Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.fw001

Polymers for Personal Care and Cosmetics

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.fw001

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.fw001

ACS SYMPOSIUM SERIES **1148**

Polymers for Personal Care and Cosmetics

Anjali Patil, Editor
Revlon
Edison, New Jersey

Michael S. Ferritto, Editor
Dow Corning Corporation
Midland, Michigan

Sponsored by the
ACS Division of Polymeric Materials: Science and Engineering

American Chemical Society, Washington, DC

Distributed in print by Oxford University Press

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.fw001

Library of Congress Cataloging-in-Publication Data

Polymers for personal care and cosmetics / Anjali Patil, editor, Revlon, Edison, New Jersey, Michael S. Ferritto, editor, Dow Corning Corporation, Midland, Michigan ; sponsored by the ACS Division of Polymeric Materials: Science and Engineering.
pages cm -- (ACS symposium series ; 1148)
Includes bibliographical references and index.
ISBN 978-0-8412-2905-1 (alk. paper)
1. Cosmetics--Materials--Congresses. 2. Polymers--Industrial applications--Congresses. I. Patil, Anjali. II. Ferritto, Michael S.
TP983.P68 2013
668.9--dc23
2013041538

The paper used in this publication meets the minimum requirements of American National Standard for Information Sciences—Permanence of Paper for Printed Library Materials, ANSI Z39.48n1984.

Copyright © 2013 American Chemical Society

Distributed in print by Oxford University Press

All Rights Reserved. Reprographic copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Act is allowed for internal use only, provided that a per-chapter fee of $40.25 plus $0.75 per page is paid to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. Republication or reproduction for sale of pages in this book is permitted only under license from ACS. Direct these and other permission requests to ACS Copyright Office, Publications Division, 1155 16th Street, N.W., Washington, DC 20036.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto. Registered names, trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

PRINTED IN THE UNITED STATES OF AMERICA

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.fw001

Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

ACS Books Department

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.pr001

Preface

Polymers are routinely used in many personal care and cosmetic products. The applications take advantage of the various properties of these polymers to impart unique benefits to their formulations. The range of properties is as varied as the class of polymers that have been utilized. Using polymers, cosmetic chemists can create high performance products. Broad spectrums of polymers — natural polymers, synthetic polymers, organic polymers as well as silicones — are used in a wide range of cosmetic and personal care products as film-formers, emulsifiers, thickeners, modifiers, protective barriers, and aesthetic enhancers.

Development of leading edge products requires better chemical and physical properties that cannot be provided by traditionally used, naturally-derived raw ingredients such as fats, oils, and waxes. Many valuable, new cosmetic ingredients come from broad polymer classes such as cellulosics, polyacrylates, polyamides, polyurethanes, polyolefins, and silicones. Today, polymers can be custom engineered to produce desired end objectives, and can be manufactured economically on a commercial scale to deliver such performance on a consistent, predictable, and reproducible basis. Molecular weights can be tailored to formulation requirements. Thermal and mechanical properties can be “tuned in” as needed. Classical chemical properties such as surface activity, solubility, hydrolytic stability, oxidation resistance, and other characteristics can also be designed in a precise and controlled manner.

This book is based on an international symposium on “Polymers for Cosmetics and Personal Care” held at the 244th National ACS Meeting in Philadelphia on August 22, 2012. The aim of this book is to cover the many facets of polymers used in cosmetics and personal care products and to bring together researchers from industries and academic disciplines from different countries. To our knowledge, this is the first compilation of progress made in the use of polymers in cosmetics and personal industry.

This book comprises a collection of papers presented in the symposium as well as several review chapters. Topics in this book have been divided into three sections as follows: Part 1 contains reviews focused on polymers described in this book, polymers used in colored cosmetic products, and organo functional silicones; Part 2 is dedicated to new synthetic methods and strategies; and Part 3 is focused on novel applications of synthetic polymers.

In the synthetic portion of the book (Part 2), there are seven chapters. Some chapters discuss specific approaches to controlling molecular architecture and other chapters prepare novel polymeric structures. For example, polymer structures can be controlled using free radical methods in order to prepare unique aqueous rheology modifiers or to create copolymers with unique properties.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.pr001

Additionally, novel materials prepared by combining poly(alphaolefins) with diphenylamine and polymers, novel cationic latex materials, and polymers with unique personal care attributes that are also biodegradable are discussed as well. There are chapters on structure-property relationship as well as on non-penetrating polymerized surfactants.

The third part of the book consists of seven chapters, too. It highlights novel applications of materials that may not be typically associated with personal care products. Such polymers include acetylene-based polymers, alkylacrylate cross-polymers, styrene/acrylate copolymers, and silicones. There are also some chapters that discuss other interesting applications of materials by utilizing the enhanced performance they impart to personal care (e.g., ion permeable microcapsules and a polymer adsorption model).

This book will be a good resource for those involved in the field of personal care and cosmetics who want to learn of recent developments. Additionally, this book will benefit the reader that would like to become acquainted with the variety of polymeric systems that can be used in personal care products and cosmetics.

The editors thank the Division of Polymeric Materials: Science and Engineering for their support of the symposium on which this book is based. We wish to thank all of the authors for their cooperation and for their high quality chapters. Finally, we thank Tim Marney, Arlene Furman and Rachel Deary from the ACS books department for their help in keeping us on task.

Anjali Patil
Revlon Research Center
2121 Route 27
Edison, New Jersey 08818

Michael S. Ferritto
Dow Corning Corporation
2200 West Salzburg Road
Midland, Michigan 48686

Editors' Biographies

Dr. Anjali Patil

Anjali Patil (Ph.D.) is a Senior Scientist at Revlon Inc. She has been working at Revlon for the last 20 years. Her work involves synthesis and use of polymers in various aspects of cosmetic products.

Anjali obtained her Ph.D. from the Indian Institute of Technology, Bombay (India) in polymer chemistry and has done her post-doctoral research at the University of Illinois at Urbana-Champaign in Organic Chemistry (Dr. David Y. Curtin) and also at the Institute for Polymers and Organic Solids, University of California, Santa Barbara (Dr. Fred Wudl).

She has been a member of ACS for the past 22 years. She has attended and chaired sessions at the National ACS meetings. She is a member of the Society of Cosmetic Chemists. She has published 9 scientific papers, issued 14 U.S. patents, and published 38 patent applications. She has recently written a monograph on "Nail Lacquer Technology," which is published by the Society of Cosmetic Chemists. Her research interests are in synthesis and application of polymers.

Anjali successfully organized the symposium sponsored by the PMSE division entitled 'Polymers for Personal Care and Cosmetics" at the fall 2012 ACS national meeting.

Dr. Michael S. Ferritto

Michael S. Ferritto (Ph.D.) is a Senior Development Specialist at Dow Corning Corporation. He has been working at Dow Corning for 17 years. His work involves the synthesis and application of silicone polymers with an emphasis on organofunctional silicones. Prior to his time at Dow Corning, he was employed at the Dow Chemical Company.

Michael obtained his Ph.D. from the University of Massachusetts at Amherst in organic chemistry and studied polymer synthesis and application of novel polymers. He completed a post-doctoral fellowship at the Michigan Molecular Institute where he studied the synthesis of novel dendrimer polymers

He has been a member of ACS for the past 30 years. He is a member of the Polymer Chemistry and Organic Chemistry Division of the ACS. He has issued 12 patents and published 7 papers. His research interest is in the synthesis of new polymers and in the application of organic chemistry to polymeric systems.

Michael has co-organized (with Anjali Patil from Revlon) the symposium sponsored by the PMSE division entitled 'Polymers for Personal Care and Cosmetics" at the fall 2012 ACS national meeting.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 12, 2013 | doi: 10.1021/bk-2013-1148.ch001

Chapter 1

Polymers for Personal Care and Cosmetics: Overview

Anjali Patil*,[1] and Michael S. Ferritto[2]

[1]Revlon Research Center, 2121 Route 27, Edison, New Jersey 08818
[2]Dow Corning Corporation, 2200 West Salzburg Road,
Midland, Michigan 48686
***E-mail: Anjali.patil@revlon.com.**

Abstract

Polymers are routinely used in many personal care and cosmetic products. The applications take advantage of the various properties of these polymers to impart unique benefits to their formulations. The range of properties is as varied as the class of polymers that have been utilized. Using polymers, cosmetic chemists can create high performance products. Broad spectrums of polymers; natural polymers, synthetic polymers, organic polymers as well as silicones are used in a wide range of cosmetic and personal care products as film-formers, emulsifiers, thickeners, modifiers, protective barriers, and as aesthetic enhancers.

This book is based on an international symposium on “Polymers for Cosmetics and Personal Care” held at the 244th National ACS Meeting in Philadelphia on August 22, 2012. The aim of this book is to cover the many facets of polymers used in cosmetics and personal care products and to bring together researchers from industries and academic disciplines from different countries. This overview chapter provides a brief description of each chapter presented in this book and is meant to provide the reader with an insight to the exciting developments described throughout.

Publication Date (Web): December 12, 2013 | doi: 10.1021/bk-2013-1148.ch001

There is no denying that cosmetics and personal care products represent a very large market for products that provide a wide range of properties to the consumer. Personal care products can be used to enhance the appearance of an individual's skin, hair, nails or teeth. Makeup is generally used to even out skin tone, hide blemishes, improve skin's appearance, moisturize and protect from UV rays at the same time. Sunscreen products protect from sun and also have anti-aging benefits. Nail polish makes nails look pretty and protects them too.

Personal care products can carry out their function as a cleansing aid while often providing an additional benefit that can last well after the cleansing has taken place. They can also provide protection in the form of an antiperspirant/deodorant and often include perfumes that impart a nice smell. These products can also provide much more than just an aesthetic sensory effect. Cosmetics can be used to help build the self-esteem for an individual that has a medical condition that can be masked by using these products. It is quite obvious that this class of consumer products can have a very large range of attributes. Consequently, a wide range of components can be used as ingredients within this class of products.

Polymers represent one class of materials that have been used as ingredients (*1*, *2*). The types of polymers that have been used are as varied as the applications which include them. Natural and synthetic materials have been utilized. The synthetic polymers used are also quite vast ranging from organic polymers based on alpha olefins to inorganic materials based on silicones. Even within a certain class of polymers, the structural variations can also dictate what kinds of properties are obtained. Features such as the degree of polymerization, the amount of branching, and the ratio of the units within a copolymer can have dramatic impact on the final performance attributes. If the copolymers are random versus block or if they are ABA or (AB)n can influence the characteristics. The chapters within this book represent some of the recent advances in how the specific properties of polymers have been used to provide some unique benefits in cosmetics and personal care products.

A large number of thickeners, mostly polymers, are used in the cosmetic and personal care industry. They not only affect the rheological profile of the formulation but also influence application of the product, water sensitivity of the formulation, and delivery of the active ingredients. Natural and synthetic ingredients are used as thickeners for a water-based system. Anhydrous systems combine one or more fatty "structuring agents" (e.g. natural or synthetic waxes, lanolin, long-chain fatty alcohols, triglycerides etc.) to impart structural rigidity and to facilitate mold release by contracting slightly upon cooling. Synthetic waxes are either mixtures of long chain hydrocarbons primarily derived from petroleum or synthesized from monomers like ethylene, vinyl acetate, vinyl pyrrolidone or organically modified dimethicones.

Polymers play a role of rheology modifier in cosmetics and personal care products. Often these products are prepared using water based formulations, and are typically low in viscosity. This is where the polymers are added to thicken and in many cases gel the formulation. To increase viscosity of water-based systems sometimes natural polymers are utilized such as polysaccharides, starch, xanthan gum, guar gum, carrageenan, alginates, pectines, gelatin, agar etc (*3*). Occasionally, natural polymers are modified for personal care use e.g. cellulose derivatives (hydroxyethylcellulose, methyl cellulose, hydroxypropylcellulose). Commonly used synthetic polymers are acrylic acid based polymers, polyacrylamides, and alkylene oxide based homopolymers and copolymers. Alkali soluble emulsions (ASE) are synthesized from acid functional and acrylate co-monomers. When the acid group is fully protonated, the polymer exists as a collapsed random coil at low pH. Viscosity is low at acidic pH and when acid groups are neutralized with alkali or organic amine, viscosity increases. Polymers like acrylates copolymers thicken by charge induced chain extension, chain entanglement and hydration.

Hydrophobically modified alkali soluble emulsions (HASE) are acid/acrylate copolymers with ethoxylated hydrophobes (*4*). When the acid groups present in the HASE polymer are neutralized with alkali, they become anionically charged and thicken by the effect of charge induced chain extension and through association of the hydrophobic groups. Polymers like acrylates/steareth-20 methacrylate copolymer build viscosity quickly, and can suspend pigments or particulates. Another type of rheology modifiers are hydrophobically modified ethoxylated urethanes (HEUR). Since these urethanes are nonionic polymers, no neutralization is required. These polymers are stable in anionic, cationic and non-ionic systems as well as in a broad pH range.

Acrylic acid based polymers are a workhorse of the industry. They can be broadly classified into 2 classes: acrylic acid cross-linked with allyl ethers of pentaerythritol or sucrose and acrylic acid cross-linked with C_{10-30} alkyl acrylates. All these acrylic acid based polymers have low electrolyte tolerance. The chapter titled “Beyond Thickening: Use of Alkyl Acrylate Cross-polymer in Personal Care Formulations” describes acrylates/C_{10-30} alkyl acrylate cross-polymers that have thickening synergy when salts and/or certai surfactants are used.

A class of polymers have been developed that can modify rheology of water based products. They are typically a hydrophilic polymers that are water soluble and have been modified by the addition of hydrophobic groups (*5*). Since there is an obvious incompatibility between these two types of polymers, it has been difficult to prepare these materials in an easy and cost efficient process.

Within the chapter titled: “Stars and Blocks: Tailoring Polymeric Rheology with “Conflicting Properties” by RAFT for Personal Care Applications”, the preparation of structural variants is described where such hydrophobic polymers are easily added to water soluble cores in one step and two step processes. There is no a need to further modify the polymers prepared with this technique. Structure property relationships are developed for the block and star copolymers that were prepared, and their performance in thickening aqueous mixtures is investigated. Additionally, by the appropriate choice of the architecture and structural components, thermally responsive systems are demonstrated.

A large number of natural and synthetic antioxidants are used in cosmetics and personal care products. Some of the commonly used antioxidants are vitamin C (ascorbic acid), butylated hydroxyanisole, butyl hydroxyl toluene, and large number of natural antioxidants such as grape seed extract, horse chestnut extract, celery extract, cucumber extract etc. Antioxidants are used to scavenge free radicals, as free radicals are known to contribute to the aging process. Free radicals contain unpaired electrons in the outer shell and these unpaired electrons

Publication Date (Web): December 12, 2013 | doi: 10.1021/bk-2013-1148.ch001

Publication Date (Web): December 12, 2013 | doi: 10.1021/bk-2013-1148.ch001

try to snatch an electron from a nearby molecule to gain stability. When the "attacked" molecule loses its electron, it becomes a free radical and this initiates a chain reaction (*6*, *7*). Ultraviolet rays also produce free radicals. Skin inhibits the pressure of being oxidized by free radicals from the environmental pollution as well as ultraviolet rays by using natural antioxidants in our bodies. Antioxidants are added to cosmetic formulations to neutralize free radicals and to help skin stay younger for a longer periods of time.

Hydrocarbons such as petrolatum, mineral oil, paraffin wax, microcrystalline wax, and ceresin wax are used in cosmetic products. Poly α-olefin (PAO) is also used in the personal care industry; one example of a PAO is hydrogenated polydecene. Hydrocarbons are used in the personal care industry due to their thermal and light stability (*8*). Due to non-greasy feel of PAO, they are used in skin care, eye shadow, makeup, and lip products. "Bifunctional Synthetic Fluid: Polyolefin-Diphenylamine" describes a novel synthesis of antioxidant bound to polymer using ionic liquid catalyst, a new way to increase solubility of an antioxidant, use of these polymers as lubricants, and a pressure DSC technique to evaluate oxidative stability of polymers.

Antioxidants and oils are also used in hair care. Hair is damaged by environmental factors as well as chemical treatments like bleaching, permanent waving, straightening, or coloring. Environmental factors include wind, rain, harsh weather, ultraviolet rays, and chlorinated swimming pool water. Grooming practices like shampooing, brushing, blow drying, and combing can damage hair, especially the cuticle. UV radiation can bleach natural melanin in the hair and can cause photo-degradation of proteins such as cystine, tyrosine, and tryptophan. This damage affects the hair color and the cuticle, which is reflected in wet and dry combing forces (*9*).

A hair conditioner can improve hair luster or shine, enhance tactile properties such as dry and wet combing, feel (soft, silky), reduce fly-away, increase volume, and improve manageability by protecting it from environmental, mechanical, and chemical damage. Hair conditioner is normally applied after shampooing the hair and then rinsed off shortly after application; this is called "rinsed-off" conditioner. It also can be a "leave-on" conditioner: as the name suggests, it can be applied as a spray, lotion, pomade, or a cream and left on the hair. The chapter entitled "Hair Care Polymers for Styling and Conditioning" focuses on polymers used in styling and conditioning applications. This chapter describes how the structure, glass transition temperature, molecular weight and acidity of the polymer affect performance of the polymer and the spray, gel, and mousse conditioning products. This chapter also describes test methods used to evaluate polymer performance and regulatory, health, and safety aspects related to manufacture and use of the polymers.

Typically, cationic polymers are used in hair conditioning products. Hair is negatively charged and therefore, cationic polymers show affinity towards negatively charged keratin. Polymer molecular weight, charge density, and hydrophobicity play a role in their interaction with hair. Natural polymers such as polysaccharides (based on cellulose and its derivatives, such as starch), hydrolyzed proteins, and gums (gum arabic, gum tragacanth) and synthetic polymers (including polyvinyl pyrrolidone homo and copolymers, polyvinyl

Publication Date (Web): December 12, 2013 | doi: 10.1021/bk-2013-1148.ch001

acetate, polyacrylates, polymethacrylates, polyvinylamides, polyurethanes, and silicones) are often used. The chapter entitled "Styrene/Acrylates Copolymer as Film Former for Improved Hair Surface Luster" describes the development of a polymer and how it can impart both hold and shine to the hair. In this chapter, a hairspray was developed using this polymer, and it was compared to conventionally used polymers for hair styling. Different instruments such as gloss meter, SEM, Dia-stron, and DMA are used for polymer property evaluation.

Opacifiers are used in personal care products such as face cleanser, liquid soap, body wash, and shampoo. to impart a milky white or creamy appearance or sometimes to hide unacceptable haziness. In general, an opacifier should have a substantially different refractive index than the formulation for it to work. There are two classes of opacifiers used in consumer products: glycol stearates or emulsions. Glycol stearates not only act as opacifiers but also impart a pearlizing effect to the formulation.

Emulsions used as opacifiers are generally styrene copolymers that are anionic in nature. They work well in systems containing anionic surfactants. To impart conditioning benefits to hair and skin formulations cationic polymers are used. Anionic opacifiers are not compatible with these formulations. The chapter titled "A Novel Cationic as an Opacifier for Cleansing Formulations" describes synthesis and evaluation of a novel opacifier. Importance of particle size for opacifiers is depicted and a method to evaluate opacity by measuring backlight scattering is described.

Polyurethanes are extensively used in cosmetic and personal care products. Both, solvent based and aqueous dispersions are used. Solvent based polyurethanes are used in nail products as secondary film-formers while aqueous dispersions are seen in mascara and skin care formulations (*10–12*). Film properties of polyurethanes depend on their structure. The chapter titled "Modern Polyurethanes: Structure-Property Relationship" explains how molecular weight, phase separation, and crosslinking density affect polymer properties. Role of soft and hard segments in determining modulus and strength of polymer and what determines stability and particle size of the dispersion are explained.

Many ingredients in cosmetics and personal care products include those obtained from polymers prepared from ethylenically unsaturated monomers (*1*). In many cases, free radical polymerization methods are employed to make these polymers. As such, there are limitations to the types of copolymers that can be prepared, and typically they will have a high polydispersity index (≥2.0) (*13*). Application of RAFT (Reversible Addition Fragmentation chain Transfer) polymerization techniques have been employed to make unique copolymers that can be used in personal care applications. These unique materials are described in the chapter titled: "Controlled Synthesis of Multifunctional Polymers with "Conflicting Properties" by RAFT for Personal Care Applications".

The RAFT process was implemented using two distinct routes. The first consists of modifying a hydrophilic polymer to add the required functional group, followed by the addition of a second block using the RAFT mediated polymerization. The second method simply uses typical RAFT conditions to make block copolymers or ABA triblock copolymer architectures. This results in materials that have potential applications in hair conditioners, hair styling formulations, lipsticks and mascaras.

There are several advantages to using active delivery systems in cosmetics and personal care compositions. One of the biggest benefits is the increased shelf life that typically accompanies the sequestering of a bioactive component, where it is protected from the degrading effects of other formulation components and/or the environment (*14*). Typically, the desired component has been physically entrapped within a polymeric matrix. There are several limitations to using this type of delivery system, such as low level of active loading and the release rate from within the matrix can be difficult to control. The materials that make up the polymer matrix may also have detrimental interactions with the entrapped active, thereby decreasing its efficacy (*15*). In the chapter titled "Biodegradable, Bioactive-Based Poly(anhydride-esters) for Personal Care and Cosmetic Applications", a novel active delivery system is described. Instead of being held within the interior of a delivery vehicle, the active ingredient is incorporated either into the polymer chain or as a pendant group and can be released at a desired rate by the hydrolytic degradation of the polymer. The hydrolysis releases the active to perform its desired action. This results in several benefits when compared to previous delivery systems, such as very high active loading levels and increased active stability.

The incorporation of several different types of actives is described. Salicylic acid is incorporated into the main chain of a poly(anhydride-ester) and the complete release within a short time is demonstrated. This active is a typical component of skin care products having anti-acne and other benefits for skin care. Antimicrobials another class of active compounds that can be incorporated as a pendant group to the poly(anhydride-ester). This system can be designed such that when the polymer degrades, not only is the antimicrobial released but the polymer backbone can be broken down to another beneficial component such as ethlyenediaminetetraacetic acid. A final example of bioactive components that can be delivered using this method is antioxidants, with ferulic acid being an example. It has been difficult to include this potent compound due to its low stability. Use of this system could lead to new personal care products that incorporate this compound.

A variety of dental issues result when the enamel is compromised. A major component of enamel is hydroxyapatite which contains calcium and phosphate ions and other constituents (*16*). The loss of the calcium and phosphate causes the enamel to erode, which is a process referred to as "demineralization" (*17*). This demineralization process can be reversed with treatments that provide calcium, phosphate and fluoride ions (*18*). The chapter titled "The Effect of Counterion, Concentration and Temperature on the Release of Bioavailable Calcium and Phosphate Ions from Ion Permeable Microcapsules for Remineralization" studies the release of calcium and phosphate from these microcapsules as a function of several controllable factors. These factors include the type of polymer used to prepare the microcapsule, the form of the phosphate ion, the associated counterion, the initial ion concentration inside the microcapsule and temperature. These materials could have potential application as an oral decay preventative treatment or as a tooth whitening product.

Publication Date (Web): December 12, 2013 | doi: 10.1021/bk-2013-1148.ch001

Anhydride functional polymers represent a class of polymers that can be soluble in water and as such are used in many personal care formulations (*19*). For example; anhydride polymers are suited for use in toothpaste, mouthwash and other oral care products. The anhydrides will open to generate acid groups and these will allow association with natural surfaces, since these are typically charged (*20*). To improve the use of the anhydride polymers in such applications, an understanding of the mechanism of adsorption onto the natural surfaces is required. Once the adsorption can be measured, the impact of various conditions can be determined.

In the chapter titled “Adsorption/Desorption Processes of pH-Responsive Copolymers on Dental Surfaces via QCM and AFM Analysis”, the mechanism of the adsorption of a maleic anhydride methyl vinyl ether copolymer is studied as a function of the conditions. The copolymer is adsorbed onto a specially prepared substrate coated with hydroxyapatite (the main component of dental surfaces) to provide an ultra smooth model of a dental surface. Both pH and concentration were varied and the mechanism and the form of the adsorbed copolymer varied with these conditions. At low pH, the ionic copolymer strongly interacts with the charged surface and results in the polymer being in a rigid conformation. The information obtained could lead to new applications in oral care formulations.

The name “silicone” refers to the class of inorganic polymers based on a silicon oxygen backbone. There is a variety of structural variants and many different organic functional groups that are included with these materials. Also, silicones have used extensively in cosmetics and personal care products. One of the reason silicones are used is because of the unique attributes these materials can impart to the formulations. For example, silicone surfactants can be found that stabilize both oil-in-water and water-in-oil emulsions (*21*, *22*). Silicone resins add mechanical strength and long-lasting characteristics to lipsticks and foundations (*23*). Low molecular weight linear silicone fluids and cyclosiloxanes are volatile but also impart a unique feel once they have evaporated (*24*). The linear silicones that have two methyl groups attached to each chain silicon atom are commonly referred to as “polydimethylsiloxanes” or “PDMSs”. The unique properties associated with siloxanes have been described in terms of the molecular attributes of these materials that are very different from organic polymers.

In the chapter titled “Silicone Wettability and Its Significance in Beauty Products”, some of the unique molecular properties are investigated using contact angle measurements. The surface energy of different silicones are measured and compared to organic oils and polymers. The different silicones include structural variants of PDMS materials, such as linear PDMS, cyclic PDMS compounds and networked structures, including gels and resins. Additionally, silicones that also have been modified with various organic groups are included in the discussion. Several personal care uses of silicones are described throughout the chapter.

A variety of synthetic and natural polymers have been used as additives in personal care applications to act as rheology modifiers, stabilizers, emulsifiers or as film formers. A method to screen the performance of the polymer additive could be valuable in quickly identifying the appropriate material of choice for the desired benefit. An important function of a polymer is as a film former for a skin application and the viscoelastic properties of the polymer will determine

Publication Date (Web): December 12, 2013 | doi: 10.1021/bk-2013-1148.ch001

how the polymer performs (*25*). In “Mechanical Characterization of Cosmetic and Viscoelastic Effects of Firming Polymers”, a method is described to screen a variety of synthetic and natural polymers for the firming effect on skin.

The screening of the mechanical performance of the polymers on a given substrate and modeling indicated a correlation in firmness and elasticity. When the applied polymer increased the firmness of the substrate, there was also an increase in the elasticity. When the polymers that displayed this increase in firmness and elasticity were then applied to skin, the same increase in these mechanical properties was demonstrated. Although the range of polymers tested was limited, this method shows the ability to quickly measure the performance of a polymer for a given mechanical property.

One of the components commonly added to cosmetic and personal care formulations is surfactants. These materials provide stability to these formulations since they also typically include water. When small molecule surfactants are used, they also have the ability to cause irritation if they penetrate into the skin (*26*, *27*). It would be desirable to have a compound that would provide the benefits of small molecule surfactants without this detrimental side effect.

In “Next Generation Mildness for Personal Care: Nonpenetrating Polymerized Surfactants for Cleansing Applications”, a class of materials described as polymerized surfactants was discussed and tested. These materials can have a variety of chemical structures and they maintain the surface activity required to stabilize aqueous formulations. In addition, since they are much larger than their small molecule counterparts, it was demonstrated that they possess a dramatically lower tendency to penetrate tissue. In addition to this mildness, the materials were also able to maintain cleansing and foaming, which are critical to performance and consumer perception. These polymerized surfactants could also be used with the small molecule surfactants, and this combination resulted in milder compositions compared to small molecule surfactants when used alone. These materials represent a new class of surfactants that provide very mild cleansers.

Publication Date (Web): December 12, 2013 | doi: 10.1021/bk-2013-1148.ch001

References

1. Gruber, J. V. Principles of Polymer Science and Technology in Cosmetics and Personal Care. *Cosmetic Science and Technology*; Goddard, E. D., Gruber, J. V., Eds.; Marcel Dekker Inc.: New York, 1999; Vol. 22; Chapter 6.
2. Lochhead, R. Y. *ACS Symp. Ser.* **2007**, *961*, 3–56.
3. Clarke, T. M. Rheological Properties of Cosmetics and Toiletries. *Cosmetic Science and Technology Series*; Laba, D., Ed.; Marcel Dekker, Inc.: New York, 1993; Vol. 13, pp 55−152.
4. Jones, C. E *Cosmet. Toiletries* **2002**, *117*, 49–60.
5. Winnik, M. A.; Yekta, A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 424–436.
6. Halliwell, B.; Gutteridge, M. C.; Cross, C. E. *J. Lab. Clin. Med.* **1992**, *119*, 598–620.
7. Halliwell, B. *Nutr. Rev.* **1994**, *52*, 253–265.

Publication Date (Web): December 12, 2013 | doi: 10.1021/bk-2013-1148.ch001

8. Butuc, G.; Morrison, D. S. *Surfactants in Personal Care Products and Decorative Cosmetics*, 3rd ed.; Rhein, L. D, Olenick, A., Schlossman, M., Somasundaran, P., Eds.; Surfactant Science Series; CRC Press: Boca Raton, FL, 2007; Vol. 135, pp 341−355.
9. Krummel, K.; Chiron, S.; Jachowicz, J. *The Chemistry and Manufacture of Cosmetics*, 4th ed.; Schlossman, M. L., Ed.; Allured books: Carol Stream, IL, 2009; Vol. 2, pp 123−163.
10. *Nail Lacquer Technology*; Patil, A. A., Sandewicz, R. W., Eds.; Monograph No. 6; Society of Cosmetic Chemists: New York, 1997.
11. de la Poterie, V. U.S. Patent 6,238,679, 2001.
12. Collin, N. U.S. Patent 6,482,400, 2002.
13. Cowie, J. M. G.; Arrighi, V. *Polymers: Chemistry and Physics of Modern Materials*, 3rd ed.; CRC Press: Scotland, 2008.
14. Gebelein, C. G.; Cheng, T. C.; Yang, V. C. In *Cosmetic and Pharmaceutical Applications of Polymers*; Plenum Press: New York, 1991.
15. Gupta, S *HAPPI* **2003**January, 49–59.
16. Mathew, M.; Takagi, S. Structures of biological minerals in dental research. *J. Res. Natl. Inst. Stand. Technol.* **2001**, *106*, 1035–1044.
17. Dawes, C. What is the critical pH and why does a tooth dissolve in acid? *J. Can. Dent. Assoc.* **2003**, *69* (11), 722–724.
18. Garcia-Godoy, F.; Hicks, J. M. Maintaining the integrity of the enamel surface: the role of dental biofilm, saliva, and preventive agents in enamel demineralization and remineralization. *J. Am. Dent. Assoc., JADA* **2008**, *139*, 25S–34S.
19. Singhal, R.; Mishra, A.; Nagpal, A. K.; Mathur, G. N. *J. Polym. Mater.* **2009**, *26*, 239.
20. Ellis, J.; Jackson, A. M.; Scott, B. P.; Wilson, A. D. *Biomaterials* **1990**, *11*, 379.
21. Hill, R. M. *Silicone Surfactants*; Surfactant Science Series; Marcel Dekker: New York, 1999; Vol. 86.
22. Petroff, L. J.; Snow, S. A. In *Silicone Surface Science*; Owen, M. J., Dvornic, P. R., Eds.; Springer: New York, 2012; Chapter 9.
23. Garaud, J. L. In *Inorganic Polymers*; De Jaeger, R., Gleria, M., Eds.; Nova Sciences Publisher: New York, 2007; Chapter 16.
24. Brand, H. M.; Brand-Garnys, E. E. *Cosmet. Toiletries* **1992**, *107*, 93.
25. Jachowicz, J.; McMullen, R.; Prettypaul, D. Alteration of skin mechanics by thin polymer films. *Skin Res. Technol.* **2008**, *14*, 312–319.
26. Jongh, C. M. d.; Jakasa, I.; Verberk, M. M.; Kezic, S. *Br. J. Derm.* **2005**, *154* (4), 651–657.
27. Jongh, C. M. d.; Verberk, M. M.; Spiekstra, S. W.; Gibbs, S.; Kezic, S. *Skin Res. Technol.* **2007**, *13* (4), 390–398.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Chapter 2

Cosmetic Science and Polymer Chemistry: Perfect Together

Anjali Patil* **and Robert W. Sandewicz**

Revlon Research Center, 2121 Rote 27, Edison, New Jersey 08818
***E-mail: Anjali.patil@revlon.com.**

Cosmetic science has evolved significantly during the past thirty years. One of the principal drivers of such advancement has been the development of new color cosmetic formulations that deliver a combination of drastically improved functional performance and outstanding aesthetic properties. The key element enabling the creation of such high performance products is the increasingly widespread use of a broad spectrum of polymers in a wide range of color cosmetic formulations. The primary reasons for this trend are rooted in intrinsic attributes of polymers. Polymers typically are more substantive to biological substrates than are many of the fatty-based raw ingredients historically used in cosmetic formulations. Polymers also can be customized readily to meet very specific performance requirements. In some formulations, polymers have supplemented fatty-based raw ingredients as a means of improving product performance. In other formulations, advanced technology polymers have completely replaced traditional cosmetic chemicals in order to create products having superior skin adhesion and wear attributes. Polymer scientists should be aware of the safety and regulatory requirements peculiar to the cosmetic industry so as to engage cosmetic chemists in a productive way.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Introduction

American industrialist Henry Kaiser is credited with having coined the adage, "*Find a need and fill it*." This advice typically is cited within a marketing context, yet it appropriately describes the ongoing relationship between cosmetic science and polymer chemistry. Classical polymer chemistry understandably might be viewed as part of a larger "smokestack industry", conversely, the term *cosmetic science* at first glance might seem to be an oxymoron. How can aesthetics be reconciled with organic chemistry? What common ground could possibly exist between lipsticks and elastomers? Are the names *Ziegler* and *Natta* as synonymous with beauty as the names *Revson* and *Lauder*? Despite what might appear to be a glaring lack of similarity, both areas truly are more alike than might be imagined. Both fields are highly scientific in nature, are quite adept at harnessing new technologies to reconcile some challenging puzzles, and financially are very profitable. In short, both cosmetic scientists and polymer chemists make high performance, high value products through skillful implementation of advanced technologies or, as Mr. Kaiser would have said, by finding needs and filling them.

The common ground shared by cosmetic scientists and polymer chemists can be summarized by one word: *performance*. During the first three decades of the 20th Century, cosmetic manufacturers sought to transform their businesses from small, artisanal "cottage industries" into modern enterprises. They did so not only by use of clever and aggressive marketing strategies, but also by use of increasingly sophisticated chemical technologies. The net result: products characterized by outstanding aesthetics and performance-driven benefits. During that era, cosmetic chemists had the unenviable task of attempting to create such products using the relatively unsophisticated raw ingredients available to them. Chemists relied almost exclusively on time-honored, naturally derived raw materials such as fats, oils and waxes. Given the inherent variability of biological systems, the chemical and physical properties of natural ingredients sometimes varied considerably from lot to lot. Not surprisingly products intended to be both aesthetically pleasing and functional did not always perform consistently. The fact that early cosmetic products enjoyed *any* commercial success pays tribute to skillful formulators who were able to comprehend and manage the variability of a relatively small "chemistry set" comprised mainly of naturally derived raw ingredients.

During the years leading up to World War II, consumers demanded increasingly more sophisticated cosmetic products. Synthetic pigments became available on a regular basis, enabling formulators of staple cosmetic products such as nail lacquers and lipsticks to broaden their shade palettes significantly. Performance attributes such as ease of application, high gloss and improved adhesion to human skin and nails became more important. Fortunately, during this same timeframe, polymer chemists were busy creating synthetic organic polymers such as polyacrylates, nylon, polyethylene and polyesters. Considered rudimentary materials today, these revolutionary new polymers represented breakthrough technologies at the time. As with cosmetic chemists, dye and textile chemists had long grappled with the inherent performance shortcomings of

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

"biopolymers" such as cotton and wool prior to the advent of synthetic polymers capable of producing "engineered fibers" having more uniform and predictable chemical and mechanical properties.

The fruits of technical labor did not go unnoticed by the cosmetic industry. Founded at New York City in 1945, the Society of Cosmetic Chemists (SCC) became the cornerstone professional organization on which the discipline of "cosmetic science" was firmly established (*1*). Then as now, the scholarly journal of SCC served as the primary tool to communicate new raw ingredient technologies, formulation techniques, manufacturing advice, and product testing methodologies. Not surprisingly, new polymeric ingredients potentially useful to cosmetic formulators began appearing in SCC literature with increasing frequency.

Creators of advanced new beauty care products took note of such technical advances and began experimenting with new polymeric ingredients in formulations previously dominated by animal- and plant-derived raw materials (*2*). Due to aggressive competition, new formulations were required to attract increasingly savvy consumers who demanded constant innovation and ever more added value. New polymeric materials clearly would benefit formulators of such complex new cosmetic products. As with their counterparts in many other industries, cosmetic chemists realized that high performance products could be achieved only by selecting raw ingredients truly capable of sustaining such performance characteristics on a predictable basis. Leading edge products required far better chemical and physical properties than could be provided by most naturally-derived raw ingredients.

Many valuable new cosmetic ingredients came from such broad polymer classes as cellulosics, polyacrylates, polyamides and hydrocarbons (*3–6*). Why this hunger for polymers in cosmetics? Once again, the word *performance* enters the equation. Clearly, very many non-polymeric synthetic raw ingredients are readily available to cosmetic chemists today. There are many formulations having performance requirements that are met adequately without the use of polymeric materials. Nevertheless, polymeric cosmetic ingredients help make higher performance attributes possible in ways that their "monomeric" counterparts cannot achieve. Polymers have structure/activity relationships that can be custom engineered to produce desired end objectives, and can be manufactured economically on a commercial scale to deliver such performance on a consistent, predictable and reproducible basis. Molecular weights can be tailored to formulation requirements. Thermal and mechanical properties can be "tuned in" as needed. Classical chemical properties such as surface activity, solubility, hydrolytic stability, oxidation resistance and other characteristics also can be designed in a precise and controlled manner. Clearly, cosmetic chemists have come to recognize and appreciate what polymer chemists have known for many years: the potential benefits of polymers in beauty care products are limited mainly by the imaginations of those who synthesize polymers and those who determine how best to use these materials in end products.

One of the many technological step-changes that have occurred in cosmetic science during the past 50 years involves the large class of polymers collectively known as *silicones*. Very many unique and important performance benefits highly relevant to the cosmetic industry have been made possible through the use of these materials. As cosmetic chemists became familiar with the solubility and compatibility profiles of various silicones used in combination with traditional organic raw ingredients, the very real benefits of silicones became apparent.

Early silicones frequently used in cosmetic applications were homopolymers of dimethyl siloxane. Known as *dimethicones*, these liquid polymers were employed in many of the same applications as organic oils, to impart hydrophobicity and lubricity on the skin (*7*). Manufacturers also began offering various organically-modified silicones that were more readily compatible with traditional cosmetic raw ingredients, and that offered a broader range of visual and tactile properties. Silicone emulsifiers were developed to enable formulation of stable creams and lotions. Perhaps the most revolutionary silicone polymers used in cosmetic applications are *silicone resins*. Produced in various forms, materials such as *trimethylsiloxysilicate* (called *MQ resins* in silicone chemistry parlance) help produce cosmetic formulations having very tenacious adhesion to skin, thus enabling creation of entirely new classes of "transfer-resistant" lip and face makeup products (*8–10*).

Up to this point, polymers have been discussed solely within the context of cosmetic formulation technology. A meaningful analysis of the engineering applications of polymers used in modern cosmetic packaging applications warrants more than a cursory discussion, and is far beyond the scope of this document. Manufacturers of sustainable cosmetic packaging materials have struggled to achieve all the protective and aesthetic properties of conventional polymeric materials, but significant advances undoubtedly will be made in the development of bio-degradable, sustainable packages exhibiting chemical and mechanical robustness equal to that of conventional packages.

Another important but less obvious application of polymeric materials in cosmetic science is process engineering. Materials storage and shipping vessels used in the cosmetic industry historically were constructed of metal. In response to a wide variety of contemporary factors (i.e. enhanced corrosion protection, energy conservation, sustainability initiatives, ease of recycling, cost control programs, reduction of tare weight to mitigate shipping costs etc.) storage and transportation equipment built with polymeric materials have become more common in the industrial environment. *Intermediate bulk containers* (sometimes called *IBC's* or *totes*) can be constructed of polypropylene instead of stainless steel. As with an analysis of polymeric packaging materials, a discussion of the use of engineering polymers in chemical processing industries is a subject worthy of a separate discussion and is beyond the scope of this chapter.

Table 1 lists the functional properties of cosmetic ingredients alongside their expected consumer benefits, then to provide examples of polymers that have been utilized commercially to meet these requirements. Examination of this table reveals that appropriately selected polymers can provide nearly every functional property needed to achieve meaningful consumer benefits in all types of cosmetic formulations. Whether the final product form is solid (e.g. lipstick, deodorant), liquid (e.g. nail lacquer, foundation makeup, shampoo) or gaseous (e.g. perfume, aerosol hair spray) one or more polymeric raw ingredients may be

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

used in combination with multiple other cosmetic chemicals to deliver the level of performance required to meet consumer needs.

Table 1. Cosmetic Ingredient Functional Properties and Consumer Benefits

Functional Property	*Consumer Benefits*	*Polymeric Examples*
Film formation	Extended product wear; enhanced skin protection; improved product aesthetics	Nitrocellulose, polybutene, polyester resins, acrylates copolymers, silicone acrylate copolymers, polyurethanes
Transfer resistance	Tenacious product adhesion; enhanced skin protection; improved product aesthetics; reduction in number of product application cycles	Trimethylsiloxysilicate (*MQ resins*), silicone elastomers
Tack	Enhanced product adhesion	Polycyclopentadiene, polybutene
Emolliency	Enhanced comfort & protection	Dimethicone
Moisturization, chapping prevention	Improved skin condition; more youthful skin appearance	Hydrogenated polydecene, polybutene
Surface activity	Ease of application; enhanced product shelf life	PEG/PPG block copolymers
Structure development	Ease of application in stick products	Polyethylene, EVOAc
Rheological control	Ease of application; enhanced product shelf life	Hydroxypropylmethylcellulose, hydroxyethyl cellulose, polyacrylic acid, polyamides
Wrinkle effacement	Mitigation of appearance of undesirable skin surface defects; more youthful skin appearance	Nylon, PMMA, polyurethane crosspolymers
Gloss reduction	Mitigation of appearance of undesirable skin surface defects; more youthful skin appearance	Polyurethane crosspolymers
Pigment surface treatment	Ease of application; novel visual aesthetics	Reactive silanes

Continued on next page.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Table 1. (Continued). Cosmetic Ingredient Functional Properties and Consumer Benefits

Functional Property	*Consumer Benefits*	*Polymeric Examples*
Ingredient encapsulation	Reduction in number of product application cycles, prevention of ingredient degradation, prolonged release of fragrance oils and active ingredients;	Acrylates copolymers, cyclodextrins
Color development	Products having novel visual aesthetics	Metal oxides and mica
Gloss enhancement	High shine appearance on lips or nails	Hydrogenated polyisobutene, Hydrogenated polydecene, phenyl silicones
Odor/flavor control	Fragrance/flavor longevity, elimination of malodors	Cyclodextrins

Technologies such as dendritic polymers might offer tremendous benefits in beauty care products once cosmetic chemists begin to understand how to best use these materials. The concept of “smart polymers” is equally intriguing, as is the field of composite polymers. In recent years, numerous smaller cosmetics brands have decided to market products identified as *natural, organic, mineral-based* and/or *bio-botanical*, largely in the hope of increasing market share among groups of consumers with whom such terms resonate positively. Conversely, larger cosmetic brands have chosen to market products based primarily on consumer-perceived performance benefits. It is interesting to observe that polymers either of natural or synthetic origin can provide important benefits regardless of specific market positioning. Driven by overarching “mega-trends” such as sustainability, environmental sensitivity, conservation of energy and natural resources, makers and users of polymers across all industries will discover creative new ways to exploit the great utility of these “compounds with many parts.” Cosmetic chemists have come to recognize and appreciate that potential benefits of polymers in beauty care products are limited mainly by the imaginations of those who synthesize polymers and those who determine how best to use these materials in end products. Equipped with high-tech polymers “in the toolbox”, successive generations of cosmetic chemists and polymer scientists undoubtedly will be more than able to support continuous efforts to “find a need and fill it.”

Film Formation

In the cosmetic industry, a “film-forming polymer” does not necessarily form a self-standing film. It can be a fluid film that enhances the wear of the product, extends sunscreen protection, imparts water or oil resistance, or improves product aesthetics. A large variety of polymers are used as film formers, such as hydrocarbons, cellulosics, polyesters, polyurethanes, and acrylics.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

- *Hydrocarbons*: Commonly used hydrocarbon polymers are polybutene, polyisobutene, polycyclopentadiene, and poly(alpha olefins), frequently abbreviated as *PAO* (*6*). They are made by polymerizing α-olefins (α-olefin is an alkene with terminal double bond, e.g. 1-decene). An example of a PAO commonly used in cosmetic formulations is hydrogenated polydecene. Polydecenes are available in a wide viscosity range, and due to their non-greasy skin feel they are used in skin care, eye shadow, makeup, and lip products (*11*). The most commonly used polybutenes are lower molecular weight polymers (400-1000 daltons) and primarily are used in lip gloss formulations as they are very shiny and have good adhesion to lip surfaces. They are also used in eye makeup, eyeliner, blushes, foundation, mascara and makeup products. Hydrogenated polyisobutenes are mainly used in lip products along with eye shadow, eyeliner, and mascara (*12*).
- *Acrylates copolymers*: Acrylates are formed by free radical polymerization of different acrylic monomers, either via solution or emulsion polymerization. They are available in 100% solids form as well as in dispersions and emulsions. They are used either alone or as secondary film-formers along with nitrocellulose in nail enamel formulations (*4*, *13*). They also are used in skin care products to extend sunscreen protection or wear. Mascara formulations often use acrylate copolymers with acid functionalities, neutralized with an alkali (*14*). As the emulsion coalesces during the drying period, a relatively durable film is formed on eye lashes.
- *Silicone acrylate copolymers*: These copolymers are prepared either by free radical polymerization of a silicone acrylic monomer with other acrylic monomers or by grafting (*15*, *16*). Some copolymers have siloxane backbones with pendant acrylic groups e.g. poly(dimethylsiloxane)-g-poly(isobutyl methacrylate) as shown in Figure 1.

  This copolymer dissolves in cosmetic solvents such as isododecane and forms shiny adhesive films. These materials are used in high-performance pigmented cosmetic products, such as lip products and mascaras (*17*). Some copolymers have acrylic backbone with pendant silicone e.g. poly(isobutyl methacrylate)-co-methyl FOSEA)-g-poly(dimethylsiloxane) is used in lip products (*18*). Acrylic silicone graft polymers also can be prepared by free radical polymerization of dimethylpolysiloxane with polymerizable acrylic/methacrylic group on end with acrylic/methacrylic monomers as shown in Figure 2 (*19*).

  These acrylates/dimethicone copolymers form adhesive films that have good water and oil resistance. They are used in various pigmented cosmetic products as well as in skin care products for enhanced sunscreen protection.
- *Polyester resins*: Polyesters are formed by the reaction between a polyol and acids or acid chlorides. Polyesters used in lip products are generally synthesized using aliphatic fatty acids and fatty alcohols.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

These polymers confer gloss, adhesion and water resistance. Polyesters used for nail enamel applications typically are produced by the reaction of dicarboxylic acids (e.g. adipic acid), polyols (e.g. glycerin, neopentyl glycol or trimethylolpropane) and acid anhydrides (e.g. maleic anhydride, phthalic anhydride or trimellitic anhydride). Such polyester resins produce soft films and often are blended with nitrocellulose to improve gloss, toughness and flexibility of nail lacquer films (*4*).

- *Nitrocellulose*: The first polymer used in cosmetic formulations was nitrocellulose (cellulose nitrate). It is produced by the esterification of cellulose (obtained from cotton fibers or wood pulp) with nitric acid and its structure is shown in Figure 3. Nitrocellulose lacquers first came into widespread use in the 1920's, mainly for automobile finishes and other industrial coatings applications (*3*).

  Nitrocellulose is a dangerous explosion and fire hazard. Nitrocellulose is particularly explosive when dry, thus it must be wetted with ethanol or isopropanol to prevent detonation in transit. It readily degrades upon exposure to many common environmental factors, such as heat, sunlight, elemental iron and alkaline compounds. Classic evidence of the degradation of nitrocellulose solutions in organic solvent mixtures is a yellowing or browning of the bulk solution. In spite of these formidable shortcomings, it still is the main film-former used in nail lacquer formulations today (*20*, *21*). Nitrocellulose is manufactured in various grades based on different solvent solubility profiles and molecular weights. Nitrocellulose used in nail products has a high degree of nitration for maximum durability and water resistance. Although it's neat films are inherently brittle, nitrocellulose forms durable, shiny films when adequately plasticized.
- *Cellulose Esters/Mixed Esters*: In order to avoid the hazards of nitrocellulose in a variety of industrial applications (including the manufacture of early motion picture film) polymer chemists undertook development of cellulose esters in the 1920's and 1930's. By esterifying the available hydroxyl groups of cellulose with acetic acid alone or with a mixture of acetic acid and either propionic or butyric acids, several useful polymers were created: cellulose acetate ("CA"), cellulose acetate propionate ("CAP") and cellulose acetate butyrate ("CAB"). These polymers do not present the explosion hazards of nitrocellulose, and they also are far more tolerant of a variety of environmental factors. They are soluble in a wide range of commonly available organic solvents, and are compatible with a broad range of plasticizers and other polymers. Cellulose esters/mixed esters exhibit very good clarity and color stability even with prolonged exposure to UV light, heat and other insults, making them particularly valuable for use in "non-yellowing" nail topcoat formulations (*3*).
- *Polyurethanes*: The first polymers containing the urethane linkage (-NCOOR-) were developed and prepared by Otto Bayer in Germany. Urethanes are esters of carbamic acid, having the structure RHNCOOR, where R is an organic radical. This basic reaction still is used in the

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

production of urethane today (*22*). Solvent based polyurethanes are used in nail products as secondary film formers and also in eye shadow, mascara, foundation and lipstick (*23*). Aqueous polyurethane dispersions are used extensively in mascaras, skin care as they form flexible films (*24*, *25*).

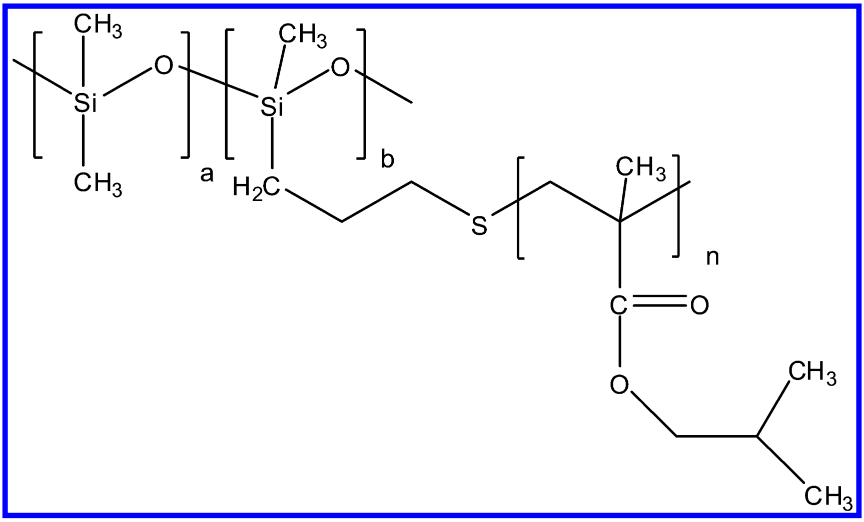


Figure 1. Poly(dimethylsiloxane)-g-poly(isobutyl methacrylate).

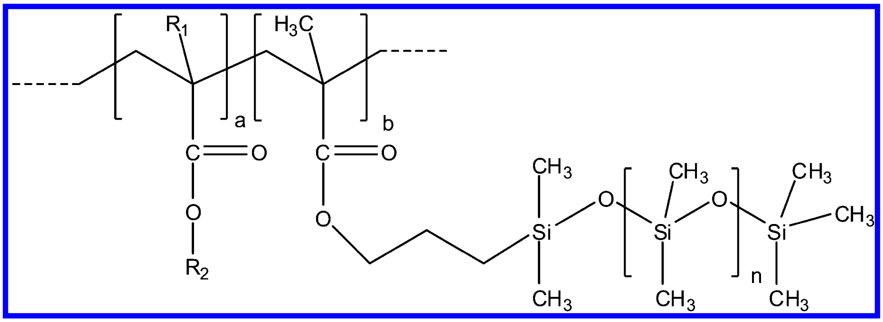


Figure 2. Acrylates/dimethicone copolymer (R_1 is H or alkyl group, R_2 is alkyl group).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

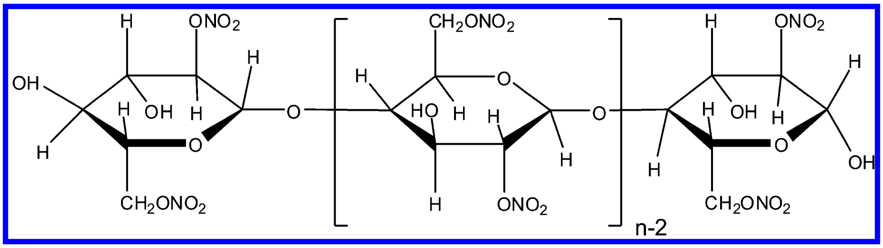


Figure 3. Structure of nitrocellulose.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Transfer Resistance

When a cosmetic product does not “kiss-off”, deposit on clothing or glasses, or when it resists removal by food (“food-proof”), it is called “transfer-resistant”. Transfer-resistant cosmetic products are less affected by water and oil as compared to conventional cosmetic products and are not easily affected by sebum or perspiration. Early transfer-resistant lip products were prepared by partially replacing the non-volatile oils with volatile solvents (*26*). These products were “kiss-proof” but they were not sufficiently durable to be described as “food-proof”. Robust food-proof products almost all have one thing in common: “MQ polymers”. In the “silicone alphabet”, an “MQ polymer” is more accurately described as trimethylsiloxysilicate.or trimethylated silica. MQ polymers are highly cross-linked structures consisting of $SiO_{4/2}$ units. Trimethylsiloxysilicate is dissolved/dispersed in volatile solvents e.g. isododecane, volatile cyclic or linear silicones e.g. cyclopentadiene, hexamethyldisiloxane, etc. It also can be dissolved in non-volatile silicones (e.g. different viscosity dimethicones or substituted dimethicones e.g. alkyl or phenyl substituted dimethicones). There are large number of lip, eye, and face products sold today containing trimethylsiloxysilicate (*8–10*).

Tack

Although tack usually is not a pleasant feeling on the skin or lips, it is necessary to promote adhesion of cosmetic products to various biological substrates. Molecular weight and glass transition temperature play a role in determining tack of the polymer. Polyisobutylene with lower molecular weight has tack and an ability to flow and wet the substrate, and also imparts shine (*27*). Polyisobutylene forms an occlusive barrier and locks the moisture in, therefore, it is used in lip gloss. Hydrogenated polycyclopentadiene is used to enhance adhesion and shine. Hydrogenated polycyclopentadiene is synthesized by ring opening metathesis polymerization of dicyclopentadiene, then the double bond is hydrogenated. This is a low molecular weight (~500 dalton) polymer that is soluble in volatile and non-volatile hydrocarbons and imparts water-resistance to the formulations along with adhesion. Hydrogenated polycyclopentadiene is used lipstick, eye liner, eye shadow, makeup, foundation, and mascara (*28*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Emolliency

An “emollient” is defined as an ingredient intended to soothe and protect skin,.thus “emolliency” means the degree of skin soothing and protection conferred by a particular cosmetic raw ingredient (*29*). Historically, cosmetic emollients were liquid and solid fatty materials derived from plant and animal sources (e.g. castor oil and lanolin, respectively). Not surprisingly, emollients also can be derived from completely synthetic feedstock (e.g. octyl dodecanol).

Polydimethyl siloxane is called the dimethicone in cosmetic industry, this name conforms to INCI (the International Nomenclature Cosmetic Ingredient) nomenclature. Dimethicone is described as a MDM polymer in the silicone alphabet. Dimethicone has flexible silicone and oxygen (siloxane) to which methyl groups are attached. Dimethicones are hydrophobic and still have high permeability to water vapor. Although dimethicones have very low glass transition temperature, they are not tacky or sticky. Due to their low surface tension (24 mN/m), dimethicones can spread easily and wet substrates (e.g. skin or lips) easily.

Dimethicones come in a broad viscosity range from 0.65 cSt to thousands of centistokes. 0,65 cSt dimethicone is volatile and is used as a solvent or a diluent, while higher viscosity dimethicones are used as protective agents. Due to its hydrophobicity, low surface tension and ability to spread easily, dimethicone is recognized by the U. S. Food and Drug Administration as a protecting agent in topical skin care products (*30*). The skin protectant monograph allows dimethicone to be claimed as an active ingredient when incorporated into OTC (over the counter) products in concentrations of 1 to 30%. An anti-chapping claim can be made for a lip product if it contains at least 1.5% dimethcone.

Moisturization

The term “moisturization” is defined as a process by which skin is made smooth and supple by keeping it relatively moist. For most biological substrates, moisture is provided mainly by water. Maintenance of the proper amount of water on the skin can be accomplished by depositing a protective, hydrophobic barrier layer over skin surfaces to prevent or retard trans-epidermal water loss (known as “TEWL”) (*31*). This tactic sometimes is called “occlusion”. It has direct parallels in the plant world: cacti and other plants living in arid regions have waxy surface layers (“cuticles”) that effectively prevent loss of precious water. Following this approach, hydrophobic liquid polymers such as hydrogenated polydecene are used to “seal in” natural moisture, thus making the skin feel and look more moist and youthful. These polymers are more substantive than their mono-molecular counterparts, and in recent years have replaced older moisturizers such as mineral oil or petrolatum. A second method of moisturization involves attracting water to skin surfaces. This type of activity is called “humectancy”. Most humectants contain one or more functionalities capable of forming hydrogen bonds with water. While the archetypal mono-molecular humectant is glycerol (a 3-carbon tri-hydroxy alcohol) polymers having similar architecture also can provide humectant benefits.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Surface Activity

Some examples of surface active polymers are poly(ethylene oxide), poly(propylene oxide), and poly(ethylene oxide-propylene oxide) copolymers. They are prepared by homo- or co-polymerization of the corresponding ether. INCI nomenclature classifies homopolymers of ethylene oxide into two categories. Ethylene oxide polymers with molecular weights below 20,000 are designated as PEG-N, where N represents the number of ethylene oxide monomer units in the polymer (*32*). When an alcohol (e.g. methanol) is used to initiate the polymerization of a lower molecular weight methyl-terminated polyether, the INCI designation is PEG-N methyl ether. Polymers with molecular weights greater than 20,000 are referred to as poly(ethylene oxides) and the INCI designation is PEG-#M, where # is a whole number and the M indicates 1000, and together they represent the approximate number of moles of ethylene oxide in the polymer.For example, PEG-3M is comprised of 3000 moles of ethylene oxide. These high molecular weight poly(ethylene oxide)s are solid materials.

The difference between poly(ethylene oxide) and poly(propylene oxide) is a single methyl group, but that difference has significant implications. Poly(ethylene oxide) homopolymers are water soluble at all molecular weights and in all proportions. In contrast, presence of the additional methyl group in propylene oxide imparts hydrophobicity to poly(propylene oxide) homopolymers, making them water-insoluble. Random EO/PO copolymers are water soluble when they contain at least 50% ethylene oxide. Not surprisingly, block co-polymerization of EO and PO produces amphiphilic polymers that legitimately can be described as “non-ionic surfactants”. An entire class of surfactants is created by adjusting the EO-to-PO ratio in various block co-polymers across the full spectrum of HLB (“hydrophilic/lipophilic balance”) values. Hydrogen bonding is responsible for the affinity between water and the EO moiety of EO/PO copolymers. Because of this situation, random EO/PO copolymers exhibit a phenomenon known as “ inverse cloud point”, defined as the temperature at which such polymers collapse upon themselves and precipitate from aqueous solution. As the solution cools, hydrogen bonds re-form, the polymer re-disperses and then re-dissolves. These polymers have a slippery feel. Due to their surface activity, they are very good for dispersing pigments or sparingly water-soluble raw ingredients into water.

Structure Development

Cosmetic products are marketed in a variety of convenient forms. “Hot-pours” (e.g. lipsticks and anhydrous blush formulations) are very popular products (*33*). They are manufactured by melting and mixing solid, semi-solid and liquid fatty raw ingredients then casting the hot molten liquid either into molds or directly into final containers. This procedure has parallels to other industrial processes, such as steel casting in a foundry or injection molding in a plastics factory. Traditionally, hot pour formulations must incorporate one or more fatty “structuring agents” (e.g. waxes, lanolin, long-chain fatty alcohols, triglycerides etc.) to impart structural rigidity and to facilitate mold release by contracting

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

slightly upon cooling. Logically, various thermoplastic polymers can be used to supplement or completely replace waxes in hot pour products.

Synthetic waxes are either mixtures of long chain hydrocarbons primarily derived from petroleum or synthesized from monomers such as ethylene, vinyl acetate, vinyl pyrrolidone or organically modified dimethicones. Polyethylene used in the cosmetic industry is a linear low molecular weight homopolymer of ethylene. Polyethylene grades used in cosmetics have a melting point below 100 °C. Polyethylene imparts structure, increases overall hardness and crystallinity of the product and therefore, is used in a large variety of cosmetic products (e.g. lipstick, eye shadow, blush, eye liner, mascara, makeup, foundation etc.). It improves stability to cosmetic stick formulations due to its compatibility with commonly used cosmetic oils. It also is a good film former which aids in the delivery of actives. Low molecular weight ethylene and vinyl acetate copolymers (EVA) are used in eye shadow, eyeliner, eyebrow pencil, lipstick, and makeup products (*34*). Presence of vinyl acetate introduces slight polarity to the polymer and makes the copolymer compatible with triglycerides commonly used in cosmetics. EVA is used to modify the rheological properties of products. Crystallinity of polyethylene is interrupted by vinyl acetate and that helps in imparting gloss to the product. Copolymers of vinyl pyrrolidone with alkenes (e.g. eicosene, hexadecane, triacontene) are used for structure building. Silicone waxes and alkyl modified silicones are used to give structure as well as different textures to stick products.

Polyethylene and ethylene/vinyl acetate copolymer frequently are used to impart structure in lipstick and lip gloss formulations. Polymeric structuring agents have some important advantages as compared to their traditional counterparts. Waxes typically are extracted from inherently variable origins such as petroleum (e.g. paraffin), animal secretions (e.g. beeswax and lanolin) and plants (e.g. carnauba and candelilla waxes). In contrast, polymeric structuring agents generally offer improved batch-to-batch reproducibility, and their chemical, mechanical and thermal properties can be tailored to meet specific performance requirements.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Rheological Control

Color cosmetic products not only must be visually appealing, but they also must be aesthetically pleasing in several other important ways. Products applied to the surfaces of the human body must exhibit acceptable tactile properties during application and throughout the wear period. Control of product rheology is an extremely important topic in cosmetic science. Solid and semi-solid products must have structural integrity across a variety of storage and use conditions, yet they also must afford smooth, even film deposition during application. Liquid formulations must possess robust structure in order to suspend various pigments, yet they also must exhibit appropriate flow and viscosity properties with each use. Because color cosmetic products frequently have shelf lives of 36 months or longer, successful maintenance of long-term product stability is dependent upon

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

the correct selection of rheology modifiers. Rheological control is a critical factor in the new product development process, thus many different types of inorganic and organic rheological control agents are marketed to address various formulation requirements.

As might be anticipated, natural and synthetic polymers enjoy widespread use as rheological control agents in a variety of color cosmetic formulations (*35*). All raw ingredients in a formulation exert varying degree of influence on the rheological profile of the product, even those ingredients whose primary intended function is not rheological control. Polymeric materials are no exception to this rule. For example, nitrocellulose is used as a primary film former in nail lacquer formulations, yet small amounts of high molecular weight nitrocellulose sometimes are added to increase lacquer viscosity. Similarly, polyurethanes or acrylics may be used to form films in mascara formulations, yet they also can be used to increase product viscosity. Because polymers can perform a multiplicity of functions in a color cosmetic formulation, when discussing polymeric rheology modifiers it is convenient to focus on those polymers whose primary function is rheology control (i.e. viscosity modification).

Both naturally-derived and synthetic polymers are used as cosmetic thickeners. For anhydrous products and some emulsions polyethylene and EVA are used. High molecular weight grades of polybutene or ethylene/propylene/styrene terpolymers are used to thicken oil-based products (e.g. lip glosses). For water-based products (e.g. eye and face products) generally cellulose ethers and polyacrylic acid and its derivatives are used. Cellulose ethers are water-soluble polymers derived from cellulose, the most abundant polymer in nature. They are used as thickeners, binders, film formers, and water-retention agents. They also function as suspension aids, surfactants, lubricants, protective colloids and emulsifiers. Water-dispersible vegetable gums (e.g. acacia, carageenan, guar and xanthan gums) often are added to emulsified formulations (e.g. liquid makeup) to increase viscosity (*36*).

Poly(acrylic acid) is a workhorse polymer for water-based systems. In cosmetic applications this polymer is lightly cross-linked or hydrophobically modified. Alkali soluble emulsions (ASE) (*35*). are synthesized from acid and acrylate co-monomers. These polymers exist as collapsed random coils at low pH when the acid groups are fully protonated. The viscosity is low at an acidic pH and when acid groups are neutralized with alkali or organic amine, viscosity increases. Polymers like acrylates copolymer thicken by charge induced chain extension, chain entanglement and hydration.

Hydrophobically modified alkali soluble emulsions (HASE) are acid/acrylate copolymers with ethoxylated hydrophobes (*37*). When the acid groups present in HASE polymers are neutralized with alkali, they become anionically charged and thicken by the effect of charge induced chain extension and through association of the hydrophobic groups. Polymers like acrylates/steareth-20 methacrylate copolymer build viscosity quickly and can suspend pigments or particulates. They are used in creams and gels.

Another type of rheology modifiers are hydrophobically modified ethoxylated urethanes (HEUR). .Since these urethanes are nonionic polymers, no neutralization is required. Polymers are stable in anionic, cationic and non-ionic systems as well as from pH 2-12. They impart a creamy feel and therefore, are used in creams, lotions, makeup, and hair care and hair color.

Polyamide resins sometimes are used to increase product viscosity in formulations where bulk clarity is desired. Ether and ester modified polyamides are used in colored cosmetic products to enhance shine and for better compatibility with cosmetic ingredients. Polyamide-8, bis-stearyl ethylenediamine/neopentyl glycol/stearyl hydrogenated dimer dilinoleate copolymer (Fig 4) is used in lipstick to improve gloss (*5*).

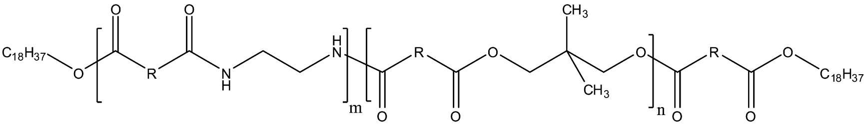


Figure 4. Bis-stearyl ethylenediamine/neopentyl glycol/stearyl hydrogenated dimer dilinoleate copolymer (where R is hydrogenated dimer dilinoleic acid).

It is not unreasonable to state that viscosity building properties vary directly with formula concentration. At low levels, a polymer may function primarily as a film former, but as polymer concentration increases, increased rheological structure is produced. When rheological control agents are added at very high levels, a liquid product gradually may become a semi-solid gel and then eventually become a solid product. Care must be exercised to ensure that end objectives are achieved.

Wrinkle Effacement

Wrinkles are commonplace skin defects, but many people regard their arrival as an ominous sign of advancing age. In their never ending quest to develop products that help create a youthful appearance, cosmetic chemists regard wrinkles as mortal enemies. Wrinkle formation is part of the skin aging process. Formulators of skin care products seek to prevent formation of wrinkles by influencing natural biological processes (e.g. skin hydration and collagen synthesis). In contrast, developers of color cosmetics primarily focus on covering and/or filling in wrinkles. A well formulated makeup product uses 3 different types of polymers to create a flawless finish: 1. film formers to fill in wrinkles; 2. polymeric powders to obscure the appearance of wrinkles; 3. polymeric humectants to attract and hold moisture to the skin. The subject of polymeric powders is intriguing.

The use of inorganic particulate materials (e.g. mica, sericite, silica or talc) to exert an "optical blurring" effect on skin is well known. More recently, synthetic polymeric "spherical powders" (e.g. nylon, polyurethanes,

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

polymethylmethacrylate) and naturally-derived polymeric powders (e.g. microcrystalline cellulose) have been used to supplement or supplant inorganic materials in makeup formulations to fill in and minimize the appearance of skin wrinkles. Occasionally, some polymeric powders also carry various surface treatments to enhance tactile properties and to increase resistance to water and sebum. Similar raw ingredients can be added to lip products (to reduce the appearance of lines and wrinkles on the lips) and nail care formulations such as "ridge filling basecoats". While use of such materials provide significant "instant gratification" by changing surface appearances, longer-term benefits may be produced by incorporating hydrogen-bonding polymers to attract and bind moisture to the stratum corneum.

Gloss Reduction

Color cosmetics products are designed to deposit pigmented films onto various substrates on the human body (i.e. eyelids, eyelashes, face, lips and nails). Such films have finishes that are glossy, matte or somewhere in between. For certain types of products (e.g. lip glosses and nail lacquers) a high gloss film usually is preferred. Glossy lips appear moist and fuller in size, while lustrous nails appear to be very highly refined. Dark-colored products such as eye liners and mascaras sometimes use glossy films to create a deeper, richer appearance. Some color cosmetic products have low gloss finishes due to very high pigment concentrations (e.g. eye shadows and lip liners).

Liquid foundation makeup formulations frequently are developed so that their films exhibit little to no luster when applied to facial skin. There are several reasons for this. Liquid foundation products originally were developed as more convenient and less messy alternatives to traditional powdered facial makeup products (i.e. loose and pressed powders). Because the appearance of facial gloss often is associated either with perspiration or an oily complexion, a primary objective of foundation makeup is shine control. A secondary benefit of a matte finish makeup product is minimization of superficial skin imperfections such as fine lines and wrinkles (*36*). This phenomenon sometimes is referred to as "optical blurring". Traditionally, inorganic materials such as clays and other silicates were used as "mattifying agents". They diminish the appearance of film gloss by scattering incident light in multiple directions. In recent years, polymeric materials such as polyurethane, polyester powders also have been used to control gloss (*38*). Although polymeric materials tend to be more costly than inorganic powders, polymeric powders offer some important advantages. Because these polymers are manufactured by "additive" rather than "extractive" processes, desired performance properties can be "dialed in" with greater specificity. Perhaps more importantly, while inorganic powders are derived from mineral sources that may contain traces of objectionable heavy metals, polymers can be manufactured to high degrees of purity, an important consideration for cosmetic products.

Pigment Surface Treatment

Colorants can be used with impunity by most industries, but color additives intended for use in food, drug and cosmetic products are regulated closely in the United States by the Food and Drug Administration ("FDA"), and by similar regulatory agencies in other global jurisdictions (*39*). Such colorants (both inorganic and organic) are approved for cosmetic use primarily on the basis of their toxicological safety as opposed to other functional properties. *Dyes* are organic colorants that can be *dissolved* in certain solvents, while pigments (both inorganic and organic) are insoluble in their vehicles and must be *dispersed* in order to make them useful in color cosmetics. Because a limited number of approved pigments must be dispersed into a chemically-diverse group of cosmetic formulations, pigment dispersion is critically important to cosmetic chemists. Both chemistry and chemical engineering are needed for successful preparation of acceptable pigment dispersions.

While pigments may be dispersed mainly by application of intense mechanical energy, it is more preferable to augment "brute force" with some "chemical finesse". This is accomplished by careful selection of the *pigment dispersion vehicle*, typically a liquid medium with which dry pigments are blended prior to mechanical energy. Polymers can provide some important benefits for pigment dispersions. Appropriate film former(s) and/or polymeric plasticizer(s) can be combined and dissolved in appropriate solvent(s) to form chemically-favorable dispersion vehicles. For example, nitrocellulose and toluene sulfonamide/epoxy resin can be dissolved into n-butyl acetate to form a suitable pigment dispersion vehicle for nail lacquer formulations. Individual pigment particles also can be *surface treated* with appropriate polymers to render them more readily dispersible in specific dispersion vehicles. For example, particles of titanium dioxide and iron oxides frequently are treated with very thin layers of dimethicone or other silicones to make their surfaces hydrophobic (*40*). Such treated pigments are more readily dispersible in various organic dispersion vehicles than their untreated counterparts. Surface treatment of pigments also can confer improved pigment suspension properties, an important consideration when formulating heavily pigmented products such as liquid foundation makeup. Hydrophobically modified pigments can enhance product application, spreading and wear properties, as they improve water-resistance of the products into which they are dispersed.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Ingredient Encapsulation

Modern color cosmetic formulations are a sophisticated combination of art and science. With thousands of raw ingredients from which to choose and infinitely many ways in which to combine them, contemporary products can be daunting to create and manufacture. Although cosmetic product chemistry might seem categorically mild, formulators are required to blend chemically-diverse materials while ensuring a high degree of safety, aesthetics and consumer value. Fortunately, advanced technologies are available to help the chemist achieve his or her desired objectives.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

It is possible to protect sensitive raw ingredients from hostile chemical environments by encapsulating them inside polymeric capsules. There are some parallels to this tactic in other consumer product industries. A popular brand of candy uses a hard confectionary shell to protect heat-labile milk chocolate from melting (thus the tag line, “Melts in your mouth, not in your hand”). “Carbonless” business forms are coated with inks encapsulated in polymeric capsules prepared from urea-formaldehyde resins; these capsules release ink upon application of mechanical pressure from a ballpoint pen.

The phrase “timed release of active ingredients” may seem to have been borrowed from the pharmaceutical industry, but it also is relevant to the cosmetics industry. While the term “active ingredient” has very specific implications in pharmacy, one or more “active ingredients” may be added to certain cosmetic formulations to produce specific performance benefits. Entrapment can be used to provide substantiation for certain marketing-driven raw ingredient claims. In this scenario, vitamins or botanical extracts known to be beneficial to the skin can be entrapped into a polymeric matrix, then released slowly over time (*41*). It is important to emphasize that it is not appropriate to use entrapment for all cosmetic active ingredients. Over-the-counter (“OTC”) drug products are regulated very closely by FDA in the U.S. and by similar regulatory agencies in other countries. OTC products contain active ingredients specified in detailed formal “monographs” issued by regulatory agencies.

Such active ingredients must be handled carefully in order to guarantee their required biological activity. Certain biopolymers can be used to promote timed release of active ingredients. *Cyclodextrins* are cyclic pentapolymers of glucose. They form hollow “open cup” structures that can be “filled” with a payload ingredient (e.g. flavor, fragrance, fatty esters, etc.). Manufacture of encapsulated raw ingredients generally is performed by third-party specialty suppliers having the necessary expertise and process equipment to produce acceptable end products. Generally, “payload” ingredients must not act as solvents for the capsules in which they will be packaged, thus cross-linked polymers are valuable for such applications. Chemical and physical properties of encapsulated ingredients must be tailored to the characteristic of their final products: encapsulates should have proper hardness, particle size and shape, solubility and surface chemistry.

Color Development

As mentioned previously, color additives intended for use in food, drug and cosmetic products are regulated closely in the United States by the Food and Drug Administration (“FDA”), and by similar regulatory agencies in other global jurisdictions. Traditional organic pigments are complex aromatic compounds; while so-called “effect pigments” are based on the chemistry of various metal oxides and mica.

Dry pigments intended for use in nail lacquer formulations must be dispersed into nitrocellulose/plasticizer mixtures under high shear using specialized equipment. This process is termed “chipping”, and is performed by special manufacturers trained to deal with the dangerous explosion and fire hazards presented by nitrocellulose (*3*). Mixed cellulose esters can be used instead of nitrocellulose to produce safer dispersions.

Gloss Enhancement

The term “gloss” refers to the ability of a surface to produce specular reflection. This property is highly prized in the color cosmetics industry because it connotes moisture, refinement and luxury. Moist lips also tend to appear larger and plumper than dry lips. Wet eyelashes appear fuller and darker, thus “wet-look” mascaras are valuable products. Matte finish nail lacquers are not mainstream products because to many users they appear dull and worn. Classic gloss promoting cosmetic ingredients are lipophilic compounds such as oils of animal, vegetable, mineral and synthetic origin (e.g. lanolin, castor oil, mineral oil and isopropyl myristate, respectively) (*42*). These materials are used extensively in lip products, an application where high gloss is important. Not surprisingly, gloss also is promoted by a wide range of cosmetically acceptable polymers.

Hydrocarbon polymers such as hydrogenated polycyclopentadiene and polydecene exhibit outstanding luster. Nitrocelllulose, styrene/acrylates copolymers, and phenyl silicones all confer significant gloss to a variety of products (*43*). Thermoplastic polyester resins (e.g. adipic acid/neopentyl glycol/trimellitic anhydride copolymer) are glossy secondary film formers in nail lacquers (*13*). Specialized proprietary “bio-polyesters” (e.g. sucrose polycottonseedate, the product of exhaustive esterification of sucrose by cottonseed oil fatty acid) are used in lip products (*44*). Aromatic groups (e.g. phenyl, benzyl) have inherently high indices of refraction, thus polymers rich in styrene monomer content (e.g. styrene/acrylates copolymers) are glossy film formers.

Odor/Flavor Control

Color cosmetics have very attractive visual impact, but they also must satisfy tactile, olfactive and sometimes gustatory aesthetic requirements. For example, fragrances are important for providing aesthetic enhancement as well as malodor control (*45*). Flavoring agents and artificial sweeteners often are added to lip product formulations to enhance taste. Unfortunately, fragrances and flavors are complex mixtures of volatile compounds that evaporate readily, making them challenging to use during manufacturing and storage. Many cosmetic products encounter significant amounts of heat during manufacturing and filling, thus preventing fragrance loss is an important consideration. Entrapment of fragrance can be a desirable tactic in such situations. Fragrance oils can be mixed with reactive monomers (e.g. acrylate monomers) then become “entrapped” upon formation of the polymer. In this situation, the polymer serves as a “fixative” by delaying release of entrapped fragrance oils. Cyclodextrins perform similar functions. “Loaded” cyclodextrins can deliver fragrance oils over time, while “empty” cyclodextrins can be added to products to scavenge malodors (*46*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Polymers and Color Cosmetics: Formulation Guidelines

As with all chemicals, polymers must be selected thoughtfully and handled with care throughout the new product development process. Many thousands of cosmetic chemicals are available to formulators of color cosmetic products, thus raw ingredient selection is not a trivial matter. The logical first step is to identify the intended biological substrate(s) to which the product will be applied: eye, face, lip and/or nail. The next task is to determine the physical form of the product (i.e. liquid or solid) and its desired performance attributes (e.g. easy application, long wear, one-coat color deposition, water resistance etc.). Finally, the proposed package must be considered: stick, tube, bottle, jar, pump, etc.). Implicit in these considerations is whether one or more polymers are required to help achieve formulation objectives. In some instances, use of time-honored non-polymeric raw ingredients may be adequate; this is particularly true for many “natural” cosmetic products. On the other hand, as demonstrated previously in this chapter, development of modern, high-performance color cosmetic products typically requires use of polymers to accomplish demanding tasks. When the use of polymers is contemplated, it is necessary to consider the following general factors:

Formulation Type and Characteristics

At the outset, it must be determined what specific physical form the new product must have in order to meet overall performance objectives. Color cosmetic products can be solids (e.g. lipsticks), semi-solids (e.g. lip gloss gels), liquids (e.g. nail lacquers) or aerosols (e.g. aerosol mousse foundation makeup). Once the basic product form has been determined, it is necessary to evaluate the various types of chemical formulations that might be used to create the desired end product. In many instances, the type of chemistry that ultimately will be used will be dictated by product history, corporate preferences or a formulator’s technical acumen. Generally, it must be determined whether the base formula will be hydrophilic or hydrophobic, and if the desired performance of the final product requires formation of relatively durable films on the skin, hair or nails. This decision helps determine which types of polymers might be added to influence product aesthetics and performance, especially the type and degree of required structure modification and/or film formation. For example, in hydrophobic formulations such as a lip gloss, incorporation of a hydrocarbon polymer (e.g. hydrogenated polydecene) would be appropriate for enhancement of adhesion, gloss and water-resistance (*11*). Similarly, the structural integrity of a lipstick can be improved by addition of polyethylene or eicosene/vinyl pyrrolidone copolymer to augment structure-building waxes such as carnauba. For high performance lip formulations, silicone resins (e.g. trimethysiloxysilicate) dissolved in a cosmetically-acceptable volatile hydrocarbon solvent (e.g. isododecane) help promote strong skin adhesion and transfer-resistance (*8–10*).

If a water-based formulation is desired, it must be determined if the product warrants use of a more complex type of formulation (e.g. an emulsion, a solution or a suspension). An aqueous suspension product such as a tinted cheek gel

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

contains large amounts of water, thus it can be thickened with a hydrophilic polymer such as polyacrylic acid or PEG-3M. If a product must be an emulsion, the type of emulsion system must be determined: oil-in-water (O/W), water-in-oil (W/O) or mixed. For example, liquid foundation makeup products requiring a light skin feel might use an O/W emulsion base, and a hydrophilic polymer such as vinyl pyrrolidone homopolymer can be added to build viscosity and form a water soluble film. Conversely, a waterproof mascara product requires hydrophobic films produced by W/O emulsions. In this application, certain hydrocarbon resins (dissolved in cosmetically-approved light petroleum distillate solvents) could prove useful for their adhesion and durable film formation attributes.

Solvent Selection

When preliminary formulation type and characteristics have been determined, the next major consideration is selection of an appropriate solvent system. In aqueous systems, water is the primary solvent, but addition of surfactants or coupling agents may be useful if one or more hydrophobic raw ingredients need to be incorporated. In some instances, small amounts of ethanol or isopropanol may be added to enhance the solvent power of water. In anhydrous systems, it is necessary to determine which polymers must be dissolved. Modern anhydrous color cosmetic formulations can use inorganic and/or organic solvent systems. Inorganic solvents are “volatile silicones” (e.g. trisiloxane, cyclopentasiloxane and low molecular weight dimethicone) commonly used to dissolve various silicone polymers (e.g. high molecular weight dimethicone etc.). These solvents are virtually odor-free and have a dry feeling when applied to skin surfaces. Evaporation rates can be adjusted by blending silicones of different boiling points.

Organic solvents vary considerably according to specific formulation requirements. Volatile hydrocarbon solvents (e.g. C7-C15 isoparaffins, petroleum distillates, isododecane, isohexadecane) can dissolve a variety of polymers (e.g. silicone resins, rosin esters, styrene/acrylate copolymers) that are useful for enhancing adhesion, hydrophobicity and transfer-resistance. Such volatile hydrocarbons frequently are used in high performance lipstick, mascara and foundation makeup formulations and therefore must be free of residual aromatic solvents. The broad category termed “oxygenated solvents” includes a variety of compounds having one or more oxygen-containing functional groups (e.g. carbonyl, ester, ether and hydroxyl). Examples of oxygenated solvents include alcohols (e.g. ethanol, isopropanol), ethers (e.g. PEG), esters (e.g. n-butyl acetate), glycols (e.g. butylene glycol), glycol ethers (e.g. dipropylene glycol mono-methyl ether), ketones (e.g. acetone) and organic carbonates (e.g. propylene carbonate). Many solvents have harsh odors and may present significant fire hazards, thus they must be handled with care. Silicone solvents generally are not irritating, but some hydrocarbons and oxygenated solvents can be harsh on the skin, therefore care must be exercised when contemplating their use in color cosmetic formulations. Nail lacquer formulations are not applied directly on skin, and can use most oxygenated solvents with impunity. With the exception of ethanol and some glycols, most oxygenated solvents see limited use in color cosmetics.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Packaging Design

A favorite slogan of industrial designers is, "Form follows function", which also is very applicable to design of packages for color cosmetic formulations. Perhaps an even more relevant expression would be, "Begin with the end in mind." Many conventional cosmetic containers are incapable of preventing evaporation of volatile solvents. More importantly, some cosmetic applicators and packages are constructed from polymers that can be attacked by certain solvents, causing package damage and eventual loss of product integrity. When the use of any volatile solvent (including water) is contemplated, it is absolutely imperative that package design engineers be informed immediately. Modern cosmetic packages frequently incorporate various "hermetic sealing" devices to prevent undesired solvent evaporation.

Manufacturing Considerations

Many color cosmetic formulations involve manufacturing and filling processes requiring application of heat. When considering the use of polymers in color cosmetic formulations, it is important to determine if process heating equipment capable of achieving required melting temperatures is available for use. More importantly, if use of volatile solvents is contemplated, it is very important to ascertain that process equipment can be sealed to prevent evaporative losses during processing at elevated temperatures. If flammable solvents must be used, electrically-powered process equipment and surrounding devices (e.g. lights, telephones, laboratory testing equipment, forklifts, fans, etc.) must be specially designed to prevent ignition of hazardous atmospheres: such installations are termed "explosion proof" ("XP"). Additionally, appropriate fire suppression equipment must be installed and maintained at locations where flammable solvents are stored and handled.

Economic Constraints

While use of polymers and solvents can facilitate the creation of numerous high value color cosmetic products, such raw ingredients sometimes may contribute to elevated costs of goods. This is not unexpected, given that synthetic polymers are "value added" raw ingredients and volatile solvents mandate the use of sophisticated packaging and processing techniques. As with all other business decisions, it is necessary to perform risk versus benefit analyses to determine if the potential benefits of polymer use outweigh their perceived disadvantages.

INCI Nomenclature

From a regulatory standpoint, it is a global requirement that all raw ingredients used in cosmetic formulations be given an "INCI name" (INCI = **I**nternational **N**omenclature of **C**osmetic **I**ngredients). The conferral of an approved INCI name on a raw ingredient does *not* indicate the raw ingredient is *approved* for use in cosmetic products. Rather, an INCI name is a formal descriptor that must be used for mandatory ingredient labeling purposes should that raw ingredient ultimately be used in a final cosmetic product. Obtaining an INCI name for a raw ingredient is a process that is neither complex nor costly. Any manufacturer planning to market a polymer or other raw ingredient to the cosmetic industry should contact the Personal Care Product Council to obtain detailed information regarding the INCI registration process (*47*).

Summary

Color cosmetic formulations have evolved considerably during the last 30 years. Time honored product formulations focused primarily on attractive appearance and pleasing textures. In today's highly competitive global marketplace, color cosmetic formulators simply cannot depend on advanced pigment technologies to achieve significant commercial success. Cosmetic consumers have become increasingly more sophisticated, and they demand multi-benefit formulations in every product category. In response to such market-driven challenges, the performance attributes of color cosmetic formulations have improved steadily and impressively. Products have become easier, safer, more convenient to use than ever. They also offer the modern consumer a greater degree of choice and a higher level of value for the money.

The products of today arguably are the very best products the cosmetic pigment industry has created, yet in today's marketplace novel aesthetics cannot "carry the day" alone. Formulation technologies must keep pace with demand for constant innovation. In light of the information presented in this chapter, it is not unreasonable to assert that modern, high performance color cosmetics simply would not exist without the judicious use of polymers. Ironically, some contemporary cosmetic products are marketed under an "all natural" banner. Many such products exploit the unfounded fear of chemicals held by some consumers, and therefore they revert back to unsophisticated formulation technologies. These are best described as "niche" products. They generally are shunned by mainstream consumers, who prefer the level of performance that simply cannot be achieved by products relying mostly on natural raw ingredients. Clearly, the futures of polymer science and cosmetic science will remained closely intertwined, as chemists from both disciplines continue to heed Henry Kaiser's old adage: "*Find a need and fill it*."

References

1. http://www.scconline.org/website/about_scc/index_about.shtml.
2. Butuc, G., Morrison, D. S. *Surfactants In Personal Care Products and Decorative Cosmetics*, 3rd ed.; Rhein, L. D, Olenick, A., Schlossman, M., Somasundaran, P., Ed.; Surfactant Science Series' CRC Press: Boca Raton, FL, 2007; Vol. 135, 341−355.
3. *Nail Lacquer Technology*; Patil, A. A., Sandewicz, R. W., Eds.; Monograph No. 6; Society of Cosmetic Chemists: New York, 1997.
4. Patil, A. A. *Household Pers. Care Today* **2008**, *1*, 48–50.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch002

5. Shah, A. N. U.S. Patent 7,989,002, 2011.
6. Bobka, E. U.S. Patent 8,246,939, 2012.
7. Klempsch, H. *The Analytical Chemistry of Silicones*; Smith, A., Ed.; Wiley: New York, 1991; Vol. 112, pp 117−132.
8. Brieva, H. U.S. Patent 5,800,816, 1998.
9. Brieva, H. U.S. Patent 7,160,550, 2007.
10. Mateu, J. R. U.S. Patent 7,682,605, 2010.
11. Scancarella, N. D. U.S. Patent 20020159960, 2002.
12. Kaori, S. U.S. Patent 20120237467, 2012.
13. Remz, H. M. *Rheological Properties of Cosmetics and Toiletries*; Laba, D., Ed.; Cosmetic Science and Technology Series; Marcel Dekker, Inc.: New York, 1993; Vol. 13, pp 153−221.
14. de La Poterie; V. U.S. Patent 7,351,405, 2008.
15. Kumar, K. U.S. Patent 5,468,477, 1995.
16. Garbe, J. E. U.S. Patent 5,209,928, 1993.
17. Calello, J. F. U.S. Patent 6,033,650, 2000.
18. Calello, J. F. U.S. Patent 5,849,275, 1998.
19. Suzuki, K. U.S. Patent 5.061.481, 1991.
20. Wilkinson, J., Moore, R. *Harry's Cosmetology*, 7th ed.; Chemical Publishing: Revere, MA, 1962; pp 516−532.
21. Wing, H. *Nail Preparations in Chemistry and Manufacture of Cosmetics*, 2nd ed.; de Navarre, M. G., Ed.;Continental Press: Orland, FL, 1975; Vol. 4, pp 983−1010.
22. (a) Dieterick, D.; Reiff, H. *Adv. Urethane Sci. Technol.* **1976**, *4*, 112. (b) Dieterick, H. *Angew. Makromol. Chem.* **1972**, *26*, 85.
23. Morlacchi, S. U.S. Patent 8,394,890, 2013.
24. de la Poterie, V. U.S. Patent 6,238,679, 2001.
25. Collin, N. U.S. Patent 6,482,400, 2002.
26. Castrogiovanni, A. U.S. Patent 5,505,937,1996.
27. Satoshi, K. U.S. Patent 4,983,388 1989.
28. Krenceski, M. A.; Johnson, J. F. *Polym. Eng. Sci.* **1989**, *29*, 36–43.
29. Blank, I. H. *The Chemistry and Manufacture of Cosmetics*, 2nd ed.; de Navarre, M. G., Ed.; Continental Press: Orland, FL, 1975; Vol. 3, pp 15−24.
30. *Code of Federal Regulations, 21 CFR Part 347 Skin Protectant Drug Products for Over-the-Counter Human Use*; Final Monograph; (see: http://www.gpo.gov/fdsys/pkg/CFR-2006-title21-vol1/pdf/CFR-2006-title21-vol1.pdf).
31. Wickett, R. P., Rhein, L. D., Babajanyan S. *Surfactants In Personal Care Products and Decorative Cosmetics*, 3rd ed.; Rhein, L. D, Olenick, A., Schlossman, M., Somasundaran, P., Eds.; Surfactant Science Series; CRC Press: Boca Raton, FL, 2007; Vol. 135, pp 57−93.
32. Lochhead, R. Y.; Fron, W. R. Encyclopedia of Polymers and Thickeners for Cosmetics. *Cosmet. Toiletries* **1993**, 108–122.
33. O'Lenick, T., Bosmann, D. C. *The Chemistry and Manufacture of Cosmetics*, 4th ed.; Schlossman, M. L., Ed.; Allured books: Carol Stream, IL, 2009; Vol. 2, pp 523−538.
34. Narebski, M. U.S. Patent .8,211,416, 2012.

35. Clarke, T. M. *Rheological Properties of Cosmetics and Toiletries*; Laba, D., Ed.; Cosmetic Science and Technology Series; Marcel Dekker, Inc.: New York, 1993; Vol. 13, pp 55−152.
36. Hollenberg, J. C.; Bosmann, D. C. *The Chemistry and Manufacture of Cosmetics*, 4th ed.; Schlossman, M. L., Ed.; Allured books: Carol Stream, IL, 2009; Vol. 2, pp 501−521.
37. Jones, C. E. *Cosmet. Toiletries* **2002**, *117*, 49–60.
38. Sandewicz, I. M. U.S. Patent 20070243220, 2007.
39. http://www.fda.gov/ForIndustry/ColorAdditives/ColorAdditivesinSpecificProducts/InCosmetics/ucm110032.htm.
40. Socci, R. L. U.S. Patent 4,832,944, 1989.
41. Peppas, L. B. *Polymeric Delivery System: Properties and Applications*; El-Nokaly, M. A., Piatt, D. M., Charpentter, B. A., Eds.; ACS Symposium Series 520, Wiley: New York, 1993; p 42.
42. http://www.meadowbrookglitter.com/hiband/cosmetic.html.
43. http://www.dayglo.com/fileshare/tech/DermaGlo-TB-2012-04-24-Email.pdf.
44. Sandewicz, R.; Finkenaur, G. *The Chemistry and Manufacture of Cosmetics*, 4th ed.; Schlossman, M. L., Ed.; Allured books: Carol Stream, IL, 2009; Vol. 2, pp 443−474.
45. Patil, A. A. U.S. Patent 20060228314, 2006.
46. Dreja, M. U.S. Patent 8,399,395, 2013.
47. www.personalcarecouncil.org.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

Chapter 3

Organo Functional Silicones in Personal Care

Tony O'Lenick[*,1] **and Thomas O'Lenick**[2]

[1]**Siltech L.L.C., 2170 Luke Edwards Road, Dacula, Georgia 30019**
[2]**SurfaTech Corporation, 1625 Lakes Parkway, Suite N,**
Lawrenceville, Georgia 30043
[*]**E-mail: tolenick@mindspring.com. Phone: (678) 442-0210.**

Abstract

Silicone compounds have been known since the 1860s; they have been commercialized since the 1940s with the pioneering work of Rochow; and now are present in almost every category of personal care formulation. The continued development of silicone compounds and efficiently applying them to the personal care market requires the use of amphiphilic silicones, that is silicones with two or more groups that have different solubilites (i.e. hydrophobic and hydrophilic). The amphiphilc nature of these silicone polymers makes them surface active or surfactant silicones. Silicone compounds that have been organo-functionalized can be made to offer the formulator both water-soluble and oil soluble materials.

Silicone Compounds

Silicone first entered the cosmetic market in the 1950s as a skin protectant (*1*). Silicone polymers have enjoyed a tremendous growth in popularity in personal care products. Simple silicone fluids are used in a wide variety of products. Low molecular weight cyclic compounds, most commonly cyclomethicone (D5), have been used in shampoos to reduce drying time (*2*), anti-perspirants as carriers for aluminum salts and actives, and in sun care products to improve spread (*3–5*). High molecular weight silicones or gums have been used in coaservate shampoos. Over the last decade silicone compounds have been employed in more and more product classes and are too numerous to mention here. Garaud published a figure that best shows the evolution of silicone products in the cosmetic field (*6*). The development has gone from very general non-sophisticated applications like defoaming in the 1950s, to more specific structure specific properties, provided by

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

organo-functional products like conditioning (1970s), aesthetic modifiers (1980s), and finally SPF enhancement and transfer resistance. Along with this shifting of product function, there have been a dramatic shifting in the type of silicone used. The products used in personal care applications in the early days of the market were primarily if not exclusively fluids and cyclics. As the formulator became more sophisticated, driven by increased consumer expectations, a shift to lower concentrations of very specialized high value organo-functional silicone polymers occurred. This has offered expanded usage.

The reason for this expanded usage is two-fold, first new advancements in silicone chemistry has provided an ever-increasing number of new compounds, which allows for their incorporation into different formulation types. Secondly, the formulator has learned how to incorporate these materials efficiently into formulation.

One of the most important things to understand when studying silicones is their unique solubility. Anyone who has taken a chemistry class knows the two major solubilities: hydrophilic or water loving and hydrophobic or water hating. While breaking solubilites down into two categories makes teaching chemistry easier, the real world isn't so simple. Silicones are not hydrophilic or hydrophobic in their simplest form. This introduces a new solubility, siliphilic or silicone loving and siliphobic or silicone hating. Dimethicones are known to possess exceptional hydrophobicity (*7*). When a drop of silicone fluid is added into water, the drop will migrate to the interface, to minimize contact with the water. If the concentration of silicone is increased, the two materials will form two distinct phases. Chemical modification can be made to the silicone to make the silicone water-soluble. Similar chemical modifications can be made to make the silicone soluble in non-polar solvents. The inclusions of oil soluble groups (alkyl silicones), or water soluble groups (dimethicone copolyols) allow the raw material manufacturer to overcome the solubility problem.

Why Silicone?

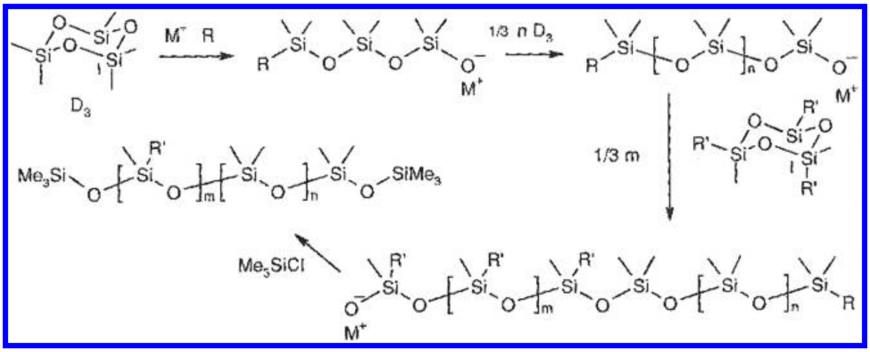
Silicones can be employed for several different reasons, the most important being their surface activity and tension. Silicones have a very flexible Si-O bond (ca. 145°) and low bending force constant for this linkage (*8*) that leads to their surface activity. The flexibility of the silicone polymer chain permits the rearrangement of the polymer backbone such that the methyl groups may orient themselves at an interface, thus allowing them to wet out (spread over) surfaces (*9*). This flexibility and branching allow for the silicone to take up a lot of free volume at the interface, hence a low surface tension and make them among the lowest-surface-energy compounds on earth (*7*). Silicone compounds typically have a surface tension of around 20 dynes/cm. Furthermore, silicones has an unique ability to lower the surface tension of water and oil at relatively low concentrations. When silicone is added into water (~ 72 dynes/cm), the surface tension drops drastically to under 30 dynes/cm where their fatty based surfactant counterpart will reduce the surface tension from in the 72 dynes/cm to 32 dynes/cm. Silicone surfactants can also be employed to lower the surface tension of oils. Oils have a surface tension in the 30 dynes/cm range. This reducing of surface tension applies to finished formulations as well. This provides a “light” or “dry” feel when compared to the same formulation without silicone.

Silicone compounds that have both silicone soluble groups and another group that in insoluble in silicone result in surface-active agents that provide unique functionality. Lower surface tension results in surface activity and makes the functionality of the silicone more effective at lower concentrations. It was noted in a concise perspective on silicones, 1993, the future of silicones is associated with more interesting, frequently functional, side chains (*10*). The rest of this chapter is dedicated to the “more interesting” silicones with functional side chains. The authors firmly believe that the use of high concentrations of silicone fluids and cyclics will be replaced in the formulation by greener, more sustainable organic materials augmented with very carefully chosen silicone polymers that modify the sensory attributes of the organics. Put another way, in comparing cosmetic formulations to gourmet meals, silicone polymers should be the spice, not the meat or potatoes.

Basic Types of Functional Silicones

Silicone fluids or “dimethicones” (MD_xM) in the absence of acid or base catalyst, are thermally and chemically stable. However, the incorporation of a reactive group (e.g. Si-H, $Si\text{-}CH{=}CH_2$) can provide an avenue to a wide variety of functional silicones. Until recently, there have been two categories of functionalized silicones: Terminal and Pendant or Comb. Recently O’Lenick Jr, introduced the world of silicones to a fourth category called Star Silicones (*8*). These star silicones have both terminal and pendant functional groups.

While the structure of the functional silicone is important, there are several other factors that must be considered when looking that the structure of a silicone polymer. The most common way to create silicones is by cationic or anionic ring opening reaction of a cyclic compound (most commonly D3, D4, D5 or D6). Below Scheme 1 (*9*) showing the anionic ring-opening polymerization.



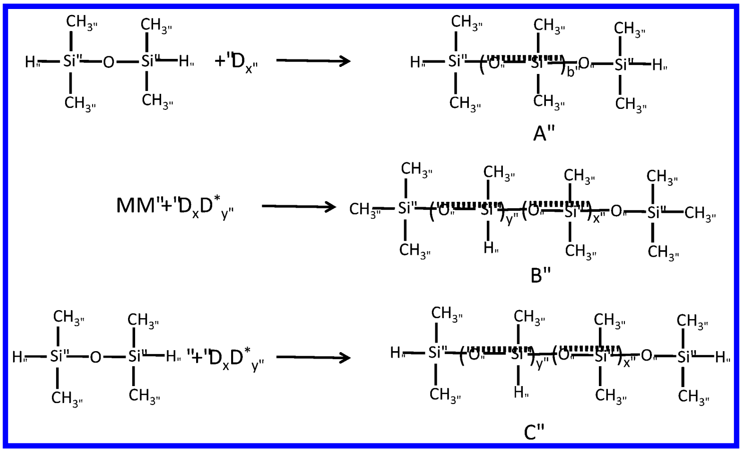
Scheme 1. (9) Shows the Cationic Ring-Opening Polymerization

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

To achieve a silicone that can be functionalized, the ring opening reaction should be conducted with a reactive starting material either M*M* or D_xD^*. Below is the Scheme 2 for functionalized silicones.



*Scheme 2. Synthetic route to **(A)** terminal, **(B)** Comb and **(C)** Star*

It is important to note that the production of silicones is an equilibrium reaction with linear silicone and cyclics. It is also possible to react two finish silicones, in the presence of catalyst, to rearrange into a silicone polymer with both un-reactive D units and reactive D* units. The ratio of D* to D units will have a drastic effect on the properties of the polymer. Some of the differences are discussed later on in the chapter.

Oil Soluble Silicones

As discussed in the section above, silicones contain hydrophobic methyl groups but aren’t soluble in all non-polar solvents. To improve the solubility in non-polar silicones are functionalized with alkyl groups. Alkyl silicones can be terminal, comb or star. The structure of the polymer determines the function of the polymer. Silicone surfactants can be employed to lower the surface tension of oils. Oils have a surface tension in the 30 dynes/cm range. This reducing of surface tension applies to finished formulations as well. This provides a “light” or “dry” feel when compared to the same formulation without silicone.

The number of “a” and “b” units in the formula above and the length of the alkyl group (the “R” structure) all are important in the ultimate properties of the silicone polymer produced. Unfortunately, the International Nomenclature of Cosmetic Ingredients (INCI) name is determined solely by the “R” group. Consequently, it does not help in the selection of a proper alkyl silicone polymer since the ratio of silicon molecules that contain only methyl groups to those that contain higher alkyl groups (i.e. organofunctional) materials is not specified.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

The length of the alkyl chain is the salient factor in determination of the melt point of the wax. Waxes based upon alkyl groups having 16 or less carbon atoms present are liquids at room temperature. At carbon lengths of 18 carbon atoms or above, the products become solid and the melt point increases as the carbon length goes up. Table 1 shows this.

Table 1. Melt point of alkyl silicones

Melt Point of Alkyl Silicones				
Product	***State RT***	***% Silicone***	***% Alkyl***	***Melt Point (%)***
Cetyl dimethicone	Liquid	50.2	49.8	-
Behenyl dimethicone	Solid	68.0	32.0	46
Behenyl dimethicone	Soft solid	45.0	55.0	37
C26 dimethicone	Solid	41.0	59.0	47
C26 dimethicone	Solid	69.0	31.0	43
C26 dimethicone	Solid	81.0	19.0	37
C32 dimethicone	Hard Solid	64.0	36.0	60

Table 2. Solublity of alkyl silicones in a variety of solvents

Solubility of Alkyl Silicones							
Product	***Water***	***Mineral oil***	***Mineral Spirits***	***Propylene Glycol***	***D5***	***350 visc Dimethicone***	***IPA***
Stearyl Dimethicone	I	S	S	I	D	I	I
Behenyl dimethicone	I	S	D	I	D	D	I
C26 dimethicone	I	S	S	I	D	D	I
Legend							
I = Insoluble			D = Dispersible		S = Soluble		

The ratio of silicon atoms bearing only methyl groups to those that bear higher alkyl organofunctionality (a measure of the percent alkyl to silicone) is a critical factor to functionality. It is the salient factor in determination of the hardness of the wax, and the degree of occlusivity of the wax. As the ratio of silicone to alkyl increases the wax becomes softer and less occlusive. A highly alkyl functionalized polymer will be occlusive, while a highly silicone functionalized material will be non-occlusive. The formulation implications to this finding is that polymers with the same INCI name will function differently in formulation, one giving a hydrophobic feeling serum and the other a much more hydrophilic feeling. A formulation with exactly the same label can feel very differently.

The solubility of alkyl silicones in a variety of solvents is shown in Table 2.

Liquid alkyl dimethicone are used in as additives for polar oils because of their improved solubility. Viscosity and skin feel can be varied easily by chemical modification of the silicone. Another very important observation made when studying alkyl silicone polymers in oils is that despite their being soluble (that is clear when added), the molecules function as surfactants. That is they first lower surface tension by increasing their concentration at the interface, then form micelles. Figure 1 shows what happens when behenyl dimethicone of added to soybean oil.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

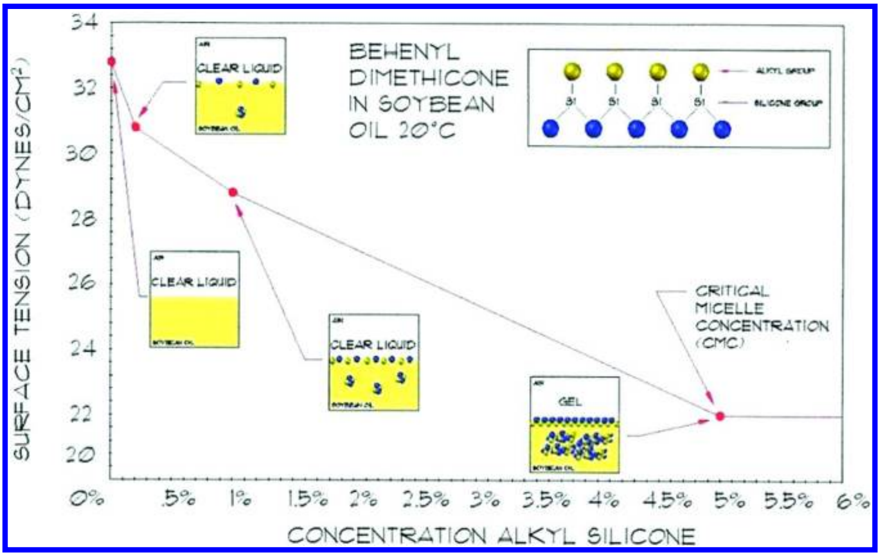
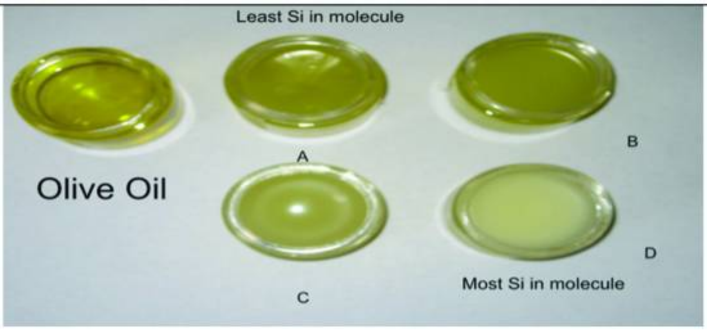


Figure 1. Critical micelle curve of behenyl dimethicone in soybean oil.

The reduction of surface tension makes the oil feel like silicone, in fact because of the low surface tension the oil mimics the feel of D5. If an alkyl silicone with a melting point above ambient is chosen, a physical gel will form upon cooling. The gel is reversible, liquefying upon heating and re-solidifying upon cooling. The gel is thixotrophic that is it liquefies under pressure.

The synthetic alteration of the ratio of silicon atoms bearing only methyl groups to those that bear higher alkyl organofunctionality in the molecule results in a change is clarity of the gel and also the occlusivity of the blend. Figure 2 shows this effect. The behenyl dimethicone added to the oil has differing amounts of silicone group present. There are some very significant trends that occur when one adds behenyl dimethicone to olive oil at 5 % wt / wt. When the percentage of alkyl in the alkyl dimethicone is high, the resulting gel is translucent, almost clear. As the amount of alkyl is reduced, the resulting 5% alkyl dimethicone / olive oil mixture will become more opaque.



Sample	**Silicone (% w/w)**	**Alkyl (% w/w)**
A	20	80
B	40	60
C	60	40
D	80	20

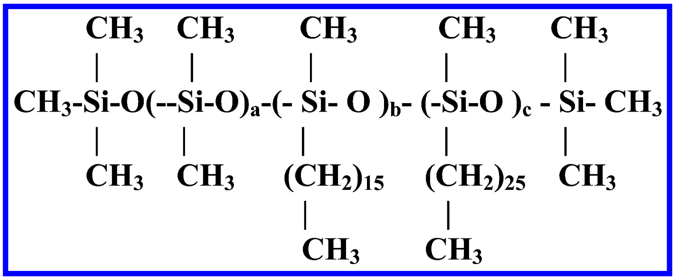
Figure 2. Behenyl alcohol in olive oil at 5.0 %.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

Multi Domain Silicones

The alkyl silicone surfactants that have been discussed until now have had a single alkyl group on the silicone backbone. A series of alkyl dimethicones have been developed which contain two different alkyl groups, one liquid at ambient temperatures and another that is solid at ambient temperatures. These polymers provide unique aesthetics to cosmetic formulations. One such polymer is shown in Figure 3.

The specific structures of the "R" groups of the solid and liquid domain have a profound effect upon the rehology and aesthetics of the product, Products of this family are thixotrophic solids that liquefy under pressure. The ability to define the polymers results in the ability to vary cushion and play time in formulations that contain this class of polymers.



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O(\text{--}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\underset{\underset{CH_3}{(CH_2)_{15}}}{\overset{CH_3}{Si}}\text{-}O)_b\text{-}(\text{-}\underset{\underset{CH_3}{(CH_2)_{25}}}{\overset{CH_3}{Si}}\text{-}O)_c\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Figure 3. Structure of a common multi-domain silicone.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

The differences between Multi Domain silicones and a “single domain silicone” are easy to ascertain by looking at the two products. The two polymers shown in the figure have exactly the same composition of C22 and C16, The first is a blend of two “single domain alkyl silicone polymers”, that is a blend of two silicone polymers, one containing all C22 pendant groups and the other polymer all C16 alkyl pendant groups. The blend of two polymers are then compared to a multi-domain alkyl silicone polymer having the two types of alkyl groups as pendant groups on the same polymer backbone.

Multi-domain silicone polymers behave in a similar manner as block co-polymers in that they can self-assemble (*11*). While these polymers aren’t block copolymers, they can self assemble into highly organized structures. When the multi-domain polymer is heated above its melt temperature (T_m), then allowed to cool to room temperature, the solid pendant groups start to “stick together” forming a domain. The solid domain forces the liquid pendant group out of its domain, since it is covalently bonded to the same polymer backbone; the liquid domain surrounds the solid domain. This leads to unique rehology. These domains produces a soft, thixotrophic wax. The thixotropic wax liquefies under pressure has a cushion effect, but has a short playtime. This means the material rubs out rapidly. If one compares a multi domain alkyl silicone polymer to a blend of alkyl silicone polymers having the two different alkyl groups on different molecules, it will become clear the two are very different. The multi-domain product will be clear to translucent and flow-able, while the blend will be a hard waxy solid. The blend will have a bimodal distribution having two different rather sharp melt points, while the multi-domain product will have a wide melting range and a wide distribution. Most importantly, the multi-domain will offer major differences in the rheology properties and the aesthetics in formulation. The multi-domain product has been referred to as vanishing petrolateum, having a significant cusion but a short play time.

To further study the difference in the two, photo microscopy was employed. As seen in Figure 4, the multi-domain silicone polymer is highly structured, while the blend of the two single domain silicone polymers is quite random and lack structure. It is this structure that accounts for the different functionality seen in the polymers. The INCI names also recognize the difference. The blend of the two single domain silicone molecules has the INCI name behenyl dimethicone and acetyl dimethicone, whilst the multi domain silicones have the INCI name benehyl / cetyl dimethicone.

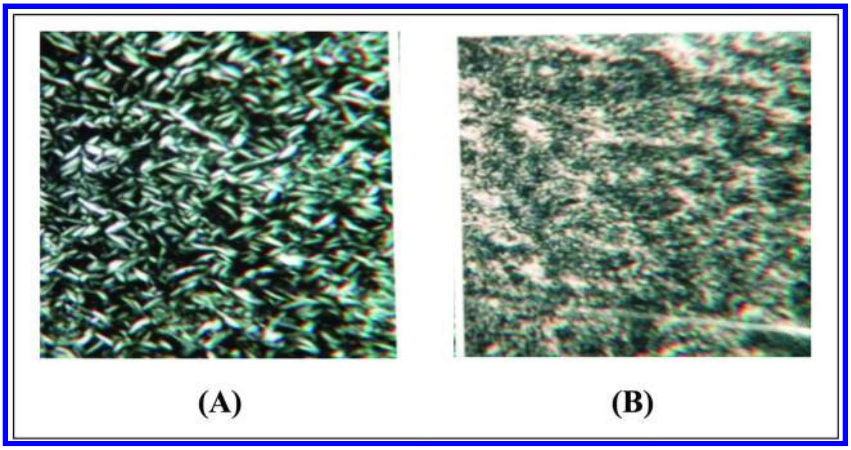


Figure 4. Photo microgram images of ***(A)*** *multi-domain polymer and* ***(B)*** *polymer blend.*

The Photo micrograms were prepared by Microtrace LLC, for Siltech LLC. Their results state: "[The polymer blend] is an opaque, waxy, white, crystalline solid at room temperature. Its color and solid phase structure are a direct result of the fact that it is composed entirely of colorless, interlocking crystals. These crystals melt at 56°C (132.8°F) when the solid becomes liquid. This transformation is entirely reversible. The multi-domain polymer, at room temperature, is a translucent, gel that flows under pressure. It is composed of two phases. The liquid phase is liquid at room temperature. The solid phase is crystalline and the relatively large, elongated crystals scatter light just enough to make the product translucent instead of white and opaque like the multi-domain or entirely transparent and colorless as would be the case if the crystals were absent. The crystalline phase melts entirely at 38°C (100.4°F) but recrystallizes when the temperature drops below this." It continues on to read "…the disappearance of most of the birefringent crystals in a thin film of the multi-domain when pressure is applied to the coverslip and their immediate reappearance once the pressure is released."

Multi Domain Properties

The ability to alter the feel of alkyl silicones by altering the ratio of the alkyl groups to each other, the ratio of silicone component, and the overall molecular weight allows the formulator to independently alter cushion and play-time. The terms cushion and playtime are commonly used to describe the feel of ingredients and formulations on the skin. If one places a compound or formulation on the index finger and rubs it on the forearm, both cushion and playtime can be evaluated.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

Cushion refers to the amount of compound that persists between the finger and forearm. That is the greater the "distance" between the finger and the forearm the greater the cushion. Honey has a great cushion. When tested in this manner there is a feeling of a great deal of material between finger and forearm. Water has little of no cushion. There is little "distance" between finger and forearm.

Playtime refers to the length of time cushion persists. If the cushion is felt for a long period of time, the playtime is said to be long. If the cushion collapses rapidly the playtime is said to be short.

This ability allows for the alteration of the feel of a variety of formulations including skin care, pigmented products and sun care products.

In most compounds the cushion and playtime are directly related. Honey has both a high cushion and high playtime. There are however materials that have a good cushion but rapidly collapse having a low playtime. Most important in this class are multi-domain alkyl silicone compounds having both liquid and solid portions in the same molecule. There are many applications in which in a high level of cushion, and a short playtime are desired. These include lipsticks, sun products and many lotions.

The inclusion of two different alkyl groups into an alkyl silicon polymer, one liquid and the other solid allow for a series of polymers that have different cushion and playtime. The ability to de-couple cushion and play time allows for the formulation of cosmetic products with very unique and tunable aesthetics. It is this type of alteration of polymers to provide a requested aesthetics to a formulation that will be the direction of future silicone polymer development.

Water Soluble Silicones

The ability to make organo-functional polymers that have a solubility in water and hydro-alcoholic formulations opens a new area of formulation possibilities for the cosmetic formulator.

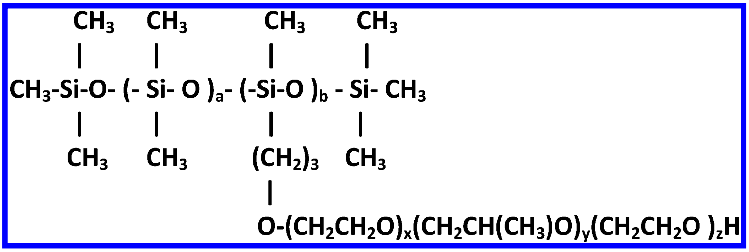
PEG/PPG dimethicone compounds are a class of silicones that have enhanced water solubility. They should be used in instances where they provide benefits. These benefits include (a) lowering of surface tension (into the range of 25 dynes/cm), (b) provide unique skin feel, (c) provide unique emulsification properties (especially in invert emulsions), (d) provide film formation, and (e) provide foaming of non-traditional formulations.

These properties are a direct result of the structure, but the structure needs to be carefully selected. PEG/PPG dimethicone polymers have increase polarity, by virtue of their polyoxyalkylene groups. It is important to note that these modifications are done by chemical reaction between a reactive silicone and a vinyl containing compound. A very common structure is shown in Figure 5.

As seen in Figure 5, there are several variables that can be modified to change the performance of the dimethicone copolyol (DMC) polymer. One of the most important is the ratio of a (silicone soluble portion) to b (water soluble portion) as well as the total number of a and b are both important to functionality. The higher the ratio of silicon atoms that have only methyl groups present (D units) in the molecule relative to those that have organofunctional groups (D* units) are less

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

water-soluble the product. Also, the molecular weight of the DMC Polymer can drastically change properties. The studies presented in this paper keep the ratio of D/D* constant.



$$\mathrm{CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}O\text{-}(\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}O)_a\text{-}(\text{-}\underset{\underset{\underset{O\text{-}(CH_2CH_2O)_x(CH_2CH(CH_3)O)_y(CH_2CH_2O)_zH}{|}}{\underset{(CH_2)_3}{|}}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}O)_b\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}CH_3}$$

Figure 5. Structure of PEG/PPG Dimethicone.

Surface Tension

When added into water at low concentrations, PEG/PPG dimethicone (DMC) migrates to the air/water interface. As more DMC is added into the water, the interface becomes saturated and a critical point is achieved. When additional DMC polymer is added, it cannot migrate to the interface, so they start to form micelles. This critical point where the interface is saturated and micelles start to form is called the critical micelle concentration (CMC). Critical micelle concentrations are determined by monitoring surface tension (*12*). It is well known that when one adds a surface-active material to water, the surface tension starts to decrease in a linear relationship with the amount of surfactant added. The moment the interface gets saturated, the surface tension stops decreasing and micelles form. Addition of more surface active agent does not decrease the surface tension.

The key to surface tension efficiency is the ability of a polymer to migrate to the interface and take up the maximum free volume on that interface. This maximization of free volume at the interface and its affinity for the interface makes the DMC extremely effective at lowering surface tension. This leads to DMC being used at very low concentrations to drastically change the properties of a solution. The molecular weight is a key concept in determining CMC. As the molecular weight increases, the CMC decreases. This is due in part to the fact that the surface can accommodate fewer “large molecules” than small molecules. The CMC of a DMC is a key property to be determined before using a specific DMC in formulation, this based upon the observation that if the DMC cannot get to the interface, it will not provide desired properties to the formulation. As will become clear subsequently, interaction with other raw materials in the formulation needs to be considered as well.

The surface tensions are related to the molecular weight of a series of PEG 8 dimethicone in which the ratio of silicone units to polyoxyalkylene units (a:b) are kept constant but increases. The results are shown in tabular form in Table 3 and in graphic form in Figure 6.

Table 3. Surface tension and molecular weight of a 0.5 wt % solution of PEG 8 dimethicone

Product	***Molecular Weight***	***Surface Tension (dynes/cm)***
A	607	21.0
B	808	21.9
C	1108	23.1
D	1610	24.8
E	2111	26.3

* Concentration is over the polymers CMC.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

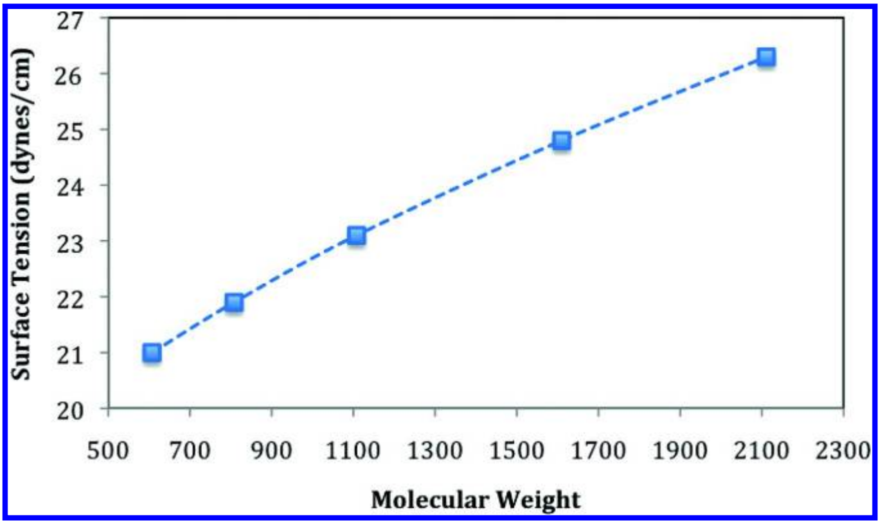


Figure 6. Molecular weight vs surface tension of a 0.5 wt % solution of PEG 8 Dimethicone.

The structure/function relationship is seen in these same compounds in both wetting times and eye irritation as shown below.

Wetting Properties as a Function of Molecular Weight

The term wetting, refers to how a material coats a surface. For example, if a water drop is placed onto a lotus leaf, the water will minimize the inter action with the leaf and have a high contact angle. If a good wetting agent is added either to the surface of the leave or in the water solution that same drop will spread out coating the surface of the leaf. In turn making the leaf "wet", this is where the term wetting comes from. Figure 7 shows and illustration of the Young's equation and how the contact angle is defined.

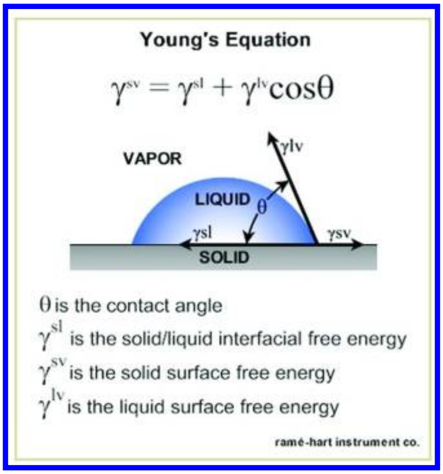


Figure 7. Contact angle illustration. Reproduced with permission from reference (13). Copyright 2013, ramé-hart instrument co. All rights reserved.

As seen in Figure 7, the contact angle is defined as the angle the water makes with the surface. In this illustration, a low contact angle ($\theta < 90$ °) means the surface is hydrophilic. Large contact angles ($\theta > 90$ °) leads to a surface that is hydrophobic.

Another measure of wetting is the time required for a standard skein of fiber, or of hair to drop in an aqueous solution. This type of wetting time is called Draves Wetting (ASTM D2281). The lower molecular weight DMC polymer has faster wetting times than their high molecular weight counterparts. The lower molecular weight polymers allow for more efficient packing efficiency and dynamics. The materials with lower molecular weight were extremely effective at the higher concentration of 1.0 % w. Their wetting speeds were almost instantaneous meaning it is controlled by the diffusion of the DMC polymer to the air/water interface. The interesting finding is that the wetting speed is lost slowly as the molecular weight is increased. The slope increases once one gets to a molecular weight over 2000. This implies that a rapid wetting conditioner can be prepared by proper selection of molecular weight. As the molecular weight of a polymer is increases, its ability to function in different capacities changes (table 4). This is due to hydrogen bonding and achieving lowest free energy.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

Table 4. Function of dimethicone copolyol vs molecular weight

Molecular Weight (Da)	*Function*
500	Wetting
2,500	Emulsification
10,000	Conditioning
50,000	Water Proofing

If the ratio of D to D* is held constant, the molecular weight of the polymers controls its wetting properties. As weight increases, the wetting ability decreases. Table 5 shows in tabular form the effect of molecular weight on wetting time and Figure 8 shows the same data in graphic form.

Table 5. Draves wetting of dimethicone copolyol with differing molecular weights

Sample	*M.W.*	*Wetting Time (Second)*
A	607	7.0
B	808	8.0
C	1108	10.7
D	1610	18.0
E	2111	256

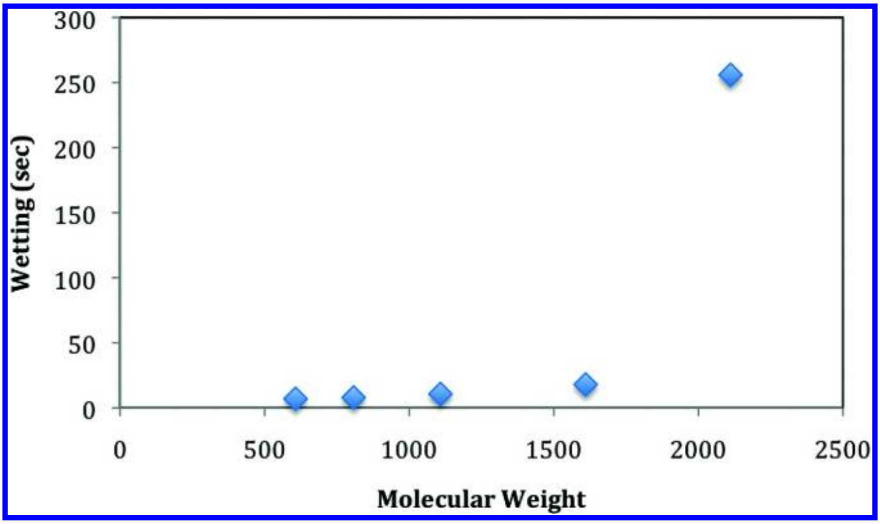


Figure 8. Wetting times of dimethicone copolyol with differing molecular weights.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

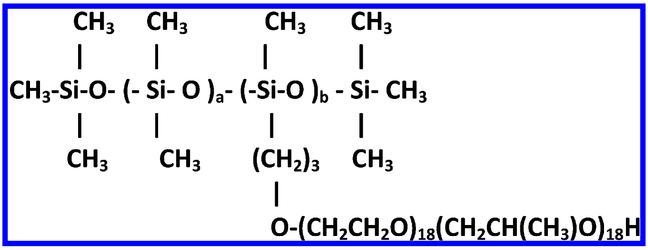
Foam

Ability to generate foam is an important functionality in any surfactant, including silicone surfactants. The ability to generate foam results from the balance of silicone portion to water soluble portion, which includes as an important variable the amount of PEG / PPG. The cylinder shake foam test data is shown in Table 6.

Table 6. Foam test for 1 % PEG 8 dimethicone

Sample	*M.W.*	*Immediate*	*3 Minutes*
A	607	90	62
B	808	90	63
C	1108	95	67
D	1610	90	62
E	2111	90	61

The above data (Table 6) indicates that changes to the PEG-8 dimethicone with the D/D* ratio evaluated has really no effect upon foam, either initial or after 3 minutes. A change was made to Sample E replacing the PEG 8 group with PEG 18/ PPG 18. This material was designated Sample F and is shown in Figure 9 below.



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-(-\underset{CH_3}{\overset{CH_3}{Si}}-O)_a-(-\underset{\underset{O-(CH_2CH_2O)_{18}(CH_2CH(CH_3)O)_{18}H}{(CH_2)_3}}{\overset{CH_3}{Si}}-O)_b-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

Figure 9. Structure of PEG 18/PPG 18 dimethicone.

Table 7 and 8 show that despite the PEG 18 /PPG 18 having a silicone backbone, the high level of alkoxylation results in a higher foaming, higher surface tension surfactant. This dispels the myth that al silicone surfactants have low surface tension. Some silicone surfactants have low surface tension, while others have fatty surfactant surface tension. The surface tension in water id determined by how the molecule orientates at the interface. If the PEG / PPG portion dominates the surface tension will be around 32 dynes/cm. If silicone dominates, the surface tension will be around 25 dynes/cm range.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

In formulation, the effect of adding the surfactant will also depend upon how the silicone surfactant interacts with other ingredients. This situation is even more complicated, but one can determine of the silicone functionality is effective by checking surface tension. If the surface tension is not reduced from around 32 dynes/cm by adding 1% silicone surfactant, the addition will have little likelihood of providing benefit. While surface tension lowering is a prerequisite of desirable surface active properties like spreadability, emulsification, and soft powdery feel, it is not true that surface tension lowering will provide the specific function specified. How a surfactant functions is structure dependant. Table 7 shows the foam properties and needs to be compared to Table 6. Table 8 shows surface tension of the two. Sample E functions like a silicone surfactant while Sample F functions like a standard fatty surfactant.

Table 7. Foam height of 1 % PEG 18 PPG 18 dimethicone

Sample	***M.W.***	***Immediate***	***3 Minutes***
F	7600	97	50

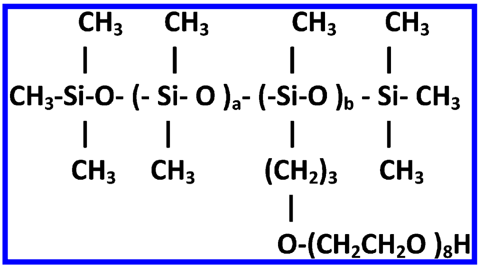
Table 8. Surface tension vs molecular weight

Sample	*Molecular Weight*	*Surface Tension (dynes/cm)*
E	211	26.3
F	7600	31.3

Star Silicones

Knowing that molecular weight as shown above has little effect upon foam properties when the D/D* is kept constant, and that inclusion of EO/PO did not improve foam, a new series of products have been made and patented (U.S. Patent 7,951,893 to O'Lenick et al, issued May 31, 2011). This class of compounds, referred to as Star Silicones, have unique properties and are a model useful in explaining the properties observed above. The structure of PEG 8 Dimethicone is shown in Figure 10.

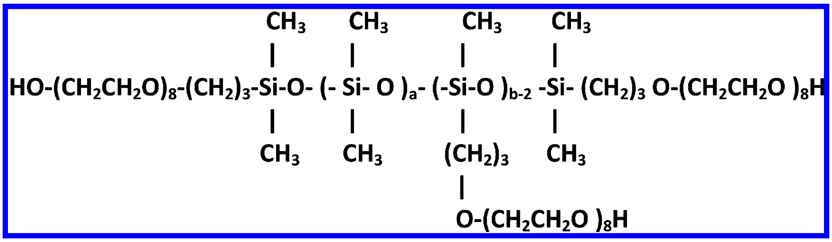
In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\underset{\underset{O\text{-}(CH_2CH_2O)_8H}{(CH_2)_3}}{\overset{CH_3}{Si}}\text{-}O)_b\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Figure 10. Structure of PEG-8 dimethicone.

The structure of the Star compound (Sample G) evaluated in shown in Figure 11.



$$HO\text{-}(CH_2CH_2O)_8\text{-}(CH_2)_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\underset{\underset{O\text{-}(CH_2CH_2O)_8H}{(CH_2)_3}}{\overset{CH_3}{Si}}\text{-}O)_{b\text{-}2}\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}(CH_2)_3O\text{-}(CH_2CH_2O)_8H$$

Figure 11. Structure of "star" PEG-8 dimethicone.

A comparison of he properties of Sample E (standard PEG8 dimethicone) and G (Star PEG 8 dimethicone) are shown below in Table 9.

Table 9. Properties of star silicones

Property	*Sample E*	*Sample G Star Product*
Surface Tension (0.5% Aqueous)	26.2	30.5
Foam Height (1% Aqueous)	90	185
Cloud Point °C)	58	89
Wetting time (seconds)	>200	>200

It is noteworthy that the surface tension of Sample G is more reminiscent of a fatty compound than of a silicone (30s dynes/cm not 20s dynes/cm). It is also quite significant that the foam level is more than twice the non-star version. Most

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

significantly is the cloud point, the temperature at which a 1% solution in water of the product becomes haze while heating. It is significantly higher. This is an indication that the water is tenaciously held to the EO group.

Eye Irritation as a Function of Molecular Weight

Not only do wetting properties depend upon molecular weight, but the molecular weight is also a controlling factor in eye irritation. Lower molecular weight polymers penetrate into the eye, causing more irritation to the eyes. As molecular weight increases, irritation decreases. However, there is a very definite molecular weight effect over which irritation becomes little or no problem as seen in Table 10.

Table 10. Draize primary ocular irritation scale

Moderately Irritating	25.1 – 50.0
Mildly Irritating	15.1 – 25.0
Minimally Irritating	2.6 – 15.0
Practically Non-Irritating	0.6 – 2.5
Non-Irritating	0.0 – 0.5

Table 11. Eye irritation of PEG-8 dimethicone

Sample	*M.W.*	*1 Day Irritation*	*7 Day Irritation*
A	607	28	4
B	808	13	2
C	1108	5	2
D	1610	4	0
E	2111	2	0

The data in Table 11 was generated on a series of PEG 8 dimethicone polymers with the same D to D* ratio, by increasing the total number of D and D* units. The eye irritation was run at 20% active and was evaluated over one and 7 days. The data is presented graphically in Figure 12.

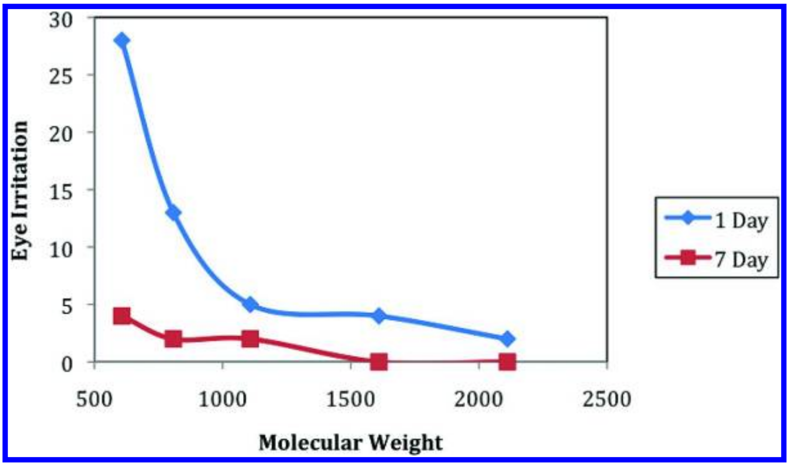


Figure 12. Eye irritation of PEG-8 dimethicone by molecular weight.

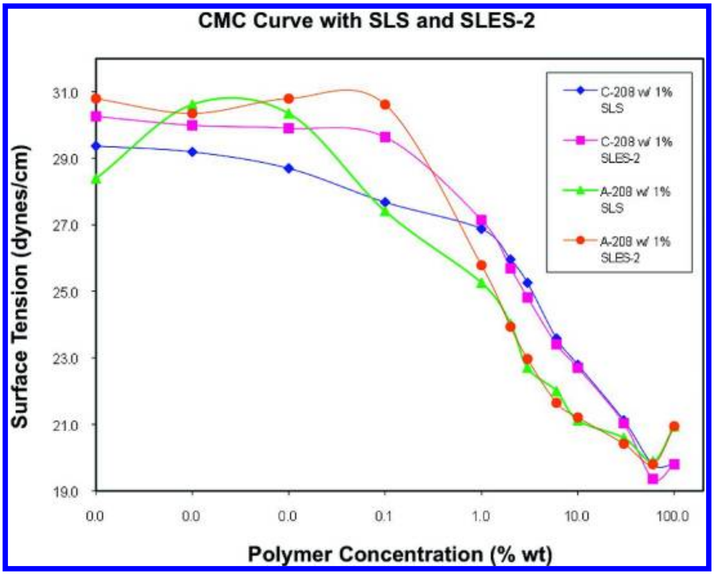


Figure 13. CMC curve with Sodium Lauryl Sulfate (SLS) and Sodium Lauryl Ether Sulfate (SLES-2).

Formulation Interactions

One of the most important factors facing the formulator of cosmetic products is how additives to formulations will interact with each other. This complication can include hydrophobic / hydrophilic interactions between ingredients, hydrogen bonding between ingredients, insolubility or limited solubility of ingredients,

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

micelluar interactions, just to name a few. This explains why there is a great deal of trouble for the formulator to adapt raw material supplier data on function of products in pure aqueous environment with data obtained in the real world. Figure 13 shows the effect of adding PEG-8 dimethicone into an aqueous solution of DI water. The graph is quite ordinary and looks like what one might expect for a CMC. Notice however that the surface tension is significantly lower than for fatty surfactants (i.e. below 30 dynes/ cm).

When the same PEG-8 dimethicone is added to a 1% solution of sodium lauryl sulfate, a completely different result is obtained. Figure 14 does not look like a CMC (critical micelle concentration) graph. This shows an interaction effect between the two surfactants as they compete for surface at the air water interface. While not a CMC graph in the classical sense, this graph and its shape are very enlightening as to the effectiveness of the silicone surfactant when added to the surfactant. Since there is no clear break point as is seen with the CMC graph, we created a new point so the effectiveness of the addition of a silicone surfactant to another surfactant vis-à-vis surface tension reduction can be determined. That term is RF_{50} and it is described below in Figure 14.

RF_{50} = the concentration of silicone surfactant added to reduce the surface tension to 25 dynes/cm

Figure 14. Definition of RF_{50} (13).

Table 12 shows the affect on RF_{50} that the addition of two different PEG-8 dimethicone molecules have on a 1% solution of two different sulfated fatty surfactants.

Table 12. RF50 values of PEG-8 dimethicone

Silicone Surfactant	***Molecular Weight***	***Co-Surfactant***	***RF_{50} (%)***
E	616.3	SLS	1.2
E	616.3	SLES-2	1.2
F	1,556.5	SLS	1.5
F	1,556.5	SLES-2	3.5

Silicone surfactant E and F both have the same ratio of groups that have only methyl groups around silicone and those with water soluble organo-functional groups present. The only difference is that the total number of each group is 2.5 times as many for F than E. They are homologues of each other.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

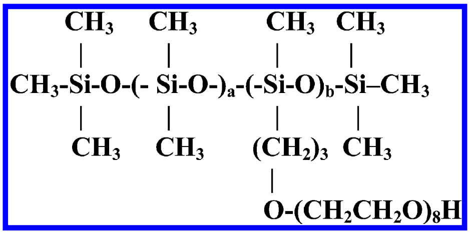
It is interesting to see from Table 12 that when SLS is used as a co-surfactant, the of the higher MW dimethicone copolyol has a RF_{50} of 1.5 %, while the lower molecular weight dimethicone copolyol has a RF_{50} of 1.2%. This shows that the low molecular weight polymer is more efficient at lowering the surface tension when a co-surfactant is involved. When comparing the RF_{50} in the samples containing Sodium Lauryl Ether Sulfate (SLES-2), the results are more dramatic. The RF_{50} for the low molecular weight PEG/PPG dimethicone polymer is 1.2, while the higher molecular weight PEG/PPG dimethicone polymer is 3.5 %. This is much more significant and is driven by the hydrogen bonding between the 2 moles of polyoxyalkylene on the SLES, making getting to the surface of the solution much harder for the larger “F” molecule.

How can this be applied when putting together a cosmetic formulation?

1. It will less efficient to use a higher molecular weight copolyol to lower surface tension effectively in SLES-2 based systems. It would be more efficient to use a lower molecular weight dimethicone copolyol.
2. The evaluation of surface tension reduction in formulation needs to be determined to maximize the effectiveness of formulations. There is simply no other alternative.

Delivery of the silicone to the surface (interface) is a prerequisite to obtaining consumer perceivable advantageous in formulations. The consumer can easily feel a difference in a formulation where there is a surface tension difference. As shown above, silicones when added into a surfactant solution with other surfactants effects the efficiency. Efficiency can be measured by RF_{50}.

Another mostly neglected structural variable that can dramatically change RF_{50} is the solubility of the silicone being added. Insoluble materials cause formulation problems, and too soluble materials result in the expensive silicone ingredient going down the drain. Products that form micro-emulsions (i.e. are thick and blue in color when added to water) are most efficient. Consider the structure in Figure 15.



$$CH_3\text{-}Si\text{-}O\text{-}(\text{-}Si\text{-}O\text{-})_a\text{-}(\text{-}Si\text{-}O)_b\text{-}Si\text{–}CH_3$$

Figure 15. Structure of PEG-8 dimethicone.

As the ratio of a D to D* changes, the water solubility will change. This is because D is a group that lowers water solubility, and D* is one that increases water solubility. A polymer with an D:D* ratio of 100:1 will be insoluble in water and one with an D:D* ratio of 1:100 will be very water soluble. Somewhere in between there will be a polymer that forms a microemulsion. It will be that polymer in the series that will offer the best effectiveness in solution. Using a wide range of D:D* ratios, the polymer can be determined which provides a microemulsion.

Water Tolerance (*13*)

In the previous section water-soluble silicones and silicone surfactants were discussed. In this section we will be discussing another important phenomenon to formulating chemist. To start our discussion we will have to first consider what happens when water is added into an anhydrous formulation. Most commonly, formulations will split or separate when water is added. Typically this is because the addition of water changes the Hydrophilic-Lipophilic Balance (HLB) of the system, thus decreasing the solubility of one of the components in the formulation. A new concept has emerged and it is called water tolerance. Basically, water tolerance is a measure of how much water can be added into a formulation before the formulation splits.

PEG/PPG Dimethicone polymers are in interesting polymer in the fact that they can be utilized to increase the water tolerance of a formulation. To test how the PEG/PPG dimethicone polymers effects the formulation, the water tolerance of the formulation has to be determined. The determination of water tolerance is based upon the fact that PEG/PPG dimethicone polymers are soluble in anhydrous isopropanol, independently of their solubility in water. Water can be added to the isopropanol solution until a haze develops. This haze signifies the water tolerance of the solution, this have allows for the concentration of water tolerated by the formulation and is called "Water Tolerance". A common procedure for determining the water tolerance is described in Table 13.

Table 13. Water tolerance test procedure for dimethicone copolyol

1. Dissolve 2.0 g of dimethicone copolyol in 100.0 g of Isopropanol.
2. Slowly titrate in deionized water into the isopropanol solution.
3. Record the number of grams of water needed to produce the first haze.

Figure 16 shows the water tolerance of specific silicone compounds. As the D:D* ratio (a:b ratio), i.e. the number of D units (hydrophobic) compared to the number of water soluble groups (D*), goes up the materials become more water insoluble and the water tolerance drops. What is very interesting and warrants consideration is the fact that 1 mole of propylene oxide will increase water tolerance as much as four moles of ethylene oxide does.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

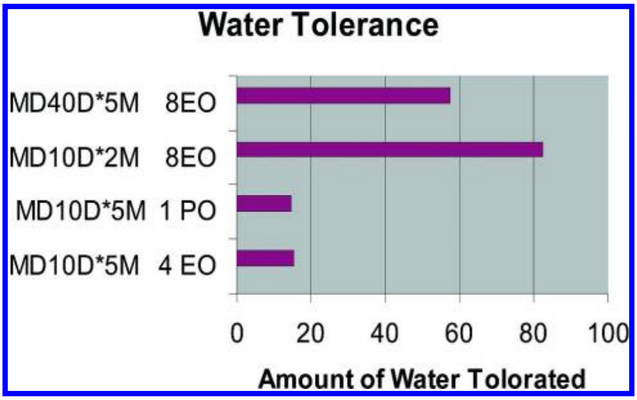


Figure 16. Water tolerance test for dimethicone copolyol.

Conclusion

Many of the most interesting properties of silicone compounds are a direct result of their amphiphilic nature. This is because amphiphilic silicone polymers lower surface tension; provide wetting, emulsification, foaming, and gellation depending upon the specific structure. What is most critical for the formulator is to consider interactions between all ingredients in the formulation. Since silicone polymers are almost always with other ingredients in the formulation, it is critically important to consider the interaction of the various components in formulations.

Many of the desirable properties silicone compounds provide to our formulations are dependant upon the silicone getting to the surface and providing the benefit consumers want. This means that successful formulations are those that overcome surface activity problems, interaction problems as well as the “standard” problems encountered in formulation. One of today’s emulsion products that provides a powdery feel from an oil literally has so many interactions, that one could do a thesis on them. Since there is never time to do that thesis, the formulation needs a series of steps that allow for rapid screening. These steps include (1) solubility (if the silicone is not soluble in the phase from which the formulator wants a benefit, there is no way to obtain that benefit); (2) surface activity (getting to the surface in preference to the other ingredients in the formulation); (3) lowering surface tension (which is a requirement to get any benefit from the surfactant) and (4) choosing a silicone that provides the desired affect at the lowest concentration. Solubility, surface activity and regular old fashion feeling of the aesthetics of a formulation will always offer the formulator the best methods to develop products. Happy Formulating!

References

1. DiSapio, A.; Fridd, P. *Int. J. Cosmet. Sci.* **1998**, *10*, 75–89.
2. Hill, M. P.; Fidd, P. GB2 074184, 1981.
3. DeBaecker, G.; Ghirardi, D. *Perfumes Cosmet.* **1993**.

4. Lanwet, M. *Cosmet. Toiletries* **1986**, *101* (2), 63–72.
5. DiSapio, A. *Cosmet. Toiletries* **1987**, *102* (3), 102–106.
6. Andriot, M.; Chao, S. H.; Colas, A.; Cray, S.; de Buyl, F.; DeGroot, J. V. , Jr.; Dupont, A.; Easton, T.; Garaud, J. L.; Gerlach, E.; Gubbels, F.; Jungk, M.; Leadley, S.; Lecomte, J. P.; Lenoble, B.; Meeks, R.; Mountney, A.; Shearer, G.; Stassen, S.; Stevens, C.; Thomas, X.; Wolf, A. T. Silicones in Industrial Applications. In *Inorganic Polymers*; Nova Science Publishers: Hauppauge, NY, 2007; available online at: http://www4.dowcorning.com/content/publishedlit/silicones_in_industrial_applications_internet_version_080325.pdf.
7. Owen, M. J. Siloxane Surface Activity. In *Silicon-Based Polymer Science: A Comprehensive Resource*; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990.
8. O'Lenick, T. U.S. Patent 7,956,151, June, 2011.
9. Grigoras, S.; Lane, T. H. *Conformation Analysis of Substituted Polysiloxanes Polymers*; American Chemical Society: Washington DC, 1990
10. White, J. W. Recent Achievements in Industrial Silicon Polymer Science. In *Progress in Organosilicon Chemistry*; Proceedings of the 10th International Symposium on Organosilicon Chemistry, Poznan, Poland, 1993.
11. Hadjichristidis, N.; Pispas, S.; Floudas, G. *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*; Wiley: New York, 2003
12. RSC website. http://www.rsc.org/chemistryworld/issues/2003/march/inkchemistry.asp; accessed 9-20-2013.
13. Siltech LLC Corporate website. http://www.siltechpersonalcare.com/pdfs/products/AP_Project.pdf, accessed 9-20-2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch003

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

Chapter 4

Modern Polyurethanes: Overview of Structure Property Relationship

Yuliya Berezkin*[*] and Marie Urick

Bayer MaterialScience LLC, 100 Bayer Road,
Pittsburgh, Pennsylvania 15205
[*]E-mail: yuliya.berezkin@bayer.com.

The intrinsic features of polyurethanes polymers - such as elasticity, clarity and tunable mechanical properties - are found to be key in industrial and personal care applications. Understanding structure-property relationships in polyurethanes is necessary when designing smart multifunctional materials for specific end-uses.

Polyurethanes have a segmented structure of block copolymers where soft and hard segments form micro domains that may result in two-phase morphology. For example, a change in the molecular weight of the soft segment may affect phase separation that, in turn, dictates a very unique thermodynamic behavior of the polymer affects its mechanical characteristics. The nature of the building blocks and polymer morphology greatly affects film forming properties, stiffness, and polymer behavior under different thermal and physical conditions.

This paper will review effects of the polymer structure on biodegradability and chemical resistance. Physical-chemical characteristics of the polymer to achieve shape memory or self-healing effects will also be discussed.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

Introduction

Polyurethanes (PURs) belong to an exciting class of polymers known for their versatile chemistry and unique properties.

Modern PURs can be found in many different end use applications—from soccer balls and Nike shoes to kitchen cabinets, bridges and cars, even cosmetics! Many technologies based on PURs have established themselves as quality standards in the coatings, adhesives and sealants industries. In Personal Care, PURs remain an emerging technology –not as commonly used as in other industries.

In order to design a PUR polymer to deliver performance specific to a targeted end use, one need understand PUR structure property relationships and the changes in behavior this relationship affects.

This article will discuss common building blocks used in the synthesis of polyurethane dispersions, stabilization mechanisms of ionic and non-ionic dispersions and film formation. Many factors in a polymer structure affect its thermodynamic and mechanical properties, chemical resistance and biodegradability. Specifically, the effects of molecular weight, phase separation and crosslinking density on polymer properties will be examined. The discussion will focus on waterborne polyurethane technology since it is most relevant to personal care—not only because of its safety and compliance with industry regulations, but also because of its ability to be tailored to deliver desired performance in various cosmetics.

Discussion

Basic Polyurethane Reactions

Otto Bayer invented PURs in 1937. Three basic reactions lie in the foundation of PUR chemistry:

Urethane bonds are formed when an isocyanate group (NCO) reacts with an alcohol or polyol as shown in Figure 1:

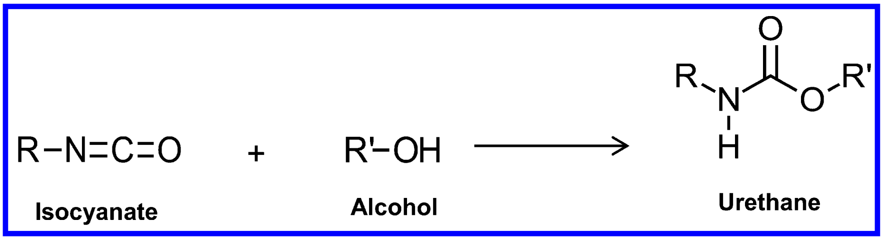


Figure 1. Urethane formation.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

Urea bonds are formed when an isocyanate NCO group reacts with an amine as shown in Figure 2:

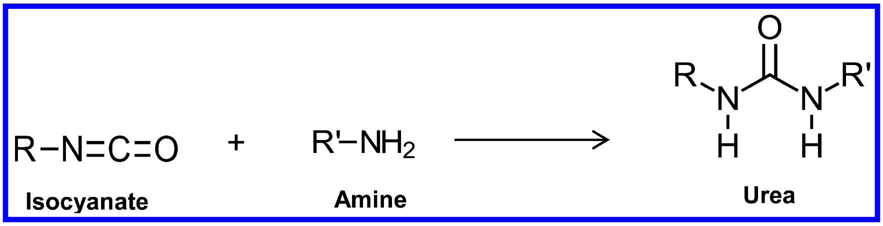


Figure 2. Urea formation.

The third important basic reaction, shown below in Figure 3, is between an isocyanate group and water:

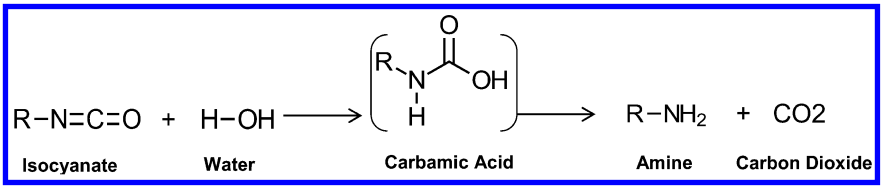


Figure 3. Isocyanate reaction with water.

Water hydrolyzes isocyanate groups to yield amines via unstable carbamic acid and the evolution of carbon dioxide. The co-formed amino groups can react with remaining isocyanate groups to form urea linkages and thus contribute to the extension of the macromolecular chain.

Unique Nature of Polyurethanes

Polyurethane polymers are unique and differ from other polymer types mainly because they are segmented copolymers consisting of soft segments formed by a high molecular weight species and hard segments formed by a low molecular weight species. This type of copolymer can have both crystalline and amorphous structures, and thus combines the benefits of both segments and the visco-elastic properties of both phases. The soft segment in polyurethanes contributes high extension and elastic recovery, while the hard segment contributes high modulus and strength to the composite.

The most interesting phenomenon which is responsible for the intrinsic elastic behavior of PURs is the formation of hydrogen bonds between PUR groups. This nature of these bonds is shown in Figure 4.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

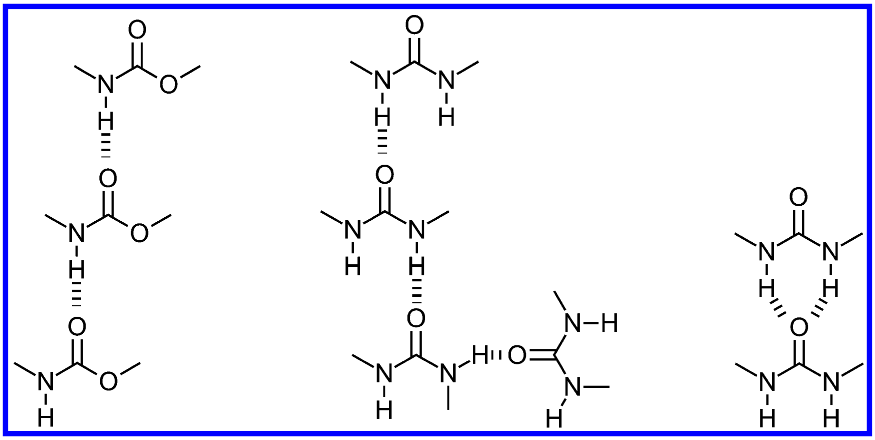


Figure 4. Hydrogen bonding in polyurethanes.

These non-covalent bonds act as crosslinks that break under strain and then easily recover upon release.

EPA regulations and consumer emphasis on green technologies propelled the use of aqueous Polyurethane Dispersions (PUDs) into many industrial and personal care applications in which they replace traditional solvent-borne resins. Simply defined, a PUD is a colloidal system in which a high molecular weight PUR polymer is dispersed in water. Figure 5 schematically depicts the idealized polymer structure and its segmented morphology.

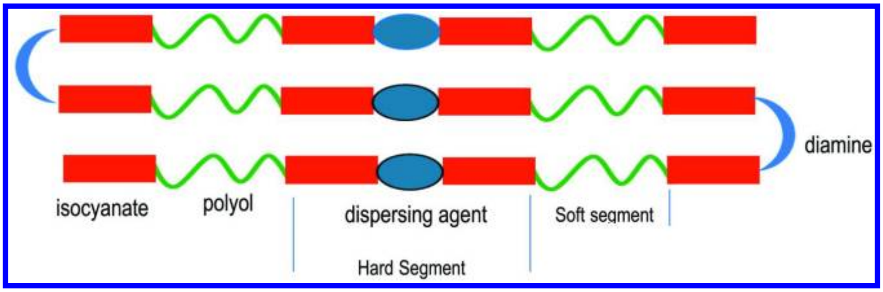


Figure 5. Polymer structure of PUD.

Polyurethane Dispersion: Building Blocks

Diisocyanates (*1*)

Among the common building blocks that are involved in PUD synthesis, isocyanates, polyols and amines are the three most influential ingredient categories that affect the polymer's properties and performance.

The choice of the isocyanate is one of the most influential factors with respect to the hard segment. Polymer performance will depend greatly on the chemical nature of the isocyanate. In synthesizing PUDs, primarily linear aliphatic and cycloaliphatic diisocyanates and their blends are preferred due to their lower reactivity towards water and light stability.

Schematic structures of aliphatic diisocyanates are shown below in Figure 6.

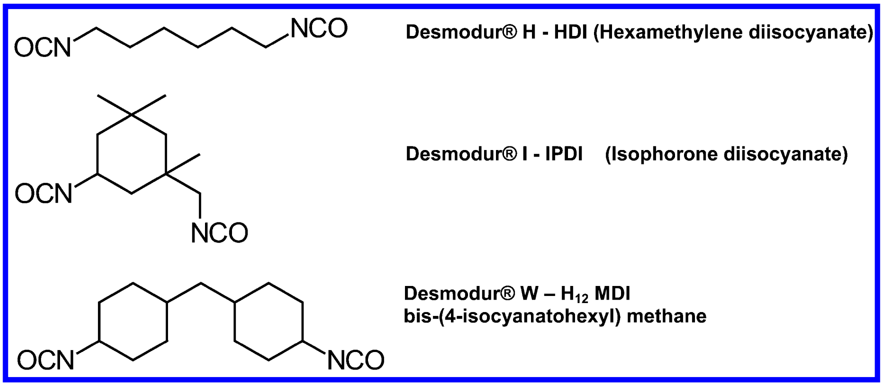


Figure 6. Aliphatic diisocyanates.

Isophorone diisocyanate, IPDI, contributes to harder and more chemically resistant materials, while hexamethylene diisocyanate, HDI, imparts great low temperature flexibility and elasticity to the polymer chain. 4,4-dicyclohexylmethane diisocyanate, H_{12}MDI, makes materials with optical clarity, excellent durability, solvent resistance and toughness. H_{12}MDI also helps to retain gloss longer. Among aliphatic diisocyanates, H_{12}MDI definitely produces the most hydrolytically stable polyurethanes. The polymer morphology of H_{12}MDI systems is also different from that of other diisocyanates, particularly methylene diphenyl diisocyanate (MDI)-based materials. MDI often forms well-defined crystalline hard segments, whereas H_{12}MDI yields smaller amorphous or semi crystalline domains. This difference in morphology results in greater tensile strength and hardness of polymers built with H_{12}MDI (*2*).

H_{12}MDI is the slowest to react because both of its NCO groups are attached to secondary carbon atoms. HDI is the most reactive among aliphatic diisocyanates because it contains only primary NCO groups. IPDI has the greatest difference in reactivity between primary and secondary NCO groups which helps better control the polymer's molecular weight, and subsequently, its viscosity.

Polyols (*1*)

Hydroxy-functional polyols often serve as co-reactants for diisocyanates and make up a majority of the resin composition. Both processing and finished properties of the polyurethane will depend to a large extent on the type of polyol

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

used in the polymer backbone. Low molecular weight diols and triols form hard blocks, while high molecular weight polyesters, polyethers and polycarbonates represent soft blocks. The chemical nature of these polyols will dictate film properties such as glass transition temperature, elasticity, modulus, solvent requirement and solubility. Typical examples of short chain polyols used in the hard segment are: ethylene glycol, 1,4-butanediol, and trimethylol propane. Hard segment content usually controls mechanical properties as well as thermal and hydrolytic stability of the finished polyurethane.

Polyesters (eg. Figure 7) are known to impart greater water resistance and hardness—but are susceptible to hydrolysis. To compensate for this weakness, urea linkages can be introduced into the polymer.

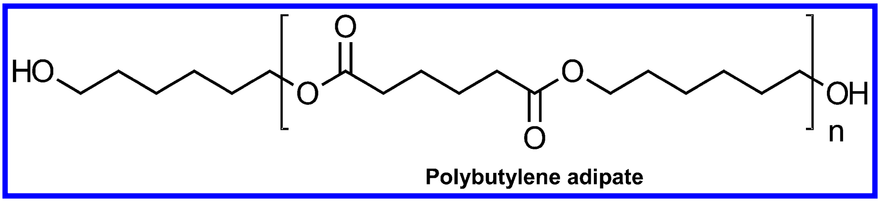


Figure 7. Typical polyester polyol.

Polyethers (eg. shown in Figure 8) are known for their flexibility and lower cost. C4 polyethers also produce materials with excellent hydrolytic stability.

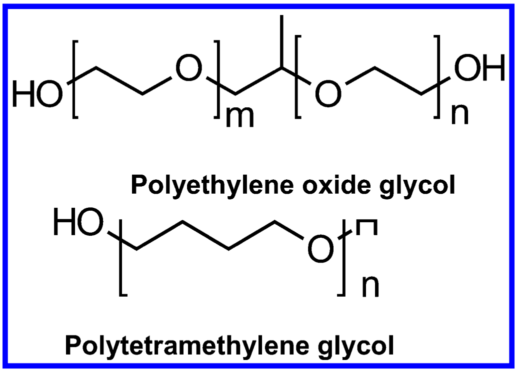


Figure 8. Typical polyether polyols.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

Polycarbonates produce materials with greater hydrolytic stability and solvent resistance (see Figure 9).

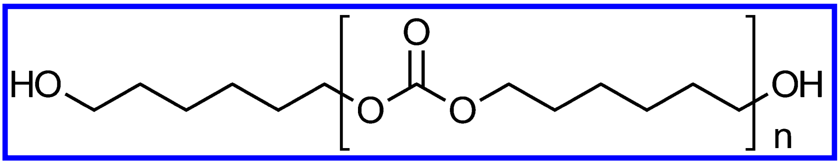


Figure 9. Polycarbonate-based polyol.

The demand for green and sustainable technologies prompted innovation in this category of raw materials. For instance, adipates and some of the glycols can be replaced with succinates and lactides, renewable raw materials sourced from plants. Soybean and castor oils are other plant-derived building blocks that can be incorporated into the polyester or polyether backbone. Such polyols will have an amphiphilic nature and will impart a softening effect on the film. New technology for making polycarbonate from carbon dioxide is emerging as well.

In order to achieve special effects, the use of hydroxyl-functional acrylates, oil-modified alkyd resins, or hydroxyl-functional polybutadienes or fluoroalkyl-containing polyethers is applicable.

To achieve faster biodegradability, polyesters made of lactic or glycolic acids can be used instead of adipates or phthalates.

Dispersing Agents (*3*)

PUR prepolymers are built as intermediate molecular weight species in the process of synthesizing high molecular weight final polymers. PUR prepolymers are typically very hydrophobic in nature. In order to disperse hydrophobic prepolymers in water, either external or internal emulsifiers are required. Internal emulsifiers (those that can be incorporated into a prepolymer backbone) are usually preferred as they impart superior stability and final dispersion properties compared to external emulsifiers (surfactants). Specifically, polymers with built-in internal emulsifiers have finer particle sizes and reduced water sensitivity. Also, high-shear dispersing processes are not required.

Internal emulsifiers contain either ionic or non-ionic hydrophilic groups. Hence, prepolymers modified with ionic groups or with hydrophilic polyether will become self-dispersing. Among ionic emulsifiers, anionic types, such as salts of sulphonic or carboxylic acids, are typically used.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

Schematic structures of internal emulsifiers are shown below in Figure 10.

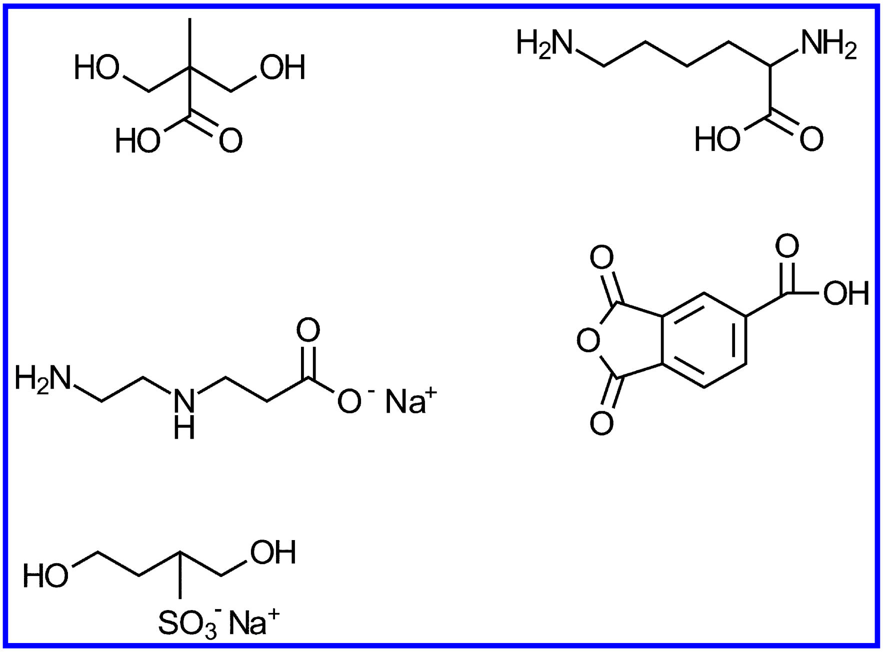


Figure 10. Internal emulsifiers.

Salts of tertiary amines will render polymers cationic. These types of PUDs are almost exclusively used in paper and leather applications.

Non-ionic emulsifiers are almost exclusively represented by polyethylene oxide polyethers similar that shown in Figure 11 below.

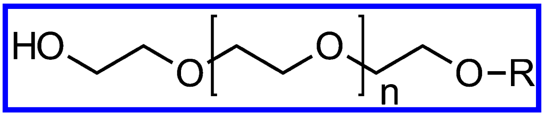


Figure 11. Non-ionic emulsifier.

The ionic dispersion is stabilized by the formation of electrical double layers between the ionic centers and their counter ions which migrate into the continuous water phase (*3*). The interference of electrical double layers from different particles results in particle repulsion. This stabilization mechanism is known as ionic repulsion and is illustrated in Figure 12. Ionic dispersions are sensitive towards electrolytes and freezing. However they are stable at high temperatures (>70°C), have an exceptionally long shelf life, and are somewhat stable under strong shear forces.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

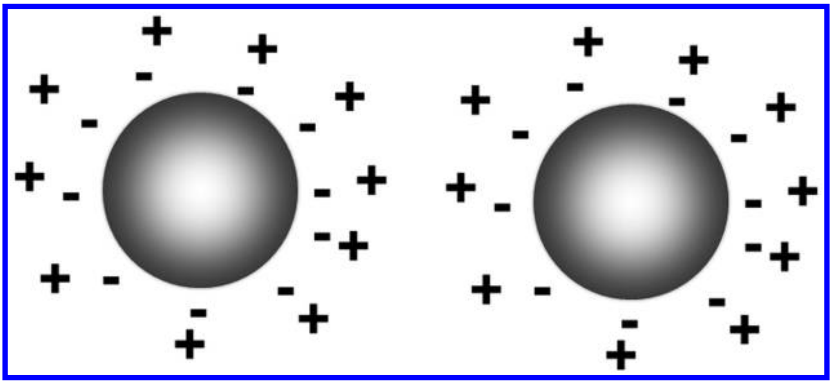


Figure 12. Ionic stabilization.

The stabilizing mechanism of non-ionic dispersions (illustrated in Figure 13) can be explained in terms of entropic or steric repulsion. When the particles approach closely, the freedom of motion of hydrophilic chains in the water phase becomes restricted, leading to a reduction of entropy. Non-ionic dispersions show greater stability to low temperatures, pH changes and strong shear, but are sensitive to degradation at high temperature

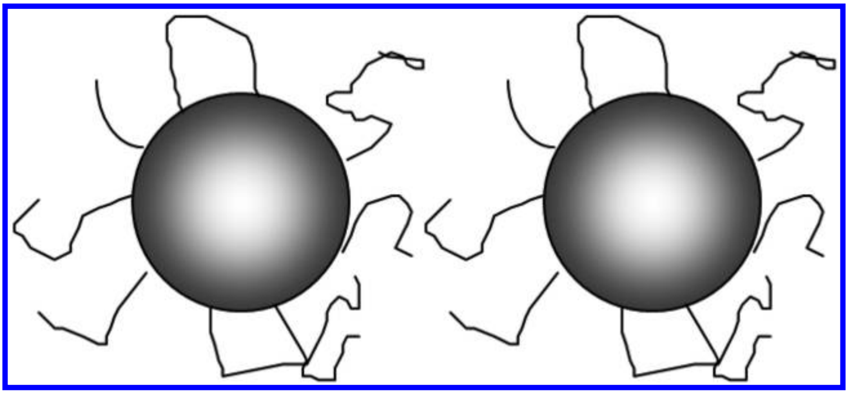


Figure 13. Non-ionic or Steric stabilization.

Greater hydrophilic modification of the polymer yields smaller particle sizes in the dispersion. However, in this case the viscosity of the dispersion tends to increase, leading to lower solids content. Ultimately, the amount of internal emulsifier in the prepolymer backbone has to be balanced to obtain a stable dispersion with the highest possible solids content.

Both stabilization types can be combined to achieve desirable synergistic effects:

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

- Lower overall hydrophilicity
- Tolerance to pH changes and towards electrolytes
- Freeze/thaw stability
- Fine particle size

Amines

In the synthesis of PUDs, water soluble amines are used as chain extenders to build up molecular weight in the final stages of the reaction. The preferred reaction is between amines and isocyanates compared to amines with water, thus making it possible to conduct reactions between amine and NCO groups in the presence of water. Typically, aliphatic linear and cyclic di- and tri-functional amines are used, depending on the desired properties of the final polymer. Urea linkages are formed as a result of the reaction between amines and diisocyanates. These usually improve the hydrolysis resistance, thermal stability and mechanical strength of the polymer.

Film Formation

In the PUD, polymer particles remain discrete as they are dispersed in water. Film formation occurs when the water evaporates and particles coalesce to form a continuous smooth matrix. Figure 14 shows stages of the film formation process from the starting point of applying raw material on the substrate to the dry-to-touch film (*2*).

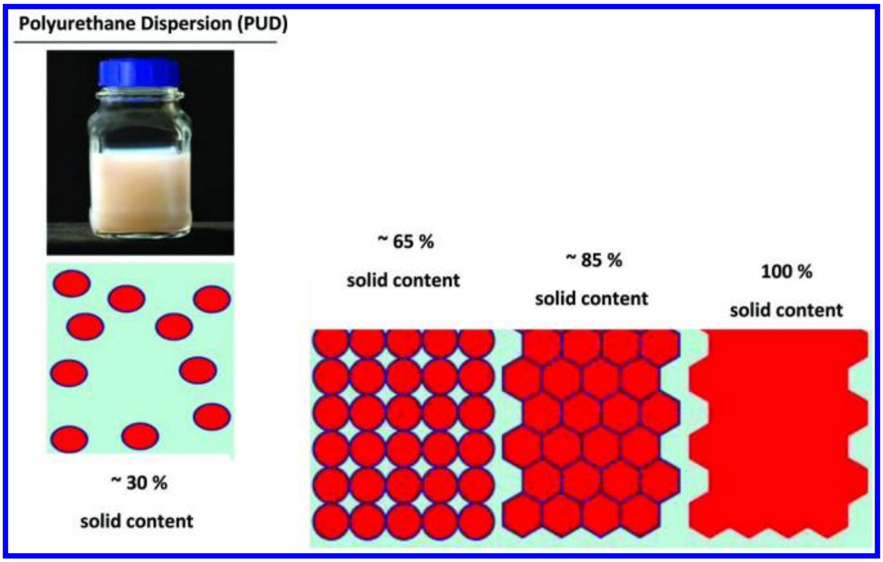


Figure 14. Film formation in PUDs.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

Hence, film formation is a physical process driven by several factors:

- Glass transition temperature of the polymer
- Minimum film formation temperature
- Humidity
- Coalescent solvent or plasticizer

The lower the glass transition temperature of the polymer, the easier it becomes to form a film. The more flexible the polymer, the lower minimum film formation temperature it will have. Brittle or very cross-linked polymers will require the help of a plasticizer or coalescent solvent to form a film at room temperature. Particle size will also influence film formation; a wide particle size distribution will lead to better packing and less water sensitivity of the film after water evaporates.

Morphology of the Polymer

Knowledge of a polymer's morphology is essential for understanding structure/properties relationships. This knowledge allows one to vary the morphology in a controlled manner in order to achieve the desired properties in a material.

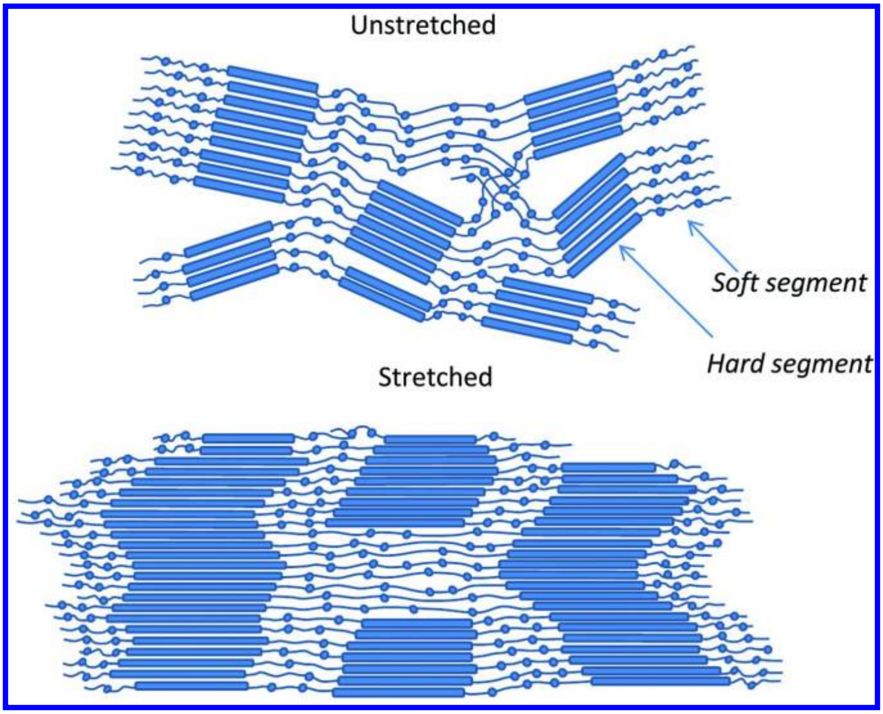


Figure 15. Molecular reinforcement due to orientation.

PURs are famous for their toughness, meaning a unique combination of strength and flexibility. This unique PUR feature can be explained from a polymer morphology standpoint. The polymer macromolecular structure in stretched and unstretched modes helps to explain this phenomenon. Molecular reinforcement is taking place in the stretched mode (as illustrated in Figure 15) (*1*).

In the unstretched form, there is phase separation between Soft and Hard Segments. As the polymer is strained, both domains become oriented in the direction of strain, causing more intense molecular interactions, which leads to molecular reinforcement.

In Figures 16 and 17, DMA graphs show a classic case—as strain increases, the point of “densification”(molecular reinforcement) is reached, whereupon stress sharply rises. This explains why PURs maintain high strength at high elongation. Moreover, the stress/strain relationship will depend greatly on the polymer composition. The influence of the structure of the soft segment on tensile strength and elongation is related to intermolecular association and crystallization during stretching. Effects of the soft segment are pronounced mainly in polymers with a continuous soft segment phase, e.g., those with soft segment content above 50%.

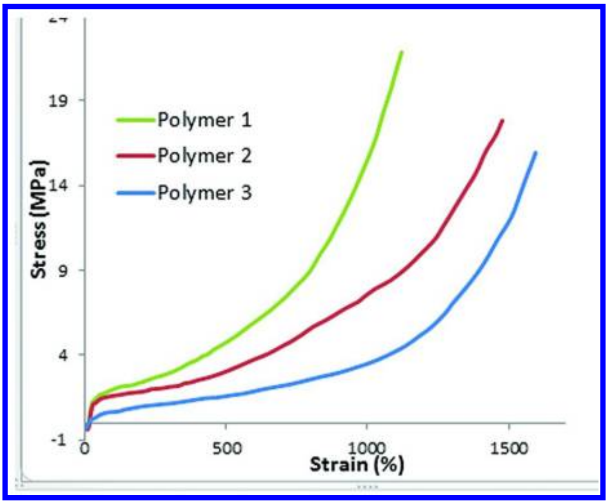


Figure 16. Stress/Strain behavior.

The graph on Figure 16 illustrates that the level of strain where the ‘densification’ phenomenon occurs depends on both Hard Segment length and content. For PURs with higher Hard Segment content, the strength increase occurs at lower strain (see example of waterborne PUR polymer Polymer 3 in Figure 16).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

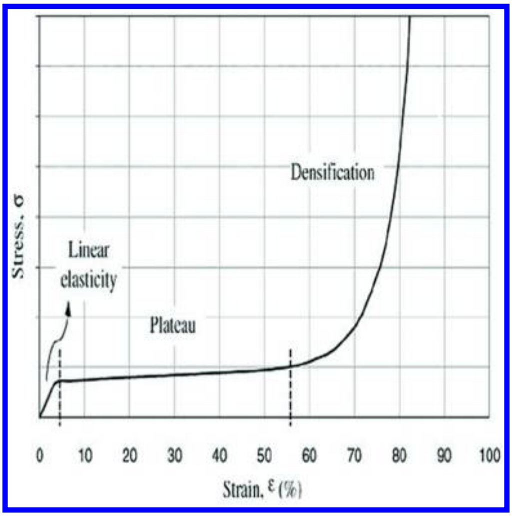


Figure 17. Densification phenomenon.

The molecular weight of the polymer will also play a role in determining final properties and the end-use of the polymer. The degree of chain extension, chain termination, and the isocyanate- to-hydroxyl ratio are the key factors affecting molecular weight. The greater the extent of the reaction between isocyanates and hydroxyl groups, the higher the molecular weight of the polymer becomes, as it is shown on Figure 19. Mechanical properties, viscosity and adhesion will greatly depend on the optimal molecular weight determined for each specific application. As shown in Figure 18 below, the tensile strength of the polymer increases significantly with increasing molecular weight, while elongation is reduced.

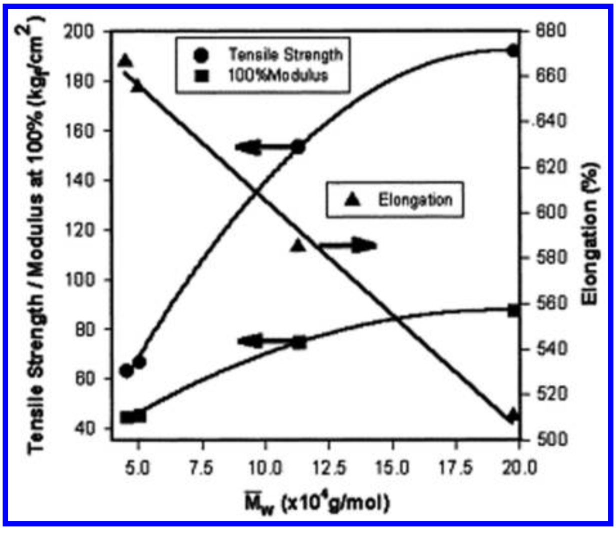


Figure 18. Tensile Strength vs. Mol. Wgt.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

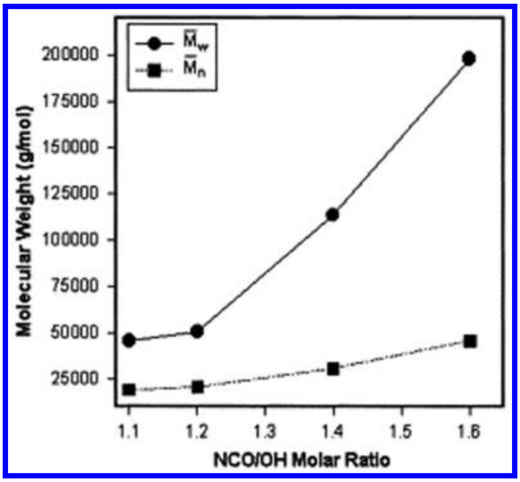


Figure 19. Effect of Index on Mol. Wgt.

Effects of Crosslinking

A polymer's hardness, chemical resistance and abrasion resistance can be increased via chemical or physical crosslinking. Chemical crosslinking is achieved via the addition of another reagent that will polymerize within the existing polymer and form IPN (interpenetrating network) structures as shown in Figure 20. If the polymer has free functional groups, OH or COOH, another reagent (aziridines, blocked isocyanates, carbodiimides, waterborne polyisocyanates and melamine formaldehydes) can react with these groups to create additional crosslinking. Equivalent weights of these functional groups affect the crosslinking density.

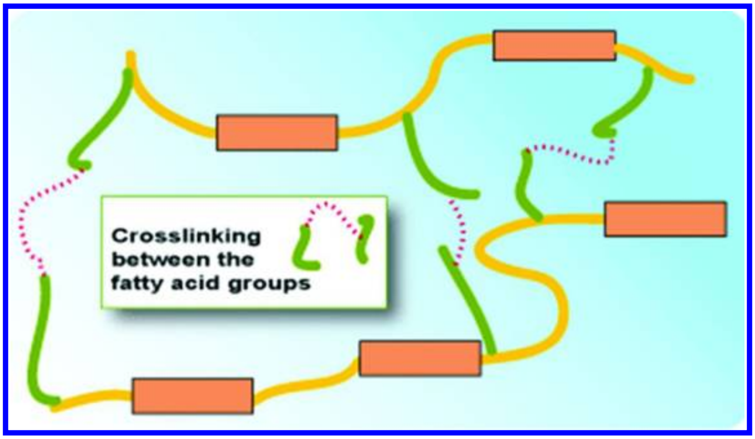


Figure 20. Chemical crosslinking.

Breathability (water vapor permeation) and moisture resistance (no film swelling occurs upon exposure to water) can be obtained with the introduction of side chains containing polyethyleneoxide ether subsequently crosslinked with one of the above listed reagents. The resulting polymer will demonstrate breathability with high moisture resistance (*4*).

Physical crosslinking is obtained when non-covalent bonds are formed between polymer chains and through phase separation.

Effects of Phase Separation

What drives phase separation versus phase mixing?

One of the factors that drive phase separation is thermodynamic incompatibilities between Soft Segments and Hard Segments—for instance, between aliphatic Soft Segments and aromatic Hard Segments or between soft and hard segments with wide differences in polarity. From a kinetic point of view, phase separation can be driven by increased mobility of either the Hard or Soft Segment. This explains the effect of annealing on segmented PURs. Increased mobility during annealing allows the polymer to rearrange into a thermodynamically more favorable arrangement (*5*).

The molecular weight of the Soft Segment is another factor affecting phase separation—the greater the distance between anchoring sites connecting Hard Segment to Soft Segment, the more mobile the Hard Segment, allowing for easier phase separation.

As hardness increases with Hard Segment content, the extent of phase mixing increases—the Hard Segment becomes dispersed in the Soft Segment domain, thereby hindering Soft Segment mobility. This increases the Soft Segment glass transition temperature, Tg. However if the Hard Segment is relatively crystallizable, increased Hard Segment content will increase its crystallizability and thus increase phase separation. These changes in phase separation affect not only the hardness of the polyurethane, but also its low-temperature properties.

Cross-linking will decrease phase separation since the crosslinks hinder mobility and therefore impede phase separation. Varying crosslink density, however, allows one to control, among other things, the modulus, softening behavior, clarity and chemical resistance of a material. Figure 21 shows the effect on crosslink density on storage modulus.

Choice of chain extender can also influence phase separation. Studies have been done that show certain chain extenders allow for more or less hydrogen bonding in the hard segment. Increased hydrogen bonding increases physical crosslinking which in turn affects crystallizability and stress-strain behavior.

Annealing drives phase separation since both Hard Segment and Soft Segment domains regain their mobility at higher temperatures allowing them to realign and even crystallize. Crystallization results in a greater degree of phase separation. The length of hard segment domains determines the limits of hard segment crystallization, determining, in turn, the melting point, and ultimate thermal stability. Introducing asymmetrical structures like 2,4 and 2,6 isomers of TDI, will break up crystallinity and favor increased phase mixing.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

Polymers with phase-separated structures form hazy films. Very transparent and glossy films are typically obtained with amorphous polymers.

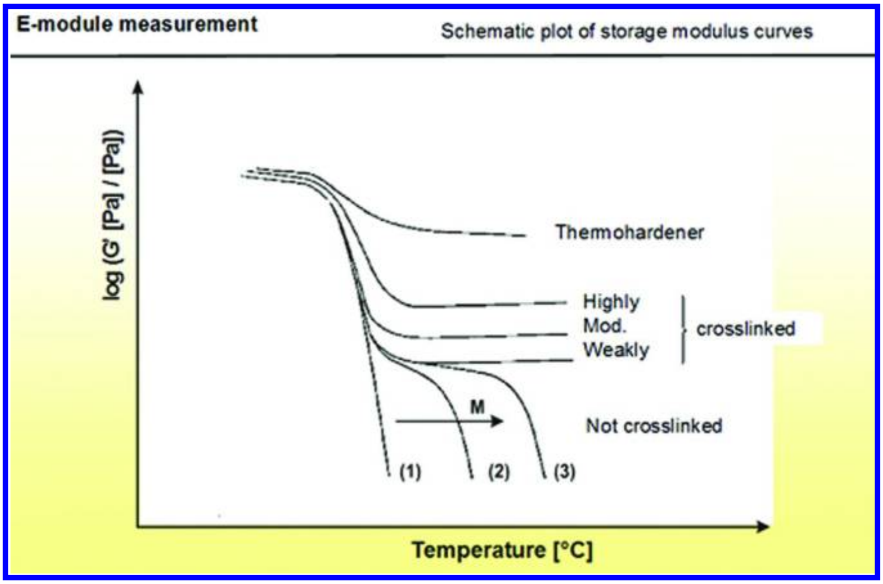


Figure 21. Schematic plot of storage modulus curves showing the effects of crosslink density. (Reproduced from Bayer MaterialScience TPU Tech Center Website.)

Conclusion

Waterborne polyurethanes are a versatile class of environmentally friendly polymers that can be designed with a wide range of properties suitable for high performance applications. They often offer a unique balance of flexibility, hardness, mechanical strength and durability combined with excellent sensorial attributes and appearance. In cosmetics, these film-forming polymers contribute to excellent water and rub off resistance, controlled delivery of actives, and long-lasting wear without sacrificing aesthetics and sensorial properties. Films made of linear polyurethanes are distinctively soft and silky to touch, having smooth transparent surfaces. In skin care applications, such polymers enhance the efficacy of active ingredients such as sunscreen filters, anti-inflammatory aids and salicylic acid, helping to achieve mild and efficacious products with excellent aesthetics. In hair care applications, waterborne polyurethanes make a difference in obtaining long lasting humidity resistance, dynamic durable styles and healthy appearances. Moreover, these polymers are generally safe and of high quality, friendly to human skin biology.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

Suggested Additional Reading

1. Szycher, M. *Szycher's Handbook of Polyurethanes*; CRC Press LLC: Boca Raton, FL, 1999; pp 4-31-4-32, 4-36, 14-1–14-3.
2. Meier-Westhues, U. *Polyurethanes: Coatings, Adhesives and Sealants*; Vincentz Network: Hannover, Germany, 2007; pp 67−68.

References

1. Szycher, M. *Szycher's Handbook of Polyurethanes*; CRC Press LLC: Boca Raton, FL, 1999; pp 4-31-4-32, 4-36, 14-1–14-3.
2. Meier-Westhues, U. *Polyurethanes: Coatings, Adhesives and Sealants*; Vincentz Network: Hannover, Germany, 2007; pp 67-68.
3. Dieterich, D. Aqueous Emulsions, Dispersions and Solutions of Polyurethanes: Synthesis and Properties. *Prog. Org. Coat.* **1981**, *9*, 281–340.
4. Anderle, G.; Lubnin, A.; Snow, G. *Breathable Polyurethanes, Blends, and Articles*. U.S. Pat. Appl. 20030195293 A1, 2003.
5. Li, Y.; Kang, W.; Stoffer, J. O.; Chu'pt, B. *Macromolecules* **1994**, *27*, 612–614.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch004

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

Chapter 5

A Novel Cationic Latex as an Opacifier for Cleansing Formulations

Fanwen Zeng,*[,1] Sylvie Doulut,[2] Miao Wang,[1,3] Alan Nakatani,[1]
Diane Routzahn,[1] and Curtis Schwartz[1]

[1]The Dow Chemical Company, 727 Norristown Road,
Spring House, Pennsylvania 19477, U.S.A
[2]The Dow Chemical Company, Avenue L.V. Beethoven, Sophia Antipolis,
06560 Valbonne, France
[3]Current address: L'Oreal USA, 200 Terminal Ave.,
Clark, New Jersy 07066, U.S.A.
***E-mail: fzeng@dow.com.**

Opacifier technology has been applied in cleansing formulations to provide an opaque and creamy appearance in consumer products. Styrene/acrylate latex (SAL) is one of the most widely used technologies. Conventionally, this opacifier technology is based on latexes stabilized with anionic groups on the surfaces. It is being used in anionic surfactant-based systems at slightly acidic to neutral pH. However, this technology is not compatible in cleansing formulations that contain a higher content of cationic polymers. In this paper, we describe a novel cationic SAL that is prepared by an emulsion polymerization process. The compatibility and long term formulation stability is markedly improved with this cationic SAL vs. the anionic counterpart where cleansing formulations contain higher content of a variety of cationic polymer ingredients.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

Introduction

Opacifier technology has been applied in cleansing formulations to provide an opaque and creamy appearance in consumer products such as detergents, hand dish, cleansers, body wash, liquid soaps, and shampoos. It modifies the appearance of a product from clear, or potentially unacceptable haziness to a uniform, luxurious, and “lotionized” appearance. There are two major classes of opacifiers in the market: small molecules such as glycol stearates and latex particles. While glycol stearates are used as an opacifer and pearlizing agent due to their near insolubility in aqueous systems, they impart a negative impact on foam properties. Latex particles based on styrene copolymers have a substantially different refractive index vs. the other ingredients in the formulations, and therefore they are efficient and cost effective in opacifying formulations through an efficient light scattering mechanism. Among them, styrene/acrylate latex (SAL) is one of the most widely used opacifiers.

Opacifier based on latex particle technology is prepared by emulsion polymerization of styrene and other co-monomers. The polymeric product is typically a milky white dispersion of polymer particles in water with polymer solid content of at least 30%. They are formulated into cleansing formulations typically at the 1% level as supplied. The particle sizes of these emulsion polymers are optimized to achieve good opacity and colloidal stability. The use of water as a dispersion medium provides attractive safety, environmental and heat removal benefits when compared to other methods of polymerization process. Furthermore, these products have a water-like viscosity and can be easily pumped at room temperature. The ease of cold process handling in plant conditions is another significant advantage for latex particle technology when compared to glycol stearates where heat/melting is required.

Typically, latex particles are stabilized through either electrostatic (anionic or cationic) repulsion or steric (non-ionic) repulsion at their surface as shown in Figure 1 (*1*). Conventional SAL opacifiers are stabilized with anionic groups or the combination of anionic groups and non-ionic groups. They are being used in anionic surfactant-based cleansing formulations such as shampoo, shower gel or liquid hand soaps at slightly acidic to neutral pH. However, anionic SAL becomes incompatible in cleansing formulations formulated with higher percentage of cationic conditioning polymers typically used to condition the skin, hair, or improve in-use feel on the skin. Cationic polymers that deliver conditioning benefits include, for example polyquaternium-7 (PQ-7), polyquaternium-10 (PQ-10) and (hydroxypropyl) guar hydroxypropyltrimonium chloride (GHPTC). We postulate that a SAL opacifier based on cationic stabilization mechanism on its surface should be more compatible in the cleansing formulations containing higher content of cationic polymers. In this paper, we describe the synthesis and properties of this novel cationic SAL. The compatibility and long term formulation stability of cationic SAL are compared with the anionic counterpart in cleansing formulations containing a variety of cationic polymer ingredients.

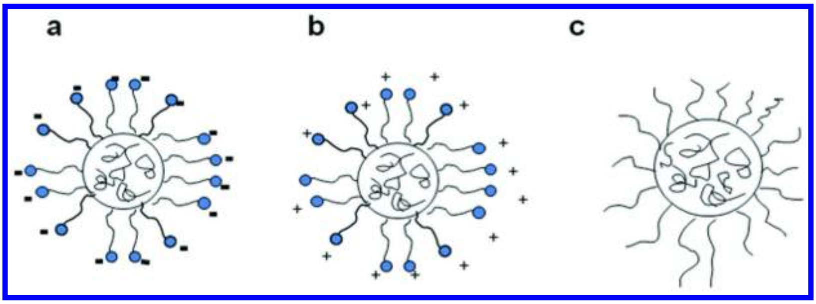


Figure 1. Schematic illustration of stabilization of latex particles by a) anionic electrostatic repulsion, b) cationic electrostatic repulsion, and c) non-ionic steric repulsion.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

Experimental

Synthesis and Properties of Cationic SAL

Cationic SAL was prepared by cationic emulsion polymerization of monomers comprising styrene, hydroxyethyl methacrylate (HEMA), and cationic monomer such as ethalkonium chloride acrylate. This material as prepared has an average polymer solid content of 35%, a mean particle size of 180 nm, and a pH of 2.05-3.3. The viscosity of this material is less than 50 cPS as measured by Brookfield viscometer (LV1, 60 rpm, 25 °C).

All Other Materials Were Used As Received

Cationic polymers: PQ-10 (Quaternized hydroxyethyl cellulose, UCARE™ JR-400) was from the Dow Chemical Company (Spring House, PA, U.S.A.); PQ-7 (Copolymer of acrylamide and diallyldimethyl-ammonium chloride, Salcare® Super 7) was from BASF (Florham Park, NJ, U.S.A.); GHPTC and hydroxypropyl GHPTC (Jaguar® C500 and C162) were from Rhodia (Cranbury, NJ, U.S.A.).

Surfactants: SLES (sodium laureth sulfate, Empicol® ESB70) and CAPB (cocamidopropyl betaine, Empigen® BSFA) were from Huntsman Corporation.

Typical Procedure To Formulate the Cationic Latex in a Bodywash Formulation Containing PQ-7 and PQ-10

SLES was dissolved in water with proper mixing, followed by CAPB. PQ was added to the above surfactant solution. The pH was adjusted to the target specification using citric acid or sodium hydroxide. The viscosity was adjusted to the target specification using for example, sodium chloride (NaCl). Finally the pre-diluted SAL in water was added to the formulation followed by other additives such as perfume and preservatives.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

Typical Procedure To Formulate the Cationic Latex in a Bodywash Formulation Containing GHPTC

With proper mixing, (hydroxypropyl) GHPTC was dissolved in water followed by pH adjustment to less than 4 (Raising the solution temperature to 45-50°C during the first steps of the process till the addition of SLES can optimize surfactant dissolution, polymer stabilization and final product stability). CAPB was then added followed by pre-diluted SAL in water and SLES. The viscosity and the pH were then adjusted to the target specifications using for example, sodium chloride (NaCl) for the viscosity and citric acid or sodium hydroxide for the pH. Finally other additives such as perfume and preservatives were added to the formulation.

Formulation Stability and Opacity

Stability of each formulation was assessed under aging conditions at 5, 25 and 45°C for at least 1 month. Opacity as measured by backscattering (BS) and its change over time as a function of position (tube height) within each sample was determined using a Turbiscan™ instrument, (model TLabExpert from Formulaction Company, L'Union, France) as shown in Figure 2 (*2*, *3*). Formulation with BS(%) of great than 30 has an excellent opacity, while formulation with BS(%) of less than 20 has a not desirable blue-gray appearance.

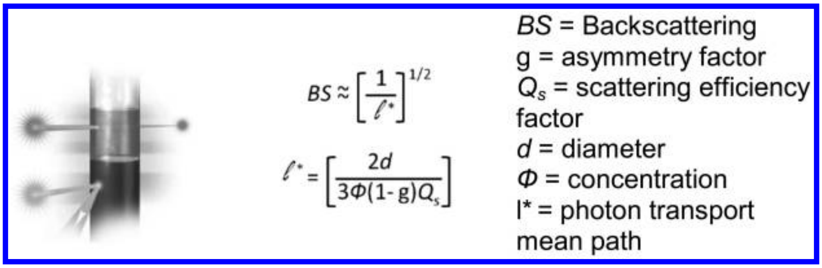


Figure 2. Formulation stability with Turbiscan and BS calculation. Reproduced with permission from http://www.formulaction.com/technology-mls.html.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

Furthermore, the formulation stability was evaluated visually and ranked as shown below.

Table I

Observation	*Rating*
Flocculation and/or sedimentation or creaming	Poor
Slight flocculation and/or sedimentation or creaming without further evolution over time	Fair
Miniscule flocculation and/or slight sedimentation or creaming without further evolution over time	Good
No flocculation , no sedimentation, no creaming	Excellent

Results and Discussion

SAL with the desired particle size is used as an opacifier in cleansing formulations to modify the appearance of the formulation through an efficient light scattering mechanism. It imparts a translucent to milky and/or lotionized appearance with uniform opacity to formulations. The opacity is affected by three important factors: refractive index (*4*), particle size and stability. Firstly, polystyrene has a refractive index of 1.59, which is significantly higher than that of air (1.0), water (1.33) and polymethyl methacrylate (1.47). Therefore, styrene-rich SAL leads to a superior opacity to acrylates or vinyl latexes. Secondly, the particle size and distribution is another factor that impacts the opacity. The most efficient light scattering occurs at the particle size close to one-half of the wavelength of visible light, i.e., 200-375 nm. Finally, the colloidal stability of SAL in formulation is critical to maximize the scattering efficiency and maintain the uniformity of opacity.

A typical cleansing formulation contains anionic surfactant such as SLES, amphoteric surfactant such as CAPB and salt. For formulations opacified with anionic SAL, the uniformity of opacity is compromised when increasing level of cationic polymers is present in the formulations. Cationic polymers such as PQ-7, PQ-10, and GHPTC are used in cleansing formulations to impart conditioning benefit to consumers. The incompatibility of anionic SAL with cationic polymers, especially at high use level and/or at low pH presents a significant technical challenge to formulators.

The stabilization and flocculation behavior of latex particle have been investigated in a wide range of systems. The electrostatic and steric repulsion between particles is the primary contributor to the stability of latex particle. For primary particles with particle size around 200 nm, the sedimentation rate is estimated to be extremely slow since the density of SAL is not significantly different from that of water. Most of the motion of the primary particles is

Brownian. Once in the formulation, the absorption of other ionic materials on the surface of latex particles can compress the electrical double layer (*5–7*). The observation of incompatibility of anionic SAL in high cationic polymer containing formulation clearly indicates that cationic polymer plays a significant role for instability. The absorption of cationic polyelectrolytes to anionic SAL can lead to the reduction of the zeta potential of the anionic SAL. This eventually results in sedimentation or flocculation/ coalescence of the opacifier latex and a decrease in the opacity for formulations as illustrated in Figure 3 (C).

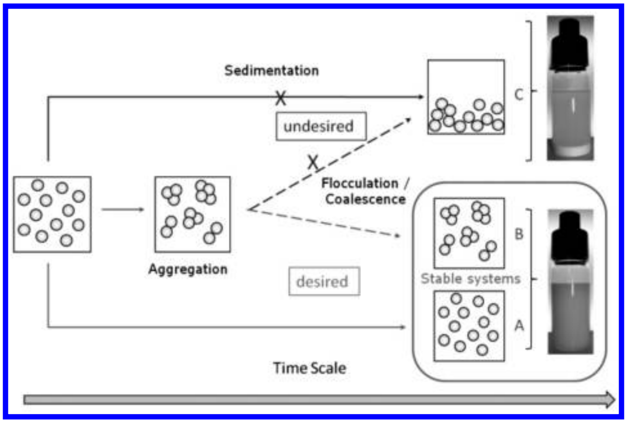


Figure 3. Stability and instability of opacifier in formulations.

We postulate that the above stability issues can be resolved if the opacifier latex is based on cationic stabilization. Syntheses of latex polymers with cationic stabilization have been reported in the literature (*8–12*). For example, Van Herk and coworkers (*8*) reported the synthesis of cationic latex particles with high cationic surface charge densities. Vancso and coworkers (*9*) described a preparation of core-shell cationic latex particles. Aslamazova and coworkers (*10*) were able to make cationic latex in a surfactant-free emulsion polymerization process. Deng and coworkers (*11*) compared the synthesis of cationic latexes by either solution or emulsion polymerization. Piet and coworkers (*12*) reported the synthesis of cationic latex by copolymerization of styrene, and 3-(methyacrylamidinoprpryl) trimethylammonium chloride. The cationic SAL material described in this paper was prepared by a proprietary process so that all targeted product specifications were met. The stability and opacity of this cationic SAL, in comparison with anionic SAL, were investigated in cleansing formulations containing commonly used cationic polymers.

Table II summarizes the stability comparison between conventional anionic SAL and the cationic SAL in four different formulations containing various amounts of PQ-7 as well as variations in the surfactant and salt levels. The use level of PQ-7 ranged from 0.2 to 0.6% while the salt level was varied from 0.6 to 2.5%. The range of CAPB was from 1.6 to 3.5%. In all cases, flocculation/coalescence

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

and sedimentation were observed for the anionic SAL-containing formulations under heat-aging conditions at 45°C. In contrast, good to excellent stability was achieved for the cationic SAL-containing formulations. These results indicate the robustness of the cationic SAL in formulation compatibility with PQ-7.

Table II. Comparison of Formulation Stability of Anionic and Cationic SAL with PQ-7

Formulations	*Formulation stability at 45 °C*	
	Anionic SAL	*Cationic SAL*
11% SLES, 3.5% CAPB, 0.6% PQ-7, 0.6 NaCl	flocculation/ coalescence	good to excellent stability
11% SLES, 2.7% CAPB, 0.2% PQ-7, 1.7% NaCl	Sedimentation	
11% SLES, 1.6% CAPB, 0.6% PQ-7, 2.5% NaCl	flocculation/ coalescence	
11% SLES - 2.0% CAPB, 0.4% PQ-7, 2.0% NaCl	Sedimentation	

Figure 4 shows the comparison of formulation stability of anionic and cationic SAL in cleansing formulations containing hydroxypropyl GHPTC under heat-aging study at 45 °C for up to 6 weeks. Each line in the graph corresponds to the light backscattering (%BS) at different days (right axis from top to bottom) as a function of the tube height for each experiment. A stable formulation should exhibit a stable value (after a stabilization period of time) to the end of heat-age study, suggesting that there is no change in opacity. Also, the line should be flat, suggesting the uniformity of opacity regardless of tube height. For anionic SAL as shown in the top figure, a large increase in the backscattering (opacity) at the bottom of tube was accompanied with a decrease of backscattering elsewhere, indicating the accumulation of opacifier at the bottom of tube. For cationic SAL, it was very interesting to observe that a large increase in backscattering occurred after few days of heat-aging mostly across the whole tube (Figure 4, bottom). Equally interesting, this increase of backscattering was maintained throughout the heat-aging study. This observation can be rationalized with the potential formation of stable small aggregates as shown in Figure 3B. This was further confirmed with ultra small angle neutron scattering (USANS) study (*13*). Overall, incompatibility of anionic SAL with GHPTC leads to sedimentation of latex particle and loss of opacity. In contrary, cationic SAL provides a stable and opaque formulation containing GHPTC.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

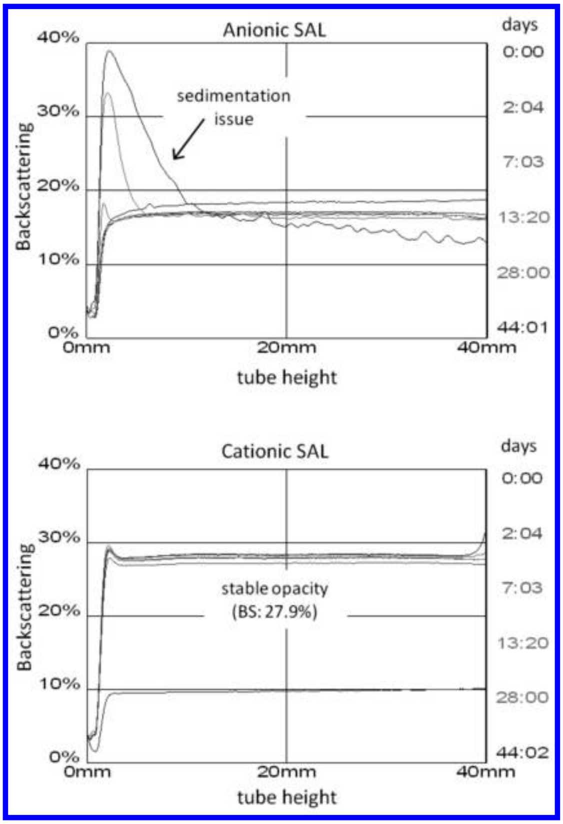


Figure 4. Stability of SAL (top: anionic; bottom: cationic) in a formulation containing 10%SLES, 3.0% CAPB, 1.0% NaCl, 0.3% guar hydroxypropyl GHPTC (Jaguar® C162) at pH 5.5. Each line corresponds to the light backscattering (%BS) at different days (right axis from top to bottom) as a function of the tube height for each experiment.

Similarly, improvement of compatibility of cationic SAL vs. anionic SAL was observed for the PQ-10-containing formulations under heat-age conditions at 45 °C as shown in Figure 5. For anionic SAL, the light backscattering (%BS) at longer heat-aged time changed constantly overtime, indicating the instability of opacity, before sedimentation occurred. In comparison, after the stabilization period (around 2 days), the light backscattering (%BS) remained constant at a high value for the cationic SAL system.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

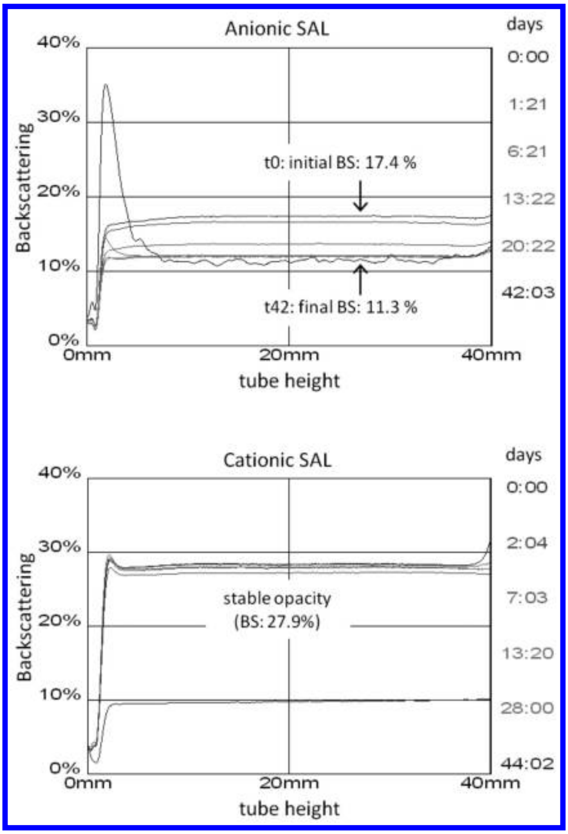


Figure 5. Stability of SAL (top: anionic; bottom: cationic) in a formulation containing 11%SLES, 2.3% CAPB, 1.8% NaCl, 0.5% PQ-10 (UCARE™ Polymer JR400). Each line corresponds to the light backscattering (%BS) at different days (right axis from top to bottom) as a function of the tube height for each experiment.

Finally, in a formulation containing a high ratio of SLES/CAPB at low pH, anionic SAL went through an aggregation, flocculation and coalescence process resulting in formulation instability (Figure 6, top), while the cationic SAL was stable throughout the heat-aging study at 40°C (Figure 6 bottom). This observation is more obvious when the delta of light scattering was compared. The graphs on the left of Figure 6 give the light backscattering per days, whereas the graphs presented on the right give the variation of the light backscattering at longer heat-aged time vs. day 1, taken as a reference. Day 1 becomes the baseline (0% delta backscattering) and was subtracted to next measurements. The profile obtained with the cationic SAL is almost perfect with all curves being superimposed at 0%.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

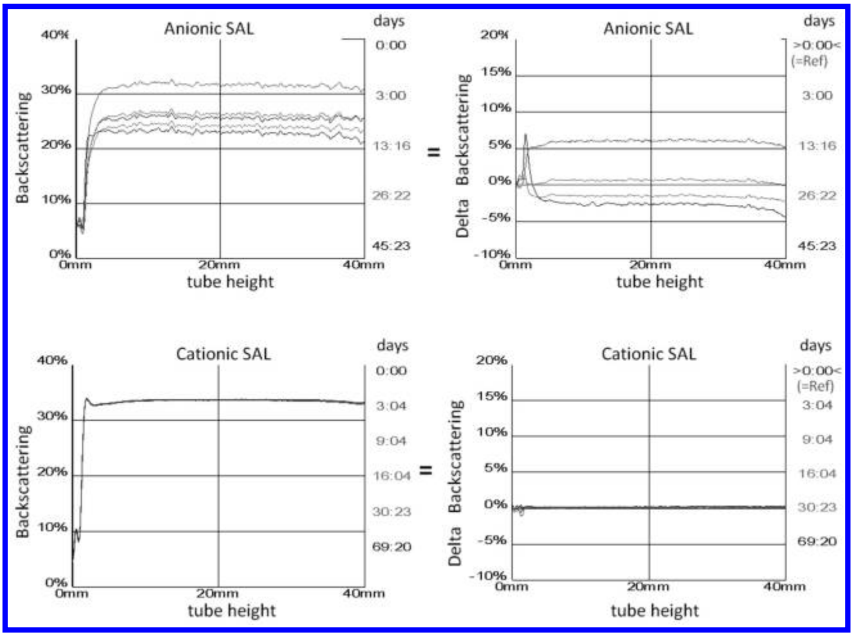


Figure 6. Stability of SAL (top: anionic; bottom: cationic) in formulations containing high ratio of SLES / CAPB at low pH (7% SLES, 3% CAPB, 0.8% NaCl at pH 4.5).

The marked improvement of compatibility and opacity of cationic SAL vs. anionic SAL in cleansing formulations containing cationic polymer can be rationalized by considering the interaction of latex particles, surfactants and cationic polymers (*7*, *14–16*). As shown in Figure 7, anionic SAL particles with negative surface charge interact with PQ to form patched adsorption. Though this interaction depends on the molecular weight, charge density and hydrophobicity of cationic polymers as well the ionic strength of the formulation, the electrostatic attraction between cationic polymer and anionic SAL is the primary driver for this patched adsorption. Through this adsorption, the cationic polymer can neutralize the latex particle charge density to zero surface zeta potential so that the latex particles are destabilized. This results in particle aggregation. Furthermore, the cationic polymer can function as a template and bridge the anionic SAL to form bridged flocculation. Both scenarios lead to sedimentation of anionic SAL and loss of opacity. For cationic SAL, the electrical repulsion of cationic polymer and latex particle prevents the above described polyelectrolytes and particle interaction. On the other hand, anionic surfactant can bind to cationic polymer either non-cooperatively or cooperatively depending on surfactant concentration. When surfactant concentration is below critical association concentration (CAC), the binding is non-cooperative. Polymer/surfactant aggregates are formed, where the charge is neutralized and solubility is decreased. In the cleansing formulations described in this study, the surfactant concentration is above the CAC, the binding is cooperative. Polymer and surfactant form "pearl-necklace" like complex, where net charge and solubility increase. Further interaction of "pearl-necklace" like complex and cationic SAL is possible, where a dynamic but stable aggregate can be formed as illustrated in Figure 7 (bottom). In this structure, the stability is maintained through the following two major opposing forces: hydrophobic interactions between "pearl-necklace" like complex and opacifier particle, and electrostatic repulsions between cationic polymer stretched chains. Overall, "pearl-necklace" like complex is sandwiched into the cationic particles to prevent them from irreversible aggregation.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch005

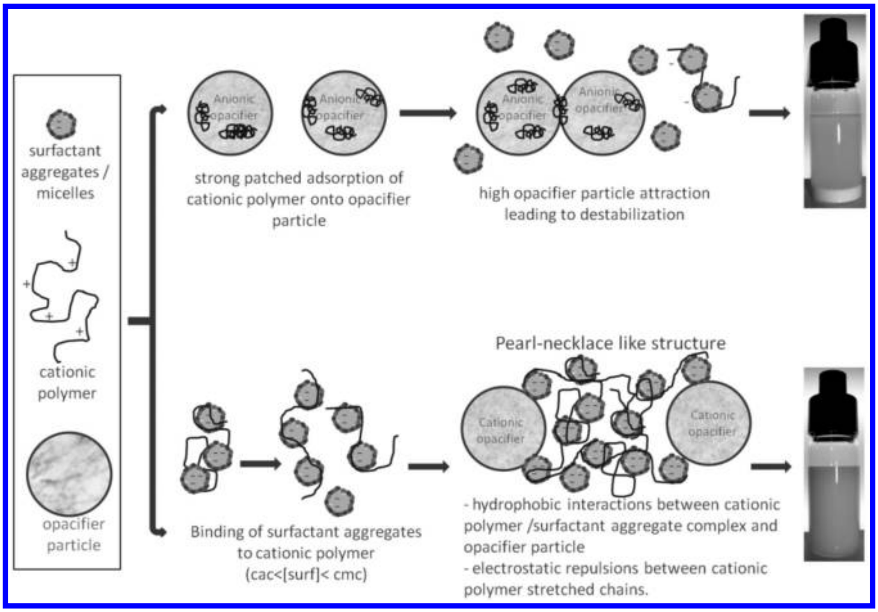


Figure 7. Interaction model of anionic and cationic SAL in cationic polymer-containing cleansing formulations.

Conclusion

A novel cationic SAL was developed with excellent compatibility in cleansing formulations containing cationic polymers. This improved compatibility over anionic SAL provides a complementary tool for formulating stable opaque products which were out of the capability of anionic SAL. The improved stability was rationalized through the complex interactions among the latex particles, surfactants and cationic polymers.

Acknowledgments

The authors gratefully acknowledge the excellent help and advice from Fabienne Bizeray, Frédéric De La Torre, Kathy Keller, Wei Gao, Martina Osti.

References

1. *Emulsion Polymerization and Emulsion Polymers*; Loverll, P. A., El-Aasser, M. S., Eds.; John Wiley and Sons: New York, 1997.
2. Mengual, O.; Meunier, G.; Cayre, I; Puech, K.; Snabre, P. *Colloids Surf., A* **1999**, *152*, 111–123.
3. Mengual, O.; Meunier, G.; Cayre, I; Puech, K.; Snabre, P. *Talanta* **1999**, *50*, 445–456.
4. Katritzky, A. R.; Sild, S; Karelson, M. *J. Chem. Inf. Comput. Sci.* **1998**, *38*, 1171–1176.
5. Napper, D. H. *Polymeric stabilization of colloidal dispersions*; Academic Press Inc.: New York, 1983.
6. Ross S.; Morrison, I. D. *Colloidal systems and interfaces*, John Wiley & Sons; 1988.
7. Fuchs, A.; Killmann, E. *Colloid Polym. Sci.* **2001**, *279*, 53–60.
8. Voorn, D. J.; Ming, W.; van Herk, A. M. *Macromolecules* **2005**, *38*, 3653–3662.
9. Dziomkina, N. V.; Hempenius, M. A.; Vancso, G. J. *Eur. Poly. J.* **2006**, *42*, 81–91.
10. Aslamazova, T.; Tauer, K. *Adv. Colloid Interface Sci.* **2003**, *104*, 273–283.
11. Deng, Y.; Yan, Z.; Yang, N. *Colloid Polym. Sci.* **1999**, *277*, 227–233.
12. van Streun, K. H.; Belt, W. J.; Piet, P.; German, A. L. *Eur. Polym. J.* **1991**, *27*, 931–938.
13. Nakatani, A.; Wang, M.; Keller, K.; Zeng, F.; Osti, M. *Soc. Cosmet. Chem Annual Scientific Meeting,* December 2011.
14. Nylander, T.; Samoshina, Y.; Lindman, B. *Adv. Colloid Interface Sci.* **2006**, *123-126*, 105–123.
15. Holmberg, K.; Jönsson B.; Kronberg, B.; Lindman, B. *Surfactants and Polymers in Aqueous Solution*, 2nd ed.; John Wiley and Sons: New York, 2003.
16. Leong, Y. K. *Colloid Polym. Sci.* **1999**, *277*, 299–305.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch006

Chapter 6

Bifunctional Synthetic Fluid: Polyalphaolefin (PAO) - Diphenylamine

Abhimanyu O. Patil* **and Satish Bodige**

Corporate Strategic Research Laboratory, ExxonMobil Research & Engineering Company, Route 22 East, Annandale, New Jersey 08801
***E-mail: Abhimanyu.o.patil@exxonmobil.com.**

1-Decene dimer with a terminal double bond (C_{20}=) was reacted with diphenylamine (DPA) using an acidic catalyst to obtain an antioxidant bound fluid. Two different alkylation catalysts were explored: Solid acid clay and 1-ethyl-3-methyl imidazolium heptachloroaluminate [$EMIM^+$][$Al_2Cl_7^-$]. In the DPA alkylation process one converts low molecular weight, volatile 1-decene dimer into a fluid with lower volatility, higher viscosity and higher viscosity index. The ionic liquid (IL) catalyst gave higher viscosity fluid than solid acid clay catalyst because of 1-decene dimer oligomerization followed by alkylation or multiple alkylations. Thus, potentially one can modify a process to design a fluid with desired viscosity and antioxidant-solubility characteristics.

Introduction

Poly-α-olefins (PAOs) have been recognized for over 30 years as a class of materials which are exceptionally useful as synthetic lubricant base stocks. They possess good flow properties at low temperatures, relatively high thermal and oxidative stability, low evaporation losses at high temperatures, high viscosity index, good friction behavior and good hydrolytic stability. PAOs are miscible with mineral oils, other synthetic hydrocarbon liquids and esters. Consequently, PAOs are suitable for use in engine oils and various other applications (*1–3*).

The term PAO has been conventionally employed as the name for these lubricant base stocks although prior to their use as such the initial olefin oligomer is hydrogenated in order to remove residual unsaturation and improve their

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch006

thermal and oxidative stability. The hydrogenation is typically performed over a supported metal catalyst. The use of PAOs as high quality lubricant base stocks has been the subject of several textbooks (*1–3*).

PAOs may be produced by the use of Friedel-Craft catalysts, such as boron trifluoride (*3*). Boron trifluoride is preferably combined with a protic promoter, typically an alcohol, water, or an acid to form a catalyst complex which may be used to promote oligomerization into products with the desired molecular weight. Branched oligomeric structure is required for a low pour point of the fluid. The alpha olefins which are generally used are those in the C_8 to C_{14} range. Olefins of this type may typically be formed by cracking or by the ethylene chain growth process.

In current low viscosity PAO process using the Friedel-Craft catalysts, the dimer or light fractions are recycled into the linear alpha-olefin feed to produce more lube base stock. These dimers or light fractions, comprising mostly of C_8H_{16} to $C_{30}H_{60}$ oligomers (average $C_{20}H_{40}$), exhibit a relatively low average molecular weight of about 280 or less and are not very desirable as feed stock because of the isomerization which accompanies the oligomerization process. Being sterically hindered, the double bonds in these light co-products are less accessible and therefore less amenable to further reaction. Thus, these dimers or light fractions are less reactive toward further oligomerization. Furthermore, they are more highly branched olefins and as a consequence of their structure, produce lube products with less desirable viscosity index (VI), volatility and thermal/oxidative stability.

An alternative to the Friedel-Craft catalyzed process is using an ionic liquid catalyst. Processes of this type may be used for producing high viscosity PAOs (*4*). An alpha-olefin oligomerization process using a non-nickel transition metal catalyst and an ionic liquid medium has been reported to obtain a trimer product (*5–7*).

Ionic Liquids

An Ionic Liquid (IL) is an organic liquid salt (100% ions) with a melting point below 100 °C. Many of the ILs are liquid over a wide temperature range (often more than 200 °C). The low melting points of the ILs can be attributed to the large asymmetric cations having low lattice energies. ILs have attracted much attention because of their unique properties which result from the composite properties of the wide variety of cations and anions (*8–16*).

Most of the ILs exhibit negligible vapor pressure at ambient conditions, which reduces the possibility of air pollution and loss of materials. ILs are highly solvating for both organic and inorganic materials. Many of them are nonflammable, non-explosive, have high thermal stability and potentially recyclable.

If we compare a typical IL, e.g., 1-ethyl-3-methylimidazolium ethyl sulfate (m.p. < - 20 °C), with a typical inorganic salt, e.g., table salt (NaCl, m.p. 801 °C), it becomes obvious why there is a difference (see Figure 1). The IL has a significantly lower symmetry. Furthermore, the charges of the cation and anion are distributed over a larger volume of the molecule by resonance. As a consequence, the solidification of the IL will take place at lower temperatures. In some cases, especially if long aliphatic side chains are involved, a glass transition is observed instead of a melting point.

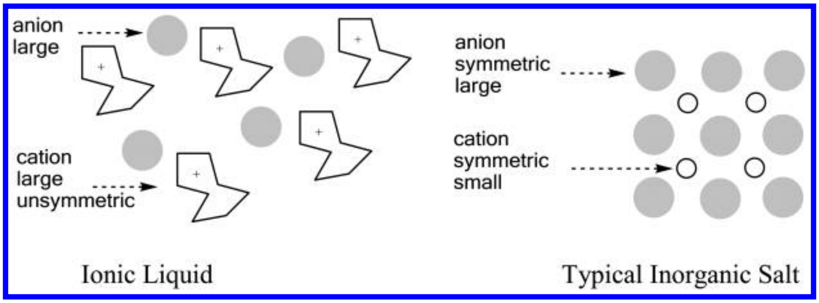


Figure 1. Cations and anions in ionic liquid and inorganic salt.

The strong ionic interaction within these substances results in a product with high thermal, mechanical and electrochemical stability. In addition, they offer other favorable properties, such as immiscibility with water or organic solvents which results in biphasic systems.

The choice of the cation has a strong impact on the properties of the IL and will often define its stability. The chemistry and functionality of the IL is, in general, controlled by the choice of the anion. The growing academic and industrial interest in IL technology is represented by the yearly increase in the number of publications: starting from far below 100 in 1990 to more than 39000 by 2012. The reason for this increase can be attributed to the unique properties of these new materials. Ultimately, the possible combinations of organic cations and anions places chemists in the position to design and fine-tune physical and chemical properties by introducing or combining structural motifs and, thereby, making tailor-made materials and solutions possible.

Ionic Liquid Catalyzed Alkylation Reactions

As noted above, ILs can be formed from the wide variety of cations and anions. Depending on the ions present, ILs may be neutral, basic or acidic in character (*8–16*). The acidic liquids can be used as catalysts for alkylation of olefins. In many instances, however, the catalyst system will be a two component system with the first component being an acidic component, i.e., a Lewis acid. For example, a typical first Lewis acid component of the catalyst system may be aluminum trichloride and the second component, as IL, may be a quaternary ammonium compound.

The catalyst system, being a liquid, may also function as the solvent or diluent for the reaction. Thus, the light PAO reactant may be alkylated directly in the presence of the catalyst system without the addition of solvent or diluent.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch006

Additives are designed to improve the performance of lubricants with respect to oxidation, wear, friction, corrosion, viscosity index, etc. One of the most significant properties is oxidative stability. Antioxidants slow oxidative degradation by neutralizing a variety of degradation chemistries, thus protecting the additives and base stocks of the formulated oils and extending their useful lifetimes and performance. Diphenylamine is a good antioxidant but is not soluble in hydrocarbons. Therefore alkylated diarylamines are used as stabilizers and/or antioxidants in a wide variety of organic materials, such as mineral oil-derived lubricants and synthetic lubricants. The mechanism of its radical inhibition is shown in Figure 2.

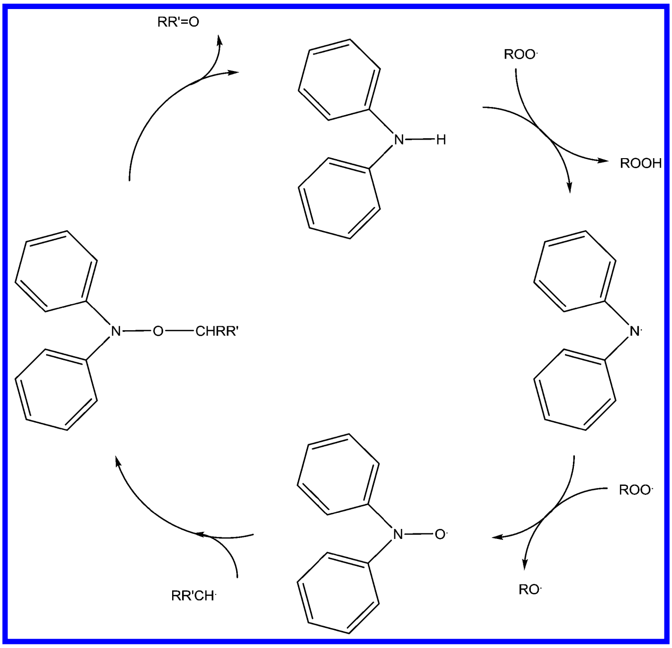


Figure 2. Diphenylamine as radical inhibitor.

In this work, 1-decene dimer was used to alkylate diphenylamine using Engelhard clay F-24 or acidic IL catalysts. The reaction scheme for diphenylamine with 1-decene using IL catalysts is shown in Figure 3. The alkylated products were characterized using IR, NMR and GPC.

IL Alkylation

The FTIR spectra of the starting 1-decene dimer showed vinyl double bond peaks at 3069, 1644 and 888 cm^{-1}. After the diphenylamine reaction catalyzed by IL, the double bond peaks disappeared and new peaks at 3450 and 1606 cm^{-1}

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch006

appeared (Figure 4). The product was examined by ^{13}C NMR to determine the composition of the product. The ^{13}C NMR results suggest that all double bonds reacted during the diphenylamine reaction.

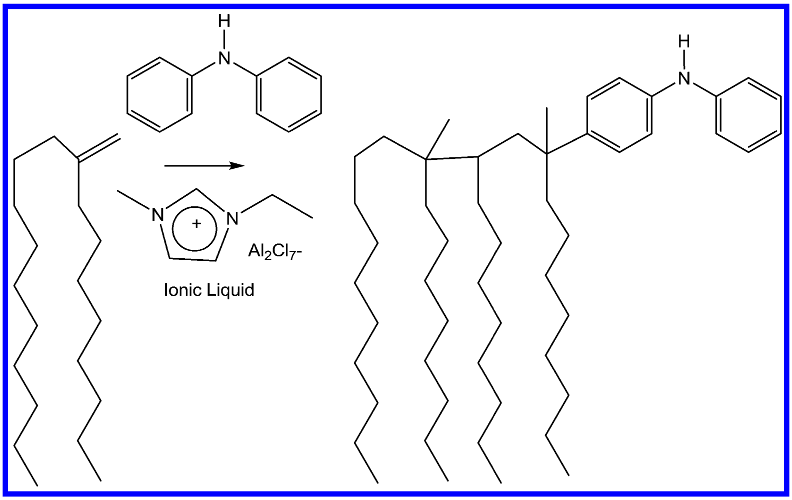


Figure 3. Reaction of diphenylamine with 1-decene dimer using ionic liquid catalyst.

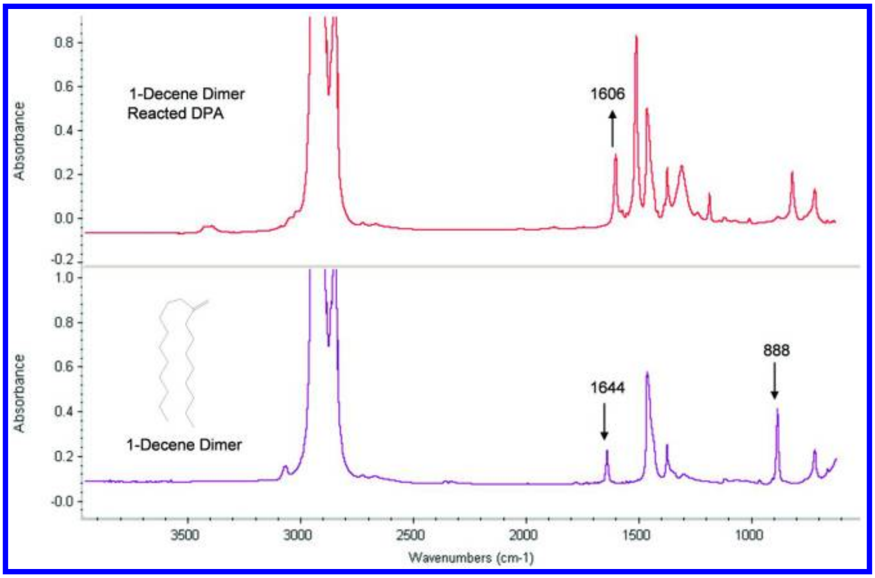


Figure 4. Infrared spectra of 1-decene dimer and and diphenylamine alkylated product using ionic liquid catalyst.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch006

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch006

Field desorption mass spectroscopy (FDMS) analysis (Figure 5) of diphenylamine-functionalized 1-decene dimer shows a major m/z peak at 729.4 due to 1-decene dimer difunctionalized with DPA and m/e peak at 449.1 due to C_{20}= monofunctionalized with DPA. The spectrum also shows peaks at 560.2 due to tetramer and peaks at 869.4 and 1009.8 possibly due to oligomerized and then alkylated PAO products. The mass spectrum x-axis in Figure 5 refers to mass/charge ratio, while m/e refers to molecular ion peak.

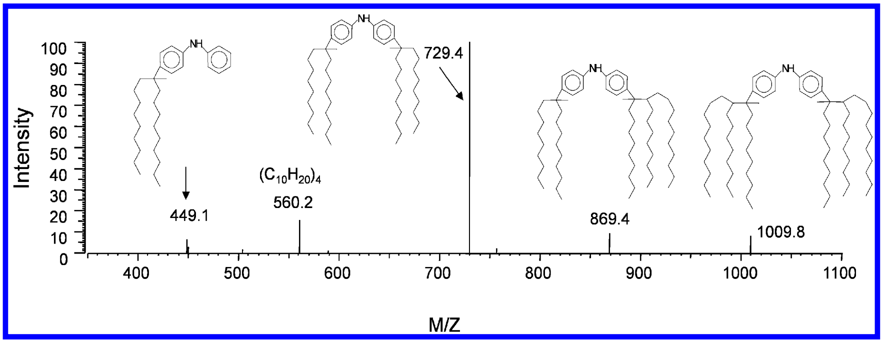


Figure 5. FIELD desorption mass spectroscopy (FDMS) OF diphenylamine alkylated 1-decene dimer.

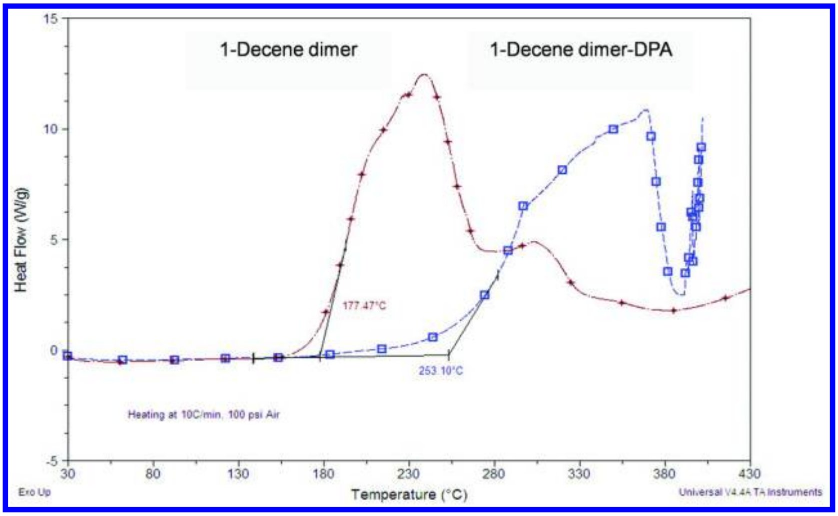


Figure 6. PDSC heating data for 1-decene dimer and dimer-diphenylamine product.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch006

Pressure Differential Scanning Calorimetry (PDSC)

Many tests are used in the lubricant industry to measure antioxidancy of products. PDSC is a technique that allows evaluation of oxidation over a temperature range. It also has the advantages of requiring only a small sample and being relatively fast. The sensitivity of oxidation data obtained upon heating depends on the sample mass, oxygen partial pressure, temperature, metallurgy of sample pan used and total operating pressure.

A DuPont (TA instruments) PDSC model 2920 with a pressure cell was used for all measurements. The cell is well calibrated for temperature (+/- 0.3 °C). The heating measurements were carried out at a heating rate of 10 oC/min and a pressure of about 100 psi in air.

Figure 6 shows the heating data obtained for the neat 1-decene dimer and the 1-decene dimer-DPA. The PDSC data showed that oxidation of diphenylamine (DPA)-functionalized product begins at 253 °C compared to 1-decene dimer which occurred at 177 °C. Thus, there is a substantial improvement in oxidation stability of the functionalized PAO.

Solid Acid Alkylation

The solid acid clay catalyzed 1-decene dimer product was also characterized using IR, NMR and GPC. The FTIR spectra of the starting dimer showed the vinyl double bond peak at 3069, 1644 and 888 cm^{-1}. After the diphenylamine reaction, the double bond peaks disappeared and new peaks appeared at 3450 and 1606 cm^{-1} The ^{13}C NMR results suggest that all double bonds reacted during the diphenylamine reaction.

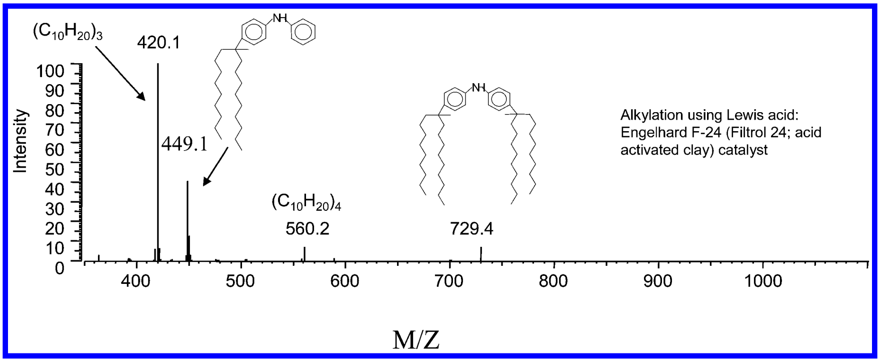


Figure 7. FIELD desorption mass spectroscopy (FDMS) of diphenylamine alkylated 1-decene dimer.

A FDMS analysis of diphenylamine-alkylated 1-decene dimer showed m/e peak at 729.4 due to dimer difunctionalized with DPA and m/e peak at 449.1 due to dimer monofunctionalized with DPA (Figure 7). If one compares the mass spectrum of IL catalyst based diphenylamine-functionalized 1-decene dimer

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch006

(Figure 5) and solid acid based product, it is clear that there are no high molecular weight peaks (i.e., m/e at 869.4 and 1009.8) in solid acid catalyst based process. This may be due to oligomerization followed by alkylation of 1-decene dimer.

The PDSC data shows that oxidation of diphenylamine (DPA)-functionalized product occurs at 257 °C compared to 1-decene dimer which occurred at 177 °C. Thus, there is a substantial improvement in oxidation stability of the functionalized PAO.

Lube Properties of the Fluids

The physical and chemical properties of synthetic fluids make them attractive for a variety of applications requiring a wider temperature operating range than can normally be achieved by petroleum-based products (mineral oils). Instead of molecular weights, synthetic lubricants like PAOs are commonly classified based on their approximate kinematic viscosity (Kv). The Kv of the liquid product was measured using ASTM standard D-445 and reported at temperatures of 100 °C or 40 °C. For lube applications, the viscosity of lubricant must permit it to flow to the surfaces to be lubricated and maintain a film thick enough to prevent excessive wear. The fluid obtained by IL catalyzed diphenylamine-functionalized 1-decene dimer has much higher viscosity than fluid obtained by solid acid catalyst alkylation reaction.

The viscosity-temperature relationship of lubricating oil is one of the critical criteria to be considered when selecting a lubricant for a particular application. The Viscosity Index (VI) is an empirical, dimension-less number which indicates the rate of change in the viscosity of an oil within a given temperature range and is related to kinematic viscosities measured at 40°C and 100 °C (typically using ASTM Method D-445 or D-2270). Fluids exhibiting a relatively large change in viscosity with temperature are said to have a low VI. The VI of both fluids were high as shown in Table 1.

Table 1. Lube properties of 1-decene dimer fluids

fluids	kv_{100}	*viscosity index*
dimer-dpa (il)	12.1	118
dimer-dpa (clay)	6.4	120
1-decene dimer	2.1	-

In summary, 1-decene dimer with a terminal double bond (C_{20}=) was reacted with diphenylamine (DPA) using two different alkylation catalysts. In the DPA alkylation process one converts low molecular weight, volatile 1-decene dimer into a fluid with lower volatility, higher viscosity and higher viscosity index (Table 1). The ionic liquid (IL) catalyst gave higher viscosity fluid than solid acid

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch006

clay catalyst possibly because of 1-decene dimer oligomerization followed by alkylation or multiple alkyations. Thus, potentially one can modify a process to design a fluid with desired viscosity and antioxidant-solubility characteristics.

Experimental Details

Preparation of IL catalyst: 2.8 g of EMIM·$AlCl_4$ ionic liquid (FW. 280, 0.01 mole) and 1.34 g of aluminum chloride (FW. 133.5, 0.01 mole) were mixed together and stirred to obtain a homogeneous mixture.

The Alkylation of 1-Decene Dimer with Diphenylamine Catalyzed by IL

8.85 g of 1-decene dimer (molecular weight 280, 0.0316 mole), 1.07 g of diphenylamine (FW. 169.22, 0.0063 mole) and 1.0 g of EMIM·Al_2Cl_7 were mixed and heated to 100 °C with a heating mantle. The reaction system was stirred overnight. Reaction was monitored by thin layer chromatography (TLC) with hexane as the eluent. The reaction mixture was filtrated through celite. The ionic liquid was removed by washing with saturated $NaHCO_3$ (200 ml x 3) and brine (200 ml) in hexane solution (200 ml). Excess unreacted 1-decene dimer was removed by vacuum distillation at 5 mmHg and 160 °C. 7.1 g of product (mono-alkylation and di-alkylation mixture) was obtained. 2.4 g of unreacted 1-decene dimer was collected. The yield was almost quantitative based on diphenylamine. Judging from TLC, almost all the product was di-substituted or PAO oligomer-substituted.

The Alkylation of 1-Decene Dimer with Diphenylamine Catalyzed by Engelhard Clay F-24)

20.7 g of 1-decene dimer (FW. 280, 0.074 mole), 2.5 g of diphenylamine (FW. 169.22, 0.015 mole) and 4.0 g of Engelhard clay F-24 catalyst were mixed in a 100 ml round bottom flask. The reaction system was brought to 100 °C and kept stirring overnight (18 hours). The reaction mixture was filtered and excess unreacted PAO dimer was removed by vacuum distillation at 5 mmHg at 160 °C. 8.5 g of product (a mono-alkylation and di-alkylation mixture) was obtained. 13.9 g of unreacted 1-decene dimer was collected. The yield was almost quantitative based on diphenylamine, i.e., the diphenylamine was substantially consumed during the reaction.

Acknowledgments

We would like to thank Chunping Wu for mass spectra.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch006

References

1. Wills, J. G. *Lubrication Fundamentals*; Marcel Dekker Inc.: New York, 1980.
2. Rudnick, L. R.; Shubkin, R. L. *Synthetic Lubricants and High-Performance Functional Fluids*, 2nd ed.; Marcel Dekker Inc.: New York, 1999.
3. Rudnick, L. R. Polyalphaolefins. In *Synthetics, Mineral Oils, and Bio-Based Lubricants*; Rudnick, L. R. Ed.; Chemical Industries: Boca Raton, FL, 2006; Vol. 111, pp 3−36.
4. Hope, K. D.; Twomey, D. W.; Driver, M. S.; Stern, D. A.; Collins, J. B.; Harris, T. V. Method for manufacturing high viscosity polyalphaolefins using ionic liquid catalysts. U.S. Patent 7,259,284, 2007.
5. Hope, K. D.; Driver, M. S.; Harris, T. V. U.S. Patent 6,395,948 B1, 2002.
6. Bagheri, V.; Eisenberg, D. C.; Ratliff, K. S.; Benda, R.; Lanier, C. W. Oligomer oils and their manufacture. U.S. Patent 6,548,724 B2, 2003.
7. Brenda, R.; Plomer, A.; Bullen, J. *J. Synth. Lubr.* **1996**, *13*, 141–157.
8. Supont, J.; Souza, R. F.; Suarez, A. Z. *Chem. Rev.* **2002**, *102*, 3667–3692.
9. Weldon, T. *Chem. Rev.* **1999**, *99*, 2071–2083.
10. Olivier-Bourbigou, H. *J. Mol. Catal. A: Chem* **2000**, *39*, 3777–3789.
11. Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789.
12. Sheldon, R. *Chem. Comm.* **2001**, *23*, 2399–2407.
13. Carmichael, A. J.; Haddleton, D. M. In *Ionic Liquids in Synthesis*; Wiley-VCH Verlag: New York, 2003; pp 319−335.
14. Olivier-Bourbigou, H.; Forestiere, A. In *Ionic Liquids in Synthesis*; Wiley-VCH Verlag: New York, 2003; pp 258−280.
15. Castner, E. W.; Wishart, J. F.; Shirota, H. *Acc. Chem. Res.* **2007**, *40*, 1217–1227.
16. Zhou, F.; Liang, Y.; Liu, W. *Chem. Soc. Rev.* **2009**, *38*, 2590–2599.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

Chapter 7

Next Generation Mildness for Personal Care: Nonpenetrating Polymerized Surfactants for Cleansing Applications

Michael J. Fevola,*[1] Frank C. Sun,[1] Russel M. Walters,[1]
and Joseph J. LiBrizzi[2]

[1]Johnson & Johnson Consumer & Personal Products Worldwide,
Division of Johnson & Johnson Consumer Companies, Inc.,
199 Grandview Road, Skillman, New Jersey 08558
[2]Current address: Ashland Specialty Ingredients, 1361 Alps Road,
Wayne, New Jersey 07470
***E-mail: mfevola@its.jnj.com**

The small molecule surfactants used in personal cleansers perform many beneficial functions, yet they can exhibit significant irritation potential. Inspired by the micelle penetration theory of surfactant-skin penetration, we have employed polymerized surfactants (PSs) to minimize irritation potential via the micelle hydrodynamic size exclusion mechanism. PSs are comprised of amphiphilic repeat units (ARUs) and overcome the problem of surfactant penetration by enabling the formation of micelles that are too large to penetrate into tissue. The physical properties of PSs can be manipulated via chemical design to provide materials that function like conventional small molecule surfactants with the benefit of a tremendous reduction in irritation potential. PSs are readily formulated into ultra-mild personal cleansers that do not compromise on product performance or aesthetics while providing new levels of mildness for skin health.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

Introduction

Surface-active agents, or *surfactants*, are essential ingredients in nearly all personal cleansing products, from bar soaps to shampoos and liquid body washes (*1*). Comprised of hydrophilic head groups that are covalently linked to lipophilic tail groups, these amphiphilic molecules exhibit distinct interfacial phenomena in aqueous media, such as self-assembly into aggregated structures, e.g. micelles or lamellae, and adsorption at air-water and oil-water interfaces (*2*). These phenomena are the fundamental drivers of surfactant-enabled processes associated with the formulation and use of personal cleansers, including viscosity building; solubilization of hydrophobic compounds, e.g. fragrances and active ingredients; detergency; and foaming. For example, the ability of surfactants to organize at air-water interfaces and lower surface tension enables the formation and stabilization of the air bubbles that comprise aqueous foams. Such foams are often formed during consumer use of surfactant-based cleansers, and foaming is an important component of the sensorial experience associated with many personal cleansing products.

Surfactants and Skin Penetration

Due to their amphiphilic nature, surfactants readily interact with biological substrates, such as the lipids and proteins that comprise the stratum corneum (SC) of the skin (*3*). During cleansing, surfactants can penetrate into the SC and damage its structure by disrupting and disorganizing lipid bilayers, solubilizing and removing lipids, and denaturing proteins (*4–7*). For example, surfactants, such as sodium dodecyl sulfate (SDS), are known to penetrate into and beyond the SC and to cause increased transepidermal water loss, inflammation, and changes in keratinocyte differentiation (*8–10*). This damage to the skin barrier and the ensuing inflammatory response are collectively referred to as *irritation*, and the small molecule surfactants typically employed in personal cleansers can present a significant irritation risk if they are not formulated properly.

A perennial goal of personal care formulators is to develop cleansing products that are exceedingly gentle on skin, yet still effective at removing dirt and oil from the body and providing copious amounts of foam. Traditional approaches to improving the mildness of surfactant based cleansers include employing surfactants with lower critical micelle concentration (CMC) values, e.g. polyoxyethylene alkyl ether sulfates in place of alkyl sulfates, and blending surfactants of different chemistries to obtain mixtures with lower CMC values, e.g. anionics with amphoterics and/or nonionics (*11–13*). The success of these approaches was explained according to the *monomer penetration model* of surfactant skin penetration, which holds that only monomeric surfactant species are capable of penetrating into the SC and causing irritation (*14*, *15*). This model assumes that at surfactant concentrations in excess of the CMC, the resulting micellar surfactant species are too large to penetrate into the SC. Thus, according to the monomer penetration model, less irritating cleansers may be obtained by decreasing the critical micelle concentration (CMC) of the surfactant system and minimizing the concentration of monomeric surfactant species.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

However, in 2003, Blankschtein and coworkers (*15*, *16*) demonstrated that surfactant micelles are indeed capable of penetrating the SC into the epidermis, leading them to propose the *micelle penetration model*, which holds that both monomeric and micellar surfactant species can contribute to irritation if the micelle hydrodynamic radius is smaller than the radius of the diffusion pathways in the hydrated SC. For example, the authors determined that SDS micelles exhibit an average hydrodynamic radius (R_h) of 20 Å, whereas the average aqueous pore radii of the hydrated SC are 10–28 Å, indicating the potential for SDS micelle penetration (*15*). Subsequent ex vivo skin penetration experiments using ^{14}C radiolabeled SDS revealed a dose-dependent penetration response above the CMC, thereby confirming that SDS micelles were indeed contributing to SDS skin penetration. In related studies, Blankschtein et al. (*15–17*) demonstrated that surfactant penetration into the SC can be reduced by additives that increase SDS micelle size, e.g. low molecular weight polyethylene glycols and ethoxylated nonionic surfactants, and that sodium cocoyl isethionate, a surfactant whose average micellar R_h value exceeds the average aqueous pore radius of the hydrated SC, is relatively ineffective at penetrating into the SC. Additionally, the group has shown that the humectant glycerol can decrease the penetration of SDS micelles into skin by effectively decreasing the average aqueous pore radius of the hydrated SC, further demonstrating the utility of the micelle penetration model (*18*, *19*)

Hydrophobically Modified Polymers for Irritation Mitigation

The technical insight provided by the micelle penetration model has led to the pursuit of new methods for irritation mitigation that target surfactant in both monomeric *and* micellar forms to minimize skin penetration and improve mildness. Previously, our group has shown that effective reduction of irritation potential can be achieved via polymer-surfactant association (*20–25*). The physical association of surfactants to hydrophobically-modified polymers (HMPs) results in the formation of HMP-surfactant complexes that are too large to penetrate into living tissue and simultaneously lowers the effective concentration of potentially irritating free micelles in solution. Addition of HMPs to surfactant systems provides an alternative substrate for surfactants to interact with during skin contact and also results in slower surfactant dynamics (*26–28*). Thus, HMPs are quite effective at inhibiting the partitioning of surfactants into the SC and preventing skin barrier damage (*29–32*). Nevertheless, the HMP-surfactant complexes and some free micelles are still available at the skin surface to provide the cleansing and foaming performance required for product functionality. Successful application of this approach requires the selection of HMPs that exhibit high surfactant binding efficiency yet do not interfere with product aesthetics, e.g. rheology, clarity, etc. (*21–25*, *33–36*).

The present chapter will review how deeper understanding of *micelle size distributions* (MSDs) has led us to a new polymer-based approach for preventing surfactant penetration, which is based on micellar hydrodynamic size exclusion. To further exploit this mechanism for minimizing irritation potential in personal cleansers, we have identified and applied *polymerized surfactants* (PSs) as a class of nonpenetrating amphiphiles that achieve tremendous improvements in mildness over conventional small molecule surfactants.

Micelle Size Distributions and Irritation Potential

According to the findings of Blankschtein et al., surfactant micelles with average micelle hydrodynamic diameter (d_H) values less than ca. 6 nm are capable of penetrating into the SC and compromising the skin barrier, while larger surfactant micelles, i.e. those having average d_H values greater than 6 nm, exhibit dramatically less skin penetration due to hydrodynamic size exclusion (*15–17*). Yet even for surfactant systems with average micellar d_H values greater than 6 nm, the MSD may still contain a significant fraction of micelles that are small enough to penetrate the SC and contribute to irritation potential.

Building on the work of Blankschtein et al., we have previously used dynamic light scattering (DLS) analysis to measure the average micelle sizes and MSDs of commercially relevant surfactants and cleansing products at concentrations in the range of in-use dilution (*22*, *37–40*). The irritation potential of these surfactant systems was measured via the transepithelial permeation (TEP) assay, an in vitro biological assay with direct correlation to skin and eye irritation (*22*, *41*, *42*). TEP values (reported as an EC_{50}, the percent dilution at which a formula will decrease epithelial barrier integrity by 50%, as measured by fluorescein dye leakage) increase as a function of decreasing irritation potential; thus milder surfactant systems display higher TEP scores.

As predicted by the micelle penetration model, surfactant systems exhibiting larger average values of micelle d_H also demonstrated higher TEP scores, i.e. lower irritation potential. However, because MSDs tend to be broad in nature, even mild surfactant blends with average micelle d_H values greater than 6 nm were found to have a significant fraction of smaller micelles, i.e. micelles having d_H values less than 6 nm, that are capable of penetrating into skin. Thus, a high foaming, yet mild cleanser cannot be achieved by simply employing a mild surfactant blend at an increased concentration: Although increasing the surfactant load will positively impact foam volume, it will negatively impact mildness because of the increased concentration of small penetrating micelles that accompanies an increase in the overall surfactant concentration (*22*).

Our previous approach to mitigate the irritation potential of these small penetrating micelles during product usage employed HMPs to decrease the overall concentration of micellar surfactant in solution without respect to micelle d_H, as shown in Figure 1. We have demonstrated that HMPs with high surfactant binding efficiency can effectively sequester a significant fraction of surfactant that would normally be present as free micelles in the absence of HMPs, and that this reduction in apparent free micelle concentration results in reduced surfactant penetration and irritation potential (*20*, *22*, *23*, *25*). However, surfactant present at concentrations in excess of the HMP saturation concentration will exist as free micelles with a distribution of sizes, and any free micelles with average d_H values less than six nm will still be capable of penetrating into the SC.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

Therefore, to achieve more effective irritation mitigation via hydrodynamic size exclusion, surfactant systems must be designed to shift the entire MSD to d_H values greater than 6 nm, as illustrated in Figure 2. In particular, we have discovered that significant decreases in irritation potential are obtained when the *small micelle fraction* (SMF), which we define as the fraction of micelles in the MSD with d_H values less than 9 nm, does not exceed 50% (*38–40*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

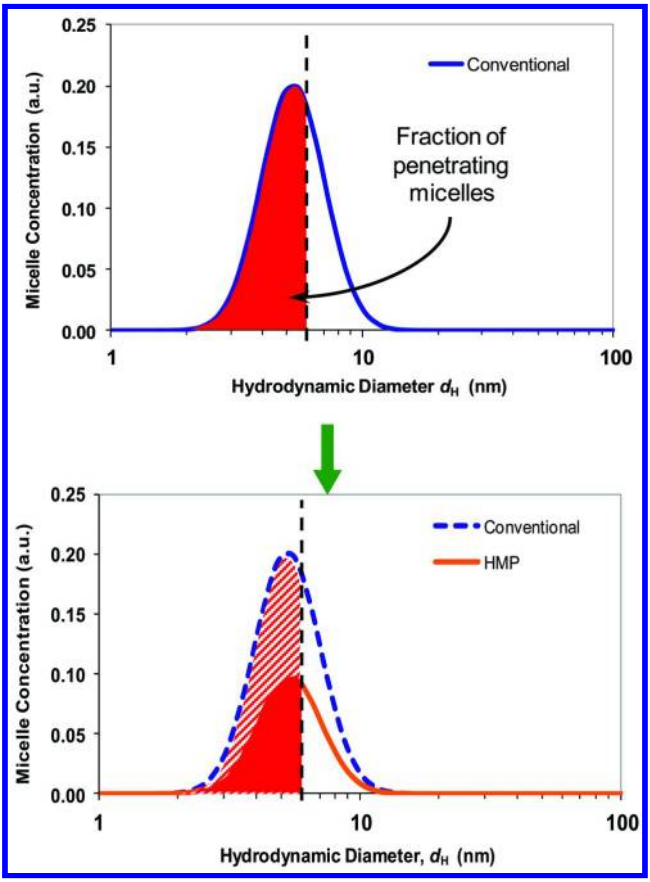


Figure 1. Conceptual diagram of polymer-surfactant association mechanism for reducing surfactant penetration with HMPs. Free micelle concentration as a function of micelle d_H shown for a conventional surfactant system (top) and a surfactant system containing a HMP (bottom). The dashed lines at $d_H = 6$ nm represent the upper size limit of aqueous pore radii in the SC as measured by Moore et al. (15).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

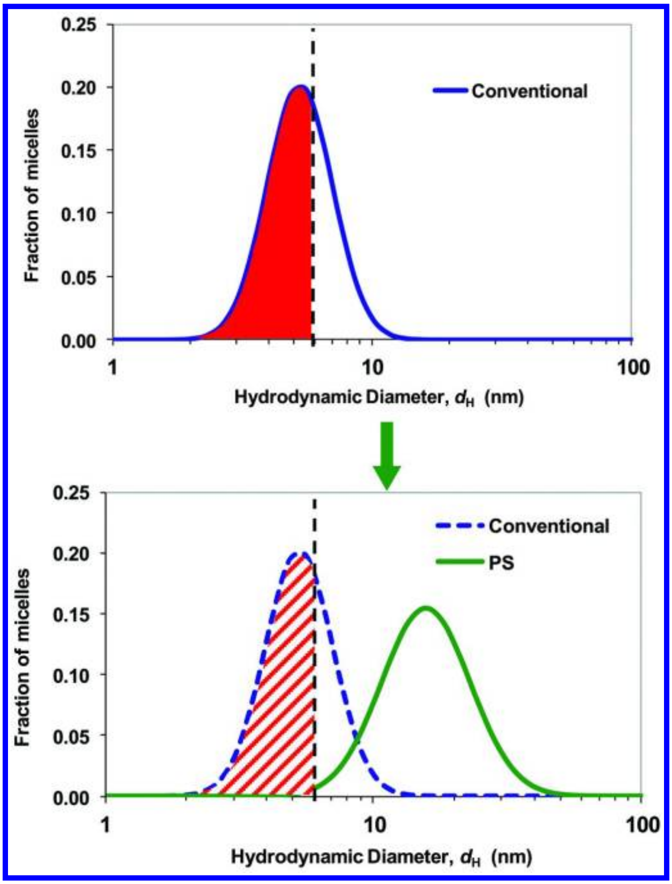


Figure 2. Conceptual diagram of hydrodynamic size exclusion mechanism for reducing surfactant penetration with PSs. Model MSDs shown for conventional small molecule surfactants (top) and comparison to micelles comprising PSs (bottom). The dashed lines at d_H = 6 nm represent the upper size limit of aqueous pore radii in the SC as measured by Moore et al. (15).

Polymerized Surfactants for Personal Cleansing

In theory, the ideal mild cleansing formulation would contain surfactants that are not capable of penetrating into skin in either monomeric or micellar forms. However, such nonpenetrating surfactants would still need to have adequate amphiphilic character to provide the surface and interfacial activity required for processes such as cleaning and foaming. In an effort to achieve this ideal balance, we have identified PSs as a class of amphiphilic macromolecules that provide the functionality of small molecule surfactants with the benefit of little or no irritation potential due to their inability to penetrate into tissue.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

Polymerized Surfactants

PSs are defined as polymers comprised of covalently-linked amphiphilic repeat units (ARUs), wherein each ARU contains both hydrophilic and lipophilic, i.e. hydrophobic, moieties (*38–40*). Also known as *polysoaps* or *micellar polymers*, PSs often demonstrate the same phenomena as small molecule surfactants in aqueous solutions, including surface activity and self-assembly into micelles (*43*). However, the covalently-linked nature of the surface-active ARUs also causes PSs to demonstrate unique properties compared to their small molecule counterparts. For instance, PSs exhibit very low CMC values (or in some cases no CMC at all) indicating that PSs exist almost exclusively in micellar form, a consequence of the ARUs being bound by a common polymer backbone. PS ARUs are also limited in their degrees of freedom compared to small molecule amphiphiles and do not pack efficiently into micelles; thus, PS micelles have significantly larger d_H values compared to micelles comprised of small molecule amphiphiles, typically an order of magnitude larger. Additionally, the solution dynamics of PSs micelles are slower compared to those of small molecule surfactants due to the enhanced stability of PS micelles and the slower diffusion of PS molecules.

Penetration of PS molecules into the SC is inhibited due to their inherent steric bulk and propensity to exist as large micelles. PSs are an extremely effective means of achieving MSDs with a low SMF and thus low irritation potential (*38–40*). PSs are also capable of comicellization with small molecule surfactants, so PSs can be blended with conventional surfactants to yield mixed surfactant systems having larger d_H values and low SMFs.

The PS approach to controlling and preventing surfactant penetration overcomes two potential shortcomings of the HMP approach, 1) the presence of small free micelles not bound to the HMP, and 2) the necessity of properly matched HMP-surfactant combinations for high surfactant binding efficiency. As mentioned earlier, HMPs bind surfactant without respect to hydrodynamic size, and therefore any free micelles not bound to HMPs will exist in a MSD which may contain a population of smaller, more dynamic micelles capable of penetration. By shifting the entire MSD to higher values, PSs eliminate this population of small micelles that would remain even in the presence of an HMP. HMPs must also be properly matched to the surfactant(s) in a given cleansing system to ensure high surfactant binding efficiency. PSs overcome this requirement by incorporating the surfactant functionality into a polymeric species that does not depend on physical, i.e. noncovalent, association to prevent surfactant penetration.

Representative PS Chemistries

A variety of synthetic approaches can be employed to prepare PS molecules (*38–40*). The common goal of these synthetic approaches is to yield a polymer comprising ARUs, which may be achieved via 1) post-polymerization modification of polymers to convert some or all of the repeat units to ARUs, or 2) polymerization of preformed amphiphilic monomers.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

PSs are readily achieved via post-polymerization modification routes that provide amphiphilic character to some or all of the repeat units in a hydrophilic or hydrophobic parent polymer. For example, 1:1 alternating copolymers of C_8 – C_{24} α-olefins and maleic anhydride (MA), such as poly(1-octadecene-*alt*-MA) (PA-18) and poly(1-tetradecene-*alt*-MA) (PA-14), are normally hydrophobic materials that are insoluble in water. However, base-catalyzed hydrolysis and neutralization of these copolymers results in PSs comprised of ARUs bearing hydrophilic dibasic succinate moieties and pendant C_6–C_{22} hydrophobic moieties (Figure 3) (*38–40*). The hydrolyzed copolymers are soluble in water and exhibit surface-active solution behavior, such as foaming. Notable examples are the sodium salts of hydrolyzed PA-18 (HPA-18) and PA-14 (HPA-14). Ring-opening of the MA groups on the PA-18 and PA-14 with hydrophilic nucleophiles also provides ARUs. PAT-18 and PAT-14 (Figure 3) were prepared via amidation of the MA groups with sodium taurate under basic conditions according to previously reported methods (*44*, *45*), to yield PSs bearing sulfonate functionalities for improved solubility under low pH conditions.

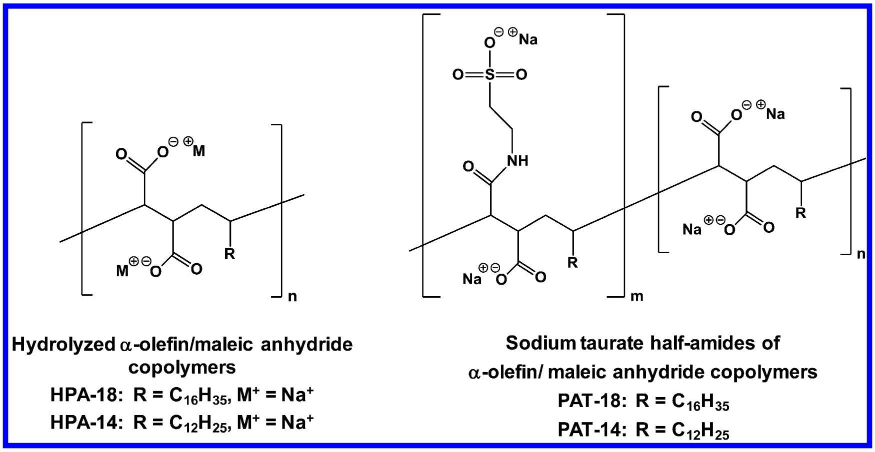


Figure 3. Chemical structures of PSs derived from post-polymerization modification of long chain α-olefin/maleic anhydride copolymers.

Free-radical homo- and copolymerization of ethylenically-unsaturated amphiphilic monomers can be used to prepare a variety of PS molecules (*38–40*), such as those shown in Figure 4. Notable examples of such monomers include sodium allyldodecylsulfosuccinate (*46*) and 2-acrylamidododecylsulfonic acid (*47*). However, due to the relatively higher cost of these specialty amphiphilic monomers, it is advantageous to copolymerize them with less expensive ethylenically-unsaturated hydrophilic conomomers, such as acrylic acid (AA). Copolymerization with hydrophilic monomers can also improve the solubility of PSs bearing ARUs that are more hydrophobic in nature.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

PSs may also be synthesized by step-growth copolymerization of amphiphilic monomers bearing two or more reactive functional groups. Such amphiphilic monomers can be covalently linked together via condensation or addition reactions with suitable difunctional comonomers. For example, O'Lenick et al. (*48*, *49*) have reported the synthesis of PSs by the base-catalyzed condensation polymerization of alkyl polyglucoside (APG) surfactants with 1,3-dichloroisopropanol to yield a complex mixture of linear, branched, and crosslinked polymeric APGs. These polymeric APGs may be further derivatized to incorporate anionic, cationic, or zwitterionic moieties to impart more hydrophilic character to the PS molecules.

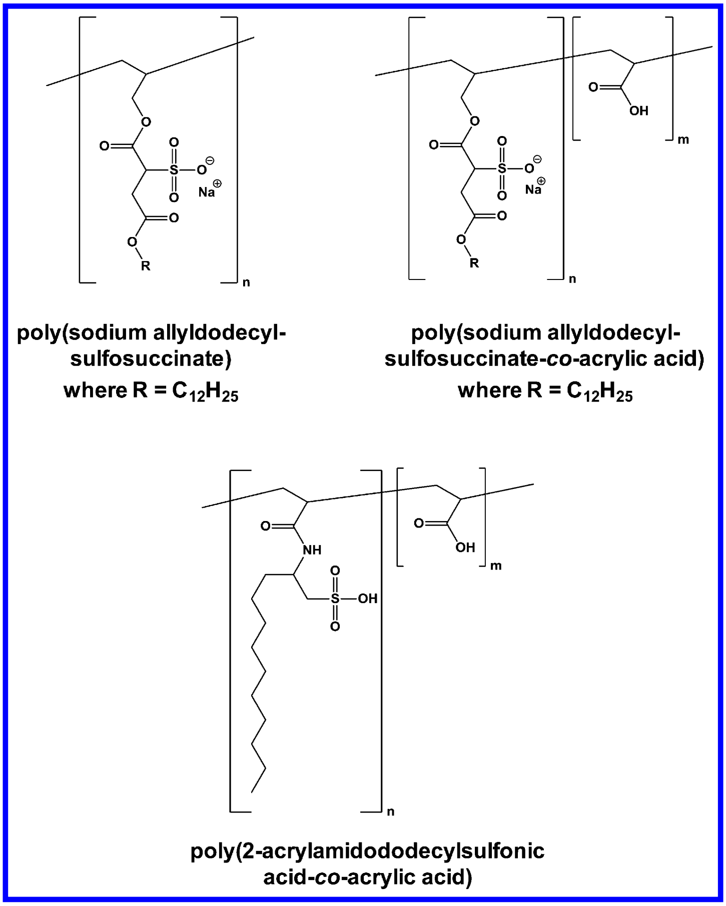


Figure 4. Chemical structures of PSs derived from polymerization of ethylenically-unsaturated amphiphilic monomers.

A key disadvantage of the step-growth approach to PS synthesis is that the degree of polymerization (DP) is governed by the Carothers equation (*50*); thus, comonomer stoichiometry must be precisely controlled and the reactions

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

driven to very high conversion in order to achieve a DP distribution composed predominately of true polymeric species that are not capable of skin penetration. If the reactant stoichiometry is not precisely controlled and the polymerization reactions are not driven to sufficiently high conversion, the DP distribution of the resulting PS will contain a significant fraction of oligomeric species (e.g. dimers, trimers, tetramers, etc.) that could be detrimental to mildness.

PS Molecular Design Principles

Although an extremely diverse selection of chemistries can be employed to synthesize PSs, the resulting molecules must fulfill certain design criteria to achieve the optimal balance of mildness and formulation performance required in personal cleansing applications. First, the PS must contain a sufficient level of ARU content to elicit surfactant behavior in aqueous solution, including surface-tension reduction, foaming, detergency, and solubilization. While PSs may require as little as 10 mol% ARU content to function as surfactants, we have discovered that PSs containing from 25–100 mol% ARU content demonstrate ideal performance (*38–40*). PSs should also exhibit low DPs, most preferably from 20–500 ARUs, which typically correspond to PS molecular weights (MWs) of 10,000–50,000 g/mol. The low DP is important to ensure low PS solution viscosities and sufficiently fast diffusion of PS molecules to air-water and oil-water interfaces.

The combination of high ARU content and low MW are especially critical to PS performance in personal cleansing applications, and contrasting molecular architectures will not possess the appropriate solution behavior. For instance, PS molecules having a *low* ARU content, i.e. less than 10 mol% ARU, and *high* MWs will tend to have lower critical overlap concentration (c^*) values and exhibit intermolecular association behavior in aqueous solution at relatively low concentrations. This intermolecular association leads to associative thickening phenomena as the polymers form networks of hydrophobic associations above c^* (*51*). Such viscosity building behavior is undesirable in PSs for personal cleansing applications, as the resulting product formulations will be too viscous or gel-like, leading to poor cleansing and foaming performance during product use.

Conversely, PS molecules having *high* ARU content and *high* MW, i.e. greater than 50,000 g/mol, demonstrate a strong propensity for intramolecular association of the ARUs (*51*). As the PS chains becomes longer and more flexible with increasing MW, the intramolecular associations cause collapse of the PS into unimolecular micelles. Such high MW unimolecular micelles tend to be kinetically “frozen”, and due to this stability they are not capable of dissociation and interfacial activity on the timescales associated with processes such as foaming and detergency.

PS Micelle Size and Mildness

The goal of employing PSs in personal cleansing formulations is to minimize and ultimately eliminate penetration of the surfactant species into skin during product use by creating micellar species that are too large to penetrate into the

SC. The validity of this approach has been demonstrated for the PS molecules shown in Figures 1 and 2. Model formulas comprising 4.8 wt % active surfactant (either a PS or a conventional small molecule surfactant) were analyzed via DLS to determine their MSDs and screened for irritation potential using the TEP assay. DLS was conducted on diluted formulations at concentrations representative of in-use dilution (typically 3% formulation in deionized water) and which correspond to the dilution ranges used in the TEP assay.

Table I. Dynamic Light Scattering and TEP Assay for Model PS Formulations (*38–40*)

Polymerized Surfactant	*Average Micelle d_H (nm)*[a]	*Small Micelle Fraction (% $d_H < 9$ nm)*	*TEP EC_{50} Value (% formula)*
HPA-18	15.1	10	No leakage
HPA-14	48.6[b]	4	No leakage
PAT-18	17.6	13	4.85 ± 1.33
PAT-14	13.0[c]	34	No leakage
AA/Acryloyldecyltaurine Copolymer	16.7	14	No leakage
AA/Sodium Allyldodecyl-sulfosuccinate Copolymer	8.4[d]	41	No leakage
Comparative Examples			
Cocamidopropyl Betaine	6.2	91	2.55 ± 0.46
Sodium Laureth Sulfate	2.7	100	3.12 ± 0.74
Sodium Trideceth Sulfate	2.6	100	1.73 ± 0.50

[a] Measured as a 3% (w/w) dilution in deionized water on a Malvern Instruments Zetasizer Nano ZS operating at 25 °C. [b] Bimodal distribution of d_H values, low peak = 15.9 nm, high peak = 148 nm [c] Bimodal distribution of d_H values, low peak = 12.9 nm, high peak = 113 nm [d] Bimodal distribution of d_H values, low peak = 3.7 nm, high peak = 21.8 nm.

The DLS data in Table I reveal that the PSs exhibit significantly larger average values of micelle d_H compared to typical small molecule surfactants used in personal cleansers. More importantly, the MSDs for the PSs contain significantly lower SMFs, indicating fewer potentially irritating micellar species are present. In contrast, the small molecule surfactants demonstrate very high SMF values, indicating that the majority of the micelles in the size distribution are capable of penetrating into and disrupting the skin barrier.

The TEP assay reveals that the model PS formulations are exceedingly mild, and in most cases, the PS formulas do not even elicit a response in the assay. The absence of dye leakage indicates that the PS micelles do not disrupt the epithelial

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

barrier and have a negligible irritation potential. For PAT-18, the EC_{50} value is relatively high, indicating a high concentration of the formula is necessary to compromise barrier integrity. On the other hand, the formulas containing conventional small molecule surfactants have relatively low EC_{50} values which correspond to increased potential for skin barrier disruption and irritation. In accordance with the micelle penetration model, we attribute the dramatically lower or nonexistent irritation potential of the PSs to their larger average micelle d_H and low SMF values. Thus, the DLS and TEP data in Table I further reinforce the utility of the micelle penetration model and reveal the ability of PSs to function as nonpenetrating surfactants with extremely low irritation potential.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

Table II. Dynamic Light Scattering and TEP Assay Data for Model PS Formulations of HPA-18 and Cocamidopropyl Betaine (*38–40*)

Ratio CAPB: HPA-18	*[CAPB] (wt % active)*	*Average Micelle d_H (nm)*[a]	*Small Micelle Fraction (% $d_H < 9$ nm)*[a]	*TEP EC_{50} Value (% formula)*
0.00	0.0	15.1	10	No leakage
0.38	1.8	19.5	3	No leakage
0.75	3.6	20.2	3	No leakage
1.00	4.8	18.1	5	No leakage
1.25	6.0	16.2	9	5.51 ± 0.20
1.50	7.2	13.8	18	4.76 ± 0.66
Comparative Examples				
CAPB only (no HPA-18)	7.2	6.2	91	2.55 ± 0.46
SLES (1.50)	7.2	5.3	94	1.34 ± 0.48

[a] Measured as a 3% (w/w) dilution in deionized water on a Malvern Instruments Zetasizer Nano ZS operating at 25 °C.

PS Compositions Comprising Mixed Micelles

Personal cleansing formulations rarely contain a single surfactant ingredient, but instead utilize multi-component surfactant systems that are formulated to maximize product performance and minimize overall formula cost. Such surfactant blends act synergistically to enhance product attributes, e.g. rheology, foam volume, lather quality, skin feel, etc., which in turn provide points of differentiation to the consumer. With this in mind, it is critical to demonstrate that PSs can be formulated with common secondary surfactants used in personal cleansing formulations and still deliver exceedingly mild products.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

Table II shows DLS and TEP data for model cleansing compositions based on 4.8 wt % HPA-18 as the primary surfactant with varying ratios of a small molecule cosurfactant, cocamidopropyl betaine (CAPB) (*38–40*). In the absence of CAPB, the HPA-18 formulation has an average micelle d_H = 15.1 nm and an SMF of 10%. This formula causes no dye leakage in the TEP assay, indicating that it has virtually no irritation potential. As the ratio of CAPB:HPA-18 in the formula is increased from zero to 0.75, the average micelle d_H increases and the SMF decreases; this is due to comicellization of CAPB with HPA-18, which causes expansion of the HPA-18 PS micelles. Deo and coworkers (*52–54*) have reported analogous comicellization behavior with both anionic and nonionic surfactants for a high MW PS, poly(octyl vinyl ether-*alt*-maleic acid) having weight-average MW = 160,000 g/mol.

The HPA-18/CAPB formulas are still quite benign up to a CAPB:HPA-18 ratio of 1.00, as indicated by the absence of leakage in the TEP assay. However, at CAPB:HPA-18 ratios above 0.75, the average micelle d_H begins to decrease and a corresponding increase in the SMF is observed. These results are attributed to the onset of homogeneous CAPB micelle formation that occurs once the HPA-18 becomes saturated with CAPB and comicellization is no longer possible (*52–54*). As the concentration of CAPB increases and more homogeneous CAPB micelles form, dye leakage eventually occurs in the TEP assay as the small CAPB micelles begin to compromise the epithelial barrier.

The ability of HPA-18 to decrease the irritation potential of CAPB via comicellization is evident from the comparative example of 7.2 wt % CAPB in the absence of HPA-18. This formula has an average micelle d_H of 6.2 nm and an SMF of 91%, and it exhibits a TEP score ca. 50% lower than the corresponding formula with HPA-18. This result is particularly surprising because the formula without HPA-18 contains 40 % less active surfactant, yet it displays a dramatically lower TEP score, i.e. higher irritation potential.

When a traditional anionic surfactant, sodium laureth sulfate (SLES), is substituted for HPA-18 in the 7.2 wt % CAPB formulation, a precipitous decrease in the TEP score is observed (Table II). This large increase in the irritation potential is attributed to the much smaller average micelle d_H (5.3 nm vs. 13.8 nm) and extremely high SMF (94 %) of the SLES-CAPB system.

Foaming Properties of PS Formulations

Foam and lather strongly influence consumer perception of cleansing products, and successful products must deliver adequate foam and lather to satisfy consumers' expectations. An important feature of PS-based cleansing systems is that their exceptional mildness does not come at the expense of foaming performance. To demonstrate the ability of a PS to substitute for a traditional high-foaming anionic surfactant, model cleansing formulations comprising 7.2 wt% CAPB and either 4.8 wt % HPA-18 or 4.8 wt % SLES were analyzed for foam generating ability. Diluted solutions (0.5 wt % formula in simulated hard water containing 130 ppm Ca^{2+}) of each formula were tested using a SITA R-2000 Foam Tester (SITA Messtechnik GmbH) operating at 30 °C and 1200 rpm. Foam volume measurements were recorded at 15 s intervals, with the maximum

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

foam volume reported at 180 s. The foam performance of the HPA-18 and SLES formulations was found to be nearly identical (Table III), indicating that substitution of HPA-18 for SLES to create a milder formula with larger average micelle d_H and lower SMF did not negatively impact foaming ability. Thus, while the design of personal cleansers classically involves a tradeoff between foam performance and mildness (*37*), we have shown that PSs can overcome this tradeoff to enable the formulation of cleansers with both high foaming performance and superior mildness.

Table III. Dynamic Light Scattering, TEP Assay, and Foam Volume Data for Cleansing Compositions Containing Either HPA-18 or SLES

Anionic Surfactant	*Average Micelle d_H (nm)*[a]	*Small Micelle Fraction (% d_H < 9 nm)*[a]	*TEP EC_{50} Value (% formula)*	*Max Foam Volume (mL)*
HPA-18	13.8	18	4.76 ± 0.66	357 ± 15
SLES	5.3	94	1.34 ± 0.48	347 ± 14

[a] Measured as a 3% (w/w) dilution in deionized water on a Malvern Instruments Zetasizer Nano ZS operating at 25 °C.

Viscosity Building for Flash Foam in PS Formulations

To provide a consumer-desirable cleansing experience, foaming cleansers should lather quickly and efficiently to produce a substantial quantity of foam during product use, e.g. upon handwashing or shampooing. A particularly critical aspect of a cleansing product's foam behavior is its propensity for *flash foaming*. Flash foaming refers to the rapid generation of significant quantities of foam upon lathering; the foam formed over short periods of lathering and/or with minimal energy input is referred to as *flash foam*, and a product that generates large quantities of flash foam is said to be a good *flash foamer*.

We have observed that foaming performance during cleanser use is related to the loss in product viscosity that occurs upon in-use dilution. This viscosity reduction is referred to as the formula's ability to *break*. Formulas that break more efficiently upon in-use dilution tend to exhibit improved flash foaming ability.

As thin or watery personal cleansers are undesirable to consumers, the formulas are typically thickened via incorporation of rheology modifiers to increase product viscosity. Such rheology modifiers include high MW linear water-soluble polymers, crosslinked water-swellable microgels, and associative micellar thickeners (*55*). The high MW polymers and crosslinked microgels possess rather large hydrodynamic volumes in aqueous solution and efficiently occupy free solvent volume with increasing concentration; viscosification is achieved in the former via chain overlap and entanglement, while the latter do so via colloidal packing and network formation (*55*). Associative micellar thickeners (AMTs) are relatively low MW (generally < 25,000 g/mol) linear or star-shaped hydrophilic polymers that are functionalized with hydrophobic endgroups (*55*, *56*). Due to the hydrophobic effect, the endgroups associate to form micelle-like aggregates in aqueous solution. Above a critical concentration, AMTs form three-dimensional networks of intermolecular hydrophobic associations; this network formation results in a dramatic increase in solution viscosity. Examples of AMTs include linear polyethylene glycol diesters, such as PEG-150 Distearate, and ethoxylated polyol esters, such as PEG-120 Methyl Glucose Dioleate and PEG-120 Methyl Glucose Trioleate.

We have discovered that PS formulations thickened with AMTs deliver superior flash foaming performance (*57*). Improvements in flash foaming have been quantified using the Modified Cylinder Shake Test (MCST), which is designed to simulate flash foaming during in-use dilution. In the MCST, 50 g of the cleanser is charged to a 500 mL graduated cylinder and then 50 g of water is carefully added on top of the formula to yield two separate layers. The cylinder is then sealed and agitated by rotating on a Gaum Foam Machine (Gaum Inc., Robbinsville, NJ) causing simultaneous dilution and foaming. The flash foam volume (FFV) is recorded as a function of the number of cylinder shake cycles, and the foam generation rate (FGR) is determined by plotting the FFV as a function of cylinder shake cycle and fitting the data to a linear function; the slope of the resulting linear fit is the FGR.

Figure 5 shows MCST data for formulations containing 4.5 wt % HPA-18 and 5.0 wt % CAPB. The formulas are thickened to similar viscosities (~9000 cP) with either an AMT (PEG-120 Methyl Glucose Dioleate, sold commercially as Glucamate™ DOE-120 by Lubrizol Advanced Materials, Inc., Brecksville, OH), or a crosslinked microgel (Acrylates Copolymer, a crosslinked alkali-swellable emulsion copolymer of ethyl acrylate and methacrylic acid, sold commercially as Carbopol® AQUA SF-1 by Lubrizol Advanced Materials, Inc.). The MCST reveals that the formula thickened with the AMT exhibits a higher FGR, which corresponds to better flash foaming.

The superior flash foaming ability of AMT-thickened PS formulas is attributed to the highly dilution-sensitive integrity of the AMT thickening network, which enables the formulas to rapidly break upon in-use dilution. Typical in-use dilution results in an AMT concentration that is below the critical concentration required for formation of the thickening network. Therefore, the concentration change that occurs during lathering triggers a precipitous decrease in product viscosity. The diluted product requires significantly less energy input to create foam due to its low viscosity. The loss in viscosity also enables the PSs to diffuse more rapidly to air-water interfaces that are formed during lathering, leading to enhanced stabilization of the resulting foam bubbles as they are formed.

In contrast, PS formulas thickened with high MW polymers or crosslinked microgels do not break as readily and thus tend to exhibit poor flash foaming. This behavior is due to the less concentration-sensitive nature of their hydrodynamic thickening mechanisms. At typical in-use dilutions, these formulas will maintain higher viscosities and require greater energy input during lathering to create foam. The higher viscosities will also impair PS diffusion to newly formed air-water interfaces, further inhibiting flash foaming in these systems.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

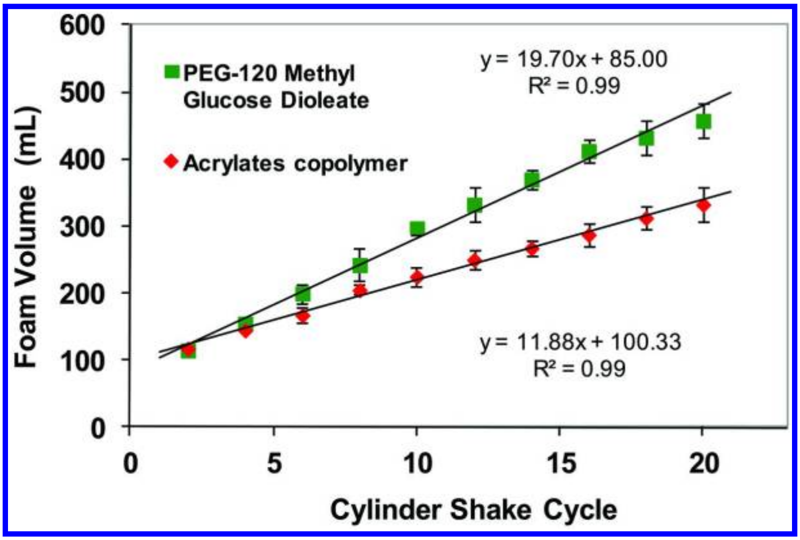


Figure 5. Determination of foam generation rate via MCST for HPA-18 formulations thickened with PEG-120 Methyl Glucose Dioleate or Acrylates Copolymer (57).

Conclusion

We have demonstrated that PSs can be used to achieve tremendous improvements in mildness over conventional small molecule surfactants via micellar hydrodynamic size exclusion. Due to their polymeric nature, PSs and PS micelles are too large to penetrate into tissue, rendering them extremely mild; nevertheless, PSs are still capable of providing the same benefits as conventional surfactants, such as cleansing and foaming, due to their amphiphilic character. PSs can also be formulated with conventional surfactants to form larger mixed micelles that demonstrate improved mildness. Viscosity building in PS formulations requires careful selection of rheology modifiers to achieve acceptable flash foaming during product use, with AMTs delivering the best performance. PSs represent a step-change in mild cleansing technology and are perhaps the mildest foaming surfactant ingredients ever developed for personal cleansing.

List of Abbreviations

AA	acrylic acid
AMT	associative micellar thickener
APG	alkyl polyglucoside
ARU	amphiphilic repeat unit
CAPB	cocamidopropyl betaine
CMC	critical micelle concentration

d_H	hydrodynamic diameter
DLS	dynamic light scattering
DP	degree of polymerization
FFV	flash foam volume
FGR	foam generation rate
HMP	hydrophobically-modified polymer
HPA-14	hydrolyzed PA-14
HPA-18	hydrolyzed PA-18
MA	maleic anhydride
MSD	micelle size distribution
MW	molecular weight
PA-14	poly(1-tetradecene-*alt*-MA)
PA-18	poly(1-octadecene-*alt*-MA)
PAT-14	sodium taurate half-amide of PA-14
PAT-18	sodium taurate half-amide of PA-18
PS	polymerized surfactant
SC	stratum corneum
SDS	sodium dodecyl sulfate
SLES	sodium laureth sulfate
SMF	small micelle fraction
TEP	transepithelial permeation

References

1. O'Lenick, A. J., Jr. *Surfactants: Strategic Personal Care Ingredients*; Allured Publishing Corp.: Carol Stream, IL, 2005.
2. Holmberg, K.; Jönsson, B.; Kronberg, B.; Lindman, B. *Surfactants And Polymers In Aqueous Solution*, 2nd ed.; John Wiley & Sons: New York, 2002.
3. Mao, G.; Flach, C. R.; Mendelsohn, R.; Walters, R. M. *Pharm. Res.* **2012**, *29* (8), 2189–2201.
4. Rieger, M. M. *Cosmet. Toiletries* **1995**, *110* (4), 31–50.
5. Polefka, T. G. In *Handbook of Detergents, Part A: Properties*; Broze, G., Ed.; Marcel Dekker, Inc.: New York, 1999; pp 433−468.
6. Ananthapadmanabhan, K. P.; Moore David, J.; Subramanyan, K.; Misra, M.; Meyer, F. *Dermatol. Ther.* **2004**, *17* (1), 16–25.
7. Saad, P.; Flach, C. R.; Walters, R. M.; Mendelsohn, R. *Int. J. Cosmet. Sci.* **2012**, *34* (1), 36–43.
8. Jongh, C. M. d.; Jakasa, I.; Verberk, M. M.; Kezic, S. *Br. J. Derm.* **2005**, *154* (4), 651–657.
9. Jongh, C. M. d.; Verberk, M. M.; Spiekstra, S. W.; Gibbs, S.; Kezic, S. *Skin Res. Tech.* **2007**, *13* (4), 390–398.
10. Törmä, H.; Lindberg, M.; Berne, B. *J. Invest. Derm.* **2008**, *128* (5), 1212–1219.
11. Masci, J. N.; Poirier, N. A. U.S. 2,999,069, 1961.
12. Masci, J. N.; Poirier, N. A. U.S. 3,055,836, 1962.

13. Verdicchio, R. J.; Walts, J. M. U.S. 3,950,417, 1976.
14. Rhein, L. D. *J. Soc. Cosmet. Chem.* **1997**, *48* (5), 253–274.
15. Moore, P. N.; Puvvada, S.; Blankschtein, D. *J. Cosmet. Sci.* **2003**, *54* (1), 29–46.
16. Moore, P. N.; Shiloach, A.; Puvvada, S.; Blankschtein, D. *J. Cosmet. Sci.* **2003**, *54* (2), 143–159.
17. Ghosh, S.; Blankschtein, D. *J. Cosmet. Sci.* **2007**, *58* (3), 229–244.
18. Ghosh, S.; Blankschtein, D. *J. Cosmet. Sci.* **2007**, *58* (2), 109–133.
19. Ghosh, S.; Hornby, S.; Grove, G.; Zerwick, C.; Appa, Y.; Blankschtein, D. *J. Cosmet. Sci.* **2007**, *58* (6), 599–620.
20. LiBrizzi, J.; Protz, A.; Ganopolsky, I.; Walters, R. U.S. 7,157,414, 2007.
21. Fevola, M. J.; LiBrizzi, J. J.; Walters, R. M. *Polym. Prepr.* **2008**, *49* (2), 671–672.
22. Fevola, M. J.; LiBrizzi, J. J.; Walters, R. M. In *Polymeric Delivery of Therapeutics*; Morgan, S. E., Lochhead, R. Y., Eds.; American Chemical Society: Washington DC, 2010; pp 221−242.
23. Walters, R. M.; Fevola, M. J.; LiBrizzi, J. J. U.S. 7,754,666, 2010.
24. Walters, R. M.; Fevola, M. J.; LiBrizzi, J. J. U.S. 7,754,667, 2010.
25. LiBrizzi, J. J.; Walters, R. M.; Fevola, M. J.; Tamareselvy, K. U.S. 7,803,403, 2010.
26. Walters, R. M.; Fevola, M. J.; LiBrizzi, J. J.; Tierney, N.; Martin, K.; Jerri, H. *Abstracts of Papers*, 239th ACS National Meeting, San Francisco, CA, Mar 21-25, 2010, American Chemical Society: Washington, DC, 2010; COLL-102.
27. Walters, R. M.; Fevola, M. J.; Gandolfi, L.; LiBrizzi, J. J.; Tamareselvy, K.; Tierney, N. K. *Abstracts of Papers 242nd ACS National Meeting*, Denver, CO, Aug 28-Sep 1, 2011, American Chemical Society: Washington, DC, 2011; PMSE-69.
28. Walters, R.; Mao, G.; Saad, P.; Mendelsohn, R.; Martin, K. *Abstracts of Papers,* 244th ACS National Meeting, Philadelphia, PA, Aug. 19−23, 2012; American Chemical Society: Washington, DC, 2012; POLY-76.
29. Draelos, Z.; Walters, R.; Hornby, S.; Appa, Y. *J. Am. Acad. Dermatol.* **2011**, *64* (2) (Suppl 1), AB24.
30. Hornby, S.; Walters, R.; Kamath, Y.; Appa, Y. *J. Am. Acad. Dermatol.* **2011**, *64* (2) (Suppl 1), AB25.
31. Walters, R. M.; Mao, G.; Gunn, E. T.; Hornby, S. *Dermatol. Res. Prac.* **2012**, *2012* Article ID 495917.
32. Draelos, Z. D.; Hornby, S.; Walters, R. M.; Appa, Y. *J. Cosmet. Dermatol.* Accepted for publication.
33. Anim-Danso, E.; Gandolfi, L.; Gunn, E. T.; Walters, R. M.; Fevola, M. J. U.S. 8,338,348, 2012.
34. Gunn, E. T. G. E.; Walters, R. M.; Gandolfi, L. R.; Lahey, K. C. U.S. 8,329,626, 2012.
35. Gunn, E. T. G. E.; Walters, R. M.; Gandolfi, L. R.; Lahey, K. C.; Mack, M. C. U.S. 8,329,627, 2012.
36. Walters, R. M.; Gunn, E. T.; Gandolfi, L.; Johnson, D.; Anim-Danso, E. U.S. 8,343,902, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

37. Walters, R. M.; Fevola, M. J.; LiBrizzi, J. J.; Martin, K. *Cosmet. Toiletries* **2008**, *123* (12), 53–60.
38. Fevola, M. J.; LiBrizzi, J. J.; Walters, R. M. U.S. 7,417,020, 2008.
39. Fevola, M. J.; LiBrizzi, J. J.; Walters, R. M. U.S. 7,446,087, 2008.
40. Fevola, M. J.; LiBrizzi, J. J.; Walters, R. M. U.S. 7,446,088, 2008.
41. Cottin, M.; Zanvit, A. *Toxicol. In Vitro* **1997**, *11* (4), 399–405.
42. Gautheron, P.; Duprat, P.; Hollander, C. F. *Toxicol. In Vitro* **1994**, *7* (1), 33–43.
43. Anton, P.; Köberle, P.; Laschewsky, A. *Makromol. Chem.* **1993**, *194* (1), 1–27.
44. Greif, N.; Potthoff-Karl, B.; Oppenlaender, K.; Ehle, M.; Oetter, G.; Slotman, W.; Buechner, K.-H. WO9716464, 1997.
45. Nieuwkerk, A. C.; Van Kan, E. J. M.; Koudijs, A.; Marcelis, A. T. M.; Sudhoelter, E. J. R. *Langmuir* **1998**, *14* (20), 5702–5711.
46. Wang, X.; Sudol, E. D.; El-Aasser, M. S. *Macromolecules* **2001**, *34* (22), 7715–7723.
47. Peiffer, D. G. U.S.4975482, 1990.
48. O'Lenick, K. A.; O'Lenick, A. J., Jr. U.S. 7,335,627, 2008.
49. O'Lenick, A. J., Jr. U.S. 7,507,399, 2009.
50. Odian, G. *Principles of Polymerization*, 4th ed.; John Wiley & Sons, Inc.: New York, 2004; pp 39−197.
51. Hashidzume, A.; Noda, T.; Morishima, Y. In *Stimuli-Responsive Water Soluble and Amphiphilic Polymers*; McCormick, C. L., Ed.; American Chemical Society: Washington, DC, 2001; Vol. 780, pp 14−37.
52. Deo, P.; Jockusch, S.; Ottaviani, M. F.; Moscatelli, A.; Turro, N. J.; Somasundaran, P. *Langmuir* **2003**, *19* (26), 10747–10752.
53. Deo, P.; Deo, N.; Somasundaran, P. *Langmuir* **2005**, *21* (22), 9998–10003.
54. Deo, P.; Somasundaran, P. *Langmuir* **2005**, *21* (9), 3950–3956.
55. Gruber, J. V. In *Principles of Polymer Science & Technology in Cosmetics and Personal Care*; Goddard, E. D., Gruber, J. V., Eds.; Marcel Dekker, Inc.: New York, 1999; pp 217−274.
56. Fevola, M. J. *Cosmet. Toiletries* **2011**, *126* (1), 12–14.
57. Fevola, M. J.; Sun, F. C. U.S.20110082065A1, 2011.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch007

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

Chapter 8

Stars and Blocks: Tailoring Polymeric Rheology Modifiers for Aqueous Media by Controlled Free Radical Polymerization

**André Laschewsky,*,[1,2] Christoph Herfurth,[1,2] Anna Miasnikova,[2]
Frank Stahlhut,[2] Jan Weiss,[1,4] Christoph Wieland,[1]
Erik Wischerhoff,[1] Michael Gradzielski,[3] and Paula Malo de Molina[3]**

**[1]Fraunhofer Institute for Applied Polymer Research IAP
Geiselbergstrasse 69, 14476 Potsdam-Golm, Germany
[2]University of Potsdam, Department of Chemistry
Karl-Liebknecht-Str. 69, 14476 Potsdam-Golm, Germany
[3]Technische Universität Berlin, Chemistry Department,
Stranski-Laboratorium, 10623 Berlin, Germany
[4]Current address: CNRS Institut Charles Sadron, Strasbourg, France
*E-mail: andre.laschewsky@iap.fraunhofer.de.**

Using *Reversible Addition-Fragmentation chain Transfer* (RAFT) polymerization as model technique for reversible deactivation radical polymerization (RDRP) methods, we explored the synthesis of complex non-ionic amphiphilic water-soluble polymers in general, and of associative telechelics in particular. *Via* straightforward one-step or two-step RAFT polymerizations, and without any further chemical transformation, various diblock, triblock, star as well as star block (co)polymers were made, and studied with respect to their thickening and gelling behaviors. By systematic structural variations and comparison, structure-property-relationships were derived. Moreover, we conferred thermo-responsiveness (of the lower critical solution temperature (LCST) type) to the hydrophilic polymer blocks, thus enabling the modulation of the rheological effects by a thermal switch.

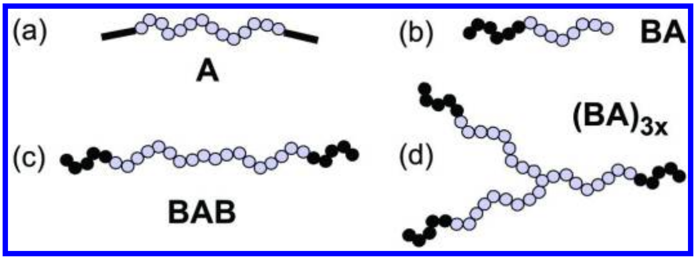
In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

Introduction

Polymer rheology modifiers are major ingredients in many cosmetics and personal care products (*1*, *2*). Within this group, the so-called “associative telechelics”, in particular in form of hydrophobically α,ω-end-capped water-soluble polymers (Scheme 1a), are highly effective for the thickening or gelling of aqueous formulations, and thus are widely applied (*2–6*). However, due to the severe boundary conditions for the synthesis of water-soluble polymers, the synthetic options for associative telechelic polymers have been limited for long. For availability, cost, and toxicological reasons, the vast majority of associative telechelics has been derived from polyethylene oxide (PEO, often named synonymously polyethylene glycol PEG) as hydrophilic building block (*5*, *7*). PEO is made by ionic polymerization, a method that is generally very sensitive and prone to side reactions. Therefore, ionic polymerization is extremely difficult to apply for the synthesis of other hydrophilic polymers than PEO.

In contrast, free radicals are mostly inert toward water and typical hydrophilic groups. Thus, classical free radical polymerization is *a priori* the most suited synthetic pathway for fabricating water-soluble polymers. Moreover, a large choice of suited, water-soluble monomers is commercially available. Yet, the inherent kinetics of the classical free radical process do not allow for an effective control over the molecular structure or architecture (*8*, *9*). This situation has changed profoundly with the evolving methods of reversible deactivation radical polymerization RDRP (formerly often called "controlled free radical polymerization") (*9–11*). These methods combine many advantageous features of free radical and of controlled ionic polymerizations, thus enabling an efficient and versatile control of molar mass, end groups and polymer architecture.



Scheme 1. Architectures of macromolecular rheology modifiers: (a) associative telechelics; (b) amphiphilic diblock copolymer; (c) amphiphilic triblock copolymer (hydrophilic block in the center); (d) amphiphilic star block copolymer (hydrophilic blocks in the center); A/open symbols signify the hydrophilic building blocks, while B/filled symbols signify the hydrophobic blocks

With the aim of exploiting the opportunities of RDRP in the synthesis of complex non-ionic water-soluble polymers as alternatives to PEO based systems, we have explored the use of the *Reversible Addition-Fragmentation*

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

chain Transfer (RAFT) (*12–14*) method for hydrophobically α,ω-end-capped water-soluble polymers, and further for more complex variants, by designing straightforward one-step or two-step polymerization strategies without the need of any further chemical transformation. The RAFT method was chosen as model technique for RDRP in our studies as it is not only extremely versatile for introducing specific end groups into polymers, but it also enables inherently a rapid verification of the extent of end group functionalization achieved (*15*, *16*). The various amphiphilic architectures addressed are sketched in Scheme 1. On the one hand, we explored the realization of classical associative telechelic structures (Scheme 1a) and of star-shaped analogs *via* RDRP methods. On the other hand we explored analogous amphiphilic block copolymer structures (Scheme 1c-d), while the corresponding diblock copolymers (Scheme 1b) served as reference.

Experimental

For experimental details, we refer to previous reports. Concerning the monomers shown in Figure 1, the synthesis of non-ionic hydrophilic monomers **AA3 - AA5** (*17*, *18*), **AA9** (*19*), **Sox1** - **Sox3** (*20*, *21*), **HEOnS** (*22*) and **MEOnS** (*22*) is described elsewhere. The other monomers used were commercial products. The synthesis of the bi-, tri- and tetrafunctional trithiocarbonates used as RAFT agents was described before (*23–25*). Trithiocarbonate RAFT agents were preferred over dithioesters in our studies, as they generally show better resistance to hydrolysis (*26*, *27*). Polymerizations were performed in bulk (styrene) or in solution, following established procedures (*24*, *28*). Details for size exclusion chromatography (SEC, SEC-MALLS), dynamic light scattering (DLS), small angle neutron scattering (SANS), visual determination of phase diagrams, and rheological studies are reported elsewhere (*24*, *28–30*). For systems described as “opaque”, 1 cm thick samples were nontransparent to the eye.

Results and Discussion

Selecting the Hydrophilic and Hydrophobic Building Blocks

For non-ionic hydrophilic building blocks, we focused on - mostly (meth)acrylic - monomers bearing amide, sulfoxide, hydroxyl or oligoethylene oxide moieties as hydrophilic groups (Figure 1) (*31*). Within this group of non-ionic monomer constituents, the acrylamides are the more common ones. In the majority of the acrylamides, namely **AA1-AA6**, the hydrophilic moiety is an integral part of the polymerizable group, while in the case of acrylic and methacrylic esters and styrenes, separate polymerizable and hydrophilic moieties are needed. All the monomers shown give rise to water-soluble homopolymers, except for **HEMA** and **Sox2**, the homopolymers of which only swell in water. If chemically cross-linked, all monomers produce permanent hydrogels.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

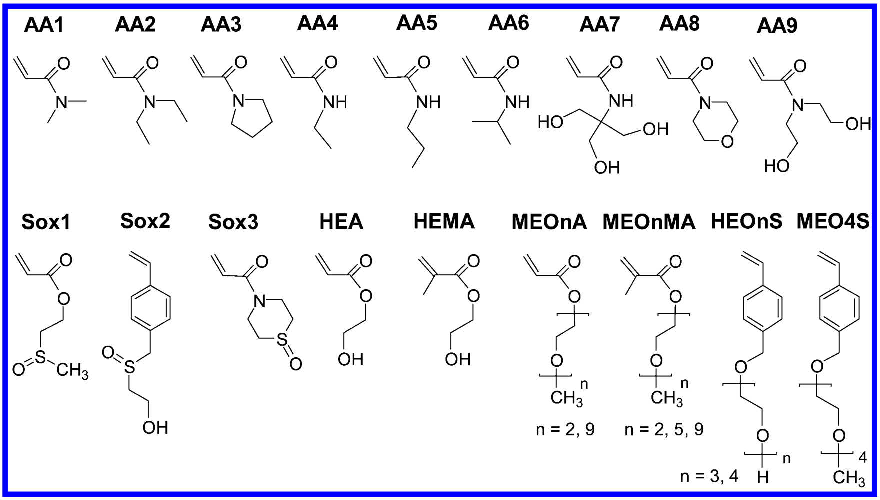


Figure 1. Non-ionic hydrophilic monomers studied.

The polymers with the highest affinity for water were obtained from **AA1**, **AA7, Sox1**, **Sox3**, and the macromonomers with oligomeric PEO side chains as **MEO9A** and **MEO9MA**. In contrast to these, the polymers derived from monomers bearing more hydrophobic substituents, such as **AA2-AA6**, **HEA, MEO2A**, **MEO2MA**, **HEO3S**, **HEO4S**, and **MEO4S**, exhibit a characteristic miscibility gap with water at high temperatures under ambient pressure, *i.e.*, they exhibit a lower critical solution temperature (LCST).

All the monomers shown can be polymerized by the RAFT method with monofunctional chain transfer agents (such as **CTA1a** or **CTA2a** in Figure 2) to give polymers with relatively low polymer dispersities (PDI < 1.3), predicted number average molar mass M_n (*i.e.*, the number average degree of polymerization DP_n, corresponds closely to the theoretically calculated value of [conversion] × [monomer concentration] / [concentration of thiocarbonyl moieties engaged] (*13*)), and mostly defined end groups. Under appropriate polymerization conditions, end group conservation is ≥ 90% (*15*, *16*, *24*). The use of non-ionic moieties as hydrophilic groups confers not only good water-solubility to the polymers, but is generally favorable for their biocompatibility, too. Polymers derived from (meth)acrylates bearing hydroxyl, oligoethylene oxide, or sulfoxide moieties as hydrophilic groups seem to exhibit particularly high biocompatibility (*32*, *33*). Additionally, the non-ionic character favors solubility of the polymers in many standard organic solvents (in marked contrast to polyelectrolytes), thus facilitating their handling and molecular analysis.

Incorporation of the Hydrophobic Building Blocks

To incorporate the hydrophobic building blocks into the telechelics, we applied two different strategies. First, we exploited the inherent need for a chain transfer agent in the RAFT process for attaching hydrophobic end groups to the

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

polymers, by engaging multifunctional RAFT agents bearing hydrophobic R or Z-groups (Figure 2). To attach identical end groups in the α- and ω-position of the polymer chains, we used symmetrical RAFT agents either of the Z-R-R-Z type (Figure 2, series **CTA1**), or of the R-Z-Z-R type (Figure 2, series **CTA2**). In the first case, the polymer chains grow from the center toward the periphery of the macromolecules ("R-approach"). In contrast, when using RAFT agents of the R-Z-Z-R type, polymer growth takes place at the macromolecular center (“Z-approach”) (*34*).

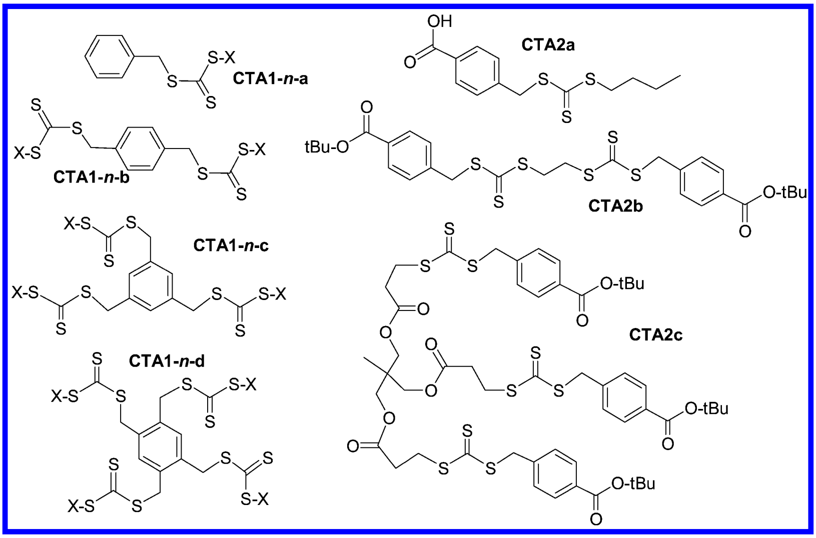


Figure 2. Multifunctional hydrophobic RAFT agents employed in the synthesis of the associative polymers (24, 25). Left column: RAFT agents (Z-R-R-Z type) used for producing hydrophobically end-capped homopolymers, with X = butyl, dodecyl, or octadecyl; “n” in the name indicates the number of carbons in the substituent X. Right column: RAFT agents (R-Z-Z-R type) used for preparing amphiphilic block and star block copolymers. Monofunctional RAFT agents ***CTA1-n-a*** *and* ***CTA2a*** *are employed for reference purposes.*

Both strategies are useful, but have their particular strengths and weaknesses (*35*, *36*). Hence, both approaches enable the synthesis of hydrophobically end-capped linear polymers (with a topology analogous to classical associative telechelics) when using bifunctional RAFT agents, via a one-step procedure. When using multifunctional RAFT agents, both enable the synthesis of hydrophobically end-capped star polymers (*37*), also in a one-step procedure. In this way, we prepared 3-arm and 4-arm star polymers (*24*). The various polymers will be abbreviated as **poly(A_x-*n*)$_f$**, where A denotes the hydrophilic monomer unit, *n* is the number of carbons in the hydrophobic end groups, and *f* is the functionality, *i.e.*, the number of (star) arms.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

The “R-approach” seems particularly attractive for the synthesis of rheology modifiers, as it allows for high molar masses while mostly suppressing the formation of small linear chains as by-products (*38*, *39*). However, this strategy implies the possibility of star-star coupling reactions, the probability of which increases with conversion and the number of arms (*35*, *38*). A set of criteria was proposed based on theoretical calculations and experimental results, in order to minimize such problems, and thus to obtain well-defined star polymers (*35*). Accordingly, star production is favored at low stationary radical concentration, for a high rate of monomer propagation, and when using a sufficiently rate-retarding chain transfer agent. While the first criterion asks for the judicious choice of the initiator and the reaction temperature, acrylic monomers and trithiocarbonates bearing benzylic R groups (see Figure 2) meet the other requirements well (*40*).

Exemplarily, the synthesis of hydrophobically end-capped star polymers was investigated in more detail with two strongly hydrophilic, non-ionic acrylic monomers, namely the small *N,N*-dimethylacrylamide **AA1** and macromonomer **MEO9A**. While both are fully water-soluble and do not show phase separation up to boiling point of water under ambient pressure (no LCST), they differ substantially in their size, and **poly-MEO9A** presents a comb structure. Polymerizations were conducted using RAFT agent series **CTA1** (Figure 2) in homogeneous solution in benzene, which is virtually inert towards radical attack. This eliminates possible chain transfer to solvent as competing process. While the use of **AA1** gave excellent results providing well-defined linear and star polymers with various hydrophobic end groups from butyl to octadecyl chains, as reported in detail elsewhere (see also Figure 3a) (*24*), the use of macromonomer **MEO9A** revealed unexpected problems (Table 1).

Though 4-arm stars of high molar mass could be synthesized at sufficiently high monomer concentrations of 40 wt%, these star polymers showed PDI values of 1.5 to 3. Even after optimizing reaction conditions, the values are rather high for polymers obtained by a well-controlled RDRP process. The difficulties seem to be aggravated rather than improved when increasing the polymerization temperature from 70 to 90 °C (while keeping the flux of initiating radicals comparably low by exchanging initiator AIBN to V-40 that requires higher decomposition temperatures) - a measure that, *a priori,* should favor star formation (*35*). Therefore, the problems encountered are attributed to the PEO side chains: H-abstraction from the α-methylene ether groups, as favored by the lone pair effect of oxygen (*41*), results in uncontrolled chain transfer of the growing radicals to monomers and polymers (*42*). In fact, this type of chain transfer reaction has been well known to occur when highly reactive oxy and peroxy radicals are involved, and has even been synthetically exploited, *e.g.*, for grafting monomers onto PEO polymers (*43–45*). Seemingly, the much more stabilized - and thus less reactive - secondary carbon centered radicals are still aggressive enough to induce similar chain transfer reactions under the conditions and synthetic constraints applying in our systems. While for linear chains this problem may be hardly notable (*17*, *46–49*), it becomes increasingly prominent with increasing degree of polymerization and number of arms for the star polymers (Table 1).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

Table 1. RAFT solution polymerisation of macromonomer MOE9A in benzene in the presence of multifunctional RAFT agents; [MOE9A] / [CTA] = 1000

CTA *used*	***[MOE9A]₀*** *[wt.-%]* [a]	***T*** [b] *[°C]*	***d*** [c] *[h]*	***yield*** *[%]* [d]	M_n^{theo} *[kg/mol]* [e]	M_n^{MALLS} *[kg/mol]* [f]	M_w^{MALLS} *[kg/mol]* [f]	***PDI*** [f]
1-*4*-c	40	70 [g]	6	56	271	264	425	1.6
1-*4*-c	40	90 [h]	3	50	241	57	90	1.6
1-*4*-c	17	90 [h]	5	7	33	24	37	1.6
1-*4*-c	40	90 [h]	5	72	346	58	108	1.9
1-*4*-d	40	70 [g]	6	58	278	276	702	2.5
1-*4*-d	40	90 [h]	5	61	295	95	170	1.8

[a] monomer concentration in benzene, [b] reaction temperature; [c] duration of the reaction; [d] by gravimetry; [e] calculated as [conversion] × [monomer concentration] / [RAFT agent engaged]; [f] from SEC in 0.05 M Na_2SO_4 in H_2O, MALLS detection; [g] using initiator azobisisobutyronitrile (AIBN); [h] using initiator 1,1′-azobis(cyanocyclohexane) (V-40).

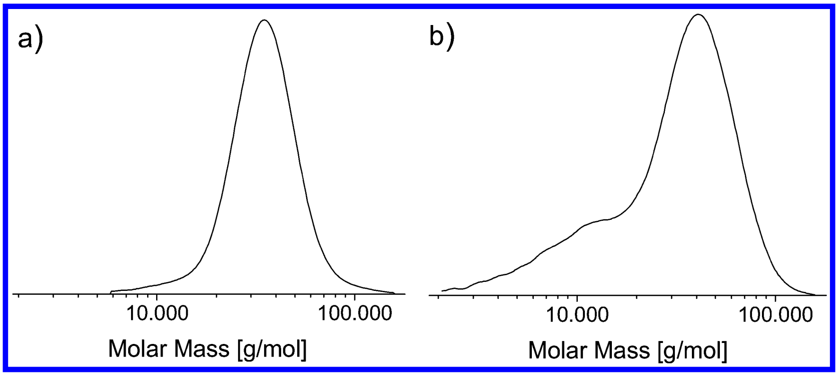


*Figure 3. Effect of solvent in the homopolymerization of **AA1** to 4-arm star polymers using tetrafunctional RAFT agents **CTA1-d** (SEC in DMF with 0.1 wt% LiBr, calibration with polystyrene standards): (a) polymerization in benzene; (b) polymerization in ethanol.*

This interpretation is supported by the finding, that molar mass distributions are broadened, too, when polymerizing **AA1** to high molar mass polymers using multifunctional RAFT agents in ethanol (Figure 3b). This contrasts markedly with the narrow molar mass distributions obtained when polymerizing in the inert solvent benzene (Figure 3a) (*24*). Different from benzene, ethanol also disposes of α-methylene groups next to an oxygen atom, which are sensibilized toward radical attack, explaining that the transfer constant to ethanol in radical polymerization of acrylic monomers is by one order of magnitude higher (*50*) This side reaction seems to pass unnoticed when producing linear polymers *via* RAFT polymerizations in ethanol (as frequently applied for very polar monomers) (*51–53*), but must be taken into account in the particularly demanding synthesis of well-defined high molar stars. Clearly, the preparation of high quality, high molar mass star polymers is feasible by RAFT, but requires careful selection of the various components and parameters of the polymerization mixture.

In our second synthetic approach, we prepared symmetrical triblock as well as star block copolymers, in which a long central hydrophilic block or star, respectively, is end-capped by short hydrophobic blocks (*54*) (*cf.* Scheme 1c-d), made, *e.g.*, from poly(2-ethylhexyl acrylate) (**polyEHA**) or from polystyrene (**polySt**). Following analogous considerations to establish appropriate reaction conditions as presented for the alkyl end-capped linear and star homopolymers above, only two consecutive polymerization steps are needed when using multifunctional RAFT agents as in Figure 2. In favorable cases, polymerizations may be implemented as one-pot reaction, producing tapered block copolymers. For carefully selected monomer combinations, such as hydrophobic maleimides together with styrene monomer **MEO4S** (*55*, *56*), the synthesis of hydrophobically end-capped water-soluble polymers can be even simplified to a one-step process, when alternating copolymerization (producing here a hydrophobic block) is followed by homopolymerization of excess styrene monomer (producing here the hydrophilic block).

In this way, the size, the hydrophobicity, and the dynamics of the hydrophobic segments (*via* its glass transition temperature) can be conveniently tailored at will. The various triblock copolymers are abbreviated in the following as $\mathbf{poly(B_y\text{-}\boldsymbol{b}\text{-}A_x\text{-}\boldsymbol{b}\text{-}B_y)}$, where A denotes the hydrophilic monomer unit and x its number average degree of polymerization, while B denotes the hydrophobic monomer unit and y its respective number average degree of polymerization DP_n. Analogously, star block copolymers are noted as $\mathbf{poly(A_x\text{-}\boldsymbol{b}\text{-}B_y)_f}$, with f being the functionality (number of arms). The synthesis of such symmetrical triblock and star block copolymers for associative thickeners based on the hydrophilic A blocks of **poly-AA6** and **poly-MEO2A** was described elsewhere in detail, for a wide variety of hydrophobic blocks of varying hydrophobicity and glass transition temperatures (*25*, *28*, *29*, *57*). Importantly, strong hydrophobic B blocks, such as polystyrene, must be kept sufficiently small, to allow the direct dissolution of the amphiphilic block copolymers in water (*25*, *58*). While for instance $\mathbf{poly(St_{11}\text{-}\boldsymbol{b}\text{-}AA6_{220}\text{-}\boldsymbol{b}\text{-}St_{11})}$ and $\mathbf{poly(St_{10}\text{-}\boldsymbol{b}\text{-}MEO2A_{150}\text{-}\boldsymbol{b}\text{-}St_{10})}$ can still be directly dispersed in water, the analogous copolymers with polystyrene blocks of y=15 required dissolution in an organic, water-miscible solvent, mixing with water and subsequent removal of the organic solvent (*e.g.*, by evaporation) to obtain homogeneous, clear aqueous solutions. Such a procedure may be feasible for model studies, but seems hardly appropriate for practical applications. In any case, one must be aware that true thermodynamic equilibrium is difficult to reach

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

in aqueous “solutions” of amphiphilic block copolymers, and that experimental results therefore may depend on the preparation paths, in particular for polymers carrying either long or strongly hydrophobic blocks (*59*).

Association in Dilute Aqueous Solution

As the hydrophobic end groups render the polymers amphiphilic, micelle-like aggregation is seen in dilute solutions (concentration < 1 wt%), *e.g.* by DLS or SANS studies. The spherical aggregates (“flower micelles” (*54*)) are small and large clusters are almost absent, despite the presence of the multiple hydrophobic end groups. In agreement, solution viscosity is low. For linear and star homopolymers with identical aliphatic hydrophobic end groups, the size of the aggregates was found to be small and hardly dependent of the number of arms and end groups, *f*. For example, all micelles formed by **polyAA1** bearing C_{12}-end groups and $x \approx 1000$ (**poly(AA1$_x$-*12*)$_f$**), show values of about 16-18 nm for the hydrodynamic radii R_H, independent of having linear (f=2, “2-arm”), 3-arm or 4-arm architecture (*60*). In contrast, the radius of gyration R_G of the aggregates decreases somewhat in this series with *f*, from 12.5 to 10.6 to 9.8 nm (*24*). The size of the amphiphilic block copolymers with short hydrophobic blocks (to enable direct dissolution in water, see above) is in the same range. As expected, R_H grows with both the lengths of the hydrophobic end groups and of the hydrophilic central block for the **poly(B$_y$-*b*-A$_x$-*b*-B$_y$)** block copolymers, as illustrated in Figure 4.

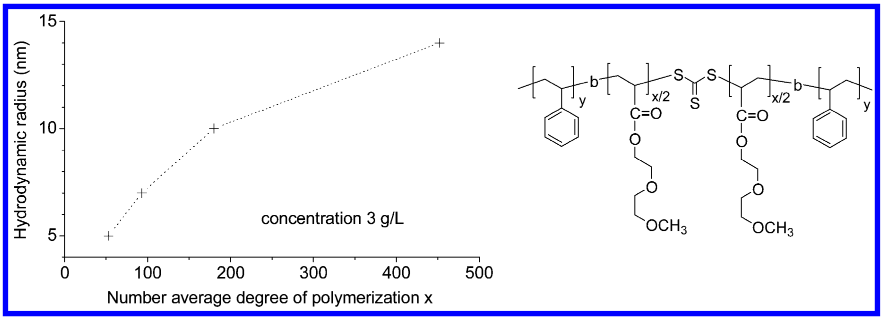


Figure 4. Evolution of the apparent hydrodynamic radius R_H for micellar aggregates of block copolymers ***poly(St$_8$-b-MEO2A$_x$-b-St$_8$)*** *with x in dilute aqueous solution. The lines are meant as guide to the eye only.*

Thickening in Semidilute and Concentrated Aqueous Solutions

When the concentration of the telechelics rises above 1 wt%, solution viscosity increases rapidly. Depending on the detailed molecular structure, complete gelling is achieved for many systems from few wt% on (Fig. 5) (*24*, *28*, *60*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

Figure 5. Tube inversion flow test for 5 wt% aqueous solutions of 3-arm star homopolymers of ***AA1*** *with molar mass $M_n \cong 100$ kg/mol bearing different hydrophobic alkyl end groups: samples from left to right* ***poly(AA1-4)$_3$****,* ***poly(AA1-12)$_3$*** *and* ***poly(AA1-18)$_3$****. Left picture: before turning; right picture: samples turned upside down after 30 s.*

DLS and SANS measurements corroborate the presence of polymer (transient and/or permanent (*3*, *6*, *61*, *62*)) networks in this concentration range. The network points consist of spherical micelles with the radius given approximately by the length of the alkyl chains constituting the hydrophobic end groups.

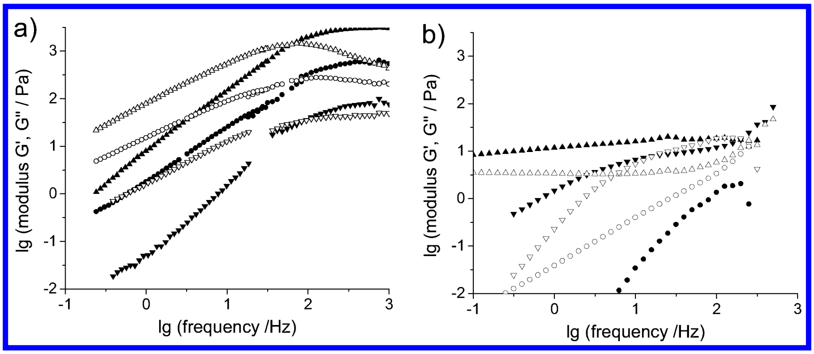


Figure 6. Oscillating rheology at room temperature; storage modulus (G', full symbols) and loss modulus (G'', open symbols) as function of the frequency: a) 5 wt% aqueous solutions of star homopolymers of ***AA1*** *(molar mass $M_n \cong 120$ kg/mol: "2-arm"* ***poly(AA1-12)$_2$*** *(▼, ▽), 3-arm* ***poly(AA1-12)$_3$*** *(●, ○), and 4-arm* ***poly(AA1-12)$_4$*** *(▲, △). (Data taken from ref. (24)) b) 3.5 wt% aqueous solutions of block and star block copolymers: BAB triblock* ***poly(St$_8$-MEO2A$_{450}$-St$_8$)*** *(●, ○) and BAB triblock* ***poly(St$_{15}$-MEO2A$_{530}$-St$_{15}$)*** *(▲, △), 3-arm star block* ***poly(St$_8$-MEO2A$_{220}$)$_3$*** *(▼, ▽).*

Thickening and gelling is not only favored by increasing the lengths of either the hydrophilic block or the hydrophobic end groups (Figure 5 and 6), but also by increasing the number of end groups (Figure 6b). All these molecular parameters enhance the gelling efficiency of the telechelics as well as the mechanical strength of the hydrogels formed (see Figures 5-8). The instructive comparison in Figure 6 demonstrates clearly that the shear modulus G_0 (high frequency limit of the storage modulus G') increases substantially with the number of arms of the polymers, for the end-capped homopolymers (Figure 6a) as well as for the amphiphilic block copolymers (Figure 6b). In contrast, the characteristic relaxation time is only weakly affected, as it is almost exclusively determined by the length of the hydrophobic alkyl end group (*30*). Thus, by tuning individually the chemical nature and the length of the hydrophilic block, and the hydrophobicity and the number of the hydrophobic end groups, gel points and mechanical properties can be adjusted in a wide range. Interestingly, the glass transition temperature of the hydrophobic end blocks seems to be of little importance for the gelling ability of the amphiphilic block copolymers, if the hydrophobic block exceeds a certain size and becomes strongly incompatible with the aqueous dispersion medium, as then, the hydrophobic interaction seems to prevail (*29*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

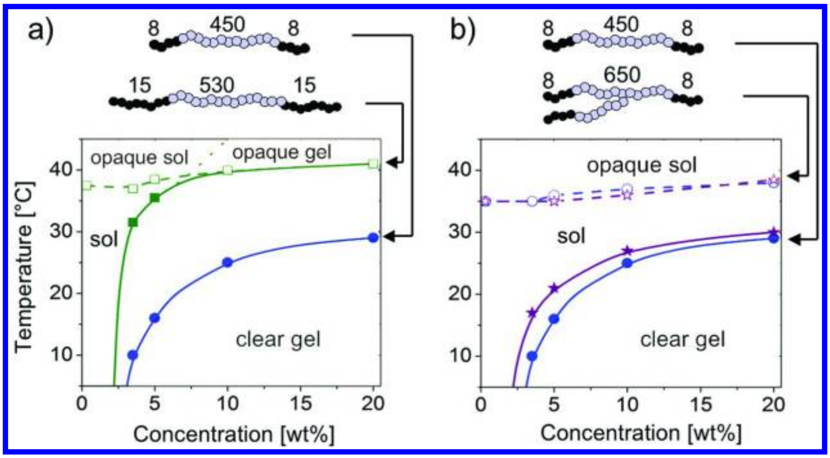


*Figure 7. Partial phase diagrams of aqueous solutions of telechelic polymers of **MEO2A** end-capped with short polystyrene blocks. Comparing the effect of the polymer architecture: (a) linear triblock copolymer analogs with increasing length of the hydrophobic block: **poly(styrene$_8$-MEO2A$_{450}$-styrene$_8$)** vs. **poly(styrene$_{15}$-MEO2A$_{530}$-styrene$_{15}$)**; b) linear triblock vs. 3-arm star block with comparable block lengths: **poly(styrene$_8$-MEO2A$_{450}$-styrene$_8$)** vs. **poly(styrene$_8$-MEO2A$_{220}$)$_3$**.*

Temperature Effects on Associative Thickening in Aqueous Solutions

In addition to polymer concentration, temperature is a key physical parameter for controlling the viscosifying and gelling power of associative polymers. Importantly, the water-solubility of many non-ionic polymers decreases with increasing temperature, until phase separation occurs, *i.e.*, they exhibit a *Lower Critical Solution Temperature* (LCST) phase transition (*63*, *64*). For polymers made from the oligoethylene oxide (macro)monomer families **MEOnA** and **MEOnMA**, LCST transitions are only absent under ambient pressure when *n* > 6 (*17*, *33*, *65*). For many classical applications, such as solubilization, this miscibility gap at elevated temperatures poses a problem and must be thoroughly taken into account, when selecting a non-ionic polymer. In contrast, this feature is most useful for designing responsive systems. Such "smart" systems are characterized by a marked change of their property profile upon exposure to a small trigger, here to a small temperature change (*63*, *64*, *66*, *67*). The passage through the LCST-type transition profoundly modifies key properties such as swelling, and consequently has a dramatic impact on the solutions′ rheology (*cf.* Figures 7- 8).

Independent of their thermo-reponsive behavior at elevated temperatures, these polymers also serve well to elucidate some basic structure-property relationships between the macromolecular structure and the ability for associative thickening. While Figures 7a and 8a illustrate the effect of increasing the length of the hydrophobic end blocks, Figures 7b and 8b illustrate the effect of multiplying the number of hydrophobic ends. They compare the linear triblock copolymer **poly(St$_8$-*b*-MEO2A$_{450}$-*b*-St$_8$)** and the analogous 3-arm star block copolymer **poly(MEO2A$_{220}$-*b*-St$_8$)$_3$**, which exhibit approximately the same hydrophilic-hydrophobic balance (HLB). Clearly, the tendency for gelling as well as mechanical strength of the gels increase with the length of the hydrophobic end caps as well as with their number. Yet, the lack of direct solubility in water for polystyrene blocks already as short as 1.5 kg/Mol (DP$_n$=15), renders the first optimization strategy impractical. A low molar mass limit for direct dispersion of the associative triblock copolymers in water is not a particularity of hydrophobic vinyl polymers as end-caps, but has been noticed for other hydrophobic blocks, too, such as polylactide (*68*, *69*). In contrast, an increasing number of short polystyrene blocks of molar mass 0.8 kg/mol increase the gel strengths without compromising the solubility in water.

Note also that while the phase transition temperature of **poly-MEO2A** is about 40°C, the crossover of the G′ and G″ curves occurs at much lower temperatures (Figure 8) (*28*). Accordingly, the hydrogels disintegrate already at temperatures considerably below the phase transition temperature of these block copolymers. However, such a behavior is not universal for thermo-responsive telechelics. Hydrogels made from analogous triblock copolymers based on N-isopropylacrylamide (**AA6**), for instance, become mechanically even more stable in the temperature window shortly above the phase transition, and collapse only when heated well above their phase transition temperatures (*29*). A similar induced gelation by high temperatures has been reported for many BAB type block copolymers made from an inner PEO block and

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

hydrophobic polylactide end-caps (*68*, *70*, *71*). Possible reasons for the observed differences between **poly-MEO2A** based and **poly-AA6** based polymers, namely thermo-liquidification vs. thermo-gelling despite analogous architectures (cf. Scheme 1) are discussed in detail elsewhere (*72*).

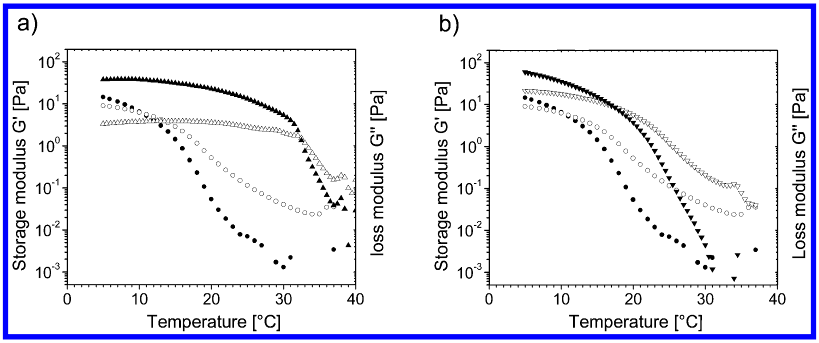


Figure 8. Evolution of the storage modulus (G', full symbols) and loss modulus (G", open symbols) of 3.5 wt% aqueous solutions of amphiphilic block copolymers with the temperature, as function of the polymer architecture. a) linear triblock copolymer analogs with increasing length of the hydrophobic block: ***poly(St$_8$-MEO2A$_{450}$-St$_8$)*** *(●, ○) and* ***poly(St$_{15}$-MEO2A$_{530}$-St$_{15}$)*** *(▲, △); b) linear triblock vs. 3-arm star block of comparable block lengths:* ***poly(St$_8$-MEO2A$_{450}$-St$_8$)*** *(●, ○) and* ***poly(St$_8$-MEO2A$_{220}$)$_3$*** *(▼, ▽). (Frequency 1Hz, data for* ***poly(St$_8$- MEO2A$_{450}$-St$_8$)*** *are taken from ref. (28)).*

In an interesting additional option, the use of thermo-sensitive blocks may help to overcome the size limitation of the hydrophobic end-caps for the direct dissolution of associative block copolymers in water. If the hydrophobic functionality is only “switched on” after dissolution of an originally water-soluble block, here by rising the working temperature above the LCST phase transition, hydrophobic aggregation of a formerly completely water soluble block copolymer can be induced. In the simplest version of an associative telechelic, this is done *via* a symmetrical binary B′-A-B′ type architecture, with a permanently hydrophilic inner A block and two thermo-sensitive B′ end-caps (Figure 9, top) (*23*, *73–78*). This approach can be further refined by designing B′-A-B″ type architectures, which contain two different thermo-sensitive B′ and B″ end-caps with sequential phase transition temperatures (Figure 9, bottom). Unfortunately, the reorganization processes and their kinetics following the thermal switching from hydrophilic to hydrophobic behavior of the end caps (with concomitant viscosifying effects), is complex and far from the scenario of a simplistic “on-off” switch (*23*, *79–81*).

A possibly interesting compromise might be the use of a non-symmetrical ternary B-A-B′ design, in which a permanently hydrophilic inner A block is framed by one permanently hydrophobic end-cap B, and one thermo-sensitive end-cap B′ (Figure 9, center) (*82–84*). While the initial water-solubility is improved in comparison to a BAB system with 2 permanently hydrophobic end

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

blocks, the dynamics of the hydrophobic association and physical crosslinking are somewhat simplified in comparison to a B′AB′ system, in which both end blocks must undergo induced aggregation. On the one hand, the initial water-solubility is improved by the presence of only one short hydrophobic and the much bigger hydrophilic block in such non-symmetrical ternary B-A-B′ systems, when applying sufficiently low temperatures (T < LCST). On the other hand, half of the micellar cross-links are already preformed when the thermo-sensitive end-caps start to aggregate when passing the switching temperature.

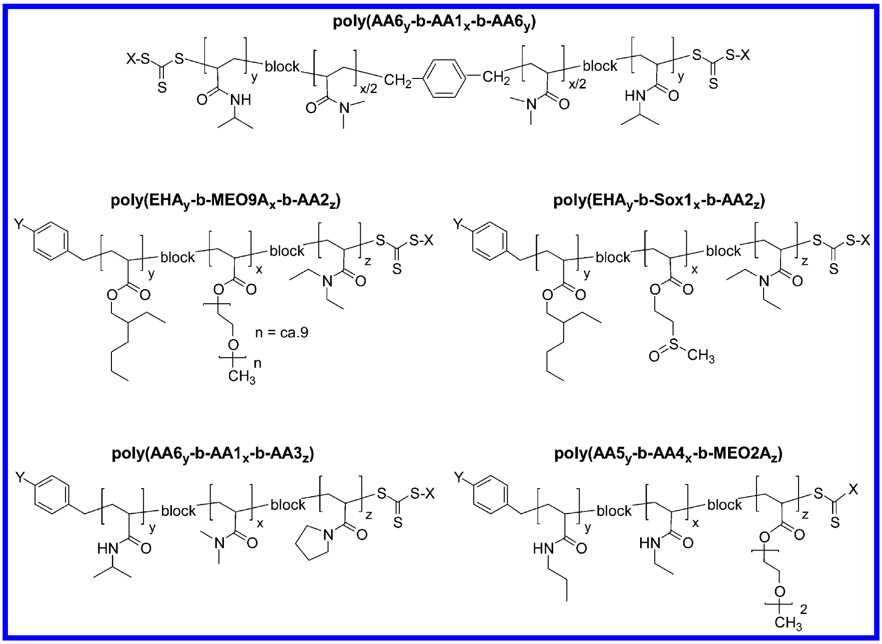


Figure 9. Examples for amphiphilic and thermo-responsive ternary triblock copolymers. Top row: symmetrical binary B'-A-B' type with a permanently hydrophilic inner A block and two thermo-sensitive B' end-caps (23). Central row: non-symmetrical ternary B-A-B' type with a permanently hydrophilic inner A block, one permanently hydrophobic end-cap B, and one thermo-sensitive end-cap B'. Bottom row: non-symmetrical ternary B'-A-B" type with a hydrophilic inner A block, and two different thermo-sensitive B' and B" end-caps (80, 81).

Yet, Figure 10 shows that even in such systems, the molecular architecture has to be designed carefully to implement the desired effects. For instance, the thermal collapse of the thermo-responsive **poly-AA2** block of copolymer **poly(EHA$_{67}$-Sox1$_{69}$-AA2$_{93}$)** occurs preferentially within the individual micelle, resulting in the formation of denser core-shell micellar aggregates. Although this leads to increased scattering in turbidimetric studies when crossing the phase transition temperature of **poly-AA2**, the hydrodynamic diameter D_h of the aggregates of about 120 nm remains virtually unchanged. In contrast, the thermal collapse of the

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

nearly identically sized **poly-AA2** block in copolymer **poly(EHA$_{79}$-MEO9A$_{550}$-AA2$_{635}$)** takes place preferentially between individual micelles. Consequently, large aggregate clusters are formed: in addition to the strongly increased scattering in turbidimetric studies, we observe a marked increase of hydrodynamic diameter from about 120 nm to nearly micrometer size (Figure 10b). Obviously, only the latter scenario may lead to temperature-stimulated thickening. Also, we note that the phase transition temperature of **poly-AA2** depends somewhat on its molar mass and the overall architecture of the polymer, in which it is incorporated. While in **poly(EHA$_{67}$-Sox1$_{69}$-AA2$_{93}$),** the collapse occurs at about 42°C, it is observed at about 48 °C in polymer **poly(EHA$_{79}$-MEO9A$_{550}$-AA2$_{635}$)**. Anyhow, the number of studies on such complex polymers is limited up to now. Clearly, much work is still needed to improve our understanding of such systems, and to decide, in which scenario the synthetic effort to obtain such increasingly complex block copolymers is counterbalanced by an improved performance as rheology modifier under practical conditions.

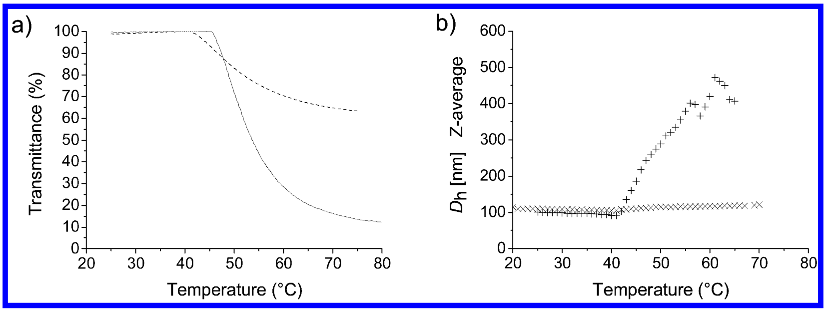


Figure 10. Thermo-induced secondary association of unsymmetrical triblock copolymers, containing one permanent and one thermo-responsive hydrophobic end-cap, in dilute aqueous solution (0.5 wt%). a) turbidimetric analysis: (-----) = copolymer ***poly(EHA$_{67}$-Sox1$_{69}$-AA2$_{93}$)*** *; (——) = copolymer* ***poly(EHA$_{79}$-MEO9A$_{550}$-AA2$_{635}$)****; b) hydrodynamic diameter D_h as function of the temperature, measured by dynamic light scattering (DLS): (×) = copolymer* ***poly(EHA$_{67}$-Sox1$_{69}$-AA2$_{93}$)*** *and (+) = copolymer* ***poly(EHA$_{79}$-MEO9A$_{550}$-AA2$_{635}$)****.*

Conclusions

The methods of RDRP, in particular of the RAFT polymerization, allow the straightforward and versatile synthesis of hydrophobically end-capped water-soluble polymers that act as associative telechelics. Only one or two reaction steps are needed, whereas post polymerization modifications are not necessary. As the pool of water-soluble monomer building blocks is large, a plethora of different structures and architectures can be easily made. Importantly, direct solubility in water is only achieved for rather short hydrophobic end blocks (block molar mass < 1.5 kg/mol). The resulting hydrophobically end-capped polymers are efficient thickeners and gelling agents. The use of star and star block structures seems particularly attractive, as these architectures confer high mechanical strength to the gels without compromising the solubility in water. Also, the use of (thermo-)responsive systems offers interesting options for particular "smart" property profiles in the future.

Our studies revealed also, that the behavior in aqueous solution depends on the detailed overall chemical structure of the end-capped polymers. Thus, the choice of a specific polymer for implementing supramolecular (and in certain cases also responsive) viscous systems is not simply a matter of its hydrophilic-hydrophobic balance and of the basic architecture, as *e.g.*, diblock vs. triblock vs. star geometry. Although this might be insinuated by the simple sketch in Scheme 1, the behavior of such associative systems cannot be predicted by a simplified model considering just size, volume fraction and distribution of the various hydrophilic and hydrophobic polymer fragments within the macromolecules. In fact, optimization of the performance as rheology modifier requires the careful tuning of the precise individual structure.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

Acknowledgments

Fonds der Chemischen Industrie FCI, Deutsche Forschungsgemeinschaft DFG, and German Federal Ministery of Eduction and Research (Bundesministerium für Bildung und Forschung) BMBF are acknowledged for financial support.

References

1. *Principles of Polymer Science and Technology in Cosmetics and Personel Care*; Goddard, E. D., Gruber, J. V., Eds.; Marcel Dekker: New York, 1999.
2. Lochhead, R. Y. *ACS Symp. Ser.* **2007**, *961*, 3–56.
3. Annable, T.; Buscall, R.; Ettelaie, R.; Whittlestone, D. *J. Rheol.* **1993**, *37*, 695–726.
4. Winnik, M. A.; Yekta, A. *Curr. Opin. Coll. Interface Sci.* **1997**, *2*, 424–436.
5. Kortemeier, U.; Venzmer, J.; Howe, A.; Grüning, B.; Herrwerth, S. *SOFW J.* **2010**, *136* (3), 30–38.
6. Chassenieux, C.; Nicolai, T.; Benyahia, L. *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 18–26.
7. Booth, C.; Attwood, D. *Macromol. Rapid Commun.* **2000**, *21*, 501–527.
8. Moad, G.; Solomon, D. H. *The Chemistry of Radical Polymerization*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2006.
9. Matyjaszewski, K.; Davis, T. P. *Handbook of Radical Polymerization*; John Wiley and Sons, Inc.: Hoboken, NJ, 2002.
10. Moad, G.; Rizzardo, E.; Thang, S. H. *Acc. Chem. Res.* **2008**, *41*, 1133–1142.
11. *Controlled and Living Polymerizations. From Mechanisms to Applications*; Matyjaszewski, K., Müller, A. H. E., Eds.; Wiley-VCH: Weinheim, Germany, 2009.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

12. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562.
13. *Handbook of RAFT Polymerization*; Barner-Kowollik, C., Ed.; Wiley-VCH: Weinheim, Germany, 2008.
14. Keddie, D. J.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2012**, *45*, 5321–5342.
15. Päch, M.; Zehm, D.; Lange, M.; Dambowsky, I.; Weiss, J.; Laschewsky, A. *J. Am. Chem. Soc.* **2010**, *132*, 8757–8765.
16. Skrabania, K.; Miasnikova, A.; Bivigou-Koumba, A. M.; Zehm, D.; Laschewsky, A. *Polym. Chem.* **2011**, *2*, 2074–2083.
17. Mertoglu, M.; Garnier, S.; Laschewsky, A.; Skrabania, K.; Storsberg, J. *Polymer* **2005**, *46*, 7726–7740.
18. Weiss, J.; Böttcher, C.; Laschewsky, A. *Soft Matter* **2011**, *7*, 483–492.
19. Laschewsky, A.; Rekai, E. D.; Wischerhoff, E. *Macromol. Chem. Phys.* **2001**, *202*, 276–286.
20. Hennaux, P.; Laschewsky, A. *Colloid Polym. Sci.* **2001**, *279*, 1149–1159.
21. Ott, P.; Gensel, J.; Roesler, S.; Trenkenschuh, K.; Andreeva, D.; Laschewsky, A.; Fery, A. *Chem. Mater.* **2010**, *22*, 3323–3331.
22. Weiss, J.; Li, A.; Wischerhoff, E.; Laschewsky, A. *Polym. Chem.* **2012**, *3*, 352–361.
23. Skrabania, K.; Li, W.; Laschewsky, A. *Macromol. Chem. Phys.* **2008**, *209*, 1389–1403.
24. Herfurth, C.; Malo de Molina, P.; Wieland, C.; Rogers, S. H.; Gradzielski, M.; Laschewsky, A. *Polym. Chem.* **2012**, *3*, 1606–1617.
25. Miasnikova, A.; Laschewsky, A. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 3313–3323.
26. Baussard, J.-F.; Habib-Jiwan, J.-L.; Laschewsky, A.; Mertoglu, M.; Storsberg, J. *Polymer* **2004**, *45*, 3615–3626.
27. Ratcliffe, L. P. D.; Ryan, A. J.; Armes, S. P. *Macromolecules* **2013**, *46*, 769–777.
28. Miasnikova, A.; Laschewsky, A.; DePaoli, G.; Papadakis, C. M.; Müller-Buschbaum, P.; Funari, S. S. *Langmuir* **2012**, *28*, 4479–4490.
29. Bivigou-Koumba, A. M.; Görnitz, E.; Laschewsky, A.; Müller-Buschbaum, P.; Papadakis, C. M. *Colloid Polym. Sci.* **2010**, *288*, 499–517.
30. Malo de Molina, P.; Herfurth, C.; Laschewsky, A.; Gradzielski, A. *Langmuir* **2012**, *28*, 15994–16006.
31. Laughlin, R. G. *J. Soc. Cosmet. Chem.* **1981**, *32*, 371–392.
32. Hofmann, V.; Ringsdorf, H.; Muacevic, G. *Makromol. Chem.* **1975**, *176*, 1929–1943.
33. Lutz, J.-F. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3459–3470.
34. Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. *Tetrahedron Lett.* **2002**, *43*, 6811–6814.
35. Chaffey-Millar, H.; Stenzel, M. H.; Davis, T. P.; Coote, M. L.; Barner-Kowollik, C. *Macromolecules* **2006**, *39*, 6406–6419.
36. Gregory, A.; Stenzel, M. H. *Prog. Polym. Sci.* **2012**, *37*, 38–105.

37. Taton, D. From Stars to Microgels. In *Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications*; Matyjaszewski, K., Gnanou, Y., Leibler, L. Eds.; Wiley VCH: Weinheim, Germany, 2007; Vol. 2, Chapter 8, pp 1007−1056.
38. Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505–1513.
39. Moad, G.; Mayadunne, R. T. A.; Rizzardo, E.; Skidmore, M.; Thang, S. H. *Macromol. Symp.* **2003**, *192*, 1–12.
40. Destarac, M. *Polym. Rev.* **2011**, *51*, 163–187.
41. Fleming, I. *Molecular Orbitals and Organic Chemical Reactions*; Wiley-Blackwell: Chichester, U.K., 2009.
42. Buller, J.; Laschewsky, A.; Wischerhoff, E. *Soft Matter* **2013**, *9*, 929–937.
43. Jabloner, H.; Vandenberg, E. J. *Polyether graft copolymers*. U.S. Patent 3,546,321A, 1970.
44. Papantoniou, C. *Hair cosmetic compositions based on grafted and crosslinked copolymers*. U.S. Patent 3,946,749A, 1973.
45. Bromberg, L. *Ind. Eng. Chem. Res.* **1998**, *37*, 4267–4274.
46. Zehm, D.; Laschewsky, A.; Gradzielski, M.; Prévost, S.; Liang, H.; Rabe, J. P.; Schweins, R.; Gummel, J. *Langmuir* **2010**, *26*, 3145–3155.
47. Liu, J.; Liu, H.; Boyer, C.; Bulmus, V.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 899–912.
48. Müllner, M.; Schallon, A.; Walther, A.; Freitag, R.; Müller, A. H. E. *Biomacromolecules* **2010**, *11*, 390–396.
49. Zehm, D.; Laschewsky, A.; Heunemann, P.; Gradzielski, M.; Prévost, S.; Liang, H.; Rabe, J. P.; Lutz, J.-F. *Polym. Chem.* **2011**, *2*, 137–147.
50. Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 1999.
51. Albertin, L.; Stenzel, M. H.; Barner-Kowollik, C.; Davis, T. P. *Polymer* **2006**, *47*, 1011–1019.
52. Pietsch, C.; Fijten, M. W. M.; Lambermont-Thijs, H. M. L.; Hoogenboom, R.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 2811–2820.
53. Zehm, D.; Ratcliffe, L. P. D.; Armes, S. P. *Macromolecules* **2013**, *46*, 128–139.
54. Halperin, A. *J. Macromol. Sci. C: Polym. Rev.* **2006**, *46*, 173–214.
55. You, Y.-Z.; Hong, C.-Y.; Pan, C.-Y. *Eur. Polym. J.* **2002**, *38*, 1289–1295.
56. Weiss, J.; Laschewsky, A. *Macromolecules* **2012**, *45*, 4158–4165.
57. Bivigou-Koumba, A. M.; Kristen, J.; Laschewsky, A.; Müller-Buschbaum, P.; Papadakis, C. M. *Macromol. Chem. Phys.* **2009**, *210*, 565–578.
58. Garnier, S.; Laschewsky, A. *Langmuir* **2006**, *22*, 4044–4053.
59. Hayward, R. C.; Pochan, D. J. *Macromolecules* **2010**, *43*, 3577–3584.
60. Malo de Molina, P.; Herfurth, C.; Laschewsky, A.; Gradzielski, M. *Progr. Colloid Polym. Sci.* **2011**, *138*, 67–72.
61. Hoffman, A. S. *Adv. Drug. Delivery Rev.* **2002**, *43*, 3–12.
62. Podhajecka, K. P. K.; Hourdet, D. *Polymer* **2007**, *48*, 1586–1595.
63. Durand, A.; Hervé, M.; Hourdet, D. *ACS Symp. Ser.* **2001**, *780*, 181–207.

64. Aseyev, V.; Tenhu, H.; Winnik, F. *Adv. Polym. Sci.* **2011**, *242*, 29–89.
65. Ishizone, T.; Seki, A.; Hagiwara, M.; Han, S.; Yokoyama, H.; Oyane, A.; Deffieux, A.; Carlotti, S. *Macromolecules* **2008**, *41*, 2963–2967.
66. Dimitrov, I.; Trzebicka, B.; Müller, A. H. E.; Dworak, A.; Tsvetanov, C. B. *Prog. Polym. Sci.* **2007**, *32*, 1275–1343.
67. Ruel-Gariépy, Eve; Leroux, J.-C. *Eur. J. Pharm. Biopharm.* **2004**, *58*, 409–426.
68. Lee, D. S.; Shim, M. S.; Kim, S. W.; Lee, H.; Park, I.; Chang, T. *Macromol. Rapid Commun.* **2001**, *22*, 578–592.
69. Hiemstra, C.; Zhong, Z.; Li, L.; Dijkstra, P. J.; Feijen, J. *Biomacromolecules* **2006**, *7*, 2790–2795.
70. Zhong, Z.; Dijkstra, P. J.; Feijen, J.; Kwon, Y.-M.; Bae, Y. H.; Kim, S. W. *Macromol. Chem. Phys.* **2002**, *203*, 1797–1803.
71. Abebe, D. G.; Fujiwara, T. *Biomacromolecules* **2012**, *13*, 1828–1836.
72. Laschewsky, A.; Müller-Buschbaum, P.; Papadakis, C. M. *Prog. Colloid Polym. Sci.*, accepted for publication.
73. Kirkland, S. E.; Hensarling, R. M.; McConaughy, S. D.; Guo, Y.; Jarrett, W. L.; McCormick, C. L. *Biomacromolecules* **2008**, *9*, 481–486.
74. Ge, Z.; Zhou, Y.; Tong, Z.; Liu, S. *Langmuir* **2011**, *27*, 1143–1151.
75. Huynh, C. T.; Nguyen, M. K.; Lee, D. S. *Macromolecules* **2011**, *44*, 6629–6636.
76. Madsen, J.; Armes, S. P. *Soft Matter* **2012**, *8*, 592–605.
77. Schmalz, A.; Schmalz, H.; Müller, A. H. E. *Soft Matter* **2012**, *8*, 9436–9445.
78. Tsitsilianis, C. *Soft Matter* **2010**, *6*, 2372–2388.
79. Sugihara, S.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2601–2611.
80. Skrabania, K.; Kristen, J.; Laschewsky, A.; Akdemir, Ö.; Hoth, A.; Lutz, J.-F. *Langmuir* **2007**, *23*, 84–93.
81. Weiss, J.; Laschewsky, A. *Langmuir* **2011**, *27*, 4465–4473.
82. Nedelcheva, A. N.; Vladimirov, N. G.; Novakov, C. P.; Berlinova, I. V. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5736–5744.
83. Reinicke, S.; Schmelz, J.; Lapp, A.; Karg, M.; Hellweg, T.; Schmalz, H. *Soft Matter* **2009**, *5*, 2648–2657.
84. Zhou, C.; Hillmyer, M. A.; Lodge, T. P. *J. Am. Chem. Soc.* **2012**, *134*, 10365–10368.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch008

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch009

Chapter 9

Biodegradable, Bioactive-Based Poly(anhydride-esters) for Personal Care and Cosmetic Applications

A. L. Carbone-Howell, M. A. Ouimet, and K. E. Uhrich[*]

Department of Chemistry and Chemical Biology, Rutgers University,
610 Taylor Road, Piscataway, New Jersey 08854
[*]E-mail: keuhrich@rutgers.edu.

Bioactive-based polyanhydride delivery systems offer advantages for cosmetics and personal care applications including the potential to increase the efficacy of topical formulations and provide preservation benefits to both delivery formulas and packaging components. Such polymers allow for the incorporation of high levels of bioactive materials, strict control over the bioactive release profile, and formulation into films and microspheres, for example. Several examples of bioactive-based polyanhydrides will be discussed including those containing hydroxy acids, antimicrobials, and antioxidants.

Introduction

In the past few decades, polymeric delivery systems have been extensively studied for pharmaceutical and medical applications to protect and deliver bioactives, leading to increased efficacy, extended half-life, and sustained drug effects (*1*). Due to their success, polymeric delivery systems have migrated into other industries including cosmetic and personal care. In cosmetics and personal care, a delivery system can be defined as "a composition or process that can enhance perceptual or measured performance of a cosmetic product" (*2*). Such delivery systems can maximize both the performance and the aesthetics of a product, thereby improving the consumer experience.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch009

The origin of delivery systems in cosmetics and personal care stems from the need to enhance the efficacy of bioactive molecules. Factors such as solubility and stability to light, water, and air limit the amount of active that can be added to a formulation (*2*). Increasing bioactive loading in a formulation, however, does not always lead to enhanced efficacy. Delivery systems are thus also designed to enhance formula efficacy by extending a product's shelf-life through protecting sensitive bioactives such as peptides, vitamins, steroids, enzymes, flavors, fragrances and preservatives (*3*).

There are several types of delivery systems employed in cosmetics and personal care that utilize entrapment or adsorption technologies including clays and zeolites, emulsions, vesicles such as liposomes and hollow microparticles (empty with no drug), and suspensions (*2*). One of the most common methods to topically deliver bioactives is through suspensions and emulsions (*3*). Microemulsions can be utilized to directly entrap actives, fragrances, or flavors. Simple oil-in-water (O/W) or water-in-oil (W/O) emulsions have been staple formulations in the cosmetic industry (*4*). Suspensions and emulsions offer methods to not only entrap but also to deliver bioactives; control over the active release profile, however, is not always straightforward. Controlling emulsion properties (e.g., droplet size) requires careful formulation techniques including proper selection of surfactants and their concentrations, addition of thickeners, order of ingredient addition and specific processing conditions (*4*). In some cases, the chosen surfactant may have negative effects on the structure of the upper layers of the skin (*4*).

Liposomes have also been frequently used in cosmetics to provide a continuous supply of bioactive to skin cells over a prolonged period of time and to increase the delivery of vitamins such as vitamins A and E (*5*). The liposome bilayer structure gives rise to a variety of vesicle-type structures including small unilamellar vesicles, large unilamellar vesicles, and mutlilamellar vesicles (*5*). Structural similarity to skin lipids and other molecules naturally occurring in the human body can be advantageous for lipisome biocompatibility. Liposomes, however, often exhibit low encapsulation efficiency, poor storage stability, and leakage of their contents (*3*).

Polymeric Delivery Systems

Polymeric delivery systems based on biodegradable polymers have been studied extensively in the fields of biomaterials, gene delivery, drug delivery, and tissue engineering (*6*). Due to their beneficial attributes, these delivery systems are becoming more prevalent in cosmetics and personal care.

Polyanhydrides are a promising class of biodegradable polymers for controlled release applications due to their surface-eroding behavior, biodegradation into non-cytotoxic products, and tunable degradation rate based on polymer composition (*7–9*). Surface erosion of polyanhydrides enables a near zero-order release of physically entrapped actives upon hydrolytic degradation (*10*). In many polyanhydride delivery systems, the active molecules are physically entrapped within the polymer matrix. This often results in low bioactive loading and limited control over the bioactive's release rate. Furthermore, the polymer's mechanical properties can be compromised by the bioactive molecule utilized during physical encapsulation due to plasticizing effects (*11*).

More recently, bioactive-based poly(anhydride-esters) have received attention as promising delivery systems for a variety of bioactive molecules. In these delivery systems, bioactives are chemically incorporated into the backbone of polymers (*12–14*) or chemically attached as pendant groups to the main polymer chain (Figure 1) (*15*). This chemical incorporation leads to high levels of active loading (up to 100%). Furthermore, bioactive release can be easily tailored by altering the composition of the polymer; the "linker" (defined herein as the molecule chemically conjugated to the bioactive) can be altered when the bioactive is chemically incorporated into the polymer backbone, while the polymer backbone can be altered when the bioactive is attached as a pendent group.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch009

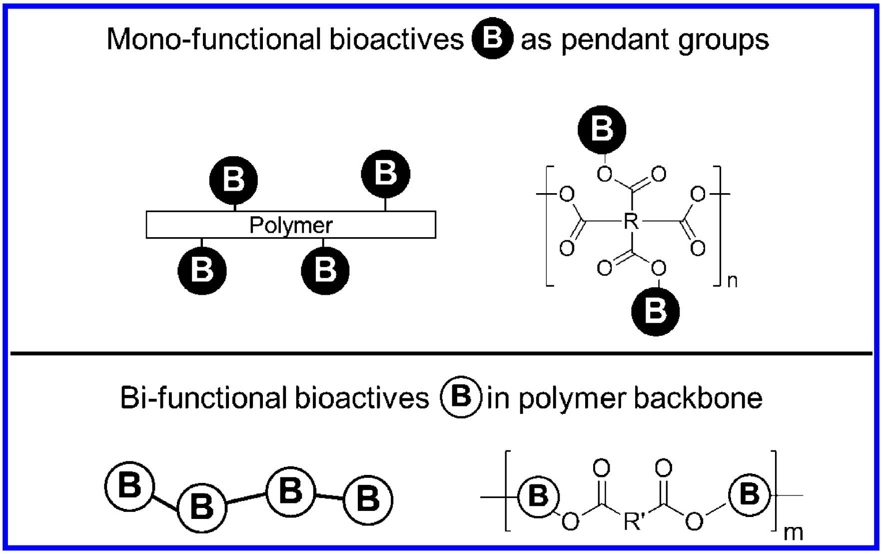


Figure 1. Representation of bioactive-containing polymers as pendant groups or within polymer backbone.

Bioactive-Based Poly(anhydride-esters)

A wide range of bioactive molecules can be incorporated into poly(anhydride-esters). Depending on the chemical nature of the bioactive, there are several synthetic routes that can be employed to chemically incorporate the bioactive into the polymer (*16–19*). Recent examples using antimicrobial and antioxidant bioactive molecules may be of particular interest for cosmetics and personal care (*15*, *18*, *20–22*). A more in-depth description of such polymers will be discussed throughout the remainder of this chapter.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch009

Salicylic Acid-Based Poly(anhydride-esters)

Salicylic acid, an over-the-counter monograph drug approved by the FDA for acne treatment, is an example of a cosmetic active for which a delivery system would be desired. In addition to its anti-acne properties, salicylic acid is often incorporated into various skin care products due to its keratolytic properties. Hydroxy acids such as salicylic acid have been utilized for skin benefits including rejuvenation and for the treatment of dry skin, wrinkles, photoaged skin, and skin pigmentation disorders (*23*). As an acid, however, this active sometimes causes skin irritation and dermatitic inflammation due its lowering of a formulation's pH (*2*, *23*, *24*). To overcome these drawbacks, a delivery system can be used. Recently, Dayan demonstrated that a porous nylon polymer-based controlled release delivery system could deliver 15% of physically entrapped salicylic acid while reducing skin irritation and prolonging the bioactive's efficacy (*25*, *26*). Rhein described salicylic acid delivery by physical entrapment in porous hydrophobic polyurethane to deliver sustained salicylic acid release (*27*). In both examples above, however, the loading and relative salicylic acid release is dependent on the porous polymeric carrier, which limits the ability to tailor the release of the bioactive material.

For biomedical applications, salicylic acid-based poly(anhydride-esters) have been designed to release chemically incorporated salicylic acid over prolonged periods of time (e.g., weeks to months) (*12*, *13*). For personal care and cosmetics, however, the delivery rate needs to be such that it is controlled, yet rapid, releasing the bioactive within 6-12 hours in most cases (*28*, *29*). To meet this degradation profile, a salicylic acid-based monomer was co-polymerized with a second, more hydrophilic diglycolic acid monomer (Figure 2). In this case, 38% of salicylic acid was released within a 48 hour time period. This offers a significant amount of release in a controlled manner over a few days. A more desirable release rate for salicylic acid, however, will be within a 12-24 hour time frame as a consumer will most likely not retain a cosmetic product in their skin for more than 24 hours due to their daily routines (e.g., face washing and showering) (*30*, *31*).

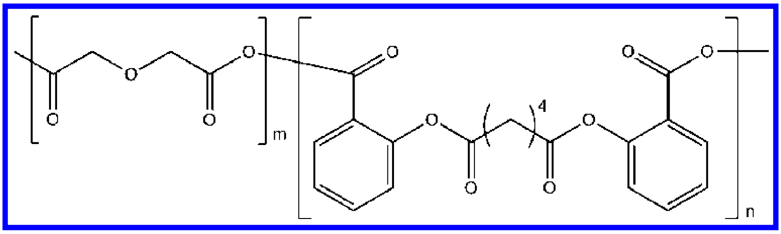


Figure 2. Chemical structure of salicylic acid-based poly(anhydride-ester) containing an adipic acid-based linker co-polymerized with diglycolic acid.

An alternative way to increase degradation rates is to incorporate a more hydrophilic linker molecule into the salicylic acid-based poly(anhydride-ester) backbone (*20*). Using a hydrophilic, diglycolic acid-based linker molecule

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch009

(Figure 3), the polymer released 100% salicylic acid within 48 hours as opposed to releasing over a timeframe of weeks and months (*13*). As with the copolymer, this system can be considered a potential candidate for releasing salicylic acid in a controlled manner over 2 days. One potential application of this polymer would be for a topical skin care formulation or overnight treatment for acne.

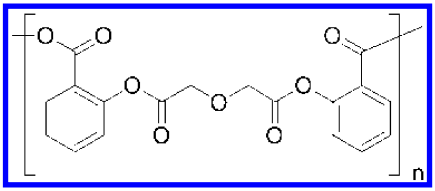


Figure 3. Chemical structure of salicylic acid-based poly(anhydride-ester) with diglycolic acid-based linker.

An additional benefit of bioactive-based poly(anhydride-esters) for cosmetic and personal care applications is that they may be employed as carriers for additional bioactive molecules. In one recent example, antimicrobials were physically incorporated into salicylic acid-based poly(anhydride-ester) discs that released both active molecules upon hydrolytic degradation (*32*). As skin care formulations often contain several bioactive molecules, the ability to use a dual delivery system may be desirable.

Antimicrobial-Based Poly(anhydride-esters)

Antimicrobials, commonly found in soaps, scrubs, and sanitizers are often utilized in personal care due to their ability to reduce infection and prevent disease transmission (*33*). In medical applications, antimicrobial-containing polymeric delivery systems can be utilized as temporary antiseptic coatings for tables, floors, and surgical suites or as controlled release systems for wound care applications (*21*).

Antimicrobial ingredients are also used in cosmetic formulations to protect the consumer from the growth of microorganisms in their products after prolonged use (*34*). Although antimicrobials are very effective in preventing microbial growth and protecting cosmetic formulas, their safety has been questioned due to surmounting negative press. Thus, trends in “preservative-free” products are becoming more prevalent to reduce potential safety issues (*35–37*). Furthermore, rather than including the antimicrobial preservative as part of the formula, the controlled release of antimicrobials from packaging components may also be advantageous to prolong product shelf-life (*38*). This aspect may be realized with the use of antimicrobial-containing polymers.

Some antimicrobials of interest for personal care contain only one functional group available for chemical incorporation into a polymer. Therefore, rather than incorporation into backbone of the polymer, they must be chemically incorporated as a pendant group on the degradable backbone (*15*, *21*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch009

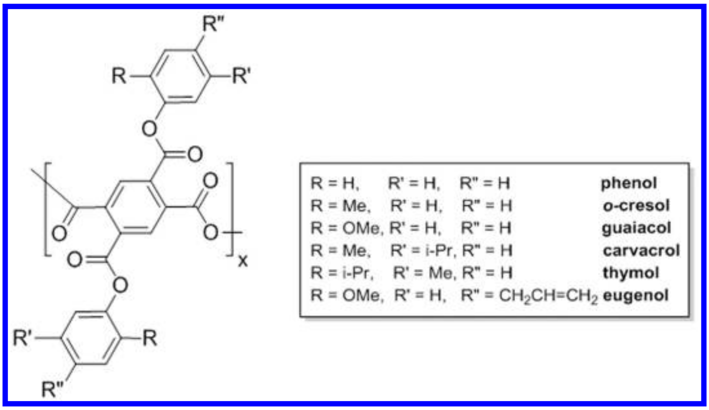


Figure 4. Chemical structure of antimicrobial-based poly(anhydride-esters).

In the case above (Figure 4), the polymer backbone is based on pyromellitic acid. Pyromellitic dianhydride was chosen as the starting material to provide a facile synthetic route for incorporation of mono-functional bioactives (*15*). To build upon this synthetic route, another type of backbone, namely ethylenediaminetetraacetic acid (EDTA), was explored (Figure 5) for its use as a chelating agent to improve cosmetic formulation stability (*39*). Chelating agents such as EDTA can work synergistically with preservatives to increase their efficacies (*40*, *41*). In this example, the polymer is completely bioactive, releasing both an antimicrobial and EDTA upon hydrolytic degradation (*21*).

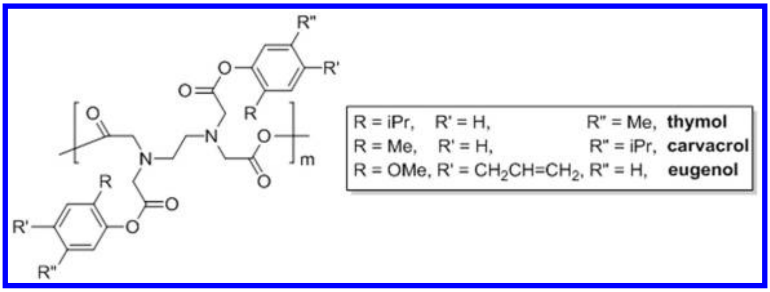


Figure 5. Chemical structure of fully bioactive-based poly(anhydride-esters).

Antioxidant-Based Poly(anhydride-esters)

Antioxidant use in cosmetic and personal care products is a growing trend due to numerous studies demonstrating their ability to protect skin from free radicals. Free radicals, generated by UV radiation, cause oxidative stress, which may lead to photodamage and result in photosensitivity, senescence, and even skin cancer (*42*). The human body combats this oxidative stress by employing antioxidants made in the body or acquired from diet and/or supplements (*43*, *44*). These antioxidants, however, are usually not in sufficient levels to overcome the stresses caused from environmental damage. Therefore, new formulation methods using topical antioxidants with photoprotective actives are needed to enhance skin protection against photodamage.

Antioxidants such as kinetin and ubiquinone (and its derivatives) have been shown to improve skin texture by energizing the skin, protecting against skin aging, and reducing detrimental photo-aging effects (*45*). These antioxidants are beneficial, but when compared to another product containing ferulic acid, a natural, potent antioxidant with many potential health benefits, and vitamins C and E, they proved ineffective or poor photoprotectors (*46*).

Topical antioxidants such as ferulic acid, vitamins C and E, and selenium, have been investigated for enhancing skin protection and reversing photoaging, but the actives' stability within such formulations poses a new issue. To overcome this stability issue, researchers have found that the addition of ferulic acid to a formulation containing vitamins C and E improved the vitamin stability and doubled their photoprotective capabilities (*47*, *48*). It is believed that the ferulic acid acts a sacrificial molecule and may also provide synergistic photoprotection (*47*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch009

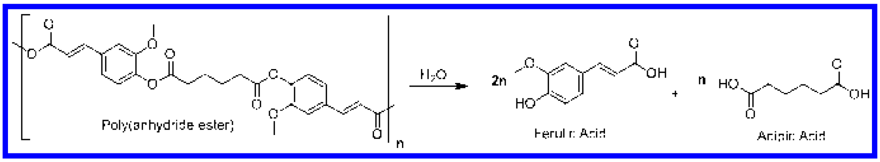


Figure 6. Chemical structure of antioxidant-based poly(anhydride-ester) and subsequent hydrolysis into ferulic acid and biocompatible linker, adipic acid.

Ferulic acid itself can be quite useful, but its limited elimination half-life (less than 2 hours) (*49*) and stability issues (degradation over time) lowers its efficacy in current formulations (*50*). Ferulic acid delivery can be improved by incorporation into a biodegradable polymer backbone (Figure 6), enabling controlled bioactive release and preventing active functional groups from degradation (*18*, *50*). In this example, antioxidant activity was comparable to that of the free bioactive, indicating increased stability (i.e., degradation and discoloration did not occur).

In addition to preventing photodamage, these molecules can be used for antimicrobial purposes. The primary function of these antioxidants when used as antimicrobials is to delay the auto-oxidation of unsaturated oils that could influence the product's odor and color, thus leading to its use as a two-fold bioactive (*38*). The antimicrobial potency, however, must be ensured as the concentration may decrease when the antioxidants perform within a formulation.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch009

Applications of Poly(anhydride-esters): Novel Forms

The described poly(anhydride-esters) not only allow for controlled drug delivery and high drug loading, but can also be fabricated into various devices depending on the end use. The described salicylic acid-based poly(anhydride-esters) have been fabricated into discs (*13*), hydrogels (*51*), and microspheres (*52*), which is a feature that small molecules alone cannot achieve and can be beneficial for personal care and cosmetic applications (Figure 7).

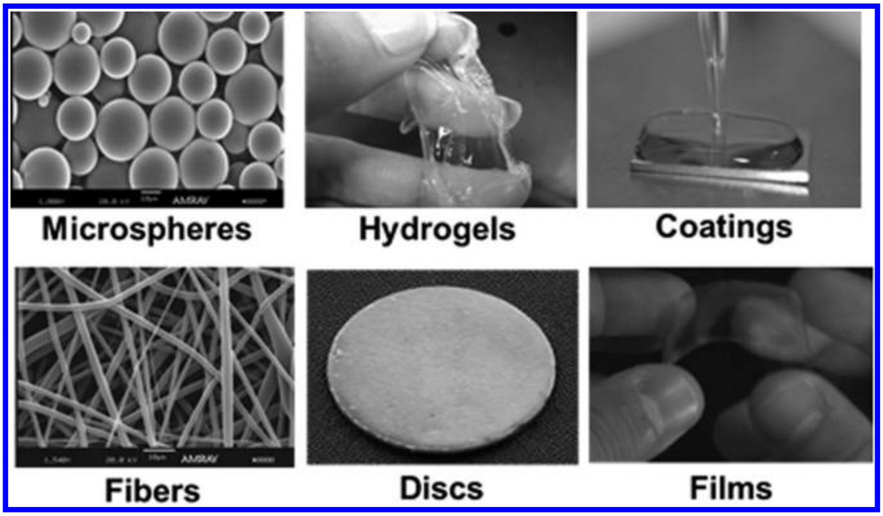


Figure 7. Bioactive-based poly(anhydride-esters) fabricated into various devices including microspheres, hydrogels, coatings, fibers, discs, and films.

Poly(vinyl pyrrolidone) (PVP) is a polymer currently used in a variety of cosmetic and personal care products as an emulsion stabilizer, thickener, and binder due to its unique rheological and film-forming properties (*53*). PVP is primarily found in eyeliners, mascaras, hair conditioners, and other products as the polymer complexes with a wide range of organic molecules such as dyes, antimicrobials, and UV absorbers (*53*, *54*). Taking a cue from the multitude of PVP usages, the aforementioned salicylic acid-based polymers were blended with PVP to formulate hydrogels, three-dimensional gel-like materials that absorb water without dissolving (*55*). This gel can be used topically to impart relevant bioactive properties as salicylic acid is released from the polymer.

The polymers can be further formulated for cosmetic applications by preparing microspheres (*56*). These microspheres are advantageous over using a disc in that the surface area is greatly increased, thus accelerating bioactive release. Furthermore, these microspheres act as carriers to encapsulate other bioactive molecules for dual release and potential synergistic activity.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch009

Summary

Polymeric delivery systems may be beneficial in cosmetics and personal care due to the ability to release active agents in a controlled manner. Rather than physically entrapping active molecules, bioactive-based polyanhydrides offer the advantages of well-controlled and tailored release rates, high bioactive loading, and the ability to formulate the polymer into various different forms including gels, films, and microspheres.

Salicylic acid-based polyanhydrides may be utilized for topical applications to deliver the hydroxy acid for treatment of acne, dry skin, wrinkles, photoaged skin, or skin pigmentation disorders. It has been demonstrated that the degradation profile can be tuned to release 100% of the chemically incorporated salicylic acid in as little as 48 hours or as long as several weeks depending on the application.

Antimicrobials and antioxidants based on phenolic derivatives have also been chemically incorporated into polyanhydrides. In one example above, the polymer is completely comprised of bioactive based on the antimicrobial and a chelating agent, EDTA. These polymers may be useful for formula or packaging preservation to prevent microbial contamination. In another example using ferulic acid-based polymers, this methodology proved beneficial for stabilizing the active while providing controlled release, ultimately improving upon current topical antioxidant formulations to mitigate or negate some of the harmful effects of oxidative stress leading to skin damage.

Acknowledgments

The authors would like to acknowledge the members of the Uhrich research group for insightful discussion.

References

1. Gebelein, C. G.; Cheng, T. C.; Yang, V. C. In *Cosmetic and Pharmaceutical Applications of Polymers*; Plenum Press: New York, 1991.
2. Gupta, S. *HAPPI* **2003** January, 49–59.
3. Somasundaran, P.; Chakraborty, S.; Deo, P.; Deo, N.; Somasundaran, T. *Nanoparticles for Cosmetics and Personal Care Formulations. Skin Delivery Systems: Transdermals, Dermatologicals and Cosmetic Actives*, 1st ed.; Blackwell Pub.: Ames, Ioawa, 2006; pp 247−56.
4. Shroot, B.; Aust, D. *Current Trends in Dermatologicals and Delivery Systems. Skin Delivery Systems: Transdermals, Dermatologicals and Cosmetic Actives*. Ames, Iowa: Blackwell Pub.; 2006; pp 129−35.
5. Lautenschläger, H. In *Handbook of Cosmetic Science and Technology*; Barel, A., Paye, M., Maibach, H., Eds.; CRC Press Taylor & Francis Group: Boca Raton, 2006.
6. Brannon-Peppas, L. Polymers in Controlle Drug Delivery. *Med. Plast. Biomater. Mag.* **1997**.
7. Göpferich, A.; Tessmar, J. *Adv. Drug Delivery Rev.* **2002**, *54*, 911–31.

8. Kumar, N.; Langer, R. S.; Domb, A. J. *Adv. Drug Delivery Rev.* **2002**, *54*, 889–910.
9. Amass, W.; Amass, A.; Tighe, B. *Polym. Int.* **1998**, *47*, 89–144.
10. Whitaker-Brothers, K.; Uhrich, K. *J. Biomed. Mater. Res., Part A* **2006**, *76A*, 470–9.
11. Siepmann, F.; Le Brun, V.; Siepmann, J. *J. Controlled Release* **2006**, *115*, 298–306.
12. Erdmann, L.; Uhrich, K. E. *Biomaterials* **2000**, *21*, 1941–6.
13. Prudencio, A.; Schmeltzer, R. C.; Uhrich, K. E. *Macromolecules* **2005**, *38*, 6895–901.
14. Schmeltzer, R. C.; Uhrich, K. E. *Polym. Bull.* **2006**, *57*, 281–91.
15. Prudencio, A.; Carbone, A. L.; Griffin, J.; Uhrich, K. E. *Macromol. Rapid Commun.* **2009**, *30*, 1101–8.
16. Schmeltzer, R. C.; Anastasiou, T. J.; Uhrich, K. E. *Polym. Bull.* **2003**, *49*, 441–8.
17. Schmeltzer, R. C.; Johnson, M.; Griffin, J.; Uhrich, K. *J. Biomater. Sci., Polym. Ed.* **2008**, *19*, 1295–306.
18. Ouimet, M. A.; Griffin, J.; Carbone-Howell, A. L.; Wu, W. H.; Stebbins, N. D.; Di, R.; Uhrich, K. E. *Biomacromolecules* **2013**, *14*, 854–61.
19. Rosario-Meléndez, R; Harris, CL; Delgado-Rivera, R; Yu, L; Uhrich, KE *J. Controlled Release* **2012**, *162*, 538–44.
20. Carbone, A. L.; Uhrich, K. E. *Macromol. Rapid Commun.* **2009**, *30*, 1021–6.
21. Carbone A. L. Ph.D. Thesis, Rutgers, The State University of New Jersey, New Brunswick, 2009.
22. Rosenberg, L. E.; Carbone, A. L.; Romling, U.; Uhrich, K. E.; Chikindas, M. L. *Appl. Microbiol. Lett.* **2008**, *46*, 593–9.
23. Gupta S. *Hydroxy Acids Delivery Systems. Skin delivery systems: transdermals, dermatologicals, and cosmetic actives*, 1st ed.; Blackwell Pub.: Ames, Iowa, 2006.
24. Kligman, A. M. Salicylic acid: An alternative to alpha hydroxy acids. *J. Ger. Dermatol.* **1997**, *5*, 128–31.
25. *Epidermal Targeting: Controlled Topical Delivery of Salicylic Acid*; Dayan, N., Basak, K., Eds.; HBA Product Development Presentations, Session PD2, New York, 2002.
26. Dayan, N.; Basak, K. A Delivery System for Salicylic Acid to Overcome the Drawbacks of its Use in Topically Applied Formulations. *C&T Manufacture World Wide Magazine* **2003**, 114–8.
27. Rhein, . L; Chaudhuri, B.; Jivani, N.; Fares, H.; Davis, A. *Int. J. Cosmet. Sci.* **2004**, *26*, 218–9.
28. Huang, X.; Brazel, C. S. *J. Controlled Release* **2001**, *73*, 121–36.
29. Peppas, N. A.; BrannonPeppas, L. *J. Controlled Release* **1996**, *40*, 245–50.
30. Abrahamse, W.; Steg, L.; Vlek, C.; Rothengatter, T. *J. Environ. Psychol.* **2007**, *27*, 265–76.
31. Wilkes, C. R.; Mason, A. D.; Hern, S. C. *Risk Anal.* **2005**, *25*, 317–37.
32. Johnson, M. L.; Uhrich, K. E. *J. Biomed. Mater. Res., Part A* **2009**, *91*, 671–8.
33. Larson, E. *Clin. Infect. Dis.* **1999**, *29*, 1287–94.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch009

34. Campana, R.; Scesa, C.; Patrone, V.; Vittoria, E.; Baffone, W. *Appl. Microbiol. Lett.* **2006**, *43*, 301–6.
35. Rastogi, S. C.; Schouten, A.; Dekruijf, N.; Weijland, J. W. *Contact Dermatitis* **1995**, *32*, 28–30.
36. Cashman, A. L.; Warshaw, E. M. *Dermatitis* **2005**, *16*, 57–66.
37. Kabara, J. J.; Orth, D. S. In *Preservative-free and self-preserving cosmetics and drugs: principles and practices*; Marcel Dekker: New York, 1997.
38. Varvaresou, A.; Papageorgiou, S.; Tsirivas, E.; Protopapa, E.; Kintziou, H.; Kefala, V.; Demetzos, C. *Int. J. Cosmet. Sci.* **2009**, *31*, 163–75.
39. *Int. J. Toxicol.* **2002**, *21*, 95–142.
40. Lundov, M. D.; Moesby, L.; Zachariae, C.; Johansen, J. D. *Contact Dermatitis* **2009**, *60*, 70–8.
41. Hart, J. R. *Ethylenediaminetetraacetic Acid and Related Chelating Agents. Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: New York, 2000.
42. Gonzaga, E. R. *Am. J. Clin. Dermatol.* **2009**, *10* (Suppl 1), 19–24.
43. Podda, M.; Grundmann-Kollmann, M. *Clin. Exp. Dermatol.* **2001**, *26*, 578–82.
44. Kohen, R.; Gati, I. *Toxicology* **2000**, *148*, 149–57.
45. Vinson, J.; Anamandla, S. *Int. J. Cosmet. Sci.* **2006**, *28*, 148.
46. Tournas, J. A.; Lin, F.-H.; Burch, J. A.; Selim, M. A.; Monteiro-Riviere, N. A.; Zielinski, J. E.; Pinnel, S. R. *J. Invest. Dermatol.* **2006**, *126*, 1185–7.
47. Murray, J. C.; Burch, J. A.; Streilein, R. D.; Iannacchione, M. A.; Hall, R. P.; Pinnell, S. R. *J. Am. Acad. Dermatol.* **2008**, *59*, 418–25.
48. Lin, F. H.; Lin, J. Y.; Gupta, R. D.; Tournas, J. A.; Burch, J. A.; Selim, M. A.; Monteiro-Riviere, N. A.; Grichnik, J. M.; Zielinski, J.; Pinnell, S. R. *J. Invest. Dermatol.* **2005**, *125*, 826–32.
49. Li, F.-Q.; Hu, J.-H.; Deng, J.-X.; Su, H.; Xu, S.; Liu, J.-Y. *Int. J. Pharm.* **2006**, *324*, 152–7.
50. Wang, Q.; Gao, X.; Gong, H.; Lin, X.; Saint-Leger, D.; Senee, J. *J. Cosmet. Sci.* **2011**, *62*, 483–503.
51. Fogaça, R.; Ouimet, M.; Catalani, L.; Uhrich, K. *Proc. ACS Div. Polym. Mater.: Sci. Eng.* **2010**, *103*.
52. Griffin, J.; Delgado-Rivera, R.; Meiners, S.; Uhrich, K. E. *J. Biomed. Mater. Res., Part A* **2011**, *97A*, 230–42.
53. Salamone, J. C. In *Polymeric Materials Encyclopedia*; CRC Press: Boca Raton, 1996.
54. Draelos, Z. In *Hair Care: An Illustrated Dermatologic Handbook*; Taylor & Francis: Boca Raton, FL, 2005.
55. Fogaça, R.; Ouimet, M. A.; Catalani, L. H.; Uhrich, K. E. Bioactive-based poly(anhydride-esters) and blends for controlled drug delivery. In *Tailored Polymer Architectures for Pharmaceutical and Biomedical Applications*; Scholz, C., Kressler, J., Eds.; ACS Symposium Series 1135; American Chemical Society: Washington, DC, 2013.
56. Rosario-Meléndez, R.; Ouimet, M. A.; Uhrich, K. E. *Polym. Bull.* **2013**, *70*, 343–51.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

Chapter 10

Controlled Synthesis of Multifunctional Polymers by RAFT for Personal Care Applications

Matthias Haeussler,* John Chiefari, Graeme Moad, and Ezio Rizzardo

CSIRO Materials Science and Engineering, Bayview Avenue,
Clayton, Vic, 3168, Australia
***E-mail: Matthias.Haeussler@csiro.au.**

The versatility of the RAFT (Reversible Addition-Fragmentation chain Transfer) technology provides enormous potential for the design and development of multifunctional polymers that are optimized for performance in a range of applications in the personal care and cosmetics areas. This contribution demonstrates the attributes of the RAFT process as a ground-breaking technology offering unprecedented control over the composition, functionality and architecture of polymers obtained through radical polymerization. Examples of block copolymer structures with distinctive physical and chemical properties are presented and the performance attributes of these polymers are highlighted.

Introduction

Polymers made from ethylenically unsaturated monomers such as acrylates, methacrylates, acrylamides, styrenes or vinyl esters are essential ingredients in many cosmetic and personal care formulations and find application as thickeners, hair fixative agents and conditioners, rheology modifiers, color dispersants, active-delivery compounds and film formers (*1*). They have traditionally been synthesized by conventional radical polymerization (RP). However, newer, more sophisticated product requirements call for the intricate control provided by techniques for reversible deactivation radical polymerization (RDRP) (*2*, *3*). These methods include nitroxide-mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

fragmentation chain-transfer polymerization (RAFT) that enable the generation of multifunctional polymers with improved properties (*2*, *4–11*). Among RDRP techniques, RAFT polymerization is arguably the most versatile one as it requires only the addition of an organic small molecule (chain transfer agent) to an otherwise conventional RP (*12*). It is now well-established for providing control over molecular weight, dispersity, composition and architecture of polymers and thereby offers a convenient route to well-defined, gradient, block and star polymers as well as more complex architectures that include microgels and polymer brushes (Figure 1) (*13–19*). The process can be applied to most monomers polymerizable by RP and is in particular important for vinyl ester and vinylamide based polymers such as poly(vinyl alcohol) (PVOH) and poly(vinyl pyrrolidone) (PVP), which are often used in cosmetic and personal care (*11*). RAFT can also be used for block or graft copolymers with polyesters (*20*), polyurethanes (*21*), polysiloxanes (*22*), poly(ethylene glycol) (*10*), polysaccharides (*23*) and other polymers frequently used in cosmetic and personal care applications (*24*, *25*).

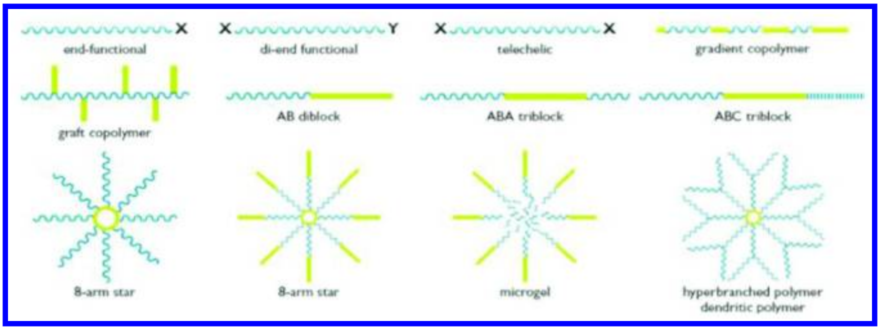


Figure 1. Idealized polymers of controlled composition, end-groups, molecular weight and structure obtainable through CDRP.

In this contribution, the RAFT process will be described placing particular emphasis on addressing end-group removal and potential odor issues, which arise with the use of sulfur containing RAFT agents. Additionally, examples of block copolymer structures with distinctive physical and chemical properties are presented and the performance attributes of these polymers are highlighted.

Experimental

Reagents

3-[Tris(trimethylsiloxy)silyl]propyl methacrylate (TrisMA) was purchased from Gelest, all other monomers were obtained from Sigma-Aldrich. The monomers were purified before use by passing them through inhibitor removal columns or by distillation immediately before use. Azobisisobutyronitrile (AIBN) was obtained from TCI and recrystallized from methanol before use.

Solvents were distilled before use. RAFT agents were synthesized according to published procedures (*7*, *10*, *13–19*). All other chemicals were purchased from Sigma-Aldrich and used as received.

Instruments

Gel permeation chromatography (GPC) was performed on a Waters Alliance e2695 liquid chromatograph equipped with a Waters 2414 differential refractometer and 3×mixed C and 1 mixed E PLgel columns (each 300 mm × 7.5 mm) from Polymer Laboratories. The eluent was tetrahydrofuran (THF) at 30 °C (flow rate: 1 mL min^{-1}). Number (M_n) and weight-average (M_w) molar masses were evaluated using Waters Empower Pro 2 software. The GPC columns were calibrated with low dispersity polystyrene standards (Polymer Laboratories) and molecular weights are reported as polystyrene (PS) equivalents. A third order polynomial was used to fit the log M_p vs time calibration curve, which was linear across the molecular weight range 2×10^2 to 2×10^6 g mol^{-1}.

Polymerization

The polymerizations were carried out according to published procedures (*7*, *10*, *13–19*) and are illustrated by the following example. A mixture of the 2-cyanopropan-2-yl dodecyl trithiocarbonate (40.8 mg, 1.18×10^{-4} mol), AIBN (0.65 mg, 3.94×10^{-6} mol), TrisMA (2.85 g, 6.75×10^{-3} mol), 2-hydroxylethyl methacrylate (HEMA; 97.6 mg, $7.5\mathrm{x}10^{-4}$ mol) and 3.25 mL 1,4-dioxane was degassed with three freeze–pump–thaw cycles, sealed under vacuum, and heated in a constant-temperature oil bath at 70 °C. After 18 h, the polymerization was quenched by cooling the reaction mixture and a sample was taken for determining the monomer conversion by the reduction of the methacrylate protons in the ^{1}H-NMR spectra (83.4 %). The polymer was precipitated twice into methanol (MeOH), filtered and washed with MeOH and dried under vacuum to a constant weight; yellow solid: M_n = 17,400; $Đ$ = 1.21.

Poly(2-(dimethylamino)ethyl methacrylate) (PolyDMAEMA) was obtained in a similar way by polymerizing a mixture of 2.26 g (1.44×10^{-2} mol) DMAEMA, 0.49 mg (3×10^{-6} mol) AIBN, 31.1 mg (9×10^{-5} mol) 2-cyanopropan-2-yl dodecyl trithiocarbonate and 2.3 mL of toluene at 70 °C for 18h. Conversion (^{1}H NMR): 63.3%, M_n = 16,700; $Đ$ = 1.28.

RAFT End-Group Modification

Hydrazine monohydrate (28.6 μL, 5.9×10^{-4} mol) was added to a solution of Poly(TrisMA-*co*-HEMA)-RAFT (1.18 g, [RAFT] = 4.72×10^{-5} mol) in 3 mL 1,4-dioxane. The solution was stirred for 1 h after which 137 mg ($1.18\mathrm{x}10^{-3}$ mol) 2-hydroxyethyl acrylate (HEA) added. The mixture was stirred overnight, precipitated twice into MeOH, filtered and washed with MeOH and dried under vacuum to constant weight. Colorless solid, M_n = 17,300; $Đ$ = 1.21.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

RAFT End-Group Removal

PolyDMAEMA (0.5g) was placed in a Kugelrohr and heated at 180 °C under vacuum (1×10^{-3} bar). Samples were taken at different time intervals and analyzed by GPC.

Discussion

Commercial Polymers

RP is a well known and key industrial process for obtaining a wide range of polymers and materials that are pervasive in our modern society – producing up to half of the total world-wide quantity by volume (*26*). In the personal care and cosmetics area, a large number of polymer additives are similarly made or can be accessed by this form of polymerization. Table 1 shows a few selected examples of currently used polymers and their function in a personal care formulation.

Table 1. Selected examples of polymers currently used for personal care applications obtained through conventional RP

Product Name	***Function***
• Acrylates/C10-30 alkyl acrylate CrossPolymer	Thickener
• Carbomers	Stabilizer, Thickener, Binders, Film Formers, Hair Fixatives, Suspending Agents
• Acrylates/dimethiconol acrylate copolymer	Film Formers
• Polyquaternium-5, 11, 15, 16, 28, 32, 37, 46, 47	Antistatic Agents; Film Formers; Hair Fixatives
• Acrylamide/ethyltrimonium chloride acrylate/ethalkonium chloride acrylate copolymer	Film Former, Hair Conditioning Agent; Skin Conditioning Agent; Slip Modifier, Thickener
• Acrylamidopropyl trimonium chloride/acrylamide copolymer	Hair Conditioner
• Styrene/acrylate copolymer	Film formers

RAFT Polymers

Conventional RP in general requires only a monomer and a radical initiator to produce the polymer (Figure 2) (*27*). Most polymer chains contain the initiator fragment as the head group and another initiator fragment or hydrogen atom/unsaturated double bond as the terminal groups, depending on whether chain termination is by combination or disproportionation of the propagating radicals

(*27*, *28*). The resulting polymer typically exhibits a relatively broad molecular weight distribution, $Đ$ ($=M_w/M_n$) ≥ 1.5, which is a consequence of superimposed chain propagation and chain termination statistics, but may be much higher for commercially produced polymers ($Đ = 1.0$ means all polymer chains are of the same length).

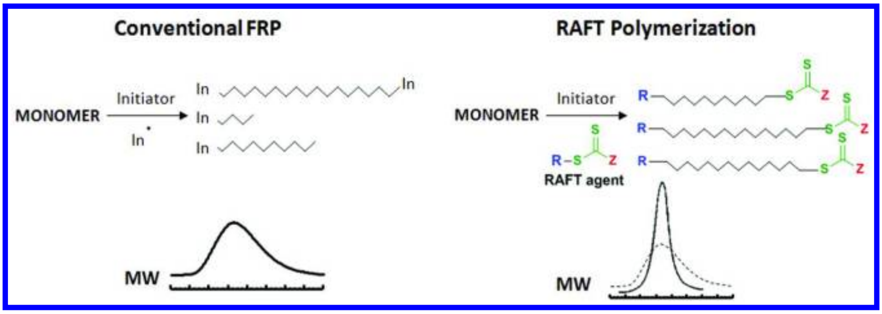


Figure 2. Comparison between conventional RP and RAFT polymerization.

The RAFT polymerization is carried out in a similar fashion to the conventional RP and, as such, also requires a monomer and a radical initiator. Additionally, a thiocarbonylthio chain transfer agent (RAFT agent) is employed to control the growth of each polymer chain. This RAFT agent functionality is retained at the end of each macromolecule and ensures the steady growth of all polymer chains, which is very different from conventional RP, where high molecular weight polymers are formed almost instantaneously after initiation. Consequently, in a RAFT-controlled polymerization, all polymer chains grow simultaneously (though intermittently) and thus are of similar length and have a narrow molecular weight distribution (typically $Đ = 1.05$-1.3) (*29*).

Because each polymer chain contains the RAFT end-group, the terminal ends are “living” though “dormant” (macro-RAFT agent). Hence, addition of a second monomer will directly result in the formation of a diblock copolymer provided sufficient initiator is present in the polymerization mixture (see below: *Mechanistic considerations*). Multiple RAFT agents, the use of different (co)monomers and the manner of their addition opens up possibilities to generate more advanced and sophisticated polymer architectures such as multiblock, gradient, polymer brush, star and dendritic structures for use as high performance polymers (some of the possible structures are shown in Figure 1).

Mechanistic Considerations and Choice of RAFT Agent

The RAFT agent consists typically of a thiocarbonylthio functional group sandwiched between the R and the Z group. The R group must be a good homolytic leaving group and needs to be matched with the type of monomers being polymerized (Note: while tertiary R groups are acceptable leaving groups with respect to both tertiary and secondary propagating radicals, secondary R

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

groups are poor leaving groups with respect to tertiary propagating radicals) (*29*, *30*). The Z group determines the bond strength of the C=S double bond and the stability of the intermediate radical and thus the activity of the RAFT agent (*19*).

In a RAFT polymerization, initiator and propagating radicals add to the C=S bond, resulting in an intermediate which can cleave (fragmentation) the bond between the R group and the thiocarbonylthio group of the RAFT agent to form a macro-RAFT agent and a radical R·. The resulting R· radical reacts with monomer to form a new propagating radical (P_n·), which adds again either to initial RAFT agent or macro-RAFT agent to kick out the R-group or another polymer chain, respectively. As a result, reversible addition−fragmentation equilibria are established as shown in Figure 3.

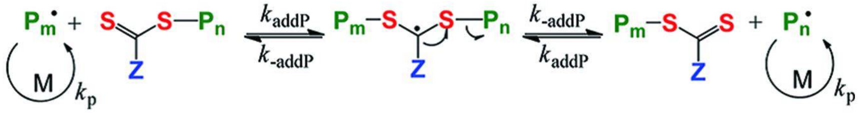


Figure 3. Addition – fragmentation equilibria occurring during a RAFT polymerization.

During the reversible addition-fragmentation step radicals are neither formed nor destroyed. Thus in the absence of side reactions, the RAFT process should therefore have no direct influence on the rate of polymerization compared to a conventional RP beyond that caused by reduction of molecular weight and the narrowing of the molecular weight distribution (see also “Polymerization times” later in this chapter). Since termination radical-radical reaction occurs, just as in conventional RP, a constant supply of initiator radicals is required to maintain the reaction.

It should be mentioned here that for all RDRP methods the control of the propagation and thus the narrow polydispersities comes at the price of reduced molecular weights. This should be taken into account where the use of high molecular weight polymers is targeted such as for thickeners. Very high molecular weights can be obtained, for example, by carrying out the polymerizations under very high pressure (1 – 10 kbar) to yield polymers with molecular weights up to 1.2×10^6 Da ($Đ = 1.03$) (*31*).

For the reasons mentioned above, it is important to select the RAFT agent according to the monomers being polymerized and reaction conditions employed. The effectiveness of RAFT agents is determined by the substituent R and Z and guidelines for selection have been proposed (Figure 4) (*13*, *14*, *32*). Dithioester and trithiocarbonate RAFT agents are good for the polymerization of more activated monomers (MAM), e.g. methyl methacrylate (MMA), methacrylic acid (MAA), hydroxypropyl methacrylamide (HPMAM), methyl acrylate

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

(MA), acrylic acid (AA), acrylamide (AM), acrylonitrile (AN) and styrene (St). Xanthates and dithiocarbamates are suited for the less activated monomers (LAM), e.g. vinyl acetate (VAc), *N*-vinylpyrrolidone (NVP) and *N*-vinylcarbazole (NVC). Recently, we reported 4-pyridinyl-*N*-methyl-dithiocarbamate derivatives that can be switched by changing the pH to allow control of both MAMs and LAMs (*33–35*).

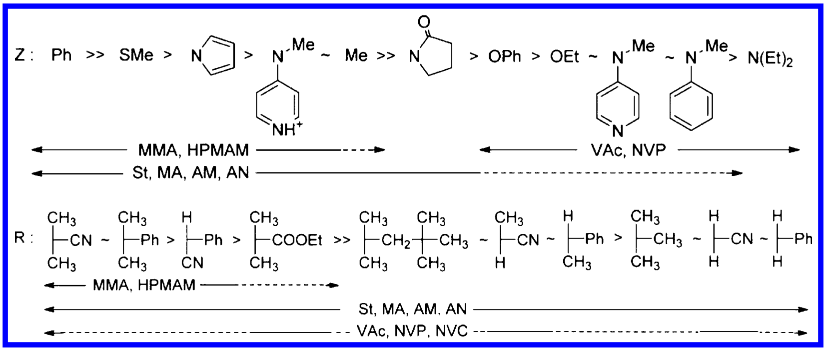


Figure 4. Guidelines for selection of the Z and R groups of RAFT agents (ZC(=S)SR) for various polymerizations. For 'Z', addition rates decrease and fragmentation rates increase from left to right. For 'R', transfer coefficients and fragmentation rates decrease from left to right. A dashed line indicates partial control (i.e., control of molar mass but poor control over dispersity or substantial retardation in the case of LAMs such as VAc or NVP). Adapted with permission from reference (18). Copyright 2012 CSIRO Publishing. Available online at: http://www.publish.csiro.au/nid/51/paper/CH12295.htm.

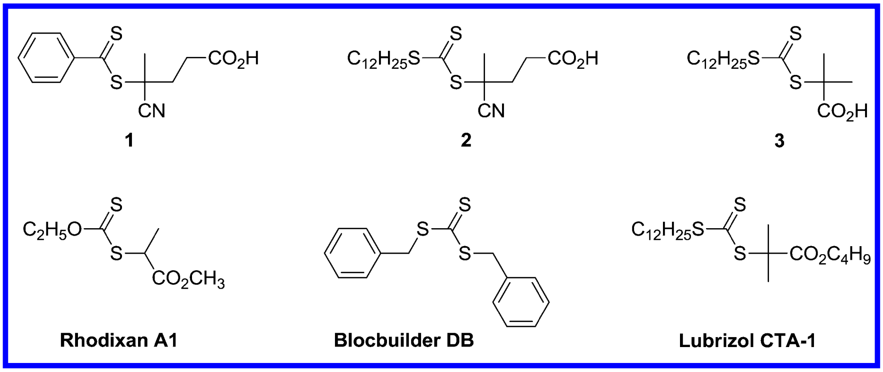


Figure 5. Commercially available RAFT agents.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

Commercial Availability of RAFT Agents

While over the past two decades a great variety of RAFT agents with different R and Z groups has been reported in the literature (*35*, *36*), from a practical point of view the polymerization of most monomers can be satisfactorily controlled by only a selected few RAFT agents. A range of RAFT agents including the carboxylic acid functional RAFT agents 1–3 are now commercially available in research quantities and are shown in Figure 5 (*37*, *38*). The industrial scale-up has been announced of the xanthate, Rhodixan-A1, by Rhodia (*39*) and trithiocarbonates, Blocbuilder DB and CTA-1, by Arkema (*40*) and Lubrizol (*41*), respectively.

Polymerization Times

Recent developments in flow chemistry and microreactor technology have changed the way polymers are synthesized in the laboratory (*42*). As shown by our group, RAFT polymerizations can not only be carried out in the traditional batch e.g. round-bottom flask, ampoules or Schlenk tubes but also be adapted for continuous flow processing using stainless steel tubular reactors (*43–45*).

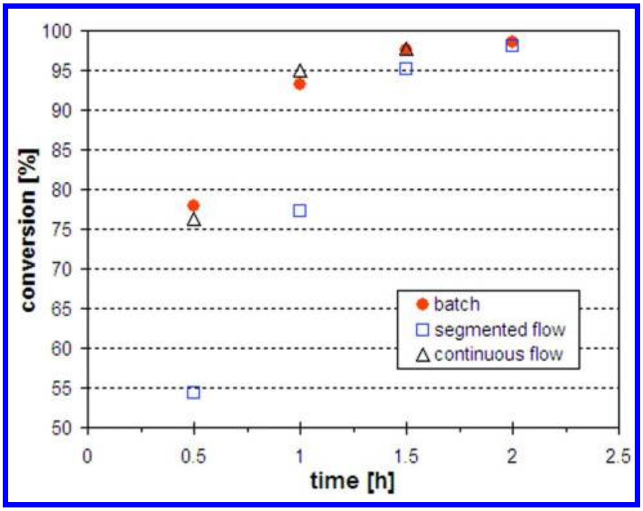


Figure 6. Polymerization of N,N-dimethyl acrylamide (DMA) in batch and under segmented and continuous flow conditions. Reproduced with permission from reference (46). Copyright (2011) American Chemical Society (46).

Reversible deactivation radical polymerizations are often perceived as exhibiting very long reaction times. Since RAFT is based on conventional RP, RAFT polymerizations can be as fast as the traditional RP. Provided RAFT agents, monomers and the chosen reaction conditions have been correctly matched, practically complete conversion of monomers can be achieved in less than 3 hours (*46*). As illustrated in Figure 6 the RAFT polymerization of dimethylacrylamide (DMA) show that under both flow reactor and batch (microwave) conditions, one can obtain high conversions and thus high polymer yields in very short times without impacting on the integrity of control.

Similar findings of very fast reaction times and high end-group purity have also been observed by other groups (*47*). For example stimulus-responsive polymers based on 2-hydroxypropyl acrylate have been reported, where nearly-complete conversion was achieved for all polymers between 45 min and 4.5 h polymerization time. Most polymers contained intact RAFT end-groups and could be transformed into block copolymers by a simple one-pot procedure.

Examples of RAFT Polymers for Personal Care Applications

The use of living radical polymerization methods to generate multi functional materials may have the most significant impact in the cosmetics industry due to the demand by formulators for polymers with “conflicting properties”. “Conflicting properties” include hydrophilic–lipophilic, hard–soft (high and low glass transition temperatures), soluble–insoluble or ionic–nonionic and are highly desired for surfactants, emulsifiers, film formers, pigment dispersants and for self–assembled structures such as vesicles and microcapsules.

An example of a readily synthesized hydrophilic–lipophilic block-copolymer is shown in Figure 7 (*10*). Butyl acrylate (BA) is firstly polymerized in the presence of a dithioester RAFT agent under standard radical polymerization conditions with AIBN as initiator at 60 °C. The resulting “lipophilic block” exhibits a molecular weight of 33,600 Da and a low dispersity of 1.13. Addition of acrylic acid into the polymerization system forms the second hydrophilic block. The final molecular weight of the polymer was determined to be 52,400 with a maintained low dispersity of 1.19.

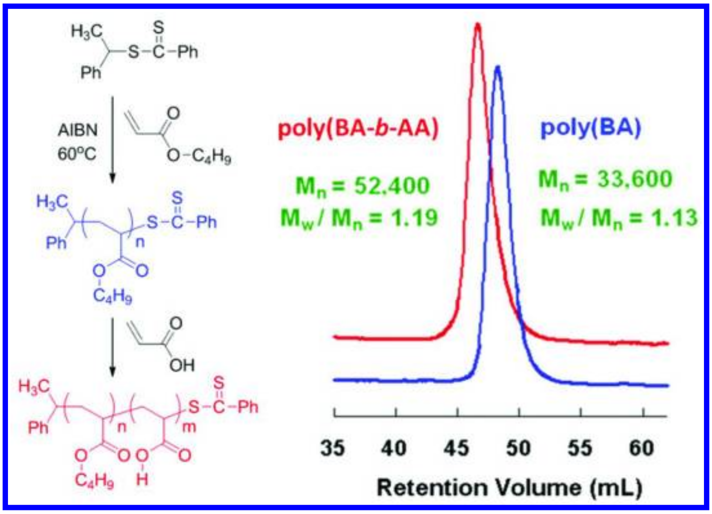


Figure 7. Formation of a hydrophilic–lipophilic block-copolymer by consecutive polymerization of BA and AA under the control of a dithioester RAFT agent (left). GPC traces of BA homopolymer and BA-AA block-copolymer (right) (10).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

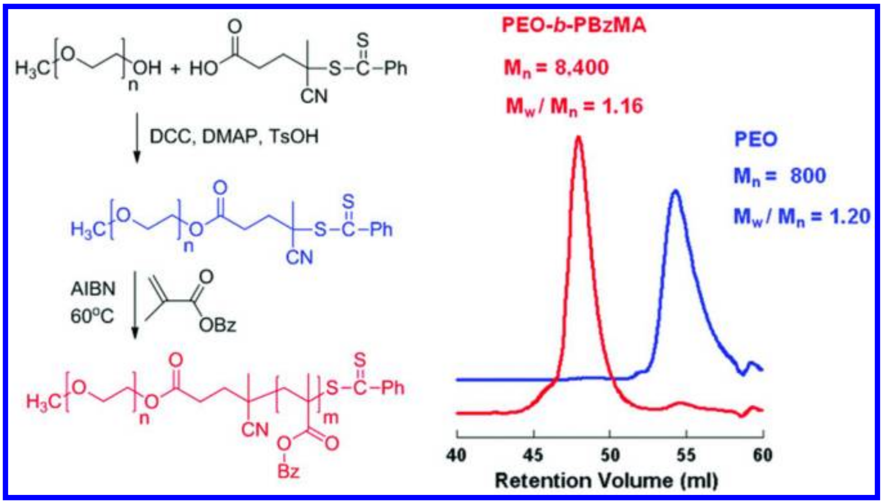


Figure 8. Formation of a macro-RAFT agent from polyethyleneoxide (PEO) and its use in the synthesis of hydrophilic–lipophilic block-copolymers (left). GPC trace of macro-RAFT agent and its block-copolymer (right).

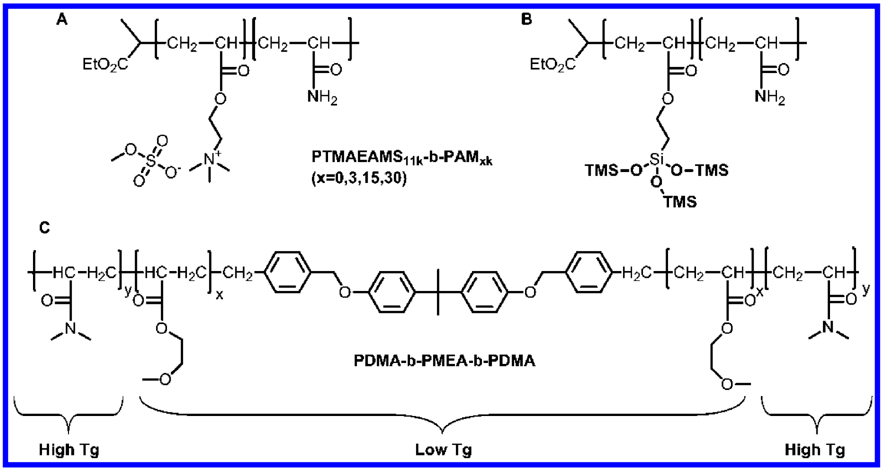


*Figure 9. Examples of block-copolymers prepared by living radical polymerization techniques. **A** Diblock ionic-neutral copolymers for improved formulations by avoiding phase separation of colloidal particles (48). **B** Diblock-copolymer with improved solubility in silicone media for use in mascara, lipstick, powders and face gels (49). **C** Elastomeric triblock-copolymer for improving bond strength in hair styling applications (50).*

While RAFT in general can only control the formation of polymers synthesized by RP, attachments of RAFT agents to other polymers frequently used in personal care such as poly(ethylene oxide) (PEO) is possible. Figure 8 illustrates such an example. An acid-functionalized dithioester RAFT agent is readily attached to a hydroxyl-terminated PEO catalysed by dicyclohexyl carbodiimide (DCC). The resulting macro-RAFT agent (M_n = 800 Da) controls the polymerization of benzyl methacrylate resulting in a block-copolymer with a molecular weight of 8,400 Da and a dispersity of 1.16 (*10*).

While such block-copolymers have been prepared in great variety, surprisingly, there are only a limited number of examples of their use for cosmetics formulations (*48–53*). These new multi-functional materials are diblock or triblock copolymers and are used as e.g. solubilizers, dispersants, film formers or adhesion promoters (Figure 9). Ionic-*block*-neutral copolymers have been prepared from a quarternary amine salt of an acrylate and acrylamide (Figure 9A) (*48*). Such block-copolymers have been proposed to be useful in hair care products such as 2-in-1 shampoos and conditioners. While the ionic block interacts with the negative charges of the cortex of damaged hair, the neutral block conditions the hair. In a similar fashion, siloxane containing block-copolymers have been prepared. Such materials exhibit increased solubility in silicon media and have been proposed to be used in mascaras, lipsticks, powders and face gel (Figure 9B) (*49*). It should be mentioned here that despite the claims in the cited patent the silicone pendant groups are hydrolytic labile and this particular polymer might be only of limited use in such cosmetic applications. The triblock based elastomers (Figure 9C) were prepared according to literature procedure and used in hair styling formulations (*50*). A number of different block compositions were investigated for adhesion, flexibility (elastic modulus E) and viscosity under a variety of relative humidity levels.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

The Issue of Color and Odor: Removal of RAFT Agent End Group

One of the most common misapprehensions with the use of RAFT in the personal care market is the perception that the color and odor associated with the RAFT agent will impact on final product formulations. There are a number of well-developed chemistries that can efficiently remove the RAFT end group.

Based on the mechanism, the growth of each polymer chain is controlled by the RAFT agent, which will remain as the end-group in the polymer. Sulfur is a common element present for example in the natural occurring amino acids of cystein and methionine and should therefore not in itself present any harm (*54–58*). However, its removal is desired for some applications. In particular the odor of low molecular weight thiols and the red and yellow color of the dithioesters and trithiocarbonates, respectively, are of concern to some formulations. Thus, a number of techniques have been developed to either completely remove the RAFT agents or transform them into functional end-groups (*59–61*). Complete desulfurization of the polymer can be readily accomplished by thermolysis yielding an unsaturated chain end (*62–64*). While this method requires the polymer to be stable to the conditions of thermolysis (typically 120-200 °C), it is applicable to most conventional polymers. Figure 10 shows two examples

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) and poly(methyl methacrylate) (PMMA) obtained through polymerization using trithiocarbonate and dithioester RAFT agents, respectively, before and after thermolysis. The trithiocarbonate containing polymer was heated under vacuum in a Kugelrohr at 180 °C for 60 min. Over the course of the thermolysis, the yellow color, originating from the trithiocarbonate RAFT end group with its typical absorption band at 309 nm, disappeared completely. Only the clean polymer was left behind (absorption at 230 nm).

The RAFT agent can also be removed as part of the synthesis procedure as demonstrated in our flow reactor (*45*). In a continuous flow reactor, the polymerization of MMA was immediately followed by a 1 h thermolysis step to remove the dithioester RAFT agent. Comparison of the color of the same polymer without the thermolysis step confirmed the complete removal.

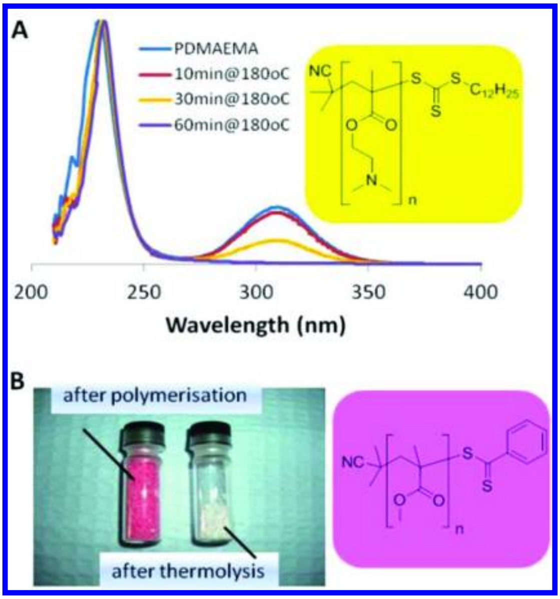


Figure 10. A) UV spectra of PDMAEMA RAFT polymers before and after thermolysis. B) Photograph of color of PMMA RAFT polymer after polymerization and after 1 h thermolysis under continues flow.

Radical induced reductions using hypophosphite salts as the H-donor are another way to sulfur-free polymers and are generally milder. They are in particular useful for lipophilic polymers as the reaction reagents and by-products are water soluble and thus easily removed (*60*).

An alternative method is to utilize the RAFT end groups by transforming them into functional end-groups. While a number of those transformations have been investigated, the most prominent ones are the radical catalyzed thiol-ene and oxidation reaction and Michael-addition to activated vinyl-groups (*59*, *61*, *65*). Figure 11 shows an example of the latter one, where the trithiocarbonate end-group of a copolymer was converted to a stable thiol-ether by treatment with excess hydrazine, followed by the addition of 2-hydroxylethylacrylate (HEA).

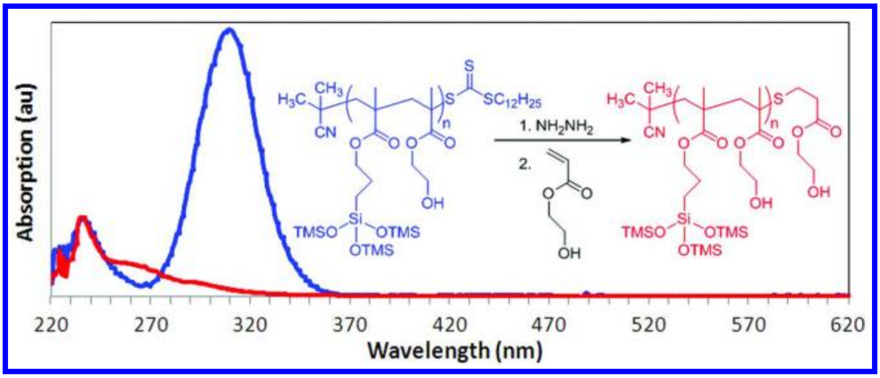


Figure 11. UV absorption spectra of a random copolymer obtained through gel permeation chromatography equipped with a photodiode array detector before and after RAFT end-group conversion.

Conclusion

The RAFT process is a versatile tool to multi-functional polymers that were previously unattainable. RAFT can be used to modify existing polymers and creates new opportunities to design and improve the performance of cosmetic products. Since RAFT is based on conventional free radical polymerization, it is readily implementable and cost effective as well as scalable. Current efforts are beginning to exploit this new technology for a wide range of applications in the personal care industry in particular for rheology modifiers, dispersants and emulsifiers.

References

1. James, V. G. In *Principles of Polymer Science and Technology in Cosmetics and Personal Care*; CRC Press: Boca Raton, FL, 1999.
2. Barner-Kowollik, C. *Handbook of RAFT Polymerization*; Wiley-VCH Verlag GmbH & Co. KGaA: Berlin, 2008.
3. Jenkins, A. D.; Jones, R. G.; Moad, G. *Pure Appl. Chem.* **2010**, *82*, 483.
4. Sciannamea, V.; Jerome, R.; Detrembleur, C. *Chem. Rev.* **2008**, *108*, 1104.
5. Nicolas, J.; Guillaneuf, Y.; Bertin, D.; Gigmes, D.; Charleux, B. In *Polymer Science: A Comprehensive Reference*; Matyjaszewski, K., Möller, M., Eds.; Elsevier: Amsterdam, 2012; p 277.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

6. Sigma-Aldrich Living Radical Polymerization Webinar (http://www.sigmaaldrich.com/materials-science/polymer-science/polymerization-webinar.html).
7. Moad, G.; Rizzardo, E.; Thang, S. H. *Acc. Chem. Res.* **2008**, *41*, 1133.
8. Matyjaszewski, K. *Radical Polymerization*; Wiley-VCH Verlag GmbH & Co. KGaA: Berlin, 2010.
9. Colombani, D. *Progr. Polym. Sci.* **1997**, *22*, 1649.
10. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
11. Destarac, M.; Charmot, D.; Franck, X.; Zard, S. Z. *Macromol. Rapid Commun.* **2000**, *21*, 1035.
12. Mayadunne, R. T. A.; Rizzardo, E. In *Living and Controlled Polymerization*; Jagur-Grodzinski, J., Ed.; Nova Science Publishers, Inc.: New York, 2006; p 65.
13. Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071.
14. Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49*, 1079.
15. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379.
16. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2006**, *59*, 669.
17. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2009**, *62*, 1402.
18. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2012**, *65*, 985.
19. Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273.
20. Jesberger, M.; Barner, L.; Stenzel, M. H.; Malmstrom, E.; Davis, T. P.; Barner-Kowollik, C. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3847.
21. Jin, Y.-Z.; Hahn, Y. B.; Nahm, K. S.; Lee, Y.-S. *Polymer* **2005**, *46*, 11294.
22. Shinoda, H.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2001**, *22*, 1176.
23. Crescenzi, V.; Dentini, M.; Bontempo, D.; Masci, G. *Macromol. Chem. Phys.* **2002**, *203*, 1285.
24. Perrier, S.; Takolpuckdee, P.; Westwood, J.; Lewis, D. M. *Macromolecules* **2004**, *37*, 2709.
25. Hao, X. J.; Nilsson, C.; Jesberger, M.; Stenzel, M. H.; Malmstrom, E.; Davis, T. P.; Ostmark, E.; Barner-Kowollik, C. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5877.
26. Braun, D. *Int. J. Polym. Sci.* **2009**, 10.
27. Matyjaszewski, K.; Davis, T. P. *Handbook of Radical Polymerization*; John Wiley & Sons, Inc.: New York, 2003.
28. Cowie, J. M. G.; Arrighi, V. *Polymers: Chemistry and Physics of Modern Materials*, 3rd ed.; CRC Press: Boca Raton, 2008.
29. Keddie, D. J.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2012**, *45*, 5321.
30. Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256.
31. Rzayev, J.; Penelle, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 1691.
32. Coote, M. L.; Henry, D. J. *Macromolecules* **2005**, *38*, 1415.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

33. Benaglia, M.; Chen, M.; Chong, Y. K.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2009**, *42*, 9384.
34. Benaglia, M.; Chiefari, J.; Chong, Y. K.; Moad, G.; Rizzardo, E.; Thang, S. H. *J. Am. Chem. Soc.* **2009**, *131*, 6914.
35. Keddie, D. J.; Guerrero-Sanchez, C.; Moad, G.; Mulder, R. J.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2012**, *45*, 4205.
36. Favier, A.; Charreyre, M. T. *Macromol. Rapid Commun.* **2006**, *27*, 653.
37. Moad, G. R. E.; Thang, S. H. *Mater. Matter* **2010**, 2.
38. Moad, G. R. E.; Thang, S. H. *Strem Chem.* **2011**, 2.
39. Destarac, M. *Macromol. React. Eng.* **2010**, *4*, 165.
40. Couvreur, L. G. O.; Laffitte, J.-A.; Magnet, S. *Polym. Prepr.* **2005**, *46* (2), 219.
41. Brzytwa, A. J.; Johnson, J. *Polym. Prepr.* **2011**, *52* (2), 533.
42. Tonhauser, C.; Nataello, A.; Lowe, H.; Frey, H. *Macromolecules* **2012**, *45*, 9551.
43. Hornung, C. H.; Nguyen, X.; Dumsday, G.; Saubern, S. *Macromol. React. Eng.* **2012**, *6*, 458.
44. Hornung, C. H.; Nguyen, X.; Kyi, S.; Chiefari, J.; Saubern, S. *Aust. J. Chem.* **2013**, *66*, 192.
45. Hornung, C. H.; Postma, A.; Saubern, S.; Chiefari, J. *Macromol. React. Eng.* **2012**, *6*, 246.
46. Hornung, C. H.; Guerrero-Sanchez, C.; Brasholz, M.; Saubern, S.; Chiefari, J.; Moad, G.; Rizzardo, E.; Thang, S. H. *Org. Proc. Res. Dev.* **2011**, *15*, 593.
47. Vo, C. D.; Rosselgong, J.; Armes, S. P.; Tirelli, N. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2032.
48. Herve, P.; Destarac, M.; Anthony, O.; Bavouzet, B.; Joanicot, M.; Wilczewska, A.; WO patent 2003050185, 2003.
49. Farcet, C.; U.S. Patent 7,585,922, 2009.
50. Frechet, J. M. J.; Hajduk, D.; Khoshdel, E.; Liu, M.; Nielsen, R. B.; Reid, E. S.; Rutherford, K. L.; WO Patent 200228357, 2002.
51. Herve, P.; Destarac, M.; Wilczewska, A.; Cadena, N.; Wilczewska, A.; WO patent 2003050195, 2003.
52. Guerret, O.; Olivier, G.; U.S. Patent 7,893,163, 2006.
53. Boupat, N. P.; Guerret, O.; Mougin, N.; Schultze, X.; Hernandez, F.; U.S. Patent 7,951,888, 2011.
54. Pissuwan, D.; Boyer, C.; Gunasekaran, K.; Davis, T. P.; Bulmus, V. *Biomacromolecules* **2010**, *11*, 412.
55. Samsonova, O.; Pfeiffer, C.; Hellmund, M.; Merkel, O. M.; Kissel, T. *Polymers* **2011**, *3*, 693.
56. Truong, N. P.; Jia, Z. F.; Burges, M.; McMillan, N. A. J.; Monteiro, M. J. *Biomacromolecules* **2011**, *12*, 1876.
57. Chang, C. W.; Bays, E.; Tao, L.; Alconcel, S. N. S.; Maynard, H. D. *Chem. Commun.* **2009**, 3580.
58. Gibson, M. I.; Froehlich, E.; Klok, H.-A. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4332.
59. Willcock, H.; O’Reilly, R. K. *Polym. Chem.* **2010**, *1*, 149.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

60. Chong, Y. K.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2007**, *40*, 4446.
61. Moad, G.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2011**, *60*, 9.
62. Chong, B.; Moad, G.; Rizzardo, E.; Skidmore, M.; Thang, S. H. *Aust. J. Chem.* **2006**, *59*, 755.
63. Postma, A.; Davis, T. P.; Moad, G.; O'Shea, M. S. *Macromolecules* **2005**, *38*, 5371.
64. Li, J. In *Name Reactions*; Springer: Berlin, 2009; p 110.
65. Dietrich, M.; Glassner, M.; Gruendling, T.; Schmid, C.; Falkenhagen, J.; Barner-Kowollik, C. *Polym. Chem.* **2010**, *1*, 634.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch010

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

Chapter 11

Mechanical Characterization of Cosmetic and Viscoelastic Effects of Firming Polymers

Chung-yi Chiang,* Lei Huang, and Naresh Ghatlia

**Unilever Research and Development, 40 Merritt Boulevard,
Trumbull, Connecticut 06611, U.S.A.
*E-mail: chung-yi.chiang@unilever.com.**

In personal care products, polymers may be used as emulsifiers, stabilizers, rheology modifiers (e.g. thickening agent), or film formers. When deposited on the skin, polymer usually doesn't penetrate the skin due to its high molecular weight and size. It remains on the skin surface to form a film, which may potentially provide conditioning benefits. One of the conditioning effects is to enhance the tactile stimulus by altering the overall mechanical properties of skin. This mechanical alteration is highly associated with the viscoelastic properties of the polymeric film forming on the skin surface. In order to select a suitable polymer from numerous choices of polymers when designing a product, it is important to have a method to screen polymers and benchmark the performances. In this report, a screening method, a mechanical measurement and its modeling methods to evaluate the mechanical effects of polymers will be presented. A variety of synthetic and natural polymers were tested, and the result suggested that synthetic polymers might provide broader ranges of designs for altering skin mechanical properties. Although most polymers seem to have similar modes of actions in enhancing skin firmness and elasticity, further investigations will be required to completely reveal the design principles and to expand the ranges of mechanical alterations that are delivered by the applications of firming polymers.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

Skin Mechanics

The mechanical property of skin is a physical representation of skin condition, which relates to both age and health. As skin ages, the mechanical behaviors of skin change and may result in unfavorable perceptions, such as loose, saggy, slack, slumped, lack of tightening, etc. These are typical signs of aging that are commonly perceived by consumers in their lives. On the other hand, dermatologists often assess the skin condition based on the mechanical response from the skin when a force or deformation (such as pinching) is applied onto the patient. It is known that aging (*1*) and photodamage (*2*) are highly correlated with the changes in skin mechanical properties. Some hereditary disorders (*3*) and diseases (*4*, *5*) have influences on the skin mechanics as well. Therefore, skin mechanics not only governs the aesthetic perception but also reflects the health condition of a person.

Viscoelasticity of Skin: Firmness and Elasticity

Skin is known as a viscoelastic material, which exhibits both viscous and elastic behaviors. The viscous property is the physical characteristic determining the permanent deformation or rearrangement of the material. The elastic property describes the resilience and the resistance of a material to defy the applied stress or strain. When a viscoelastic material is subjected to a constant stress, the occurrence of molecular rearrangement in the material is called “creep”, and the resistance to the deformation corresponds to the “stiffness” of the material. When the applied stress is removed, the recovery to its original shape is the physical phenomenon of “elasticity”. In consumer language, “firmness” is the attribute commonly used and understood by consumers, and it is equivalent to “stiffness” that is defined in scientific language. Thus, both firmness and stiffness may be used interchangeably when describing the physical properties of a material. Most consumers believe that a firm and elastic skin is a young and healthy skin. Of course, it becomes unrealistic if the skin exceeds normal ranges of firmness and elasticity. As a matter of fact, the skin firmness and elasticity have been found to correlate with the chronological age in literature (*6–9*). In the published results, instrumental measurements showed directional increases in skin extensibilities and decreases in Young’s moduli when the age increases. This indicates that skin firmness decreases as skin ages. In addition, the measurement on skin elastic recovery after deformation suggests that skin elasticity also decreases with chronological age. These reported instrumental observations are concluded in the same way that how consumers generally perceive the mechanical changes in the skin when a person is getting older. It is for sure that firmness and elasticity are two important mechanical characteristics not only for evaluating the condition of the skin but also for perceiving the chronological age of the person.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

Polymers in Skin Care Products

Since skin firmness and elasticity are related to the age and these properties are perceivable by people, firm and resilient skin is highly desired by consumers in the skin care industry. Improving skin firmness and elasticity have become the key functional benefits when consumers are searching for anti-aging products. To counteract and defy the unfavorable consequences caused by skin aging, different technical approaches have been used in anti-aging products. Of these approaches, active ingredients that stimulate cell activities in proliferation, hydration, and extracellular matrix production to improve skin's intrinsic mechanical properties are usually costly and required long-term investments in researches to prove the safety and efficacy. Besides, a lot of actives that may affect or alter biological functions of cells are highly regulated and subject to numerous legal restrictions in many countries. In the US, Food and Drug Administration (FDA) constantly monitors consumer products that claim or imply to change cell functionalities. Companies may get warning or even penalties if they violate the regulations and definitions of cosmetic and personal care products. Therefore, polymers that can induce immediate and temporary effects on skin mechanical properties (*10*) are considered to be cost effective, safe, and easy to be used in commercialized personal care products. What this type of polymer can provide are cosmetic and sensorial effects that enhance the sensory cues of anti-aging benefits. Based on our knowledge, most anti-aging products on the market usually combine both approaches of utilizing bioactives and polymers. While the bioactive functioning at the cell level may take longer time to show its anti-aging effect, the firming polymer can provide the cosmetic effect that is an instant sensory cue to the consumer. In this report, we will focus on the characterizations of the polymers that are used in the applications of improving skin firmness and elasticity.

Testing Methods and Materials

Mechanical Testing Method

Creep test was frequently used as the testing method to evaluate the viscoelastic properties of materials. In a typical creep test, a constant stress is applied to the sample, and the time-dependent increase in strain is monitored (Figure 1). The result of creep test will provide information about both stiffness and elasticity of the sample. When the constant stress is on ($t > t_0$), the degree of extension within a certain period of time is relevant to the stiffness of the sample. When the stress is off ($t > t_1$), the degree of remaining strain is relevant to the elasticity of the sample. In this paper, the device used to perform creep test is Cutometer MPA 580 (Courage–Khazaka Electronic GmbH) with aperture size of 2 mm in diameter. The constant suction pressure (σ_0) was set to 300mbar with on-time (t_1-t_0) of 3 seconds. The off-time (t_2-t_1) was set to 3 seconds for the sample to relax. 3 repeated cycles of creep test (n=3) were carried out to complete one measurement. For each sample, 9 measurements (N=9) were performed to evaluate the viscoelasticity of the sample.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

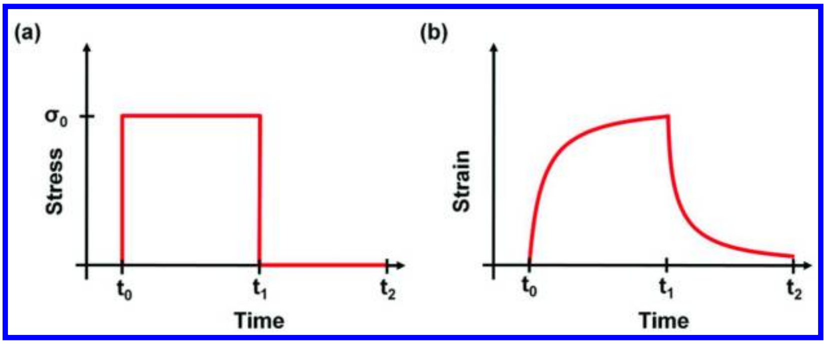


Figure 1. (a) The applied stress and (b) the responding strain with the time in one creep testing cycle. (see color insert)

Mathematical Models of Viscoelasticity

Two types of models were used to analyze the creep tests. The first one is the conventional Cutometry model (*11*). In this conventional model, various parameters were defined to assess the viscoelastic properties of sample based on the time-dependent elongation curve (Figure 2). There are five U parameters and ten R parameters defined in this analytical model. U parameters are defined by the amounts of elongation at particular time points. Ue is the amount of extension at 0.1 second after the suction is on and Ur is the amount of recovery at 0.1 second after the suction is off. Ue and Ur are immediate elastic extension and relaxation, respectively. These two parameters are mainly driven by the elastic components in the sample. A small Ue indicates the sample is firm. For an ideal elastic material, Ue and Ur should be the same, indicating the amount of elastic deformation can be fully recovered. Therefore, R5 is defined to assess the ratio of Ur and Ue. For an ideally elastic material, R5 is equal to 1. Uv is the amount of inelastic extension from the time point t_0+0.1 to the time point t_1 before the suction is turned off. A higher Uv suggests the sample tends to creep more and therefore it is less elastic. The parameter R6 is defined as Uv/Ue, which is the ratio between viscous and elastic deformations under a constant stress. If R6 is zero, it indicates that the material behaves like a pure elastic material. The higher the R6 is, the more the material is like a viscous fluid. Uf is the total elongation during the period of time (t_1-t_0) when suction is on, and it also relates to the overall firmness of the material measured in the given period of time. It is important to note that Uf is totally dependent on the time of suction for any viscoelastic material. Ua is the amount of total recovery given by a certain relaxation time (t_2-t_1). R1 is the residual or permanent deformation (Uf-Ua) after the first creep cycle, R2 is the ratio of recovery (Ua/Uf) after the first creep cycle, and R7 is the ratio of immediate recovery (Ur/Uf) after the suction is truned off. If more than one creep cycle (n>1) is used to test the sample in the measurement, R3 and R4 are the last maximal and minimal deformations respectively in the last creep cycle. R9 is the amount

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

of creep elongation occurring in the additional creep cycles (for n>1 cycles). In general, the R parameters are defined to assess the firmness and elasticity of the sample based on the deformation.

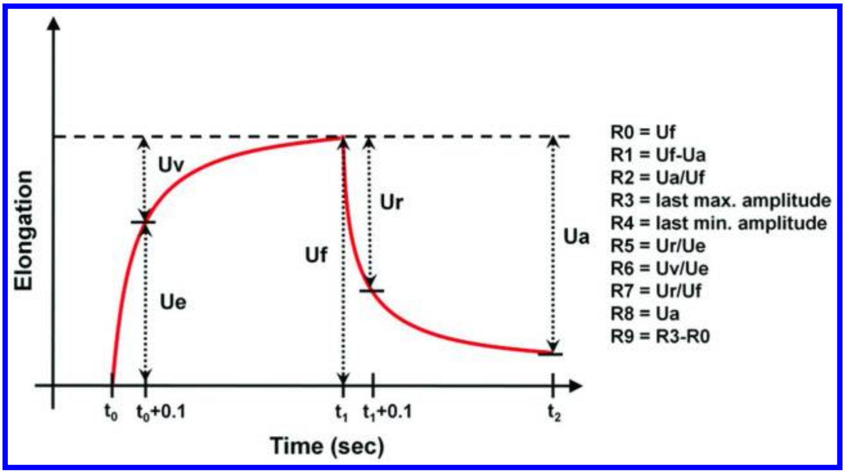


Figure 2. Conventional Cutometer analysis and the definitions of parameters. t_0 *is the time when suction is turned on,* t_1 *is the time when suction is turned off, and* t_2 *is the designated time point to complete on testing cycle. (see color insert)*

The conventional Cutometry model is simple and convenient when processing and analyzing the data. It is very useful and reliable to use the R parameters such as R2, R5, R6, and R7 for evaluating the elasticity of material. However, the firmness assessment highly depends on the sample dimension in this model. For the same material, a thicker sample will have more deformation than a thinner sample under the same stress. Therefore, the U parameters and R parameters (e.g. R0) that are defined by the amount of deformation or recovery may not be appropriate for a comparison of any two samples unless the dimensions of these two samples are identical.

The other analytical model used to assess the viscoelasticity in this report is Standard Linear Solid (SLS) model. A Voigt form of SLS model can be used to simulate the creep test conducted by Cutometer (Figure 3). The Voigt form is chosen because the mechanical properties along the suction direction are of the measurement interest, and this model fits the theme of skin's multiple-layered structure and surface coating of firming polymer. The constitute equation of this model to describe the creep test performed by Cutometer is

$$\varepsilon = \frac{\sigma_o}{E_1} + \sum_{n=2}^{4} \frac{\sigma_o}{E_n}(1 - \exp(-\frac{E_n}{\eta_n}t)) \qquad \text{eq 1}$$

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

where ε is the strain, σ_0 is the constant stress applied to the sample, E_n is the elastic modulus of spring component, η_n is the viscous modulus of dash-pot component, and t is the time point in the test. To evaluate the overall elastic and viscous properties of the sample, three equivalent properties are defined. The equivalent elastic modulus (E_{eq}) and equivalent viscous modulus (η_{eq}) are

$$E_{eq} = \frac{H(E_1, E_2, E_3, E_4)}{4} \qquad \text{eq 2}$$

$$\eta_{eq} = \frac{H(\eta_2, \eta_3, \eta_4)}{3} \qquad \text{eq 3}$$

where H is the harmonic mean function. From eq 2 and eq 3, the equivalent relaxation time (τ_{eq}) can then be defined as

$$\tau_{eq} = \frac{\eta_{eq}}{E_{eq}} \qquad \text{eq 4}$$

It is important to note that the sample thickness needs to be taken into account to measure the mechanical modulus. Unlike some of the parameters in conventional Cutometry model, the modulus obtained from SLS model will be eligible for the comparison among different samples.

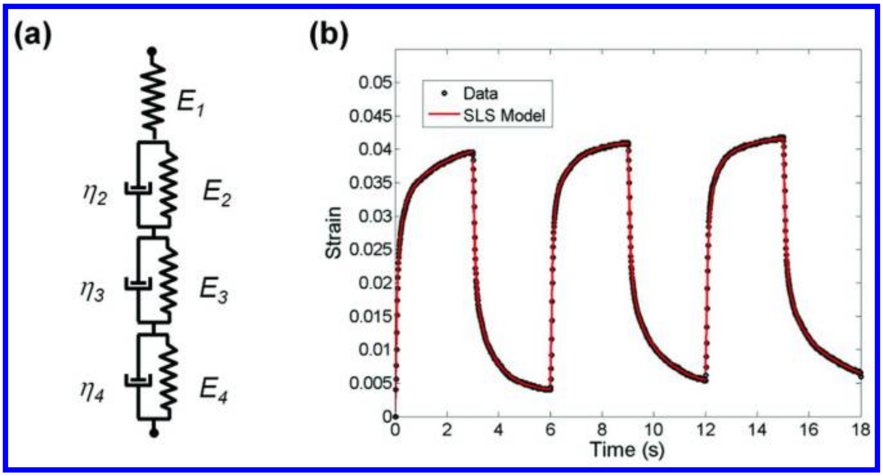


Figure 3. (a) Voigt form of SLS model. (b) An example of cyclic creep measurement carried out by Cutometer and data modeling with SLS model. (see color insert)

Based on our unpublished validation, two parameters were determined to be the primary indexes for measuring firmness and elasticity: equivalent elastic modulus (E_{eq}) from SLS model and R7 from conventional Cutometry

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

model. Although the other parameters may provide the same information about firmness and elasticity, only E_{eq} and R7 will be discussed in this report. To better understand the meanings of parameters derived from the two creep models and their correlations with firmness and elasticity perceptions, a balloon at two different inflation conditions was used for the demonstration. It is known that a balloon is firmer when it is totally inflated and the elasticity of balloon remains the same regardless its inflation status. Shown in Figure 4, E_{eq} of the balloon at the highly inflated status is ~2.5 times higher than that at the partially inflated status ($p<0.001$). The rubber material of balloon becomes stiffer as it is stretched more due to the non-linear elasticity and strain hardening effect. On the other hand, there is no significant change in R7 when changing the inflation status of the balloon, which suggests that the elasticity of balloon doesn't change with the inflation status. Since the balloon behaves like a pure elastic material, the elasticity of balloon is expected to be independent of the inflation status. This simple demonstration shows that the firmness and elasticity can be effectively assessed by measuring E_{eq} and R7 using Cutometer.

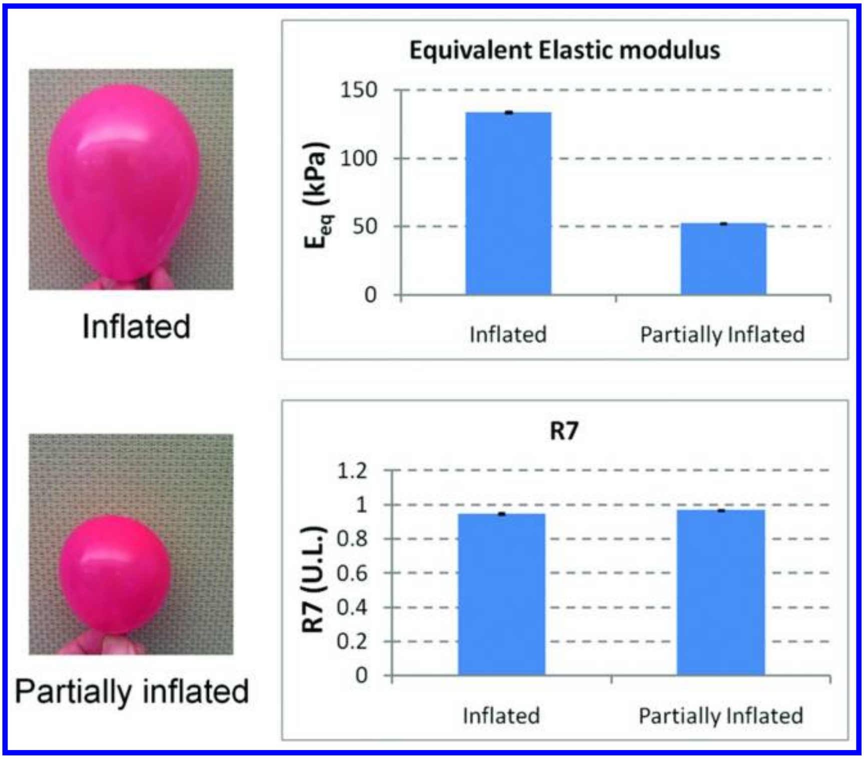


Figure 4. The E_{eq} and R7 for the same balloon at two different inflation conditions. (see color insert)

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

Viscoelastic Substrate to Mimic Skin Mechanical Properties

A variety of viscoelastic materials potentially could be used to mimic the mechanical behaviors of skin. Polyurethane (PU) was selected as the substrate to simulate skin mechanical properties because a range of viscoelasticity could be adjusted by controlling the compositions of hard and soft segments in its chemical structure (*12*). Polyurethane plates (5 cm x 5 cm) were purchased from Beaulax Co., Ltd. The thickness of the PU plate was 6 mm. According to the manufacturer, the hardness of the purchased polyurethane plate was ~5, measured by Durometer (Teclock GS-721N E-type equipped with the constant pressure loader Teclock GS-710) using measuring protocol JIS K 6253E. From our Cutometry measurement, E_{eq} of the polyurethane substrate was ~750 kPa and R7 was ~0.45. According to our clinical data, the ranges of E_{eq} and R7 of skin measured using Cutometer are highly dependent on the measurement site and the person's age. E_{eq} may range from 300 kPa to 900 kPa, and the R7 may range from 0.4 to 0.8. A substrate that fully resembles the viscoelasticity of the targeted skin type would be the ideal choice for the simulated testing. It is believed that the polyurethane substrate that we used in the experiments may be in the higher range of E_{eq} and the lower range of R7 than the human skin typically has.

Firming Polymers and Sample Gels

Various synthetic and natural polymers with instant firming effects were provided by Ashland Inc., Air Products and Chemicals Inc., Bayer Inc., NOF Corp., and Silab Inc. Most of the synthetic polymers used in the application of skin care are block copolymers and graft copolymers, which may contain both hydrophilic and hydrophobic blocks/branches, as well as the charged groups to increase inter- and intra-molecular interactions. An example of synthetic polymer that is used as the firming ingredient in skin care product is shown in Figure 5. In this polyimide copolymer, it contains polypropylene oxide and polyethylene oxide blocks on the side chains as the hydrophilic branches, and tertiary amines and carboxylic acids as the hydrophilic and charged side groups. The functional groups in this type of copolymer may provide a uniform film formation and interfacial adhesion on the skin (*13–15*). Most of the natural polymers tested in our experiment were proteins and polysaccharides, which were extracted from natural sources such as plants. The raw materials obtained from suppliers might have been diluted in solvent or mixed with other ingredients. In order to mimic the product application procedure, each firming polymer was prepared in a gel base that was made of 0.5% Carbopol® Ultrez 21 (Lubrizol Corp.), 0.25% Glydant™ Plus Liquid (Lonza Group Ltd.), and 0.125% sodium hydroxide by mass fractions in water. Four concentrations (1%, 3%, 5%, and 10% w/w) of firming polymer gels were prepared using the polymer raw materials from suppliers without any further dilution or concentration.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

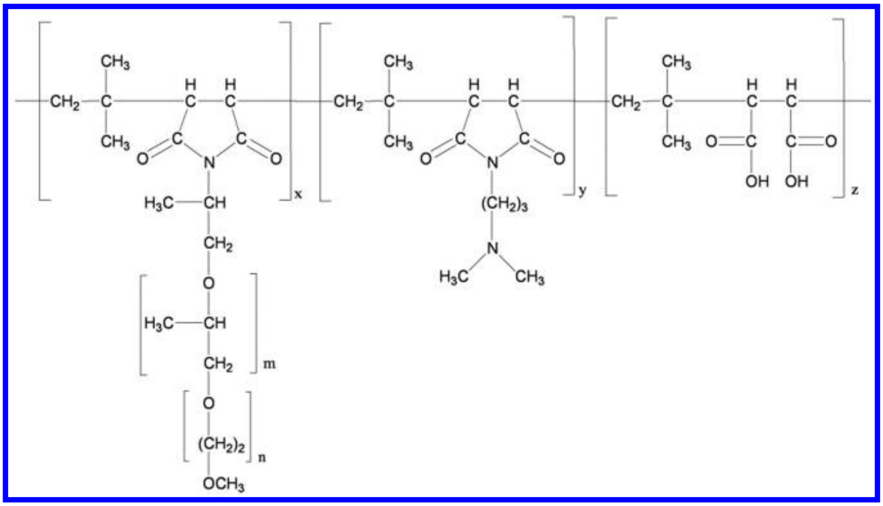


Figure 5. Chemical structure of Polyimide-1, which is a block copolymer serving as a firming ingredient in skin care products.

Sample Testing Procedure

The whole experimental procedure was carried out in a laboratory with controlled temperature (21°C) and humidity (RH=45%). All the measurements were first performed on the untreated polyurethane plates to obtain the baseline properties. The firming polymer gel was then applied onto the polyurethane plate (~6mg/cm^2) and incubated for 40 minutes to dry before conducting the creep test. Each sample was divided into 9 regions. One measurement was carried out on each region and totally 9 measurements (N=9) were collected for statistical analysis for each sample. The change from baseline for each mechanical property (ΔE_{eq} or ΔR) was defined as the performance index to show the degree of mechanical alteration.

Mechanical Effects of Firming Polymers

Visual Effects of Firming Polymers

Most firming polymers delivered by the simple Carpobol gel in our study could form continuous films on the polyurethane substrates after drying. Depending on the interaction within the polymer and the interfacial interaction between polymer film and substrate, some firming polymers may induce tightening effects that are strong enough to change the appearance of PU substrate. For example in Figure 6, both samples were coated with firming polymer gels. The lifting effect from the polymer Syn-2 (on the right) was stronger than the other polymer Syn-0 (on the left). This lifting effect was caused by the tightening action of the firming polymer film that was deposited on the PU substrate. The top surface of the substrate shrank and the surface firmness increased. This example

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

shows how the tightening effect could be visualized and how the polymer could potentially influence the change of appearance if applied onto skin. Polymers exhibiting such lifting effects may serve as cosmetic ingredients to provide instant tightening/lifting of skin.

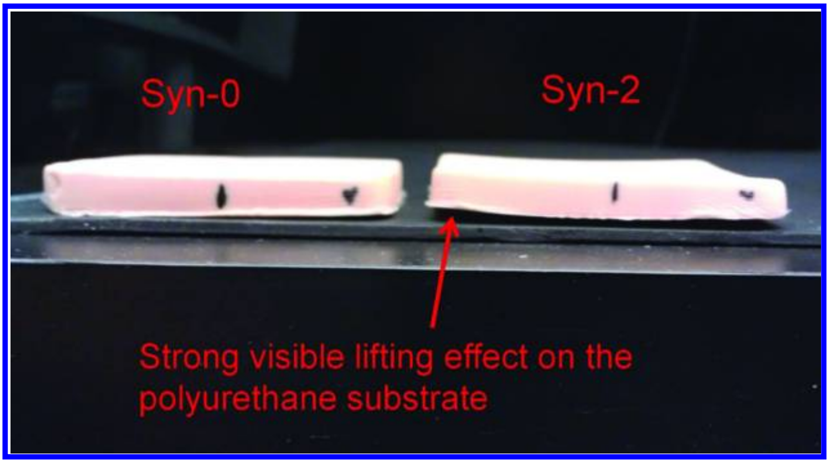


Figure 6. The visible lifting effect was induced by the firming polymer that was coated on the viscoelastic substrate. (see color insert)

Quantification of Mechanical Effects

Although the visual effects may be perceivable, it can be marginal and difficult to quantify the degree of the mechanical alteration that is provided by a firming polymer. Therefore, instrumental measurements on viscoelasticity could help to quantify the mechanical effects of polymers. Cutometer has been widely used to assess skin elasticity in clinical practices (*16–18*), so it is suitable to carry out the measurements on viscoelastic substrates that simulate skin mechanical properties. Combining with the SLS model described earlier in this paper, both elasticity and firmness of the substrate can be evaluated from the creep test performed by Cutometer. Shown in Figure 7, the mechanical alterations of polymer Syn-0 on the substrate proportionally increase with the polymer concentration in the formulation. The higher the concentration of polymer Syn-0 in the product will provide higher degree of mechanical enhancement in both firmness (Figure 7a) and elasticity (Figure 7b). However, polymer concentrations higher than 10% w/w were not tested due to the issues of phase stability and sample processing. It is possible that the mechanical alteration may become nonlinear or plateaued at the higher mass fractions. Depending on the chemical and physical properties of the polymer, the relationship between mechanical enhancement and polymer concentration may be linear, non-linear, proportional, inversely proportional or even independent. Besides, it is noted that the gel base without any addition of firming polymer also has certain impact on altering the

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

mechanical properties of substrate. This is because the Carbopol Ultrez 21 is an acrylate copolymer, which may form a polymeric film and alter the mechanical properties of the substrate like the firming polymer. Thus, it is also likely that the Carbopol may shield the actual efficacy of firming polymer.

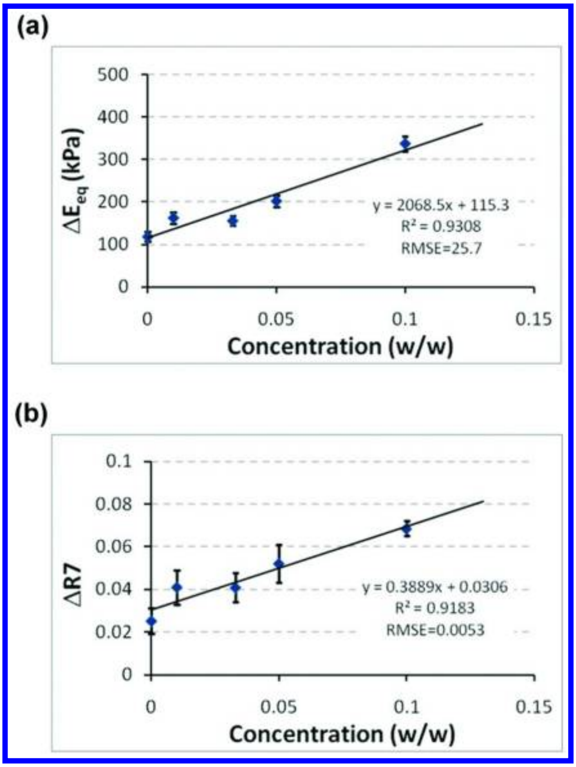


Figure 7. The changes in (a) elastic modulus and (b) R7 at various concentrations of polymer Syn-0. (see color insert)

In order to understand how the chemical structures of polymers could affect the mechanical properties, all the polymers were compared at 10% w/w in the same base formulation of Carbopol gel. The mechanical alterations of a variety of synthetic and natural polymers depositing on polyurethane substrates were plotted in Figure 8. The mechanical alteration in firmness is shown on the x-axis and that in elasticity is on the y-axis. Most polymers that were tested in this study showed similar linear dependency between firmness and elasticity. In other words, when a firming polymer is deposited on the PU substrate, elasticity increases proportionally with the increase of firmness. Although some polymers may outperform the others at the same concentration, the ratios of ΔE_{eq} to ΔR7 for most polymers are within the similar range, which is $\Delta E_{eq}:\Delta R7 \approx 6000:1$. This indicates the modes of actions to enhance mechanical properties at the molecular level have high similarities among these polymers. One synthetic polymer (Syn-2) was found to have a significantly stronger influence on firmness than the other polymers (ΔE_{eq}:$\Delta R7 \approx 12000$:1). Polymer Syn-8 seems to have stronger enhancement in elasticity among these polymers (ΔE_{eq}:$\Delta R7 \approx 1300$:1). And, polymers Nat-6 and Syn-9 have adverse effects on both firmness and elasticity, where both mechanical properties decrease after the applications. These two polymers seem to remain plasticizing effects after depositing onto the skin-mimicking substrates. From our preliminary analysis, it is not clear yet how the functional groups or chemical structures of polymers affect the degrees of mechanical alterations. For all the polymers tested in this study, the synthetic polymers (Syn-X) seem to have a broader range of mechanical alterations while the natural polymers (Nat-X) have a narrower range of effects. However, there is still a range of white space on this mechanical alteration map where these polymers can't reach yet.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

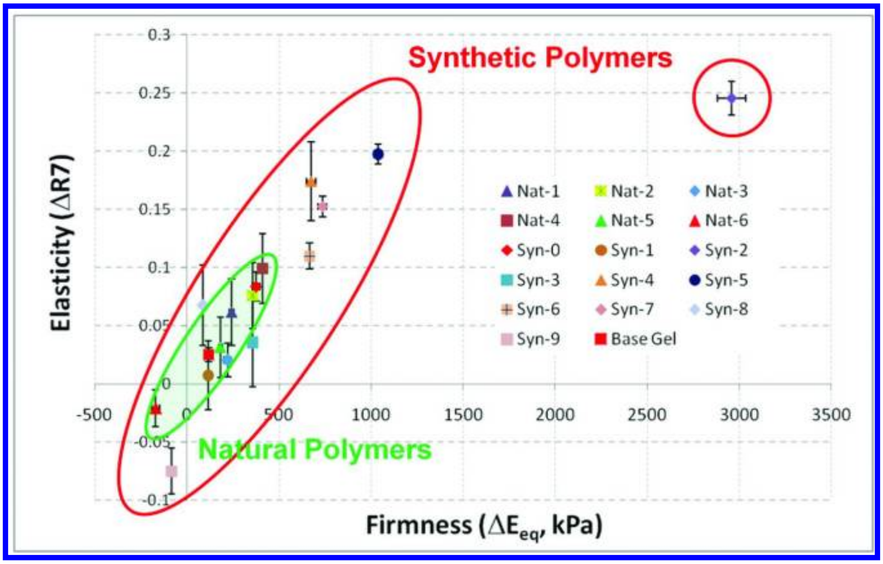


Figure 8. The range of mechanical enhancement provided by polymers in the gel formulation. All the polymers on this chart were formulated and tested at 10% w/w. (see color insert)

Although the mechanisms and molecular structures that govern the ratios between firmness and elasticity performance still need to be investigated further, it is believed that synthetic polymers may provide a wide diversity of options for formulating a product to achieve the desired mechanical enhancement. It is highly important to continually research polymers that can achieve various ranges of mechanical alterations in order to create the preferred sensory. Besides, separated studies on consumer perceptions are required in order to identify the perceivable and acceptable ranges of mechanical alterations on skin.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

Influence of Other Ingredients

In a typical skin care product, other ingredients besides polymers may be added to provide users the claimed benefits, to facilitate active delivery, to generate specific rheological properties, or to preserve the product. These ingredients may potentially affect the mechanical performance of the firming polymer in the product. Polymers with ionic functional groups are known to be sensitive to pH and ionic strength (*19*). Charged ingredients may have influences on the mechanical properties of polymers because charged molecules may change the ionic strength and the electrostatic interactions in the formula. Other interactions such as hydrogen bonds may also impact the performance of firming polymer. For example, niacinamide, which is used as an anti-aging ingredient in skin care products, is known as a hydrotropic agent. According to our experiments, the presence of niacinamide (3% w/w) in the formulation may lower the mechanical enhancement of the firming polymer (Figure 9). This is likely due to the interactions between niacinamide and polymer that disturb the inter- and intra-molecular interactions of polymer itself. Likewise, the addition of firming polymer potentially may bind the niacinamide in the formulation and retard its delivery from the product that is applied on skin. These factors will need to be considered when designing a formulation.

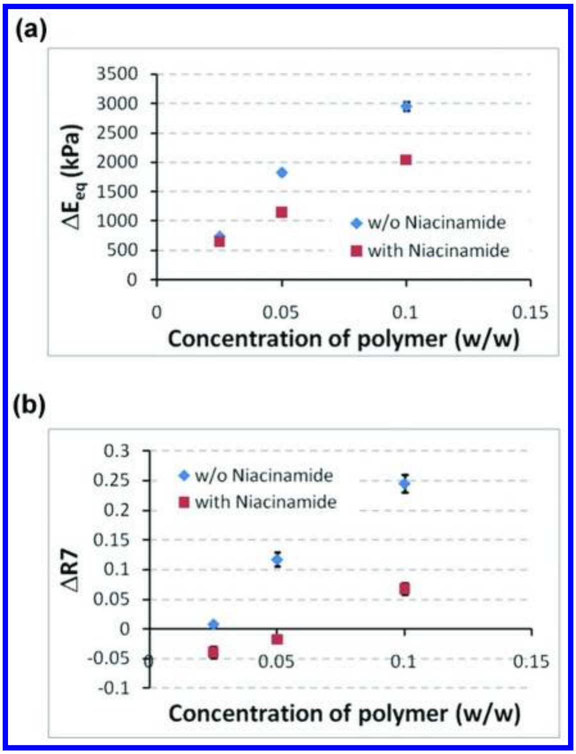


Figure 9. Effect of niacinamide on the mechanical performance of firming polymer Syn-2. (see color insert)

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

Conclusion

The testing and modeling method discussed in this report may provide a simple way to pre-screen polymers and benchmark the mechanical performance. It potentially can be used to select high performer and to further tune the formulation in order to achieve the desired mechanical effects. It is found that the tunable range of mechanical enhancement using the existing firming polymers is still limited but potentially can be expanded by designing new chemical structures of polymers. This will require more research to reveal the mechanism of how the chemical structures influence the mechanical properties of polymeric films on the substrate and skin. Shown in the experiments that simulate the product application on the skin, the so-called firming polymer may provide the mechanical enhancement in the substrate firmness, and the increase of firmness is found to be accompanied with the increase of elasticity. In our clinical tests on human skin using the firming polymers that showed high performances in the simulating tests, firming polymers indeed provided the measurable benefits in increasing firmness and stimulating the tactile sensations of consumers. This clinical result will be published in a separated report.

To formulate a polymer for providing mechanical benefits can be a big challenge since other ingredients may potentially alter the designed performance. The addition of firming polymers may also change the properties of products such as transparency and viscosity due to the interactions between polymers and other ingredients. Many other factors may need to be considered in order to create a successful formula. Although these firming polymers in skin care products are designed for cosmetic purposes, the mechanical effect that is applied to the skin may potentially stimulate skin biology and have anti-aging benefits in the long term. This is a research area that still needs to be explored more and it may open up new technologies and applications of polymers in the personal skin care.

Acknowledgments

We thank Mr. Timothy Monos for collecting the data of polymers with niacinamide. Also, we thank Ashland Inc., Air Products and Chemicals Inc., Bayer Inc., NOF Corp., and Silab Inc. for providing polymer samples used in our experiments.

References

1. Bischoff, J. E.; Arruda, E. M.; Grosh, K. *J. Biomech.* **2000**, *33*, 645–652.
2. Nishimori, Y.; Edwards, C.; Pearse, A.; Matsumoto, K.; Kawai, M.; Marks, R. *J. Invest. Dermatol.* **2001**, *117*, 1458–1463.
3. Heidbreder, A. E.; Ringelstein, E. B.; Dittrich, R.; Nabavi, D.; Metze, D.; Kuhlenbaumer, G. *J. Clin. Neurosci.* **2008**, *15*, 650–653.
4. Yoon, H. S.; Baik, S. H.; Oh, C. H. *Skin Res. Technol.* **2002**, *8*, 250–254.
5. Dobrev, H. P. *J. Am. Acad. Dermatol.* **1999**, *40*, 436–442.
6. Pierard, G. E.; Henry, F.; Castelli, D.; Ries, G. *Gerontology* **1998**, *44*, 159–161.

7. Cua, A. B.; Wilhelm, K. P.; Maibach, H. I. *J. Invest. Dermatol.* **1990**, *94*, 516–516.
8. Escoffier, C.; de Rigal, J.; Rochefort, A.; Vasselet, R.; Leveque, J. L.; Agache, P. G. *J. Invest. Dermatol.* **1989**, *93*, 353–357.
9. Zahouani, H.; Boyer, G.; Pailler-Mattei, C.; Ben Tkaya, M.; Vargiolu, R. *Wear* **2011**, *271*, 2364–2369.
10. Jachowicz, J.; McMullen, R.; Prettypaul, D. *Skin Res. Technol.* **2008**, *14*, 312–319.
11. Elsner, P.; Wilhelm, D.; Maibach, H. I. *Br. J. Dermatol.* **1990**, *122*, 607–614.
12. Song, M.; Chen, H.; Jiang, C. D.; Zhao, B.; Li, X. Y. *Macromol. Theory Simul.* **2002**, *11*, 845–870.
13. Koberstein, J. T. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 2942–2956.
14. Tiggelman, I.; Hartmann, P. C. *Prog. Org. Coat.* **2010**, *67*, 76–83.
15. Awaja, F.; Gilbert, M.; Kelly, G.; Fox, B.; Pigram, P. J. *Prog. Polym. Sci.* **2009**, *34*, 948–968.
16. Choi, J. W.; Kwon, S. H.; Huh, C. H.; Park, K. C.; Youn, S. W. *Skin Res. Technol.* **2013**, *19*, 349–355.
17. Ohshima, H.; Kinoshita, S.; Oyobikawa, M.; Futagawa, M.; Takiwaki, H.; Ishiko, A.; Kanto, H. *Skin Res. Technol.* **2013**, *19*, 238–242.
18. Dobrev, H. *Skin Res. Technol.* **2000**, *6*, 239–244.
19. Hu, Y. H.; You, J. O.; Auguste, D. T.; Suo, Z. G.; Vlassak, J. J. *J. Mater. Res.* **2012**, *27*, 152–160.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch011

Chapter 12

Styrene/Acrylates Copolymer as Film Former for Improved Hair Surface Luster

Fanwen Zeng,*,[1] Miao Wang,[1,2] Jennifer Collin,[1] Alan Nakatani,[1]
Michaeleen Pacholski,[1] John Reffner,[1] and Curtis Schwartz[1]

[1]The Dow Chemical Company, 727 Norristown Road,
Spring House, Pennsylvania 19477
[2]Currently, L'Oreal U.S.A., 200 Terminal Avenue, Clark, New Jersey 07066
***E-mail: fzeng@dow.com.**

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

Shine (luster) is one of the most sought-after and desirable criteria for a hair care product, including hair styling. The purpose of a hair fixative polymer is to hold the hair style in place. In order to deliver hair shine, silicone is typically added as a separate ingredient in the formulation. However for the amount of silicone required to deliver shine to the hair in a hair styling or fixative product, the hold performance of the fixative polymer becomes compromised. This study describes the development and results of the Styrene/Acrylates Copolymer hair fixative that delivers both hold and shine to the hair, and the polymer properties behind it.

Introduction

Shine is one of the most sought-after and desirable criteria for a hair care product. Shine is a sign of beauty, health and cleanliness. Loss of hair shine or dullness can occur due to hair damage from environmental factors such as sun, harsh cold weather or use of excessive hair treatments such as bleaching, coloring, and product build-up. Common approaches to restore hair shine include: 1) repairing the damage and brittleness; 2) removing build up; 3) moisturizing and increasing elasticity; and 4) smoothing to help the cuticles to lie flat. Cosmetic ingredients used in personal care formulations to aid hair shine are for example, naturally derived triglyceride oils; silicone oils such as cyclomethicone, dimethicone, phenyl trimethicone, amodimethicone trimethylsiloxy amodimethicone; and esters such as PPG-3 benzyl ether myristate. While they impart shine benefit to hair, there are some drawbacks to these materials, mostly in leaving an undesirable feel on the hair, or reduction in hair volume, or both.

Hair styling (fixative) polymers are the active cosmetic ingredients used in hair styling products (*1*, *2*). Hair styling polymers are typically excellent film-formers that can change the texture or shape of hair, or hold it in place in a certain hair style. Hair styling products exist in various product forms such as hair spray, hair gel, hair mousse, and pomade. Depending on product forms, hair styling polymers are designed so that they are compatible with the formulation. Various copolymers ranging from poly(acrylates), poly(vinyl pyrrolidone), poly(vinyl acetate) poly(urethanes), and polyesters have been utilized in hair styling products. While the conventional hair styling polymers such as poly(acrylates), poly(vinyl pyrrolidone) and their copolymers provide excellent hold performance, formulators have been relying on adding silicone to provide shine. This results in the compromise of hold performance for shine benefit. In this paper, we describe the synthesis of a novel styrene/acrylate copolymer with high refractive index. The physical properties, shine, and hold performance of this new polymer in hair styling products were investigated in comparison with conventional hair styling polymers.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

Experimental

Polymer Synthesis

The styrene/Acrylate copolymer was prepared by thermally initiated emulsion polymerization of monomers consisting mostly of styrene, butyl acrylate, methacrylic acid, as well as other co-monomers. This material has an average polymer solids of 40%, a mean particle size of 200 nm, and a pH of 3.5-4.0. The viscosity of this material is less than 10-20 cps as measured by Brookfield viscometer (LV2, 60 rpm, 25 °C).

Formulation

Hair spray aerosol formulations were prepared by dispersing 8-10% solids of the polymer sample in 200 proof ethanol, fully neutralized by aminomethyl propanol to pH 8.0-8.5. The aerosol can was charged with 50% of the above solution, and then charged with 50% of dimethyl ether under pressure.

Hair gel formulations were prepared by dispersing 1-2% solids of the polymer sample in DI water, fully neutralized by aminomethyl propanol to pH 7.5-8.0 followed by addition of an anionic rheology modifier to thicken the formulation.

Hair Treatment

Untreated hair swatches 8 inches long, weighing 2 g (European Dark Brown Hair, International Hair Importers, NYC, NY) were first positioned on cylinder for initial baseline measurement. Hair swatches were then sprayed at 30 cm distance for 1 second, and air dried for 15 minutes before measurement. Each sample test was repeated on 5 separate hair swatches.

Shine Measurement by Expert Panel Evaluation

The tresses were evaluated in a shine box by six panelists. The shine results are a ranking of best (value of 1) to worst (value of 5). Results of the six panelists were averaged to give the rating.

Shine Measurement by Bossa Nova Technologies (Culver City, CA, U.S.A.)

Polarized illumination coupled to a polarization analysis was used to differentiate between the specular (Gloss) and diffuse light. The light source was a neon light (6 Watts, 5500K color temperature). The data collected was then analyzed using equations and theories that consider the various band geometries of the specular and diffuse profiles.

Film Gloss

A Micro-TRI-Glossmeter was used for measuring the film gloss. A 5 mil wet film was cast on a porous tile substrate, and air dried. Readings were taken at 20 and 60 degree angles. A 3 unit difference in measurement can be recognized by the naked eye, with higher readings corresponding to glossier surfaces.

Stiffness Analysis by Dia-Stron

The hair tresses prior to curling were on the average 8 inches long and weighed 2.0±0.1 grams. They were washed using Tressemme® Deep Cleansing Shampoo (Unilever, UK) , then curled wet onto a 22 millimeter (mm) x 70 mm curler and held in place with a bobby pin. The curled tresses were allowed to dry on the lab bench overnight, or in a 45°C oven for 1 h. The curled tresses were then sprayed with test formulations from a distance of 30 cm in the hood, one second for both front and back of the curls. The curled, treated tresses were dried in a 45 °C oven for 1 h. Before the curl compression testing, the curler was removed carefully without disturbing the tress. The curled tress was placed on the miniature tensile tester, model MTT160 instrument (Dia-Stron Limited, UK). The curl was compressed to 25% of its initial diameter; the force-displacement curve was recorded. The peak force F (mgf) is reported to characterize curl stiffness.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

High Humidity Curl Retention (HHCR)

Curled tresses were prepared and treated as in the Diastron curl compression test above. After drying, the curlers were gently removed from the tresses and the curls were suspended by clips in a humidity chamber at 90% relative humidity (RH), 25°C. The initial curl length was recorded. The length of the curled tresses was recorded at intervals over 8 hours. Curl retention was determined as [(L(0)-L(t))/L(0)-L(i))x100] where L(0) is fully extended curl length, L(i) is initial curl length and L(t) is curl length at a specific time. Higher values indicate better humidity resistance performance.

Dynamic Mechanical Analysis (DMA)

Solutions of the samples were cast in perfluorinated polymer Petri dishes and allowed to air dry in a convection hood. The samples dried very slowly and the time required to air dry sufficiently so the resultant films could be handled was approximately 2 weeks. After 2 weeks the films were still pliable and somewhat tacky to touch. The films could be removed from the Petri dishes without breakage and strips, approximately 5 mm wide, could be cut from the films with scissors. The strips were placed back into the Petri dishes and allowed to dry further in the convection hood, approximately one week. The dishes were then placed in a mild oven (50 °C) to assist with the final stages of drying for 3 days. Experience has shown that trying to speed the drying protocol results in films containing a considerable number of voids. Finally, the samples were removed from the oven and placed under vacuum for approximately 2 weeks to remove last traces of moisture and solvent.

The film samples were tested on the TA Instruments Q800 Dynamic Mechanical Analyzer (DMA) using tensile film clamp fixtures. Each sample was tested from -50 °C to approximately 120 °C at a heating rate of 2 deg/min using the Temp Ramp/Freq Sweep Test in the DMA Multi-Frequency-Strain Mode. The applied frequency was 1 Hz. The Procedure Parameters were as follows: Applied Strain = 0.0075%; Preload Force = 0.01 N; and Force Track = 125%. A Soak Time of 5 minutes was employed before the start of data acquisition. The dynamic storage and loss moduli (E' and E" respectively) as well as tan δ were recorded as a function of temperature.

Results and Discussion

The principle function of hair styling polymers is that the polymeric materials deposit, adhere and form mostly seam and spot welds between hair fibers to hold the hair style in place. even in high humidity conditions or conditions where there is hair movement. The performance of hair styling polymers is strongly dependent on the polymer design and the resulting polymer properties. For example, the glass transition temperature (Tg) of the polymer can affect the film properties, stiffness, tackiness, and film dry-time. The polymer molecular weight can affect the formulation viscosity, which in turn affects spray particle size on hair fibers, which in turn affects hold. The spray particle size will have an impact on the

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

number and ratio of seam and spot welds. Typically, the polymer should be soluble in the formulation, can be removed from the hair through washing with water/shampoo, yet is resistant to high humidity. These performance properties are controlled through an optimum incorporation of both hydrophobic and hydrophilic sections in the polymer. The cohesive and adhesive strength of the polymer to hair fibers can influence the aesthetics of hair styling, in which non-flaking is desirable. If the polymer does not adhere to the hair fibers and/or has low cohesive strength, flaking can occur.

Acrylates copolymers are one of the most versatile classes of polymers that are currently used in hair styling polymers. Due to the availability of various side chain groups of (meth)acrylate monomers and excellent polymerization kinetic profiles with other monomers, Acrylates copolymers can be designed to be soluble in various hair spray formulations. Among them, alkaline soluble emulsion polymers became popular in the industry due to their versatility and economic efficiency. As supplied, the polymeric products are typically a milky white dispersion of polymer particles in water with high polymer solid content of at least 40%. They have a water-like viscosity and can be easily pumped to the production kettle at room temperature. Latex polymers with various glass transition temperatures, molecular weights, hydrophobicity, and morphology can be readily accessible. Typically, these latex polymers contain monomers with carboxylic acid groups. At polymerization pH, these carboxylic acid groups are protonated and the corresponding latex polymers have limited solubility in water. Upon neutralization with base, such as commonly used AMP-95® (2-Amino-2-methyl-1-propanol) (The Dow Chemical Company, Spring House, PA, U.S.A.), a clear solution is formed, resulting in excellent film forming properties upon drying.

Latex polymers containing high refractive index monomers have been marketed in the floor care industry to produce excellent gloss and gloss retention. It is our intention in this paper to incorporate this concept to provide shine benefit to hair styling polymers with all characteristics as described above. Styrene/Acrylates copolymer described in this paper has a general chemical structure as illustrated in Figure 1. It has a high refractive index compared to Octylacrylamide/Acrylates/ Butylaminoethyl Methacrylate copolymer (OABMC), a conventional hair styling polymer and silicones as shown in Figure 2.

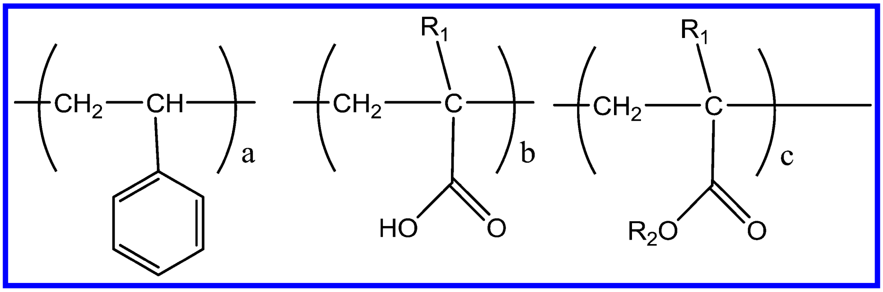


Figure 1. Chemical structure of Styrene/Acrylates copolymer (R_1= H, Me).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

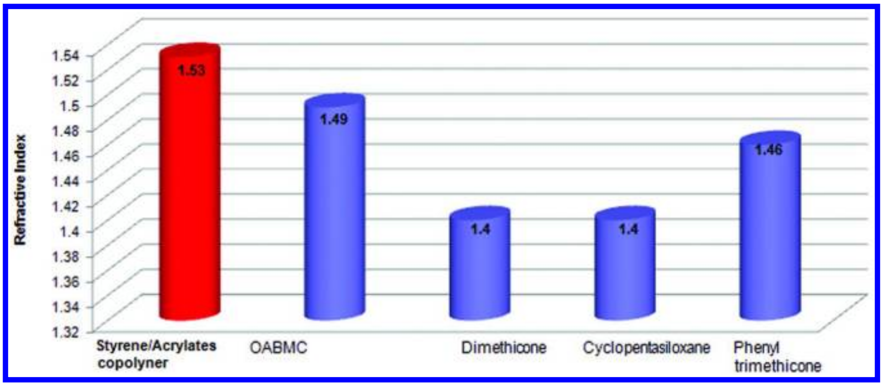


Figure 2. Comparison of polymer refractive index.

Styrene/acrylates copolymer was formulated into a variety of hair spray formuations , for example 55% VOC with 1,1-difluoroethane (Dupont's Dymel® 152a propellant), 55% VOC with dimethyl ether (DME) propellant, and 80% VOC. Table 1 shows a typical 55% VOC DME aerosol spray with styrene/acrylates copolymer. Shine and hold, the most important performance targets, were evaluated with several test protocols. In all studies, styrene/acrylates copolymer was directly compared with one commercial spray sample containing a polymer blend of Vinyl Acetate / Crotonates /Vinyl Neodecanoate Copolymer (VACVEC) and OABMC, and another commercial spray sample containing only OABMC.

Table 1. 55% VOC DME Aerosol Spray with Styrene/Acrylates Copolymer

Phase	*Ingredient*	*%Weight*
A	Ethanol	27.0
A	Styrene/Acrylates Copolymer	12.50
A	2-Amino-2-methyl-1-propanol	1.5
A	Water	31.0
B	Dimethyl Ether	28.0

Comparison of hair shine benefit from Styrene/Acrylates Copolymer with VACVEC/ OABMC blend and OABMC was obtained from both expert panel evaluation study and shine measurement with Bossa Nova Technologies (*3*–*5*). Figure 3 shows a comparison study of shine rating from expert panel evaluation. Higher shine rating was obtained for two Styrene/Acrylates Copolymer prototypes than OABMC. A more objective shine measurement is based on goniophotometer developed by Bossa Nova Technologies. Figure 4 shows the principle of shine measurement and data analysis from Bossa Nova Technologies.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

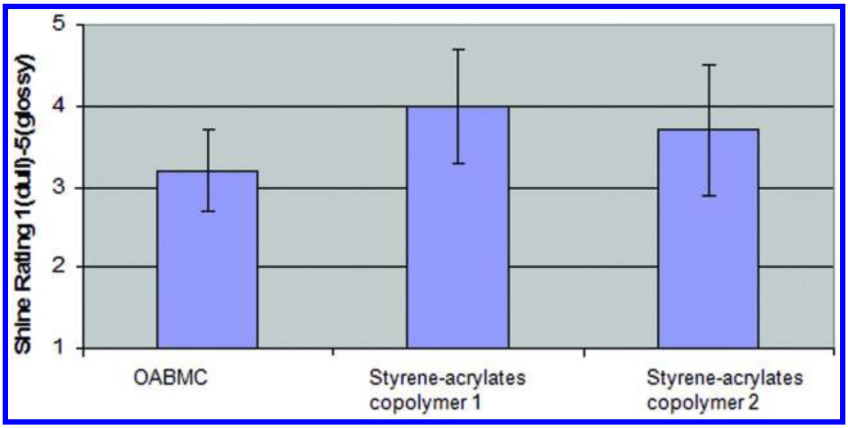
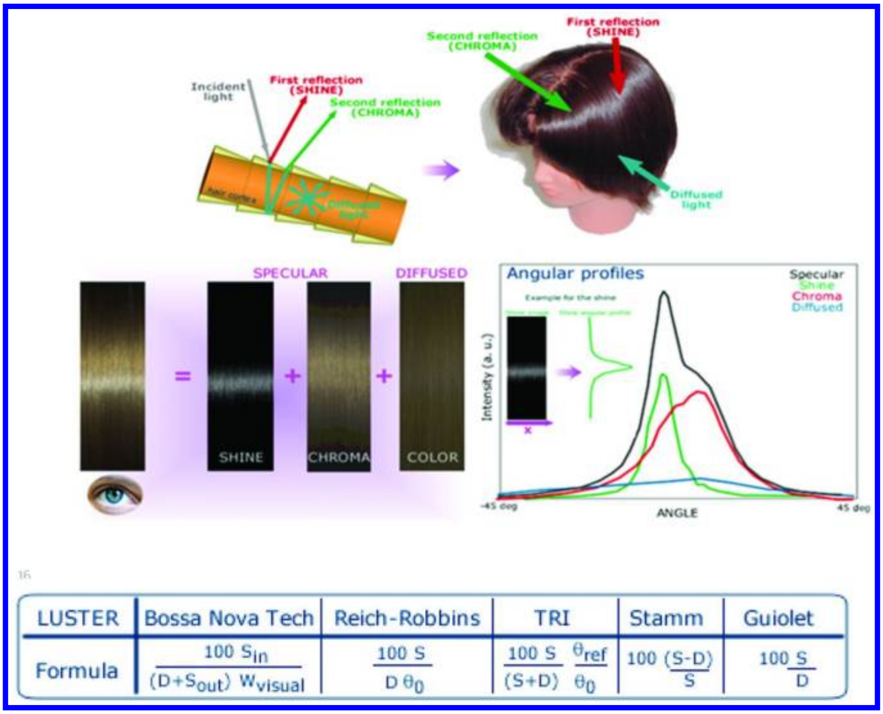


Figure 3. Comparison of shine rating from an expert panel evaluation study.



LUSTER	Bossa Nova Tech	Reich-Robbins	TRI	Stamm	Guiolet
Formula	$\frac{100\ S_{in}}{(D+S_{out})\ W_{visual}}$	$\frac{100\ S}{D\ \theta_0}$	$\frac{100\ S}{(S+D)}\ \frac{\theta_{ref}}{\theta_0}$	$100\ \frac{(S-D)}{S}$	$100\ \frac{S}{D}$

Figure 4. Shine (luster) measurement and data analysis from Bossa Nova Technologies. Images courtesy of Bossa Nova Technologies (4). Available at: http://www.bossanovatech.com/samba_hair_system.htm.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

Hair tresses treated with Styrene/Acrylates Copolymer, VACVEC/ OABMC blend and OABMC respectively were subjected to shine evaluation with the Bossa Nova method. The corresponding shine (or luster) was calculated by employing either Reich-Robbins equation or Bossa Nova equation. As shown in Figures 5 and 6, Styrene/Acrylates Copolymer provides a much better shine benefit to hair than VACVEC/ OABMC blend and OABMC for both calculation methods. Therefore, both subjective expert panel evaluation and objective Bossa Nova measurement demonstrate that Styrene/Acrylates Copolymer delivers a superior shine performance in comparison with the conventional polymers.

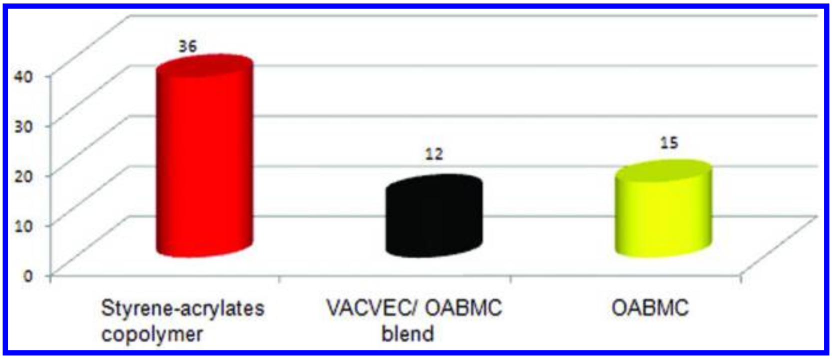


Figure 5. Comparison of shine performance in 55 VOC 152(a) aerosols with Reich-Robbins equation.

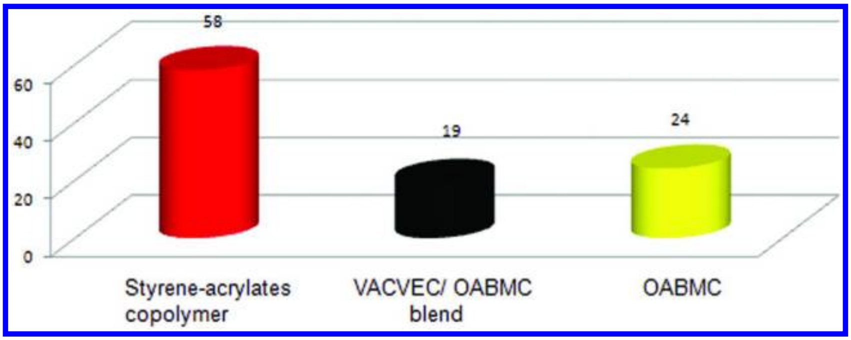


Figure 6. Comparison of shine performance in 55 VOC 152(a) aerosols with Bossa Nova equation.

The Styrene/Acrylates Copolymer provided higher shine performance to hair in comparison with conventional hair styling polymers. It is equally important that Styrene/Acrylates Copolymer can at least match the hold performance of the conventional hair styling polymers. A battery of hold measurement studies were performed to compare the performance of Styrene/Acrylates Copolymer with the conventional hair styling polymers: VACVEC/ OABMC blend and OABMC. Comparison of hold performance as measured by high humidity curl retention

(*6*), curl droop test, oscillation bouncing test, and Dia-stron curl compression (*7*) were shown in Figures 7, 8, 9 and 10, respectively. In high humidity curl retention and curl droop test, Styrene/Acrylates Copolymer has a very similar curl retention as VACVEC/ OABMC blend and OABMC. For oscillation bouncing test, Styrene/Acrylates Copolymer has a slighly better curl retention than OABMC, which is better than VACVEC/ OABMC blend. In Dia-stron curl compression study, Styrene/Acrylates Copolymer has higher peak stiffness and stiffness modulus than OABMC, which is better than VACVEC/ OABMC blend. The last two hold performance studies are in good agreement with each other. Based on all of these data, Styrene/Acrylates Copolymer has a silimar or slightly better hold performance than the conventional hair styling polymers.

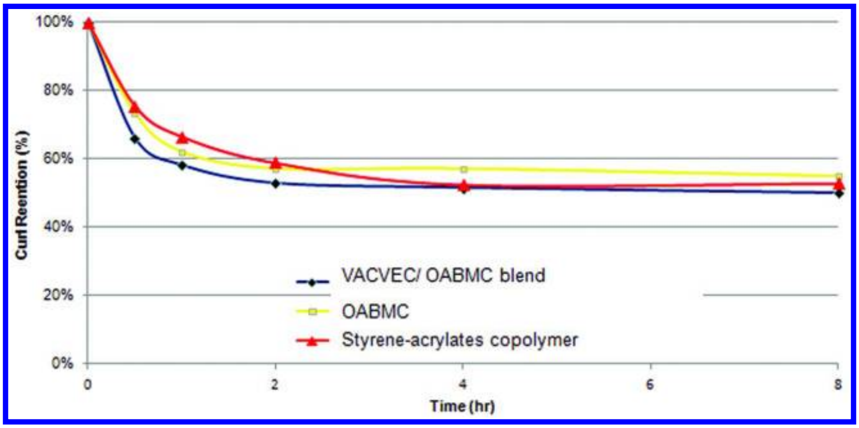


Figure 7. Comparison of High Humidity Curl Resistance at 90% RH, 25°C.

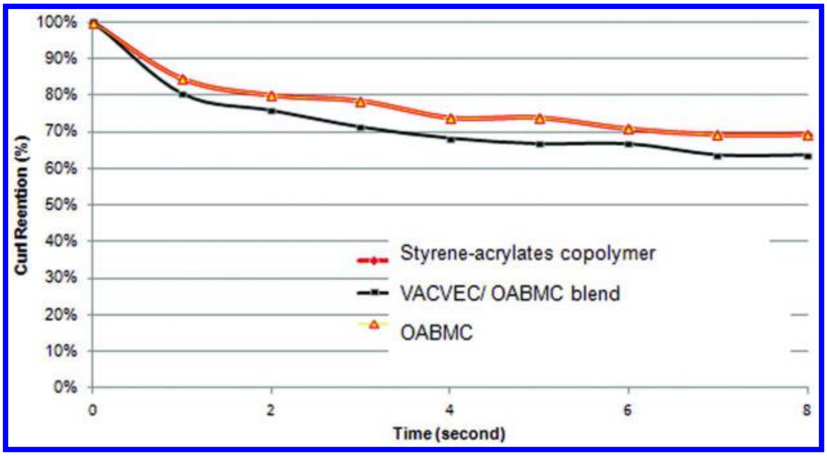


Figure 8. Comparison of Hold Performance byCurl Droop Test.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

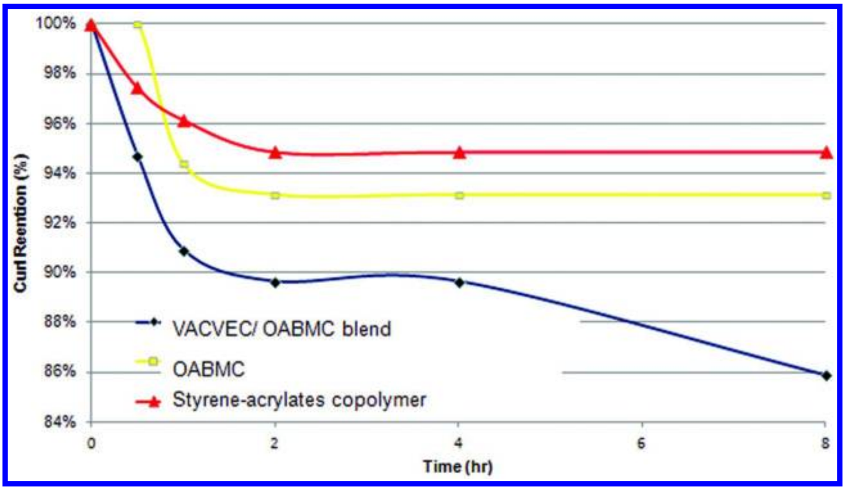


Figure 9. Comparison of Hold Performance byOscillation Bouncing Test.

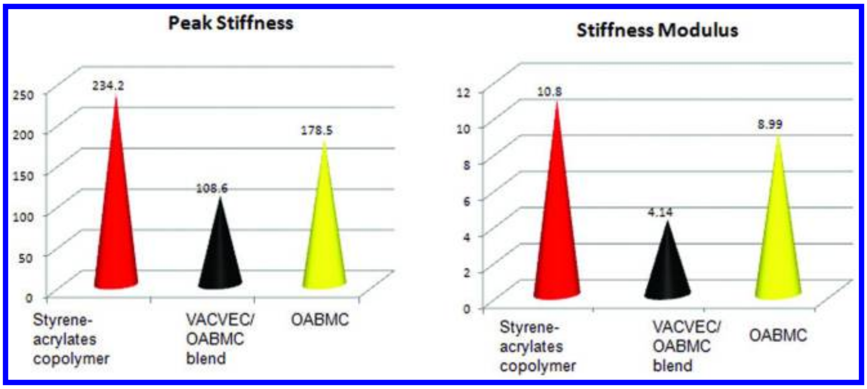


Figure 10. Comparison of Hold Performance by Dia-stron Curl Compression.

To explain the superior shine and hold performance, we investigated several polymer properties of Styrene/Acrylates Copolymer in comparison with the conventional hair styling polymers. The polymer film formation properties such as film smoothness and homogeneity (*8*) should play a beneficial role for hair shine as described above. As shown in Figure 11, Styrene/Acrylates polymer showed lower surface tension at early times compared to OABMC in ethanol solution. This lower Dynamic Surface Tension (DST) would provide better flow out and wetting of the formulation on hair prior to the formulation drying.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

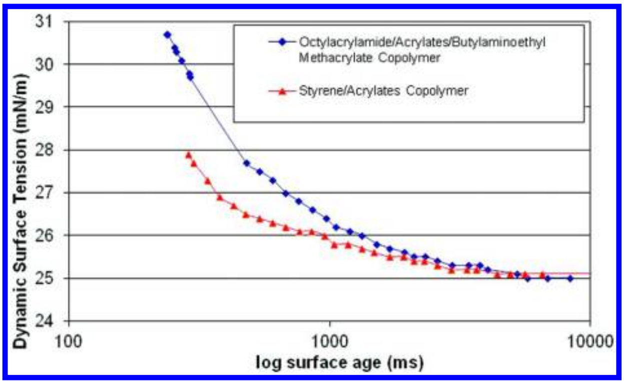


Figure 11. Dynamic surface tension of 5% polymer in ethanol solution.

Polymer molecular weight exerts direct impact on formulation viscosity as well as spray particle size. Scanning electron micrograph (SEM) surface analysis shows that fine spray particle size results in a smooth surface coverage, while large spray particle size results in cohesion between hair fibers and a coarse surface coverage. As shown in Figure 12, the molecular weight of Styrene/Acrylates Copolymer was fully optimized (left graph) so that a smooth surface was achieved. Both low DST and optimized MW for smooth surface spray should lead to a higher film gross. Figure 13 shows the comparison of film gloss as measured by micro-tri-glossmeter for 20 and 60 degree gloss. Styrene/Acrylates Copolymer has a higher gloss at both angles than VACVEC/ OABMC blend and OABMC. One needs to keep in mind that the film gross measurement employs different physics mechanism vs. the hair shine measurem.ent.

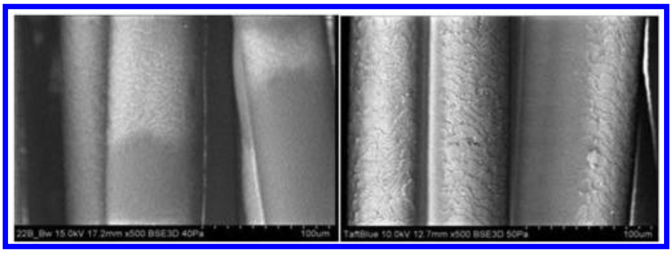


Figure 12. SEM surface analysis of hair treated with polymer with various molecular weight (left: optimized, right: un-optimized).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

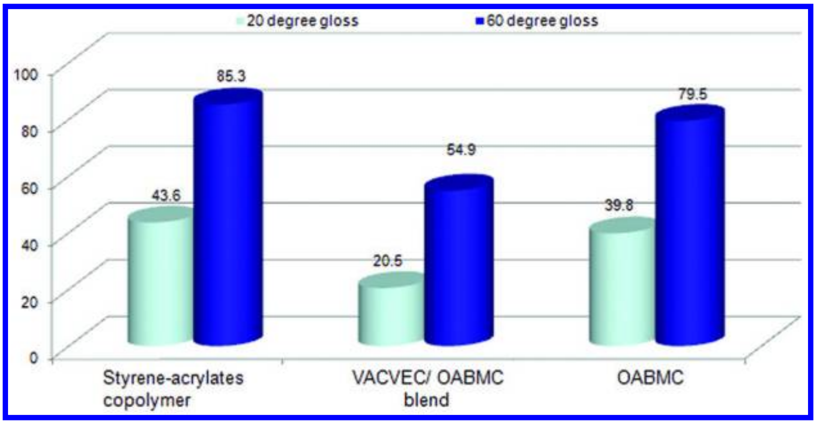


Figure 13. Comparison of film gloss as measured by micro-tri-glossmeter.

Finally, the mechanical properties of film formed from Styrene/acrylates copolymer was analyzed with Dynamic Mechanical Analysis (DMA). As shown in Figure 14, Styrene/acrylates copolymer has a high storage modulus at temperature up to 50 °C. This result is consistent with the strong hold performance of Styrene/acrylates copolymer as a hair styling polymer in the temperature range practiced by consumers.

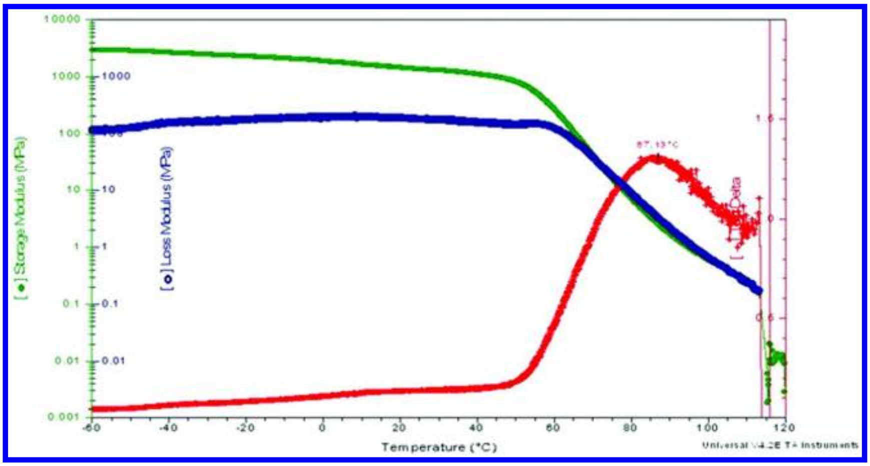


Figure 14. DMA of Styrene/acrylates copolymer film.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch012

Conclusion

The Styrene/acrylates copolymer was demonstrated to provide proven better hair shine and equivalent hold in various hairspray formulations when compared to the conventional hair styling polymers. The better hair shine performance is achieved through a combination of the polymer's high refractive index and superior product delivery, which impacts the polymer flow across the hair surface. This results in the formation of a smooth reflective film which gives outstanding shine while maintaining the hair hold performance. The Styrene/acrylates copolymer provides formulators a useful tool to achieve both shine and hold from a hair fixative polymer without compromise.

Acknowledgments

The authors gratefully acknowledge advice and support from Mark Westmeyer, Martina Osti, Kathy Keller, Diane Routzahn, and Wei Gao.

References

1. Lochhead, R. Y. In *Cosmetic Nanotechnology, Polymers and Colloids in Cosmetics*; Morgan, S. E., Havelka, K. O., Lochhead, R. Y., Eds.; ACS Symposium Series 961; American Chemical Society: Washington D.C., 2007; pp 5−9.
2. Ashton M. In *The Chemistry and Manufacture of Cosmetics: Volume II Formulating*; Schlossman, M. L., Ed.; Allured Publishing Corporation: Carol Stream, IL, 2000; pp 327−358.
3. Reich, C.; Robbins, C. R. *J. Soc. Cosmet. Chem.* **1993**, *44*, 221–234.
4. Lefaudeux, N.; Lechocinski, N.; Clemenceau, P.; Breugnot, S. *J. Cosmet. Chem.* **2009**, *60*, 153–169.
5. Gao, T.; Pereira, A.; Zhu, S. *J. Cosmet. Chem.* **2009**, *60*, 187–197.
6. Micchell, A. L.; Koehler, F. T. *J. Soc. Cosmet. Chem.* **1968**, *19*, 863–880.
7. Jachowicz, J.; McMullen, R. *J. Cosmet. Chem .* **2002**, *53*, 345–361.
8. Osterhold, M.; Glockner, P. *Prog. Org. Coat.* **2001**, *41*, 177–182.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

Chapter 13

Beyond Thickening – Use of Alkyl Acrylate Crosspolymer in Personal Care Formulations

Daphne Benderly* **and Yelena Zolotarsky**

Presperse Corporation, 635 Pierce Street, Somerset, New Jersey 08873
***E-mail: dbenderly@presperse.com.**

Polymeric thickeners have been used for decades in personal care applications. One class that is widely used is INCI name carbomer, crosslinked homopolymers of acrylic acid. A newer class of thickener is INCI name acrylates/C10-30 alkyl acrylate crosspolymer, crosslinked copolymers. One disadvantage of both carbomers and current offerings of acrylates/C10-30 alkyl acrylate crosspolymers is unrecoverable loss of viscosity upon addition of electrolytes.

One approach to alter electrolyte resistance in acrylates/C10-30 alkyl acrylate crosspolymers is to vary the structure of the crosslinked copolymer – for example crosslink density and extent of hydrophobic modification. Performance of different structures of crosslinked copolymer thickeners in model systems (gels, surfactants, emulsions) is demonstrated. The thickening mechanism upon addition of salt described. For some thickener structures, an added benefit is the development of a distinctive texture. This texture can be used to differentiate consumer products, giving a unique offering.

Introduction

Polymeric thickeners have been used for decades in personal care applications. One well-known type is the carbomer family, which are cross-linked homopolymers of acrylic acid, and are used in the water phase of formulations. These polymers are used in a variety of systems – aqueous, hydroalcoholic,

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

emulsions, toothpaste, and others, and provide a shear thinning rheology (*1–4*). A disadvantage of carbomers is poor electrolyte tolerance leading to a significant reduction in viscosity when electrolyte (salt) is present. Salt can be introduced into a personal care formulation either as a component of one of the ingredients (for example surfactant), or from the inclusion of a salt forming active ingredient.

A newer class of polymeric thickener is a crosslinked copolymer, acrylates/C10-30 alkyl acrylate crosspolymer, defined in INCI as "a copolymer of C10-30 alkyl acrylate and one or more monomers of acrylic acid, methacrylic acid or one of their simple esters crosslinked with an allyl ether of sucrose or an allyl ether of pentaerythritol" (*5*). This thickener structure gives better electrolyte tolerance than carbomer, and is also used in many types of personal care products.

The thickening mechanism of carbomer and crosslinked acrylate copolymers is well known. The polymer as supplied is acidic and the polymer chains are tightly coiled. After the polymer is dispersed in water and neutralized, the carboxyl groups on the polymer backbone dissociate, becoming negatively charged. These negative charges repel each other, and the polymer chains uncoil. As a result, thickening occurs and a gel is formed. When electrolytes are added to this gel, the anionic charges are neutralized, the polymer chains collapse back to their initial coiled state and viscosity is lost (*1–4*).

While the INCI name describes a general polymer structure, the exact structure and behavior of a hydrophobically modified crosslinked polymer can be altered by varying structural parameters such as the degree of crosslinking, the nature and extent of hydrophobic modification, and others. The focus of this paper is the performance that can be obtained with different grades of acrylates/C10-30 alkyl acrylate crosspolymers. The main parameter evaluated is viscosity build (thickening efficiency). However, other formulation benefits such as unique texture can be obtained. An unexpected thickening synergy was found between two crosspolymers and several surfactants.

Experimental

Materials

Three grades of acrylates/C10-30 alkyl acrylate crosspolymer were evaluated in this work. Aqupec SER W300C (Polymer 1) and Aqupec SER W150C (Polymer 2) were obtained from Sumitomo Seika. Ultrez 20 (Polymer 3) was obtained from Protameen Chemicals. The exact structure of each polymer is proprietary, but in general Polymers 1 and 2 are lower in crosslinking density than Polymer 3. The crosslinking density of Polymer 3 is considered typical for current commercial grade thickeners. Polymer 2 is lower in the extent of hydrophobic modification, as compared to Polymer 1.

Euxyl PE 9010 preservative was obtained from Schulke. USP grade sodium chloride and sodium lauroyl sarcosinate were obtained from Universal Preserv-A-Chem. Jeelate SLS-30 (sodium lauryl sulfate) was obtained from Jeen. Pellicer L-30 (sodium dilauramidoglutamide lysine) was obtained from Presperse. Amphosol HCA (cocoamidopropyl betaine) and Bioterge AS-40

(Sodium C14-16 olefin sulfonate) were obtained from Stepan. Suganate 160 (sodium laurylglucosides hydroxypropylsulfonate) and ColaTeric 1C (Sodium cocoamphoacetate) were obtained from Colonial Chemicals. Chemoryl LB-30 (oleyl betaine (and) sodium lauroyl lactylate) was obtained from Protameen Chemicals. Sodium hydroxide was obtained from Sigma Aldrich.

Formulation Preparation

The various personal care formulations were prepared using an IKA stirrer. Gels were prepared with a high lift mixing blade. Surfactant systems were prepared using a low lift mixing blade. Emulsions were prepared using a Silverson homogenizer.

Instrumentation

Viscosity was measured using a Brookfield RV-DV II+ Pro viscometer at 20 rpm, using an appropriate spindle. pH was measured using a Thermo Scientific Orion 3 Star pH meter. Adhesiveness was evaluated using a Brookfield Texture Analyzer.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

Results and Discussion

Hydrogel Salt Tolerance

The model system used for the first stage of evaluation of the polymeric thickeners is a 1% polymer hydrogel. The salt level was varied from 0% to 3% and the pH was varied between 5.5 and 12, using sodium hydroxide as a neutralizing agent. The hydrogels also contained 0.5% preservative.

Viscosity results for gels at pH 6.5 are presented in Table I, and shown graphically in Figure 1. Polymer 3, with a higher (commercially typical) level of crosslinking results in a thick gel when no salt is present. When electrolyte (salt) is added, a large drop in viscosity is seen. Conversely, Polymers 1 and 2, with lower extent of crosslinking, show little thickening when no salt is present. When salt is added, the viscosity increases significantly. For these polymers, the presence of a salt is necessary to obtain thickening. Polymer 2 requires the presence of a higher level of salt before thickening occurs, and can tolerate a higher level.

The mechanism proposed for the “salt thickening” exhibited by Polymers 1 and 2 is shown in Figure 2. As discussed above, typically for this type of structure when electrolyte is added the electrostatic repulsion between charged side chains is cancelled. The electrolyte balances out the charges on the side groups and the polymer chains return to the original coiled state. The gel “dethickens” and loses viscosity.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

Table I. Brookfield viscosity for 1% polymer hydrogels for different salt contents (pH 6.5)

Polymer	*Salt level (%)*	*Viscosity (cps)*
1	0	6,000
	1	22,950
	2	14,200
2	0	1,200
	1	6,450
	2	18,650
	3	10,600
3	0	28,350
	1	10,900

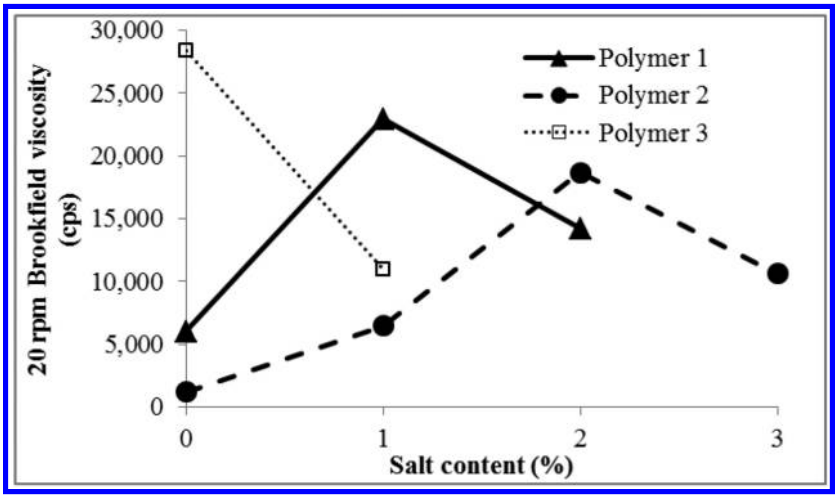


Figure 1. Brookfield viscosity for 1% polymer hydrogels for different salt contents (pH 6.5).

However, Polymers 1 and 2 are less cross-linked than Polymer 3 and have more chain flexibility. This flexibility allows the side chain hydrophobic groups to be brought close together when the polymer chains return to the coiled state. These hydrophobic groups can associate, acting as a virtual cross-link point. This association results in gel thickening.

In essence, there is a two stage thickening process for Polymers 1 and 2. The first stage is the same as described above for carbomers and typical crosspolymers. The polymer chains are neutralized and uncoil. This open structure is destroyed when electrolytes are added, and the chains coil back. In the second stage, this

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

chain collapse allows for a hydrophobic interaction between the side groups, and results in gel thickening. This process occurs rapidly, and was completed within a minute of salt addition for the samples described here.

Comparing Polymers 1 and 2, Polymer 2 contains less hydrophobic modification. Therefore, a higher salt concentration is required to coil the chains and bring the hydrophobic groups to self-association.

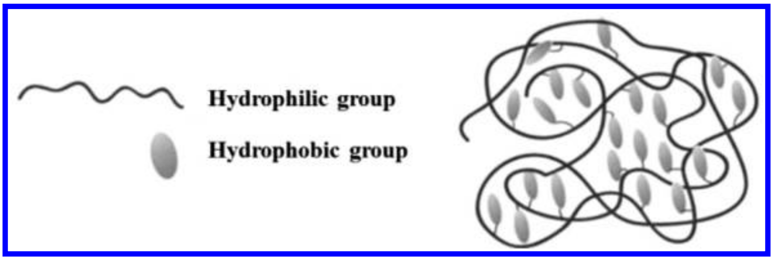


Figure 2. Interaction of hydrophobic groups in polymers such as 1 and 2, upon electrolyte addition (not to scale).

Hydrogel Texture and Sensory

The texture of the hydrogels differs with the chemical structure of the polymeric thickener. Incorporation of Polymers 1 or 2 (with lower crosslink density and salt activated thickening) gives a gel with a unique “bouncy” texture and reduced tackiness, compared to a gel with Polymer 3. These parameters are difficult to quantify.

Gels of similar viscosity with either Polymer 1 or 3 were evaluated with a Brookfield Texture Analyzer, using a back extrusion probe. Each gel was prepared at the optimal salt content – 1% for Polymer 1, 0% for Polymer 3.

In this test, a measure of adhesiveness is the area under the retraction curve. For the Polymer 3 gel (typical crosslink density), the adhesiveness was approximately 26 mJ, while for the Polymer 1 gel (lower crosslink density), the adhesiveness was approximately 14 mJ. This correlates with the gel “bouncy” feel. These gels also differ in sensory profile. After application to the skin, a gel with Polymer 1 gives a “wetter” feel than a gel with Polymer 3. Further work is planned in this area.

Thickening Efficiency in Surfactant Systems

Polymers 1, 2 and 3 were incorporated in a model cleansing (surfactant) system. Salt can be used as a thickener for surfactant systems, but provides a Newtonian flow profile rather than a shear thinning profile (*6*). In addition, exceeding the optimum salt loading (“oversalting”) can lead to a significant and irrecoverable loss in viscosity (*6*, *7*). Therefore, there are practical advantages to reducing salt level and using an additional thickener other than salt. The cleansing formulation used in the evaluation is shown in Table II. The formulation contains approximately 13% surfactant solids, which contribute electrolytes to the system.

Table II. Base formulation for cleansing system

Ingredient	*% w/w*
D.I. Water	QS
Na_2EDTA	0.09%
Propylene Glycol	0.9%
Ammonium Lauryl Sulfate	18.6%
Ammonium Laureth Sulfate	13.9%
Cocamidopropyl Betaine	9.3%
Sodium chloride	Varies
Acrylates/C10-30 alkyl acrylate crosspolymer	Varies
NaOH	to reach pH 6
Preservative	0.15%

Table III. Brookfield viscosity for cleansing system, 0.5% polymer

Polymer	*Polymer level (%)*	*Salt level (%)*	*Viscosity (cps)*
N/A	0	0.5	9,440
1	0.5	0	6,900
2			3,000
3			2,900

Viscosity results for samples with 0.5% polymer only (no salt) are given in Table III, and shown graphically in Figure 3. A comparison is shown to the viscosity of the system thickened with 0.5% salt only. Salt is an effective thickener for this formulation base, and Polymer 1 is more effective than Polymers 2 or 3. Polymer 1 gives thickening even without added salt, possibly due to interaction with the electrolytes present in the surfactants.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

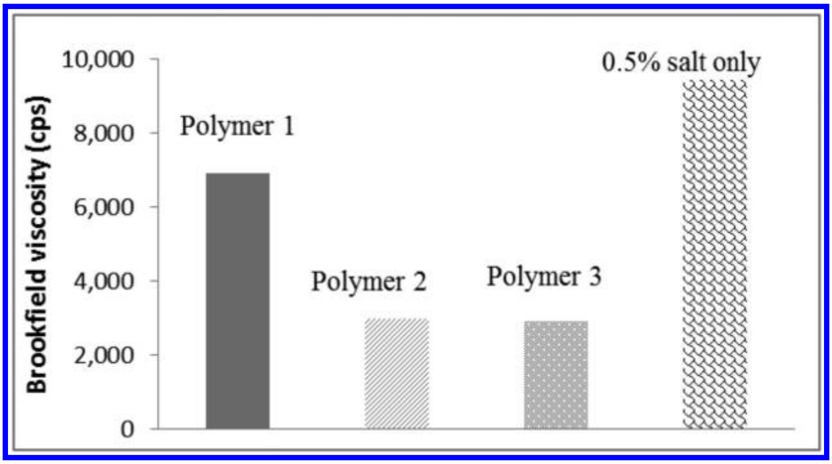


Figure 3. Cleansing system viscosity using 0.5% polymer, no salt.

Since both salt and the polymers investigated are effective in thickening the surfactant system, a combination was evaluated. The polymer level used was 0.15% and the salt level 0.3%. Viscosity results are shown in Table IV and displayed graphically in Figure 4. Polymer 1, with the lower level of crosslinking and greater chain flexibility, is the most efficient. In the presence of salt, Polymer 2 shows greater thickening efficiency than Polymer 3.

Table IV. Viscosity for cleansing system, 0.15% polymer 0.3% salt

Polymer	*Polymer level (%)*	*Salt level (%)*	*Viscosity (cps)*
N/A	0	0.5	9,440
1	0.15	0.3	13,580
2			8,100
3			5,900

A salt curve for a polymer content of 0.15% is shown in Figure 5. Polymer 3 (standard level of crosslinking) gives little thickening in this system. Polymer 1 with a low loading of salt gives a higher viscosity than the use of 0.5% salt only. The practical application of a thickener such as Polymer 1 in this system is that the danger of oversalting in production is reduced, as less salt is added to the formulation. When salt and polymer are used in combination, lower polymer levels (i.e. lower cost) can be used, in comparison to using polymer only. In addition, the “bouncy” texture observed with the hydrogels with Polymer 1 or Polymer 2 is also present in the surfactant system. The balance between texture and viscosity can be altered by the use levels of polymeric thickener and salt.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

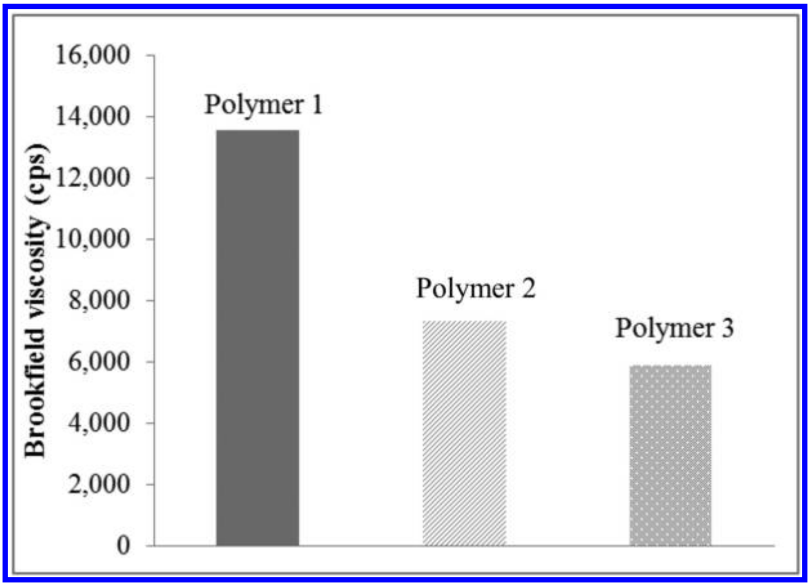


Figure 4. Cleansing system viscosity using 0.15% polymer, 0.3% salt.

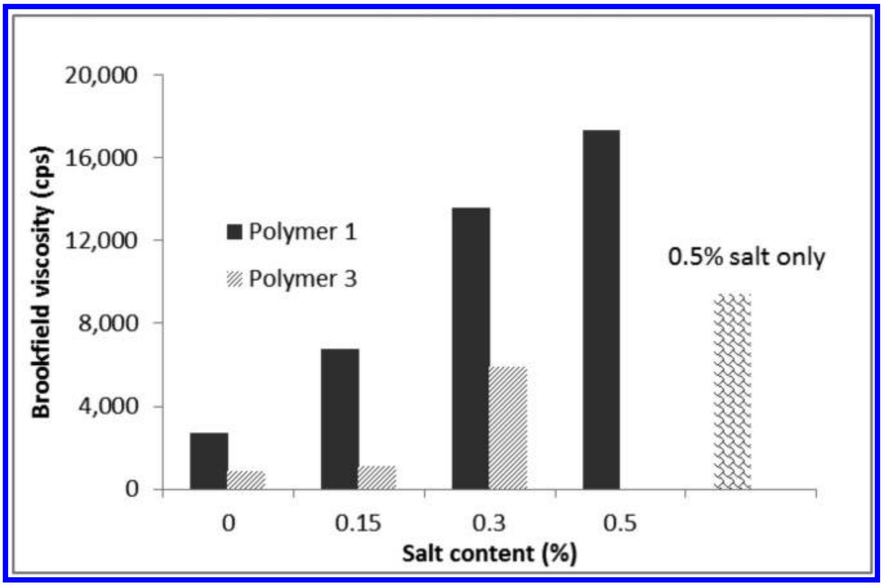


Figure 5. Salt curves in cleansing system, using 0.15% of Polymer 1 or Polymer 3 and different salt levels.

Synergistic Thickening with Preservative

Interactions have been reported in the literature between nonionic polymers and anionic surfactants (*2*, *8*, *9*). Interactions have not been reported for carbomer or acrylate crosspolymers (charged polymers) and anionic surfactants. Since Polymer 1 showed greater thickening efficiency in surfactant systems, it was of interest to study possible interactions.

The first potential interaction evaluated was with the preservative used in the hydrogel formulation. The preservative is a commercial mixture of phenoxyethanol and ethylhexylglycerin. The ethylhexylglycerin component has a surfactant like structure.

For the hydrogel study reported in the section above, the preservative was used at a 0.5% level. Hydrogels were prepared at a lower and higher preservative loading level, to study the effect of preservative level. Polymer 1 was evaluated with salt in the system, while Polymer 3 was evaluated without and with salt. The Brookfield viscosity results are shown in Table V.

Table V. Brookfield viscosity (cps) for hydrogels with different preservative levels

Polymer	*Salt level (%)*	*Preservative level (%)*	*Viscosity (cps)*
1	1	0.25	15,300
		0.50	22,500
		0.75	26,900
3	0	0.25	28,100
		0.50	28,350
		0.75	26,950
	1	0.25	16,000
		0.50	10,900
		0.75	12,650

As expected, no thickening synergy is seen between the preservative and Polymer 3. Surprisingly a strong effect is observed with Polymer 1. This type of synergy between preservative and acrylate crosspolymer thickener has not been previously reported in the literature.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

Synergistic Thickening with Typical Surfactants

This synergistic thickening was further investigated with a number of surfactants used in personal care formulations. In the first stage, hydrogels with 0.75% polymeric thickener and 0.75% NaCl were prepared to pH 6. This ratio of salt to polymer was the optimal ratio, based on the gel results reported in Table I. A low level of surfactant was added to these hydrogels.

Table VI. Brookfield viscosity (cps) for hydrogels with 0.75% polymer, 0.75% NaCl and surfactants

	Viscosity (cps)		
Surface active agent	*Polymer 1*	*Polymer 2*	*Polymer 3*
None	9,650	2,140	4,080
0.5% Sodium Lauryl Sulfate	21,500	5,650	3,710
0.5% Cocamidopropyl Betaine	14,150	32,650	2,690
0.18% Sodium Dilauramidoglutamide Lysine	14,900	N/A	5,290
0.5% Sodium Laurylglucosides Hydroxypropylsulfonate	16,500	N/A	2,570
0.5% Oleyl Betaine (and) Sodium Lauroyl Lactylate	13,550	N/A	N/A

Table VII. Brookfield viscosity (cps) for hydrogels with 0.75% Polymer 1, 0.25% surfactant, without and with 0.75% NaCl

	Viscosity (cps)	
% salt	*0*	*0.75*
no surfactant	80	9,650
Cocamidopropyl Betaine	19,800	20,000
Sodium Laurylglucosides Hydroxypropylsulfonate	9,720	14,450
Sodium Lauroyl Sarcosinate	8,880	17,850
Sodium C14-16 olefin sulfonate	23,350	3,510
Sodium Cocoamphoacetate	13,500	16,700

The Brookfield viscosity results are shown in Table VI. No thickening synergy is seen with Polymer 3. Both Polymers 1 and 2 surprisingly show significant thickening synergy. This synergy is the subject of a patent application (*10*), and could explain the improved thickening efficiency of Polymer 1 in the surfactant system results of Table III.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

This study was continued with Polymer 1, using a lower surfactant level and examining also the effect of salt addition. Hydrogels were prepared with 0.75% polymer, 0.25% surfactant, without salt and with 0.75% salt. The Brookfield viscosity results are shown in Table VII. All the surfactants evaluated showed thickening synergy with Polymer 1, although they differ in the details of the effect of salt addition.

Table VIII. Brookfield viscosity (cps) for hydrogels with 0.5% Polymer 1 and cocamidopropyl betaine without and with salt

	Viscosity (cps)	
Surfactant level	*0% NaCl*	*0.5% NaCl*
0%	316	3,210
0.25%	9,250	11,500
0.5%	19,300	11,800

A further evaluation was conducted using a 0.5% level of Polymer 1, without and with 0.5% salt. The Brookfield viscosity results, measured at 20 rpm, are shown in Table VIII. Comparing the results in Tables VI through VIII shows that different combinations of polymer level, salt level and surfactant level can achieve similar viscosity values. These levels can be chosen to tailor product texture and raw material cost.

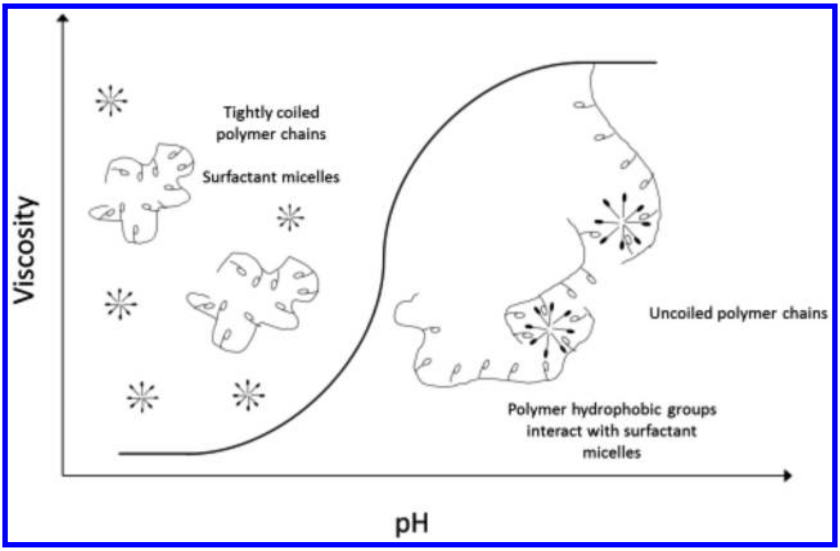


Figure 6. Possible interaction of hydrophobic groups in thickener such as Polymer 1, with surfactant micelles (not to scale).

The mechanism proposed for the higher thickening efficiency for Polymer 1 in the presence of surfactants is shown in Figure 6. The greater chain flexibility due to the lower crosslinking level allows the hydrophobically modified polymer to interact with the surfactant micelles, leading to greater thickening.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

Table IX. Base system for O/W emulsion system

	INCI Name	*w/w*
Phase A	Distilled Water	QS
	Na2EDTA	0.10%
	Acrylates/C10-30 Alkyl Acrylate Crosspolymer	Varies
	Propylene Glycol	2.00%
Phase B	Isohexadecane, Isododecane, C13-15 Alkane	5.00%
	Octyl Palmitate	3.00%
	Myristyl Myristate	3.00%
	Glyceryl Stearate and PEG-100 Stearate	3.25%
	Ceteryl Alcohol	0.75%
	Ceteth-20	0.40%
Phase C	Sodium Hydroxide	To pH approx. 5.5
	Distilled Water	QS
	Phenoxyethanol & Ethylhexylglycerin	1.00%
	Total	100%

Thickening Efficiency in Emulsion Systems

A commercially important formulation type in cosmetic products is emulsions. An emulsion is formed when one liquid is dispersed in a second liquid, in which it is not miscible (*6*). One common type is oil-in-water (O/W), in which the dispersed phase is oil. Emulsion rheology can be controlled using a water-phase thickener. Polymers 1 and 3 were evaluated as thickeners in the emulsion system shown in Table IX. The viscosity results are shown in Table X. Polymer 1 shows significantly greater thickening efficiency than Polymer 3. The “bouncy” texture observed in the hydrogels was observed in the emulsion samples as well.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

Table X. Brookfield viscosity (cps) for O/W emulsion system with different thickeners

Polymer level	*Polymer 1*	*Polymer 3*
0.2%	26,250	12,650
0.3%	39,750	28.600

Conclusions

Polymeric thickeners are commonly used in personal care formulations. The class of acrylates/C10-30 alkyl acrylate crosspolymers is a general description, in which polymers can differ in characteristics such as crosslink density and extent of hydrophobic modification.

By varying these parameters, factors such as thickening efficiency, electrolyte tolerance and formulation texture are affected. This provides insight into interactions occurring in the system. The novel texture can be of interest to product formulators. An unexpected finding for two of the acrylates/C10-30 alkyl acrylate crosspolymer structures studied is synergistic thickening with commonly used surfactants. This polymer structure exhibits not only synergy with surfactants, but also greater thickening efficiency in both surfactant and emulsion systems.

Acknowledgments

The authors would like to acknowledge the technical discussions and input of the technical staff at Sumitomo Seika. The assistance of Brookfield Engineering for the measurement of texture is acknowledged.

References

1. Clarke, M. M. In *Rheological Properties of Cosmetics and Toiletries*; Laba, D., Ed.; Marcel Dekker, Inc.: New York, 1993; pp 55−152.
2. Lochhead, R. Y. In *Rheological Properties of Cosmetics and Toiletries*; Laba, D., Ed.; Marcel Dekker, Inc.: New York, 1993; pp 275−311
3. Fevola, M. J. *Cosmet. Toiletries* **2011**, *126*, 692–697.
4. Tsolis, P.; Ollagnier, M. *Cosmet. Toiletries* **2012**, *127*, 560–563.
5. Personal Care Products Council. *On-Line INFOBASE*; Acrylates/C10-30 Alkyl Acrylate Crosspolymer http://online.personalcarecouncil.org /jsp/Home.jsp, (accessed March 16, 2012).
6. Schueller, R.; Romanowski, P. *Beginning Cosmetic Chemistry*, 3rd ed.; Allured Books: Carol Stream, IL 2009; p 316

7. Reich, C.; Chupa, J. In *Harry's Cosmeticology*, 8th ed.; Rieger, M. M., Ed.; Chemical Publishing Co.: New York, 2000; p 623.
8. Nagarajan, R. *J. Chem. Phys.* **1989**, *90*, 1990–1994.
9. Sivadasan, K.; Somasundaran, P. *Colloids Surf.* **1990**, *49*, 229–239.
10. Provisional patent application number 61/684,975

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch013

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

Chapter 14

Silicone Wettability and Its Significance in Beauty Products

Michael S. Ferritto[1] and Michael J. Owen*[,2]

[1]Dow Corning Corporation, Midland, Michigan 48640, U.S.A.
[2]Michigan Molecular Institute, Midland, Michigan 48640, U.S.A.
***E-mail: michaelowen01@chartermi.net.**

Silicones have been used in cosmetic and personal care products for over 50 years. Although polydimethylsiloxane (PDMS) remains the principal silicone polymer in these applications, a wide range of other silicone types are now utilized. Perceived benefits of incorporation of silicones into beauty products can sometimes be difficult to quantify. However, considerable data on fundamental properties that are relevant to silicone attributes in this area are available such as surface energy and hydrophobicity. Much of this information comes from contact angle measurement of liquids such as water, a useful index of hydrophobicity, and *n*-hexadecane, an indication of oleophobicity. These data are reviewed and compared with other oils and polymers of interest in the light of fundamental attributes of significance such as low intermolecular forces and polymer backbone architecture and flexibility.

Introduction

The central attribute that accounts for the widespread use of silicone fluids in cosmetic and personal care products is their ability to spread upon human skin and hair. This is a consequence of the low surface tension or energy exhibited by common silicone polymers, a lower surface energy than can be attained by typical hydrocarbon-based oils. In this chapter we review the surface energies of some different classes of silicones that are useful in cosmetic and personal care applications and explore the origins of this useful wetting behavior.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

It is conventional to refer to the surface tension of liquids and the surface energy of solids. The surface tension of an oil or liquid can be directly measured provided that the viscosities are not too high. For a solid such as skin or hair direct determination is not possible so recourse is made to a variety of contact angle approaches. These methods are not discussed in detail here. Numerous reviews are available in the literature; see, for example, (*1*). Most of the available pertinent data for solids is either critical surface tensions of wetting (γ_C) (*2*) or surface energies (γ_{SV}) obtained by the Owens and Wendt (*3*) approach. The former property is confusingly called a tension not an energy because it is the surface tension (γ) of the liquid that just wets the solid (contact angle, $\theta = 0$). The latter property has the benefit of separating the polar (γ^p) and dispersion force (γ^d) components of the solid substrate.

A definitive value for the surface energy of human skin or hair is not to be expected because of the range of skin and hair types, the variety of treatments possible, environmental factors such as relative humidity and variations in the methods of measurement and choice of contact angle test liquids. However, most reports suggest that values in the range of 20-30 mN/m are commonly encountered for both substrates. For example Schott (*4*) notes that γ_C for untreated human skin falls in the range of 22-30 mN/m while Robbins (*5*) quotes surface energy ranges from a variety of contact angle approaches of 25-28 mN/m for virgin hair, 24-26 mN/m for conditioned hair and 28-30 mN/m for chemically bleached hair.

Wetting by Silicones – Liquid Surface Tension Characteristics

This 20-30 mN/m surface energy range that encompasses many skin and hair types is a particularly interesting one for silicone materials. The most common silicone is polydimethylsiloxane (PDMS) and its surface tension lies at the lower end of this range (16-21 mN/m, depending on molecular weight) implying that spreading of PDMS is likely to occur on these substrates. One can anticipate spreading if the Spreading Coefficient (S) is positive:

$$S = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \qquad \text{(i)}$$

where S is solid, L is liquid and V is vapor (air). No values appear to be available for the interfacial tension γ_{SL} for PDMS and hair or skin but comparison with known values of PDMS/other polymer interfacial tensions suggests it will only be a few mN/m. For example, γ_{SL} for polypropylene (γ_C = 29 mN/m)/PDMS is 3.2 mN/m. Thus, a positive spreading coefficient can be predicted for a PDMS of surface tension 20 mN/m for almost all the surface energy ranges quoted in the previous paragraph. Most hydrocarbon oils have a surface tension higher than 30 mN/m and should exhibit a negative spreading coefficient on surfaces such as skin and hair. Table 1 shows some surface tensions of common oils and selected silicone fluids to illustrate this point.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

Table 1. Liquid Surface Tension of Various Oils and Silicones

Oil	*Surface Tension (mN/m)*	*Temp. (°C)*	*Ref.*
Castor oil	39.0	20	(*6*)
Olive oil	36	20	(*7*)
Peanut oil	35.5	20	(*8*)
Cottonseed oil	35.4	20	(*6*)
Coconut oil	33.4	20	(*6*)
Corn oil	33.4	20	(*8*)
Soybean oil	31.2	25	(*9*)
PDMS	21.3 (∞)(f)	20	(*10*)
PMTFPS(a)	24.4 (∞)	25	(*10*)
PHDFDMS(b)	18.5 (M_n ~ 19,600)	25	(*11*)
PDES(c)	25.7 (Unknown MW)	RT	(*12*)
POMS(d)	30.4 (600-1000 cS)	25	(*13*)
PTDMS(e)	35.0 (700-1200 cS)	25	(*13*)

(a) PMTFPS is polymethyltrifluoropropylsiloxane, the most common fluorosilicone polymer. (b) PHDFDMS is polyheptadecafluorodecylmethylsiloxane, a more highly fluorinated fluoropolymer. (c) PDES is polydiethylsiloxane. (d) POMS is polyoctylmethylsiloxane. (e) PTDMS is polytetradecylmethylsiloxane. (f) ∞ indicates the surface tension of a hypothetical infinite molecular weight material obtained by extrapolation using the LeGrand and Gaines equation (*14*). For POMS and PTDMS only single values are available so no extrapolation is possible.

The second law of thermodynamics indicates that systems will change spontaneously in the direction of minimum total free energy. Hence, for a polymer such as PDMS which contains both high (partially ionic siloxane backbone) and low (pendent methyl groups) surface energy entities, it is expected that the latter will accumulate in the surface and dominate surface behavior. This assertion is supported by the small polar component of solid surface energy that is measured by the Owens and Wendt approach (1.1 mN/m) (*3*). Langmuir's principle of the independence of surface action (*15*) extends this concept by envisioning separate surface energies for each of the different parts of complex molecules and asserting that the surface energy of such a material is determined by the composition and orientation of the outermost groups, independent of the underlying components.

Zisman and his colleagues (*2*) applied this principle to their critical surface tension of wetting studies of polymers to show that the surface energy of hydrocarbon and fluorocarbon substituent groups decreases in the order of $–CH_2$-

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

> -CH_3 > -CF_2- > -CF_3. The same order can be seen for the liquid surface tension of hydrocarbon- and fluorocarbon-containing low molecular weight oligomers as shown in Figure 1. This order of component surface activity offers a simple explanation of the difference in surface energy between organic oils and silicones reflected in Table 1. Methylene –CH_2- groups dominate the structure of the former with relatively few methyl (CH_3-) groups. For example, palmitic acid ($C_{16}H_{32}O_2$), the most common fatty acid constituent of vegetable oils, has 14 methylene groups for every methyl one. Conversely, for silicones at least one methyl group is generally found along the siloxane backbone on each monomer unit.

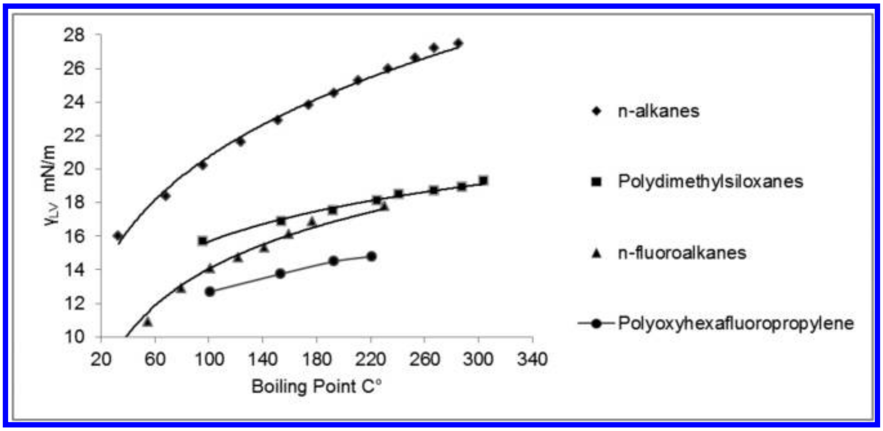


Figure 1. Dependence of surface tension at 20°C on boiling point for a variety of hydrocarbon- and fluorocarbon-containing compounds. Reproduced with permission from reference (16). Copyright 1980 American Chemical Society.

The trends in liquid surface tension values of the silicones in Table 1 can also be accounted for by this Zisman order simplification. For instance, in PTFPS one of the methyl groups is replaced by a $CF_3(CH_2)_2$- group. CF_3- is of lower intrinsic surface energy than CH_3- but the two –CH_2- group are of higher surface energy, so the higher surface tension of PMTFPS than PDMS, although somewhat unexpected, can be rationalized. One might suggest that dispensing with the ethylene bridge between the fluorocarbon group and the silicon atom would result in an interesting low surface energy polymer but the bridge is required to ensure adequate thermal and hydrolytic stability. The PHDFDMS polymer is not a commercial material and is not of interest to cosmetic and personal care product formulators but it is included in the table to demonstrate that a more highly fluorinated fluorosilicone where the methyl group is replaced by a $CF_3(CF_2)_7(CH_2)_2$- entity does have a lower surface tension than PDMS of similar molecular weight.

The higher surface tension of PDES is similarly accounted for by the inclusion of the extra methylene groups. This is an interesting polymer that is attracting interest in personal care applications. It is more compatible than PDMS with many hydrocarbon oils but, like PTFPMS, although its surface tension is increased compared to PDMS, it is still substantially below that of common hydrocarbon oils. It is not just low intermolecular forces between methyl groups that accounts for the unusual properties of PDMS. The extremely flexible siloxane backbone also plays an important role. The bulkier alkyl and fluoroalkyl groups detract from this flexibility and retaining one methyl group per silicon atom is a way of salvaging some of the flexibility benefit. The diethylsiloxane is the only other disubstituted siloxane polymer that is produced in commercial quantities. To the present time this production has been almost wholly in Russia but increasing attention is now being paid to PDES in Europe and the U.S.A..

The low surface tension advantage of silicones over hydrocarbon oils is not shared by polyalkylmethylsiloxane homopolymers such as POMS and PTDMS. These polymers have $CH_3(CH_2)_7$- and $CH_3(CH_2)_{13}$- groups, respectively, replacing a methyl group on each silicon so they are much more hydrocarbon-like than PDES. Of course, it is possible to prepare polyalkylmethylsiloxane-polydimethylsiloxane copolymers to tailor desired surface tension and compatibility characteristics.

Wetting of Silicones – Contact Angles and Solid Surface Energy Aspects

Table 2 lists advancing water and n-hexadecane contact angles on some selected hydrocartbon, fluorocarbon and silicone substrates. The water contact angles are a straightforward index of hydrophobicity; likewise, *n*-hexadecane contact angle values offer a simple measure of oleophobicity. The table also contains γ^d dispersion force components of surface energy calculated from the Girifalco, Good, Fowkes, Young equation (ii) (*17*), with the exception of polyethylene and polypropylene, taking γ_{LV} of *n*-hexadecane as 27.7 mN/m:

$$\gamma^d_{SV} = \gamma_{LV}(1 + \cos\theta)^2/4 \qquad \text{(ii)}$$

As expected, the contact angle of *n*-hexadecane is essentially zero on these somewhat higher surface energy polymers. The γ^d values for these polymers are taken from the Physical Properties of Polymers Handbook (*18*) determined by the Owens and Wendt approach using water and methylene iodide as the contact angle test liquids.

These γ^d values reflect the surface energy trend established by Zisman and co-workers from critical surface tension of wetting studies. *n*-perfluoroeicosane is a solid fluoroalkane, $C_{20}F_{42}$; its surface is a close-packed hexagonal array of CF_3- groups so it effectively sets the lower limit for the surface energy that can be achieved with fluorocarbon-based materials. Expectedly, none of the fluorosilicones have lower surface energies than *n*-perfluoroeicosane but the most highly fluorinated one, PHDFDMS, is reasonably close to the limit.

The most interesting aspect of the water contact angle values is the relatively large spread quoted for PDMS. It is surprising that there is not a more definitive value for a polymer so noted for its hydrophobicity. See (*10*) for a more detailed discussion of this topic.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

Table 2. Solid Surface Properties of Selected Polymers

Polymer	θ_{water} *(°) [Ref.]*	$\gamma_{n\text{-}hexadecane}$ *(°) [Ref.]*	γ^d *(mN/m)*
Polyethylene	94 (*18*)	<5 (*22*)	32.0
Polypropylene	116 (*18*)	<5 (*22*)	28.6
PDMS	108-122 (*10*)	41(a) (*23*)	21.3
PMTFPS	104 (*19*)	51 (*19*)	18.4
PMNFHS	115 (*20*)	63 (*20*)	14.6
PHDFDMS	121 (*11*)	69 (*11*)	12.8
PTFE	108 (*18*)	47 (*18*)	19.6
n-perfluoreicosane	122 (*21*)	76 (*21*)	10.7

(a) This is the instantaneous value of the drop contact angle; *n*-hexadecane swells PDMS and the contact angle diminishes with time as the drop is absorbed.

Interfacial Tension and Langmuir Monolayers

We have already noted the similarities between the solid surface energies and water contact angles of PDMS and hydrocarbons such as paraffin wax and the liquid surface tensions of low molecular weight PDMS and the *n*-alkanes (Figure 1). Both classes of materials can be properly considered hydrophobic and of low surface energy; their differences are of degree, not type. The same is not true for their interfacial tension against water (*24*) as shown in Figure 2. Here, no hydrocarbon can be found with a similar interfacial tension to PDMS. All low molecular weight PDMS oligomers have a significantly lower interfacial tension with water than any of the *n*-alkanes. This is a consequence of the polar siloxane backbone. Aided by its high chain flexibility, it can orient at the interface with water to achieve substantially lower interfacial tensions as a result of hydroxyl/siloxane interactions.

This interfacial affinity for water also enables PDMS to spread on water allowing for its study by the Langmuir trough technique. Figure 3 shows a surface pressure versus area isotherm for a relatively low molecular weight PDMS (*25*). Four regions are evident; an initial low surface-pressure region (A_1- A_2) followed by a rise in surface pressure (A_2-B) which leads to a plateau region (B-C) followed by a final small rise and a very small second plateau before reaching the collapse point. There has been much varied interpretation of this isotherm. The traditional interpretation maintained that all Si and O backbone atoms remain in the surface in the A_1-A_2 region and that the A_2-B rise was a transitional region to the B-C plateau which consisted of 6-unit helices with axes parallel to the surface. The latest view (*26*) supported by sum frequency generation vibrational spectroscopic studies is that in the A_1-A_2 region the methyl groups are completely disordered.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

The A_2-B region is an asymmetric layer with one methyl normal to the surface and the other parallel. In the B-C region these asymmetric layers fold horizontally. A recent survey of this Langmuir monolayer field has been provided by Esker and Yu (*27*).

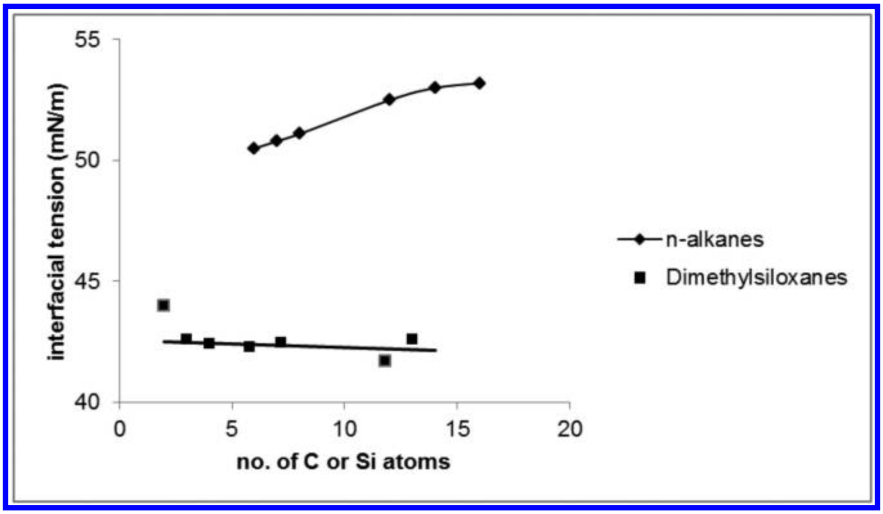


Figure 2. Interfacial tensions of n-alkanes and PDMS oligomers against water. Reproduced with permission from reference (10). Copyright 2012 Springer Science + Business Media B. V.

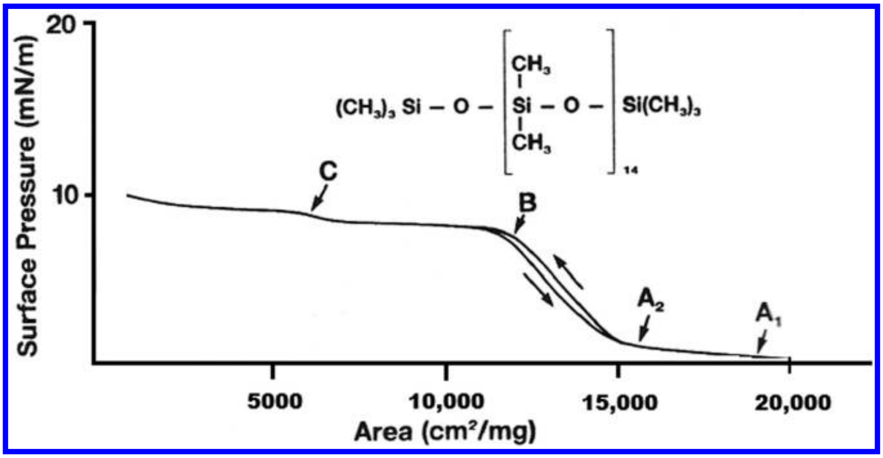


Figure 3. Langmuir trough isotherm for PDMS. Reproduced with permission from reference (25). Copyright 1971 John Wiley and Sons, Inc.

Not all silicones behave as PDMS. Noll and co-workers (*25*) suggest three classes of behavior. In class 1 two transformation points A_2 and B are observed. Class 2 has only one transformation point, A_2, and no B (i.e. no plateau) whereas class 3 has no transformation points whatsoever. Examples of class 1 are PDMS, PMTFPS, polymethylethylsiloxane, and polymethylphenylsiloxane. Silicones with hydrophilic pendent groups, such as polymethylhydroxymethylsiloxane, generally fall in class 2. Silicones in class 3 spread slowly and no appreciable surface pressure is developed. Those with bulkier aliphatic and aromatic pendent groups such as polymethylhexylsiloxane fall in this class, as does PDES.

Other Silicone Characteristics

Although low surface energy and consequent hydrophobicity are central to the role of silicones in cosmetic and personal care products, there are other important characteristics that are relevant to these applications. Notable amongst these are low toxicity, UV stability, high water and oxygen permeability, and the unique soft feel conferred on skin and hair. Even the dominant spreading capability is dependent on other features, primarily viscosity and molecular weight. The fact that silicones are available in a very wide range of viscosities and molecular weight provides a useful formulating variable. All these characteristics of silicones, particularly PDMS, are a consequence of five fundamental properties, namely: the low intermolecular forces between methyl groups, the compact size of the methyl group, the high flexibility of the siloxane backbone, the high siloxane bond energy and the partial ionic nature of the siloxane bond.

The low surface tension of PDMS is sufficient evidence of the dominance of non-polar, low intermolecular forces between the molecules. Another manifestation of this is provided by the Shih and Flory equation of state (*28*) which yields a measure of the intermolecular energy per unit volume of a compound that is known as the characteristic pressure (p*). Expectedly, p* increases as surface energy increases for the relatively few polymers reported by Shih and Flory. The lowest p* is for PDMS with a value of 341 J/cm^3. No fluoropolymer is included in their study but they quote a value of 362 J/cm^3 for *n*-hexane, which is close to that of hexamethyldisiloxane at 358 J/cm^3.

A low glass transition temperature, T_g, of a polymer segment is an indication of pronounced backbone flexibility and a low energy barrier to rotation about the Si-O main chain bonds; other factors such as pendent group size also have an effect. PDMS benefits from both the compact size of the methyl groups, the smallest possible alkane substituent (its van der Waals radius is 200 pm (*29*)) and the intrinsic flexibility of its backbone. Only an atom such as hydrogen (120 pm) or fluorine (135 pm) is smaller. The backbone architecture is also a factor with its alternating small, unsubstituted oxygen atoms and larger, substituted silicon atoms. Table 3 lists the T_g's of a variety of silicone polymers together with the lowest reported fluoropolymer T_g that we are aware of (*30*). Although the fluoropolymer has a lower T_g than PDMS it should be noted that it has pendent atoms not groups so the siloxane backbone could still be more flexible than the ether backbone. The several siloxanes with lower T_g's support this

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

contention. Although the ethyl groups in PDES are bulkier than the methyl groups in PDMS, they also help separate the chains so perhaps the latter effect is the more significant. The lowest siloxane value is for PD_5, a polymer of D_5H, pentamethylcyclopentasiloxane reported by Kurian and coworkers (*31*), that consists of cyclopentasiloxane rings linked by siloxane linkages. One can suppose that the smaller hydrogen on each methylhydrogensiloxane unit and the separating effect of the rings both contribute to the very low T_g value of this rather unusual siloxane polymer.

Table 3. Glass Transition Temperatures

Polymer	*T_g (K)*	*Ref.*
PD_5	122	(*31*)
PDES	134	(*32*)
PMHS(a)	135	(*32*)
PMES(b)	138	(*32*)
Co-poly(CF_2CF_2O-CF_2O)	140	(*30*)
PDMS	150	(*33*)
PMNFHS	198	(*20*)
PMTFPS	203	(*33*)

(a) PMHS is polymethylhydrogensiloxane. (b) PMES is polymethylethylsiloxane.

Although of great importance in the high temperature applications of silicones, the siloxane bond energy of 445 kJ/mol (*34*) is not a critical factor when used on skin or hair. Hoffmann (*35*) notes that the bond energies of carbon and silicon with other elements are similar (within 50 kJ/mol) for a large variety of elements. A marked exception is Si-O which is nearly 100 kJ/mol stronger than C-O. The 1.7 difference in Pauling (*36*) electronegativities of oxygen and silicon equates to an ionic nature of their bond of 41%. This results in increased susceptibility to nucleophilic or electrophilic attack than is the case for wholly covalent bonds. This is a potential Achilles heel of all hetero-atom polymer backbones. In practical terms, the pH stability range of spread PDMS monolayers on water (two-dimensional exposure to H_2O) is 2.5-11 and for aqueous silicone surfactants (three-dimensional exposure) is 4-9.

A variety of these silicone surfactants are available for use in aqueous as well as non-aqueous systems. Some can lower the surface tension of water to *circa* 20 mN/m, thereby providing aqueous systems with the same wetting benefits that unmodified silicones offer oleophilic compositions. In addition to surface activity the other essential for surfactancy is solubility in or compatibility with the selected medium. As silicones such as PDMS are insoluble in water, the desired solubility

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

is achieved by modification with hydrophilic entities attached to the PDMS. This most commonly is a polyoxyethylene chain although other hydrophiles similar to those found in other classes of surfactant are utilized such as sulfates, quaternary ammonium salts, betaines and saccharides.

The molecular origin of this ability of silicone surfactants to attain lower aqueous surface tensions than conventional organic surfactants can be directly attributed to the flexibility of the siloxane backbone allowing the methyl groups with their low intermolecular interactions to dominate the outermost surface. In contrast, the alkyl of alkylaryl hydrophobes of most hydrocarbon surfactants are comprised mostly of $–CH_2$- methylene groups that pack loosely at the surface as most hydrophiles occupy a larger cross-sectional area than an alkyl chain so packing is dictated by hydrophile/hydrophile interaction.

Silicone surfactant behavior has been recently reviewed by Petroff and Snow (*37*). They are also the subject of a book by Hill (*38*), which also includes a chapter by Floyd (*39*) on applications in the personal care industry. Petroff and Snow note that in recent decades one of the most intriguing aspects has been the "superwetting" behavior of a particular class of low molecular weight, trisiloxane-based, silicone surfactants. Aqueous mixtures of these surfactants exhibit very rapid spreading on low energy, hydrophobic surfaces such as are encountered in cosmetic and personal care application. The phenomenon has been associated with a number of physical properties of the surfactants including: low equilibrium surface tension, a high rate of dynamic surface tension lowering, the presence of lamellar phases of surfactanr bilayer aggregates, and aspects of Marangoni flow. Despite the considerable attention paid to this phenomenon there is not yet complete agreement on its origin.

Applications

Personal care products and cosmetics producers and formulators do not use the usual scientific nomenclature such as polydimethylsiloxane (PDMS) to describe silicone polymers. Instead they have adopted the convention authorized by the Food and Drug Administration in the U.S.A. to describe ingredients on package labels. This system is known as the INCI/(CFTA) nomenclature: i.e. International Cosmetic Ingredient (Cosmetic, Toiletries and Fragrance Association (*39*). PDMS is known as "Dimethicone" in this system and each silicone polymer type has its own INCI/(CFTA) name, such as "Aminopropyl Dimethicone" for aminopropyl-functional PDMS.

Silicones have been used in personal care products for more than half a century. The first product was a hand lotion introduced in 1958 at the suggestion of a major cosmetics company that had noted with interest the softening properties of a Dow Corning Corporation leather treatment product and enquired if the unique silicone properties could help dry, damaged skin (*40*). Connock (*41*) suggests that no single class of materials has had such an impact on modern cosmetic formulations as the silicones. PDMS was the first silicone to make a significant impression, initially owing to its waterproofing properties in barrier

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

creams but soon after to improve the skin-feel of cosmetic compositions and reduce the "soaping" effect of the triethanolamine-stearate emulsions which were popular at the time.

A major breakthrough in silicone-based ingredients in the 1970's was the use of volatile cyclics known as "Cyclomethicones" such as octamethycycloltetrasiloxane (D4) and decamethylcyclopentasiloxane (D5). These are quick-drying solvents primarily used in deodorants and antiperspirants although the widely reported benefits in altered skin feel consequent to such use imply that not all of the cyclics evaporate on application. There is currently concern regarding their accumulation in the environment. Unquestionably, they are globally dispersed (*42*) but whether or not this presents a risk to human health or the environment is a subject of considerable current debate. For instance, the Scientific Committee on Consumer Safety of the European Committee (*43*) concluded that cyclomethicone (D4, D5) does not pose a risk for human health when used in cosmetic products but felt that the Commision Services should consider whether an environmental risk assessment associated with their use in cosmetic products is required.

Nowadays, virtually every type of silicone, including cross-linked linear polymers (elastomers and gels) and resinous polymers have utility in cosmetic and beauty products. A few examples are listed as follows. Readers requiring more detail should consult the recent review by Garaud (*44*). Aminofunctional silicones are used in hair conditioners to increase substantivity to hair and increase and prolong ease of combing. Alkylmethylsiloxanes provide controlled compatibility with organic oils. Silicone surfactants improve spreading of aqueous formulations and also function as emulsifiers. Both oil-in-water and water-in-oil type silicone emulsifiers are available. Vesicle-forming silicone surfactants offer a novel delivery system for personal care ingredients such as vitamins. Fluorosilicones, being more oil repellant than equivalent dimethylsiloxanes, are useful for sweat-proof products such as sunscreens and in conditions for sebum control. Polydiethylsiloxane (PDES) is claimed to provide more body and cushion than dimethylsiloxanes of equal viscosities. They also wet many colored pigments better than PDMS. Silicone resins are used in color cosmetics to provide longer-lasting wear and non-transfer performance for lipsticks and foundations. Silicone elastomer microspheres confer a unique "dry, silky, powdery" feel to skin-care products.

It must be confessed that from a scientific viewpoint, some of these claims are rather qualitative because perceived benefits of silicone incorporation in cosmetic and beauty products can be difficult to quantify. This is particularly so for the characteristics that rely on sensory impressions of skin or hair feel such as enhanced softness, silkiness and smoothness. This is the reason that the present work has focused on measurable quantities such as contact angles. Another widely-practiced solution to these difficulties is to employ human test panels. Response to touch is clearly, at least in part, a surface phenomenon that in some instances can be quantified to a certain extent. One example relates to skin conditioning formulations where the primary function of the silicone in the formulation is to improve emolliency which is partly dependent on spreadability and also on lubrication. Based on panel evaluations, Brand and Brand-Garnys

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

(*45*) established that silicone fluids display greater emolliency than mineral oils of comparable viscosity. More quantitatively, they were also able to show using a skin friction device that the friction factor for PDMS was three times lower than that for the mineral oil. Note also that combing force measurements of treated hair tresses is another quantitatively established laboratory test that is widely used to evaluate hair conditioning formulations (*46*).

In conclusion, as put by CES, the European Silicones Centre (*47*); silicones are an outstanding success because they provide qualities people need and want and benefits that last. The shine and gloss, spreadability, softness and silkiness that silicones confer on beauty products are a direct result of basic properties such as low surface energy and hydrophobicity which arise from fundamental attributes such as low intermolecular forces between the substituent groups along the silicone chains (methyl groups in the case of PDMS, the most commonly encountered silicone) and the unusually high flexibility of the siloxane polymer backbone.

References

1. Owen, M. J. In *Comprehensive Desk Reference of Polymer Characterization and Analysis*; Brady, R. F., Ed.; Oxford University Press: New York, 2003; Chapter 15.
2. Zisman, W. A. In *Contact Angle, Wettability and Adhesion*; Fowkes, F. M., Ed.; Advances in Chemisty Series; American Chemical Society: Washington, DC, 1964; Vol. 43, p 1.
3. Owens, D. K.; Wendt, R. C. *J. Appl. Polym. Sci.* **1969**, *13*, 1741.
4. Schott, H. *J. Pharm. Sci.* **1971**, *60*, 1893.
5. Robbins, C. R. *Chemical and Physical Behavior of Human Hair*, 5th ed.; Springer: New York, 2012; p 346.
6. Chakrabarty, M. M. In *Chemistry and Technology of Oils and Fats*; Allied Publishers PVT Ltd.: Mumbai, 2003; p 49.
7. Florence, A. T.; Attwood, D. *Physicochemical Principles of Pharmacy*, 4th ed.; Pharmaceutical Press: London, 2006; p 179.
8. Halpern, A. *J. Phys. Colloid Chem.* **1949**, *53*, 895.
9. http://etc-cte.ec.gc.ca/databases/OilProperties. *Environmental Science and Technology Centre (ESTC); Environment Canada Databases; Oil Properties*, accessed May 7, 2013.
10. Owen, M. J.; Dvornic, P. R. In *Silicone Surface Science*; Owen, M. J., Dvornic, P. R., Eds.; Springer: New York, 2012; Chapter 1.
11. Kobayashi, H.; Owen, M. J. *Makromol. Chem.* **1993**, *194*, 1785.
12. Fox, H. W.; Taylor, P. W.; Zisman, W. A. *Ind. Eng. Chem.* **1947**, *39*, 1401.
13. Gelest, Inc., Product Information (Products ALT-143 and ALT-173). *Silicone Fluids: Stable, Inert Media*; 2012, p 18.
14. LeGrand, D. J.; Gaines, G. L. *J. Colloid Interface Sci.* **1969**, *31*, 162.
15. Langmuir, I. *J. Am. Chem. Soc.* **1916**, *38*, 2221.
16. Owen, M. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 97.
17. Fowkes, F. M. *J. Phys. Chem.* **1962**, *66*, 382.

18. Falsafi, A.; Mangipudi, S.; Owen, M. J. In *Physical Properties of Polymers Handbook*, 2nd ed.; Mark, J. E., Ed.; American Institute of Physics: New York, 2006; Chapter 59.
19. Owen, M. J. *J. Appl. Polym. Sci.* **1988**, *35*, 895.
20. Kobayashi, H.; Owen, M. J. *Macromolecules* **1990**, *23*, 4929.
21. Yung, Y. C.; Bushan, B. *Langmuir* **2009**, *25*, 14165.
22. Inagaki, N. *Plasma Surface Modification and Plasma Polymerization*; Technomic Publishing Co.: Lancaster PA, 1996; p 85.
23. She, H.; Chaudhury, M. K.; Owen, M. J. In *Silicones and Silicone-Modified Materials*; Clarson, S. J., Fitzgerald, J. J., Owen, M. J., Smith, S. D., Eds.; ACS Symposium Series 729; American Chemical Society: Washington, DC, 2000; p. 322.
24. Kanellopoulos, A. G.; Owen, M. J. *Trans. Faraday Soc.* **1971**, *67*, 3127.
25. Noll, W.; Steinbach, H.; Sucker, C. *J. Polym. Sci., Part C* **1971**, *34*, 123.
26. Kim, C.; Gurau, M. C.; Cremer, P. S.; Yu, H. *Langmuir* **2008**, *24*, 10155.
27. Esker, A. R.; Yu, H. In *Silicone Surface Science*; Owen, M. J., Dvornic, P. R. Eds.; Springer: New York, 2012; Chapter 7.
28. Shih, H.; Flory, P. J. *Macromolecules* **1972**, *5*, 758.
29. Brown, W. H.; Foote, C. S.; Iverson, B. L.; Anslyn, E. V. *Organic Chemistry*; Brooks/Cole: Pacific Grove, CA,2012; p 299.
30. Schiers, J. In *Modern Fluoropolymers*; Schiers, J., Ed.; Wiley: New York, 1997; Chapter 24.
31. Kurian, P.; Kennedy, J. P.; Kisliuk, A.; Sokolov, A. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **2002**, *40*, 1285.
32. Dvornic, P. R. In *Silicon Containing Polymers*; Jones, R. G., Ando, W., Chojnowski, J., Eds.; Kluwer: Dordrecht, 2000; Chapter 7.
33. Lee, W. A.; Rutherford, R. A. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 2003; p 111.
34. Beezer, A. E.; Mortimer, C. T. *J. Chem. Soc. A* **1966**, 514.
35. Hoffmann, A. *Chem. Eng. News* **2003** September8, 56.
36. Pauling, L. *J. Phys. Chem.* **1952**, *56*, 361.
37. Petroff, L. J.; Snow, S. A. In *Silicone Surface Science*; Owen, M. J., Dvornic, P. R., Eds.; Springer: New York, 2012; Chapter 9.
38. Hill, R. M. *Silicone Surfactants*; Surfactant Science Series, Vol. 86; Marcel Dekker: New York, 1999.
39. Floyd, D. T. In *Silicone Surfactants*; Surfactant Science Series, Vol. 86,; Hill, R. M., Ed.; Marcel Dekker: New York, 1999; Chapter 7.
40. www.dowcorning.com/content/publishedlit/01-4027-01.pdf. *Highlights from the History of Dow Corning Corporation, the Silicone Pioneer*, accessed May 7, 2013.
41. www.connock.co.uk/articles_silicones.htm. *Advances in the use of Silicones in Cosmetics*, accessed May 7, 2013.
42. Genualdi, S.; Harner, T.; Cheng, Y.; MacLeod, M.; Hansens, K. M.; van Egmond, R.; Shoeib, M.; Lee, S. C. *Environ. Sci. Technol.* **2011**, *45*, 3349.
43. European Commision Scientific Committee on Consumer Safety. *Opinion on Cyclomethicone (D4/D5)*; SCCS/1241/10, 22 June, 2010.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch014

44. Garaud, J. L. In *Inorganic Polymers*; De Jaeger, R., Gleria, M., Eds.; Nova Sciences Publisher: New York, 2007; Chapter 16.
45. Brand, H. M.; Brand-Garnys, E. E. *Cosmet. Toiletries* **1992**, *107*, 93.
46. Klamath, Y. K.; Weigmann, H-D. *J. Soc. Cosmet. Chem.* **1986**, *27*, 111.
47. www.silicones-eu/applications/personal-care. *Silicones in Personal Care Animation*, accessed May 7, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Chapter 15

Hair Care Polymers for Styling and Conditioning

Osama M. Musa[*] and Michael A. Tallon

Ashland Specialty Ingredients, 1361 Alps Road, Wayne, New Jersey 07470
[*]E-mail: omusa@ashland.com. Tel.: (973) 628-3265.

Many books have been written on the use of polymers in the Personal Care Industry. This chapter is written from a molecular scientist's perspective relating the structural functionality within the polymer molecule to its critical performance attributes as a hairspray, gel, mousse, or conditioner. Topics covered include; the choice and quantity of monomers; molecular weight and its distribution; physical characteristics such as flexibility or stiffness, durability of hold, shampoo removability, luster versus gloss, lubricity, conditioning, along with regulatoryand safety factors. Additionally, the fundamental principles for the evaluation tests applied on the polymer to substantiate its performance attributes, and exactly what is being measured. This chapter provides a fundamental understanding of this field from a pragmatic viewpoint while still highlighting the science behind it.

Introduction

Human hair serves many useful functions, but these are typically overlooked in today's culture. For example, hair exhibits a highly complex multi-laminate composite structure to impart distinct advantages. For example, hair inhibits exposure of the scalp to solar radiation such as infra-red heat that could result in sun-stroke while the melanin pigment inside the hair fiber acts as a natural UV filter to prevent photodamage (*1*). Moreover, oils secreted by the body coat the fibers to give them water resistency and aids in preventing fiber entanglement or knots in the hair.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Psychological factors such as aesthetic beauty and age are also involved in the visual perception of hair. A properly groomed coif imparts a perception of tidiness (organization), cleanliness (health), self-esteem (confidence), in addition to enhancing the physical appearance of the individual. Furthermore, some psychologists believe individuals' hairstyles can reveal their personality traits (*2*). Additionally, the graying of hair is a primary visual cue of the person's age and has distinct psychological implications regarding youth, or the lack of health and vigor. So it is not surprising that a multi-billion dollar industry has arisen to support these aesthetic perceptions.

This chapter will primarily focus on structure/properties inter-relationships for hair care polymers used in styling and conditioning, as well as the fundamentals behind the evaluation methods used to elucidate or substantiate their novel properties. In particular, styling, conditioning, and shine, are three major attributes readily perceived by the consumer, so these attributes are thoroughly evaluated by the manufacturer before a launch of a new hair care product. Interestingly, if the consumer does not immediately perceive a difference upon the first application of a new product, he/she will tend not to buy that product again. Therefore, immediate satisfaction with the product is required to keep the consumer using it, regardless if it takes several applications to achieve the same result.

Hence, the bar is set rather high to achieve immediate customer satisfaction. Each attribute such as styling or conditioning contain several sub-attributes essential for the total aesthetic experience. For instance, under styling, the hold can be stiff, soft, or flexible. Another critical aspect to style is durability of hold. Most consumers do not want their hair glued together as if they were using shellac, aka "*helmet-hair*", but rather would like to be able to run their fingers through it while still retaining its shape. Therefore, the dried polymer film coating the hair fiber cannot be brittle resulting in loss of style due to physical manipulation, or even worse, flaking-off resulting in an observable residue on the shoulders as depicted in Figure 1.

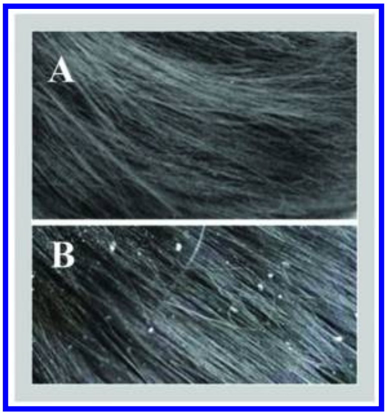


Figure 1. a) Before Brushing b) After Brushing Flaky Residue due to Brittleness of polymer resin.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Hair is commonly exposed to varying weather conditions such as extremes of humidity on rainy days, or high relative humidity because of geographical regions. High Humidity Curl Retention(HHCR) is therefore an essential testing parameter for styling performance, since the hair must not droop or lose its shape under these conditions (*3*).

In this test, a hair tress is curled and fixed in place by a styling resin, then it is placed in a humidity chamber at 28 °C and 90% relative humidity (RH) for 4 hours. The percent droop, as measure by its initial length to that after exposure determines its performance, as monitored initially, at 90 minutes and subsequently at 4 hours, as shown in Figure 2. Another visual aspect is the clarity of the dried film, as it must remain transparent when rewetted and cannot be compromised by turning cloudy as this affects color and shine, which is unacceptable by the typical consumer.

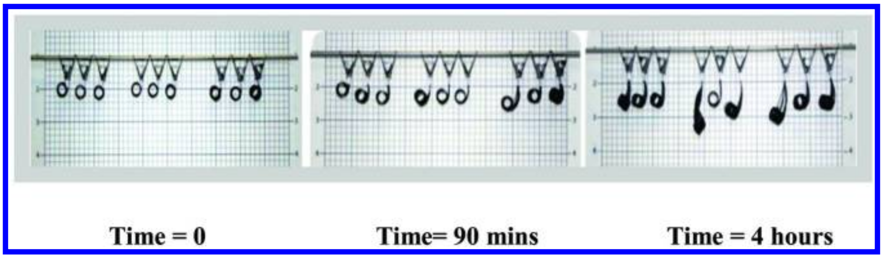


Figure 2. High humidity curl retention test at 28 °C and 90% RH.

However, today's hair-styling regimes have become ever more stressful upon the fragile nature of hair. In particular, styling tools like hot-irons and blow-dryers make hair more brittle. Chemical treatments such as relaxers, bleaching, and oxidative hair coloring just exacerbate this situation even further.

Moreover, as the hair grows , the ends of the fibers receive less and less of the natural protective oils of the scalp. Consequently, the sebum fails to reach the ends of the hair fibers so they are not lubricated. The repetitive mechanical stress of daily brushing or combing upon these unlubricated portions of the hair can result in fractures, pitting, and cracks (*4*). This results in dry, brittle ends, which are prone to splitting. shearing, and fracturing of the cuticle scales themselves, or even worse, the complete removal of the whole cuticle layer itself. Thus, the hair appears to be more frizzy and duller due to diffuse reflectance.

To minimize this damage, synthetic cationic polymers are commonly used in conditioning products as are some cellulosic polymers. These polysaccharide-based biopolymers are tacitly considered *"Green-Conditioners"*. A chemical modification to these cellulosic polymers, quaternization, results in several of the better known polyquaternium polymers used in conditioning and styling products today, such as Polyquaternium-4 and Polyquaternium-10.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Both synthetic cationic and cellulosic polymers provide lubricity so that knotting and hair damage is minimized and makes the hair feel soft, silky, and shiny as important performance attributes for conditioning.

Hence, conditioning polymers must provide luster and feel silky to the touch of the hair to be considered useful. Additionally, they must lower the frictional forces of combing or brushing so that knotting of the hair does not occur. Luster from a polymer is usually the result of fiber alignment of the individual strands and the refractive index of the resin, while manageability and prevention of fly-away hair can be ascribed to the insulating power of the polymer with respect to the highly negatively charged hair surface of each strand of damaged hair (*5*).

Genetic factors are also involved with respect to styling and conditioning given the uniqueness of African , Caucasian, and Asian hair types, as depicted in Figure 3. For example, the shape of Caucasian hair is slightly elliptical, Asian hair is circular, while African hair is oval-shaped (*5*, *6*).

Likewise, Asian hair is thicker with an average fiber diameter of 100 μm, while Caucasian hair thickness is nominally 60 μm, and African hair has cross-sectional dimensions of 80 μm by 50 μm. Similarly, the exposed portion of the cuticle on Asian hair can be as low as 5 μm, while that of Caucasian and African hair are both 10 μm. Therefore, Asian hair tends to be straighter and more difficult to shape into a curl, while African hair is curlier and harder to straighten.

This difficulty arises from the fact that the depth of the cuticle layer and the area of the medulla is roughly the same for all three hair types, but the cross-sectional area for the Asian cortex is almost three time larger than Caucasian hair. Because the cortex is responsible for maintaining the shape of the hair fiber as it exits the follicle by the alignment of the keratin helical bundles located within the cortex section, the Asian cortex contains more helical bundles per fiber making it more difficult to realign these bundles to alter the shape of the fiber. This would be analogous to reshaping a thin wire into a curl versus a thick cable made up of many individual wires. Hence, the bending of a hair fiber is mainly influenced by the cortex, while the torsional twisting of a fiber is controlled by the cuticle layer.

In contrast, African hair tends to be curlier as it exits the follicle. But like Asian hair, African hair exhibits a larger cross-sectional area than Caucasian hair, and is more difficult to reshape by straightening because of the higher level of keration bundles present per unit fiber. This requires chemical relaxers to achieve this goal, resulting in damage to the hair and requiring conditioning thereafter. Hence, ethnic hair types are not at all equivalent. Each requires its individualized ethnic styling system to achieve maximum overall consumer satisfaction.

Other aspects to styling and conditioning polymers deal with the local preferences and regional regulatory governance of these products within a particular country. Both impact the necessary performance requirements. For example, in Asian countries silicone polymer’s feel and water repellency is highly admired in a hair care product. In contrast, Europe is trying the phase out the use of silicones as they are neither biodegradable nor ecotoxicology--friendly. In the Philippines, most days are highly humid (90% RH) while in Saudi Arabia the climate is extremely arid. Consequently, each region has a unique environment and weather pattern that dictates different performance issues with respect to styling or conditioning.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

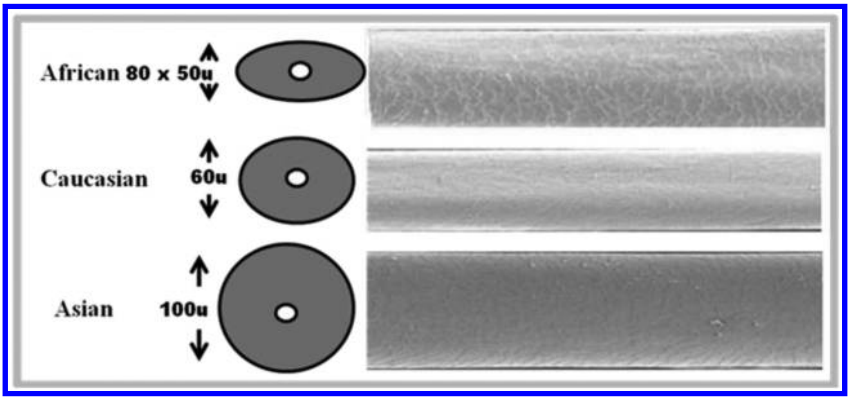


Figure 3. SEM photomicrographs of African, Caucasian, and Asian hair types.

Likewise, each local regulatory body has its own perceptions and regulations regarding consumer and environmental safety. Therefore, monomers that are not registered within a given country cannot be used for personal care products there even though they are registered everywhere else in the world. Similarly, China requires animal testing of products for consumer safety, while Europe has banned this practice as of 2013 (*7–9*).

In the U.S.A., Volatile Organic Compounds (VOCs) are constantly being monitored and regulated to protect the populace against the inadvertent contamination of drinking water (*10*), to protect the ozone layer (*11*, *12*), and to prevent the build-up of greenhouse gases (*13*, *14*). The result of which is lower VOC hairsprays, such as 55% ethanol/water. However, Europe and Asia still use hairsprays that contain high levels of ethanol, such as 100-80% in formulations for its quick drying attribute.

Another Human Health and Safety initiative established in Europe is the European Community regulation on chemicals and their safe use, EC-1907/2006, better known as REACH. . It deals with the **R**egistration, **E**valuation, **A**uthorization and Restriction of **Ch**emical substances within the European Union (E.U.). The law went into effect on June 1, 2007. The aim of REACH is to improve the protection of human health and the environment through a better understanding of the intrinsic properties of chemical substances being sold. The REACH Regulation places greater responsibility on industry to manage the risks from chemicals and to provide safety information on these substances.

Manufacturers and importers are therefore required to gather information on the properties of their chemical substances, which will allow their safe handling, and to register this information into a central database run by the European Chemicals Agency. The regulation also calls for the progressive substitution of the most hazardous chemicals when suitable alternatives have been identified. One of the main reasons for developing and adopting the REACH Regulation was that a large number of substances had been manufactured and sold in Europe for many years, sometimes in very high amounts, and yet there was insufficient information on the potential risks that they may pose to human health and the environment.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

All of these regulations and regional initiatives result in a non-uniform set of laws that have not been harmonized throughout the globe, and considerable resources are expended just to register a single product in all of these different countries and world regions alone. Hence, the synthetic chemist needs to be aware of these restrictions on the use of certain chemical substances in particular countries when constructing a Personal Care polymer that is intended to be used globally.

Lastly, the delivery of the product has its own unique set of parameters that the polymer must exhibit. For example, hairsprays require polymers with very low acidity as they can corrode unlined tin or aluminum composite cans and take on different colors from the leached metal ions present (*15*). Additionally, a low solution viscosity is ideal to obtain the proper spray pattern/profile and quick drying characteristics imparted by the aerosol's particle size.

There are several ways that this can be achieved. For example, a lower hairspray viscosity profile can be achieved if the polymer's rheology is shear thinning or pseudoplastic (*16*), whereby the measure of a fluid's resistance to flow decreases with an increasing rate of shear stress. In other words, stress applied onto a viscous polymer solution by agitation or rubbing between the hands results in a lower solution viscosity by disrupting the associative forces between the polymer chains allowing alignment of the chains and thereby exhibiting a thixotropic behavior. In contrast, delivery of the styling product in a mousse form ideally is highly viscous to maintain the foam stability and the tactile "*cushioning*" effect when rubbed between the hands or onto the hair (*17*).

In summary, there are countless factors involved in the construction of a hair care polymer that are never recognized by the public at all. The case of a simple hair-fixative polymer no longer has relevance today, instead these polymers are now high performance materials exhibiting multiple benefits within the same molecule. Moreover, the incremental advancements over the past several decades have made these types of polymers difficult to improve upon from the consumer's perspective. Yet intense research goes on to construct the perfect polymers for particular hair types, geographic regions, or applications.

This chapter will cover the most important parameters and properties needed in a hair care Polymer. We will focus on relating the structure of the polymer to its physical and chemical characteristics and how these relate to its performance. We will also cover other factors that influence these performance attributes such as the product's form, percent neutralization, and other additives used in conjunction with the polymer to achieve its overall performance in a meaningful way. Lastly, the analytical methods used to evaluate performance will also be covered to elucidate their role in the evaluation process from laboratory to commercial scale.

Styling Polymers for Hair Care

Out of the hundreds of commercially available polymers in the marketplace, only a select few can make the grade to achieve all of the necessary performance attributes yet still be cost effective too! As a result, we start with the cost of

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

the polymer as a primary driver for product development. From a pragmatic viewpoint, one cannot expect to develop a \$50 hairspray/mousse/gel for the whole world market. Most people just cannot afford to pay that much in a highly industrialized country, let alone in emerging markets such as India, South America, and China, where sales growth rates are extremely attractive from a financial viewpoint.

As a result, the synthetic chemist needs to know the pricing structure required to deliver the proposed benefits outlined by a specific need in the marketplace. Hence, the cost and availability of the raw materials, along with the processing costs of manufacture can be some of the most difficult selection criteria to achieve for a commercially feasible product, which still exhibits all the required performance attributes. As a first step, a focus on the chemistry involved in generating styling polymers for hairsprays, mousses, and gels needs to be considered.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Hairsprays

Some early styling gels used natural polymers and solvents like vegetable gums dissolved in alcohol. One popular ingredient was gum arabic, which is made from the sap of certain species of the acacia tree. Gum tragacanth is another herbal gum that is used to stiffen hair. Others use modified natural polymers based on cellulose like hydroxyethylcellulose. But the most widely used hairspray polymers in the marketplace are based on synthetic polymers.

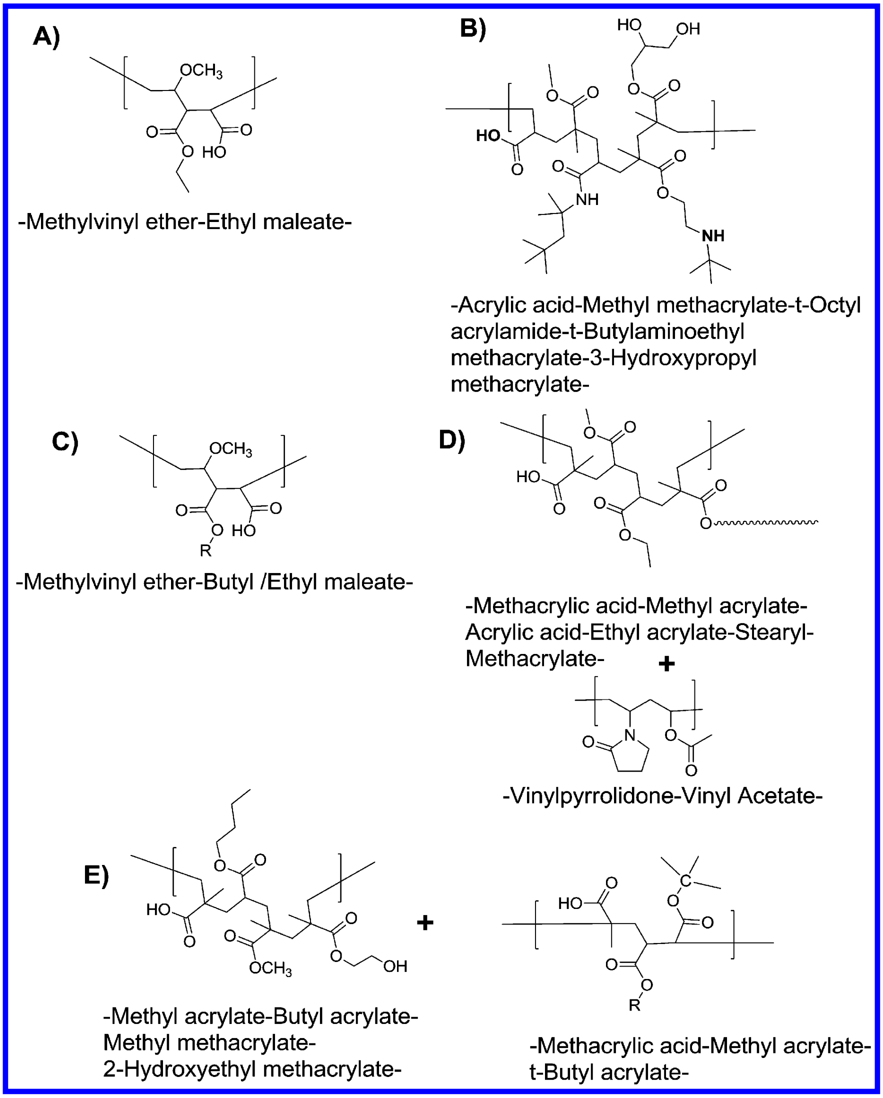
Illustrated in Figure 4 are the chemical structures of several popular hairspray resins currently in use today. It should be noted that either a single polymer or a blend of polymers can be used to achieve the desired performance characteristics. It is noteworthy that a current trend to use two polymers with a high and low glass transition temperature (T_g)to achieve efficacy is gaining momentum today, which will be discussed in detail later. The next consideration deals with the types of functional groups that are present in the polymer. These are presently primarily based on (meth)acrylate esters, vinyl esters, vinylpyrrolidone, and amides, or combinations thereof.

The reason for this is not strictly performance-based but in consideration of that hairsprays generate an aerosol mist that may be inhaled into the lungs. So, from a health and safety point of view, many large companies will not jeopardize their brand name without a massive amount of toxicological data proving that the ingredients are safe to be inhaled (*18*, *19*). In fact, even trace impurities present in the ingredient mixtures are highly scrutinized at concentrations down to parts per million (ppm) or even parts per billion (ppb) if they are known to be carcinogens.

It is very costly to generate all of the needed inhalation data and other comprehensive consumer safety data, like the localized lymph-node assay (LLNA), ocular irritation, reproductive toxicity, and ecological-toxicity to name a few. The cost to generate all of this consumer and environmental safety data can reach into the millions of dollars. Therefore, many large personal care companies are very conservative in what goes into their products, and they only use ingredients that have a proven track record to be safe for as much as several

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

decades in use without any health concerns exhibited (*18–20*). Consequently, acrylates, methacrylates, vinyl-esters, vinylpyrrolidone, and vinyl-amides have stood the test of time in hairsprays for their safety, so polymers using these types of monomers are highly preferred.



-Methylvinyl ether-Ethyl maleate-

-Acrylic acid-Methyl methacrylate-t-Octyl acrylamide-t-Butylaminoethyl methacrylate-3-Hydroxypropyl methacrylate-

-Methylvinyl ether-Butyl /Ethyl maleate-

-Methacrylic acid-Methyl acrylate-Acrylic acid-Ethyl acrylate-Stearyl-Methacrylate-

-Vinylpyrrolidone-Vinyl Acetate-

-Methyl acrylate-Butyl acrylate-Methyl methacrylate-2-Hydroxyethyl methacrylate-

-Methacrylic acid-Methyl acrylate-t-Butyl acrylate-

Figure 4. Chemical structures of popular hairspray polymers used today.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Table I. Physical and Chemical properties of some popular hairspray resins

Hairspray polymer(s)	*Polymer A 55% VOC*	*Polymer B 55% VOC*	*Polymer C 80% VOC*	*Polymers D PVP/VA + Acrylates-SM 80% VOC*	*Polymers E Acrylates + Hydroxy-acrylates 80% VOC*
Hold Type	**Stiff**	**Stiff**	**Stiff**	**Stiff**	**Stiff**
Dried Film Clarity (Subjective)	**Clear**	**Clear**	**Clear**	**Clear**	**Clear**
Acidity meq/g	**4.95**	**2.29**	**4.00**	**0 / 1.16**	**2.95 / 2.10**
T_g °C	**102**	**135**	**96**	**115 / 38**	**97 / 52**
Mol. wt. Kda	**125**	**39**	**115**	**57 / 103**	**31 / 70**
Specific Viscosity	**0.40**	**0.43**	**0.41**	**0.43 / 0.47**	**0.34 / 0.40**
Refractive Index @ 25°C, λ = 598 nm	**1.42**	**1.49**	**1.42**	**1.45 / 1.45**	**1.46 / 1.46**
HHCR 90-mins	**90**	**97**	**93**	**94**	**93 / 96**
HHCR 4-hours	**85**	**95**	**90**	**94**	**91 / 85**
Initial Curl Droop	**1%**	**1%**	**1%**	**5%**	**--/--**

Continued on next page.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Table I. (Continued). Physical and Chemical properties of some popular hairspray resins

Hairspray polymer(s)	*Polymer A 55% VOC*	*Polymer B 55% VOC*	*Polymer C 80% VOC*	*Polymers D PVP/VA + Acrylates-SM 80% VOC*	*Polymers E Acrylates + Hydroxy-acrylates 80% VOC*
Tack-time secs	**22**	**50**	**11**	**37**	**13 / 18**
Dry-time secs	**44**	**55**	**21**	**52**	**29 / 30**
Stiffness					
1-10 scale	**8**	**5**	**7**	**7**	**4 / 6**

The next commonality among these polymers is that they all contain an acidic functionality. The presence of acid groups on the polymer aids in water solubility, and enables removability of the polymer when shampooing/ washing. If the polymer is not effectively removed from the hair between applications by shampooing, then polymer build-up occurs resulting in a heavy residue and unacceptable matted-feel to the hair by the consumer.

The need for any polymeric acidic or basic groups at all arises from the fact that many neutral water-soluble polymers tend to absorb moisture readily from the atmosphere. This hygroscopic property results in failure of the resin to withstand the High Humidity Curl Retention test for several reasons. First, the water absorbed tends to make the polymer tacky by plasticizing it and lowers the stiffness of hold (*21*, *22*). This results in an unacceptable droop of the hairstyle and unpleasant feel to the hair.

To obviate this consequence, a much higher molecular weight polymer with significantly higher viscosity can be used to help slow down and reduce diffusion of water into the dried polymer film from a kinetic viewpoint, as well as the higher molecular weight will increase the overall stiffness of the polymer even though it may be plasticized by water, but that compromises removability and the aerosol/ pump spray pattern, particle size, and dry time. Hence, these negative attributes by neutral water soluble polymers tend to limit their use..

In addition, the typical use level of a polymer in a hairspray formulation is approximately 4-5 weight % to achieve proper holding performance. Given this high necessary level of polymer incorporation results in several practical consequences. For instance, hairspray resins need to be both of low acidity because they can corrode unlined spray cans, and low viscosity in order to be atomized into a fine mist, so as to be optimally delivered from an aerosol formulation.

Therefore, some of the polymer's acid groups are typically neutralized within the formulation thereby generating an ionic charge on the polymer to give it some water solubility for removal when washing. The choice of acid groups over basic groups arises from that the fact that basic groups still require an acid to be neutralized. But acidic salts can still corrode the tin-oxide lining, so to lessen this effect, corrosion inhibitors can be added as well.

However, pump hairspray formulations can tolerate a higher polymeric acidity value as they tend to be delivered in plastic containers instead of pressurized tin/ metal cans, but they still need to exhibit a lower solution viscosity for optimal spray patterns and quick drying attributes. Yet, the particle size of the aerosol droplet should not be less than 1-10 microns since particles of such size can be inhaled deep into the lungs and cause irritation resulting in health concerns (*18–20*).

Another approach to give some water solubility for removal during shampooing is to use both acidic and basic groups within the same polymer chain so that it is self-neutralizing. These types of polymers exhibit an isoelectric point, the pH at which the net charge on the molecule is zero, so that the number of positive and negative charges is equal. Hence, the synthetic chemist can control by design and construction the balance of charges to achieve this or not by choice of the quantity of cationic to anionic functionalities present within the same

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

polymer chain. Likewise, the pK_a or pK_b values for these functionalities can be chosen to deliver pH specific attributes.

This polyelectrolyte effect tends to lead to associative interactions between polymer chains thereby setting up an internal network structure, which tends to make the polymer solution thixotropic. This optimally results in a shear-thinning behavior so that a lower solution viscosity is obtained upon agitation or shear as it moves to the nozzle of the spray device. However, after application the associative forces within the resin, primarily due to the Columbic attraction of positive and negative charges, realign themselves to reestablish the internal network structure again, thereby raising the bulk viscosity of the formulation on the hair increasing its hold/stiffness (*21*).

In theory, associative thickening is a practical solution to achieve water solubility while temporarily decreasing the solution viscosity during spraying and reestablishing an increased bulk viscosity after application for strength of hold. However, toxicologists have expressed some concern that basic-type ammonium groups can pose a health concern for inhalation, so typically they are not readily used, or if so at very low concentrations such as 1-2 weight %. Therefore, most hairspray resins will be constructed with acidic groups that are neutralized with either 2-amino-2-methyl 1-propanol (AMP), tri-isopropanol amine (TIPA) salts, or triethanol amine (TEA) since these ammonium salts have been thoroughly analyzed for their safety (*20*). In contrast, basic group containing resins are used for styling products in the form of mousses and gels since they are not inhaled.

This brings us to what would appear to be a simple decision of how to effect neutralization of the resin. In fact, this is not a simple or straightforward matter at all. Formulators have capitalized on the fact that the choice of neutralizer and at what level of neutralization to use has severe impact on the performance of the resin (*22*, *23*). Most notably film clarity, water resistance, and film hardness are affected by the degree of neutralization and the type of neutralizer used.

For example, beside methyl (meth)acrylate, larger simple alkyl (meth)acrylate esters such as ethyl, propyl, butyl, etc.., are not completely water soluble; on the contrary, they give excellent humidity resistance . But for shampoo removability (meth)acrylic acid is commonly included in the backbone of the polymer. In its acid form, the polymer is not highly water soluble at all, and still provides high humidity resistance. However, upon complete neutralization of the (meth)acrylic acid portion of the polymer results in a water soluble resin, and poor humidity resistance due to hygroscopic effects.

Hence, an intermediate balance of neutralization is required to tailor the performance characteristics to the desired result. Optimally the polymer would be minimally neutralized to be removed by shampoo and no more, so that the remaining acidic groups do not contribute to hygroscopic absorption of moisture resulting in tackiness, plasticization by water on the polymer resulting in hair droop, and lastly, hazy film clarity due to incompatibility of water with highly hydrophobic ester-containing polymers like butyl (meth)acrylate monomers.

Likewise, the type of neutralizer will affect the performance attributes of the hairspray resin. For example, dimethyl-stearamine is a highly hydrophobic neutralizer that is only compatible in high VOC and hydrocarbon propellant -containing formulations. If water is still entrained in the film upon drying with

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

this neutralizer, then a cloudy film will result. Long chain hydrocarbon length may still be required if the polymer is brittle, and more flexibility is needed to obviate this shortcoming.

Similarly, 2-amino-2-methyl propanol(AMP) and tri-isopropanolamine(TIPA) are common organic neutralizers used in the industry today but are typically delivered in water for safety reasons. However, the presence of water results in incompatibility with butyl/longer chain stearyl-(meth)acrylate comonomers. Given these consequences, both the polymer and the neutralizer manufactures will test the performance attributes relative to type and level of neutralization as part of the normal testing regime, and this information is usually included in their product brochures for evaluation by the hair care companies in their selection process for new hairspray formulations (*23*, *24*).

If this neutralization issue was not complicated enough, then include hydrocarbon compatibility from the propellant system used. The propellant system could consist of simple organics like butane/propane or more costly dimethyl ether(DME) to complex fluorocarbons. However, with on-going and ever changing regulatory requirements, formulators are moving towards the use of hydrofluoroolefins as propellant systems in the future, since these do not contribute to either global warming or ozone-depletion.

Usually these propellants have some solubility in the alcoholic formulations and therefore alter the solubility of the polymer in the formulation. This is known as hydrocarbon compatibility or propellant-tolerance. If the polymer is not completely soluble in the single or two-phase formulation, there is a higher probability it will plug the orifice of the spray nozzle due to microparticulate formation resulting in complete failure of delivery or an unacceptable spray pattern as the formulation sputters out onto the hair. This can arise for a number of different reasons. For example, the choice of neutralizer may affect the polymer's solubility in a particular propellant/solvent system as can be seen in Figure 5. This behavior can result from the difference between a soluble polymer/neutralizer pair to a miscible, or completely immiscible polymer/neutralizer pair resulting in precipitation or formation of microparticulates in DME depending on the polarity, hydrophilicity, or diluents of the neutralizer itself.

For instance, alkyl-amine neutralizers that do not contain water are more hydrophobic and are typically more soluble in hydrophobic anhydrous systems, while more polar alkanol-amines that contain water are more soluble in hydrophilic hydroalcoholic systems. Furthermore, the alkyl-propellant system such as butane is not compatible with polar formulations with a high content of water. Therefore, incompatibilities can occur with different components of the formulation. Likewise, the neutralizer can alter the overall polarity of the polymer when neutralized to form a particular polymer/neutralizer pair that it is now incompatible in the formulation and/or the propellant system/formulation pair.

Moreover, the temperature profile on a polymer's solubility can occur such that the polymer is no longer soluble/miscible in the solvent/propellant system. This behavior is known as the Cloud point of a particular polymer in a particular solvent. The cloud-point temperature (CTP) is the temperature at which phase separation starts. At this temperature the solution becomes turbid/cloudy

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

due to the formation of polymer-rich emulsion droplets or aggregation into microparticulates. Cloud-point is dependent on polymer concentration, solvent used, and other additives that maybe present, and is temperature-dependent. Usually increasing temperature increases the solubility of a low molecular weight compound, but for polymers this is not always the case. For instance, another basis for this outcome can be due to the alteration of the polymer's conformation in solution whereby at elevated temperature a polymer will be more extended and expose associative regions within the polymer chain that can lead to interchain flocculation and subsequent precipitation. This occurrence is usually reversible and the polymer will redissolve back into solution at lower temperature because the polymer refolds back into its original conformation thereby hiding these associative regions within the polymer chain. The lowest cloud point is referred to as the lowest critical solution temperature (LCST), while the highest temperature is known as the HCST.

This cloud point behavior affects the freeze-thaw stability of the formulation too, and it is monitored during the long-term stability testing regime or advanced heat ageing studies for most hair care products. The consequence of this property can therefore be affected by the geographical locale, such as hot versus cold climates, so that the cloud point of the polymer needs to be evaluated as this outcome can limit the use of the product to specific regions of the globe due to its local temperature.

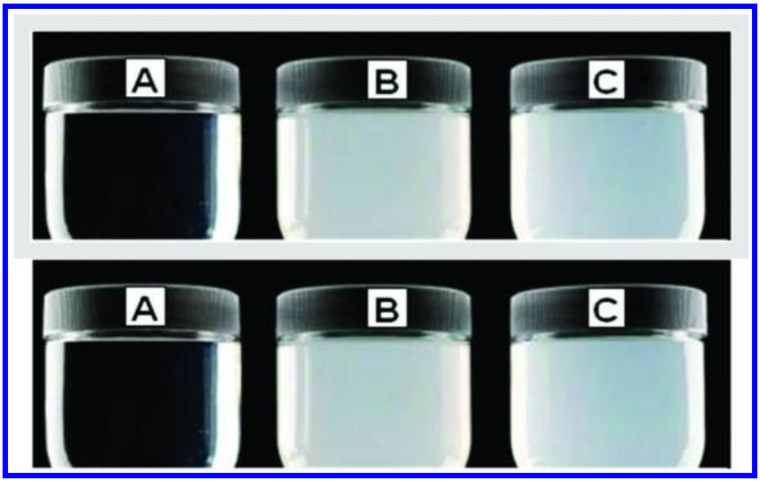


Figure 5. A-anhydrous AMP, B-Triethanolamine, C-Tri-isopropanolamine.

A number of analytical tests can be applied to evaluate how efficiently the polymer is removed from the hair by shampooing. The simplest way to evaluate the formation of a shampoo resistant residue in the whole formulation is to use

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

a clear glass slate/slide. A specific amount of sample is placed onto the glass and allowed to air-dry to a film. At this point, a number of other observations on the film can be made, such as film clarity and hardness, but we shall focus on removability for now.

The glass slide/support is then shampooed and rinsed to mimic washing and finally air-dried. If the resin/formulation comes off and leaves no observable residue it passes this test, but if not, it fails. This simple pass/fail test is still in use today by cometic chemists. If one wants to be more sophisticated, then the slide can be placed into a UV-visible spectrophotometer and the percent transmittance can be determined to give a less subjective evaluation. However, since hair is a different substrate than glass the removability of the resin itself is still typically analyzed on a hair tress and the feel of the hair determined after shampooing and drying to ensure removabilty.

In cases where removability fails, mid-infrared spectroscopy (mid-IR) for organic compound identification can be used to determine if there is any inhomogeneity within the polymeric material, or if some other incompatible organic components are present. X-Ray fluorescence spectroscopy (XRF) can be used as a complementary technique for inorganic compound identification.

In practice, if there is sufficient residue to scrape off the glass slide it can then be placed in a compression cell by sandwiching the sample between two diamond windows and pressurized until transmissive. Fourier-transform IR microscopy can then be used to obtain a fingerprint of the organic functional groups present by their characteristic group absorption frequencies.

Likewise, the thin residue can be analyzed directly from the glass slide by using an Attenuated Total Reflectance (ATR) accessory that is only a surface analysis method. The IR beam is transmitted through a ZnSe crystal to generate an evanescent wave along the surface of the crystal penetrating roughly 2 microns deep into the sample that is in direct physical contact with the crystal (*25*). The wavelength of energy absorbed by the sample is directly correlated to the vibrational excitation generated by stretching, bending, and wagging of the sample compound's functional groups allowing identification of the chemical entities present. Since this is a non-destructive analysis, it can be followed by XRF for inorganic identification.

In the best case scenario, X-ray fluorescence spectroscopy can be used to identify inorganic elements that maybe correlated back to known inorganic species present in the sample, but this is a destructive technique so that is why mid-IR is used first on a given sample. This technique works by irradiating the sample with X-rays, the effect of which is to kick out an electron from the inner valence shell of an atom within the molecule. This leaves an electronic void in the inner shell that needs to be refilled by another electron to relieve this unstable high energy state. Therefore, an electron from an outer valence shell fills this void and, in doing so, emits a characteristic fluorescence photon due to its decay to the lower atomic orbital. Multiple emissions are observed as the outer shell electrons cascade to their lower orbital's in turn, thereby elucidating the element's identity.

Depending on the atom's identity, its total number of valence shells and associated electrons , and which electrons decay back to fill the unoccupied orbital provides information used to deduce which elements and at what quantities are

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

present in the sample. As one would expect, heavier atoms/elements with an abundance of electrons are more sensitive to this technique because of their larger electronic-cloud than lighter atoms/elements. Typically, elements including and higher than sodium are preferentially detected in a quantitative fashion. Hence, inorganic analysis of helium, lithium, beryllium, or boron in a sample is less sensitive by this method. Even with this limitation, XRF is still an extremely powerful tool.

Once the delivery and removability of the polymer have been established, the stiffness and durability of hold are the next critical parameters needed for evaluating styling performance. Stiffness and Durability are by far the most important performance attributes for any hairspray resin, so quite a number of tests are performed to evaluate these characteristics. Before we describe these in-depth, let us look at styling from a holistic view.

Figure 6, depicts the two types of fixation structures generated by an aerosol mist falling upon hair fibers that have already been styled. In particular, when two fibers cross over each other a spot-weld is generated to hold them in place. Likewise, the aerosol droplet can be deposited along two parallel fibers allowing it to flow along the two hair shafts to make a seam-weld. Both of these structures have different physical characteristics with respect to stiffness and durability (*26*).

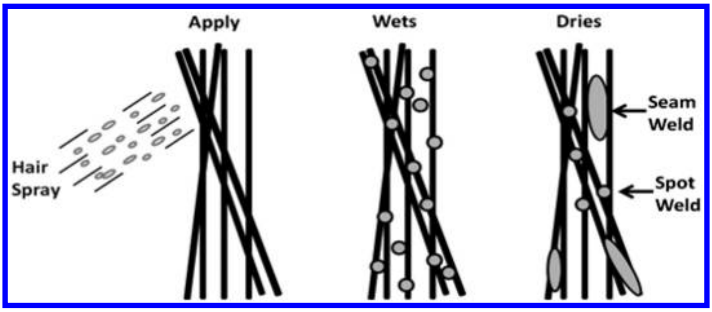


Figure 6. Examples of seam-welds and spot-welds of hair fixative spray.

Depending on the hairstyle, both spot-welds and seam-welds are formed but to differing degrees. Seam-welds will arise if the formulation has a low surface tension and low solution viscosity to easily wet the hair fiber This creates the clumping effect so often desired by people with curly hair since they want their hair to look curly instead of frizzy. These types of products also impart volume to the hair by increasing stiffness from the root, which lifts it away from the scalp. This type of hold is very susceptible to disruption due to physical manipulation, such as combing, touching and windy conditions.

In contrast, spot- welds can arise from either high surface tension formulations or extremely small particle size droplets that quickly evaporate before they can wet the hair fiber properly. Usually, both are present to give a conglomerate of fixation points to the whole hair fiber assembly.

Theoretically, a high preponderance of spot-welds should give rise to a more flexible hold than seam-welds, however in reality spot-welds are more susceptible to high humidity given the higher surface area of the deposit so that it fails the benchmark high humidity curl retention test. Therefore, the strength of hold is usually controlled by the amount of polymer in the hairspray formulation, and the identity of monomers chosen to construct the polymer along with its molecular weight and glass transition temperature rather than the spray pattern of the nozzle and the wetability of the formula onto the hair fiber.

The glass transition temperature T_g of a polymer is an important physical characteristic of the resin with respect to temperature. Strictly speaking it is defined as the temperature where an amorphous polymer will crossover from a hard or brittle glassy behavior to a more pliable or rubbery consistency. This occurs before an actual melting point is ever reached, even in a crystalline polymer. It represents the amount of energy/temperature needed to initiate rotational motion of the functional groups present within a polymer molecule thereby allowing for individual chains to slide past each other more easily.

This behavior is clearly demonstrated by comparing poly-methyl methacrylate T_g 85-165°C versus poly-methylacrylate T_g 14-15°C. The presence of the methyl group attached to the polymeric backbone hinders both rotation about its own backbone, but more importantly it hinders the slip of individual polymer chains past each other giving rise to a significantly higher Tg for methacrylate polymers than acrylate polymers. Furthermore, as the pendant functional group size increases from methyl to butyl methacrylate the T_g drops from 110 °C to 20 °C due to more space between polymer chains permitting for easier slip between chains (*27*).

Therefore, the T_g of a polymer is an inherent property of its monomer constituents, and tacitly how large the polymer molecule actually is, such as its molecular weight. At temperatures below its T_g the polymer will be hard and less pliable, while at temperatures above its T_g the polymer will be more flexible and elastic. Hence, stiffness can be controlled by the polymer chemist by design into the polymer chain by the choice of monomers used to either exhibit a strong stiff hold or a soft flexible hold.

The polymer chemist can also manipulate the T_g of a polymer by taking a stiff high T_g polymer and adding a plasticizer to it. This is usually a small molecule that inserts itself between polymer chains to increase the free volume or interfacial space between chains. It has a net effect to lower the frictional forces between the chains and lower the apparent T_g observed thereby making it more flexible and less brittle. Let us look at two practical examples of this behavior.

First, if we compare the two chemical structures depicted in Figure 4, for polymers A versus C, the only difference is the length of the side-chain ester group being completely ethyl opposed to a combination of butyl and ethyl. From Table I, we observe that the apparent T_g drops from 102 °C to 96 °C going from 100% ethyl to 20% butyl/80% ethyl ester incorporation. This becomes more obvious if we compare the PVP/VA copolymer composition in Table II.

Polyvinyl acetate(PVA) exhibits a T_g around 30° C, while PVP is around 170 ° C. As the content of the lower T_g monomer vinyl acetate VA is decreased while the higher T_g monomer vinylpyrrolidone VP is increased results in a significant

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

rise by 48 °C in overall T_g of the resultant copolymer is observed. Hence, the overall flexibility or stiffness of the polymer can be controlled by the identity of the monomers used along with the concentration of the monomers used to construct it.

Table II. Comparison of T_g versus PVP/VA composition

PVP/VA Grade	*335*	*535*	*635*	*735*
T_g	69 °C	96 °C	106 °C	117 °C
VP to VA ratio	30/70	50/50	60/40	70/30

Likewise, if we evaluate a homopolymer of polyvinylpyrrolidone PVP versus its molecular weight grades demonstrates that the T_g for a low molecular weight PVP of 9,000 daltons is 130 °C, whereas a high molecular weight PVP of 3 million daltons is 176 °C, Table III. The largest difference observed in T_g is going from low molecular weight to intermediate, K15-K30 (*28*). Once you reach intermediate to high molecular weight the difference in T_g is not that significant, Table III.

Table III. Comparison of T_g versus molecular weight for PVP homopolymers

PVP Grade	*K-15*	*K-30*	*K-60*	*K-80*	*K-90*	*K-120*
T_g	130 °C	163 °C	170 °C	172 °C	174 °C	176 °C
M. wt.	9,000	60,000	345,000	435,000	1 million	3 million

So both its chain length and the monomers used to construct the polymer will give rise to the observed T_g and thereby its relative stiffness. Focusing our attention back to Table I, demonstrates that most of the hairspray resins exhibit an apparent T_g between 96-135 °C. Therefore, at ambient temperature of 25-30 °C the polymer is rigid and exhibits a stiff hold. However, we also observe from Table I that two formulations contain two different polymers with drastically different T_g values. In particular, hairspray resin D contains PVP/VA with a T_g of 115°C and a Stearyl-methacrylate type copolymer exhibiting a T_g of 38°C. Likewise, hairspray resin E contains an Acrylate copolymer with a T_g of 97°C and a type Hydroxy-acrylate copolymer exhibiting a T_g of 52°C.

The use of a blend of polymers with dramatically different T_g values has gained popularity lately since the higher T_g polymer maybe stiffer but also brittle resulting in a lack of durability to hold. Similarly, the lower T_g polymer maybe more flexible at ambient temperature of 25-30 °C , but also exhibits less stiffness. If the flexible polymer provides durability of hold while the stiffer polymer provides

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

strength of hold, then it is possible that a blend of polymers could achieve the best of both worlds. A stiff hold without being brittle, yet flexible enough to be manipulated for styling (*29*).

Tacitly tied to the T_g is the solution viscosity, which in turn is correlated to its chain-length or molecular weight. For hairsprays there is an optimal range of viscosity in order to achieve the proper spray pattern by the nebulizing orifice of the spray nozzle heads that are commercially available. Therefore, it is not surprising that all the commercial hairspray polymers listed in Table I, exhibit a specific viscosity around 0.40 to achieve this target viscosity. The values listed are determined as a 1 wt.% polymer in ethanol by capillary viscometry at 25 °C, with or without salt to remove polyelectrolyte effects. Therefore, since ethanol exhibits an absolute viscosity of 1.074 centipoise(cp) or millipascal-sec at 25 °C, then the absolute viscosity of these polymer solutions from Table I are in the range of 2.5-2.7 cps at 25 °C.

Similarly, the molecular weight ranges of these polymers are approximately in 40-125 kilodaltons(Kda) or 40,000-125,000 amu. The large breadth of the chain length is a consequence that resistance to flow, aka viscosity, is not just related to chain size but also interactions between chains as well as those with the surface of the evaluating instrument. Hence, the monomer(s) identity influence these interactional forces, such as hydrogen-bonding, ionic salt interactions, dielectric, Van der Waals, etc…, to the observed viscosity.

Moreover, the apparent viscosity observed can be dramatically altered by the presence of a very small fraction of high molecular weight polymer, so the polydispersity or variability of the chain size is also involved, along with the physical architecture such as linear versus branched, comb vs. brush, short-chain vs. long-chain branching, and so on. Since the complexity of the solution properties of polymers are beyond the scope of this text, it will suffice to say that the viscosity of polymer solutions are typically included into sales specifications to ensure the least variability in product performance on a batch to batch basis.

The next performance attribute of a hairspray polymer to consider is stiffness versus brittleness. Scientifically, a polymer is stiff because of the lack of free rotation about the polymeric backbone of the molecule due to either a compact rigid methyl group or ring-structure along the mainchain, or due to compact yet rigid pendant groups(isopropyl or pendant ring structure as in PVP) preventing rotation between neighboring atoms along the backbone. In addition to this, how difficult different polymer chains can slip past each other or ionic interactions(salt bridges) and or hydrogen-bonding interactions between polymer chains will give rise to stiffness too, and results in a higher T_g polymer (*27*).

However, a polymer is brittle if the interchain interactions are so strong that neighboring chains are in intimate physical contact, and there are no free-volume voids or interfacial spaces for groups to rotate or move around when a stress is applied. Hence, fracture of the overall film should occur along the least path of resistance, which should be predominantly along the interchain interactions.

In contrast, a flexible polymer exhibits free rotation about its polymeric backbone of the molecule, and can contain larger but more flexible pendant groups like straight chain alkyl (n-butyl or higher stearyl group) or alkoxide(polyethylene glycol) groups that can move around due to voids between polymer chains, resulting in a lower T_g polymer. Additionally, these larger pendant groups tend to hinder interchain interactions such as hydrogen-bonding because of their steric bulk resulting in a larger separation between polymer chains. These can be viewed as free-volume voids or interfacial spaces that permit absorption of an applied stress by rearrangement of the molecule by rotation of its backbone and/or pendant functionalities thereby being more pliable.

With this in mind, if we refocus our attention back to a high and low T_g polymer blend, we can rationalize that if the low T_g polymer chain intercalates between the two high T_g polymer chains then the overall result would yield a larger separation between the two stiff polymer chains and generation of interfacial spaces for rearrangement/movement when stress is applied, hence a more flexible behavior for the composite material. Likewise, the composite material containing these two polymers would also exhibit a stiffer hold strength than the flexible polymer alone since the higher T_g polymer can be viewed as stiff rods within a gum-like semi-solid of the lower T_g polymer (*28*).

In summary, compact rigid functionalities that are also H-bond acceptors in comonomers such as vinylpyrrolidone, methyl methacrylate, and ethyl maleate are used in conjunction with H-bond donors like (meth)acrylic acid, maleic acid or maleate half acids results in stiff high T_g polymers that are also brittle due to tight H-bonding interactions between polymer chains. Conversely, bulky yet flexible functionalities in stearyl-methacrylate, n-butyl or t-butyl acrylate are copolymerized with (meth)acrylic acid results in lower T_g polymers, which are more flexible by providing more space between polymer chains thereby allowing for polymeric mobility of functional groups to slip past each other more easily.

With respect to adhesion to hair, all of these polymer functionalities listed in Table I are H-bond acceptors that can interact with the H-bond donor groups in the Keratin proteins on the hair surface (*30–32*). In particular, the side chains of Threonine, Serine, Tyrosine, and Arginine can readily participate to form H-bonds with the polymer's carbonyl groups, since there is a high preponderance of these amino acids in the cuticle layer, Table IV.

One special case worth mentioning is copolymer B in Figure 4, comprised of H-bond donors like t-butylaminoethyl methacrylate, t-octylacrylamide, glyceryl methacrylate with H-bond acceptors methyl methacrylate and acrylic acid results in a stiff high T_g polymer 135°C even though these bulky comonomers should give rise to a lower T_g copolymer. This result arises from the finding that if H-bond donors and H-bond acceptors are equally spaced away from the polymer's backbone then they can still give rise to tightly bonded intramolecular interactions within the polymer chain itself resulting in a stiffer and higher T_g copolymer. But the larger bulky groups of t-butylaminoethyl and t-octyl located further away from both the H-bonding network and polymer backbone hinders interchain interactions thereby giving rise to a durable hold copolymer instead of a brittle one.

Analytical evaluation of stiffness, toughness, brittleness, and durability are some of the most important attributes for a hairspray polymer. Therefore, over the years subject tests like ***"initial crunch"*** of a hair curl with fixative applied compared to multiple compressions thereafter, has been replaced with more sophisticated tests using a tensiometer setup devised by Jachowicz *et al*, known as ***Omega-Loop*** testing, or Dynamic Hairspray Analysis (*33–35*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Table IV. Amino acid composition of Cuticle, Cortex, and Medulla Proteins

Amino Acid	*Cuticle Mole%*	*Cortex Mole%*	*Medulla Mole%*
Alanine	0.0	4.3	5.7
Arginine	4.2	6.1	2.6
Aspartic acid	3.3	5.2	6.7
Cysteic acid	0.8	0.3	0.0
Glycine	7.1	5.6	4.3
Glutamic acid	9.5	11.7	38.7
Half-cystine	24.3	16.8	0.0
Histidine	0.0	0.8	1.4
Isoleucine	2.1	2.9	1.9
Leucine	4.8	5.9	10.0
Lysine	0.0	2.5	10.6
Methionine	0.4	0.6	0.6
Phenylalanine	1.1	1.6	0.0
Proline	11.5	7.7	2.3
Serine	16.2	12.4	3.9
Threonine	6.0	7.7	2.0
Tyrosine	1.5	2.1	4.6
Valine	7.3	5.8	4.6

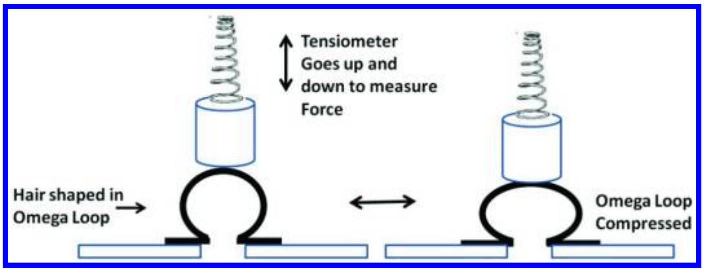


Figure 7. Omega Loop setup with fixative spray on hair.

The experimental setup in its simplest form is depicted in Figure 7. The method utilizes hair tresses formed in Omega Loops. A set quantity of material is applied onto the hair and allowed to dry under controlled humidity. The

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

mechanical properties of the treated omega loops are then measured with the texture analyzer or tensiometer. The probe is programmed to depress the tress to a certain depth corresponding to a specific back pressure or height and then retract. As the probe goes through its cycle the texture analyzer measures the forces that the probe encounters.

The following physical parameters are calculated from the force data:

F0 – maximum force of untreated hair
F1 - maximum force in the 1st deformation of fixative-treated hair
F10 - maximum force in the 10th deformation of fixative-treated hair
F1/F0 = stiffness parameter
F10/F1 - ratio of maximum forces in the 10th to 1st deformation
Stiffness ratio = Resiliency
E10/E1 - ratio of elastic modulus or resistance to change in the 10th to 1st deformation = Flexibility
H10/H1 - ratio indicating plasticity or deformity = Extendibility

The elasticity and flexibility of virgin versus polymer-treated hair fiber assemblies can be investigated by employing hair shaped into omega loops, or even straight hair. The mechanical testing procedure consists of subjecting omega-loop-shaped hair to multiple bending deformations at 25% strain in a commercially available texture analyzer, model TA-XT2, from Texture Technologies Corp., with a load sensitivity of 0.1 g. XTRA Dimensions software, version 3.7, from StableMicro Systems or equivalent, is used to collect and display the data.

A total of ten deformations are typically carried out, and elasticity or flexibility parameters can be evaluated from the data such as (a) the force at 8% deformation, typically within the elastic region of bending deformation for hair shaped into an omega loop, (b) maximum force in the first (F(1)) and tenth (F(10)) deformation cycles, (c) elastic modulus in the first (E(1)) and tenth (E(10)) deformation cycles, and (d) the change in hair sample dimensions between the first (H(1)) and tenth (H(10)) deformation cycles.

Parameters such as stiffness ratio of untreated versus treated hair were employed to characterize the treated hair tress' resiliency F10/F1, flexibility or resistance to breakage E10/E1, and plasticity or deformity H10/H1, respectively.

The data obtained can then be plotted as force/distance or stress/strain curves as in Figure 8. For a brittle polymer, it is readily apparent that during the first deformation the polymer film shatters as in graph a), when compared to a flexible polymer in graph b). But this shattering effect is believed to be associated with the breakage of [hair-polymer-hair] junctions, not that of the polymer is coming off the fiber itself.

Additionally, the force ratio of untreated hair to fixative-treated hair measures the flexibility of untreated hair to the rigidity of treated hair. This force ratio can also be described as a stiffness parameter. The ratio of F10/F1 is the flexibility of the treated fiber assembly that also reflects the force required for interfiber bond breakage as a result of the deformations imposed. This is called the stiffness ratio or resiliency of the [hair-polymer-hair] contact points.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

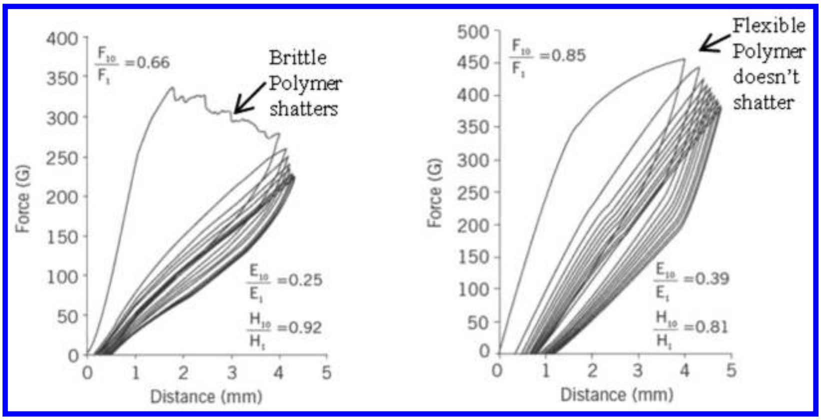


Figure 8. Dynamic Hairspray Analysis of hair with a) brittle fixative or b) flexible hairspray applied.

The same data can also be described in terms of initial height (H0) of the omega-loop to that after the first deformation, H1/H0, followed by subsequent cycling H2/H0, H3/H0,etc…. The resulting change in deformation distances H10/H1 is calculated as (2xH1 – H10/ H1) reflects the sample's plasticity or deformity where a ratio of one would indicate completely flexible with no plasticity or deformity observed to that of zero where completely inflexible and plastic or deformed.

Lastly, the slope of the force curve F1 corresponds to the elastic modulus E1. Likewise, the change in the **slope** of each force curve F1 to F10, corresponding to E1 to E10, and reflects the sample's elasticity or its propensity/resistance to change its shape due to the deformations imposed. This data can be put into tabular form, as shown in Table V.

Table V. Stiffness, Resiliency, and Plasticity Parameters for Hairspray Treated Hair

Sample	*F1-max Grams*	*F1 @ 1mm Grams*	*F10/F1 Stiffness*	*E10/E1 Resiliency*	*H10/H1 Plasticity*
Brittle Polymer A	**345 ±5**	**200**	**0.66 ±0.01**	**0.25 ±0.01**	**0.92 ±0.01**
Flexible Polymer B	**450 ±1**	**225**	**0.85 ±0.01**	**0.39 ±0.01**	**0.81 ±0.01**

This type of data can be evaluated under a variety of experimental conditions, such as 50 vs. 90% RH, temperature, solvent composition, neutralizer used, etc… One extremely interesting finding using this methodology was the comparison of 100% ethanol(VOC), 80% VOC, and 55% VOC formulations. It was found that as the water content increased from 0% to 45%, the strength of the polymer's hold increased, even though the dry time/tack time were longer. In fact, the tack time could easily be calculated by the negative force exerted on the probe as it tried to rise back off the omega-loop, while the dry time could be resolved as the maximum force without this negative oscillatory force, as summarized in Table I.

Furthermore, it was observed that as the water content in Low VOC formulations increased from 0% to 45%, the strength of the polymer's hold onto the fiber increased. This finding was rationalized as providing more intimate contact between the polymer and the surface of the hair fiber, along with the swelling of the hair fiber so that the polymer exhibited better adhesion to the cuticle scales and defects areas on the hair fiber itself (*34*).

Additionally, it was observed that the type of hair could affect the strength of the polymer's hold. In particular, fine Caucasian hair exhibited better hold when treated than thicker Asian hair, when the opposite result was expected. After further in depth analysis, it was found that the greater surface area of fine hair was responsible for better adhesion of the polymer to the hair surface thereby generating a higher population of fiber-polymer-fiber junctions, as well as a denser packing of the fibers together due to the smaller diameter of the fine hair fibers, additively these factors result in better hold than to thicker Asian hair (*34*).

In contrast, the lager diameter Asian hair results in a lower number of fibers per unit weight compared to fine hair, so they do not pack as dense as fine hair, thereby resulting in a lower population of fiber-polymer-fiber junctions, so it is less stiff than hairspray treated fine hair. After obtaining these results it was also realized that when hair tresses are constructed they are assembled by weight, not by number of fibers per tress. Consequently, Asian hair tresses would contain a lower number of fibers/tress because of their larger diameter, while fine Caucasin hair would contain a higher number of fibers/tress.

Therefore, when comparing between hair types, both a weight average and a number average of fibers are required to truly understand the system under investigation, since they both will have an impact on the observed results obtained. These findings are a testament to the versatility and reproducibility of this technique to generate meaningful scientific data about Hair Properties with respect to Personal Care Fixatives (*35*).

Another inherent and important property of the polymer is its refractive index that correlates to both its gloss or shine, as well as the clarity of the dried polymer film. The electronic cloud surrounding five and six membered rings are very good reflectors of visible light and yield very high refractive indices of 1.45-1.55 resulting in a mirror like reflection of light that adds luster and shine to hair. Luster is another optical psychological cue to how healthy and young the individual is. Therefore, this performance attribute is desired in a hairspray resin too. From a reference perspective, healthy shiny hair exhibits an RI around 1.50

Table VI summarizes the refractive indices for several homopolymers indicating the clarity and how glossy the polymer film displays. The highest results are obtained with aromatic ring structures like poly-styrene, and halogenated poly-aromatics (*36*). Likewise, halogenated monomers with large electron clouds also exhibit higher RI values in an additive fashion as demonstrated by polyvinyl-chloride-1.54 and vinylidene chloride-1.60.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

The next groups of high RI polymers are saturated ring structures like PVP-1.53 and poly-e-caprolactam-1.53. It's noteworthy to mention that although both PVP and PVCAP have almost identical RI values, but PVCAP films are still shinier than PVP. We believe this is due to how smooth the surface of the film is, resulting in more specular reflection than PVP as described below. Similarly, methacrylate esters 1.49-1.46 are slightly more clear and glossy than acrylates esters 1.48-1.45, whereas only a modest drop in clarity/gloss is observed by increasing from the chain-length from ethyl to stearyl methacrylate 1.48 to 1.45, respectively.

Table VI. Refractive Index for Select Homopolymers

Polymer	*Refractive Index*	*Polymer*	*Refractive Index*
Poly-styrene	**1.592**	**Poly-2-chlorostyrene**	**1.6098**
Poly-vinylchloride	**1.539**	**Poly-vinyldichloride**	**1.600**
Poly-e-caprolactam	**1.530**	**PVP**	**1.530**
Poly-methylmethacrylate	**1.489**	**Poly-methylacrylate**	**1.479**
Poly-ethylmethacrylate	**1.485**	**Poly-ethylacrylate**	**1.469**
Poly-n-butylmethacrylate	**1.483**	**Poly-n-butylacrylate**	**1.466**
Poly-t-butylmethacrylate	**1.464**	**Poly-acrylic acid**	**1.527**
Poly-stearylmethacrylate	**1.452**	**Poly-vinyl acetate**	**1.467**
Poly-t-octylacrylamide	**1.446**	**Poly-methylvinyl ether**	**1.467**
Poly-hydroxyethyl methacrylate	**1.453**	**Poly-hydroxypropyl methacrylate**	**1.446**

Therefore, it is not surprising that the stiffer high T_g monomers used in the hairspray resins illustrated in Figure 4, also exhibit excellent clarity and gloss as demonstrated by their high refractive indices 1.49-1.42, Table I. Moreover, even low T_g monomers still exhibit superb clarity and gloss 1.46-1.45. Hence, outstanding clarity and gloss are essential performance attributes for any hairspray polymer, regardless of its stiffness or flexibility of hold.

Not only is the gloss and clarity of the polymer film important, but another important optical property is the ratio of specular to diffuse reflection. This gives rise in part to the notion of luster mentioned earlier. This concept is illustrated in Figure 9. In particular, the smoothness of the surface can be elucidated by its specular reflection, while the roughness of the surface can be evaluated by its diffuse reflection. The higher the ratio of specular/diffuse reflection, the greater the smoothness of the surface, which in turn also indicates how well the hairspray formulation wets the hair and creates a smooth even film covering the hair fiber (*37*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

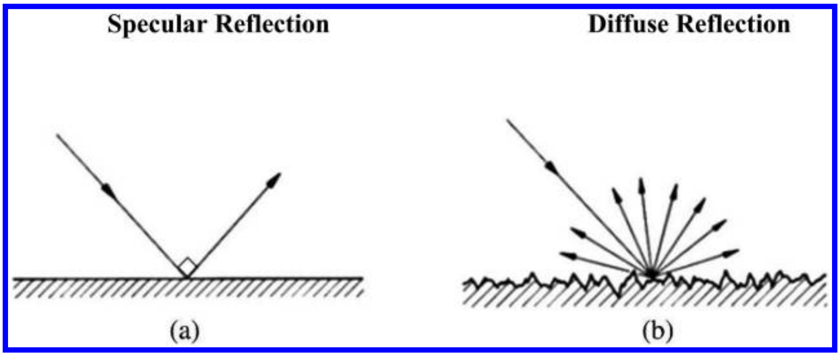


Figure 9. Specular Reflection versus Diffuse Reflection of Light.

But analytical evaluation of luster on hair is more complex than just shine/ gloss or refractive index alone. In particular, the physical integrity of the of the hair fiber itself will affect luster. For example, the repetitive stress exerted by the daily brushing and thermal styling such as blow-drying, curling or flat-ironing hair will damage the outer surface of the hair fiber known as the cuticle. This damage results in cracking, pitting, and sometimes complete loss of some of the scales resulting in a dull and flat appearance to the hair due to diffuse reflectance. Products to repair the damaged hair are commercially available and will be covered in the conditioning polymers section. Hairspray polymers that can flow into and level these defect areas, along with refractive index matching of the resin to hair itself 1.5 will enhance luster.

For example, everyone has seen a spider-crack after a pebble has hit a car windshield. Because air has a different refractive index(1.0) than glass(1.49) it refracts visible light and is readily observed. If you fill in the void occupied by air with a transparent material with the same refractive index as glass results in the crack's complete disappearance from the windshield. This is refractive index matching. If the polymer can fill in these defect areas of the hair's cuticle, the damage will appear to disappear thereby enhancing luster. Hence, another reason why the refractive index of the hairspray resins is also important. Similarly, hair fiber alignment is also important to luster. If the fibers are aligned in a parallel fashion then a reduction in diffuse reflection occurs thereby increasing specular reflection and shine.

Luster is commonly defined as the ability of a given material to produce a bright reflection. But there is also a geometrical component to luster, such as the reflection band occurs at the peaks of wavy hair and not at the trough regions. Hence, luster contains both specular and diffuse components, while gloss measures only specular reflection on a flat surface. This differenc becomes more appearant as depicted in Figure 10. Gloss would therefore measure the specular reflection as the shine-band, and ignore the chroma and diffuse bands. Therefore, gloss could be readily defined by the Refractive Index of the polymer alone, but that would only tell half the story. Since luster also contains the diffuse components of the chroma and diffuse bands, the optical clarity of the film itself with respect to its optical transmitivity needs to be considered as well. This is one reason why the optical clarity of the film is evaluated as a performance parameter since it contributes to this luster attribute. So in Hair Care, Luster is actually the additive width of the Shine, Chroma, and Diffuse bands along with their summed intensities. The larger and more intense these bands reflect back the optical light, the more Luster is perceived by the observer.

To analytically evaluate luster requires both optical and digital analyses, and can be achieved by mounting a hair tress onto a cylinder. A collimated light source providing an incident angle of approximately 30° is situated relative to the optical axis of the digital camera or detector. Linear polarizers are placed in front of the light source and the camera. This permits detection of all the reflected light (specular and diffuse) when the polarizers are parallel, and diffuse reflection when they were perpendicular (*38*, *39*).

This geometric arrangement permits deconvolution of the observed polarized light into three component bands that are spatially separated at specific locations along the hair fiber. The **shine-band** occurs at the incidence angle of reflection by specular reflection off the surface of hair, the colored **chroma-band** occurs by the penetration of light into the hair fiber and reflected back at the rear of the fiber. This band is colored because the light passes thorough the melanin pigment inside the fiber. Likewise, the colored **diffuse-band** results from diffuse reflection by refraction of light entering and leaving the hair fiber, as depicted in Figure 10, (*40*). Using polarization and digital imaging permits these individual components to be quantified in a more analytical manner rather than the variable subjective evaluation by visual analysis.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

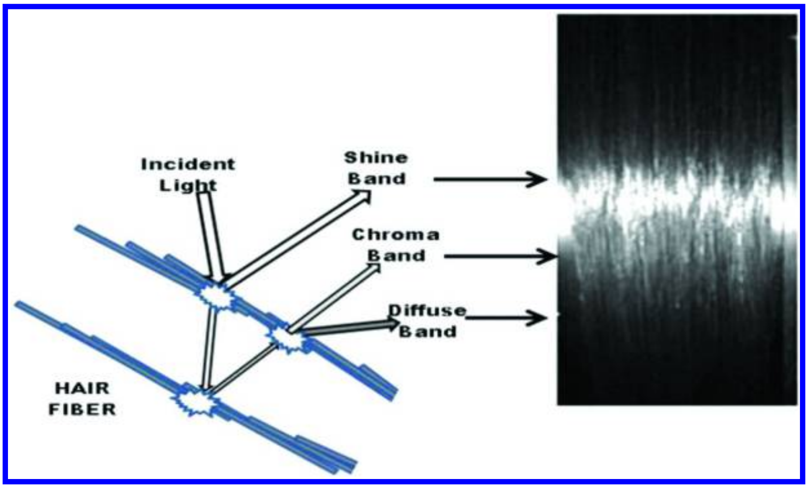


Figure 10. Specular Reflection versus Diffuse Reflection of Light on Hair.

The pixilated image from this experimental setup can then be analyzed by image analysis software programs to obtain intensity/luminosity curves along the fiber that can be integrated to yield luster parameters quantitatively. Its noteworthy, that the various hair types and coloration of the hair will influence these values.

In particular, hair that lacks any pigment such as natural white or lightly colored blonde hair types will yield two specular reflection bands corresponding to the front and back-face reflections (*41*), in comparison to red brown, and black hair colors.

Likewise, the hair's color or pigmentation will also affect the luminosity detected, since darker pigmented brown or black hair will absorb some of the light from the source naturally, and hence yield lower luminosity curves. Therefore, this type of luster analysis needs to be performed on individual hair types and/or colors to yield meaning scientific data, and cannot be directly compared across all types/colors simultaneously. Usually, this analysis is best suited for comparison of treated versus untreated hair with various hair styling ingredients, but has the added advantage in that it is on the actual substrate, instead of a surrogate material.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Gels and Mousses

A hair gel is a styling product that is used to stiffen hair into a particular hairstyle. Hair gels are probably one of the favorite styling products of those who prefer to wear their hair in curls. They help to define and sustain curl pattern and provide shine, while minimizing frizz. The properties of hair gel are highly dependent upon which ingredients and at what level are present, the hair type upon which it is being used, and the climate in which the consumer lives.

The composition of a hair gel includes water as the main ingredient, followed by polymers for film-forming. Film-forming polymers can include lactam-based, polyurethane-based, acrylic copolymer, polyacrylates, acrylates copolymer, and other copolymers are also all fixative agents found in hair gels. Emulsifiers for non-water soluble components, viscosity modifiers and thickeners, such as carbomer, fragrance, preservatives, and additives used to impart moisture, shine, and UV protection, and to modify the properties of the film that is formed.

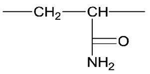
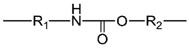
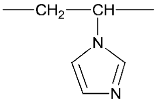
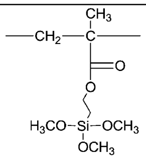
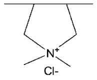
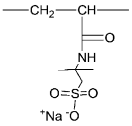
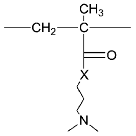
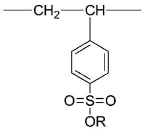
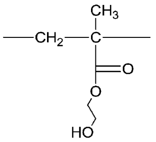
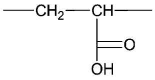
Even with all its active and inactive ingredients, a hair gel would be virtually clear and colorless if a colorant was not added. The color of dye a manufacturer chooses for its gel is more the result of branding than anything having to do with the product's function. Some manufacturers choose bright colors, like yellow, orange and blue, to market their products to young consumers. Others choose black or brown to match the hair color of their target audiences. Still other manufacturers leave their gels colorless or white for a classic appearance. The end result is always a translucent product, however. Since gels are nearly odorless on their own, it's not uncommon for manufacturers to add perfume to their formulations for a light, added scent.

It should be pointed out that how a product is applied to the hair can also influence other performance attributes that can provide auxiliary benefits. For instance, hair gels can be applied to either damp or dry hair. If added to damp hair, the gel can be spread through the hair and left to air-dry or more commonly is brushed and blow-dried. In contrast, a Mousse is a different product form that is generally applied to only damp hair, and then styled. Both product forms can impart auxiliary styling benefits such as volume, body, and shine, besides the primary benefit of hold.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Mousses are more complex product form than gels, however, all of the performance attributes and testing techniques discussed earlier still apply to both styling gels and mousses, like gloss and omega-loop testing. The only difference is the product form in which it is delivered. So we will focus on the similarities and differences between these two categories of materials, and their unique characteristics and requirements when compared to hairsprays.

Table VII. Structural Diversity of monomers used in Gels and Mousses

Monomer Name	Polymer Structure	Monomer Name	Polymer Structure
Acrylamide		**Urethanes**	
Vinyl-Imidazole		**Silicone containing monomers**	
Diallyl-dimethyl - ammonium chloride		**Sodium aminomethylpropyl sulfonate**	
Dimethylamino (ethyl or propyl) methacrylate esters or amides		**Sulfonated Styrene**	
2-Hydroxyethyl-methacrylate		**(Meth)acrylic Acid**	

First of all, styling gels and mousses are not aerosolized into a fine mist so that inhalation concerns are dramatically reduced. Therefore, a wider variety of monomers can be used to construct the hair styling polymer, Table VII. In particular, Acrylamide, Vinyl-imidazole, Diallyl-dimethyl-ammonium chloride DADMAC, Methacryloyl Ethyl Betaine, Dimethylamino(ethyl or propyl) methacrylate esters or amides, 2-hydroxyethyl-methacrylates, urethanes, silicone containing monomers and macromers, polyesters using diglycols like cyclohexanedimethanol with phthalates, and isophthalates, sodium aminomethylpropylsulfonates, and sulfonated polyesters or polystyrenes, etc…

Given the structural diversity of these monomers allows one to control even more aspects of styling, such as the tactile properties of "feel" during and after application, lubricity, and a light or heaviness to the hair itself. Additional attributes may include volumizing, root-lift, and conditioning. The importance of these tactile and styling benefits are apparent because these are experienced during application of the product onto the hair with the individual's hands, as well as the requisite styling properties needed for its ultimate performance.

Likewise, both gels and mousses can use much higher viscosity polymers than hairsprays so that the molecular weight range can be in the millions instead of the thousands for hairsprays, and/or larger polydispersities can be tolerated. Moreover, additional components are used in gels and mousses that are critical for performance such as rheological modifiers or thickeners in gels or surfactants and emulsifiers for foam-bloom in mousses.

Many polymers are rheological /viscosity modifiers themselves and are very useful in gels and mousses because they help to thicken and maintain the viscosity of the product, which gives the desired product consistency to the consumer. It is much easier to apply a styling product to one's hair if it doesn't seep between your fingers such as when scooped up as a gel or sprayed as a foam into your hands.

Likewise, the polymer scientist can manipulate the rheological profile of the polymer depending on the medium of the formulation. This is observed when a copolymer of vinyl-pyrrolidone-co-dimethylaminopropyl methacrylamide(PVP-DMAPMA) was compared to the same polymer but modified with lauryl-chloride (PVP-DMAPMA-quat) to generate its quat counterpart.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

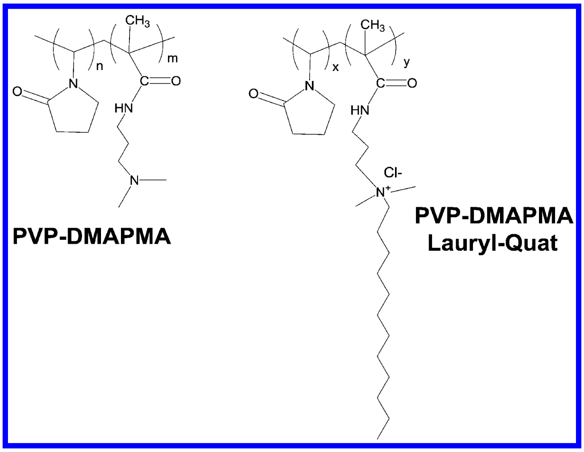


Figure 11. Chemical structures for PVP-DMAPMA and PVP-DMAPMA-Lauryl-quat.

In particular, the viscoelastic properties of PVP-DMAPMA and its hydrophobically modified analogue, PVP-DMAPMA-Lauryl-quat, Figure 11, were compared in the concentration range from 1 to 20% with dynamic and Brookfield rheometers. In addition, gel permeation chromatography/multi-angle laser light scattering light scattering data were obtained to characterize the molecular weights and radii of gyration for these polymers (*42*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

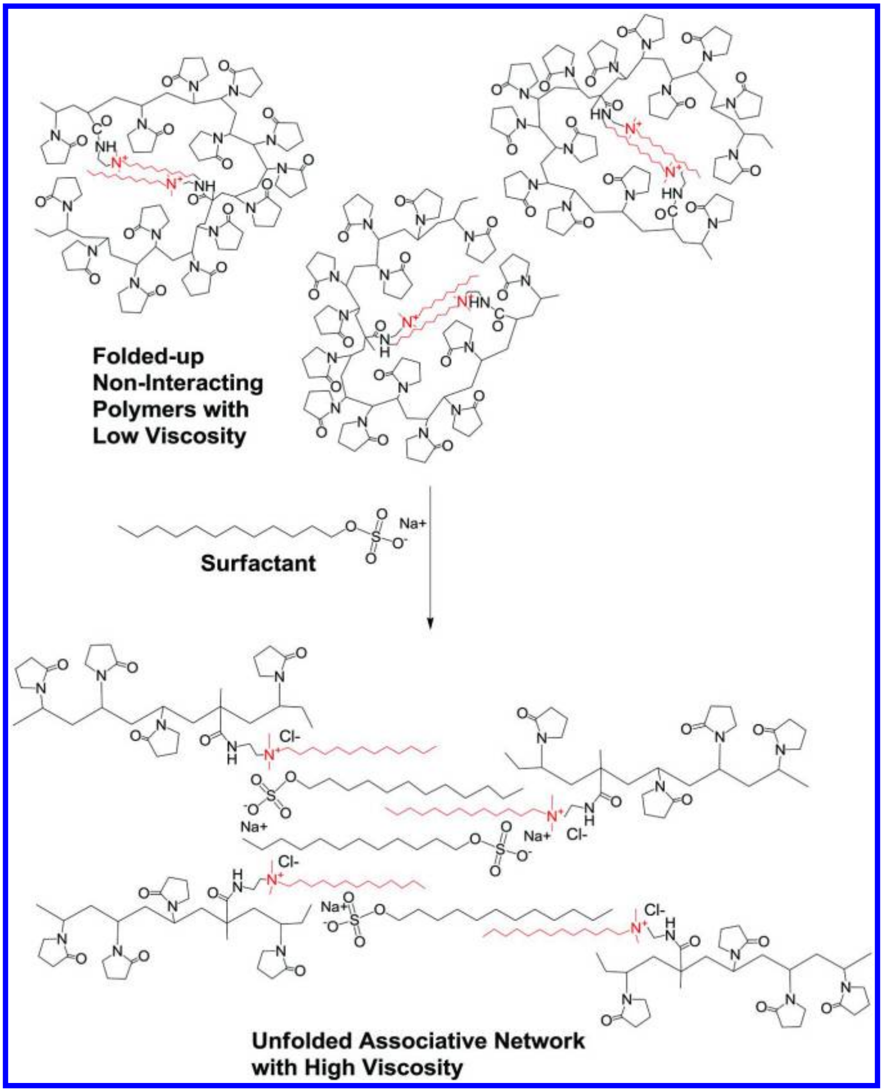


Figure 12. Model for Associative Thickening of PVP-DMAPMA-Lauryl-quat in the absence and presence of surfactant. (see color insert)

The PVP-DMAPMA-Lauryl-quat was constructed to unfold from a compact conformation into an extended-one depending on the presence or absence of a particular charged entity being present. In particular, the PVP-DMAPMA-Lauryl-quat should be compact in water alone, but in the presence of anionic surfactant and/or anionic thickening agent, it would unfold into an extended conformation thereby increasing the bulk viscosity of the gel or mousse, as well as synergistically through hydrophobic interactions by an associative thickening mechanism, Figure 12.

As expected, The hydrophobically modified PVP-DMAPMA-Lauryl-quat was more compact and less viscous by an order of magnitude than its unmodified counterpart, PVP-DMAPMA, even though both polymers were characterized by similar molecular weights, in dilute (1% w/w) and semi-concentrated solutions (<5% w/w). This finding is consistent with an intramolecular association of the positively charged quaternium group bearing a large hydrophobe interacting within its own backbone with pyrrolidone and/or methacrylamide functionalities in water. Therefore, it was expected that in the presence of anionic surfactants the opposite would be true, such as PVP-DMAPMA-Lauryl-quat should exhibit a higher viscosity than the parent PVP-DMAPMA.

Indeed, the mixtures of PVP-DMAPMA-Lauryl-quat with anionic surfactants, such as sodium dodecyl sulfate and sodium laureth-2-ether-sulfate, showed strong interactions by exhibiting viscosity maxima and flocculation points corresponding to the surfactant/polymer alkyl group and surfactant/polymer charge concentration ratios in the range of 1–2. PVP-DMAPMA-Lauryl-quat also showed network formation by significant viscosity buildup in combination with two nonionic surfactants, which included C_{14-15} Pareth-7 and C_{12-13} Pareth-3. In contrast, PVP-DMAPMA did not to interact with anionic and nonionic surfactants. This example provides a case study on how a polymer scientist can construct a particular polymer to behave differently depending upon the medium it resides by design.

Likewise, many polymers used in gels and mousses are pseudoplastic and exhibit shear-thinning so that an even spreading of the formulation occurs onto the hair fibers as the fingers run through the hair during application and subsequent combing or brushing. This provides an even coat and homogenous distribution of styling product across the hair fiber population.

Some typical rheological /viscosity modifiers used in gels and mousses include a lightly crosslinked poly-acrylic acid commonly known as Carbomer that swells and thickens upon neutralization with a base. Other thickeners not requiring neutralization include hydroxymethyl or hydroxyethyl, or hydroxypropylmethyl-cellulose, and/or carboxymethyl-hydroxyethyl-cellulose, carboxymethyl hydroxypropyl guar, and acrylates/C10-130 alkyl acrylate copolymer.

Cationic polymers are also quite popular for use as conditioning agents in gels and mousses. These polymers have been chemically modified to have positive charges along their backbone. Since hair is negatively-charged, these polymers become bound electrostatically to the surface of the hair when applied and resist being rinsed off by the water. They can form clear, glossy films and act as an anti-static agent for more manageability of hair. They typically provide

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

good wet and dry combing results and impart a smooth feel to the hair. These will be discussed more fully in the conditioning polymer section. Some examples of conditioning polymers used in gels and mousses are Polyquaternium-4, Polyquaternium-6, Polyquaternium-7, Polyquaternium-10, Polyquaternium-11, and Polyquaternium-69. Likewise, cellulosic polymers like cationically modified HEC or Guar with hydroxypropyl trimethylamonium chloride.

A key property in a styling gel is its optical clarity, while a mousse can be clear or opaque. If the gel is not completely crystal-clear in the see-through container or in the hands, the perception is that a hazy gel being applied onto your hair that is unwanted and will make your hair appear dull and dirty, even though it's not when applied as a thin film. The visual clarity or appearance of the gel in the container is exaggerated by the much larger path length the light must traverse through than the portion in the hand. Clarity is usually measured by optical methods using visible light such as nephelometry, or more commonly used method of turbidity measurements in units of NTU.

Nephelometry is the measurement of scattered light. This technique requires a special measuring instrument, where the detector is set at an angle to the incident light beam. Turbidimetry is the measurement of unscattered light, i.e. light transmitted through a turbid solution. This method of measurement is carried out using an spectrophotometer (absorptiometer).

In turbidimetry, consideration must be given to the question of color of the final solution as this will lower the transmitted light by absorption. Likewise, removal of all air-bubbles present is a prerequisite prior to measurement. If the solvent and dispersed particles are both free from color then a wavelength in the blue or near ultraviolet should be selected for maximum sensitivity. If color is present, a colored filter must be used or a different wavelength must be chosen for the measurement. Visually, the absence of haze correlates to < 10 NTU, while a slightly hazy solution is approximately around 10-20 NTU and very hazy is 100 NTU.

To improve the optical clarity of the gel, sometimes non-ionic surfactants and/or Polyethylene glycol (PEG) is used. PEG is a water-soluble polymer that can be chemically reacted with a variety of alkyl groups to improve the surfactancy and clarity of hair gels. The number associated with the PEG in the International Nomenclature of Cosmetic Ingredients-(INCI) nomenclature is indicative of the number of PEG repeat units present. The higher the number, the greater the water solubility of the modified molecule. These modified molecules can be used as emulsifiers, viscosity modifiers, surfactants, humectants, and especially solubilizers. Examples include Oleth-20, Polysorbate-20, PEG-40, Hydrogenated Castor oil, and PEG-75-Lanolin.

For setting performance, film forming polymers are still needed to provide stiffness and hold in styling products for hair gels and mousses. One example of a popular polymer used in gels is poly N-vinyl-2-pyrrolidone (PVP), an excellent film-former, substantive to hair, forms clear films, completely water soluble. However, it absorbs moisture in humid weather that can make it sticky or tacky to the touch, whereas in dry weather, it can become brittle and flake-off. PVP is used for superior optical clarity because is completely soluble in water or hydroalcoholic solvents found in hair gels.

In contrast, mousses maybe contained in an opaque containers or maybe opaque itself so that the clarity of the polymer solution itself is circumvented, but more importantly the dried film must be optically clear itself. Therefore, another popular styling polymer mostly used in mousses is polyvinyl acetate (PVA) that resists absorption of moisture in humid weather that leads to better hold under high humidity conditions, is more flexible in dry weather so that it doesn't flake, but is not as substantive to hair as PVP. It is only soluble in hydroalcoholic solvents or water with a high level of surfactants and emulsifiers. Therefore, it is not surprising that a copolymer of PVP/VA provides the best of both worlds, and is used in both Gels and Mousses. It is a copolymer of PVP and PVA and is used to avoid the limitations of each these two homopolymers when used separately. Additionally, it comes in various comonomer ratios so that the formulation can tailor a stiff (VP rich) or flexible (VA rich) hold as exhibited by its T_g in Table II.

In contrast to hair gels, Mousses are a more complex product form. In particular, most provide hold and are also used as hair volumizers as well. Volumizers are used to temporarily add volume, body, and shine to thin, dull, and limp hair. Hair volumizers are also used by balding men and women with thinning hair to make their hair mass look denser. Volumizers also contain humectants, which work by attracting moisture from the surrounding areas to the hair strand, thereby swelling the hair and making it look thicker. Likewise, various polymers present in the mousse coat the hair strand, making it look thicker and glossier as a result of the thickness of the film coat itself, as well as its effect on fiber interactions, resulting in the appearance of a greater mass of hair as a whole when viewing the head.

Root-lift is another attribute of volumizers in mousses. The spray or lotion form of volumizers is applied on damp hair, near the roots of the hair, then the person flips his/her head downward and gradually blow dries the hair. The direction of the air being blown follows along the shaft of the hair, and once the hair is dry, the person can flip his/her head back up. This strategy makes the hair appear to be more fuller, and not appear as limp and flat. One approach to evaluate this volume enhancement uses laser stereometry to determine hair volume (*43*).

Another attribute specific to mousses is foam-bloom. When the mousse is dispensed by pump or aerosol, it is aerated into a foam. The size and consistency of the foam generated is an important performance parameter for mousses, and is scrutinized thoroughly. For example, foam characteristics are a key component for the identity of a mousse due to the fact that they largely dictate the consumer's first sensory experience. Therefore, three key foam characteristics that require special attention are Foam-density, Foam Bloom-rate, and Foam-strength (*44–46*).

The simplest is Foam density and is measured by weighing a known volume of fully formed foam, which typically falls in the range of 0.05 g/ml to 0.2 g/ml. This parameter is tacitly correlated to Foam-strength. Usually the higher the density the higher the strength, but also the heavier feel on the hair. This is because we are not considering the % water in the formulation.

Numerically, a high foam density means a higher percentage of liquid is present in comparison to the percentage of air-entrained. Therefore, very high values of foam density relates to a watery consistency to the foam. Conversely, very low values means that the air/propellant content within the foam-ball is

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

higher than the amount of formulation actually present, so a smaller amount of the product is actually being applied to the hair. Hence, for volumizing it may not be desired to have a heavy foam for limp hair.

Next, Foam bloom rate describes foam development during and after dispensing, and can be viewed as a continuum from very slow bloom rates to very fast bloom rates. Here, foam bloom is rated on a scale from 1 to 3 using the following definitions and benchmarks, Table VIII.

Table VIII. Bloom Rate Definitions and Benchmarks

Bloom Rate Rating	***Observed Behavior***
1	**Product dispenses as a fully formed foam. Very fast bloom rate.**
2	**Product dispenses as a partially formed foam and the foam continues to grow after dispensing. Moderate bloom rate.**
3	**Product dispenses as a thin liquid and the foam grows slowly after product dispensing . Very slow bloom rate.**

Foam strength describes the way the foam breaks down when it is mechanically manipulated, and can be viewed as a continuum from very weak foams to very strong foams. Here, foam strength is rated on a three point scale using the following definitions and benchmarks, Table IX. Additionally, usually the higher the molecular weight of the polymer the stronger the foam-strength, as shown in Figure 10. In actuality, we are observing the foam's body, not its actual strength in Figure 13.

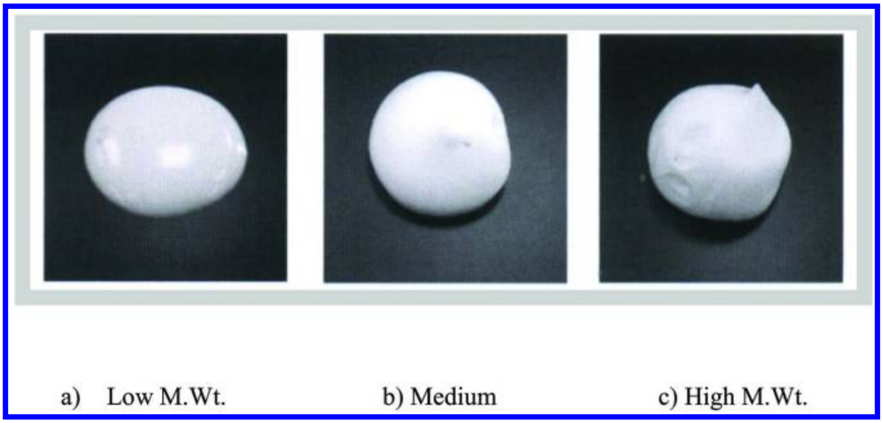

a) Low M.Wt. b) Medium c) High M.Wt.

Figure 13. Foam Strength vs. Molecular Weight of polymer: a) Low b) Medium c) High molecular weight.

Table IX. Foam Strength Definitions and Benchmarks

Foam Strength Rating	*Observed Behavior*
1	**Foam completely collapses when touched.**
2	**Foam splits open when touched and remaining untouched foam stays intact.**
3	**Foam does not break down when touched three times.**

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Foam strength is also related to the molecular weight of the polymer or thickener used. In particular, it is desired to have a moderate to strong foam strength so that when the user rubs it between the hands a sensory "cushioning effect" is felt that is usually attributable to a higher molecular weight polymer. In stark contrast though, if the foam strength is too strong, then one can never work it into the hair, thereby defeating an easy and pleasurable working experience in applying the product.

In this section we have discussed some similarities and some differences that are important to the performance of hair gels and mousses. Indeed, each has unique requirements, but they also have many similarities to each other too. It is not surprising that the perfect polymer(s) for either a gel or a mousse has been identified given the complexity of each product form and the other ingredients in which it is combined with.

Hence, modification of the film properties of hair gels and mousses are the subject of continuing research and development, both at the academic and corporate level. Some polymers provide excellent hold, but are too brittle and can cause flaking or lack durability throughout the day. Others may be stiff and durable, but may be susceptible to moisture and cause frizzy or dull hair in humid environments. Still others may provide all the desired hold and shine properties and be indifferent to climate, but may be difficult to remove with shampoo and can cause unattractive build up problems. It is also desirable that a hair gel or mousse maintain its properties over a broad range of temperatures, which can be another difficult obstacle to overcome.

It is quite obvious that polymer research is still required to improve upon the attributes of Hair Gels, Mousses, and Hairsprays too. Therefore, the authors have covered the hair care fundamentals and basic techniques to analyze the desired properties required for their optimal performance.

In conclusion of this section on Hairstyling Polymers, we have demonstrated that hairsprays, gels, and mousses are not just simple fixatives of the previous century, but these molecules have evolved into high performance materials with a whole variety of performance attributes required to achieve their desired results. As scientists continually improve upon the characteristics of these polymers, even greater insight into the complexities of these types of products will be realized..

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Conditioning Polymers

For centuries, harsh soaps would strip the natural oil of the Sebum from the hair surface thereby making hair more prone to damage by brushing or combing resulting in frizzy hair. Likewise, fly-away hair with no body or manageability is due to the electrostatic repulsion of the negative charges on the surface of the individual hair fibers when hair is combed thereby making matter worse. Therefore, natural oils have been used to condition human hair for hundreds of years. These natural products are still in use today. For example, Coconut oil is still very popular in India, while Jojoba oil from the Southwest U.S. can be found in many conditioners and cosmetics too.

These waxy oils serve to lubricate the hair fiber like Sebum to inhibit the formation of tangles and knots, while also providing more manageability, softness, and luster to the hair. Today's conditioners are still used to thwart these undesirable properties by damaged hair, but have also advanced to include moisturizers, thermal protectors, damage repair, hold and style, hard-water sequestrants, and pH adjusters.

Conditioners fall into two major categories; Neutral or Cationic. Neutral conditioners include natural oils, fatty alcohols, and hydrophobically modified hydroxyethyl-cellulose(HEC). These molecules can soften and insulate the hair fiber and provide lubricity, but they are easily washed off the hair with shampoo. Furthermore, the modified biopolymer HEC is too lubricious and when used in a high level imparts a greasy feel. Obviously this is an unwanted attribute as a conditioner. Therefore, cationic conditioners predominate the conditioner market as the primary conditioning agent. However, there are cases where non-ionics are blended with cationics in a small percentage that impart a particular property, such as an enhanced feel or rheology

Cationic polymers not only condition the hair but also provide styling and hold properties too. In particular, these high molecular weight polymers contain positive charges along the molecule, and since hair is negatively-charged, the polymer becomes bound electrostatically to the surface of the hair and resists being rinsed off by water. This substantivity has been directly correlated to its cationic charge density, Tables Xa-b. Therefore, they are substantive to hair even after multiple shampooing. These types of molecules are found in Shampoos. Conditioners, Styling Gels, and Mousses. Because of these attributes, cationic polymers are quite popular in hair conditioner formulations.

Additionally, these polymers cause the cuticles on the surface of the hair to lie flat, which gives a smoother texture and shiny appearance to the hair. Because the conditioning polymer insulates the electrostatic surface of the hair there is no repulsion between individual fibers, thereby permitting fiber alignment in a parallel fashion resulting in more smoothness and shine to the coif as a whole. It also helps lubricate each strand from adjacent strands during combing, which prevents tangling and tearing that makes both wet and dry combing easier, Figure 14.

Interestingly, the edges of the cuticle scale tend to become the most damaged by heat and repetitive combing thereby puckering-up the edge of the cuticle scale and fracturing the edges, respectively (*47*). The heat damage by a hot-iron is depicted in Figure 15, and would appear to have melted the cuticles, but upon closer inspection they are actually slightly puckered, Figure 16.

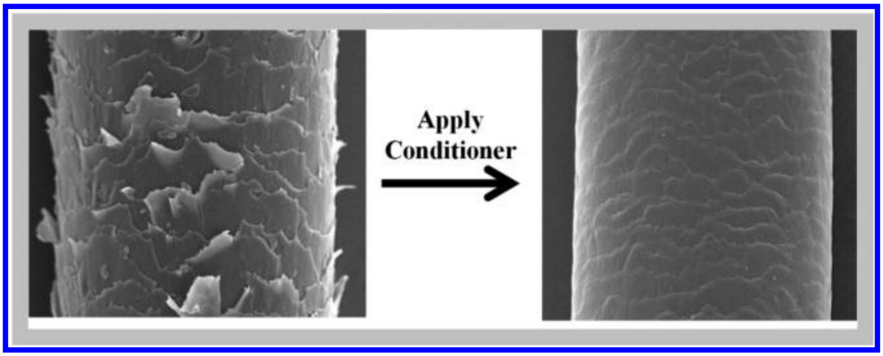


Figure 14. Thermally/ Chemically damaged hair before and after use of a conditioner.

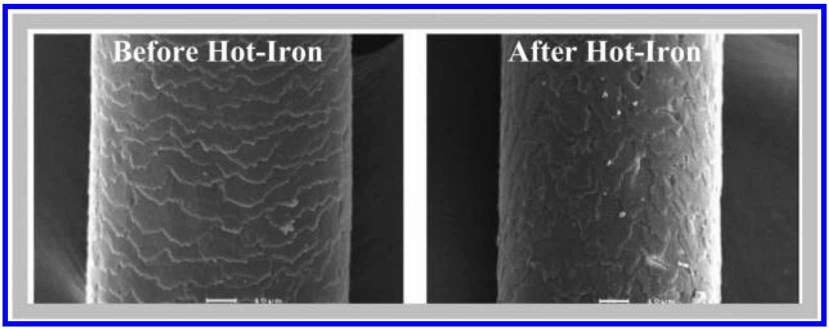


Figure 15. Thermally damaged hair before and after use of a hot-iron.

There are products available in the marketplace to prevent this thermal damage, or repair the damaged hair fiber itself, but discussion of these topics would be too lengthy here, so the reader is referred to these articles for further reading (*47–52*).

The thermally and mechanically damaged areas of the cuticle tend to have more of an anionic charge as evidenced by selective deposition or complexation of the cationic conditioner to these particular areas as depicted in Figure 16. The conditioner relaxes the cuticle scales so that they lie more flat and appear more smooth. Fluorescently labeled conditioner makes this selective deposition toward the edges of the damaged cuticle scales even more apparent as is depicted Figure 17.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

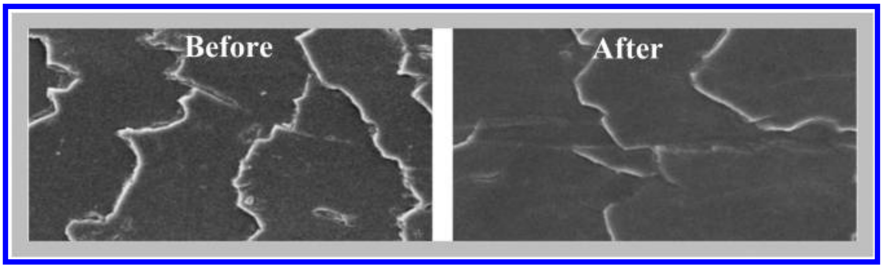


Figure 16. Thermally/ Chemically damaged hair before and after use of a conditioner; note smoothing of cuticle edges.

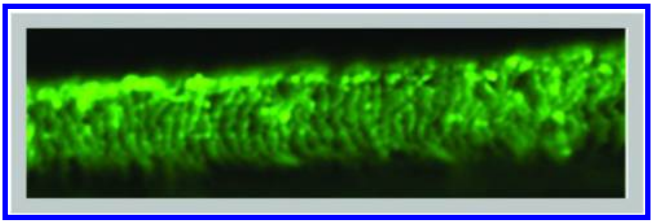


Figure 17. Fluorescently labeled conditioner after shampooing localized at cuticle edges. (see color insert)

To evaluate the substantivity of the conditioner on the hair after multiple shampooing, an anionic dye method that measures polymer concentration on hair confirms the lack of polymer build-up after at least 15 shampoo cycles (*53*, *54*).

These types of cationic conditioning polymers are known as Polyquaterniums(PQ) in the INCI naming system. In fact, as of 2013 there were 101 different Polyquaterium molecules registered for use as a conditioners in the marketplace. The numerical value of the Polyquaterium is derived by its sequential order in registering the molecule with the Personal Care Council that assigns the INCI name. Hence, PQ-1 was the first and PQ-101 is currently the last registered.

The chemical structures for the top ten most popular Polyquateriums used today are summarized in Tables VIIIa-b. These polyquats as they are commonly referred to, tend have very large molecular weights ranging from 0.5-1.0 x 10^6 daltons. Most of the polyquateriums come in differing molecular weight ranges, low-high, so that the values listed for each is an average value from either the major supplier, or its typical use grade.

Three out of the ten polyquateriums are polysaccharide-based biopolymers and are tacitly considered *"Green-Conditioners"*, while seven are based on synthetics. Cellulose is a typical naturally-occurring polysaccharides with a straight-chain polymeric backbone composed of repeating units of anhydroglucose that are β- 1,4-linked. In contrast, guar contains an anhydromannose-backbone with anhydrogalactose side-chains in a 1-6 linkage.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Cellulose in its natural state is not very water soluble at all, due to its crystalline structure and extensive hydrogen-bonding network between adjacent chains denoted by the squiggly-lines in Figure 18. In fact, the cumulative sum of two hydrogen-bonds per glucose molecule that are each 2 Kcal/M along a single 10,000 unit chain can amount to 40,000 Kcal. That's enough stabilization energy to light up 465 light bulbs of 100-watt each for an hour. However modification by addition of hydroxyethyl groups onto the cellulose by ethylene oxide allows this crystalline structure to be disrupted, which permits the polymer to become more soluble in water, which makes it more easily used by personal care formulators.

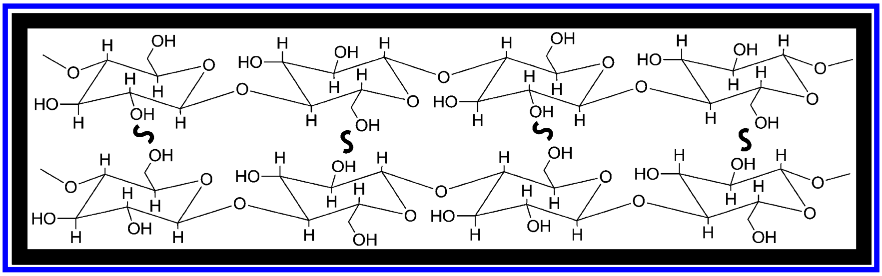


Figure 18. Extensive Hydrogen-bonding network of adjacent Cellulose chains.

The solubility of cellulose is not only dependent upon the polymer chain length that can range into the millions, but as well as the degree of substitution of the hydroxyethyl groups on the individual chain. Because the neighboring straight chains can pack so tightly against each other due to the lack of branching off the primary alcoholic carbon has serious implications when adding hydroxyethyl-groups on the overall rheology and flow of an aqueous HEC solution.

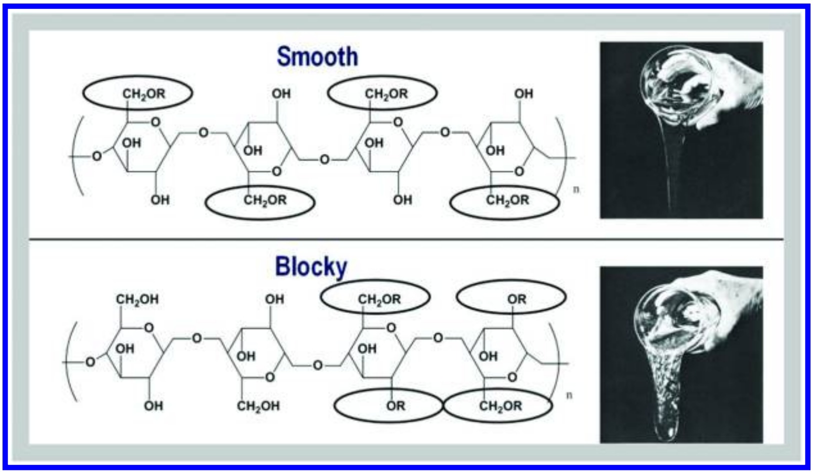
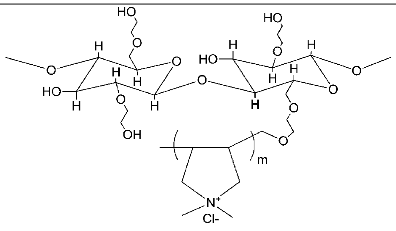
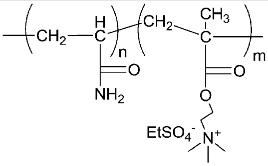
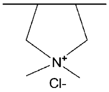
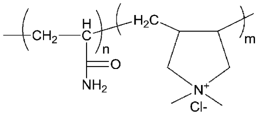
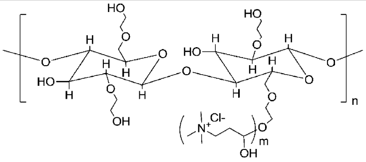


Figure 19. Flow properties of homogenous vs. blocky modification onto Cellulose chains.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

For example, a thin homogenous fluid is obtained when modification is evenly distributed along the chain thereby inhibiting interchain hydrogen-bonding. In stark contrast, a thick globby fluid is obtained when the addition is blocky resulting from sections of the backbone that still strongly hydrogen-bond to each other across chains, as evidenced by the flow properties illustrated in Figure 19.

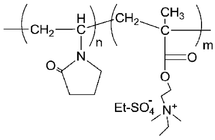
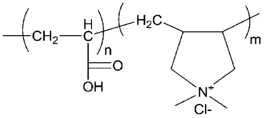
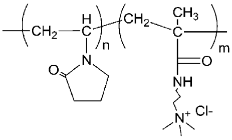
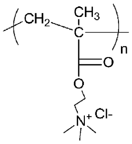
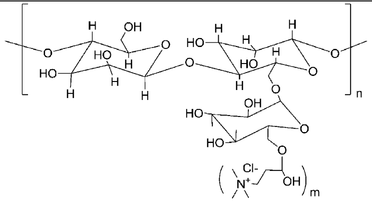
Table Xa. Chemical Structure for Popular Polyquaterium Conditioners

INCI Designation	Polymer Structure	Cationic Charge Density meq/dry g
Polquaterium-4 (HEC-DADMAC)		**1.1-1.5**
Polquaterium-5 (AM-TMAEMA)		**0.2**
Polquaterium-6 Poly(DADMAC)		**≤ 6.2**
Polquaterium-7 (AM-DADMAC)		**2.8-3.0**
Polquaterium-10 (HEC-HPTMAC)		**1.0-1.3**

Cellulosic polymers are typically used to thicken shampoos or conditioners, or to stabilize emulsions, and also occasionally to impart conditioning properties. A chemical modification of these cellulosic polymers (quaternization), produces several of the better known polyquaternium polymers used in conditioning and styling products today, such as Polyquaternium-10 and Polyquaternium-4. We shall delve into the chemistry behind these molecules in some detail.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Table Xb. Chemical Structure for Popular Polyquaterium Conditioners

INCI Designation	Polymer Structure	Cationic Charge Density meq/dry g
Polquaterium-11 (VP-DMAEMA)		**0.95-1.0**
Polquaterium-22 (AA-DADMAC)		**3.7-4.8**
Polquaterium-28 (VP-MAPTAC)		**1.4**
Polquaterium-37 Poly(TMAEMA)		**≤ 4.2**
Polquaterium-74 (Guar-HPTMAC)		**0.3-2.0**

Polyquaternium-4 is an hydroxyethyl-cellulose polymer that has been modified with diallyl-dimethyl-ammonium chloride (DADMAC). It performs well as a hair conditioner, and is cost-effective. It is a superior film-former on the hair, and has been found to exhibit very high curl retention even in high humidity. It is very substantive to hair, but exhibits some build-up despite shampooing. It exhibits a low/med cationic charge density of 1.1-1.5 meq/g but has an intermediate to high molecular weight (0.5-1.0 x 10^6) daltons. It is also very stiff due to its molecular weight, and is thus outstanding for use in hair gels. The presence of the acetal group in the glycosidic backbone limits its use to a pH range of 3-7, whereas higher pH values start to degrade the molecular weight of the polymer over time.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Polyquaternium-5 is a copolymer of acrylamide/trimethylaminoethyl methacrylate exhibiting a very high molecular weight (4 x 10^6) that provides excellent lubrication and slip in hair care products. It exhibits superior slip properties at low use levels such as 0.1-0.25% as supplied. It also exhibits nice wet-feel and dry-feel during/after application. Improved wet and dry combing, excellent application feel, and improved manageability to hair. It is also known to enhance foaming and interact with keratin to give good conditioning. The polymer is claimed not to interact with anionic surfactants due to its very low cationic charge density of 0.2 meq/g. The presence of the ester group in the quat-side chain limits its use to a pH range of 3-7, whereas higher pH values start to degrade the cationic portion of the polymer over time.

Polyquaternium-6 is a homopolymer of poly-DADMAC that exhibits the highest cationic charge density, ≤ 6.2 meq/g , of the whole polyquaterium class. It is extremely substantive to hair despite its molecular weight, which comes in high and low viscosity versions. It can provide excellent conditioning effect for hair even in low concentration, generally at 0.5%~1%. The product can offer moist, glossy and rich foam. It can make the hair more smooth for combing, and the antistatic ability to give hair a smooth, silky and lustrous feeling. It is added into moisturizing cream, bath foam, shaving cream and deodorant, as it contributes to excellent skin feel. The suggested concentration is 1%~2%. The product can also improve dispersions, which are used in hair and skin care. The lack of any degradable groups in this polymer permits its use to a pH range of 3-12.

Polyquaternium-7 is a copolymer of Acrylamide/DADMAC with a medium/high cationic charge density of 2.8-3.0 meq/g. It contributes luster and a soft, silky feel, and provides rich, creamy foam to shampoos with excellent slip, lubricity, and snag-free wet combability without excessive buildup. It also imparts excellent dry combability. Panel studies document excellent hair softness and wet hair feel during washing, rinsing and after rinsing. Additionally, it helps hold curls without flaking, with high solids and low viscosity, it maximizes freight economy and flexibility in formulations Suggested starting concentration can be as low as 0.25% (as-supplied) making it cost-effective. The presence of the amide group in this polymer permits its use to a pH range of 3-10.

Polyquaternium-10 is a quaternized hydroethyl-cellulose polymer which has been reacted with 2,3-epoxypropyltrimethyl-ammonium chloride exhibiting a medium cationic charge density of 1.0-1.25 meq/g , but relatively high molecular weight (0.5-1 x 10^6) daltons. Polyquaternium-10 (PQ-10) was the first cationic polymer introduced into conditioning shampoos, and is a water-soluble polymer that has film forming properties. PQ-10 forms a smooth uniform, clear, glossy film that likely translates into better hair appearance(ref). It exhibits moderate substantivity without build-up, while providing hair volume enhancement. In addition, wetting force measurements of a single hair fiber coupled with SEM techniques demonstrate that the polymer complex is uniformly deposited to give a smooth hair surface. Like PQ-4, the presence of the acetal group in the glycosidic backbone limits its use to a pH range of 3-7, whereas higher pH values start to degrade the molecular weight of the polymer over time.

Polyquaternium-11 is a copolymer of VP/DMAEMA (vinyl pyrrolidone and quaternized dimethylaminoethyl methacrylate). This polymer has a medium charge density of 0.95-1.0 meq/g, and often has quite high molecular weight. It gives good wet and dry combing results and imparts a smooth feel to the hair. The fact that it is a copolymer of VP and an acrylate means it will be somewhat less susceptible to humidity than just VP alone, but it may be more susceptible to failure by high humidity than the polyquat-4 due to the fact that some VP is present in it. Polyquat-11 is generally recommended for mousses and creams, where it can moisturize as well as aid in styling. This polymer is water soluble but could lead to some build-up over time if one were not using a clarifying shampoo occasionally. The presence of the ester group in the quat-side chain limits its use to a pH range of 3-7, whereas higher pH values start to degrade the cationic portion of the polymer over time.

Polyquaternium-22 is a copolymer of DADMAC/Acrylic acid exhibiting a cationic charge density of 3.7-4.8 that is extremely substantive to hair despite having a relatively low molecular weight, 1.5 x 10^3 daltons. It contributes luster and a soft, silky feel, and provides rich, creamy foam to shampoos. It also provides excellent slip, lubricity and snag-free wet compatibility without excessive buildup, while imparting excellent dry compatibility. Panel studies document excellent hair softness and wet hair feel during washing, rinsing and after rinsing, and helps hold curls without flaking when used at 1.0% in shampoo and conditioners. The lack of any degradable groups in this polymer permits its use to a pH range of 3-12.

Polyquaternium-28 is a copolymer of Vinyl pyrrolidone/ Methacrylamido propyl-trimethylammonium chloride (VP/MAPTAC) that has medium cationic charge density of 1.4 meq/g, with relatively high molecular weight, 1 x 10^5 daltons. It is a conditioning additive for shampoo formulations. The polymer is substantive to hair and delivers excellent combability, rich lather and manageability. It also delivers excellent lather properties and permits cold processing during formulation. Recommended skin care applications include body care, face and body wash and facial care formulas. The presence of the amide group in this polymer permits its use to a pH range of 3-10.

Polyquaternium-37 is a homopolymer of trimethylaminoethyl methacrylate that exhibits a high cationic charge density of ≤ 4.2 meq/g with a unique narrow range molecular weight of 4 x 10^5 daltons, that provides effective conditioning and flexible hold at low use concentrations, imparting non-greasy detangling, improves dry comb and fly away, while building volume and sheen. Also effective as a cationic emulsifier, and softening agent in crèmes and lotions. As a cationic thickener with a high yield value its available either as 100% high bulk density and low dusting powder or as a dispersion in Mineral Oil or Propylene Glycol Dicaprylate/Dicaprate and is self thickening with no neutralization required. Recommended use-level is 0.1-3.0% , and that at 0.5% provides 7-13,000 cps, and once dispersed in water you can add up to 70% EtOH. Compatible w/ iron oxides, sunscreens, and self tanners with excellent water proofing film former with elegant skin-feel. The presence of the ester group in the quat-side chain limits its use to a pH range of 3-7, whereas higher pH values start to degrade the cationic portion of the polymer over time.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Polyquaternium-74 is another modified polysaccharide. This product is reacted with hydroxypropyltrimonium chloride as a quaternized modification of another naturally occurring polymer, guar gum or polysaccharide, which functions in a very similar manner to Polyquaternium-10. Chemically, guar gum is a polysaccharide composed of the hexoses; galactose and mannose. The backbone is a linear chain of β 1,4-linked mannose residues to which galactose residues are 1,6-linked at every second mannose, forming short side-branches. It contains low/medium cationic charge density of 0.3-2.0 meq/g.

Some studies have shown that this polymer can provide superior detangling and wet combing properties to Polyquaternium-10 when used in a conditioning shampoo. Guar gum is economical because it has almost eight times the water-thickening potency of cornstarch, hence only a very small quantity is needed for producing sufficient viscosity. Thus, it can be used in various multiphase formulations: as an emulsifier because it helps to prevent oil droplets from coalescing, and/or as a stabilizer because it helps to prevent solid particles from settling. Like PQ-4 and PQ-10, the presence of the acetal group in the glycosidic backbone limits its use to a pH range of 3-7, whereas higher pH values start to degrade the molecular weight of the polymer over time.

We would be remiss if we did not mention silicone-polymers and oligomers such as poly-dimethylsiloxane and dimethicone with respect to conditioning shampoos. However, these molecules are more used in rinse-off applications for feel than conditioning. For leave-in application they lend for conditioning, shine, and reduced comb-drag. In fact, there is no substantivity of silicone/siloxanes to hair unless used with another polyquaterium by coacervate formation.

This conclusion is substantiated by silicone deposition onto hair by basically three techniques. Since silicone/siloxane oils/waxes contain an inorganic element, silicon, X-ray fluorescence, or atomic absorption can be readily used to quantify the level of silicone present. Likewise, a newer technique that uses hydrolysis of the Si-O bond by a strong acid to form a trimethicone analyte followed by gas chromatography can also be used with more specificity towards only siloxane-containing molecules, not just the detection of elemental silicon alone (*55–57*).

In addition, siloxanes can be extremely expensive depending on the type used. Therefore, their use is limited to 0.2% maximum, and are used to deposit onto the surface of the hair and act to reduce combing friction, provide an emollient effect, impart gloss and reduce static charge between hair strands. Examples of silicones include dimethicone, amodimethicone, cyclopentasiloxane, cyclomethicone, dimethicone copolyols, and dimethiconol.

Now that we have reviewed the chemistry of the major molecular entities in the conditioner area, let us now focus on the analytical techniques used to substantiate their performance claims (*58–60*). The top performance attributes for conditioning polymers are wet/dry combability, slipperiness, detangling, smoothness and sheen, fly-away reduction, and finally hair volume.

Frictional forces such as comb-drag can be measured to evaluate wet and dry combability. Using a tensiometer such as an Instron or Texture Analyzer, a stationary comb is passed through a moving hair tress being pulled-up by an Instron testing instrument as depicted in Figure 20. The higher the frictional forces from comb-drag the more energy needed to pass a comb through the hair tress. This

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

can be displayed as a bar-graph or a plot of force versus distance illustrated in Figure 20. This measurement can be made on hair versus the same tress treated with conditioner in both the wet and dry state.

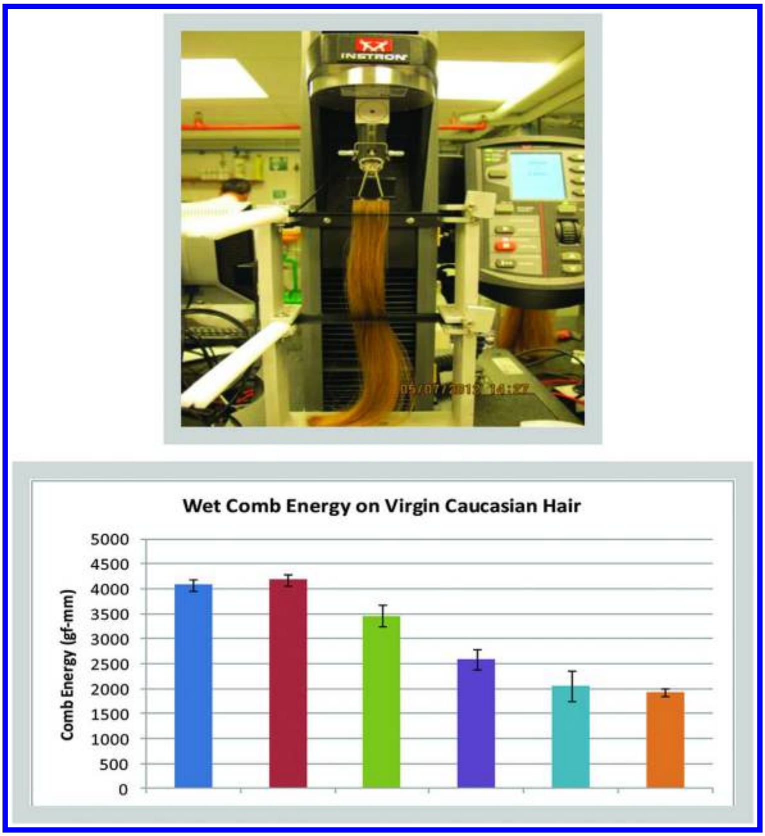


Figure 20. Comb-drag measurements on a hair tress with an Instron. (see color insert)

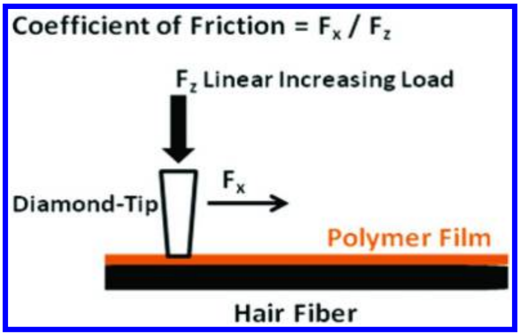


Figure 21. The Coefficient of Friction measurement using a mechanical tester. (see color insert)

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Likewise, frictional forces in the dry state can be correlated to surface smoothness, as illustrated in Figure 21. Likewise, repetitive stress from combing or brushing everyday results in damage to the cuticle edges making them more anionic in character resulting in a higher negative charge at the cuticle edges. Application of a cationic conditioner neutralizes these charges thereby insulating the fiber so that fly-away hair or repulsive fiber-fiber interactions do not occur, as depicted in Figure 22. This conclusion has been verified by our laboratory's own findings with fluoresencently labeled conditioner, Figure 17, as well as atomic force microscopy.

Figure 22. Cationic Conditioner neutralizes/insulates Anionic surface of Hair.

The last analytical technique used to evaluate the resin's properties on hair, is atomic force microscopy or scanning-force microscopy, known simply as AFM. This instrument uses the tip of an extremely small needle that approximates the width of one-atom across at the tip. In actuality, its width is closer to 1-10 nm or 10-100 angstroms. This needle is attached to one end of a cantilever face-side down, while a mirrored-surface is located on the top surface of the cantilever or backside up, Figure 23.

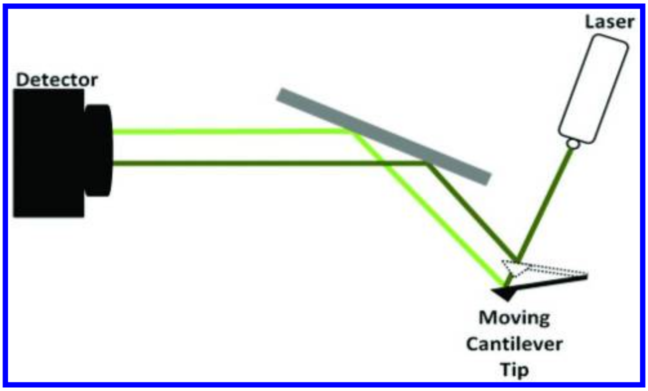


Figure 23. Measuring deflection of an AFM cantilever tip by a laser-beam. (see color insert)

A laser-beam is used to bounce off of the mirrored-surface of the cantilever to measure its exact distance in the vertical direction, whereby the reflected light is detected on an arrayed detector. The up and down motion at the tip as it taps along the surface of the substrate under investigation generates a topological or contour

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

map of the surface(tapping-mode). Depending on the model, the resolution that can be achieved is astounding, close to 1 nm, far exceeding that of a scanning electron microscope (SEM).

Additionally, the interaction of the tip with the surface of the substrate can be monitored in the phase-modulated mode, so that one can measure how soft or hard the surface is. This permits the observation of microdomains of heterogeneity on the surface. For example, polymer deposits on the hair fiber's surface can be localized to specific locations of the cuticle layer, like the edge's of the scales for conditioners, or on the surface of a particular scale or in a damaged area like a scored cuticle, Figure 24.

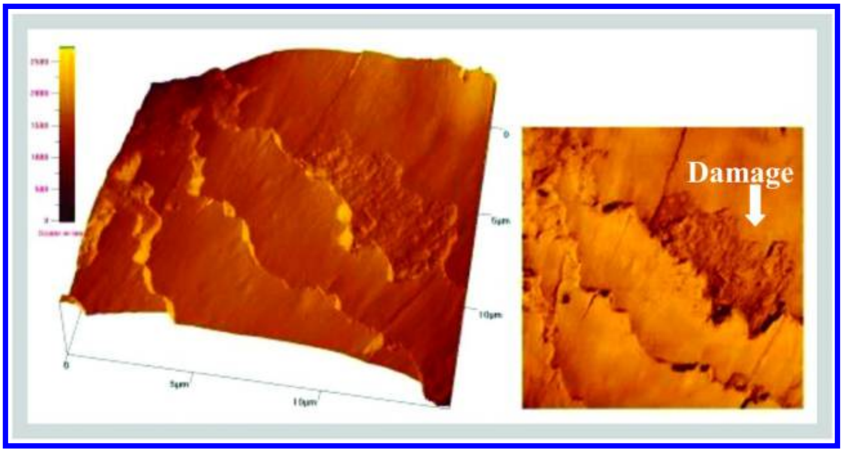


Figure 24. AFM images of Damaged Hair. (see color insert)

Therefore, AFM is used in conjunction with SEM as an image analysis tool because it provides for x,y, and z coordinate mapping instead of just x and y. AFM also exhibits better resolution with no sample preparation needed, and is non-destructive compared to SEM. Finally, the observation of inhomogenieties on the surface of the substrate can be readily observed.

In conclusion, we have covered many of the commercially important polymers used in hair care for styling, conditioning, and damage repair, and the methodologies employed to evaluate the properties of these molecules. Moreover, the fundamental bases of how these analytical techniques work and what information can be extracted from them have been covered. Furthermore, we have tried to correlate the structure of these polymers to their chemical and physical behavior when used. We hope this information provided will provide enlightenment into the science behind cosmetic products like hairsprays, conditioners, and damage repair, as well as just how complex these products truly are!

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Acknowledgments

The authors gratefully acknowledge Raymond Rigoletto and David Streuli for review of this chapter, and providing insightful discussions regarding their application knowledge in the Personal Care arena. Special thanks to Bill Thompson and Yan Zhou for SEM and AFM images. Likewise, we thank our colleagues, past and present, and senior management here at Ashland Specialty Ingredients for their support, knowledge, data, and expertise in the preparation of this manuscript.

References

1. Jung, K.; Herrling, T.; Blume, G.; Sacher, M.; Teichmüller, D. Detection of UV Induced Free Radicals in Hair and their Prevention by Hair Care Products. *SOFW J.* **2006**, *132*, 32–36.
2. Diller, V.; Muir-Sukenick, J. *Face It: What Women Really Feel as Their Looks Change*; Willens, M., Ed.; Hay House Inc.: New York, 2010
3. Micchelli, A. L.; Koehler, F. T. Polymer Properties Influencing Curl Retention at High Humidity. *J. Soc. Cosmet. Chem.* **1968**, *19*, 863–880.
4. Ramaprasad, K. R.; Ruetsch, S. B.; Weigmann, H. D.; Kamath, Y. K. Combing damage to hair cuticle structure. *Int. J. Cosmet. Sci.* **2008**, *30* (1), 76–84.
5. Robbins, C. R. *Chemical and physical behavior of human hair*, 5th ed.; Springer: Clermont, FL, 2012
6. Hitchinson, P. E.; Thompson, J. R. The cross–sectional size and shape of human terminal scalp hair. *Br. J. Dermatol.* **1997**, *136* (2), 159–165.
7. Article 25 (1) (g) and Article 25 (5) of Regulation 1223/2009/ European Commission, 2009.
8. Article 37 of Regulation 1223/2009/European Commission, 2009.
9. Article 3 of Directive 76/768/EEC, 1976.
10. Proposition 65 Safe Drinking Water and Toxic Enforcement Act of 1986-State of California, 1986.
11. Final regulation order - Regulation for reducing emissions from consumer products, California Air Resource Board, www.arb.ca.gov, 2010.
12. Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans, U.S. Environmental Protection Agency, www.epa.gov, 2005.
13. Kyoto protocol to the United Nations framework convention on climate change, United Nations, www.un.org, 1997.
14. Definition - Volatile organic compounds (VOC), 40 CFR 51.100(s), U.S. Environmental Protection Agency, 2009.
15. Howard, D. M. Principles of corrosion of metal containers by cosmetic products. *J. Soc. Cosmet. Chem.* **1969**, *20*, 17–29.
16. Carre, A.; Eustache, F. Spreading Kinetics of Shear-Thinning Fluids in Wetting and Dewetting Modes. *Langmuir* **2000**, *16* (6), 2936–2941.
17. Arzhavitina, A.; Steckel, H. Foams for pharmaceutical and cosmetic application. *Int. J. Pharm.* **2010**, *394*, 1–17.

18. Carthew, P.; Griffiths, H.; Keech, S.; Hartop, P. Safety assessment for Hairspray resins; Risk assessment based on rodent inhalation studies. *Inhalation Toxicol.* **2002**, *14* (4), 401–416.
19. Loretz, L.; Api, A. M.; Barraj, L.; Burdick, J.; Davis de, A.; Dressler, W.; Gilerti, E.; Jarrett, G.; Mann, S.; Laurie-Pan, Y. H.; Re, T.; Renskers, K.; Scrafford, C.; Vater, S. Exposure data for personal care products: hairspray, spray perfume, liquid foundation, shampoo, body wash, and solid antiperspirant. *Food Chem. Toxicol.* **2006**, *44* (12), 2008–2018.
20. Cosmetic Ingredient Review Expert Panel. *Int. J. Toxicol.* **2002**, *21* (Suppl. 3), 1–50.
21. Fonnum, G.; Bakke, J.; Hansen, F. K. Associative thickeners. Part I: Synthesis, rheology and aggregation behavior. *Colloid Polym. Sci.* **1993**, *271* (14), 380–389.
22. Martiny, S. Acetylenic polymers for hair styling products. *Int. J. Cosmet. Sci.* **2002**, *24* (3), 125–134.
23. Dallal, J.; Rocafort, C. *Hair and Hair Care*; Johnson, D. H., Ed.; Marcel Dekker, Inc.: New York, 1997; Chapter 5, pp 105−164.
24. Wickett, R.; Sramek, J.; Trobaugh, C. Measurement of the adhesive strength of hair-hairspray junctions. *J. Soc. Cosmet. Chem.* **1992**, *43*, 169–178.
25. Mirabella, F. M., Jr. *Practical Spectroscopy Series; Internal reflection spectroscopy: Theory and applications*; Marcel Dekker, Inc.: New York, 1993; pp 17−52.
26. Rigoletto, R.; Mahadeshwar, A.; Foltis, L.; Streuli, D. Advances in Hair Styling. *Cosmet. Toiletries* **2012**May, 372–379.
27. Ebewele, R. *Polymer Science & Technology*; CRC Press: Boca Raton, FL, 1996; Chapter 4, pp 95−115.
28. Buera, M.; Levi, G.; Karel, M. Glass Transition in Poly(vinylpyrrolidone): Effect of Molecular Weight and Diluents. *Biotechnol. Prog.* **1992**, *8*, 144–148.
29. Marlier, L.; Selter, M. Bimodal Polymers for Next Generation Hair Styling Products. *SOFW J.* **2004**, *130*, 61–68.
30. Robbins, C. R.; Kelly, C. H. Amino acid composition of human hair. *Text. Res. J.* **1970**, *40*, 891–896.
31. Ward, W. H.; Lundgren, H. P. The formation composition and properties of the keratins. *Advances in Protein Chemistry*; Academic Press: New York, 1955; p 9.
32. Clay, R. C.; Cook, K.; Routh, J. I. Studies in the composition of human hair. *J. Am. Chem. Soc.* **1940**, *62*, 2709–2710.
33. Jachowicz, J.; Yao, K. Dynamic Hairspray Analysis I: Instrumentation and preliminary results. *J. Soc. Cosmet. Chem.* **1996**, *47*, 73–84.
34. Jachowicz, J.; Yao, K. Dynamic Hairspray Analysis II: Effect of polymer, hair-type, and solvent compositions. *J. Cosmet. Sci.* **2001**, *52*, 281–295.
35. Jachowicz, J.; McMullen, R. Mechanical analysis of virgin and polymer-treated hair fiber assemblies. *J. Cosmet. Sci.* **2002**, *53*, 345–361.
36. Katritzky, A. R.; Sild, S.; Karelson, M. A. Correlation and Prediction of the Refractive Indicies of Polymers by QSPR. *J. Chem. Inf. Model* **1998**, *30* (6), 1171–1176.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

37. Torrance, K. E.; Sparrow, E. M. Theory of Off-Specular reflection from roughened surfaces. *J. Opt. Soc. Am.* **1967**, *57* (9), 1105–1112.
38. McMullen, R.; Jachowicz, J. Optical properties of hair-Effect of treatments on luster quantified by image analysis. *J. Cosmet. Sci.* **2003**, *54*, 335–351.
39. McMullen, R.; Jachowicz, J. Optical properties of hair-Detailed examination of specular reflection patterns in various hair types. *J. Cosmet. Sci.* **2004**, *55*, 29–47.
40. Gao, T.; Pereira, A.; Zhu, S. Study of shine and hair surface smoothness. *J. Cosmet. Sci.* **2009**, *60*, 187–197.
41. Gao, T.; Landa, P.; Gallagher, K. Hair color vibrance factor to characterize Shine and Color Intensity. *Cosmet. Toiletries* **2012**, *127* (1), 48–56.
42. Jachowicz, J.; McMullen, R.; Wu, C.; Senak, L.; Koelmel, D. Effect of hydrophobic modification on the rheological properties of poly(N-vinylpyrrolidone-co-dimethylaminopropylmethacrylamide). *J. Appl. Polym. Sci.* **2007**, *105* (1), 190–200.
43. McMullen, R.; Zisa, F.; Jachowicz, J. Measurements of hair volume by laser stereometry. *J. Cosmet. Sci.* **2009**, *60*, 171–185.
44. Sanders, P. Molecular Complex Formation in Aerosol Emulsions and Foams. *J. Soc. Cosmet. Chem.* **1966**, *17*, 801–830.
45. Sanders, P. Stiffness measurements of Aerosol Foam. *Aerosol Age* **1963**, *8*, 7–33.
46. Breuer, M.; Tsai, H. C. Measuring viscoelastic properties of shaving foams. *J. Soc. Cosmet. Chem.* **1984**, *35*, 59–71.
47. Jachowicz, J.; McMullen, R. Thermal degradation of hair. I: Effect of curling irons. *J. Cosmet. Sci.* **1998**, *49*, 223–244.
48. Rigoletto, R.; Zhou, Y. Polyelectrolyte Complex for Mending Damaged Hair. *Cosmet. Toiletries* **2009**, *124* (3), 76–87.
49. Rigoletto, R.; Zhou, Y.; Foltis, L. Semi-permanent split-end mending with a polyelectrolyte complex. *J. Cosmet. Sci.* **2007**, *58*, 451–476.
50. Zhou, Y.; Rigoletto, R.; Koelmel, D.; Gillece, T.; Foltis, L.; Moore, D.; Qu, X.; Sun, C. The effect of various pretreatments on protecting hair from thermal damage by hot flat ironing. *J. Cosmet. Sci.* **2011**, *62* (2), 265–282.
51. McMullen, R.; Jachowicz, J. Thermal degradation of hair. II. Effect of selected polymers and surfactants. *J. Cosmet. Sci.* **1998**, *49*, 245–256.
52. Tate, M. L.; Kamath, K.; Ruetsch, S. B.; Weigmann, H. D. Quantification and prevention of hair damage. *J. Soc. Cosmet. Chem.* **1993**, *44*, 347–371.
53. Faucher, J. A.; Goddard, E. D. Influence of surfactants on sorption of a cationic polymer by keratinous substrate. *J. Colloid Interface Sci.* **1976**, *55*, 313–319.
54. Weigman, H. D.; Kamath, Y. K. Modification of human hair through fiber surface treatments: characterization by wetability. *Cosmet. Toiletries* **1986**, *101*, 37–49.
55. Nazir, H.; Lv, P.; Wang, L.; Lian, G.; Zhu, S.; Ma, G. Uniform-sized silicone oil microemulsions: preparation, investigation of stability and deposition on hair surface. *J. Colloid Interface Sci.* **2011**, *364* (1), 56–64.
56. Brown, M. A.; Hutchins, T. A.; Gamsky, C. J.; Wagner, M. S.; Page, S. H.; Marsh, J. M. Liquid crystal colloidal structures for increased silicone

deposition efficiency on colour-treated hair. *Int. J. Cosmet. Sci.* **2010**, *32* (3), 193–203.

57. Grabner, D.; Xin, L.; Hoffmann, H.; Drechsler, M.; Schneider, O. The solubilisation of a water insoluble functionalized silicone oil in an aqueous surfactant solution: a novel mechanism for the solubilisation process. *J. Colloid Interface Sci.* **2010**, *350* (2), 516–522.
58. Wu, W. J.; Alkema, J.; Greg, D. S.; Basset, D. R. Quantitative methods for evaluating optical and frictional properties of cationic polymers. *J. Cosmet. Sci.* **2001**, *52*, 51–65.
59. Erazo-Majewicz, P.; Roberts-Howard, C.; Oldham, E.; Lynch, C.; Graham, J.; Usher, C.; Joneja, S. Linking enhanced deposition agent functionality with aesthetic performance. *J. Soc. Cosmet. Chem.* **2011**, *62* (2), 101–108.
60. Hossel, P.; Dieing, R.; Norenberg, R.; Pfau, A.; Sander, R. Conditioning polymers in today's shampoo formulations – efficacy, mechanism and test methods. *Int. J. Cosmet. Sci.* **2000**, *22* (1), 1–10.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch015

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

Chapter 16

The Effect of Counterion, Concentration, and Temperature on the Release of Bioavailable Calcium and Phosphate Ions from Ion Permeable Microcapsules for Remineralization

**Michelle A. Falbo,[1] Matthew Q. Schmidt,[2] Theresa A. Greving,[2]
Michael T. Davidson,[2] William A. McHale,[3] Mark A. Latta,[1]
and Stephen M. Gross*,[1,2]**

[1]Department of Oral Biology, School of Dentistry, Creighton University, Omaha, Nebraska 68178
[2]Department of Chemistry, College of Arts and Sciences, Creighton University, Omaha, Nebraska 68178
[3]Premier Dental Products Company, Plymouth Meeting, Pennsylvania 19462
***E-mail: stephengross@creighton.edu.**

The objective of this study was to measure the release of biologically available ions from microcapsules with ion permeable membranes as a function of counterion, concentration and temperature. A heterogeneous polymerization technique was utilized to prepare a series of microcapsules using an ethylene glycol based polyurethane containing different aqueous solutions of potassium phosphate dibasic, sodium phosphate dibasic, potassium phosphate monobasic, calcium nitrate, calcium chloride and calcium acetate. Ion release profiles were studied as a function of initial ion concentration within the microcapsule, ion type and counterion type, and temperature. The preparation of microcapsules with controlled release profiles appears promising based on counterion selection and concentration.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

Introduction

Dental caries will develop under acidic conditions that promote enamel dissolution in the oral environment (*1*). The majority of enamel is made of hydroxyapatite (HAP) $Ca_{10}(PO_4)_6(OH)_2$, but often has other components such as carbonate ions incorporated into its structure (*2*, *3*). Enamel structure is lost when ions dissociate from the material. This process is known as demineralization. It takes place when the oral environment is undersaturated in calcium and phosphate ions and when the pH drops below the critical pH of enamel (*3*). Varying environmental conditions can influence the rate and depth of mineral loss (*4*). Ions will dissociate from the structure until the mineral and surrounding fluid are just saturated with respect to the tooth. The pH of the saliva typically indicates whether or not the enamel will dissolve (*1*). Ions such as calcium, fluoride, and phosphate have been known to reduce the effects of demineralization and encourage remineralization (*1*, *5*). Tooth enamel is also capable of rebuilding in the oral environment, as long as the conditions are optimal. If the pH of the saliva rises above the critical pH, and the oral environment is supersaturated with calcium and phosphate ions, the enamel can remineralize (*3*).

Calcium and phosphate are key components of hydroxyapatite, however, fluoride can also be incorporated to create fluorapatite (FAP), $Ca_{10}(PO_4)_6F_2$ (*2*). FAP can form in conditions that do not favor HAP formation; for instance, FAP is less soluble than HAP and can precipitate in a more acidic environment (*6*, *7*). Fluoride can also inhibit bacterial growth and protect the enamel against acid dissolution. Its overall effectiveness has become of particular interest among dental practitioners. Products such as varnish, mouthwash, and sealants have all incorporated fluoride to avert the affects of bacterial decay and demineralization.

The philosophy of dental care is beginning to shift away from invasive, restorative solutions to preventative approaches that target the early stages of enamel loss. Patient care is shifting focus to early detection (*8*). It is known that the early stages of enamel loss can be reversed (*9*). This reversal can occur naturally in the oral environment when conditions are optimal (i.e. increased pH, supersaturation of ions). These conditions are not always prevalent, however, and the incentive to develop external treatments for enamel repair remains.

Several therapies incorporate calcium, fluoride, and phosphate ions for remineralization. For instance, calcium and phosphate have been utilized in the form of amorphous calcium phosphate (ACP) and casein-phosphopeptide amorphous calcium phosphate (CPP-ACP) (*11*, *12*). ACP and CPP-ACP are believed to reverse the effects of decay by contributing to the formation of HAP. Products such as Enamelon™ and Recaldent™ have incorporated these structures and their clinical effectiveness has been reviewed (*10*, *13*, *14*). Fluoride has also been incorporated into dental therapies. Varnishes such as Duraphat® were introduced to maximize fluoride release near the tooth surface (*15*, *16*). However, dental varnishes are not suitable for extended ion release beyond a few hours. Sustained release can realistically be achieved from materials that have a significantly longer lifespan in the oral environment. Products such as dental composites, glass ionomer cements (GICs), and resin-modified glass ionomer

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

cements (RMGICs) are capable of providing ions for long-term release (*17–19*). RMGICs and GICs have been used to promote remineralization and discourage bacterial decay over a longer period of time by incorporating a glass capable of releasing fluoride ions.

Other work has been done to maximize the remineralizing potential of the dental restoratives. As discussed previously, calcium and phosphate have been studied in the form of ACP (*11*, *17*, *20*). However, ACP may still be unstable when incorporated into composites because of its rapid conversion to HAP. In an effort to delay this transformation, Si and Zr have been added to create Si-ACP and Zr-ACP (*20*). These hybrid forms were observed to delay the conversion of ACP to HAP (*20*). Factors affecting fluoride release from dental restoratives have also been studied. Specifically, fluoride ions have been incorporated into GICs, and efforts to gauge their optimal efficiency have been conducted. One study reported that the concentration of the ‘activating solution’ added to the cement played a significant role in the release of fluoride, irrespective of the counterion (*21*). However, it has also been suggested that the counterion can influence fluoride uptake from glass ionomer cements (*22*).

Recently, our research group determined that the diffusion of calcium, fluoride, and phosphate ions from aqueous solutions entrapped in polyurethane microcapsules was possible (*23*). In the previous study, it was found that the chemical structure and initial salt concentration in the microcapsule were significant variables in determining the control of ion release rate. The goal of this study was to assess the effect of the counterion on the release of calcium and phosphate ions from semi-permeable microcapsules for remineralization. Additionally, the initial salt concentration in the microcapsule was greatly expanded up to 7.1 M and the effect of temperature was measured. We believe these microcapsules have the potential to be incorporated into a variety of dental materials capable of releasing calcium, phosphate and fluoride ions at targeted release rates over extended periods of time.

Materials and Methods

Materials

Ethylene glycol, 1,4-butanediol, and cyclohexanone were purchased from Sigma Aldrich. Concentrated sulfuric acid, calcium chloride, calcium acetate hydrate, sodium phosphate dibasic heptahydrate and methyl benzoate were provided by Acros Organics. Potassium phosphate monobasic, potassium phosphate dibasic, and ethyl alcohol (denatured) were purchased from Fisher Scientific. Calcium nitrate tetrahydrate was obtained from Alfa Aesar. Toluene-2,4-diisocyanate was obtained from Fluka. Mixed hexanes were purchased from Pharmaco-AAPER. Nanopure water was generated by a Thermo Scientific Barnstead filtration system.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

Prepolymer Synthesis

The microcapsule shell was made of a polyurethane based prepolymer. Toluene-2,4-diisocyanate was reacted with ethylene glycol in cyclohexanone at 70°C in an inert atmosphere.

Microcapsule Synthesis

Microcapsules were synthesized using a reverse emulsion which had an excess of oil to water by volume, as reported previously (*23*). The oil phase consisted of the ethylene glycol polyurethane prepolymer, an emulsifying agent, and methyl benzoate. The oil solution was heated to 70 °C in a custom-made stainless steel reactor that was submerged in a Büchi BS-490 heating bath. To create a reverse emulsion, the aqueous salt solution was added to the reactor slowly. The reactor mixed at 4000 rpm by a Caframo BDC 6015 stirrer. A stoichiometric excess of the associated diol-containing monomers was subsequently added to the reaction to quench the isocyanate functionalities remaining in the prepolymer. After the synthesis, microcapsules were isolated via centrifugation using a Fisher Centrific 288 centrifuge. It was found the microcapsules were between 1 and 2 micrometers in size (*23*).

Ion Release Studies

Microcapsules containing six different aqueous salt solutions containing either calcium or phosphate salts ions werer prepared. These salts included calcium chloride, calcium acetate, calcium nitrate, potassium phosphate monobasic, potassium phosphate dibasic, and sodium phosphate dibasic. Microcapsules of a known mass were rinsed with nanopure water and placed into a custom made poly(vinyl chloride) cylinder secured with fiberglass mesh, as previously reported (*23*). For ion release measurements, microcapsules (and cylinder) were submerged in 100 mL of nanopure water with a stir-bar contained in an Erlenmeyer flask. The flask was submerged in a water bath held at 25°C by a Julabo ED Heating Immersion Circulator and the solution was stirred at 500 rpm on a Thermo Scientific Variomag Telesystem stirplate. For all experiments, 1 mL aliquots were taken in triplicate at time zero, 1 minute, 15 minute, 30 minute, 1 hour, 3 hour, 12 hours, and at 12 hour intervals thereafter (for a total of 96 hours). Nanopure water replaced the same volume after each aliquot was taken.

Phosphate Ion Detection

In order to determine the concentration of phosphate ion in a given aliquot, the classic molybdenum blue method was used (*24*). A Tecan Infinite M200 spectrophotometer was used to measure absorbance values of the molybdenum complex at 882 nm. Each measurement was performed in triplicate.

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

Calcium Ion Detection

Potentiometry was used to determine the concentration of calcium ions (*25*). An ELIT 1265 calcium specific electrode was used for calcium ion detection. An ELIT 001N silver chloride electrode served as our reference.

Statistical Analysis

Standard deviations were calculated for each sample and a Tukey's comparison was performed on the data collected over the entire experiment.

Results

Phosphate and calcium ion release was studied due to its importance to the remineralization process. The figures report 'normalized' data, meaning that the concentrations refer to ion release per gram of microcapsule.

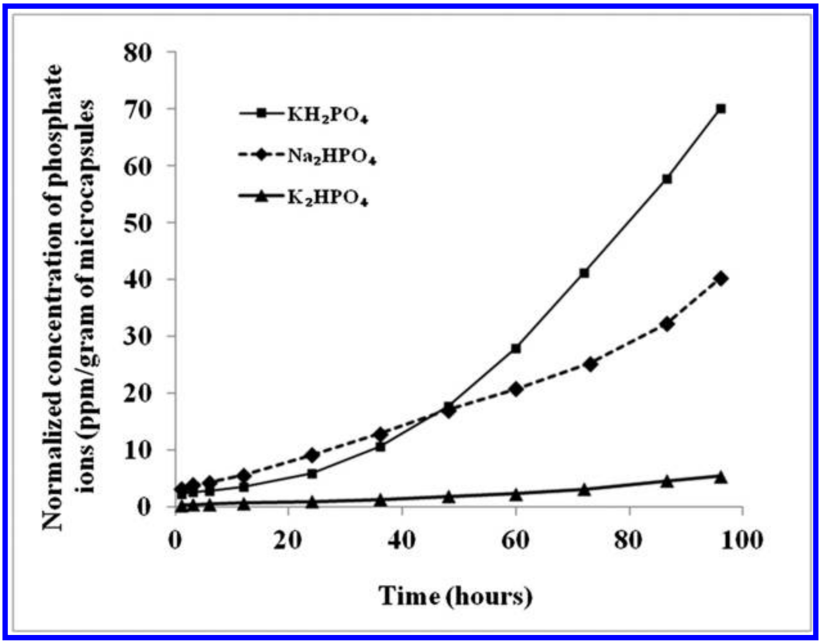


Figure 1. Normalized concentration of phosphate ions released in ppm per gram of microcapsules submerged in nanopure water as a function of time in hours. The figure represents the release of phosphate ions from microcapsules containing 0.5 M potassium phosphate monobasic, 0.5 M potassium phosphate dibasic, and 0.5 M sodium phosphate dibasic.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

Effect of Counterion

Three different 0.5 M aqueous solutions of potassium phosphate dibasic, potassium phosphate monobasic and sodium phosphate dibasic were encapsulated in ethylene glycol based polyurethane microcapsules. Figure 1 reports the concentration of phosphate ions released as a function of time for each salt solution. As seen in Figure 1, the microcapsule with potassium phosphate dibasic salt solution resulted in the slowest diffusion of phosphate ion from the microcapsule over the first 100 hours. The sodium phosphate dibasic and potassium phosphate monobasic solutions released phosphate ions at approximately the same rate over the first 50 hours of measurement. From hours 50 to 100, the potassium phosphate monobasic salt solution released phosphate ions from the microcapsule at a rate greater than the sodium phosphate dibasic solution.

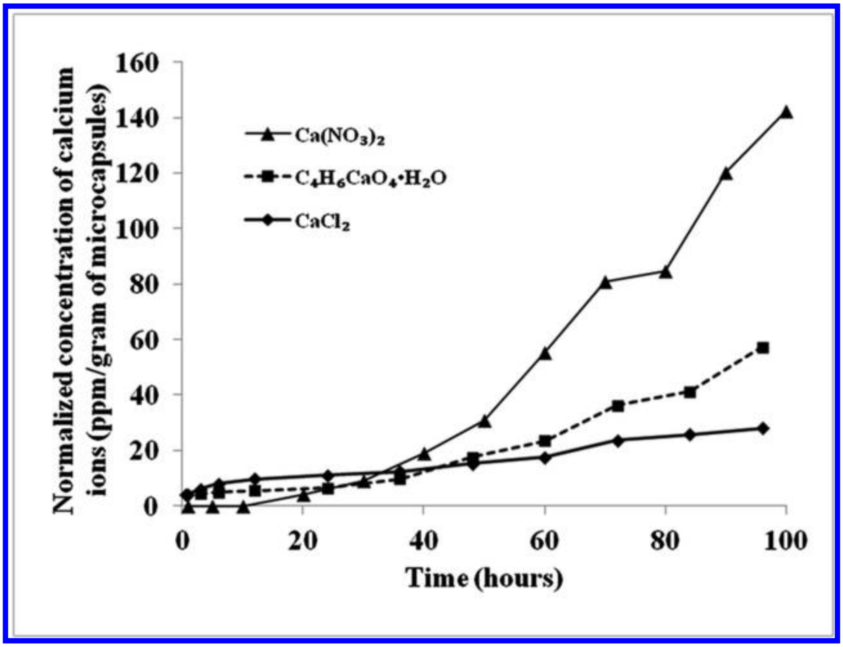


Figure 2. Normalized concentration of calcium ions released in ppm per gram of microcapsules submerged in nanopure water as a function of time. The figure represents the release of calcium ions from microcapsules containing 1.0 M calcium nitrate, 1.0 M calcium acetate, and 1.0 M calcium chloride.

Aqueous solutions of calcium salts were additionally prepared to determine the role of counterion identity on release rate. 1.0 M aqueous solutions of calcium nitrate, calcium acetate and calcium chloride were prepared in ethylene glycol based polyurethane microcapsules. Figure 2 shows the concentration of calcium ions released as a function of time for each salt solution. As seen in Figure 2, there was not much differentiation of calcium release rate as a function of counterion

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

over the first 40 hours. After the first 50 hours, the calcium nitrate solution released calcium ions at the fastest rate, followed by calcium acetate, which in turn released calcium ions at a greater rate than calcium chloride.

Effect of Concentration

Ethylene glycol based polyurethane microcapsules containing aqueous solutions of potassium phosphate dibasic salt were prepared at concentrations ranging from 0.5 M to 7.1 M. Figure 3 shows the concentration of phosphate ion released as a function of initial salt concentration at different time intervals. As seen in Figure 3, the release of phosphate ions is directly proportional to the initial salt concentration in the microcapsule over the first 12 hours of measurement. However, from hours 24 to 72, the 7.1 M solution released phosphate at a rate slower than the 6 M solution. As a result, the release rate of phosphate ions occurred at a concentration lower than the most concentrated solution used in the study.

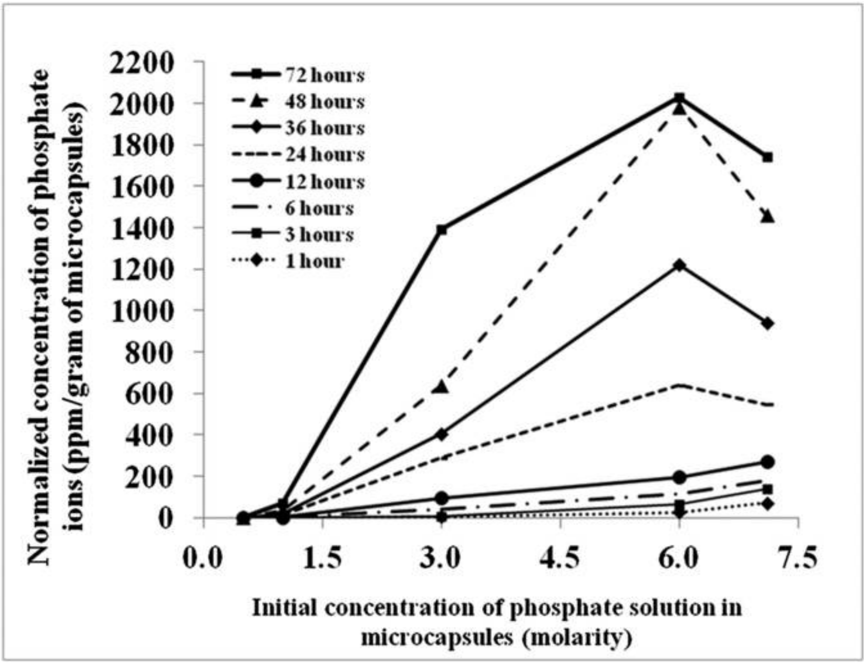


Figure 3. Normalized concentration of phosphate ions released in ppm per gram of microcapsules submerged in nanopure water. The figure represents the release of phosphate ions from microcapsules containing potassium phosphate dibasic at 0.5 M, 1.0 M, 3.0 M, 6.0 M, and 7.1 M. Phosphate ion release is illustrated as a function of initial concentration of phosphate solution in microcapsules at different release times.

Ethylene glycol based polyurethane microcapsules containing aqueous solutions of calcium nitrate salt were prepared at concentrations ranging from 0.5 M to 6.6 M. Figure 4 shows the concentration of calcium ion released as a function of initial salt concentration at different time intervals. As seen in Figure 4, the release of calcium ions is proportional to the initial concentration of calcium in the microcapsule. The greater the initial concentration of calcium contained in the microcapsule, the greater the release rate of calcium from the microcapsule. The 6.6 M solution released calcium ions at a much greater rate than the other initial concentrations over the first 39 hours of measurement. However, there appeared to be a reabsorption of some calcium back into the microcapsule establishing equilibrium at the 72 hour measurement for the 6.6 M sample. This reabsorption has not been observed in any of the other experiments.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

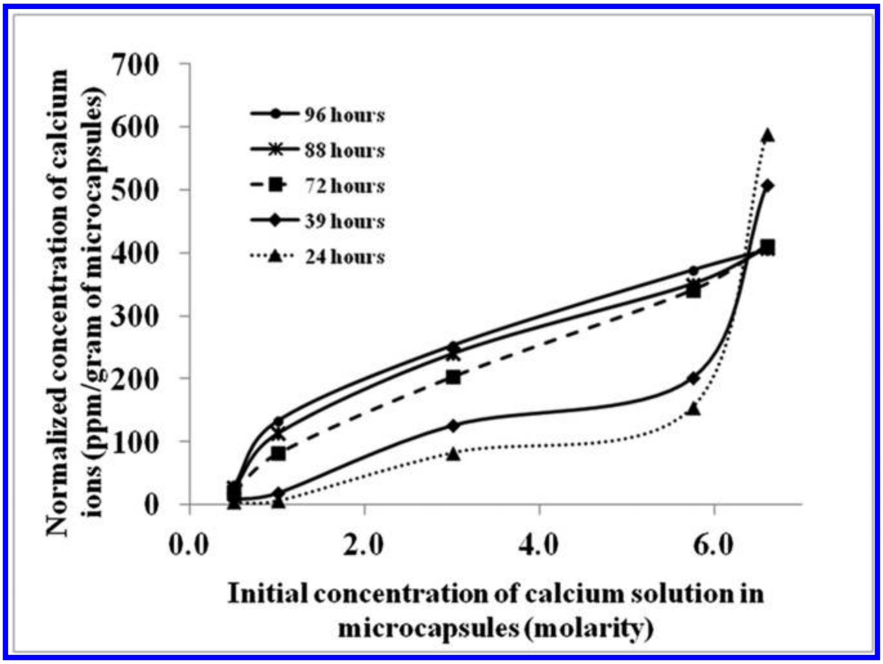


Figure 4. Normalized concentration of calcium ions released in ppm per gram of microcapsules submerged in nanopure water. The figure represents the release of calcium ions from microcapsules containing calcium nitrate at 0.5 M, 1.0 M, 3.0 M, 5.75 M, and 6.6 M. Calcium ion release is illustrated as a function of initial concentration of calcium nitrate within the microcapsules at different release times.

Microcapsules containing an aqueous solution of 2.4 M potassium phosphate dibasic salt were prepared in ethylene glycol based polyurethane microcapsules. Ion release studies were performed at 25 °C and 37 °C. Figure 5 shows the

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

concentration of phosphate ions released as a function of time at each temperature. As seen in Figure 5, the release rate of phosphate ions as a function of time increased with temperature. The microcapsules submerged in water at 37 °C released phosphate ions at a rate approximately three times greater than the microcapsules submerged in 25 °C water over the first 12 hours of the experiment. Over the next 88 hours of the experiment, the 37 °C sample released at a rate of approximately 1.2 times faster than the 25 °C sample.

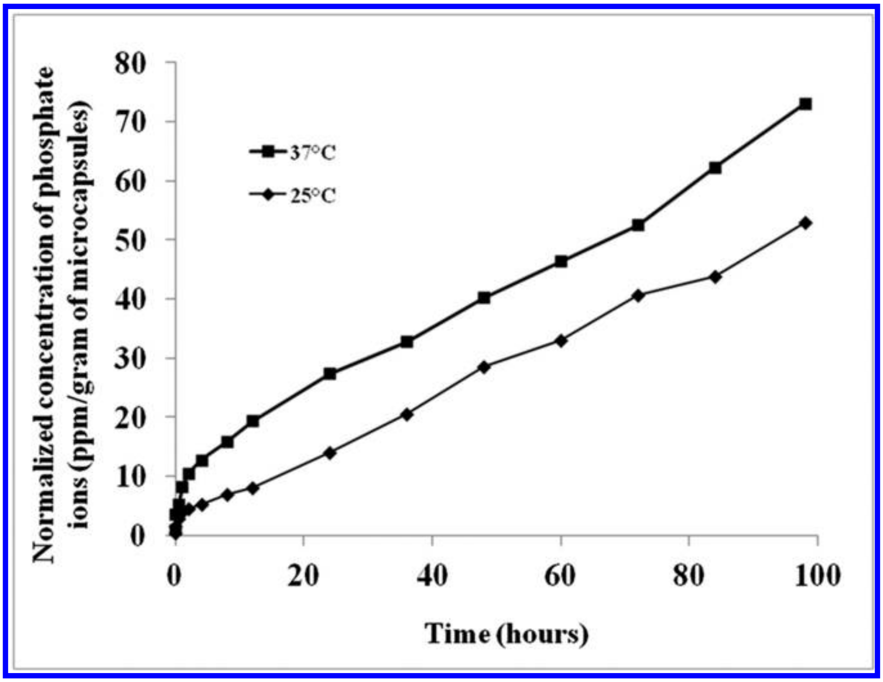


Figure 5. Normalized concentration of phosphate ions released in ppm per gram of microcapsules submerged in nanopure water at 25 °C and 37 °C as a function of time in hours. This figure represents the release of phosphate ions from ethylene glycol based microcapsules containing 2.4 M potassium phosphate dibasic.

Discussion

There are both thermodynamic and kinetic factors that are known to affect the ultimate release rate of ions from the microcapsules used in this study. The ion must first undergo sorption into the microcapsule membrane, which is subsequently followed by diffusion across the membrane (*26–29*). Some studies suggest that convection can play an important role in permeation through a membrane (*30*, *31*). Temperature and membrane thickness are important factors effecting the rate of permeation (*32*). Based on SEM analysis, the microcapsules thickness is likely to be constant as the microcapsules size were the same and synthesized under identical conditions. The free volume that exists in the microcapsule membrane is present as statistical fluctuations that come and go on the same timescale as the motions of the ions passing through the membrane. Thus, the rate of diffusion depends on the free volume and the mobility of the polymer chain segments. In these experiments, all of the microcapsules were synthesized from the same polyurethane, therefore, these effects should be negligible.

Our initial study of ion permeable microcapsules involved changing the chemical composition of the microcapsule itself, changing the initial concentration of salt inside the microcapsule, and the identity of the salt itself (*23*). This initial study demonstrated the ability to tune ion release from ion permeable microcapsules by changing these variables. It was found that the identity of the microcapsule structure was an important variable for controlling ion permeability rate, but this was sensitive to the initial concentration of the salt in the microcapsule.

In the initial study by Davidson, et al., it was found that the fluoride ion released at a rate that was greater than the calcium ion which in turn released faster than the phosphate ion. It seemed that the role of counterion could have played a large role in this observed order. In this paper, three different calcium salts and three different phosphate salts were encapsulated in the ethylene glycol based polyurethane microcapsules at a constant initial concentration. The release of a given ion is determined by a number of factors that affect the ion itself and its counterion (*33–36*). These variables include the size, polarity, polarizability, valency, specific interactions with the polymer chains of the membrane itself (e.g. hydrogen bonding), partition coefficients and diffusion coefficients.

As seen in Figure 1, the release profiles of microcapsules with three different phosphate ion containing salts with an initial concentration of 0.5 M was measured for 100 hours. Over the course of the experiment, the potassium phosphate dibasic salt permeated the microcapsule at the slowest rate, decisively slower than the monobasic form. Presumably, the divalent form of the salt has a slightly smaller size with an additional ion dissociated and a higher charge density than the monovalent form. This could create greater interactions between the polymer membrane and the divalent phosphate ion, thereby decreasing the rate of permeability. In comparing the sodium phosphate dibasic salt and the potassium phosphate dibasic salt, the sodium phosphate dibasic salt diffused at a greater rate through the membrane than the potassium phosphate dibasic salt. This is likely explained by the significantly smaller size of the sodium cation compared to the potassium cation.

The effect of counterion on permeability was also measured for the calcium ion. Calcium ion release as a function of time was measured from ethylene glycol based microcapsules containing 1.0 M solutions of calcium nitrate, calcium acetate, or calcium chloride. As seen in Figure 2, over the first 40 hours of release measurments there is not a significant statistical difference in the permeation of calcium ions based on counterion. However, as the experiment progressed, the rate of calcium ion permeation through the membrane increased for the nitrate ion relative to the acetate ion, which in turn permeated at a greater rate than

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

the chloride ion. In the experiment determining the effect of counterion on the phosphate ion, the cation and the valency of the anion were changed. In this experiment, only the identity of the anion was changed. In the case of changing the anion structure, it appeared that despite the fact that the nitrate and acetate ions were larger than the chloride ion, the negative charge on the nitrate and acetate ions are resonance stabilized. This resonance stabilization likely lead to decreased intermolecular interactions between these counterions compared to the chloride counterion.

The next series of experiments focused on the role of initial salt concentration in the microcapsule on the rate of ion permeability from the microcapsule. This variable was originally studied by Davidson, et. al. In the previous study, the rate of ion release increased significantly as the initial concentration of potassium phosphate dibasic increased from 0.5 to 1.0 to 3.0 M inside the ethylene glycol based polyurethane microcapsule. As only one microcapsule chemical structure and the same ion were used in this series of experiments, it is assumed that these results are explained by the rate of diffusion across the membrane. It was assumed the diffusion process was Fickian in nature, and the relationship $\delta C/\delta t = -\delta/\delta x\ [D(C)\delta C/\delta x]$ where D is the diffusion coefficient and C is the concentration of the diffusant inside the membrane, could be used to describe the effect of concentration on the diffusion coefficient. It has been observed that the diffusion coefficient can actually increase exponentially with local permeant concentration, effected by the degree of plasticization of the membrane (*37*). As the concentration of ions inside the membrane increases, the diffusion coefficient of the ion across the membrane increases.

In this study, a larger range of salt concentrations was studied for the potassium phosphate dibasic salt. Additionally, the effect of initial concentration of calcium nitrate solutions on calcium permeability rate was measured. Figure 3 represents the release of phosphate ions from microcapsules containing potassium phosphate dibasic at 0.5 M, 1.0 M, 3.0 M, 6.0 M, and 7.1 M. As seen in the Figure, the initial potassium phosphate dibasic concentration increased inside the microcapsule, the rate of ion release increased over the first 12 hours. However, over the next 60 hours, a maximum rate of phosphate ion diffusion from the microcapsule was observed at a concentration lower than the highest concentration studied.

This phenomenon is likely due to an increase in viscosity of the salt solution within the microcapsule. As the salt concentration increases, the viscosity of the salt solution increases. The effects of viscosity have been explained using the interionic attraction theory, which states that as the number of ions increase, a space lattice forms which is resistant to external forces due to the interionic forces within the structure (*38*). Viscosity also has a pronounced affect on diffusivity. The correlation between these two variables can be observed in the Stokes-Einstein equation (*39*), which shows that the diffusion coefficient and viscosity are inversely related. An increase in the mass percent of salts in water has also been shown to increase the kinematic and dynamic viscosities of the solution (*40*–*42*), over all measured temperatures (*41*, *42*). When comparing binary systems of potassium phosphate dibasic and water at different mass fractions and temperatures, it has been shown that as the mass fraction of the salt increases,

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

kinematic viscosity increases (*40*). In fact, the dynamic viscosity of potassium phosphate in an aqueous solution has been shown to increase in an exponential fashion as the mass percent of the salt increased (*41*). Therefore, it seems plausible that by increasing the concentration of the salt within the microcapsule, an increase in the viscosity of the solution occurred, thereby decreasing the diffusion of ions. This was especially true for the 7.1 M microcapsules.

Figure 4 depicts the rate of calcium ion permeability released from microcapsules with initial concentrations of 0.5 M, 1.0 M, 3.0 M, 5.75 M, and 6.6 M. Calcium ion release is illustrated as a function of initial concentration of calcium nitrate within the microcapsules at different release times. For calcium ion release, the range of concentrations studied was lower than phosphate ion release due to the lower solubilty of calcium nitrate compared to potassium phosphate dibasic. For the calcium ion, as the initial concentration of the ions in solution increased, the rate of calcium permeability increased. Although a maximum of permeability that was lower than the highest concentration measured was not observed for calcium nitrate, a relative sharp increase in permeation rate was observed upon going from 0.5 M to 1.0 M, compared to the increase in permeation rate going from 1.0 M to 5.75 M. This is likely due to the increase in viscosity of the salt solution. An interesting phenomenon in permeability was observed from the microcapsules initially containing 6.6 M salt. A great burst release of calcium ion was observed over the first 24 hours. The total amount of ion released appeared to subsequently decrease over the remaining time of the experiment, likely reestablishing an equilibrium.

Microcaspules incorporated into dental materials ultimately reside in the oral environment. Therefore, identifying the actual effect of increased temperature on ion diffusion rate through the membrane was measured. The normalized concentration of phosphate ions released in ppm per gram of microcapsules submerged in nanopure water at 25 °C and 37 °C as a function of time in hours is reported in Figure 5. This figure represents the release of phosphate ions from ethylene glycol based microcapsules containing 2.4 M potassium phosphate dibasic. As expected, as the temperature increased, the initial rate of ion diffusion across through the polymer membrane increased. It has been well established that the diffusion coefficient is directly proportional to the temperature of a system. In this specific system, when the concentration gradient across the membrane was the greatest, the 12 °C increase in temperature resulted in a threefold increase in the release rate of phosphate ions over the first 12 hours of measurement. As the concentration gradient across the membrane decreased over time, the temperature differential resulted in an approximate 1.2x increase in phosphate ion release over the remainder of the experiment.

In conclusion, ion permeable microcapsules containing aqueous solutions of phosphate or calcium ions have the potential to improve remineralization and whitening products. By varying the initial concentration of the salt in the microcapsule, the chemical structure of the microcapsule, the counterion of the remineralizing ion being released and the quantity of microcapsule incorporated into a specific continuous phase, targeted release rates of calcium and phosphate ions can be achieved over a given period of time.

Acknowledgments

The authors would like to acknowledge the Nebraska EPSCoR's University-Industry R&D Partnership Phase I and Phase II grants, the Premier Dental Products Company and GL Materials Research LLC for support of this research. MAL and SMG are member/managers of GL Materials Research LLC and have a financial interest with the Premier Dental Products Company.

References

1. Hicks, J.; Garcia-Godoy, F.; Flaitz, C. Biological factors in dental caries: role of saliva and dental plaque in the dynamic process of demineralization and remineralization (part 1). *J. Clin. Pediatr. Dent.* **2003**, *28* (1), 47–52.
2. Mathew, M.; Takagi, S. Structures of biological minerals in dental research. *J. Res. Natl. Inst. Stand. Technol.* **2001**, *106*, 1035–1044.
3. Dawes, C. What is the critical pH and why does a tooth dissolve in acid? *J. Can. Dent. Assoc.* **2003**, *69* (11), 722–724.
4. Sperber, G. H.; Buonocore, M. G. Effect of different acids on character of demineralization of enamel surfaces. *J. Dent. Res.* **1963**, *42*, 707–723.
5. Garcia-Godoy, F.; Hicks, J. M. Maintaining the integrity of the enamel surface: the role of dental biofilm, saliva, and preventive agents in enamel demineralization and remineralization. *J. Am. Dent. Assoc., JADA* **2008**, *139*, 25S–34S.
6. Ten Cate, J. M.; Featherstone, J. D. B. Mechanistic aspects of the interactions between fluoride and dental enamel. *Crit. Rev. Oral Biol. Med.* **1991**, *2* (2), 283–296.
7. Ten Cate, J. M. Current concepts on the theories of the mechanism of action of fluoride. *Acta Odontol. Scand.* **1999**, *57*, 325–329.
8. Pitts, N. B. Are we ready to move from operative to non-operative/preventive treatment of dental caries in clinical practice? *Caries Res* **2004**, *38*, 294–304.
9. Featherstone, J. D. B. The continuum of dental caries—evidence for a dynamic disease process. *J. Dent. Res.* **2004**, *83* (Spec Iss C), C39–C42.
10. Zero, D. T.; Martinez-Mier, E. A.; Ferreira-Zandona, A.; Ando, M.; Gonzalez-Cabezas, C.; Bayne, S. The biology, prevention, diagnosis and treatment of dental caries. *J. Am. Dent. Assoc., JADA.* **2009**, *140* (9) (suppl), 25S–34S.
11. Tung, M. S.; Eichmiller, F. C. Amorphous calcium phosphate for tooth remineralization. *Compendium* **2004**, *25* (9), 9–13.
12. Reynolds, E. C.; Cain, C. J.; Webber, F. L.; Black, C. L.; Riley, P. F.; Johnson, I. H.; Perich, J. W. Anticariogenicity of calcium phosphate complexes of tryptic casein phosphopeptides in the rate. *J. Dent. Res.* **1995**, *74* (6), 1272–1279.
13. Reynolds, E. C. Calcium phosphate-based remineralization systems: scientific evidence? *Aust. Dent. J.* **2008**, *53*, 268–273.
14. Zero, D. T. Recaldent™—evidence for clinical activity. *Adv. Dent. Res.* **2009**, *21*, 30–34.

15. Øgaard, B.; Seppä, L.; Rolla, G. Professional topical fluoride applications—clinical efficacy and mechanism of action. *Adv. Dent. Res.* **1994**, *8* (2), 190–201.
16. Strohmenger, L.; Brambilla, E. The use of fluoride varnishes in the prevention of dental caries: a short review. *Oral Dis.* **2001**, *7*, 71–80.
17. Skrtic, D.; Hailer, A. W.; Takagi, S; Antonucci, J. M.; Eanes, E. D. Quantitative assessment of the efficacy of amorphous calcium phosphate/methacrylate composites in remineralizing caries-like lesions artificially produced in bovine enamel. *J. Dent. Res.* **1996**, *75* (9), 1679–86.
18. Williams, J. A.; Billington, R. W.; Pearson, G. J. A long term study of fluoride release from metal-containing conventional and resin-modified glass-ionomer cements. *J. Oral Rehab.* **2001**, *28*, 41–47.
19. Itota, T.; Carrick, T. E.; Yoshiyama, M.; McCabe, J. F. Fluoride release and recharge in giomer, compomer, and resin composite. *Dent. Mater.* **2004**, *20*, 789–795.
20. Skrtic, D.; Antonucci, J. M.; Eanes, E. D. Amorphous calcium phosphate-based bioactive polymeric composites for mineralized tissue regeneration. *J. Res. Natl. Inst. Stand. Technol.* **2003**, *108* (3), 167–182.
21. Dhondt, C. L.; De Maeyer, E. A. P.; Verbeeck, R. M. H. Fluoride release from glass ionomer activated with fluoride solutions. *J. Dent. Res.* **2001**, *80* (5), 1402–1406.
22. Hadley, P. C.; Billington, R. W.; Williams, J. A.; Pearson, G. J. Interactions between glass ionomer cement and alkali metal fluoride solutions: the effect of different cations. *Biomaterials* **2001**, *22*, 3133–3138.
23. Davidson, M. T.; Greving, T. A.; McHale, W. A.; Latta, M. A.; Gross, S. M. Ion permeable microcapsules for the release of biologically available ions for remineralization. *J. Biomed. Mater. Res., Part A.* **2012**, *100A*, 665–672.
24. Murphy, J.; Riley, J. P. Single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* **1962**, *27*, 31–36.
25. Harwood, J. E. Use of an ion-selective electrode for routine fluoride analyses on water samples. *Water Res.* **1969**, *3*, 273–275.
26. Lyman, D. J.; Kim, S. W. Aqueous diffusion through partition membranes. *J. Polym. Sci.: Symp. No. 41* **1973**, 139–144.
27. Flynn, G. L.; Yalkowsky, S. H.; Roseman, T. J. Mass transport phenomena and models: theoretical concepts. *J Pharm. Sci* **1974**, *63*, 479–510.
28. Theeuwes, F.; Gale, R. M.; Baker, R. W. Transference a comprehensive parameter governing permeation of solutes through membranes. *J. Membr. Sci.* **1976**, *1*, 3–16.
29. Gelotte, K. M.; Lostritto, R. T. Solvent interaction with polydimethylsiloxane membranes and its effects on benzocaine solubility and diffusion. *Pharm. Res.* **1990**, *7*, 523–529.
30. Clément, R.; Jonquières, A.; Sarti, I.; Sposata, M. F.; Teixidor, M. A. C.; Lochon, P. Original structure-property relationships derived from a new modeling of diffusion of pure solvents through polymer membranes. *J. Membr. Sci.* **2004**, *232*, 141–152.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

31. Fíla, V.; Bouzek, K. The effect of convection in the external diffusion layer on the results of a mathematical model of multiple ion transport across an ion-selective membrane. *J. Appl. Electrochem.* **2008**, *38*, 1241–1252.
32. Kaibara, K.; Saito, K.; Kimizuka, H. Self-diffusion of a cation through cation exchange membrane and membrane permeability. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3712–3714.
33. Makino, K; Ohshima, H; Kondo, T Electrostatic interaction of ion-penetrable membranes. Effects of ionic solubility. *Colloid Polym. Sci.* **1987**, *265*, 911–915.
34. Miyoshi, H. Diffusion coefficients of ions through ion exchange membrane in Donnan dialysis using ions of different valence. *J. Membr. Sci.* **1998**, *141*, 101–110.
35. Sakai, Y.; Kadota, K.; Hayashita, T.; Cattrall, R. W.; Kolev, S. D. The effect of the counter anion on the transport of thiourea in a PVC-bases polymer inclusion membrane using Capriquat as a carrier. *J. Membr. Sci.* **2010**, *246*, 250–255.
36. Goli, E.; Hiemstra, T.; Riemsdijk, W. H. V.; Rahnemaie, R.; Malakouti, M. J. Diffusion of neutral and ionic species in charged membranes: Boric acid, arsenite and water. *Anal. Chem.* **2010**, *82*, 8438–8445.
37. Marais, S.; Métayer, M.; Nguyen, T. Q.; Labbé, M.; Perrin, L.; Saiter, J. M. Permeametric and microgravimetric studies of sorption and diffusion of water vapor in an unsaturated polyester. *Polymer* **2000**, *41*, 2667–2676.
38. Jones, G.; Dole, M. The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. *J. Am. Chem. Soc.* **1929**, *51*, 2950–2964.
39. Noda, A.; Hayamizu, K.; Watanabe, M. Pulsed-gradient spin-echo ^{1}H and ^{19}F NMR ionic diffusion coefficient, viscosity, and ionic conductivity of non-chloroaluminate room-temperature ionic liquids. *J. Phys. Chem. B* **2001**, *105*, 4603–4610.
40. Chenlo, F.; Moreira, R.; Pereira, G.; Vazquez, M. J. Viscosity of binary and ternary aqueous systems of NaH_2PO_4, Na_2HPO_4, Na_3PO_4, KH_2PO_4, K_2HPO_4, and K_3PO_4. *J. Chem. Eng. Data.* **1996**, *41*, 906–909.
41. Telis-Romero, J.; Coimbra, J. S. R.; Gabas, A. L.; Garcia Rojas, E. E.; Minim, L. A.; Telis, V. R. N. Dynamic viscosity of binary and ternary mixtures containing poly(ethylene glycol), potassium phosphate, and water. *J. Chem. Eng. Data.* **2004**, *49*, 1340–1343.
42. Goncalves, C. B.; Trevisan, N.; Meirelles, A. J. A. Kinematic viscosity of systems containing polyethylene glycol + salt + water at 298.2 K. *J. Chem. Eng. Data.* **2005**, *50*, 177–181.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch016

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

Chapter 17

Adsorption/Desorption Processes of pH-Responsive Copolymers on Model Dental Surfaces via QCM and AFM Analysis

Yan Zong, Yuhong Wei, and Sarah E. Morgan*

School of Polymers and High Performance Materials,
The University of Southern Mississippi, 118 College Drive, #5050,
Hattiesburg, Mississippi 39406
***E-mail: sarah.morgan@usm.edu.**

The stimuli-responsive adsorption of polyelectrolytes to biosurfaces provides an important vehicle for development of protective coatings, delivery of therapeutic agents, and cosmetic applications. Developing a fundamental understanding of the mechanisms and kinetics of adsorption/desorption processes of polymeric systems to biological surfaces is of critical importance in predicting performance and designing new formulations. This study describes quartz crystal microbalance and atomic force microscopy analysis of a poly(methyl vinyl ether-alt-maleic anhydride) copolymer (Gantrez® S97 BF) adsorption on dental mimicking surfaces to determine properties including thickness, morphology, viscoelasticy, and rate of adsorption/desorption of the polymer layer as a function of solution environment. A nanoscopically smooth model dental surface was developed for AFM analysis of the adsorbed thin film. It was found that solution pH, salinity, and polymer concentration affected the adsorption process and morphology of the adsorbed polymer layer. A higher rate of adsorption, greater stability, and a more homogeneous deposited film were observed for solutions with pH 4 than for those with pH 7, which was attributed to the charge state of polymer and

In Polymers for Personal Care and Cosmetics; Patil, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

substrate at the solution pH. Dramatic changes in polymer adsorption and film properties were observed as a function of polymer concentration with respect to the critical overlap concentration.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

Introduction

The alternating copolymer of methyl vinyl ether with maleic anhydride is known to be an effective bioadhesive for dental surfaces (*1*, *2*). The prevailing theory for the mechanism of adhesion of hydrolyzed maleic anhydride copolymers onto teeth is the ionic bonding interaction of copolymer carboxylate ions with calcium ions on the tooth surface (*3*). The primary mineral component of teeth is hydroxyapatite (HAp), a calcium phosphate (CaP) complex with the general formula $Ca_{10}(PO_4)_6(OH)_2$ (*4*). In order to optimize performance of formulated products for oral care applications, it is of interest to gain understanding of the mechanisms and kinetics of the adsorption and desorption processes of maleic anhydride copolymers on dental surfaces. One of the challenges in studying thin film adsorption onto natural surfaces is the inherent roughness and variability of these substrates, which may result in variable performance and introduces difficulty in evaluation using nanoprobe and other surface analytical techniques. In this study, we have used model surfaces to study the adorption/desorption properties of Gantrez® S97 (G-S97), a poly(methyl vinyl ether-*alt*-maleic acid/salt/ anhydride) copolymer produced by International Specialty Products Inc. (ISP®), using quartz crytal microbalance with dissipation monitoring (QCM-D) and atomic force microscopy (AFM) techniques.

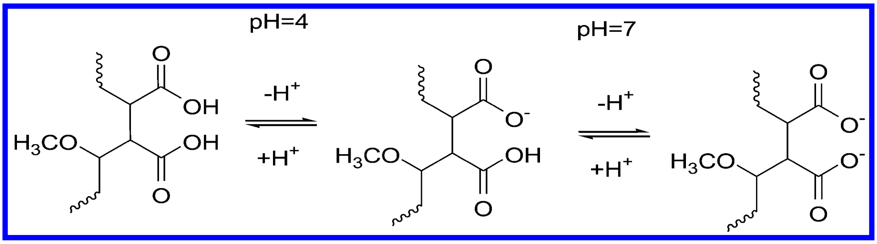
Maleic anhydride groups hydrolyze partially or totally in water, providing water solubility to the polymers and allowing them to be readily formulated in toothpaste, mouthwash or other oral care products to help to control the formation and growth of tartar. Additionally, the anhydride group of the copolymers can be used to bond with other compounds with a degradable ester linkage. On reaction of the anhydride group, water solubility is maintained through the residual carboxylate group. These properties make Gantrez® polymers useful as vehicles for delivery of therapeutics (*5*, *6*). Most importantly, Gantrez® polymers demonstrate dental adhesion properties, resulting from the electrostatic interaction or hydrogen bonding between carboxylic acid groups on the polymers and functional groups on the hydroxyapatite surface (*3*, *7*, *8*). Due to their strong adhesion to the tooth surface, they have also been used in dental adhesives.

In this study Gantrez® S-97 BF (G-S97), a free acid version of the Gantrez® series polymers, was selected as the model polymer. G-S97 is pH responsive and possesses two pKa's, with values of pK_{a1}=3.47 and pK_{a2}=6.47 (Scheme 1) (*9*).

While it is widely accepted that ionic interactions between the polyelectrolyte and the dental surface dominate the adhesion behavior of the polymer, the mechanisms and the kinetics of the adsorption/desorption process are not well understood. QCM-D (*10–14*) is a powerful technique for *in-situ* adsorption/desorption studies of biopolymer and synthetic polymer systems from solution. The quartz crystal surface can be modified to study interactions with

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

different substrates. The technique is sensitive to nanogram level mass changes on the surface and also provides information about the viscoelastic nature of the adsorbed thin film. Thus, both the deposition process and conformational rearrangements during the adsorption process can be evaluated. In this study, HAp coated QCM-D slides (to simulate dental surfaces) were used to evaluate G–S97 adsorption/desorption processes and kinetics for solutions of varying polymer concentration and pH. To the best of our knowledge, such studies of the kinetics of adsorption/desorption processes onto dental mimicking surfaces have not been previously reported.



Scheme 1. Protonation and deprotonation of maleic acid moiety of G-S 97 upon pH change

To further elucidate the mechanisms of adsorption for these polymers, the morphologies of thin films produced from the solutions were analyzed using AFM. To evaluate the nanostructure of these films, it was necessary to develop a nanoscopically smooth substrate with composition similar to that of the dental surface. Phosphorylation (*15*) of a cleaned silicon wafer was employed to provide a thin film of CaP to mimick the dental enamel surface. This smooth CaP surface allowed determination of the structure of the thin films produced from adsorption of polymer from solutions of varying concentration and pH, to complement the QCM-D studies. Ellipsometry evaluation provided information about the thickness of the adsorbed films, and solution viscosity studies were performed to determine the critical overlap concentration of the polymer in solutions of varying pH.

Experimental

Materials

Gantrez® S97 (G-S97) was kindly provided by ISP Technologies, Inc., Wayne, NJ, U.S.A.. Sodium chloride (NaCl, ≥99.5%) was purchased from Sigma-Aldrich. All chemicals were used as received. 100 mM NaCl solution, which was used as the solution for all polymer samples, was prepared by dissolving NaCl in 18.2 MΩ cm ultra pure water. G-S97 solutions of desired concentrations were prepared in the aforementioned NaCl solution and the pH was adjusted using NaOH.

Substrates

The QCM-D slides used were quartz sensor crystals, an AT-cut piezoelectric quartz crystal 14 mm in diameter and 0.3 mm in thickness coated with a 10nm thick hydroxyapatite layer (QSX 327, Biolin Scientific, Inc. Linthicum Heights, MD, U.S.A.). Before performing QCM analysis, all QCM-D slides were cleaned using UV/ozone treatment for 15 min, followed by immersion in a solution of 2% sodium dodecyl sulfate (SDS) in 18.2 MΩ cm ultra pure water for 30 min at room temperature. The slides were then rinsed with 18.2 MΩ cm ultra pure water and further cleaned using UV/ozone treatment for 10 min.

A nanoscopically smooth model dental surface was developed following a modification of the phosphorylation approach reported by Kim *et al.* (*15*) Silicon wafers (Silicon Inc. Boise, Idaho, U.S.A.) were cut into 12×12 mm^2 pieces to use as substrates for further development. Before modification all pieces were treated with piranha solution (25% H_2SO_4, 75% H_2O_2) for 30 min, then immersed in 18.2 MΩ cm ultra pure water for 20 min, and then dried with a slow stream of N_2. The cleaned substrates were immersed into a mixed solution containing 10 mM phosphorus oxychloride ($POCl_3$) and 10 mM 2,4,6-collidine in acetonitrile at 70°C for 12 h and 24 h, respectively. The modified substrates were placed into a 0.5 mM $CaCl_2$ solution for 20 min. The thickness changes after each step were monitored by ellipsometry.

Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)

The QCM-D slide is a disk shaped piezoelectric quartz crystal sensor, which is usually sandwiched between two gold electrodes contacted with an electronic oscillator. When an AC voltage is applied across the electrodes, the crystal sensor oscillates at different frequencies. The quartz crystal can be coated with different materials to provide deposition surfaces for study of chemical and/or biological adsorption. During the adsorption process, changes in frequency (Δf) and dissipation factor (ΔD) caused by adsorbed materials on QCM-D slides are simultaneously recorded. The resonant frequency of the crystal, f, will decrease as the adsorbed mass (m) increases. If the film is rigid, the frequency change $\Delta f = f_0 - f$, where f_0 is the resonant frequency of bare crystal in the medium, is proportional to the adsorbed mass. The relationship was described by Sauerbrey in 1959 (*16*):

$$\Delta m = -\frac{C\Delta f}{n} \tag{1}$$

where n is the overtone number (n=1, 3, 5, 7……) and C is the constant (C=0.177 mg m^{-2} Hz^{-1}) that reflects the sensitivity of the device to a change in mass. Since the AC voltage applied to the electrodes is operated intermittently, there is decay in oscillation due to energy losses. The dissipation factor D (unitless), which reflects the energy dissipation, provides information about the ratio of energy lost (E_{lost}) to the energy stored (E_{stored}) and is related to the time constant τ (*17*, *18*):

$$D = \frac{E_{lost}}{2\pi E_{stored}} = \frac{R}{\omega L} = \omega RC = \frac{1}{\pi f \tau} \tag{2}$$

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

where *f* is the resonant frequency, and the angular frequency (*ω*) can be varied to determine the resistance (*R*), inductance (*L*), and capacitance (*C*) of the crystal. QCM-D records the dissipation change in the dissipation factor: $\Delta D = D - D_0$ during the adsorption process, where *D* is the dissipation factor when polymer is adsorbed, and D_0 is the dissipation factor of bare crystal. ΔD is proportional to energy losses associated with the adsorbed materials.

In this study a QCM-D E4 system (Q-sense Inc., Gothenburg, Sweden) was used at 24±1 °C to monitor both adsorption and desorption of G S97 on a HAp surface. For the QCM-D study, G-S97 was prepared as 0.05, 0.2, 1, 4 and 5 mg/mL solution samples with pH 4 and 7 for each concentration. 100 mM NaCl solution and 18.2 MΩ cm ultra pure water were used to rinse adsorbed samples once the adsorption/desorption achieved equilibrium state (as defined by formation of a stable baseline). Four separate resonant frequencies (overtones, *n*) were used to drive oscillation of the shear wave through the sensor crystal. The changes in frequency (Δf) and dissipation factor (ΔD) were recorded simultaneously as a function of time at 5 MHz (fundamental overtone, $n = 1$), 15 MHz ($n=3$), 25 MHz ($n = 5$), and 35 MHz ($n = 7$). Since the noise at 5 MHz was very large, we neglected the data on fundamental overtone (n=1), as reported previously by other researchers (*19*, *20*). Each measurement was repeated at least two times. The maximum change in Δf was repeatable to within ±0.5 Hz and that of ΔD to within $\pm 0.2\times 10^{-6}$.

Atomic Force Microscopy

The morphology of adsorbed G-S97 samples was investigated by AFM (Digital Instruments, Santa Barbara, CA: Dimension 3000) in tapping mode. A silicon probe (Veeco, Camarillo, CA) with a nominal force constant of 40 N/m and resonance frequency of 335–345 kHz was used to image all samples. AFM images were taken at a scanning size of $0.5\times0.5\ \mu m^2$, and the resolution was held constant at 512×512 data points. Both height and phase images were collected simultaneously. AFM images were taken in air in a temperature (25°C) and humidity (50%) controlled room, and were processed using Gwyddion v2.30 software. At least three macroscopically separated areas were imaged for each sample and representative images are displayed. The image root-mean-square (rms) roughness is calculated as the root-mean-square average of the height deviations taken from the mean data plane, according to Equation 3 (*21*).

$$R_{rms} = \sqrt{\frac{1}{N}\sum_{j=1}^{N} r_j^2} \tag{3}$$

where N is the total number of pixels and r_j is the vertical distance of pixel *j* from the mean surface-height plane.

To prepare the samples for AFM study, model dental surfaces were immersed for 3 h in 5 mg/mL G S97 solutions of pH 4 and pH 7. The substrates were then quickly dipped in 18.2 MΩ cm ultra pure water to remove salt and dried with a weak stream of nitrogen.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

Intrinsic Viscosity

Intrinsic viscosity ($[\eta]$) measurements were used to estimate the critical overlap concentration ($C^*= 1/[\eta]$) of the polymer solutions. The apparent viscosities of G-S97solutions were measured using an Ubbelohde viscometer at 5 different concentrations. For each concentration, inherent viscosity, $\ln(\eta/\eta_0)$/c, and reduced viscosity, η_{sp}/c were calculated from the apparent viscosity measurements and plotted against polymer concentration to prepare a Huggins-Kraemer plot (*22*). Intrinsic viscosity was calculated from the extrapolation of the plots to the Y intercept.

Results and Discussion

Quartz Crystal Microscopy Analysis of the Adsorption Process

The adsorption of G-S97 onto hydroxyapatite coated surfaces was evaluated as a function of solution pH and polymer concentration using QCM-D. The experiments were conducted in four stages, as illustrated in Figure 1. First, 100mM NaCl stock solution was pumped over the HAp coated QCM-D slides until a stable baseline was obtained, when no change in frequency (f) or dissipation factor (D) was observed. In the second stage, polymer solution was injected into the flow line and pumped at a steady rate until a second stable baseline was observed, assumed to be the point at which the maximum level of polymer adsorption to the substrate was achieved. In the third step, a 100 mM NaCl rinse solution was pumped through the system to remove any loosely associated polymer from the adsorbed layer. Finally, a DI water rinse was applied and a final baseline recorded. A decrease in Δf is related to an increase in adsorbed mass, while an increase in ΔD is related to an increase in the viscoelastic response of the adsorbed polymer (*16–18*).

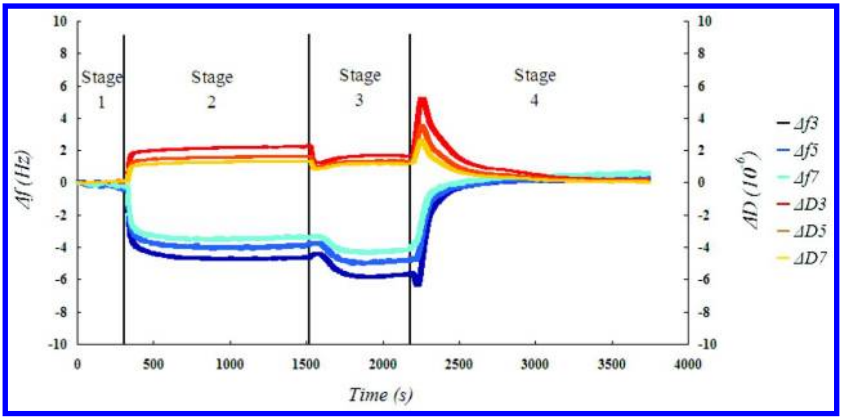


Figure 1. Representative QCM-D traces for polymer adsorption on HAp coated QCM-D slide: 0.05 mg/mL Gantrez® s 97 at pH 4.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

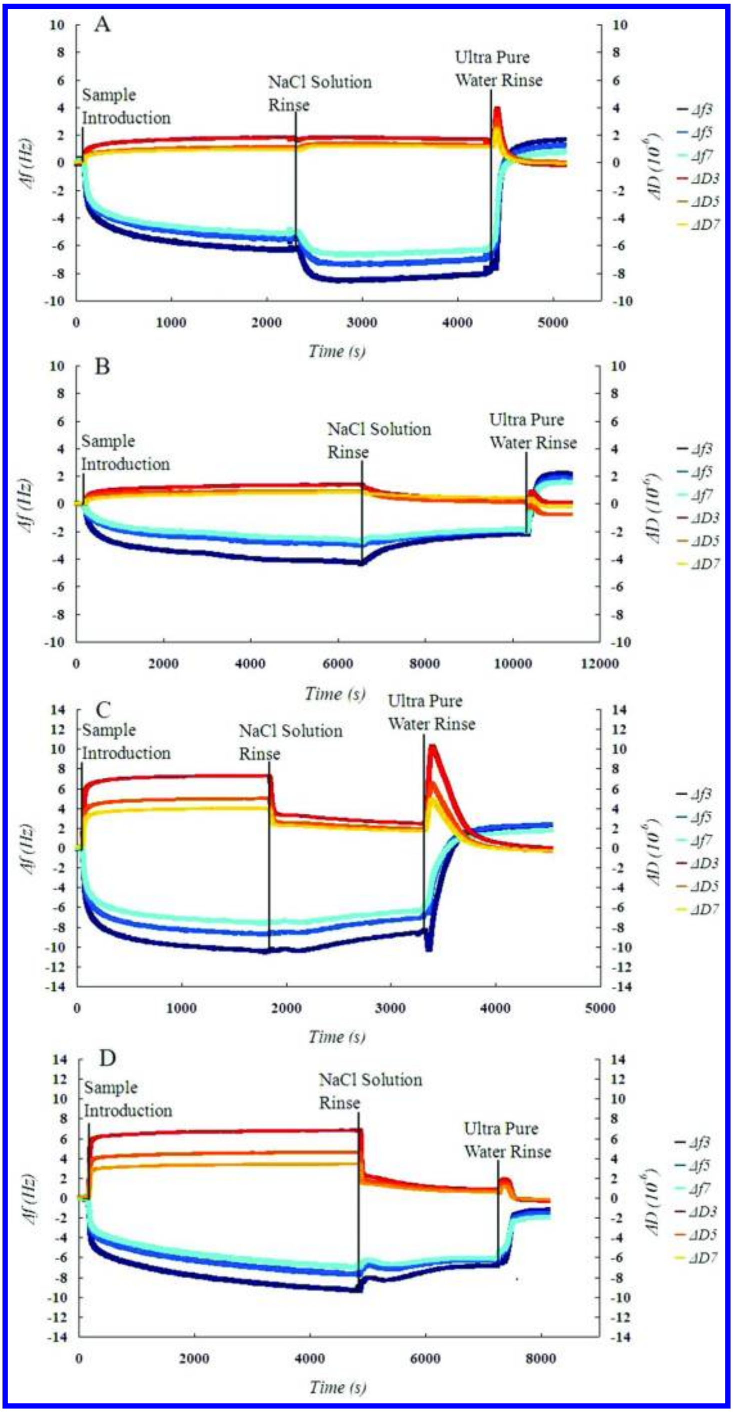


Figure 2. Adsorption of Gantrez® s 97 from solutions at different concentrations and pH levels: (A) 0.2 mg/mL (below C) at pH 4; (B) 0.2 mg/mL (below C*) at pH 7; (C) 5mg/mL (above C*) at pH 4; (D) 5mg/mL (above C*) at pH 7 as a function of time for three overtones (n=3, 5, and 7; f_0=5MHz) at 24±0.1 °C.*

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

Polymer solutions of five different concentrations were evaluated. The critical overlap concentrations (C*s) of G-S97 solutions were determined to be 3.3 mg/mL at pH 4 and 2.4 mg/mL at pH 7 from intrinsic viscosity measurements. Thus three solutions were prepared at concentrations below C* (0.05, 0.2 and 1mg/mL) and two above C* (4 and 5 mg/mL). Figure 2 shows representative QCM-D traces for polymer solutions at concentrations below C* (Fig. 2A = pH 4, Fig. 2B = pH 7) and above C* (Fig. 2C = ph 4, Fig. 2D = pH 7). Immediately upon introduction of polymer solution, the frequency decreased and the dissipation factor increased for all of the polymer solutions. The extent to which f and D changed and the rate at which the changes occurred were dependent upon polymer concentration and solution pH.

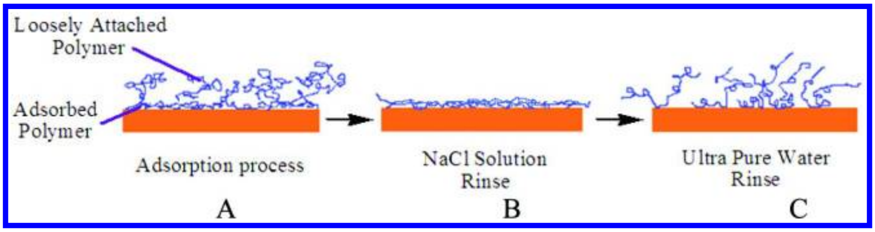
Table 1 provides a summary of measured Δf values for polymer solutions of different concentrations and pH at the equilibrium adsorption stage. In general, Δf values are lower for polymer concentrations below C* and the values increase with increasing concentration. Above C*, however, Δf appears to be constant. For a given polymer concentration, Δf is greater for solutions at pH 4 than for those at pH 7. This is attributed to the changes in the charge states of the HAp substrate and the polymer at different solution pH values. At pH 4, the HAp is expected to be positively charged, while the Gantrez polymer should have partial negative charge. At pH 7, the HAp is expected to have neutral charge, while the Gantrez polymer should be fully ionized (*9*, *23*, *24*). Thus, at pH 4 a higher level of ionic interaction is expected between the substrate and the polymer, corresponding to higher levels of adsorbed mass and greater Δf values.

For the solutions with concentration higher than C*, larger changes in dissipation factor and in the separation between overtone curves for ΔD measurements were observed. Large increases in ΔD indicate that the adsorbed layer does not behave as a purely elastic solid, but rather as a viscoelastic material with a significant viscous component. On application of the saline rinse, a sharp reduction in ΔD was observed for the high concentration solutions, with minimal changes in Δf (and thus minimal change in adsorbed mass). This indicates that the viscous layer most likely consisted of a small amount of loosely associated polymer that was removed with the saline rinse, as illustrated in Scheme 2. For the solutions with concentration below C*, only small changes in dissipation factor were observed. It is interesting to note that for the pH 4 solution of low concentration, a decrease in Δf (corresponding to an increase in adsorbed mass) was observed after injection of the saline rinse solution. This may be attributed to adsorption of salt by the charged G-S97 polymer.

Table 1. Changes in frequency of the third overtone ($\Delta f3$) at the equilibrium stage of the polymer adsorption process

Polymer concentration (mg/mL)	*$\Delta f3$ at pH4 (Hz)*	*$\Delta f3$ at pH 7 (Hz)*
0.05	-4.7	-3.0
0.2	-6.3	-4.2
1	-6.7	-5.1
4	-10.3	-9.4
5	-10.4	-9.4

For all solutions, when the DI water rinse was applied a gradual increase in Δf was observed until a stable baseline was reached, indicating removal of the adsorbed polymer layer from the HAp surface. The dissipation factor demonstrated an increase followed by a decrease to a stable baseline, indicating initial formation of a loosely attached viscous layer followed by removal of the polymer from the surface.



Scheme 2. Polymeric adsorption and desorption processes for polymer layers formed from high concentration (above C) G-S97solutions: (A) adsorbed polymer was covered by a loosely attached viscous layer; (B) salt solution removed the viscous layer; (C) adsorbed polymer was gradually rinsed off by ultra pure water*

The pH of the polymer solution had a large influence on the rate of adsorption and equilibration for the G-S97 solutions. For polymer solutions of pH 4 (Fig. 2 A and C), the saturation plateau was achieved at around 2000 s regardless of the polymer concentration. For solutions of pH 7 (Fig. 2 B and D), on the other hand, equilibrium was not reached even after 4000 s. Many factors have been reported to affect the polymer adsorption process onto a target surface, including polymer structure (*10*, *25*) solution conditions (*26*, *27*) and polymer-surface interactions (*13*). The greater rate of adsorption for the pH 4 solutions is attributed to electrostatic interactions between the oppositely charged substrate and polymer, as was previously reported by Zhang and coworkers (*27*). At pH 7, the polymer-surface interactions are weak due to the reduced ionic interactions, resulting in slower adsorption.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

Adsorption Kinetics

The adsorption kinetics of polyelectrolytes can be described as a three-step mechanism (*28*, *29*). The first step is the mass transport process, in which polymers diffuse to the proximity of the surface. The second step, the attachment onto the target surface, occurs when polymer chains begin to interact with the surface through secondary interactions including hydrophobic, *van der Waals*, hydrogen bonding, and electrostatic interactions (*30–32*). The last step is the rearrangement of adsorbed polymers in order to achieve a more stable state. A systematic study of the properties of the adsorbed layer, such as initial adsorption rate, adsorbed mass, layer thickness as well as the topography and morphology of the adsorbed layer, helps provide understanding of the adsorption kinetics.

The strength of the polymer-substrate interaction can be determined from the initial rate of polymer adsorption, if it is assumed that all macromolecules approaching the target surface during this initial stage can be absorbed. To further understand the effect of solution pH and polymer concentration on adsorption behavior, mass increase as a function of time for the first minute of polymer solution flow was determined and is shown in Figure 3. The rate of adsorption, as determined from the initial slope of the curve, is higher for solutions of pH 4, attributed to the stronger electrostatic interactions between the charged G-S97 and HAp surface at low pH.

Figure 4 shows mass uptake as a function of time for the polymer solutions over the entire equilibration stage. We first attempted to fit the data to a pseudo-first-order rate equation following equation 4 (*33*):

$$\Gamma_t = \Gamma_{max}(1 - e^{-kt}) \tag{4}$$

where Γ_t and Γ_{max} are the real-time and the maximum mass uptake values, respectively. This model significantly underestimated the initial rate of adsorption and provided poor fit to the data. We then attempted to fit the data to the sum of two first order rate expressions, following the method reported by Sedeva *et al.* (*13*), using equation 5.

$$\Gamma_t = \Gamma_{max1}(1 - e^{-k_1 t}) + \Gamma_{max2}(1 - e^{-k_2 t}) \tag{5}$$

In Figure 4 the black curves represent experimental data and the red curves are generated from the model fit to equation 5. Correlation coefficients and the plots indicate a high degree of agreement between the model and the experimental data. Model fit parameters and correlation coefficients are shown in Table 2. The model fit indicates that there are two stages present in the equilibration adsorption process: (1) a fast initial adsorption step related to electrostatic interactions between the polymer and the model surface and (2) a relatively slow secondary adsorption step dominated by diffusion of the polymer chains.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

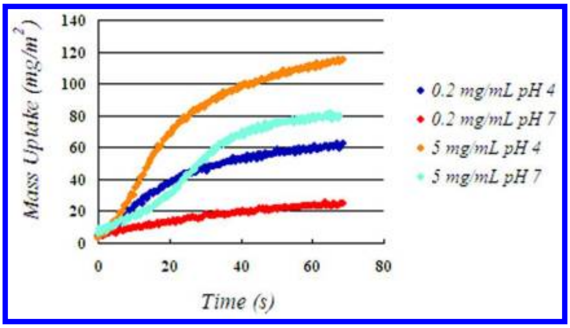


Figure 3. Initial mass uptake as a function of time for 0.2 and 5 mg/mL G-S97 solutions at pH 4 and 7.

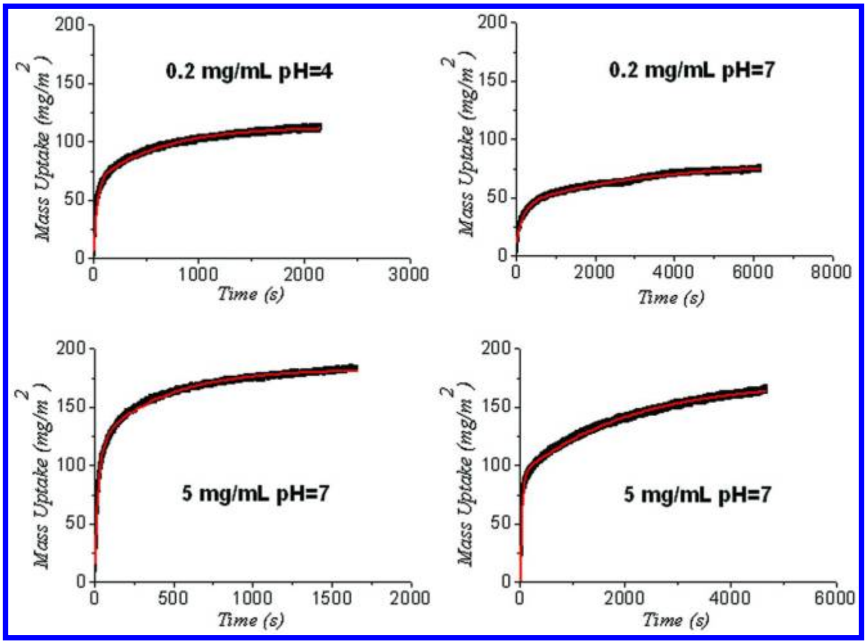


Figure 4. Mass uptake as a function of time throughout Stage 2 equilibrationfor 0.2 and 5 mg/mL G-S97 solutions at pH 4 and 7. Red line represents model fit tosummation of two first order expressions following reference (13), black line represents experimental data.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

Table 2. G-S97 Adsorption kinetic parameters for G-S97 solutions on HAp QCM-D slides: 1) 0.2 mg/mL at pH 4; 2) 0.2 mg/mL at pH 7; 3) 4 mg/mL at pH 4; 4) 4 mg/mL at pH 7. Determined from fitting to a summation of two first order expressions using OriginPro 8.0

	Γ_{max1} (mg/mL)	k_1 (s^{-1})	Γ_{max2} (mg/mL)	k_2 (s^{-1})	R^2
1	58.4±0.3	0.0305±0.0003	47.5±0.1	0.0016±0.0001	0.994
2	32.1±0.1	0.00054±0.0001	36.1±0.1	0.0003±0.0001	0.993
3	53.2±0.1	0.0023±0.0001	103.4±0.4	0.036±0.0003	0.995
4	80.0±0.1	0.0005±0.0001	94.7±0.2	0.026±0.0001	0.995

For this analysis, the mass uptake was calculated using the Sauerbrey model. The Sauerbrey model assumes a rigid film in the calculation of the adsorbed mass from the measured change in frequency. In the calculation of k_1 the mass change was evaluated only in the first minute of polymer deposition, when it is reasonable to regard the adsorbed polymer layer as a rigid film, since the adsorbed amount is very small, the polymer is well dispersed, and it can be assumed to homogeneously deposit onto the target surface. Further evidence to support this assumption is the overlapping of Δf traces during the initial stage, which is indicative of a rigid adsorbed layer (*34*). Alagha *et al.* (*14*) compared the mass of a viscous layer calculated using the Sauerbrey equation with its corrected mass calculated with the Voight model, and reported good agreement of the two models at the initial stage of deposition. It must be noted that the calculated adsorbed mass may include both polymer and water associated with the swollen adsorbed polymer chain.

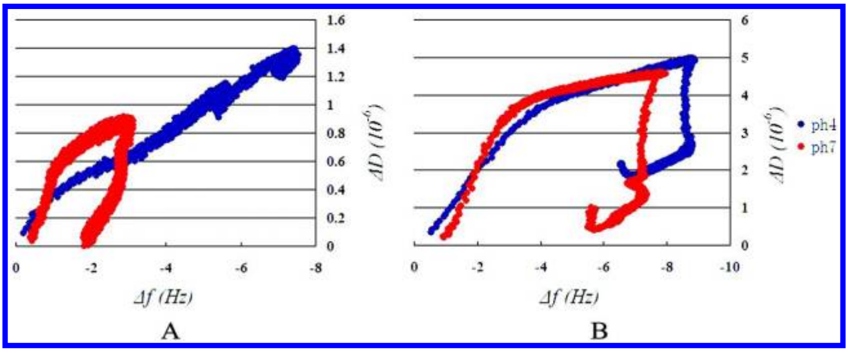


Figure 5. D-f plot for adsorption and desorption of (A) 0.2 mg/mL and (B) 5 mg/mL G-S97 solutions at pH 4 and 7.

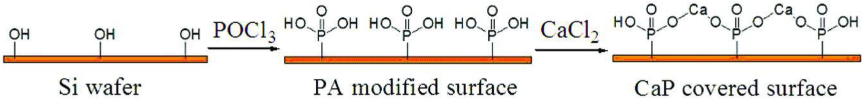
Examination of the frequency and dissipation factors as a D-f plot is a more effective way to investigate adsorption and desorption kinetics than evaluation of the raw QCM-D data, as it shows dissipation change per unit mass, which provides an indication of conformational changes during the process of adsorption (*13*, *35*).

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

If the D-f plot shows a linear relationship, it is assumed that the adsorbed layer maintains a constant conformation during the adsorption process. However, if the relationship is non-linear, this is indicative of a rearrangement of the adsorbed polymer chains. A sharp drop in the D-f plot indicates loss of mass from the adsorbed layer (*36*).

Figure 5 displays D-f plots for adsorption (during polymer solution flow) and desorption (during the NaCl solution rinse) of 0.2 (below C*) and 5 mg/mL (above C*) G-S97 solutions at pH 4 and 7. For solutions with concentration below C* pH has a dramatic effect on the D-f plot (Fig. 5A). For the pH 4 solution a linear relationship between ΔD and Δf is observed, suggesting that a compact, rigid layer formed on the surface and no conformational change occurred. For the pH 7 solution, on the other hand, initially a higher slope is observed followed by a change to a lower slope, indicating a transformation of the adsorbed polymer from a viscous to a more rigid layer (*14*). After the NaCl rinse solution was applied a sharp drop in the D-f curve is noted, indicating desorption of the polymer from the surface. The differences in the D-f plots for the two solutions are attributed to the differences in the charge states of the HAp surface and the polymers in solution at the different pH values. The negatively charged polymer is expected to deposit in a relatively extended state onto the positively charged HAp surface at pH 4. At pH 7, on the other hand, the HAp surface is neutral, attraction of the polymer to the surface is weaker, and polymers adsorb in a random conformation with loops and tails extending from the surface (*37*). Differences in conformation of adsorbed polyelectrolytes as a function of the nature of the charged surface were also reported by Guzman and coworkers (*29*). For solutions of concentration above C*, on the other hand, pH appears to have a smaller effect on adsorption/desorption behavior. D-f plots for the solutions of 5 mg/mL G S-97 demonstrated similar trends at pH 4 and 7 (Figure 5B): they both had much higher ΔD values (over 4×10^{-6}) than those demonstrated for the samples of concentration below C* (less than 1.4×10^{-6}), and both showed discontinuities for Δf values between -7 and -8 Hz. The adsorption/desorption behavior from the solutions above C* is attributed to the development of a viscous layer made up of loosely attached polymer chains, which is primarily driven by polymer-polymer interactions. The large dissipation factor of the loosely attached viscous layer overwhelms the portion due to the electrostatically bound rigid layer. Thus differences are observed for the high polymer concentration solutions of different pH only after the removal of the loosely bound layer with the saline rinse.

Model Surface Development



Scheme 3. Development of nanoscopically smooth model dental surface via phosphorylation

Table 3. CaP layer thickness and water contact angle for phosphoric (PA) modified and CaP coated model surfaces as a function of reaction time of phosphorylation

Reaction time	*CaP layer thickness* (nm)*	*Water contact angle of PA modified surface± (°)*	*Water contact angle of CaP covered surface (°)*
12 h	0.2±0.1	34.8±1.8	25.1±4.3
24 h	0.7±0.1	52.4±2.4	31.2±3.9

* Measured by ellipsometry. ± Cleaned silicon wafer is completely water wetting.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

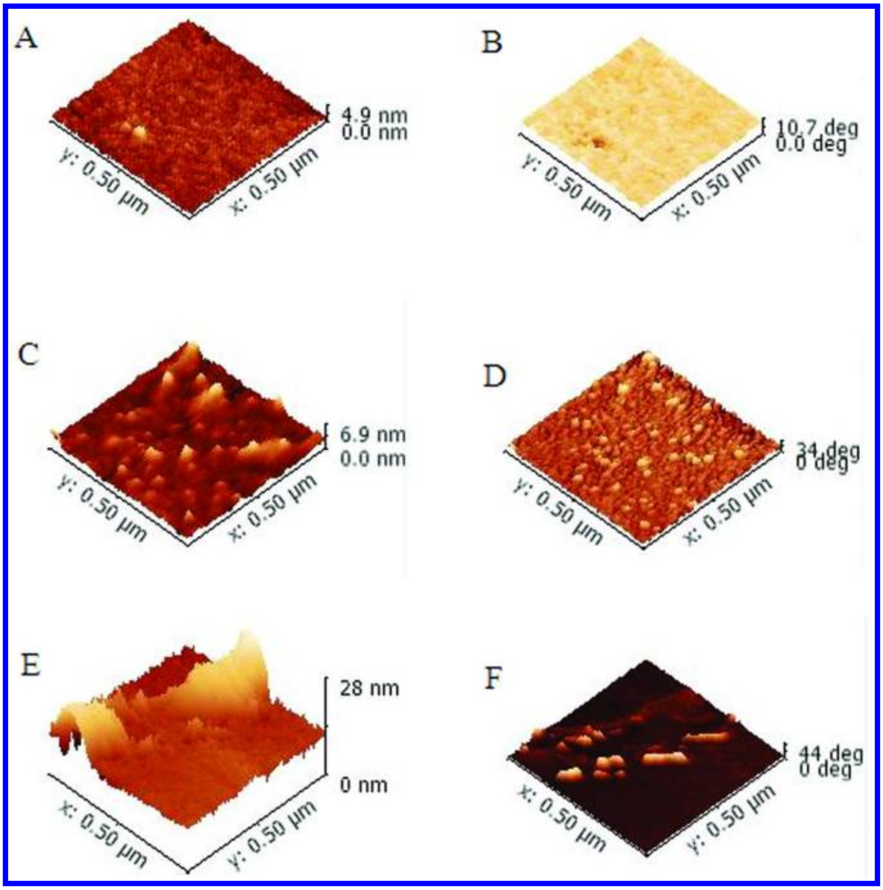


Figure 6. 3D AFM images of pH related adsorption on CaP model surface (left: height, right: phase): (A) and (B) blank CaP model surface; (C) and (D) G-S97adsorption at pH 4; (E) and (F) G-S97 adsorption at pH 7.

The QCM-D slides exhibit roughness values of several hundred nanometers, and are thus not suitable for AFM studies of the adsorbed thin films. We developed a nanoscopically smooth model dental surface for AFM analysis using a modified phosphorylation approach following that reported by Kim *et al.* as shown in scheme 3 (*15*). The thin layer of calcium phosphate provides a model surface to mimic the composition of the tooth surface. Table 3 shows thickness of the coating layer (measured by ellipsometry) as a function of reaction time and water contact angle of the surface for each step of the phosphorylation process. The thickness of the CaP layer was found to be 0.2 nm after 12 h reaction and 0.7 nm for 24 h reaction. Longer reaction time may increase the roughness of the surface and result in larger measured contact angle. The incorporation of calcium in the phosphoric acid coating was indicated by the change in water contact angle.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

Morphology Study

AFM height and phase images of the neat CaP surface are shown in Figures 6A and 6B, respectively. The surface is smooth and fairly featureless, with a measured RMS roughness of 0.3 nm. Images of the polymer-coated surfaces obtained from solutions of pH 4 and pH 7 are found in Figures 6C and D and 6E and F respectively. The polymer films adsorbed from the pH 4 solution are continuous, and cover the surface with small raised features 10-30 nm in width and measured RMS roughness of 0.7 nm. The homogenous coverage and smooth film surface resulted from the strong electrostatic interactions between the polymer and the surface at pH 4, which allowed strong adsorption and even dispersion of the polymer. The thickness of the adsorbed film was measured to be 2–3 nm by ellipsometry, consistent with the assumed extended charged polyelectrolyte deposition on the surface. The films deposited from pH 7 solutions, on the other hand, appear to be discontinuous and show larger sheet-like deposits that are several hundred nanometers to microns in length. The thickness of this irregular film was measured to be 5-8 nm by ellipsometry and the RMS roughness measured by AFM was 3.3 nm. The poor coverage on this surface is attributed to the weaker interactions between polymer and substrate at pH 7, and the deposition of polymer in a more random, globular conformation. The observed morphological features in AFM images support the conclusions drawn from QCM-D analysis, in which the adsorbed layers obtained from pH 4 solutions appear to be rigid films, while those obtained from pH 7 solutions appear to be viscoelastic, with a viscous, loosely attached outer layer made up of entangled polymer molecules (*37*).

Conclusions

The adsorption of G-S97 on dental mimicking surfaces was studied using QCM-D, AFM, and ellipsometry analyses. The studies showed that the adsorption mechanisms and kinetics were impacted by the pH of the deposition solution, attributed to differences in the charged state of the HAp surface, and to the concentration of the polymer in solution. At pH 4, the HAp substrate

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

was positively charged, resulting in strong electrostatic interactions between the partially negatively charged polyelectrolyte and the surface. Under these conditions and with low polymer solution concentration the adsorption rate was relatively high, and a flat, compact, rigid polymer layer was formed that homogeneously covered the model surface. No conformational changes were observed during deposition of this layer and the desorption of the polymer during the NaCl solution rinse was negligible. At pH 7 the charge density of the HAp surface was sharply reduced, resulting in lower levels of electrostatic interaction of the negatively charged polymer molecules with the surface. The polymer adsorbed onto the surface with loop and tail structures, and films were inhomegeneous due to weak polymer-surface interactions. High measured dissipation factor for films deposited under these conditions suggested the formation of a loosely attached polymer layer entangled with the loop and tail structures, which was removed by a saline rinse. Adsorption was found to be proportional to polymer concentration for dilute solutions, but it reached saturation at or above C*. A viscous layer formed by loosely attached polymer chains was observed in all solutions of concentration greater than C*, attributed to polymer-polymer interactions in concentrated solution. Adsorbed polymer was gradually removed from the polymer during ultra pure water rinse, indicating that a certain level of ionic strength is necessary to maintain adsorption on the dental surface. The results of these findings provide information on the kinetics of adsorption, morphology of adsorbed layers, and desorption processes of pH responsive polymers in contact with pH responsive dental-mimicking surfaces, and should prove useful in defining avenues for advancement of new polymer systems and formulations for oral care applications.

Acknowledgments

Funding from the PFI program of the National Science Foundation award no. IIP-0917730 is gratefully acknowledged. We thank Michael Fevola and Frank Sun at Johnson & Johnson Consumer & Personal Products Worldwide for helpful discussions, recommendations and materials.

References

1. Liang, N.; Rajaiah, J. U.S. Patent 5,872,161, 1999.
2. Kolias, F. G.; Wong, E.; Gasman, R. C. U.S. Patent 6,124,374, 2000.
3. Smith, D. *Br. Dent. J.* **1968**, *124*, 381.
4. Miles, A. E. W.; Allan, J. H. *Structural and Chemical Organization of Teeth*; Academic Press: New York, 1967.
5. Singhal, R.; Mishra, A.; Nagpal, A. K.; Mathur, G. N. *J. Polym. Mater.* **2009**, *26*, 239.
6. Heller, J.; U.S. Patents 4,261,969, 1981.
7. Ellis, J.; Jackson, A. M.; Scott, B. P.; Wilson, A. D. *Biomaterials* **1990**, *11*, 379.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

8. Yoshida, Y.; Meerbeek, B.; Nakayama, Y.; Snauwaert, J.; Hellemans, L.; Lambrechts, P.; Vanherle, G.; Wakasa, K. *J. Dent. Res.* **2000**, *79*, 709.
9. *Gantrez® Copolymers Technical Profile*; International Specialty Products Inc (ISP®), 1999.
10. Tsuchida, A.; Matsuura, K.; Kobayashi, K. *Macromol. Chem. Phys.* **2000**, *201*, 2245.
11. Höök, F.; Vörös, J.; Rodahl, M.; Kurrat, R.; Böni, P.; Ramsden, J. J.; Textor, M.; Spencer, N. D.; Tengvall, P.; Gold, J.; Kasemo, B. *Colloids Surf., B* **2002**, *24*, 155.
12. Olanya, G.; Iruthayaraj, J.; Poptoshev, E.; Makuska, R.; Vareikis, A.; Claesson, P. M. *Langmuir* **2008**, *24*, 5341.
13. Sedeva, I. G.; Fornasiero, D.; Ralston, J.; Beattie, D. A. *Langmuir* **2009**, *25*, 4514.
14. Alagha, L.; Wang, S.; Xu, Z.; Masliyah, J. *J. Phys. Chem. C* **2011**, *115*, 15390.
15. Kim, S. M.; Ahn, S. J.; Lee, H.; Kim, E. R.; Lee, H. *Ultramicroscopy* **2002**, *91*, 165.
16. Sauerbrey, G. *Z. Phys. A: Hadrons Nucl.* **1959**, *155*, 206.
17. Lüthgens, E.; Herrig, A.; Kastl, K.; Steinem, C.; Reiss, B.; Wegener, J.; Pignataro, B.; Janshoff, A. *Meas. Sci. Technol.* **2003**, *14*.
18. Höök, F.; Rodahl, M.; Brzezinski, P.; Kasemo, B. *Langmuir* **1998**, *14*, 729.
19. Irwin, E. F.; Ho, J. E.; Kane, S. R.; Healy, K. E. *Langmuir* **2005**, *21*, 5529.
20. Dutta, A. K.; Belfort, G. *Langmuir* **2007**, *23*, 3088.
21. Sahagun, C. M.; Morgan, S. E. *ACS Appl. Mater. Interfaces* **2012**, *4*, 564.
22. Linow, K. J. *Acta Polym.* **1983**, *34*, 447.
23. Zhang, J.; Maeda, M.; Kotobuki, N.; Hirose, M.; Ohgushi, H.; Jiang, D.; Iwasa, M. *Mater. Chem. Phys.* **2006**, *99*, 398.
24. Mafé, S.; Garcıa-Morales, V.; Ramırez, P. *Chem. Phys.* **2004**, *296*, 29.
25. Ondaral, S.; Wågberg, L.; Enarsson, L.-E. *J. Colloid Interface Sci.* **2006**, *301*, 32.
26. Saarinen, T.; Österberg, M.; Laine, J. *Colloids Surf., A* **2008**, *330*, 134.
27. Zhang, X.; Sun, Y.; Gao, M.; Kong, X.; Shen, J. *Macromol. Chem. Phys.* **1996**, *197*, 509.
28. Gregory, J. *Polym. Int.* **1995**, *36*, 102.
29. Guzmán, E.; Ortega, F.; Baghdadli, N.; Cazeneuve, C.; Luengo, G. S.; Rubio, R. n. G. *ACS Appl. Mater. Interfaces* **2011**, *3*, 3181.
30. Silva, R. A.; Urzúa, M. D.; Petri, D. F. S. *J. Colloid Interface Sci.* **2009**, *330*, 310.
31. Van de Steeg, H. G. M.; Cohen Stuart, M. A.; De Keizer, A.; Bijsterbosch, B. H. *Langmuir* **1992**, *8*, 2538.
32. Rojas, O. J.; Ernstsson, M.; Neuman, R. D.; Claesson, P. M. *Langmuir* **2002**, *18*, 1604.
33. Chiem, L. T. H., L.; Ralston, J.; Beattie, D. A. *J. Colloid Interface Sci.* **2006**, *297*, 54.
34. Steinem, C.; Janshoff, A. *Piezoelectric Sensors*; Springer: New York, 2007; Vol. 5.

35. Slavin, S.; Soeriyadi, A. H.; Voorhaar, L.; Whittaker, M. R.; Becer, C. R.; Boyer, C.; Davis, T. P.; Haddleton, D. M. *Soft Matter* **2012**, *8*, 118.
36. Sedeva, I. G.; Fetzer, R.; Fornasiero, D.; Ralston, J.; Beattie, D. A. *J. Colloid Interface Sci.* **2010**, *345*, 417.
37. Morgan, S. E.; Jones, P.; Lamont, A. S.; Heidenreich, A.; McCormick, C. L. *Langmuir* **2006**, *23*, 230.

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ch017

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ix002

Subject Index

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ix002

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ix002

Publication Date (Web): December 5, 2013 | doi: 10.1021/bk-2013-1148.ix002