Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.fw001

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ACS SYMPOSIUM SERIES **1151**

# Introduction of Macromolecular Science/Polymeric Materials into the Foundational Course in Organic Chemistry

**Bob A. Howell**, Editor
*Central Michigan University*
*Mt. Pleasant, Michigan*

**Sponsored by the**
**ACS Division of Chemical Education**

American Chemical Society, Washington, DC

Distributed in print by Oxford University Press

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.fw001

**Library of Congress Cataloging-in-Publication Data**

Introduction of macromolecular science/polymeric materials into the foundational course in organic chemistry / Bob A. Howell, editor, Central Michigan University, Mt. Pleasant, Michigan ; sponsored by the ACS Division of Chemical Education.
pages cm. -- (ACS symposium series ; 1151)
Includes bibliographical references and index.
ISBN 978-0-8412-2878-8 (alk. paper)
1. Macromolecules--Congresses. 2. Polymers--Congresses. 3. Chemistry, Organic--Congresses. I. Howell, B. A. (Bobby Avery), 1942- editor of compilation. II. American Chemical Society. Division of Chemical Education, sponsoring body.
QD380.I64 2013
547'.7--dc23
2013041536

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.

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PRINTED IN THE UNITED STATES OF AMERICA

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# 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.

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# Preface

## The Need To Provide Some Introduction to Polymeric Materials in Foundational Chemistry Courses

Currently most undergraduate programs in chemistry provide inadequate training in the area of polymeric materials. This despite the fact that these materials are largely responsible by the quality of life that everyone enjoys and that most chemistry graduates, at whatever level they decide to seek employment, will work in a polymer or a polymer-related area. This situation has been recognized by the ACS Committee on Profesional Training. Current committee guidelines contain the expectation that a treatment of polymeric materials will be a part of all foundational courses in chemistry. This is, perhaps, most readily done for the foundational organic chemistry course. Most commercial polymers commonly used by the consuming public are organic in composition and are formed by simple, easily-understood organic reactions. The preparation of polymeric materials can be used to illustrate many of the fundamental concepts of organic chemistry. Inclusion of some treatment of polymeric materials serves to stimulate student interest and enthusiasm for the course and to emphasize the central role that these materials occupy in their daily lives and the overall well-being of society.

The importance of polymeric materials in modern society may be reflected in several simple illustrations. For example, the construction of a modern home is strongly dependent on these materials. The exterior of the home is often vinyl siding, i.e., poly(vinyl chloride) [PVC]. It can be pigmented in any attractive color, is durable (lasts longer than other components of the house) and does not require maintenance. Beneath the vinyl siding is 2 or 4 inches of styrofoam insulation. This insulation is made from foamed poly(styrene). Beneath the insulation, covering the sheeting is usually a barrier layer of Tyvec, a poly(amide). The sheeting is plywood which is comprised of thin wood laminates held together with a phenol-formaldehyde adhesive. Beneath the sheeting is spun fiberglass insulation, an inorganic polymer. The next layer forms the interior of the wall and is constructed from dry wall (sheet rock). Dry wall is a layered structure containing gypsum as a main component held in place by sheets of a cellulosic polymer. The surface of the dry wall facing the interior of the house is coated with an acrylate polymer applied as a latex containing a suitable pigment. Thus several polymers are utilized just for wall construction to say nothing of the interior of the house (Figure 1).

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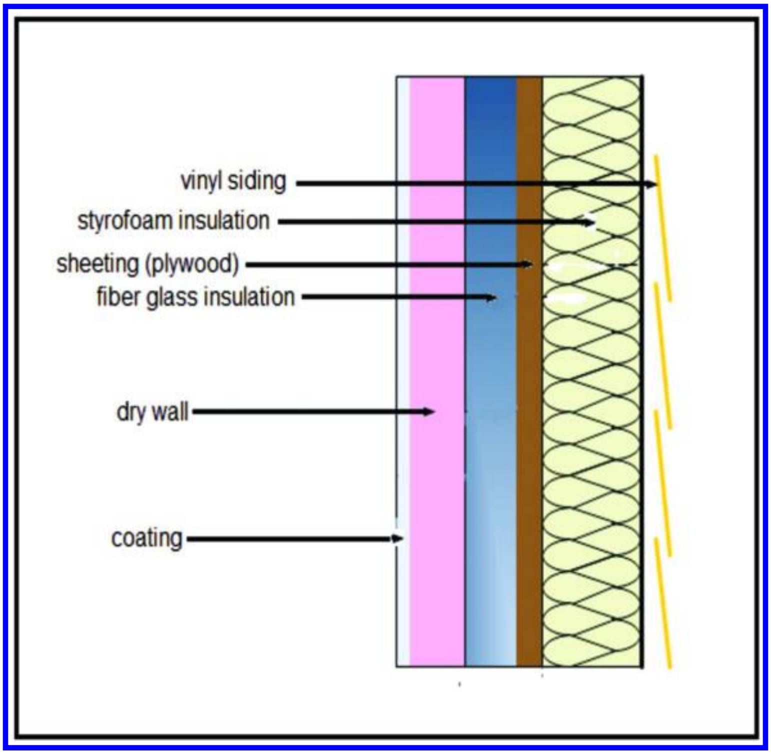

*Figure 1. Polymeric Components of a Typical Home Wall*

Plumbing pipe for the house is constructed from PVC, as is the tile in the kitchen and bathroom and portions of the roofing shingles. Window blinds may also be from PVC. Carpets are made nylon or acrylic fiber [poly(acrylonitrile)]. Light coverings are from general purpose poly(styrene). Surfaces of tables and furniture may be from an acrylonitrile-butadiene-styrene (ABS) polymer. This material can be given the appearance of any common wood grain but, of course, is much durable and resisitant to damage than is wood. Housings for common appliances (washer/drier units, dishwashers, refrigerators, freezers, etc) are made from ABS. These housings are lightweight, resilient and durable. If a chair is backed into a refrigerator the housing does not dent or break but rebounds to its original shape. Covers for couches are woven from nylon fiber (very durable) and coated with a poly(siloxane) or fluorocarbon polymer to resist staining. Simple kitchen utensils (bowls, pitchers, etc.) may be made from poly(ethylene) or poly(propylene). The non-stick surface on baking and fry pans is made from poly(tetrafluorethylene) [Teflon]. And this is but a partial listing and does not reflect polymeric components of food packaging, the food itself, personal care items, medicines, and the like that may be present in the home.

The automobile sitting in the driveway also contains many polymeric components. In fact, its construction is strongly dependent on the availability of polymeric materials. In the interior, the dash is from PVC. Seat covers may

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be from the same material. The seats themselves are made from poly(urethane). Gears in dashboard instruments are made from nylon or poly(oxymethylene) [Delrin]. Polymers are prominent in other areas as well. Side panels are made from ABS, fenders and valve covers from poly(propylene), light covers from poly(styrene), bumpers from poly(carbonate), exhaust manifolds and brake lines from nylon, fuel tanks from poly(ethylene), wiring insulation from PVC, battery covers from poly(propylene), gaskets from neoprene [poly(chloroprene)] or siloxane polymers, protective coatings from poly(urethane), and on and on, not to mention several elastomers contained in the tires.

Similar examples could be drawn from the areas of medicine, personal care, food or several others. However the pervasiveness, and utility of polymeric materials in supporting the modern lifestyle should be apparent from this brief listing.

Not only is modern society dependent upon the availability of polymeric materials but the polymer industry makes a significant ccontribution to US GDP and provides employment for most chemists. Clearly, some treatment of polymeric materials should form a component of foundational courses in chemistry. There are many ways that polymeric materials may be included in the beginning course in organic chemistry. All of these serve to illustrate important concepts of organic chemistry, to broaden student awareness of the prominent role that organic chemistry and polymeric materials play in their lives, and to enhance student interest in and enthusiasm for organic chemistry. Several ways that polymeric materials and concepts have successfully been incorporated into the beginning organic chemistry course are described in the chapters that follow.

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# Editor's Biography

## Bob A. Howell

Bob Howell is a native of western North Carolina (Ashe County). He received the B.A. degree in chemistry at Berea College (1964), a Ph.D. in physical-organic chemistry at Ohio University (1971), and completed a postdoctoral assignment with Professor Walter Trahanovsky at Iowa State University (1971-74). He is currently Professor, Department of Chemistry, Central Michigan University, where he has taught the sophomore-level organic chemistry course for over thirty years. Enhancing student interest in and enthusiasm for this course has been a longtime goal. Demonstrating the importance of organic chemistry/polymeric materials in the daily lives of students has been an effective means of engaging the student and promoting student performance. In addition to this course, he has taught a range of courses including Industrial Chemistry and Polymer Chemistry, as well as upper-level organic chemistry courses. He has twice been the recipient of major teaching awards.

His research interests are broad-ranging in the area of organic/polymer chemistry. A current major focus is the development of non-toxic, biodegradable, environmentally-friendly flame retardants based on renewable biomaterials.

He has long been active in several professional societies, most prominently the American Chemical Society (ACS) and the North American Thermal Analysis Society (NATAS). He is currently a member of several ACS committees and the NATAS Executive Board. He is Fellow of both the ACS and NATAS and is the 2012 recipient of the NATAS award for outstanding achievement, which recognizes distinguished accomplishment in the field of thermal analysis of generally wide interest and impact.

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## Chapter 1

# Integration of Macromolecular/Polymeric Topics Within the Foundational Organic Chemistry Content and the Polymer Education Committee

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Just as chemistry stands at the apex of most of science, so also do polymers. Polymers are a bridge to many topic areas in science, medicine, environment, communications, and engineering and to all of the major disciplines of chemistry. Polymers are a natural bridge between teaching material and the world of practice. It serves as a clear and persuasive connection between material presented to students at all levels and reality that science is important and pervasive. It is clearly apparent in the curriculum materials called organic chemistry. Here is presented material describing PolyEd and its many programs and the effort to assist teachers and various American Chemical Society programs to utilize polymers to enhance this natural connection between teaching material and the real world.

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# Introduction

The Polymer Education Committee, PolyEd, was formed in 1974 in response to an observed need that polymers and polymer-related examples can contribute to the teaching of basic concepts throughout the academic and post-academic career of students (*1–3*). Use of polymers is also important in conveying to society the importance between the real world and the developing world of science. Further, they are the single most important class of materials. Polymers are the materials of life, of commerce, of health, of communication, etc.

Polymers are a **natural** bridge between "the real world" and science. Using polymers allows much of the basic science knowledge to be presented. The use of polymers also encourages the application and importance of materials and concepts derived from this basic science knowledge in the world of practice that captures the student and teacher and shows the application and importance of science. Thus, polymers are an ideal vehicle for the conveyance of science from K through post graduate, including the general public.

PolyEd has had association with Nobel Prize winners Paul Flory, Linus Pauling and Alan McDiarmid; American Chemical Society Presidents including Eli Pearce, Elsa Reichmanis, Ann Nalley, Charles Overberger, William Bailey, Gordon Nelson and Mary Good; and College Presidents Angelo Volpe and L. (Guy) Donaruma and Priestley Medal winners Paul Flory, Linus Pauling, Mary Good and Edwin Vandenberg.

At times there are those that divide the terms macromolecules and polymers with the term polymers employed to describe synthetic materials while the term macromolecules used to describe biological materials (*4*, *5*). Here, we will use these terms interchangeably. Polymers/macromolecules are important as inorganic as well as organic materials and natural materials. Table 1 gives some important examples of the divergence of polymeric materials. Our focus here is on organic materials.

Equations 1 through 4 are examples of organic polymer syntheses that are cited in Table 1 and that should be considered in foundational organic content.

Equations 1 and 2 outline the synthesis of two important condensation reactions. Equation 1 describes the synthesis of monomeric and polymeric, poly(ethylene terephthalate), esters. The synthesis of poly(ethylene terephthalate), PET or PETE, is the extension of monomeric ester synthesis. Both are equilibrium processes. PET is the most widely synthesized fiber sold under a variety of tradenames including Dacron and Kodel. It is also employed as a plastic that composes most of the soda and water bottles produced today. This illustrates the importance of ester synthesis in the world that students are familiar with. The formation of PET employs ethylene glycol as the diol and again, students can be reminded of the wide uses of ethylene glycol including use in antifreeze. Mechanistic discussions are also appropriate to introduce at this juncture. Further, the synthesis of ethylene glycol from natural "green" materials allows discussion of "green chemistry" in commercial production of items they are familiar with.

Equation 2 describes the synthesis of nylon 66. This is simply the extension of monoamide formation and also allows the comparison between synthetic amide formation and natural amide formation reactions resulting in protein formation.

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## Table 1. Polymer Classes-Natural and Synthetic

***Inorganic Natural***

- Clays
- Concrete
- Pottery
- Bricks
  - Sands
  - Glasses
- Rock-like
  - Agate
  - Talc
  - Zirconia
  - Mica
  - Quartz
- Ceramics
- Graphite/diamond
- Carbon nanotubes
- Silicas

***Inorganic Synthetic***

- Fibrous glass siloxanes
- Poly(sulfur nitride)
- Poly(boron nitride)
- Silicon carbide

***Organic/Inorganic***

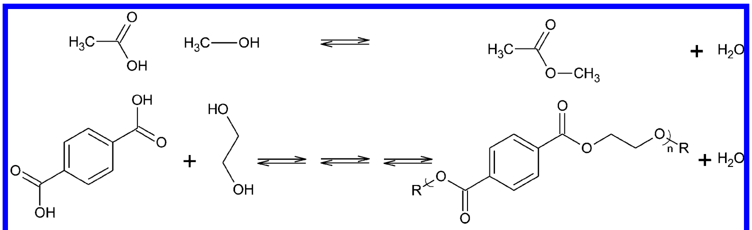
- Polyphosphazenes
- Poly(phosphate esters)
- Polysiloxanes
- Sol-gel networks

***Organic Natural***

- Proteins
- Nucleic Acids
- Lignins
- Polysaccharides
- Melanins
- Natural rubber
- Cellulose

***Organic Synthetic***

- Polyethylenes
- Polystyrene
- Nylons
- Polyesters
- Polyurethanes
- Polyacrylates and methacrylates
- Polytetrafluoroethylene
- Poly(vinyl chlorides)
- Polycarbonates
- Polypropylene
- Phenolic plastics
- Poly(vinyl alcohol)
- Poly(ethylene oxide)



**Equation 1. Synthesis of simple esters, top, and poly(ethylene terephthalate), below, where R represents simple chain extension and n is the chain length.**

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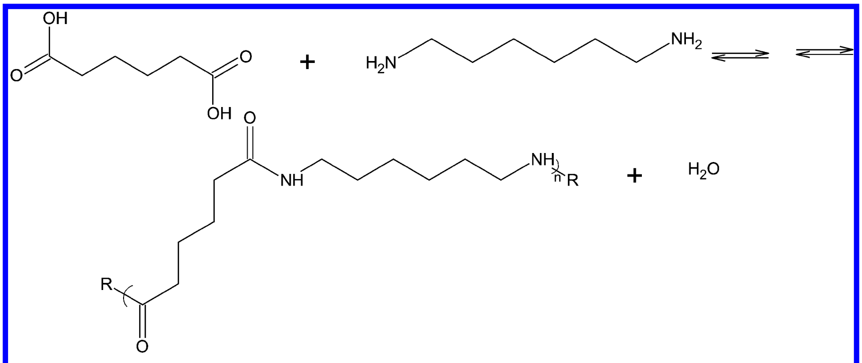
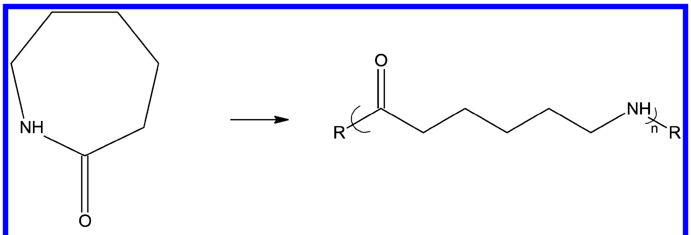


**Equation 2. Synthesis of nylon 66 where R represents chain extension.**

Nylon 6, structurally and physically similar to nylon 66, is formed from the ring opening polymerization, ROP, of caprolactam as described in Equation 3.



**Equation 3. Synthesis of nylon 6 from the ring opening of caprolactam.**

Nylon 66 and nylon 6 are used as a plastic for bicycle wheels, tractor hood extensions, skis for snowmobiles, skate wheels, etc. As a fiber, they are used in clothing, fabrics, and rugs.

The formation of most of the vinyl polymers is described in Equation 4.

$$H_2C{=}CXH \longrightarrow -(-CH_2-CXH-)_n$$

**Equation 4. General description for the formation of vinyl polymers.**

When X = H we have the general repeat unit for polyethylene. When X = Cl we have the repeat unit for poly(vinyl chloride); R = phenyl for polystyrene; R = methyl for polypropylene; etc.

These important polymers will be further discussed in other chapters in this book. Further, most polymer text books contain expanded discussions of these important polymers along with applications, properties, etc. (*4–14*).

## PolyEd

PolyEd is an organization dedicated to service and education. It is supported by the American Chemical Society Divisions of Polymer Chemistry and Polymeric Materials: Science and Engineering and by various foundations and industry. It is diverse in its programming featuring efforts from pre-school to post school and including public education. It is dedicated to the education of the general public with regard to the basic nature of science as it underpins our daily lives assisting in our appreciation and understanding of the world about us. We believe this appreciation and understanding of science will result in a more informed society that is better able to appreciate, contribute and utilize the scientific advances and technological tools that underpin our rapidly changing technologically intense society.

It has working relationships and cooperates with many education related groups including the Division of Chemical Education, Rubber Division, SOCED (American Chemistry "Society Committee on Education"), AICHE (American Institute of Chemical Engineers), SPE (Society of Plastics Engineers), NSTA (National Science Teachers Association) and with polymer education groups throughout the world.

## Programs

PolyEd programs are generally housed within four Directorates each chaired by an Associate Director. These Directorates are the Precollege Directorate, College/University Students Directorate, College/University Faculty Directorate and Industrial/Government Professionals Directorate. Other programs are more “stand alone”. Examples of programs contained within PolyEd are indicated below.

* Award for Excellence in Polymer Education by High and Middle School Teachers: PolyEd provides awards to high school and middle school science teachers for excellence in polymer education. The national award winner receives an expense-paid trip to a NSTA national meeting and will have opportunities at the meeting to interact with a Polymer Ambassador. The national winner also receives a $1000 cash award. It encourages and gives special recognition to those teachers who are pioneering the teaching of polymers at the pre-college level. Areas included in selecting those receiving the award include use of polymers in the classroom, developing novel approaches to the teaching of polymers, influencing other teachers, and educating the general public. Many of the “winners” become “Polymer Ambassadors” within IPEC (Intersociety Polymer Education Council).

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- * Education symposia at regional and national meetings: Hands-on polymer chemistry demonstrations and experiments are presented at workshops offered at national and regional meetings for chemistry educators.
- * Participates in K-12 teacher training with the support of NSF funding that allowed the creation of the MaTR (Macromolecular Teacher Resource) Institute that is housed at the University of Wisconsin – Stevens Point.
- * Media: This effort catalogues both production and location of polymer-related media content.
- * Undergraduate Research Recognition Awards: These awards recognize outstanding undergraduate research through awards for top papers that are presented by undergraduates at the national American Chemical Society meetings.
- * AkzoNobel Award for Outstanding Graduate Research: This award honors a recent PhD for an outstanding thesis during the preceding three years.
- * AkzoNobel Outstanding Student Symposium Award: This award is given to a graduate student for an outstanding presentation at the AkzoNobel Award Symposium, part of the PMSE program at each ACS fall national meeting.
- * Course Development Information: Model syllabi are available to assist faculty interested in developing courses and / or options in polymer chemistry. Copies are available from the POLYED Center. Send an email to polyed@uwsp.edu to request a copy.
- * Catalogue of short courses: Assembles a partial listing of short courses that is available from the PolyEd home web site.
- * National Chemistry Week and Other Outreaches: PolyEd teacher outreach activities focus on workshops for precollege teachers in conjunction with the Intersociety Polymer Education Council, IPEC. Several PolyEd award winning teachers now offer workshops for other teachers as IPEC Polymer Ambassadors. The PolyEd subcommittee on National Chemistry Week works with ACS's National Chemistry Week Office to develop materials that illustrate the importance and contributions of chemistry to society. Recent efforts have been aimed at elementary school students and their parents.
- * Outstanding Organic Chemistry Award: Recognizes the outstanding organic chemistry students in over 300 colleges and universities. It is an award for outstanding performance by an undergraduate chemistry major in the two-semester organic sequence. Recipients receive an award letter and certificate. Faculty should nominate students by going to http://forms.uwsp.edu/chemistry/polyed/application.htm. PolyEd is currently working with CRC Press in an attempt to offer winners the CRC Handbook of Chemistry and Physics.
- * Textbook author Committee: Encourages, alerts, and supplies information to authors of textbooks including potential authors, editors and publishers of chemistry and chemical engineering textbooks encouraging them to integrate polymer topics in their text. Also

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develops and works with authors, editors and publishers in developing polymer-related materials.

* Visitation Program: Members of PolyEd visit college and university campuses helping them develop courses in polymers and assisting them in the integration of polymer subject matter in their curriculum.

* Polymer Curriculum Development Awards: Curriculum development awards of \$10,000 and \$2500 are available from PolyEd to improve the teaching of polymer science. Grants are made for the development of curricular materials or to assist institutions in offering courses in polymer chemistry. The award allows PolyEd to develop material in a number of areas including computerized polymer simulations and laboratory programs.

* Industrial Teachers: Locates industrial scientists who are willing to teach polymer courses or present polymer topics at the college level. This effort also seeks to “connect” the industrial/governmental teachers to schools that request this service. A related effort is underway to identify industrial sites that are willing to give tours to local K-12 and college level groups.

* Surveys polymer activity within colleges and universities: Information about colleges and universities that offer courses or programs in the polymer area has been compiled and articles about this appear periodically in the Preprints of the ACS National Meeting Program for the Division of Polymeric Materials: Science & Engineering. These provide statistical information about the number of colleges and universities with coursework in the polymer area and the names of the institutions.

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Further information concerning any of these programs can be obtained from the National Information Center for Polymer Education at the University of Wisconsin-Stevens Point under the leadership of John Droske. The Center serves as the clearing house for distribution of information about PolyEd programs and resources. Materials are distributed to teachers at all levels, from K to college as well as to scientists employed in government and industrial labs. The Center provides programmatic support of several of the PolyEd awards. It also offers a special section devoted to teachers that includes an overview with definitions of polymers and appropriate material divided into the four groupings of K-5, 69, High School, and University. This area of helps continues to expand.

The Center also operates a Web Page (www.polyed.org) that describes PolyEd programs as well as acting as a depository for the results of certain programs supported by PolyEd.

## Integration of Macromolecules/Polymers into the Organic Foundational Course Content

One of the continued foci of PolyEd is the integration of polymer topics and fundamentals into existing foundational courses. In the 1980s PolyEd formed committees to develop topics and materials that would be useful to assist teachers in integrating polymer topics into the undergraduate courses. These reports were published in the Journal of Chemical Education (*15–20*).

For the current effort, committees were again formed to develop topics (and associated material) that would be useful, appropriate, and applicable for introduction of polymer concepts and examples in each of the foundational courses- Inorganic Chemistry, Biochemistry, Physical Chemistry, Organic Chemistry, Analytical Chemistry as well as General Chemistry. These committees are also to develop guidelines as to the level and depth of coverage of these topics; creating specific illustrations, and developing broad guidelines as to the proportion of time to be spent on polymer related topics and examples.

One of the major impediments to teaching polymers in the undergraduate curriculum involves the lack of faculty with knowledge of the fundamentals of polymers. Several attempts have been made to overcome this obstacle. One is to encourage scientists from the polymer industry to offer polymer courses at various academic institutions. This has proven to be moderately successful.

Another approach is being taken that will hopefully address this problem more directly. A polymer short course was offered at the Boston 2007 national ACS meeting and others followed with more planned. The courses are free to all who attend. The courses are intended for teachers who have or have not had prior polymer exposure and are aimed to both allow the participants to teach a free standing course in polymers and to integrate polymer topics and fundamentals into the core for fondational courses. It is envisioned that each “class” will have between 15 to 30 participants. Eventually, it is possible that there will be two somewhat distinct offerings, one focusing on the integration of polymers into existing courses and the second one focusing on the introduction of a course in polymers.

The committee that undertakes the approval of chemistry programs in the US is the American Chemical Society Committee on Professional Training, CPT. CPT currently approves about 630 such programs from small colleges to essentially all of the major universities in the US. For CPT approval programs are to offer the typical underpinnings which is generally a year of general chemistry with laboratory. They are then to offer the equivalence of five semesters of core or foundational course work divided between organic, physical, analytical, inorganic and biochemistry. Included in this are approximately four semester long experiences in laboratory. This allows programs to be flexible and creative in the offering of programs specific to their institution. Four (12 semester credit hours) in-depth courses fill out the requirements. These in-depth courses can be the current second semester offerings of courses or newly develop coursework. This allows programs wanting to offer a program of coursework in polymers without requiring additional courses above those typically offered in prior degree programs. Thus, a polymer emphasis can include two courses (an academic year) in organic chemistry, one semester courses in analytical and inorganic chemistry, two semester courses in physical chemistry, and two courses in polymers with one or two polymer-associated laboratories. The in-depth coursework is then the second semester of organic and physical chemistry, two lecture courses in polymers, and one laboratory course in polymers. The newly developed

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guidelines are accessible by Googling Committee on Professional Training American Chemical Society.

The 2008 **ACS-Committee on Professional Training Guidelines for Bachelor's Degree Programs** contains the following recommendation: **"students should be exposed to the principles of macromolecules across foundational areas"**. To assist CPT in efforts to integrate polymers/macromolecules in foundational courses, an active committee led by the co-authors of the present paper was formed.

Following is a description of the objective/goal of these committees.

*Objective: To develop material that allows the fundamentals and applications of macromolecules/polymers to be integrated into foundational courses*

*Goal: To enhance foundational courses through integration of macromolecules/polymers into foundational courses*

*Four groups of scholars, one for each of the four content areas of organic, inorganic, physical and analytical, from academics and industry will develop material that allows the introduction and illustrates how foundational courses can be enhanced through the use of macromolecules/polymers, M/P. M/P are all about us being integral materials that allow our society to exist. They have contributed to the growth of society and will be essential for the sustainability of society including solving problems in the environment, communications, construction, medicine, .... The fundamentals that apply to M/P are inherent to the understanding of science and the world about us. While some of these fundamentals vary from those important to understanding smaller molecules, most are simple extensions of fundamentals already presented in foundational courses.*

*The groups will develop material that is not limited to but includes*

*symposia*
*publications*
*definitions*
*laboratory experiences*
*class room demonstrations*
*historical and societal perspectives*
*course packets that can be inserted into present topic areas*
*etc.*

*Committees are encouraged to be creative and may develop different approaches to the presentation of similar material.*

*The type of material that is developed by each of the foundational course committees, FCCs, will be guided by the particular committee and the FCCs will not be lock-stepped but encouraged to be creative in developing the type and mode of developing material suitable to the particular foundational course.*

*We view these groups as being structured to be ongoing with the material caught by the PolyEd web site for delivery to those seeking the material (users). Within a year it is anticipated that sufficient material will be developed that allows a paper to be sent to the Journal of Chemical Education and within two years that a symposia will be developed for a national ACS meeting that will be cosponsored*

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*with the Division of Chemical Education and the associated foundational course ACS division.*

The Philadelphia national ACS (2012) symposium and this book are part of this effort.

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch001

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch002

## Chapter 2

# Incorporation of Polymeric Materials To Enhance Interest and Learning in the Foundational Organic Chemistry Course

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A discussion of alkenes usually occurs early in the first organic course and offers a wonderful opportunity to engage the student. The most important societal/commercial reaction of alkenes is vinyl polymerization. Discussion of vinyl polymerization permits the introduction of radical chemistry in a relevant, easily appreciated manner. More importantly, it can be used to illustrate the importance of polymeric materials in the daily lives of students. Common examples include: poly(acrylonitrile) [Orlon] for clothing [almost always one or more students will be wearing a sweater made from Orlon ("synthetic wool") or carpeting and as a precursor to carbon fiber for composite fabrication for aerospace; poly(vinyl chloride) [PVC] for siding for home construction, floor tile, plumbing pipe, and many other uses; poly(acrylates) as coatings; poly(styrene) for inexpensive wine tumblers, culterary, light covers, etc. A bit of history can be included here as well: low-density poly(ethylene) for radar insulation during WW II; poly(methyl methaerylate) [PMMA, Plexiglass] for the fabrication of canopies for fighter aircraft during WW II [this also offers an opportunity for a brief description of the origins of the Rohn and Haas Company]. Examples of this kind tend to strongly engage the interest of students [generates an appreciation of how organic chemistry impacts their well-being and "hooks" them on the course.

In Introduction of Macromolecular Science/Polymeric Materials into the Foundational Course in Organic Chemistry; Howell, B.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch002

## Introduction

Polymeric materials are pervasive in modern society. The high standard of living enjoyed by citizens of the developed world would not be possible in the absence of these materials (*1*). Everything from housing to transportation to clothing to personal care items to wholesome food and on and on is positively impacted by polymeric components. In addition, most chemists, at any level B.S., M.S., or Ph.D., work in a polymer or polymer-related area. Yet the treatment of polymeric materials in the undergraduate curriculum is generally quite inadequate. In response to this situation, the ACS Committee on Professional Traning recommends that polymeric materials be incorporated into the foundational courses in chemistry. This may be very readily done for the first course in organic chemistry.

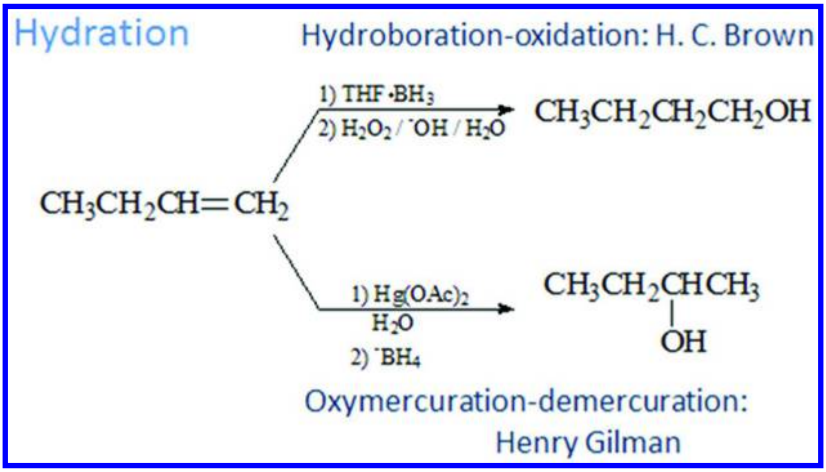
## Results and Discussion

Polymeric materials may be introduced very early in the first semester of the sophomore-level organic chemistry sequence. For most traditional courses, a treatment of alkenes occurs within the first few weeks. This offers a wonderful opportunity to introduce polymeric materials and to utilize them to illustrate several fundamental properties of organic compounds. Introduction of polymeric materials at this point also serves to generate student interest and enthusiasm and to make students much more aware of their surroundings and the impact of organic chemstiry in their everyday lives. As has been previously noted

> *"If students understand why information is important and useful, if their curiosity is piqued, if they are appropriately challenged, and if they perceive relevance of content, they will be willing to exert more effort and will perform better as a result."*
>
> -Michael Theall

As a class alkenes have a much greater impact on national GDP and citizen well-being than is reflected in most standard beginning organic chemistry textbooks (*2*). Cracking of light naptha from petroleum refining provides the small olefins on which much of the chemical industry is based (*3–5*). Ethylene alone accounts for almost half of all organic chemicals produced (*3–6*).

Even before the introduction of the concept of polymerization there is the opportunity to engage student interest *via* historically important personalities. A fundamental reaction of alkenes is simple hydration to form alochols. This is commonly accomplished in one of two ways depending on the product desired. hydroboration-oxidation to form the less-substituted alcohol or oxymercuration-demercuration to form the more substituted alcohol (Scheme 1). Both reactions are highly regioselective and lead to excellent conversion of alkene to alcohol.



Scheme 1. *Hydration of Alkenes.*

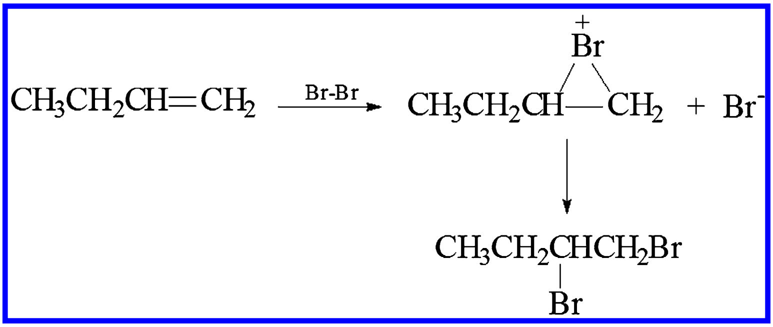
Hydroboration - oxidation was developed by H.C. Brown for which he received the Nobel Prize in 1979 (*7–9*). This was an important development for it allowed the generation of the anti-Markovnikov alcohol from an alkene. Students are impressed that they are learning a reaction of significance as mere beginners. It is also helpful to remind students, at his point, that knowledge that they get essentially for free required the effort and time of many individuals in the laboratory to establish. There are a myrid of stories about H.C. Brown that students enjoy and find instructive (all help them to remember hydration of an alkene to form the less-substituted alcohol). Perhaps, the one that students enjoy most concerns the origins of his interest in organoborane chemistry. Brown was an undergraduate (it is good for the students to reflect on the fact that everyone starts - even very famous individuals - as an undergraduate) at the university of Chicago during the depression where he met his wife-to-be. Neither had very much money. Since he had a birthday coming, she wanted to get him a gift. She went to the bookstore to get something. The least expensive thing available was a small volume on boron which she purchased and presented to him for his birthday - his introduction to boron chemistry!

Hydration of an alkene to form the more-substituted alcohol is readily accomplished by oxymercuration-demercuration. This process also represented a significant development. It permits the ready conversion of an alkene to the Markovnikov alcohol in excellent yield using a simple procedure (Scheme 1). The Markovnikov alcohol may be prepared by acid-catalyzed hydration of the alkene but this process often leads to low yields of the desired alcohol or products of rearranged structure. The early development of organomercury chemistry may be attributed to Henry Gilman. Gilman enjoyed an extraordinary career, all spent at Iowa State University (*10*). He began there in 1919 and was active through the mid-1980s. Over that period he published over 1300 research papers and trained dozens of students. This accomplishment is all the more impressive when one considers that he was blind for the second half of his life. This was

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch002

before the advent of all the electronic gadgets now available. To keep abreast of the literature, students were assigned to come to his home each evening and read aloud journal articles. Students are properly impressed by Gilman's life and accomplishments - how tough can a course in organic chemistry be compared to that?

Another, simple reaction that comes early and has associated with it an inspirational story is the bromination of alkenes. The intermediate in this reaction, a bromonium ion, had been postulated for some time but it remained for George Olah in the 1960s to first observe this species spectroscopically (Scheme 2).



Scheme 2. Bromination of an Alkene.

Olah escaped from Hungary during the Soviet invasion of 1956. He came to Canda and was able to secure employment with Dow Chemical in Sarina where he worked with Friedel-Crafts Chemistry (and actually wrote a four-volyme treatise on the subject). During this period he learned about strong acids - knowledge which he put to good use after moving to Case Western Reserve University where he had access to an NMR spectrometer. He had developed a strongly-ionizing, non-nucleophilic mixture of antimony pentafluoride and sulfur trioxide, so called "magic acid", which permitted the generation of long-lived ionic species which could be ovserved by NMR spectroscopy. Most were carbocations but one was the bromonium ion. For his work on carbocation structure, Olah received the Nobel Prize in 1994 (*11*).

Vinyl polymerization represents the most important reaction of alkenes (Scheme 3). In terms of impact on the well-being of society or contribution to national GDP, it dwarfs all other reactions of alkenes combined. Not only is it an important reaction of alkenes but a discussion of polymerization permits the reinforcement of several fundamental concepts that students have already encountered in a review of the concepts of general chemistry (bonding, reactivity, conjugative stabilization, etc.) or the study of alkanes (structural preference, steric requirements, conformational stability, ring strain, etc.)

For vinyl monomers, radical polymerization is the most widely practiced in industry. It is robust, widely applicable, and tolerant of reaction conditions. An early example of vinyl polymerization is the discovery and production of low density poly(ethylene).

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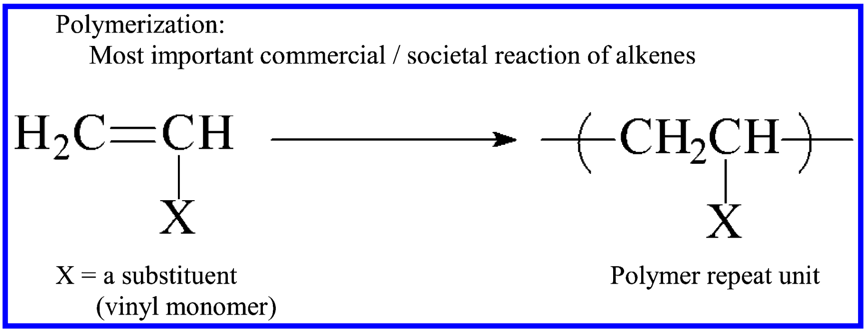


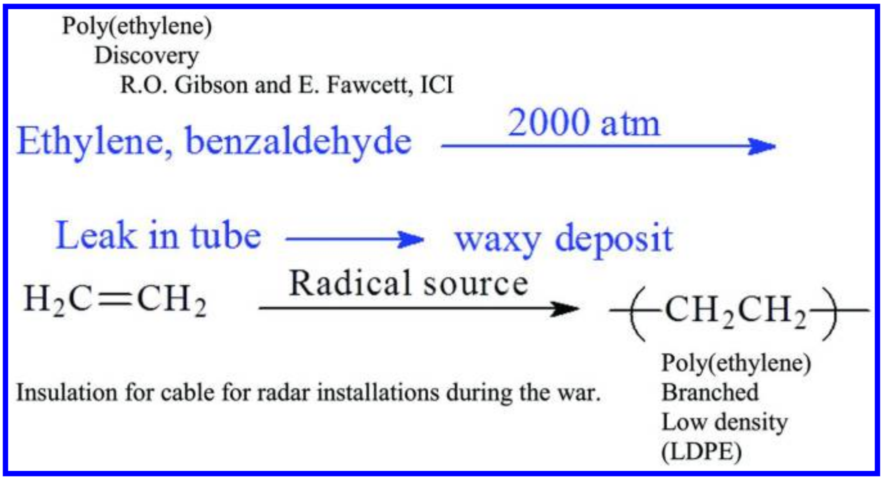
*Scheme 3. Vinyl Polymerization*

The discovery of ethylene polymerization is of particular interest to students and emphasizes the importance of careful observation in science. Discovery was by accident and came as a consequence of repeated attempts to induce reaction of ethylene with aldehydes at high pressure (Scheme 4). It was finally discovered that there was a small leak in the tube which permitted ingress of small amounts of oxygen. Some students will remember from their general chemistry experience that molecular oxygen is a diradical. The oxygen present initiated polymerization of ethylene to produce a waxy solid which was ultimately demonstrated to be poly(ethylene). Of course, much better initiators than oxygen were soon found. The polymer formed has a branched structure which accounts for its oberserved density. This material is now known as low density poly(ethylene), LPDE. Students readily relate this to the relative boiling points of branched *versus* unbranched alkanes which they have just encountered. The question to them is why butyl branches predominate. This permits a discussion of both radical reactivity and considerations of steric effects just encountered in the study of alkanes. The propagating radical is reactive and may abstract a hydrogen atom (chain transfer) as well as add monomer. Most generally chain transfer is intramolecular and occurs through a relatively strain-free six-membered activated complex to generate a new radical from which propagation occurs to leave a butyl branch (Scheme 5). Students readily relate this to their newly-acquired knowledge of cycloalkane stability.

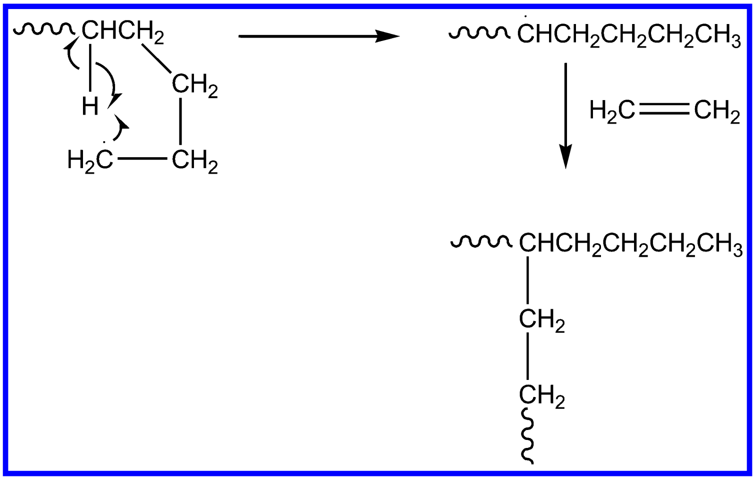
The advent of poly(ethylene) came at a very opportune time, just prior to WW II. The British had developed radar but found that paper insulation for cables was unreliable for many radar installations. This problem was solved by the use of poly(ethylene) for cable insulation. Radar was widely used by the Allies and had a very positive impact on the outcome of the war.

1-Alkenes (α-olefins) cannot be polymerized using radical techniques owing to the prominence of allylic chain transfer. Poly(propylene) was immediately of interest after the introduction of poly(ethylene). However, attempts to polymerize propylene lead to the formation of an oil of about a 1000 g/mole. This is a consequence of chain-transfer to monomer to generate an allyl radical (Scheme 6). This provides an opportunity to reinforce concepts of stability and conjugative delocalization of electron density that students have just reviewed.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch002



*Scheme 4. Discovery and Production of Low Density Poly(ethylene)*



*Scheme 5. Origin of Butyl Branches in Low Density Poly(ethylene)*

The problems of both branching in poly(ethylene) and the inability to polymerize α-olefins, of course, were solved by Karl Ziegler in the late 1940s. Ziegler developed coordination polymerization for the generation of an essentially linear poly(ethylene) with greater density and much better mechanical properties than those of them currently available low density poly(ethylene). This material is known as high density poly(ethylene), HDPE. Students can readily appreciate major differences between LDPE and HDPE by considering the difference between the common garbage bag and a dishpan. A consideration of the properites of these materials provides an opportunity to dsicuss some of the properites of semicrystalline polymers. Students are already aware of planar zig-zag structure of linear poly(ethylene) [linear poly(ethylene) is, after all, just a large alkane] and the tendency of larger alkanes to close pack to form crystalline solids. Will the same occur for poly(ethylene)? Here a good analogy is provided by a strainer of cooked spaghetti noodles. If a student (or anyone) finds a noodle end and begins to pull it from the mass, what happens? For a time, it pulls away freely but then stops. Why? Entanglement - the noddle is entagled with many others and to pull further would break the strand. The case is similar for poly(ethylene). Portions of chains free of entanglements may organize to form crystalline regions but a portion of the chain is trapped in the entangled portion, the amorphous region [the same is true for all semicrystalline polymers; for this reason no polymer is ever fully crystalline]. This leads naturally to a discussion of phase transitions for polymeric materials. How can these materials be manipulated to make items such as garbage bags or dishpans? The concept of a melt temperature ($T_m$), i.e., the temperature at which crystalline regions begin to lose organization is readily accepted by analogy with behavior of smaller alkanes. The idea of a glass transition temperature, $T_g$, i.e., the temperature at which the chains in the amorphous region can move past each other without breakage, can be readily illustrated with the experience of bending a piece of glass tubing [glass is but a simple inorganic polymer; the tubing is the polymer which has been formed into shape and allowed to cool to below $T_g$]. Almost all students have done this [middle school, high school, general chemistry]. To do this a portion of the tubing is heated, usually in a flame, to a temperature at which it becomes flexible, i.e., above $T_g$. The tubing is placed into the desired shape and allowed to cool. The shape is retained in the cooled (polymer below $T_g$) tubing. Students are very much aware from their experience with glass tubing that polymers below $T_g$ are brittle (if the tubing is rapped on the table, it shatters). Above $T_g$ they are flexible. Which raises the question, if the $T_g$ for poly(ethylene) is about -150°C, how is the dishpan able to maintain its shape? The answer, of course, is the development of crystallinity after the item is formed. These concepts may be developed further in subsequent courses but a rather simple description is sufficient to provide students with an appreciation of fundamental properites of polymers and how they can be manipulated to form useful articles of commerce.

The utilization of Ziegler coordination catalysts for the polymerization α-olefins, in particular propylene, was recognized by Natta [the story of how this occurred and the consequent loss of a good friendship makes an interesting interlude for students]. Coordination polymerization of α-olefins permits the formation of stereoregular polymers and provides an opportunity to introduce the concept of taticity. Most students have some dim acquaintance with coordination compounds from their general chemistry experience. They can readily appreciate that as the monomer approaches the metal center, it does so with the alkyl substituent away. This leads to a polymer chain with the placement of the substituent the same in every mer unit. This is the case for poly(propylene). Considering the planar zig-zag representation, all the methyl groups appear on the same side. This referred to as an isotactic arrangement. If the substituents alternate from side to side along the planar zig-zag, the structure is syndiotactic. If they are randomly placed along the structure, it is atactic.

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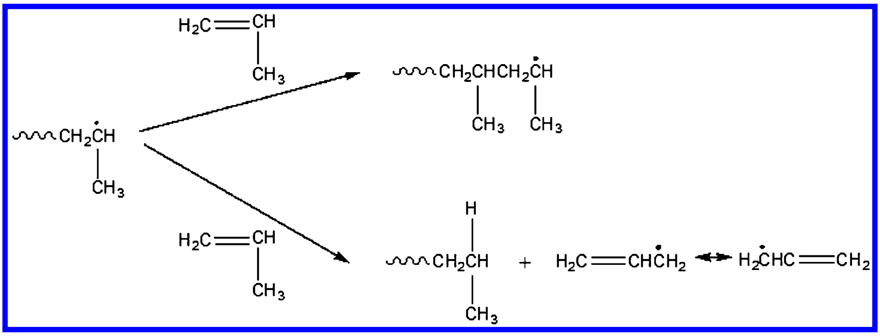

*Scheme 6. Efficient Chain-trasnfer to Monomer in the Attempted Radical Polymerization of Propylene)*

Ziegler catalysts are heterogeneous, i.e., they are supported on some inert material such as silica or alumnia. More recently homogeneous catalysis for coordination polymerization has been developed by both Dow and Exxon (Scheme 7). In this case, the coordination catalyst is soluble in the monomer. This permits the copolymerization of ethylene with an α-olefin. The result is a branched poly(ethylene) but with uniform branch size dependent upon the identity of the comonomer. The extent of branching may be controlled by the level of comonomer in the polymerization mixture or the structure of the catalyst. The Dow material is derived from 1-hexene as comonomer and thus contains butyl branches. The Exxon material contains hexyl branches derived from 1-octene as comonomer. These materials are referred to as linear low density poly(ethylene), LLDPE, and have properties intermediate between those of LDPE and HDPE. They are lower in cost than HDPE but have properties sufficient to displace HDPE in some applications. [The story of the development of these materials provides another interesting vignette for students - the catalysts used are almost identical in structure and each company was sure that the other was infringing its patent - several years of litigation ensued].

Ziegler (*12*) and Natta (*13*) receieved the Nobel Prize in 1963 [Natta's award may represent the only time that the prize has been presented for an application].

Poly(styrene) is another vinyl polymer with an interesting history and broad impact (Scheme 8). General purpose poly(styrene) has many attractive properties. It is lightweight, transparent and relatively inexpensive. These properties make it ideal for use for light coverings, pastry shells, tumblers and plastic cutlery. However, it is brittle (an amorphous polymer below $T_g$). Many students (most have little money) have had the experience of buying plastic cutlery for a picnic, usually at Wal-Mart. Their tendency is to buy the least expensive available. It looks great – transparent - but when, at the picnic, they drive it into their chicken, it breaks. The next time, they buy the white cutlery sitting on the shelf adjacent to the transparent items. It costs somewhat more but upon being drivien into barbqued chicken it flexes and does not break. This cutlery is made from poly(styrene) that is toughened by the incorporation of an elastomer, poly(butadiene) - high impact poly(styrene) or HIPS. The poly(butediene) present absorbs energy and stops crack propagation.

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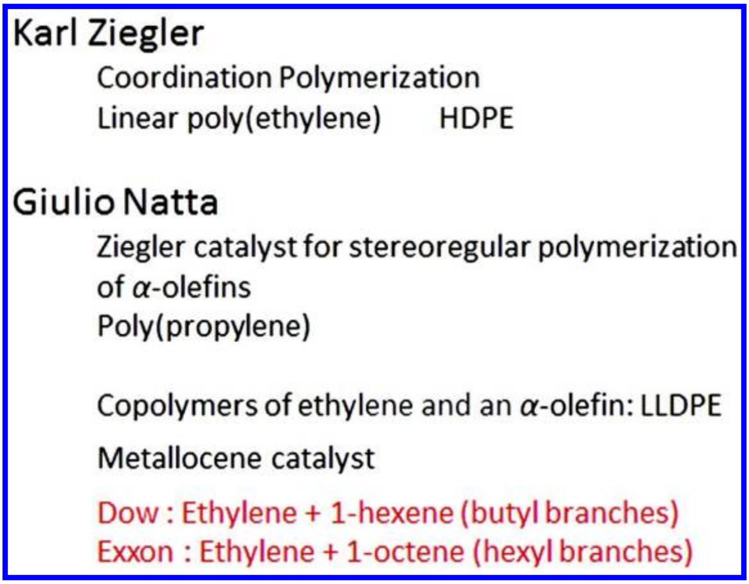


**Karl Ziegler**

Coordination Polymerization
Linear poly(ethylene) HDPE

**Giulio Natta**

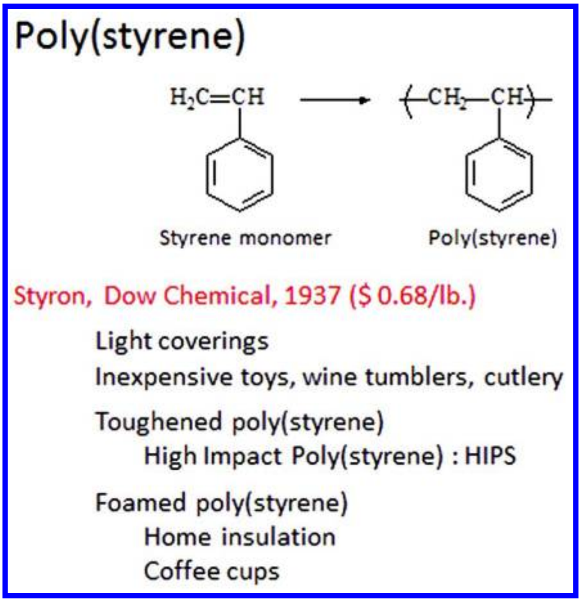
Ziegler catalyst for stereoregular polymerization of α-olefins
Poly(propylene)

Copolymers of ethylene and an α-olefin: LLDPE

Metallocene catalyst

Dow : Ethylene + 1-hexene (butyl branches)
Exxon : Ethylene + 1-octene (hexyl branches)

*Scheme 7. Coordination Polymerization of Ethylene and 1-Alkenes*



**Poly(styrene)**

Styron, Dow Chemical, 1937 ($ 0.68/lb.)

Light coverings
Inexpensive toys, wine tumblers, cutlery

Toughened poly(styrene)
    High Impact Poly(styrene) : HIPS

Foamed poly(styrene)
    Home insulation
    Coffee cups

*Scheme 8. Generation and Uses of Poly(styrene)*

When asked where they have encountered poly(styrene) most students will respond “as coffee cups”, and in fact, some foamed poly(styrene) is used for that purpose. It works very well – a thin layer of foamed poly(styrene) prevents the fingers of a student holding the cup from being burned. However, a much larger use of foamed poly(styrene) is for home insulation. Most homes constructed in the northern U.S., e.g., Michigan, contain 2-4 inches of poly(styrene) foam between the exterior vinyl sididng and the sheeting. This insulation is very effective in preventing heat loss during long winter months.

Styrene polymerization provides an excellent opportunity to discuss the mechanism of radical polymerization (Scheme 9). In fact, it offers a much more meaningful presentation of a radical chain process than is possible for the chlorination of alkanes (which the students have already seen).

Azo compounds or perozides are the most common initiators for styrene polymerization. It is useful to discuss the bond lability in these molecules and the stability of the radicals produced. This allows a reinforcement of the concepts of both inductive and conjugative affects. It is instructive to note that little initiator is required (usually about one mole percent based on monomer). As for any chain process, the propagation reactions continually generate reactive species, in this case, a carbon radical. Propagation always occurs in a head-to-tail fashion to generate the more stable radical, a benzylic radical which is conjugatively stabilized (head-to-tail addition is true for most vinyl monomers – almost any substitutent is better than hydrogen for stabilizing the propagating radical). This provides yet another opportunity to remphasize concepts of bonding, π-electron delocalization, stabilization, etc., previously learned.

A question to be raised is whether or not propagation will continue forever. Students will generally respond that it will not but without an understanding of why not. For vinyl polymerization generally, there are two prominent (charge transfer may also contribute in some cases) processes which limit propagation. These are radical coupling and disproportionation. For the manufacture of general purpose poly(styrene) termination is essentially by radical coupling. This places a head-to-head unit in the polymer mainchain, i.e., places the two large groups adjacent to each other. This provides another opportunity to discuss steric strain. The head-to-head linkage is thermally labile and limits the processing temperature for the polymer (*14*, *15*).

Although general purpose poly(styrene) is a large volume commodity polymer it is not nearly as useful as some of its copolymers (Scheme 10). In particular, the polymer containing acrylonitrile, butadiene and styrene (ABS) is an extremely useful material [the copolymer is actually a graft polymer - a copolymer of styrene and acrylonitrile grafted onto poly(butadiene) but these details can await a later course]. ABS has good appearance and mechanical properties but, in particular, is extremely durable. Almost all home appliances (refrigerators, dishwashers, washer/dryer units, etc.) have housings made from ABS. If the appliances is impacted (e.g., a chair is backed into it) it does not bend or break but simply rebounds to its original shape. Its durable properites also make it useful for the construction of automobile side panels. It has another feature which makes it attractive for the construction of furniture, particularly, table tops, surfaces of dressers, etc. It can be given the appearance of most wood grains to provide an attractive appearance but, of course, is much longer lasting than the wood itself would be.

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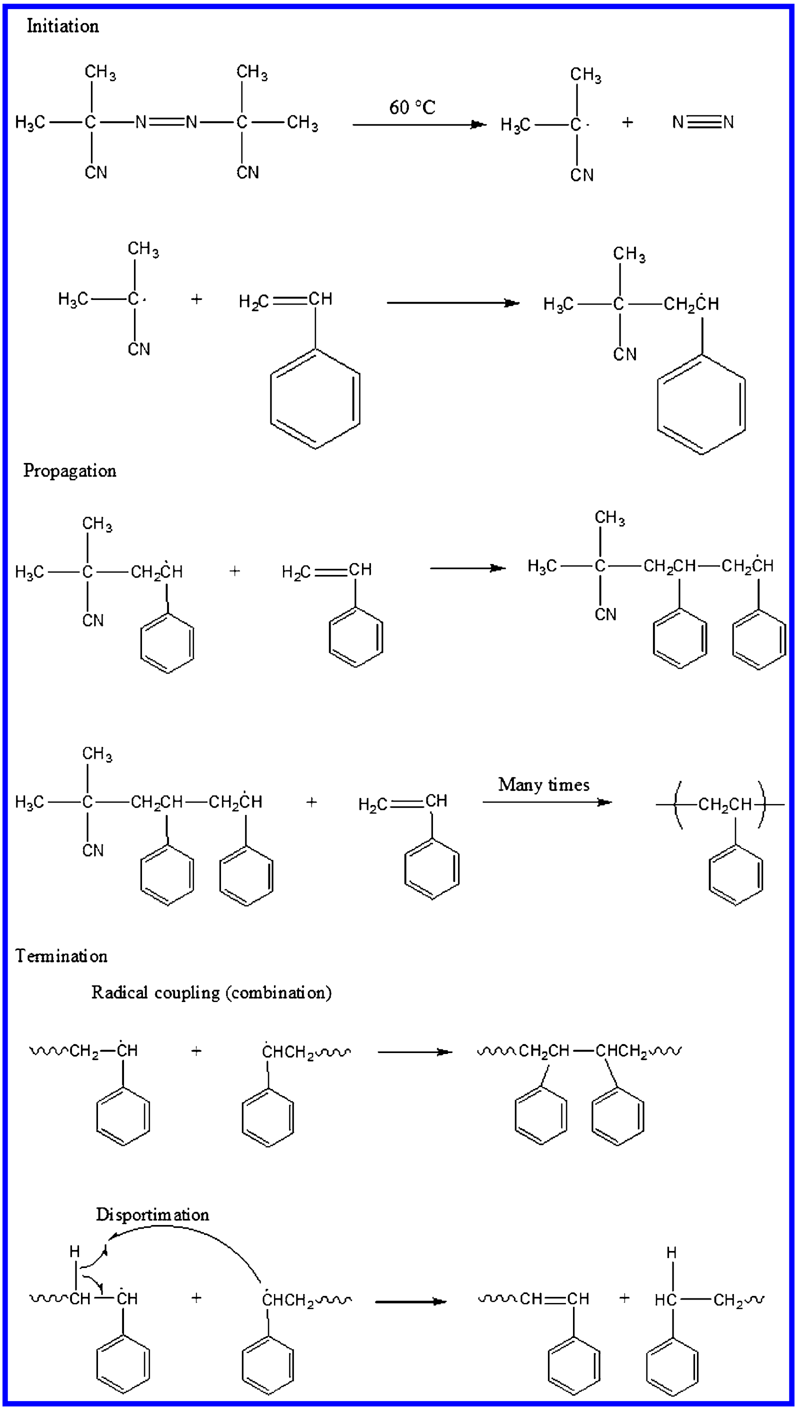

*Scheme 9. Radical Polymerization of Styrene.*

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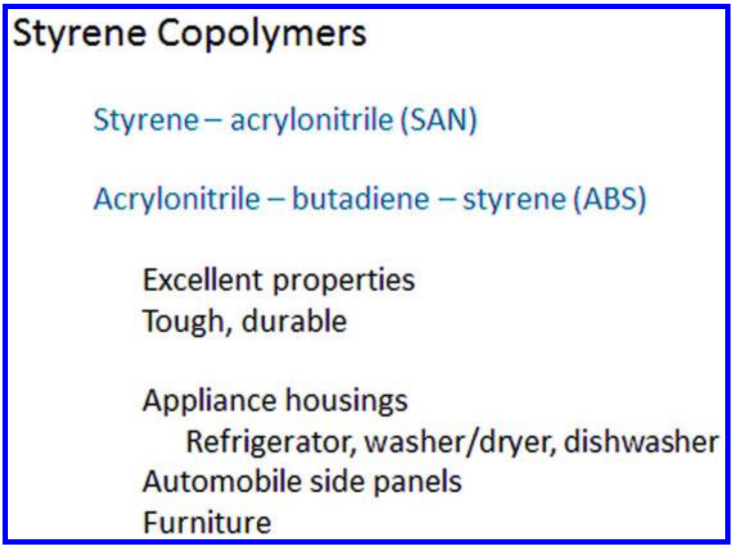

Styrene Copolymers

Styrene – acrylonitrile (SAN)

Acrylonitrile – butadiene – styrene (ABS)

Excellent properties
Tough, durable

Appliance housings
  Refrigerator, washer/dryer, dishwasher
Automobile side panels
Furniture

*Scheme 10. Major copolymers of styrene.*

Poly(vinyl chloride) [PVC] is another important vinyl polymer that students encounter regularly in their daily lives (Scheme 11). Most students drive an automobile. The dash, sometimes the seat covers and the roof, the insulation for wiring in the electrical system, and several other components are made from PVC. So is the tile in their kitchens and bathrooms. However, the major uses for PVC is in home siding and plumbing. Many new homes contain vinyl siding as the exterior surface. It can be pigmented to achieve any desirable color, is extremely durable and does not require maintenance. Huge amounts of PVC are used in the production of pipe. Most plumbing in new construction is made from PVC as is sewer pipe, pipe for highway drainage (it is much more durable and long-lasting than concrete used in these applications), and much more. Interestingly, it was not the discovery of PVC that lead to its commercial development. It was known for many years before it became a commercial product. PVC is hard to process and requires heavy plasticization to make it useful. Waldo Semon at B.F. Goodright learned how to plasticize PVC so that is could be formulated into useful items. This led to a whole new industry. A discussion of plasticization provides an opportunity to again review the notion that to be processed polymer chains must be able to move past each other without breaking. Plasticizers are small molecules, often esters, which facilitate this process. The incorporation of a plasticizer lowers $T_g$, the glass transition temperature, for the polymer and makes it flexible at lower temperature.

Poly(methyl methacrylate) [PMMA] is another vinyl polymer with an interesting story and two very important applications (Scheme 12). PMMA was developed by the Rohm and Haas company in the years before WW II. It came into its own as a commercial product during the war and, as so many polymeric

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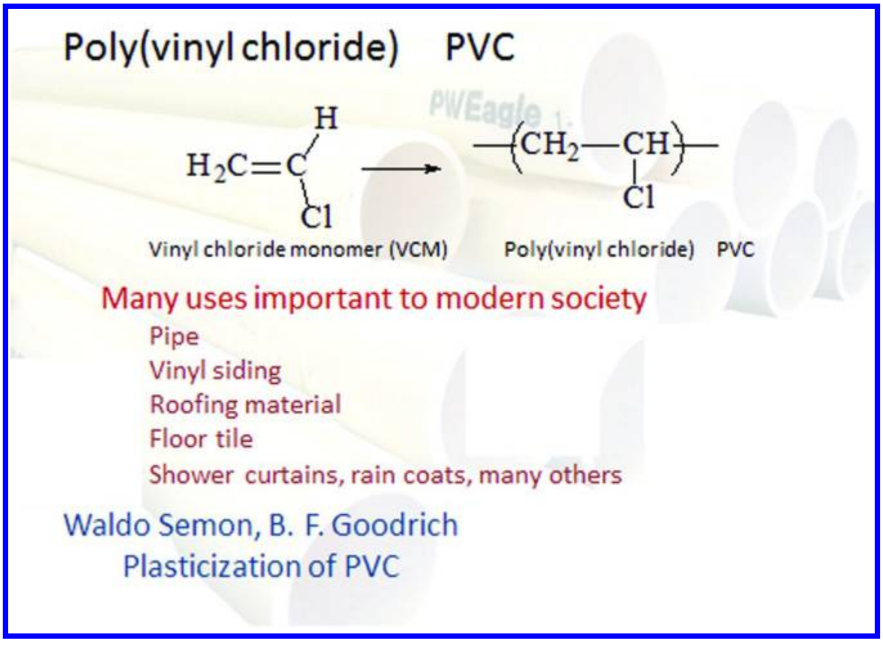
materials did, had a major impact on the conduct and outcome of the war. About half of the production of PMMA is formulated as a plastic [Plexiglass] which is transparent, tough, durable and does not shatter on impact. This made it an ideal replacement for standard glass (which shatters on impact to spray sharpnel around) in the canopoies of fighter aircraft. It is still used in this application for both military and commercial aircraft. It is also used for the construction of storm doors and windows (this is mandated by many local building codes - every year there are dozens of accidents - many serious - caused by hurried individuals missing the crash bar and driving their hand/arm through the glass door). Plexiglass is an excellent material which has had a very positive impact on the well-being of society.

The remaining 50% of PMMA production is used in the formulation of water-based coatings. These are usually sold as a latex containing approximately 50% solids. Most are pigmented for use as paints. Anyone (including students) who has used oil-based paints has a full appreciation for these materials. Most students have some experience with paints and are aware of what happens if the brush is not cleaned soon after use. This produces an opportunity to discuss cross-linking and the function of the coating to generate a protective film on the surface to which it is applied.

Acrylates were also developed by Rohm and Haas and are widely used as coatings. This arose from Rohm's early interest in acrylate polymerization (Scheme 13).



Poly(vinyl chloride) PVC

$$H_2C{=}CH(Cl) \longrightarrow -\!\!\left(CH_2-\underset{Cl}{CH}\right)\!\!-$$

Vinyl chloride monomer (VCM) Poly(vinyl chloride) PVC

Many uses important to modern society

- Pipe
- Vinyl siding
- Roofing material
- Floor tile
- Shower curtains, rain coats, many others

Waldo Semon, B. F. Goodrich

Plasticization of PVC

*Scheme 11. Uses of Poly(vinyl chloride)*

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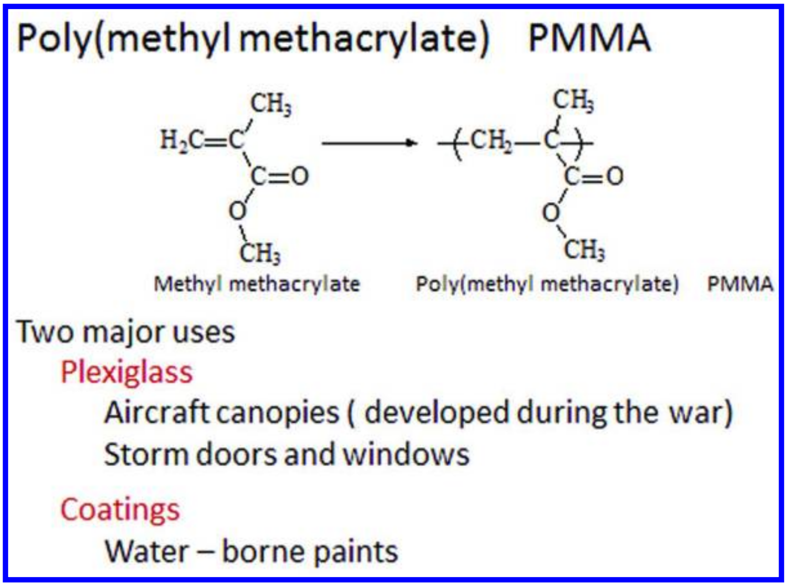


Poly(methyl methacrylate) PMMA

Two major uses

Plexiglass

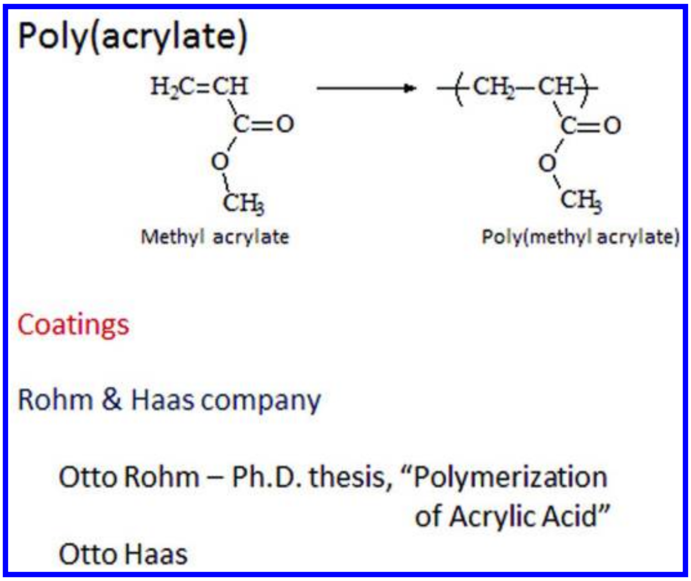
Aircraft canopies ( developed during the war)

Storm doors and windows

Coatings

Water – borne paints

*Scheme 12. Uses of Poly(methyl methacrylate)*



Poly(acrylate)

Coatings

Rohm & Haas company

Otto Rohm – Ph.D. thesis, "Polymerization of Acrylic Acid"

Otto Haas

*Scheme 13. Development of Poly(acrylate)s*

Poly(acrylonitrile) [PAN] is a vinyl polymer that all students have encounterd and most own several items of clothing containing it (Scheme 14). Its trade name in the United States is Orlon and it has largely replaced wool, a natural poly(amide), for the production of sweaters and carpeting. If students are asked to identify their favorite sweater material they will usually respond with wool. If asked where wool comes from, someone will probably say sheep. But then where are sheep raised? Eventually, New Zeland will be identified and, in fact, there are more sheep in New Zeland than people. Are there enough sheep to provide sufficient wool so that everyone can have a wool sweater? After a bit of thought, the answer is obvious – what is an enterprising student of chemistry to do? Make something that has all the good qualities of wool but which can be produced in much larger volume, doesn't shrink or itch in high humidity, and can be incorporated into clothing of a variety of styles and color. Inevitably, someone in the class will be wearing an Orlon sweater or shirt (students delight in checking their neighbor's labels).

Many students have "graphite" tennis rackets or golf clubs and are aware of their great strength, flexibility and light-weight. These are made from carbon fiber/polymer composites. The carbon fiber reinforcing material is responsible for the strength of these items. Most carbon fiber is produced from poly(acrylonitrile). The fiber produced has outstanding strength and is the material of choice for the generation of polymer composites needed in aerospace applications. It is instructive for students to reflect on the stresses that materials encounter in space flight.

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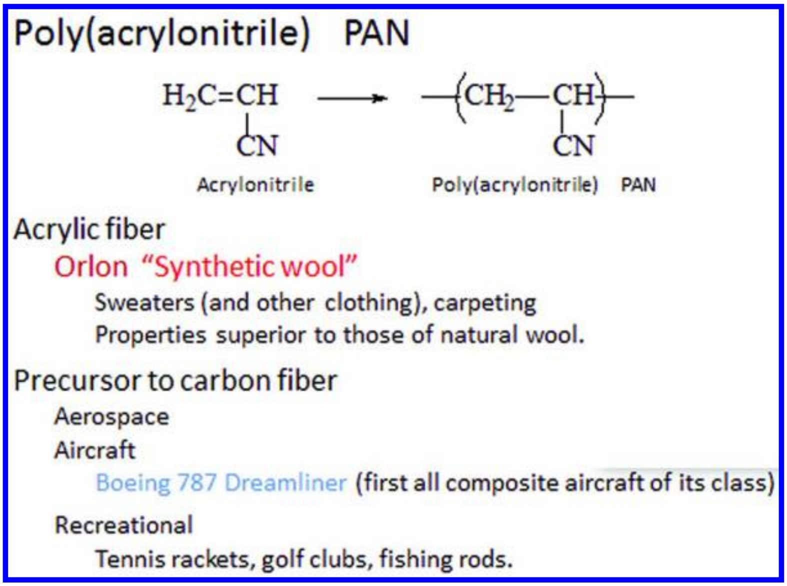


Poly(acrylonitrile) PAN

Acrylic fiber

Orlon "Synthetic wool"

Sweaters (and other clothing), carpeting

Properties superior to those of natural wool.

Precursor to carbon fiber

Aerospace

Aircraft

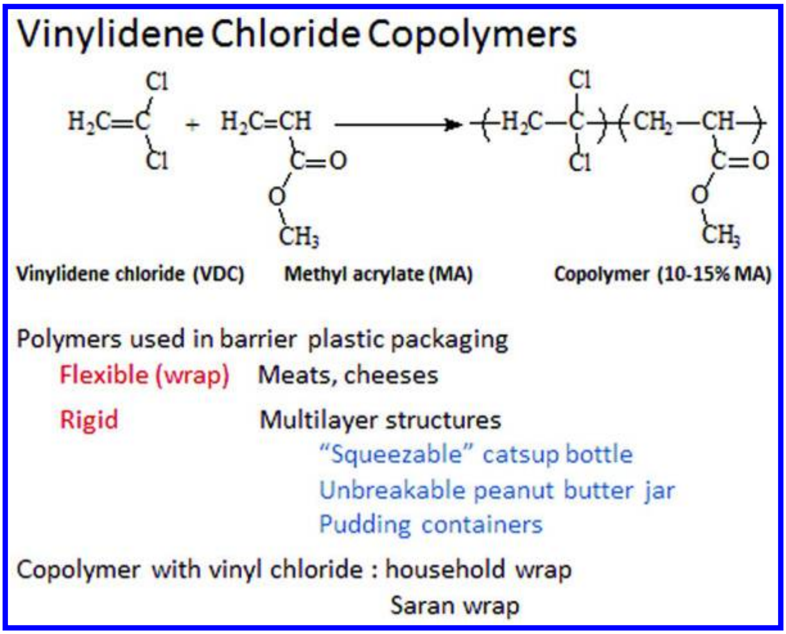
Boeing 787 Dreamliner (first all composite aircraft of its class)

Recreational

Tennis rackets, golf clubs, fishing rods.

*Scheme 14. Uses of Poly(acrylonitrile)*

Vinylidene chloride copolymers containing a few mole percent comonomer, usually alkyl acrylates, principally methyl acrylate, have unique properties which make them useful in food packaging (Scheme 15). These materials display good barrier to the transport of small molecules (oxygen etc.) and to flavor and aroma molecules. They are used in both flexible (wrapping for meats, cheeses, etc.) and rigid [a thin layer between layers of a much less expensive structural polymer, often poly(propylene)] applications. The vinylidene chloride polymer prevents the ingress of oxygen so that spoilage does not occur and the loss of flavor/aroma molecules so that flavor scalping on the supermarket shelf is avoided. These are excellent materials widely used in the barrier plastics packaging industry. A film made from the copolymer containg about 15% vinyl chloride is the common household wrap, Saran wrap, which students will have encountered. They will have noted that Saran wrap is more expensive than either Glad or Handi wrap. Glad wrap and Handi wrap are made from poly(ethylene) and are transparent to the transport of oxygen. If these are used to cover leftovers they keep the dust off but do not prevent oxygen transport (this is usually okay since leftovers are usually consumed within a few days). For long-term storage, e.g., in a freezer, Saran wrap is much better. Some of the students will have seen the TV commercial in which two steaks are wrapped, one in Handi wrap and one in Saran wrap, placed on the stage and a lion is released. He always finds the steak in the Handi warp because he can’t smell the one in Saran wap.


Vinylidene Chloride Copolymers

Polymers used in barrier plastic packaging

Flexible (wrap) Meats, cheeses

Rigid Multilayer structures

“Squeezable” catsup bottle

Unbreakable peanut butter jar

Pudding containers

Copolymer with vinyl chloride : household wrap

Saran wrap

*Scheme 15. Use of Barrier Polymers in Food Packaging*

Poly(tetrafluoroethylene) [Teflon] is a vinyl polymer which most students have encountered - usually as a coating for non-stick (some allege that they cannot make Brownies without it) cookware (Scheme 16). This is certainly not its most prominent use but it does serve to illustrate the properties of high thermal stability and non-stickiness.

It is used for wiring insulation in aircraft and space modules. Students are aware that similar writing in their automobile has PVC insulation and that the wiring is bundled over the fender. If there is a short in one of the wires, sufficient heat may be generated to ruin the insulation on the entire bundle and, of course, the engine stops. When asked how they would respond if this happened to them as they were driving along the freeway, most studetns will respond that they would coast to the shoulder and call AAA (everyone has a cell phone - constructed, of course, largely from polymeric materials). This is obviously not an option at 30,000 feet so the additional cost of Teflon is justified for aircraft wiring.

Teflon is also used in the construction of buildings in earthquake-prone areas. A Teflon layer under the foundation allows the surface of the earth to move, i.e., slide, without transmitting the energy to the structure of the building thus allowing it to escape damage.

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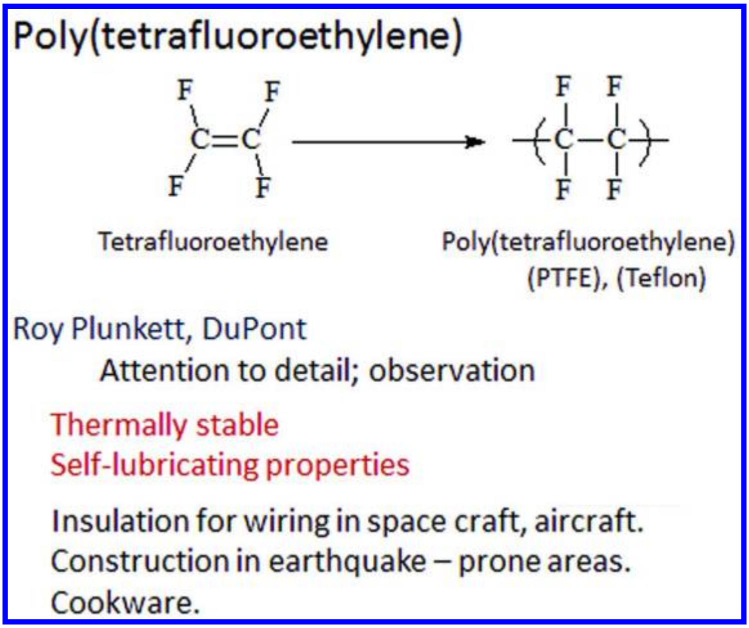


Poly(tetrafluoroethylene)

Tetrafluoroethylene

Poly(tetrafluoroethylene)
(PTFE), (Teflon)

Roy Plunkett, DuPont
Attention to detail; observation

Thermally stable
Self-lubricating properties

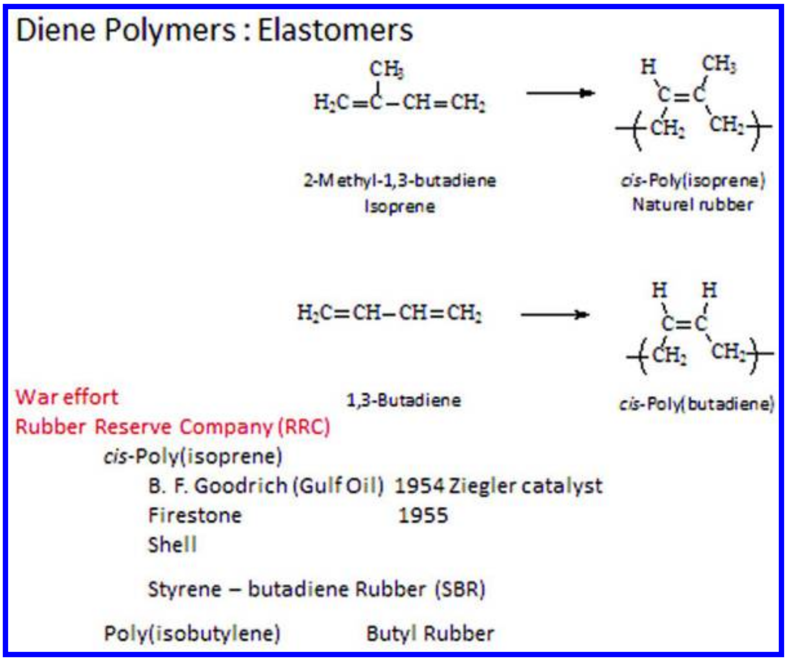
Insulation for wiring in space craft, aircraft.
Construction in earthquake – prone areas.
Cookware.

*Scheme 16. Properites and Uses of Poly(tetrafluorethylene)*

One of the most remarkable features of the Teflon saga is the story of its discovery. It was discovered by Roy Plunkett at DuPont who was exploring the use of tetrafluoroethylene in various reactions. The tetrafluoroethylene came in a small cylinder (a lecture bottle). To obtain the appropriate quanitity for use, it was common practice to place the cylinder on a balance, open the cylinder valve and transfer gas until the proper reduction in mass of the cylinder was observed. As the story goes, Plunkett completed this procedure for a reaction on a Friday afternoon.

The following Monday he attempted to use the cylinder of tetrafluoroethylene in the same way. No gas flowed from the cylinder. Yet, the mass of the cylinder was the same as on Friday. Most people would have thrown the cylinder away and started afresh with a new one. Instead, Plunkett asked that cylinder be sawed open. He found the walls to be covered with a film of a polymeric material - and thus was born Teflon. This provides a great opportunity to remind the students of the importance to paying attention to detail and the crucial role of observation in any scientific endeavor.

All students drive an automobile and, with a little thought, are aware of the crucial role of elastomers in the operation of that device (Scheme 17). Elastomers, as the name implies, are polymeric materials which may be distorted but which quickly regain their original shape when the distorting force is removed. Students readily appreciate how important it is that their automobile tires do not break when they impact a pothole (particularly, for Michigan roads). Structures of elastomers must contain a unit which provides a restoring force when the material is relieved of stress. This may be readily illustrated using diene polymers. The *cis* double bond in the structure functions in this role. Students are farmiliar with 1,4-addition of simple reagents (hydrogen halide, halogen) so the same process in polymerization is not alien to them. Prior to WW II, U.S. requirements for rubber were not large and were met by importation of natural rubber, *cis*-poly(isoprene), from French plantations in the far East. A discussion of natural rubber offers, aside from a recollection of history, an opportunity to emphasize the importance of 1. stereochemistry and 2. enzyme catalysis.



Diene Polymers : Elastomers

War effort
Rubber Reserve Company (RRC)
*cis*-Poly(isoprene)
B. F. Goodrich (Gulf Oil) 1954 Ziegler catalyst
Firestone 1955
Shell
Styrene – butadiene Rubber (SBR)
Poly(isobutylene) Butyl Rubber

*Scheme 17. Elastomer Production*

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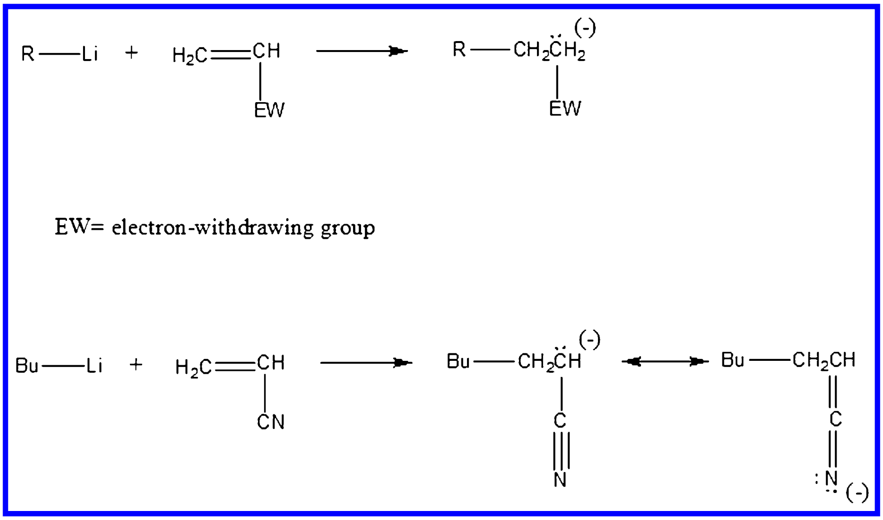
*Cis*-Poly(isoprene) is elastomeric while the trans isomer is brittle and of no use in building tires. The *trans* structure is the thermodynamically preferred yet the *heva* plant produces only the *cis*. The students are already impressed that they are sitting in class continuously conducting hundreds of organic reactions – in water at 37°C! How is that possible? Enzyme (protein) catalysis. This represents another good example of enzyme catalysis (they will, of course, learn much more about these kinds of things in subsequent courses - a brief discussion here provides only a teaser for things to come).

The lack of access to rubber producing areas created a crisis in the United States. Without tires for trucks and aircraft the war effort could not go forward. This led to the creation of the Rubber Reserve Company to pool the resources of the rubber companies, several academic institutions and the government to address the problem. The synthesis of *cis*-poly(isoprene) represented a significant challenge (the *trans* form is most readily generated) that wasn't satifactorally overcome until after the war. Today most "natural" rubber arises from synthesis. In the meantime, styrene-butadiene rubber was developed by the Dow Chemical Company. It is still a major component of tire manufacture. Poly(isobutylene) was developed for use in the manufacture of inner tubes for truck and airplane tires. It is still used for this purpose and is the only commercial polymer produced by cationic polymerization.

A discussion of elastomers leads naturally to an introduction to anionic polymerization and the formation of block polymers. The range of monomers suitable for anionic polymerization is much smaller than that for radical polymerization. The monomer must contain an electron-withdrawing group suitable for stabilization of an anionic propagating species. This provides an opportunity to re-emphasize conjugative delocalization as a means of stabilization. Monomers which work well are styrene, acrylonitrile, and alkyl acrylates/methacrylates which can undergo Michael-type addition. This is illustrated for the polymerization of acrylonitrile (Scheme 18).



*Scheme 18. Monomer Requirements for Anionic Polymerization*

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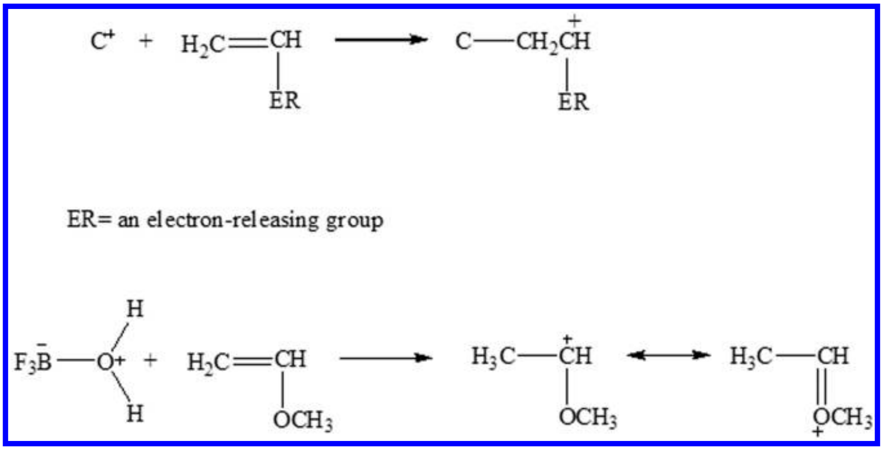
The demands for anionic polymerization are also much more stringent than for radical polymerization: scrupulous purity of monomers, solvents; absence of moisture and air. Initiators (often *sec*-butyllithium) and propagating species are carbanions which are rapidly quenched by any protic agent.

Anionic polymerization does, however, offer some very positive features. Initiation is complete within the time of mixing so that all chains are being propagated at the same time. This leads to polymers of very low dispersity. Anionic polymerizations is not self-terminating. Each chain end is a macroinitiator. If more monomer is added the chain grows anew (polymer molecular weight is increased). More importantly, if a second monomer is added a new chain segment grows and a block copolymer is formed. To terminate the reaction a protic agent, usually methanol, must be added. Because of the reactive nature of chains ends, anionic polymerization is referred to as living polymerization.

Cationic polymerization is not as prominent as anionic polymerization but it provides similar opportunity for a discussion of the stabilizing influence of substituents. In this case the monomer must bear an electron-releasing substitutent to stabilize a cationic propagating species (Scheme 19). The most widely used substrates for cationic polymerization are alkyl vinyl ethers. It may be remembered that isobutylene is the only monomer used in the commercial practice of cationic polymerization.



*Scheme 19. Monomer Requirements for Cationic Polymerization*

Finally, students may be asked to look around the room in which they are sitting and identify the polymers that they see. The number is remarkable (see Scheme 20). As in other areas of their environment, the modern classroom would not be possible in the absence of polymeric materials.

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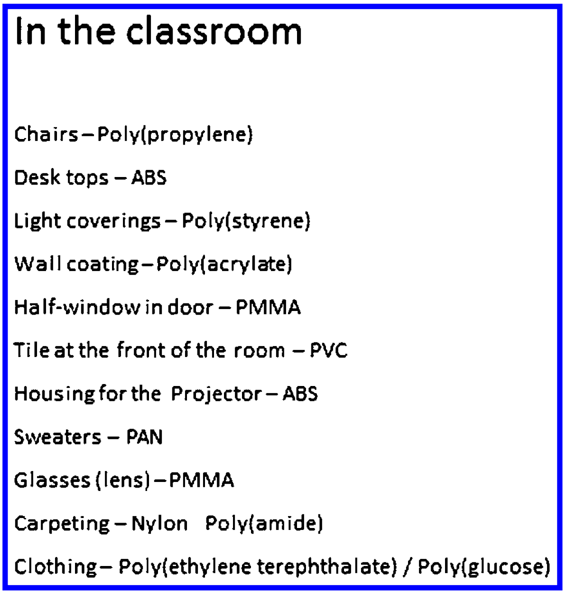
In the classroom

Chairs – Poly(propylene)

Desk tops – ABS

Light coverings – Poly(styrene)

Wall coating – Poly(acrylate)

Half-window in door – PMMA

Tile at the front of the room – PVC

Housing for the Projector – ABS

Sweaters – PAN

Glasses (lens) – PMMA

Carpeting – Nylon Poly(amide)

Clothing – Poly(ethylene terephthalate) / Poly(glucose)

*Scheme 20. Polymeric Materials In the Typical Undergraduate Classroom*

## Conclusions

The introduction of polymeric materials in the foundational organic chemistry course requires little time or effort and can begin as early as the treatment of alkene chemistry (early in the first semester). Vinyl polymerization is the most important societal/commercial reaction that alkenes undergo. It hugely affects student's lives (and those of everyone else). They could not live in the comfort that they do without these materials. A discussion of polymerization (as one of the alkene reactions), polymers, and common items generated from them is a wonderfully expansive thing for most students. They are often unaware of how pervasive in their daily lives and how beneficial these materials are. They all shop at Wal-Mart but are generally unaware that virtually everything they buy contains polymeric materials in one form or another.

Inclusion of polymeric materials provides, in addition to some fundamental chemistry, a glimpse of the historical context in which these materials were developed and some of the individuals responsible for the development. It also provides many opportunities to reinforce many concepts that students have just seen in a review of general chemistry topics and the study of alkanes. Students begin to appreciate the broad nature of organic chemistry and its impact on the society in which they live.

Student's enthusiasm for and active participation in the class often significantly improve as a consequence of some discussion of polymeric materials. This increased enthusiasm leads to enhanced performance as reflected by scores on the ACS first term organic exam administered at the end of the semester.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch002

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch002

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch003

## Chapter 3

# Using Polymer Synthesis, Reactions and Properties as Examples of Concepts in Beginning Organic Chemistry

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Sophomores in a traditional organic chemistry course benefit in many ways from using polymer chemistry as an illustrative tool. While many organic chemists view polymer chemistry as a separate discipline, there are countless instances where polymer chemistry and organic chemistry overlap. Using polymer properties, synthe-sis, and reactions as part of an organic chemistry course does not require that one knows polymer chemistry in detail. In fact, what makes polymer chemistry examples useful is that they do not introduce new concepts. They just reinforce what students learn in the traditional functional group approach to teaching organic chemistry. By using real materials that students encounter on a daily basis as subjects for problems as lecture anecdotes, as demonstrations, or as explanative illustrations in an office discussion, the dry and sometimes arcane facts of organic chemistry become more meaningful. Incorporation of polymer chemistry is no different than incorporating green chemistry, environmental chemistry, or biological chemistry examples. Any of these examples enrich the course because students realize the relevance of what they are learning in organic chemistry to broader issues that include the many materials that are products of modern polymer chemistry.

In Introduction of Macromolecular Science/Polymeric Materials into the Foundational Course in Organic Chemistry; Howell, B.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch003

# Introduction

Using polymer chemistry to illustrate the concepts of beginning organic chemistry is easy and requires no polymer chemistry expertise. Using polymer chemistry in organic chemistry is easy as the examples are just the same organic reaction mechanisms, synthetic reactions, or physical concepts that any organic chemistry instructor is already familiar with. Polymer synthesis, reactions and properties as examples of concepts in beginning organic chemistry thus reinforce what students are learning in the traditional functional group approach to teaching this subject. There are opportunities to deal with polymer concepts too, but that is not necessary for polymer examples to be effective instructional tools. By using real materials students use on a daily basis as the subject for a problem, a lecture anecdote, a demonstration, or an explanative illustration in an office discussion, it is possible to make the litany of arcane organic chemistry facts meaningful in a broader context.

The sophomore organic courses at Texas A&M University are taught with traditional lectures. These three credit classes vary from ca. 40-60 students in an honors or majors section to a maximum of 105 students in a regular section. There are no required recitations or tutorials. Aside from the majors section, most of the clientele for this course are students whose nominal goal when starting organic is some sort of professional career in biological science – an M.D. or M.D./Ph.D, a physician's associate, nursing, dental, pharmacy, or a D.V.M. degree. There is a biochemistry department that is separate from chemistry and biochemistry majors along with a substantial number of lower level chemical engineers makeup most of the rest of the population of the students in these sophomore organic chemistry courses. There are multiple sections of both the off- and on-sequence courses to accommodate the ca. 1800 students in spring 2013 who are taking organic chemistry at Texas A&M University. While we do not use common exams for these classes, there are agreed upon chapters that should be covered and a common textbook (currently McMurry). The commonality of chapters is especially important in the first semester as it is not certain that a student will have the same instructor in the second semester. Even within this scenario where students are largely focused on a biologically oriented career and where there can be over a dozen or more different sections, I have found polymer chemistry to be an extremely useful way to reinforce the concepts and principles of sophomore organic chemistry. I have found that students like knowing that what they are learning is actually relevant to everything from drug delivery to clothing to electronics to the plastic action figure they so enjoyed at age five. Moreover, it really is not hard to use polymer chemistry examples to show students that organic chemistry literally is the fabric of modern society.

Many students I have encountered in my nearly 40 years at Texas A&M take organic chemistry with a measure of trepidation. OChem as it is commonly known is a course that is a hurdle for want-to-be doctors or chemical engineers. It can be a killer course for a chemical engineering major as it is taken along with physics and some of the higher level math courses. It is a course where students supposedly memorize the equivalent of a phone book and have to deal both with seemingly irrelevant and esoteric terminology and the graphical language

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of organic chemistry. However, while OChem can be an obstacle for some in their putative careers, it most certainly is not an obscure academic topic without relevance to an eventual doctor or engineer and polymer chemistry examples illustrate that. Using polymers also helps me at least to achieve my goals of giving students more than a headache full of facts. Since polymers at first glance seem to be different than the simplest molecules they draw, the fact that polymers often behave and are prepared using the same principles and reactions that we discuss with regard to small molecules reinforces the concepts I am trying to explain in organic chemistry. I incorporate polymer chemistry examples in exactly the same way as I incorporate green chemistry, biological chemistry, and the impacts and history of technology. In some cases, polymer chemistry examples and these other examples are one and the same. Whatever the example, the result is a richer story and a course that is no longer just a collection of dry and seemingly irrelevant facts.

In this short chapter, I have provided a series of examples where I use polymer chemistry to accomplish the goals outlined above. I have not included everything I do but have instead included select examples from chapters throughout a typical sophomore book. While the specific examples here and many others are not in the book I use, it is easy to incorporate them as useful illustrations of organic concepts.

## Thermodynamics and the Gibbs Equation

While favorable kinetics are always a factor in chemistry, a chemical process is only successful if the change in free energy, ΔG, is negative. This idea as exemplified in the Gibbs equation (equation 1) and is as important in organic chemistry as it is in any other branch of chemistry.

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

Most often organic books deal with the importance of a reaction being exothermic by discussing the differences in bond strength between the starting materials and products. This focus on enthalpy changes reinforces ideas about bond strength and while oversimplified, can serve as a predictor for the success of many reactions. However, entropy is also important and many reactions and chemical processes are affected by unfavorable entropy. This effect can be illustrated with a simple example like that shown in Figure 1.

The obvious physical changes seen in a polymer's solubility in Figure 1 can be demonstrated in lecture by simply placing a vial containing a 1 weight percent aqueous solution of the commercially available polymer poly(*N*-isopropylacrylamide) (PNIPAM) successively in cups of hot water and then in ice water. An even simpler demonstration in a small class is to prepare some samples in sealed capillaries taped to a hard surface like a small piece of wood that can be passed around and literally just be touched by students for 30 seconds or so to trigger the precipitation. When using this more personal demonstration, I use capillary tubes containing a PNIPAM solution with some salt so that the solubility changes in Figure 1 can be triggered by the heating provided by a student's warm finger touching the capillary for a short time. While this second experiment uses fragile glass melting point capillary tubes, taping these tubes to a hard surface makes it so they cannot easily be broken. Free standing tubes, like any melting point capillary, could break more easily and I only use them in an office setting with people who are unlikely to crush a capillary tube in their fist. The demonstration that uses hot and cold water always works. The demonstration where students use their own body heat to trigger the LCST and clouding event works generally though some people with poor circulation and cold fingers can fail to trigger the LCST event (*1*).

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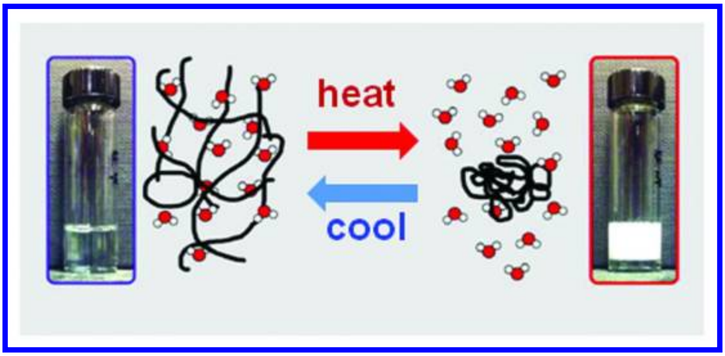
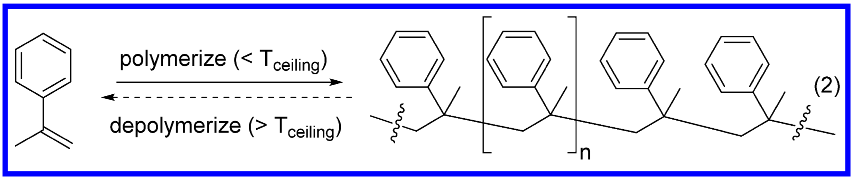


*Figure 1. The visible changes seen when a vial containing a dilute solution of a polymer with a Lower Critical Solution Temperature (LCST) is heated above or cooled above or below the LCST temperature.*

Either the larger demonstration with hot and cold water or the individual experiments with melting point capillaries use the LCST behavior of polymers in solution to demonstrate that the concepts of $\Delta H$ and $\Delta S$ are both important in a chemical process. While the explanation for LCST events can be complex and can involve many sorts of polymers (*2*), the simplified explanation I use in an organic chemistry class for PNIPAM is that this polymer is soluble cold because of the favorable hydration due to hydrogen bonding where waters of hydration are associated with each carboxamide monomer unit of the macromolecule (*3*). The hydrogen bonding of the protons of solvent water to the amide groups of the PNIPAM polymer generates a negative $\Delta H$ that contributes to a negative and favorable $\Delta G$ at room temperature. However, unlike low molecular weight molecules whose solubility increases with heating, macromolecules exhibit different behavior above some critical temperature. That is because a macromolecule has 1000s of monomer units in a single molecule. This degree of polymerization means that several 1000s of water molecules have to become more organized as molecules of hydration if each repeat unit is hydrated. While this hydration may produce a negative and favorable ΔH term, this organization is entropically unfavorable. That unfavorable entropic aspect of this organization leads to a net positive -TΔS term in the Gibbs equation. With an appropriate macromolecule and solution components, the negative ΔH term and the net positive -TΔS terms together can be adjusted to slightly favor a negative ΔG for dissolution near room temperature. This is the case in the example in Figure 1. However, in such a case, heating even just a few degrees with just a warm finger is sufficient to make the net positive -TΔS term larger in magnitude than the negative ΔH which changes ΔG and triggers a precipitation event. The cooler room temperature then reverses the precipitation process.

While this experiment might seem to be just a parlor trick, it is possible to relate this phenomenon to broader real problems. For example, this same process has been suggested to be the basis of a 'smart' window for a greenhouse providing a mechanism for plants to be shielded from sun and to control the resultant overheating with autonomous window clouding. Since this is a reversible process, subsequent clearing occurs on cooling allowing plants to later benefit from sunlight during a cooler part of the day (*4*). In our own research we prepared polymers where this LCST phenomenon significantly changes the chemistry of aqueous solutions or catalysts (*5–7*). For example, we have used the LCST behavior of PNIPAM copolymers to prepare 'smart' catalysts that turn exothermic reactions off and then back on. Such catalysts separate from a solution of a substrate when a reaction overheats (*6*, *7*) turning off a reaction in response to an exotherm. In this example, phase separation as a result of an exotherm effectively removes catalyst from the solution containing the substrate stopping the reaction. This precipitation event however only stops the reaction temporarily. Subsequent cooling after the exothermic reaction event redissolves the catalyst and restarts the reaction. A third example is effect of hydration on protein structure. Heightened hydration of proteins by water on cooling can lead to cold denaturation of a protein. In this case, increased solubility of the protein on cooling disrupts a protein's tertiary structure (*8*). This LCST experiment or demonstration can be used in multiple places in an organic course.

A final example where entropy and polymer chemistry is relevant would be polymerization chemistry itself. Students commonly assume that reactions are more likely to go to completion if they are heated. That is generally true. However, reactions that have a very unfavorable ΔS are exceptions to this rule. Polymerizations are a particularly good example of this. For example, polymerization of α-methylstyrene (equation 2) is favorable at low temperatures.



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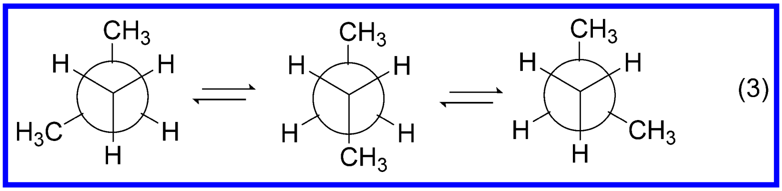
However, on heating above a so-called 'ceiling temperature' poly(α-methystyrene) depolymerizes (*9*). In this instance, the ΔG for this polymerization becomes positive and unfavorable at the ceiling temperature where ΔH equals -TΔS. Above this temperature depolymerization is thermodynamically favored. This effect is common in polymerization reactions. A similar effect is seen in cyclohexene polymerization in a ring-opening metathesis polymerization process (*10*) and is discussed below where the concept of ring strain is discussed in connection with ring-opening metathesis polymerization (*vide infra*).

## Acyclic and Cyclic Conformational Analysis

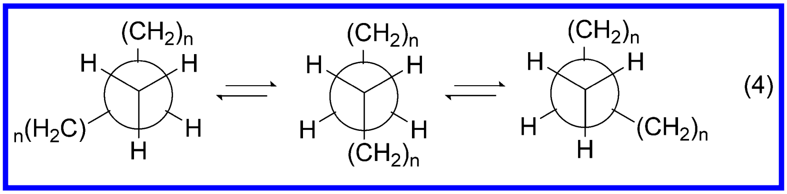
Conformational analysis and the issues associated with isomerization about carbon single bonds in acyclic and cyclic structures are a feature of most first term organic courses. Polymer chemistry is relevant here too. For example, when I discuss rotation about single bonds in terms of the equilibrium between gauche, anti and gauche butanes (equation 3) I note that the difference in energy between these conformers is much less than the energy available at room temperature.



(3)

As a result these isomers equilibrate rapidly. This is of course not the case in an environment where the thermal energy is much less. Thus, on some very cold distant planet, these species would not readily interconvert and would be isolable, separable species as bond rotation would no longer be facile.

I can make this argument with words but polymers provide a physical example of the effects of temperature on the dynamics of carbon-carbon bond isomerization. If one considers essentially the same set of structures for a carbon-carbon bond in polyethylene one would draw a very similar set of gauche, anti, and gauche conformers (equation 4).



(4)

Just as is the case for butane, the relatively facile rotation about the carbon-carbon bonds of polyethylene contributes to this polymer's segmental mobility that makes polyethylene a 'flexible' and 'tough' material for a milk bottle or a garbage bag.

However, at very low temperatures in liquid nitrogen this segmental mobility like the bond rotation that converts gauche to anti butane is no longer facile. This then changes the polyethylene from a 'flexible' plastic to a rigid glass. This can be easily illustrated by taking a polyethylene bag and vigorously tossing it against a wall or stomping it. Neither type of abuse has any effect on the plastic bag's integrity at room temperature. However, if you have a student hold open the bag and pour in a liter or so of liquid nitrogen, you end up with a bag full of liquid nitrogen. That itself attracts students' attention as the bags inevitably leak and there is a lot of frosty air. However, the more interesting part relevant to equations 3 and 4 comes from flinging the bag against a wall. This should involve a wall that is far enough from the students that no debris reaches them. That process leads to significant destruction of the bag, showing the effect of temperature on bond rotation in terms of segmental motion of polymers, a demonstration of the temperature dependence of conformational isomerism.

Polycyclic hydrocarbons provide a second way to discuss isomerism that is a consequence of single bond rotations. In this case, I begin by discussing the ring structure and conformational mobility of *cis*- versus *trans*- decalin – small molecules that are included in most text discussions (Figure 2). I usually note the rigidity of the latter and its importance in the structure of simple steroids that students know of – cholesterol being an obvious example. I then go on to mention that the same rigidity in *trans*-decalin or cholesterol can be important in organic materials that contain polycyclic organic species. Since students have usually at this point in the course not seen much in terms of functional groups, I use as examples all carbon organic materials - one real material and one hypothetical simplified organic framework molecule both of which have polycyclic hydrocarbon networks. The first of these is a hypothetical porous polymer organic framework formed with adamantyl groups. A partial structure of diamond serves as a second real example of a material with a rigid organic structure (Figure 3). Students are generally familiar with the idea that diamonds are a hard substance but are surprised to know that diamonds are really just a network of chair cyclo-hexanes without hydrogens. The porous organic framework, even though it is a hypothetical structure, allows me to talk about real polymer organic frameworks and the potential for new types of solid porous materials in energy and separation applications.

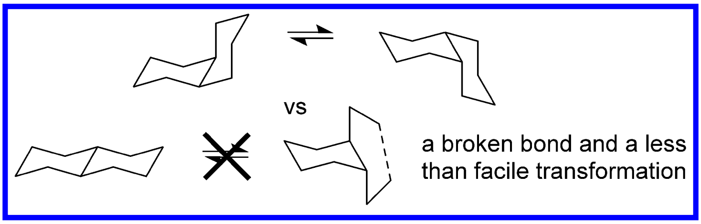


*Figure 2. Conformational isomerism in cis- and trans-decalin.*

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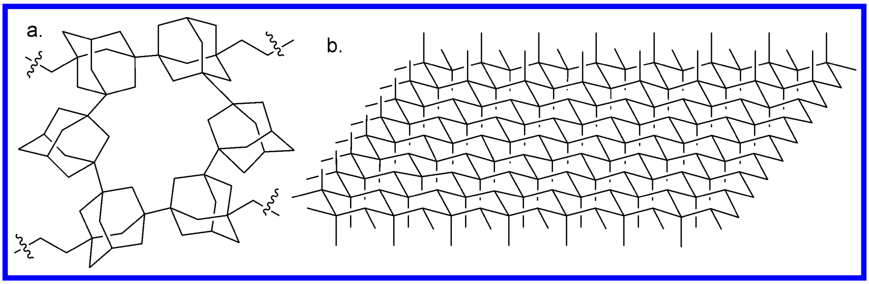

*Figure 3. Structure of rigid solids: a) a hypothetical porous organic network polymer, and b) diamond with one sheet of an extended chair cyclohexyl-like structure.*

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## Structural and Stereochemical Isomerism

Diastereomerism like the other stereochemical concepts introduced in sophomore organic chemistry courses has ample analogies in materials and polymer chemistry. Just as discussing how vision depends on an *Z* to *E* isomerization of rhodopsin provides students with a biologically relevant example of double bond stereoisomerism discussing how *E*/*Z* stereochemistry in organic polymers affects polymer properties can be useful. I use the example of the naturally occurring, biological polymer **1** as the basis for this discussion (Figure 4). This naturally occurring polymer of isoprene is the rubber material produced by rubber trees (*11*). Like its synthetic analog, *Z*-1,4-polybutadiene, *Z*-1,4-polyisoprene can be used to produce products that have the elastomeric properties of a racquet ball. In contrast, the *E*-1,4- diastereomeric form of polyisoprene while also elastomeric, is more rigid. The atactic stereorandom form of 1,2-polyisoprene is more amorphous and polymers containing this structurally isomeric form of an isoprenyl repeating unit do not bounce at all. While actual rubber products formed from these linear polymers typically contains some sulfur crosslinking or in many cases include other copolymers, I find it convenient to use two or three samples of materials that have similar properties as 'examples' of the various stereoisomeric forms of polyisoprene. While the three samples I use may not actually be the *Z*-1,4-, *E*-1,4- and atactic (i.e. stereorandom) 1,2-polyisoprene shown in Figure 4, the samples I've assembled have physical properties that are comparable to those of balls prepared from *Z*-1,4-, *E*-1,4- and atactic (i.e. stereorandom) 1,2-polybutadiene that a colleague once had. Unfortunately those original materials are now lost. I now use for this demonstration "Happy" and "Sad" balls that are commercially available (*12*) along with a rigid ball that I suspect is probably polystyrene but which I allege is *E*-1,4-polyisoprene. I use the 'Happy' ball as a *Z*-1,4-polyisoprene example and the 'Sad' ball as an example of atactic 1,2-polyisoprene. Bouncing these balls in class illustrates the consequences of structural and stereochemical isomerism of the three types of polyisoprene shown in Figure 4 on a material's physical properties. The alleged *Z*-1,4-polyisoprene 'Happy" ball bounces with youthful energy when it is tossed against walls, the ceiling or a chalkboard. In contrast, the rigid ball bounces some but not well and with an audible sound like that suggests it is a more rigid material. The "Sad" ball that is alleged to contain stereorandom 1,2-polyisoprene bounces very poorly. Older toys (e.g. "A Bad Case of Worms" that were marketed by Mattel in the 1980s) are better examples of this material as the material used in those toys would actually stick when thrown against a wall and then ooze down the wall. These toys sometimes are available on eBay but are expensive 'collectors' toys. While the 'Sad' ball's properties are not this notable, this ball is more available and has properties different enough from the other two materials to make the point that stereochemistry and structural isomerism matter for materials just as is the case of biological and low molecular weight organic materials.

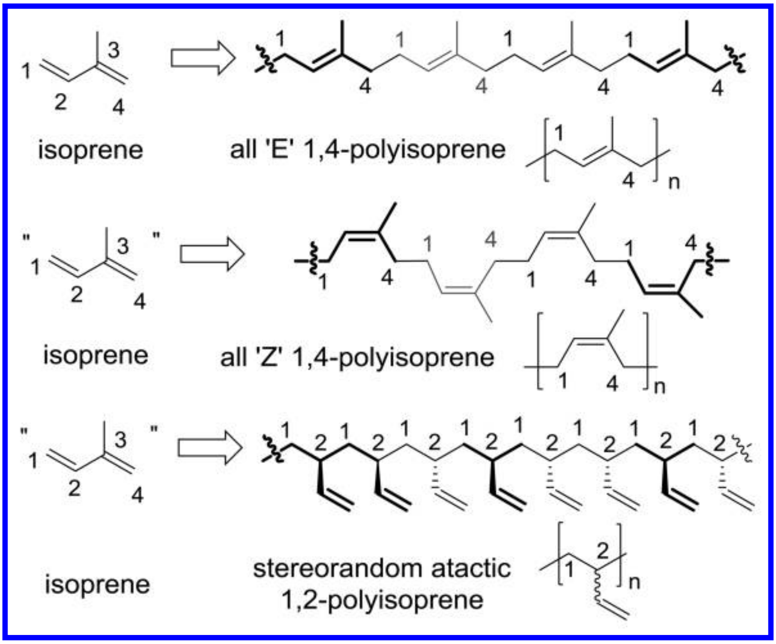

*Figure 4. Structural and stereoisomerism in polyisoprene.*

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## Ring Strain

The Baeyer theory about the stability of different sized rings and more modern concepts of stability of simple cyclic organic molecules are discussed early in chapters that describe carbocyclic rings. The concepts introduced at this point in an organic chemistry course can be reinforced using Ru-metathesis polymerization reactions. While a detailed discussion of the mechanism of the metathesis polymerization process and the catalyst structure is outside the scope of a sophomore class, the reaction is important enough to warrant inclusion in the sophomore curriculum. Of the three principle variants of this reaction – ring-closing metathesis, cross metathesis, and ring-opening metathesis polymerization (ROMP) – ROMP is the variant that fits well as an example to illustrate the consequences of the concept of ring strain in the context of a synthetic reaction. I have in the past included examples of our own green chemistry approaches to catalyst design as an example in this case (*13*). However, a more general example would emphasize the importance of ring strain for monomers that polymerize. In this polymerization process, a Ru catalyst can polymerize a strained substrate like cyclobutene to form a high molecular weight polymer because the energy gained by ring-opening of this strained ring helps generate a favorable negative ΔH that drives an otherwise entropically unfavorable polymerization process. In contrast, cyclohexene is a poor substrate for this polymerization. The difference between the two monomers is that cyclobutene is highly strained and forms a polymer with relatively unstrained carbon-carbon double bonds. The release of ring strain is an important factor driving an otherwise entropically unfavorable reaction to form a macromolecule (Figure 5). The difference between cyclobutene as a substrate and the less successful cyclohexene substrate is that the latter has relatively little strain and thus little enthalpic driving force to overcome the unfavorable entropy associated with forming a single macromolecule from 100s or 1000s of monomer molecule precursors (*10*).

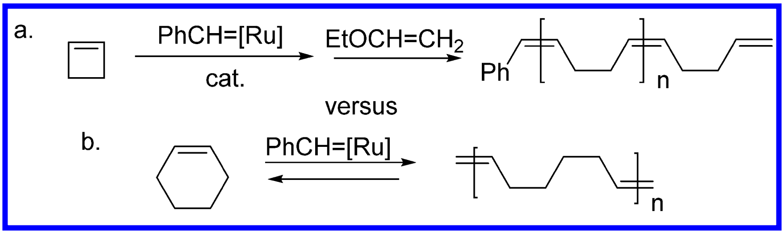

*Figure 5. The favorable ring-opening metathesis polymerization (ROMP) of (a) cyclobutene using a Ru-benzylidene initiator and (b) the less favorable process with cyclohexene.*

ROMP chemistry can be further elaborated using as an example a piece of sports equipment. At one point, Easton Sports Inc. made a composite baseball bat out of wood and dicyclopentadiene using metathesis polymerization to first polymerize dicyclopentadiene through the strained double bond of the bicyclic ring and then to crosslink the resulting polymer through the remaining double bond. This example uses baseball or more specifically baseball equipment and the common experience of most students who at college or earlier played baseball to illustrate both ring strain and the importance of organic molecules in everyday life. Professors like myself who are old enough to remember sand lot baseball with wooden versus aluminum bats and baseball enthusiasts know that the major leagues use bats made of a hardwood like ash instead of the aluminum bats used at lower levels of the game. Students though may not realize that it is the propensity of wooden bats to break that led to the widespread adoption of aluminum bats. This reflects the fact that there is enough ‘good’ ash for the limited major league baseball market, but that the broader market that includes lower level baseball and recreational baseball would require more ‘good’ ash than is available. Using poorer grades of hardwood in place of the more expensive

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‘good’ ash leads to broken baseball bats. In this case, a polymerization using ROMP chemistry addresses the issue that there is only a limited amount of ‘good’ ash available. By soaking a piece of ‘bad’ ash in dicyclopentadiene and polymerizing and crosslinking this monomer with ROMP, you get a composite wooden bat strengthened by ROMP polymerization that is the equivalent of a bat made of natural ‘good’ ash.

## Acetals

Carbonyl chemistry is a centerpiece of any organic chemistry course. The formation and cleavage of acetals is a reaction that students encounter often in this course. It is a reaction that has relevance in biological chemistry since polysaccharides are polymers where sugars are linked one to another via acetal bonds. It is also a reaction of importance in polymer chemistry. Two commercial polymers, Delrin **2** and Celcon **3**, both are polyacetals. These materials differ in that Delrin is a homopolymer of formaldehyde with ester end groups. Celcon is formed from 1,3,5-trioxolane with some ethylene oxide as a comonomer and contains random $–CH_2CH_2O$- groups and $–CH_2CH_2OH$ chain ends with the bulk of the chains being made up of repeating $–(CH_2O)_n$- acetal groups. Acetal stability, the conditions for acetal hydrolysis, and the mechanisms by which acetals and esters hydrolyze are common concepts students are expected to know when they cover carbonyl chemistry. The chemistry of these groups is all involved in the uses of these polymeric materials. These examples have the further advantage of illustrating the practical consequences of simple carbonyl chemistry in the real world as these materials were at the heart of a major class action case in the 1990s that involved the use of Delrin and Celcon in plumbing parts. While the details of those class action cases and the actual facts of those cases are muddied by the claims and counterclaims of the litigants and by the large scale monetary interests of the plaintiffs and defendants involved in this series of very publicly reported cases (*14*), the potential for depolymerization of high molecular weight polyacetal like that in Delrin that could contain 1000s of formaldehyde monomer units as a result of a single chain scission event illustrates a practical consequence of acetal hydrolysis. As shown in Scheme 1, a polyacetal like Delrin capped with esters that undergoes a basic hydrolysis of the terminal ester group will form a hemiacetal that can then unzip in a series of base catalyzed steps. This chemistry which can be understood mechanistically accounts for the description of Delrin as being unsatisfactory for use in the presence of 10% aqueous NaOH (*15*). In contrast, Celcon is predicted to be more base stable as the hydroxyl end groups will not decompose in base and acetals are base stable. However, in acid neither polymer would be stable and neither is recommended for use in strongly acidic environments (*15*). This example shows students how a knowledge of an organic chemistry concept like the stability of carbonyl derivatives to aqueous base and acid can allow them to understand a very practical problem related to the stability of plumbing parts. This example is also easy to extend or can be substituted by a discussion of the acid-catalyzed cleavage of the chain of biopolymers present in cotton that also contain acetal linkages.

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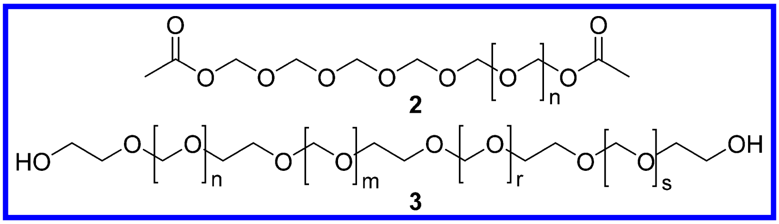

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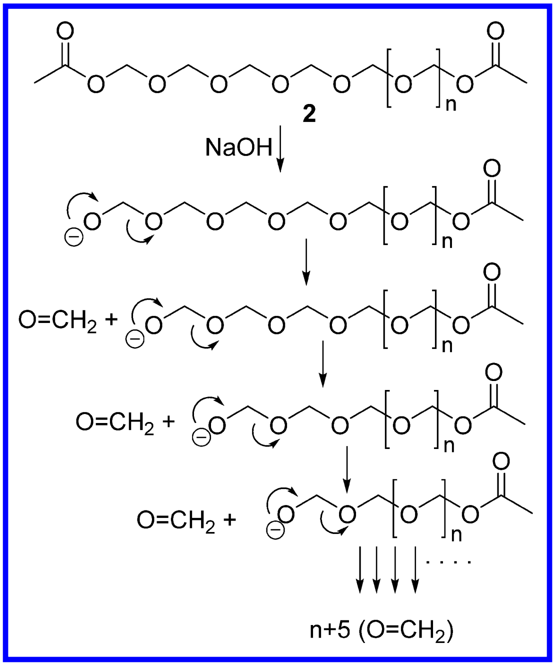
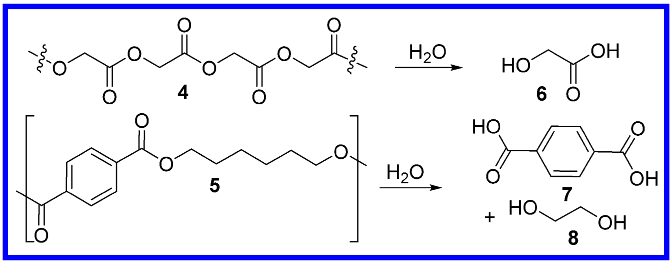
**3**



*Scheme 1. Basic hydrolysis of the ester end group of Delrin followed by anionic unzipping of the entire polymer chain.*

## Ester Hydrolysis

The design of materials that degrade in their environment to form benign small molecules has been of interest since the 1960s. A simple example of this chemistry is the chemistry of the polyester poly(glycolic acid) **4** (Scheme 2) which was developed in the early 1960s as an absorbable suture material to replace sutures that either degraded more slowly or not at all (*16*). In this case, the fate of braided multifilament fibers prepared from this simple polyester derived from glycolic acid can be contrasted with the fate of thread prepared from the synthetic polyester poly(ethylene terephthalate) (Dacron, **5**). These examples can be used to discuss both ester hydrolysis and ester hydrolysis products. In the first case, the poly(glycolic acid) can undergo hydrolysis to form the naturally occurring product glycolic acid **6** that is already present in a physiological environment. In the second case, hydrolysis would generate terephthalic acid **7** and ethylene glycol **8**, products that are not naturally present in a physiological environment.



*Scheme 2. Hydrolysis of poly(glycolic acid)* ***4*** *to form glycolic acid* ***6*** *and of poly(ethylene terephthalate (PET)* ***5*** *to form terephthalic acid 7 and ethylene glycol* ***8****.*

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## Aldol Chemistry

Aldol reactions and reverse aldol reactions are featured in every discussion of the carbon-carbon bond formation and carbon-carbon bond scission processes in carbonyl chemistry. Both aldol-like and retro aldol-like processes can be discussed using as an example one of the oldest synthetic plastics – Bakelite **9**. Bakelite is a highly crosslinked plastic formed from an aldol-like reaction of phenol and formaldehyde. A bit of chemistry known to those who collect vintage Bakelite objects from the early 20th century is that the polymerization reaction that forms Bakelite from phenol can be reversed by a variety of procedures (*17*). One very simple test that can be carried out as a demonstration is to place an object made from Bakelite into some moderately hot water. When this experiment is be carried out with a vintage Bakelite billiard ball using a 400 mL plastic beaker and hot tap water, it is possible to detect the odor of carbolic acid (phenol) in only a few minutes. The amount of carbolic acid produced is quite small but the odor is quite distinct. Presumably this phenol is formed in a process like that shown in Scheme 3 via a multistep process that includes as a final step a retro aldol-like reaction.

### Michael Chemistry and Anionic Polymerization

Michael addition reactions like those that occur in a Robinson annulation, in the Bakelite chemistry discussed above, or in biosynthesis are still other carbonyl chemistry reactions that have many analogies in polymer chemistry. An example of a polymerization that most students have experimental experience occurs when one uses superglue. This common household item works by means of a Michael reaction that repeats over and over again to produce a polymer product (Scheme 4). Here a very reactive Michael acceptor like **10** that has an ester and nitrile group to stabilize an intermediate carbanionic group polymerizes on exposure to traces of moisture. As many students may know, this can even occur with the moisture present on skin leading to the cautionary statements on superglue packages about avoiding skin contact. What many students may be unaware of is that this same chemistry with the isobutyl cyanoacrylate shown in Scheme 4 is used to form poly(isobutyl cyanoacrylate) - a tissue compatible analog of superglue that is used as an alternative to sutures and stables in closing surgical incisions (*18*).

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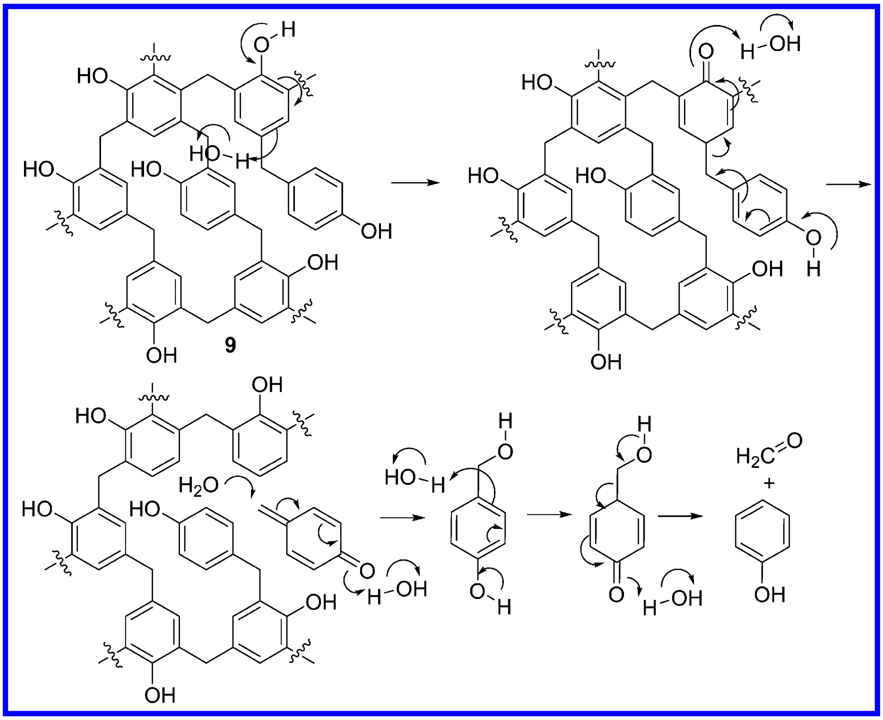
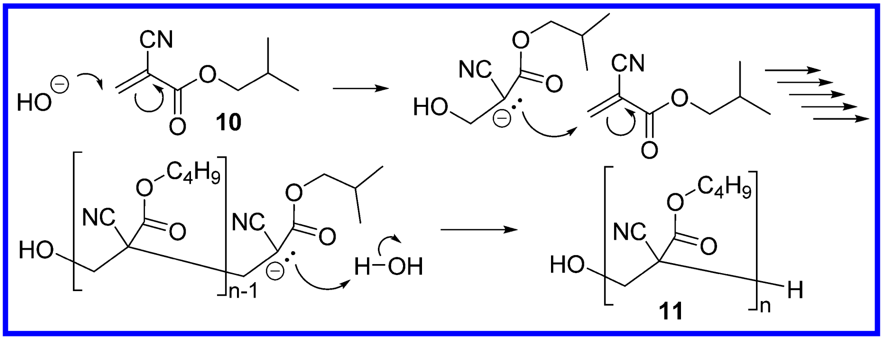


*Scheme 3. Retro aldol-like depolymerization of Bakelite in hot water to form phenol.*



*Scheme 4. Michael addition polymerization of isobutyl cyanoacrylate, a superglue like material that is biologically compatible enough for use as a replacement for sutures and stables in closing wounds and surgical incisions.*

## Green Chemistry Routes to Polyesters and Polycarbonates

Green chemistry is an issue of consequence. It is an issue students readily relate to as many are concerned about environmental issues. This topic can be easily incorporated into a sophomore organic course in a variety of ways. The

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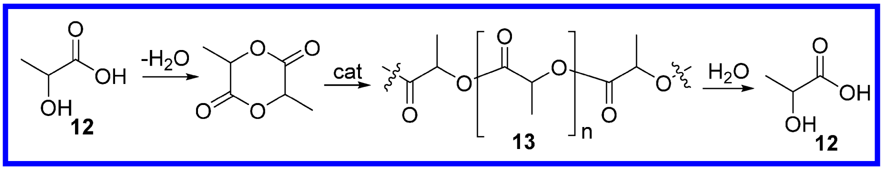
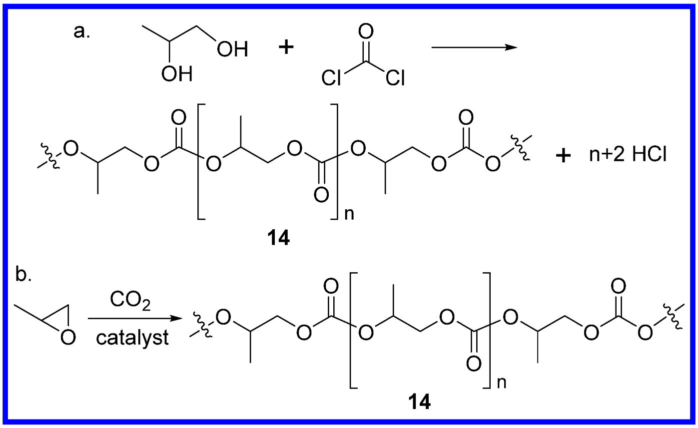
aforementioned example of a biodegradable polyester would be one example. Indeed, biodegradable lactic acid-derived materials now are available to replace the poly(ethylene terephthalate) bottles that some decades ago largely replaced glass bottles (*19*). In this case the cyclic lactide monomer is derived from sustainable resources. This polymer **13** derived from the cyclic ester dimer of the sustainable monomer **12** can replace a conventional polymer like poly(ethylene terephthalate) (*5*) (Scheme 5) which is formed from starting materials prepared from non-renewable petrochemical resources. The polymer **13** not only has the advantage of being a product of sustainable resources but has the additional advantage that it degrades after its use to form the biologically compatible product lactic acid (**12**) just as the degradable sutures mentioned above degrade to biologically innocuous products.



*Scheme 5. Synthesis of the sustainable polymer polylactide by a ring-opening polymerization and the subsequent natural lactic acid hydrolysis product produced in an eventual polymer hydrolysis reaction.*

Another example of green chemistry that involves carbonyl chemistry is the formation of polycarbonates. A polycarbonate like **14** for example can be formed by a polymerization that involves the reaction of epoxides and carbon dioxide in place of a less atom efficient synthesis of this same polymer **14** from more hazardous starting materials. This example is especially apt as it illustrates a number of green chemistry principles – the use of catalysis, atom economy, and the formation of products that degrade into benign materials. In the process shown in Scheme 6, a propylene oxide monomer and carbon dioxide in the presence of a catalyst form the polycarbonate **14** (*20*). This reaction occurs under relatively moderate conditions because of the use of a catalyst. In this polymerization, every atom of the starting materials is incorporated into the products. These two aspects of the reaction are in direct contrast to the classical route to the synthesis of the same polycarbonate that would proceed via reaction of propylene glycol and phosgene. While the propylene oxide used in the first reaction is a potentially toxic alkylating agent, its toxicity is moderate compared to that of phosgene which was used in World War I as a poison gas. Second, while the first reaction is a sterling example of atom economy, the second reaction produces two equivalents of HCl that would have to be converted into a more innocuous salt by the addition of NaOH. That neutralization step would produce on a kg of NaCl/kg of product basis more waste NaCl salt than product polymer – waste that would have to be disposed of in an expensive environmentally responsible manner. Avoiding generation of such chemical waste that could pose unknown future problems makes the $CO_2$-based polymerization especially attractive.



*Scheme 6. A conventional synthesis (a) of a polycarbonate from propylene glycol and phosgene that produces more waste than product polymer versus an atom efficient catalytic route (b) to the same polymer using propylene oxide and carbon dioxide.*

## Standards of Success in Formation of Amides from Carboxylic Acids and Amines

A final example illustrates how important very simple polymers are in commerce and industry and how critical it is to achieve high yields with exact stoichiometric balance of reagents. In this case I first discuss silk (**15**) and the synthesis of Nylon 6,6 (**16**). I typically begin this discussion by illustrating the predominant structure of the natural polypeptide that is present in silk and mention the importance of silk as a commodity for the past several thousand years. I specifically note that silk's availability was compromised in the 1930s by the developing conflicts in Asia and note the efforts by the Caruthers team at DuPont to develop a synthetic alternative to what at that time was a difficult to obtain natural polymer. While the chemistry can certainly be discussed as a mechanism, I find it also useful to mention here the problems of what many might consider to be a pretty trivial synthetic reaction – amide formation from reaction of an activated carboxylic acid derivative and an amine. What I discuss here is that for a condensation polymerization like this, it is critically important to insure that there is both a high conversion of the starting materials to products and that the ratio of the two reactants is precisely controlled. Assuming a strict stoichiometric balance of the diacid derivative and the diamine, one present students with the simplest form of the Caruthers equation (equation 5) (*21*).

$$\overline{DP} = \frac{1}{(1 - p)} \qquad (5)$$

$\overline{DP}$ = degree of polymerization; p = conversion

A brief survey of students about what they consider a high yield for a reaction often yields numbers like 90%. One can then use this 0.9 value as the value for the

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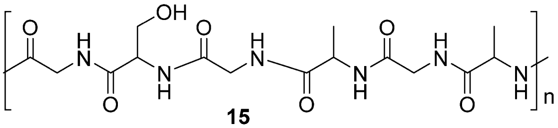
conversion p in equation 5 to the average degree of polymerization and show that their Nylon would on average be a decamer – a material unlikely to have much utility as a fiber and most certainly not a good candidate for a Nylon climbing rope for their next rock climbing adventure. This discussion can be continued to include the possibility of a stoichiometric imbalance where one includes an r value in equation 6 (r is the initial ratio of the less abundant monomer to the more abundant monomer – a number that is always less than or equal to 1) and show that a reaction that goes to 100% conversion with a ca.10% excess of one reagent over another will only yield on average a 20-mer which further complicates the process for synthesis of high molecular weight products.

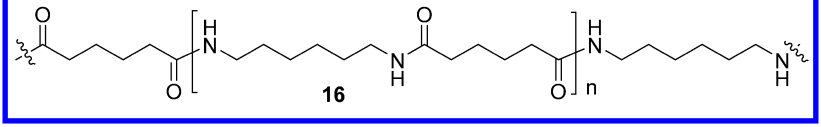
$$\overline{DP} = \frac{(1 + r)}{(1 + r - 2rp)} \qquad (6)$$

$\overline{DP}$ = degree of polymerization; p = conversion
r = stoichiometric balance

The original Carothers solution to this problem of using elevated temperature of 260 – 280 °C to effect condensations of salts of an amine and a carboxylic acid provides an example of organic acid/base chemistry being used to address what might otherwise be significant technical challenge for large scale syntheses.



**15**



**16**

## Summary

Polymer chemistry is a rich source of examples to use to teach and illustrate the concepts taught in a typical sophomore organic chemistry course. There are countless examples from polymer chemistry where a polymer's synthesis, its reactivity or its properties have biological, medical, materials, environmental and historical relevance. Such examples like the examples detailed in the discussion above can easily be choseboth n to reinforce organic chemistry concepts and to provide students with a broader view of organic chemistry. Using such examples in an organic lecture does not require any detailed knowledge or really much knowledge at all of polymer chemistry. Whether it is the consequence of isomerism on molecular properties, synthesis, mechanisms or theory, there are amply ways to use polymer chemistry to enrich the undergraduate curriculum.

## Acknowledgments

Support of my work using polymers in organic chemistry and catalysis by the Robert A. Welch Foundation (A-0639) and the National Science Foundation

(CHE-0952134) that has provided some of the examples above and that has been the basis for my ability to introduce these polymer examples into my sophomore courses is gratefully acknowledged.

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch003

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch004

## Chapter 4

# Extrapolation from Small Molecules to Polymers: A Simple and Effective Way To Promote Interest in Both Organic Chemistry and Polymer Chemistry

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Two methods to integrate polymer chemistry within the regular organic chemistry curriculum are presented. The first method extrapolates small molecule synthetic methodology to the synthesis of polymers. For example, the common organic reaction, Fischer esterification, is extended to the synthesis of diesters and polyesters. This approach is also used to introduce polyamides. The second method relies on a clear understanding of reaction mechanism in order to divert a small molecule synthesis to the synthesis of a polymer. Examples include extrapolation from the base-catalyzed hydrolysis of epoxides to the synthesis of polyethyleneglycol and extrapolation from conjugate addition to superglue.

## Introduction

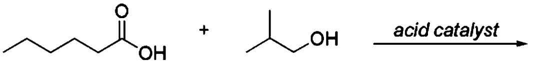
Over many years of teaching organic chemistry it has become apparent to me that connections between everyday life and the topics in organic chemistry are essential to stimulate student interest. One of the best ways to do this is to make connections between organic chemistry and polymer chemistry throughout the course. Presenting a separate polymer section towards the end of the course is much less effective because the students' interest has been won or lost many months earlier. I have developed several different approaches to integrate polymer chemistry throughout the organic chemistry curriculum. The two most effective methods I use will be described here. Both methods involve extrapolation from discrete small-molecule reactions to the synthesis of polymers. The first method is reaction-based while the second method is mechanism-based.

## Reaction-Based Strategy

In this approach I first present a method for the synthesis of a family of small molecules with the emphasis on the prediction of reaction products as well as the selection of reactants given a specific target molecule. In a logical way, this knowledge is extrapolated to the synthesis of polymers. Two of the best reactions to use this approach with are the Fischer esterification reaction and the synthesis of amides from acid chlorides and amines.

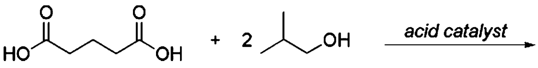
### From the Synthesis of Esters to the Synthesis of Polyesters

The Fisher esterification reaction involves the acid-catalyzed reaction of carboxylic acids with alcohols. Students should be able to predict the structure of an ester given the structure of the carboxylic acid and the alcohol used. So, in class I would begin the extrapolation of the Fischer esterification reaction to the synthesis of polyesters with a simple question based on equation 1: Can you predict the product of this reaction?



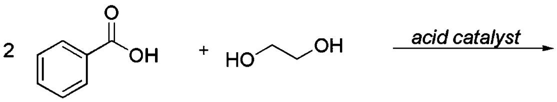
(1)

The first extrapolation is to stretch this to a question that involves reaction of a diacid with an excess of alcohol as shown in equation 2. Many students will predict that this will yield a diester.



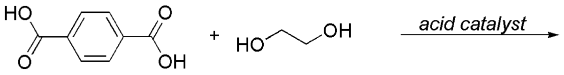
(2)

I then ask students to suggest another set of reactants, ***not*** including a diacid, that, using the Fischer esterification reaction, will also yield a diester. Generally a student will suggest reaction of a diol with an excess of acid, as shown in equation 3.



(3)

At this stage I pose the question: What product would be formed on reaction of a diol with a diacid? I intentionally draw a pair of reactants that will yield a well known product such as terephthalic acid and ethylene glycol as shown in equation 4.



(4)

It is rare for students to immediately be able to predict the product. It is always an interesting exercise to draw the product, ester-linkage by ester-linkage, starting on one edge of the teaching surface and drawing out the polyester stepwise across the board or computer screen. This is shown in the series of structures in Figure 1 which would be drawn as one growing structure.

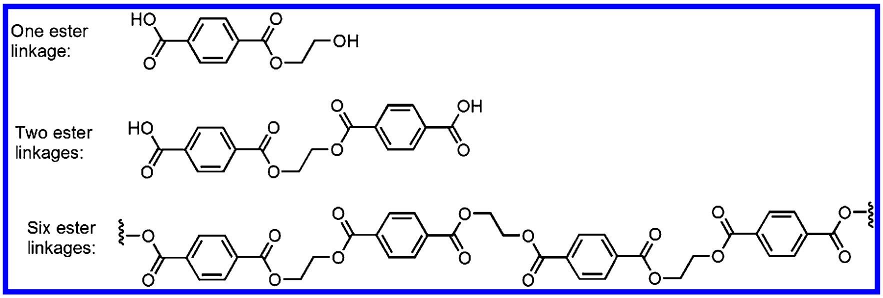


*Figure 1. Stepwise drawing of the polymer formed by reaction of terephthalic acid with ethylene glycol ideally drawn as a single growing structure.*

It doesn't take many ester linkages for students to see the trend. When at least 6 ester linkages have been drawn it is possible to identify and highlight the repeating unit in the structure. This can be achieved with colors or by circling the repeating unit for emphasis as shown in Figure 2. This is then followed by drawing out the repeating unit as commonly done for polymers.

*Figure 2. Identification of the repeating unit within polyethylene terephthalate.*

The logical extrapolation from synthesis of an ester to a polyester is so straightforward that some of the mystique of polymers is removed. This is a good time to tell students that they are most likely quite familiar with this polyester either as the "polyester" used in fabrics, or as the PETE used in clear beverage

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch004

bottles. Most students are aware of, and interested in, recycling and many will recognize the recycling symbol for PETE. This then provides an opportunity to talk about polymers in general, the history of polymers or polymers and recycling. For example, recycled PET bottles are used to manufacture insulating fleece fabrics.

The discussion is readily extended to the synthesis of another interesting group of polyesters. To begin, I pose the question: What single compound could be used to synthesize a polyester using this reaction procedure? Students may suggest a variety of molecules that contain an acid and an alcohol group on opposite sides of a molecule, for example 4-hydroxy benzoic acid or glycolic acid shown in Figure 3.

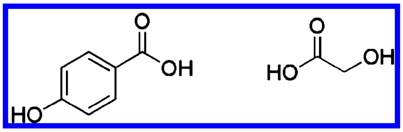


*Figure 3. Hydroxy acids suitable for the formation of polyesters.*

I then direct the discussion to use of glycolic acid and draw out several ester linkages as before and the repeating unit as shown in Figure 4. This is a particularly interesting polymer since polyglycolic acids are more readily hydrolyzed than PETE and have found application as medical sutures (stitches) that dissolve over a few weeks.

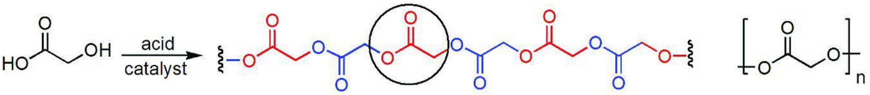


*Figure 4. Formation of polyglycolic acid from glycolic acid and recognition of the repeating unit.*

The discussion can also be diverted to the synthesis of triesters and then to triglycerides. This basic reaction can therefore make connections between the synthesis of interesting and useful small molecules, the synthesis of useful polymers, and important biological molecules. While I use the Fischer esterification reaction, other synthetic methods, for example transesterification, can be used.

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## From the Synthesis of Amides to the Synthesis of Polyamides

The synthesis of amides is another reaction that is particularly amenable to this extrapolated synthetic approach. I normally start the process by challenging students to predict the amide formed on reaction of an acid chloride with an amine and follow this with a di-acid chloride and excess amine. Finally I ask students to predict the product of reaction of a di-acid chloride with a diamine. I often use the related series of compounds shown in Figure 5 to ensure that an interesting polymer is formed.

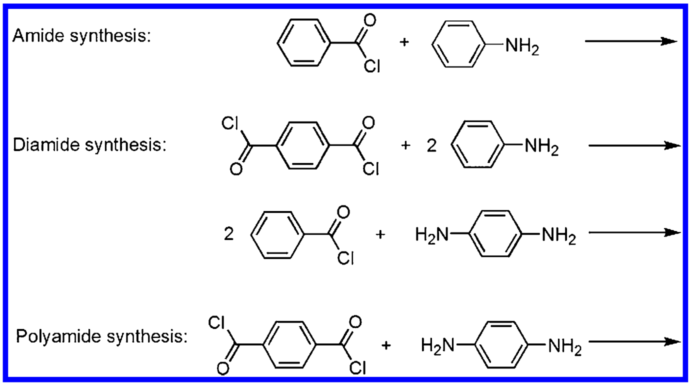


*Figure 5. Extrapolation from amide synthesis to polyamide synthesis through synthesis of diamides.*

If the extrapolation from esters to polyesters has been presented, this sequence is usually well understood and predictable for most students'. The sparkle returns to students eyes when you inform them that the predicted polymer shown in Figure 6 is one they have certainly heard of, Kevlar.

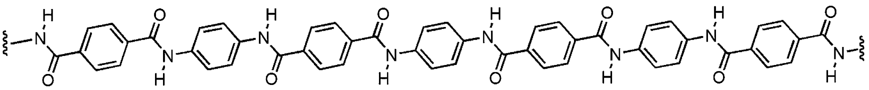


*Figure 6. Part of the polyamide formed using the reagents given in Figure 5.*

This provides an opportunity to discuss the physical properties of polymers. With Kevlar the rigidity of the two benzene rings coupled with interstrand hydrogen bonding is critical to its strength. Adjacent strands of the polyamide line up to maximize C=O---H-N hydrogen bonding between all adjacent strands as shown in Figure 7.

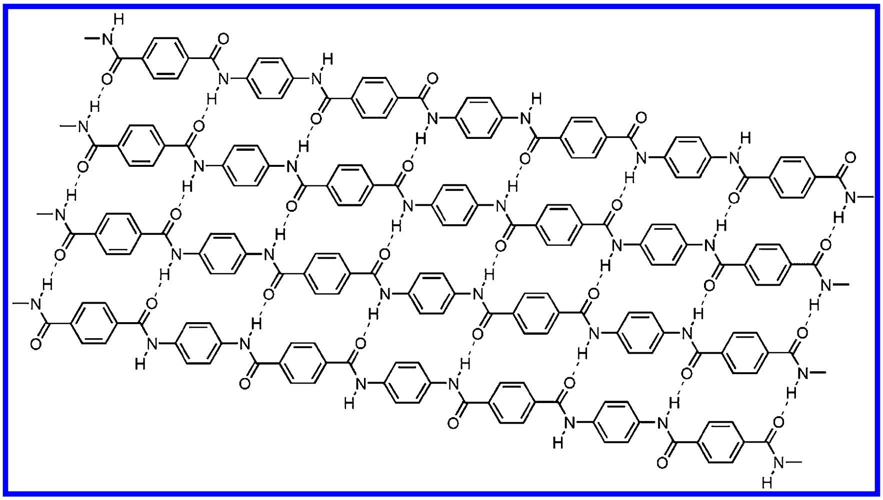
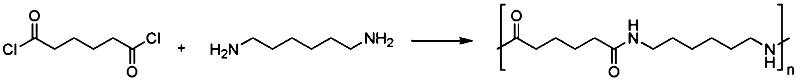


*Figure 7. Interstrand hydrogen bonding in a polyamide.*

Ideally, the presentation of Kevlar should be coupled with the formation of an aliphatic polyamide. I normally choose nylon-6,6 which can be prepared by reaction of adipoyl chloride with hexamethylene diamine as shown in equation 5.



**(5)**

Students are familiar with the flexibility of an aliphatic carbon chain and, with prompting, will understand the big difference in physical properties of the aromatic polyamide and the aliphatic polyamide. This is a particularly attractive reaction to present because the lecture presentation can be complemented by an elegant lab experience. In that experiment, an aqueous solution of hexamethylene diamine is prepared in a beaker and a solution of adipoyl chloride in cyclohexane is carefully layered over the diamine solution. Polymerization takes place at the interface between the two solutions and students can then hook the polymer and pull it out of the beaker and roll up a long strand of polyamide. This is an experiment that students go home and tell their parents about. It's that "cool"! This is an opportunity to discuss the early application of nylon in parachutes during World War II and in nylon stockings, as well as common current applications for example nylon rope, clothing and mechanical components including screws.

It is also interesting, and important, to draw connections between synthetic and naturally occurring polymers. At this juncture I present polyamides like silk (shown in Figure 8).

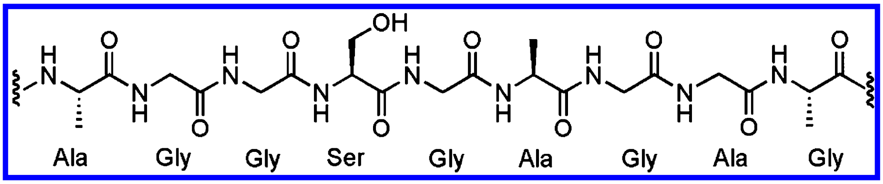


*Figure 8. Portion of a strand of silk.*

## Mechanism-Based Strategy

Teaching organic chemistry with a strong emphasis on mechanism allows several logical entries into polymer chemistry. In this approach I develop a good understanding of a reaction mechanism and then, based on this mechanism, I lead a discussion to rationalize how changing the reaction conditions results in the logical synthesis of polymers.

### From the Base-Catalyzed Synthesis of Glycols to the Synthesis of Polyethylene Glycol

The first example starts with the base-catalyzed hydrolysis of epoxides to form 1,2-glycols that can be diverted to the synthesis of polyethylene glycol. The base-catalyzed reaction starts with nucleophilic attack of hydroxide anion on the epoxide with concommitant ring opening to form an alkoxide intermediate. In an aqueous solution, the alkoxide is protonated by water to form the 1,2-diol and hydroxide as shown in Figure 9.

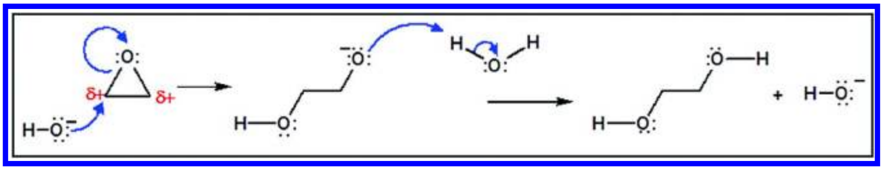


*Figure 9. Mechanism of base-catalyzed hydrolysis of ethylene oxide to form 1,2-ethanediol (ethylene glycol).*

I then challenge students to imagine what would happen if there were no proton donor (water) in the reaction mixture. I emphasize that the first step of the reaction does not involve water and would therefore proceed as before. I remind the students that apart from the catalytic amount hydroxide there would be a large excess of very reactive ethylene oxide in the solution. The alkoxide reacts with ethylene oxide as hydroxide did (path b in Figure 10). Thus in the absence of water, or any other proton donor, the reaction is diverted from path (a) to path (b). We discuss how the product of that reaction is again an alkoxide and will also react with ethylene oxide. After several iterations of this are shown, it is reasonable to develop the idea of a repeating unit either using color or circling the (-$CH_2CH_2O$-)

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units. To provide a clear understanding of the mechanism, a termination step, protonation with a trace amount of water, is shown.

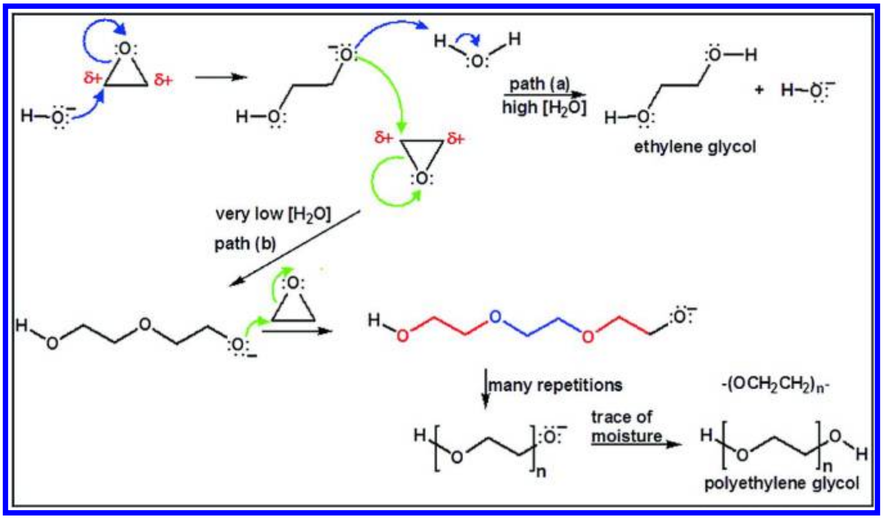

*Figure 10. Mechanism of the synthesis of polyethylene glycol developed from the mechanism of base-catalyzed hydrolysis of ethylene oxide.*

Polyethylene glycol is an interesting polymer with a great variety of uses. It is approved by the FDA for use and has been used in drug delivery, skin creams, tooth paste, laxatives, and many more common products. Challenge students to look for it in the ingredient list of common products.

## From the Synthesis of Ethers to the Synthesis of Butyl Rubber

Another example I find to be useful is the acid-catalyzed addition of alcohols to alkenes. Thus, the acid-catalyzed reaction of isobutylene with methanol yields MTBE (*t*-butyl methyl ether). This reaction begins with regioselective protonation of the alkene followed by nucleophilic addition of the methanol and, finally, deprotonation as shown in Figure 11.

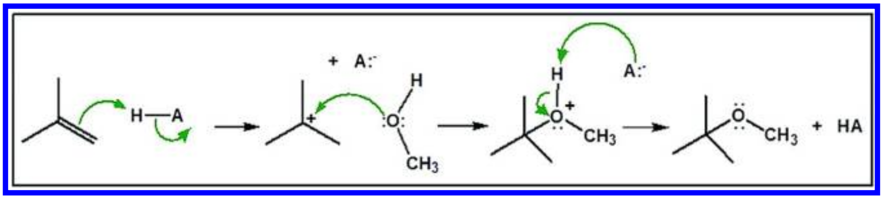

*Figure 11. Mechanism of the synthesis of t-butyl methyl ether by acid-catalyzed addition of methanol to 2-methylpropene (isobutylene).*

In Introduction of Macromolecular Science/Polymeric Materials into the Foundational Course in Organic Chemistry; Howell, B.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

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After discussion of the mechanism, I ask students to predict what would happen if the alcohol was left out of the reaction vessel. I encourage them to use the mechanism as the basis for their prediction. I remind them that it is reasonable for the protonation of the alkene to proceed irrespective of the presence or absence of the alcohol. We then discuss the fact that the excess alkene would attack the carbocation and further note that that reaction results in the formation of another carbocation. Reaction of this cation with another molecule of isobutylene again yields a cation and many repetitions of this result in the formation of a long-chain polymer. The polymer growth could be terminated by addition of the conjugate base to the cation (shown in Figure 12) or elimination to form a terminal alkene.

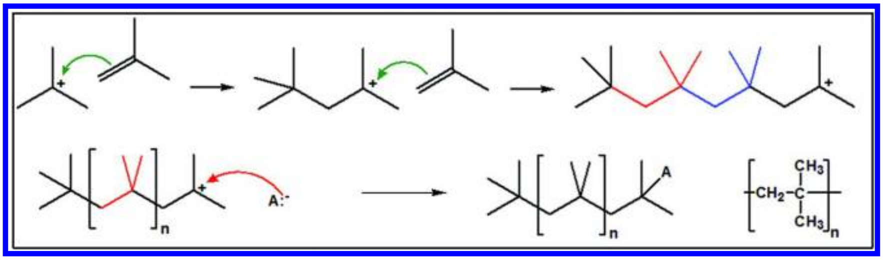

*Figure 12. Mechanism of the acid-catalyzed synthesis of butyl rubber from isobutylene.*

The polymeric product, butyl rubber, is fairly common and is found in chewing gum, butyl rubber gloves, inner tubes and as stoppers for bottles and vials.

## From Conjugate Addition to Superglue

There are several "must discuss" polymers and one of them is superglue. Superglue can be introduced when presenting conjugate addition to α,β-unsaturated carbonyls (shown in Figure 13).

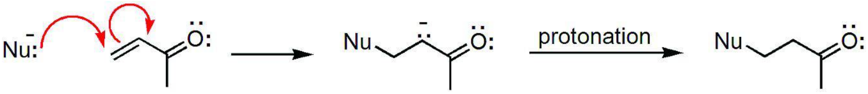

*Figure 13. Conjugate addition of nucleophiles onto α,β-unsaturated systems.*

The application of cyano acrylates as superglue or as medical glues is well established. These compounds are known to stick to anything and moisture is sufficient to start the polymerization reaction. The key to their increased reactivity is the presence of the second electron withdrawing group, the cyano substituent, which enhances the electrophilic nature of the β-carbon (shown in Figure 14) as well as stabilizing the enolate anion formed on conjugate addition.

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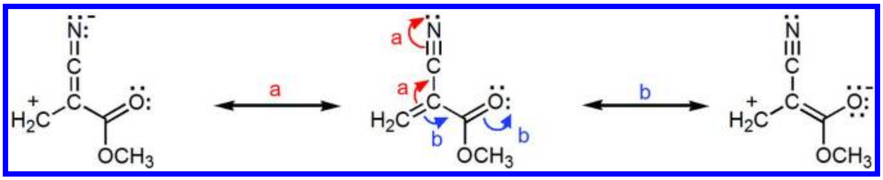

*Figure 14. Resonance picture of the electron delocalization resulting in increased electrophilicity of the β-carbon.*

The first two steps of the polymerization process are shown in Figure 15. Further iterations of the addition can be drawn out and followed by a termination step (for example protonation with water). The repeating unit can be identified and drawn.

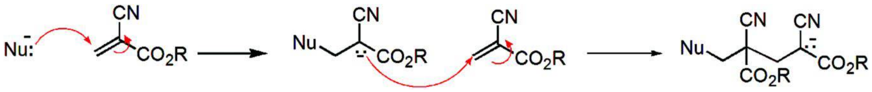

*Figure 15. Addition of hydroxide to a cyanoacrylate and the reaction of the product anion with a second molecule of cyanoacrylate.*

## Conclusions

The introduction of polymer chemistry throughout the organic chemistry course is an excellent way to stimulate interest in both polymer chemistry and organic chemistry. This has been overwhelmingly apparent to me over many years as I have observed students literally sit up and pay closer attention each time I use this approach. It is important to choose both interesting and common polymers. While most organic chemistry textbooks include a chapter on polymers it is, unfortunately, normally near the end of the textbook. As a result, the opportunity to interest students early in the course is lost. In my opinion and experience, it is far more effective to integrate examples throughout the course.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch004

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch005

## Chapter 5

# Integrating Macromolecules into Undergraduate Organic Chemistry Courses

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Integration of macromolecular principles with existing topics allows for ready incorporation into undergraduate organic chemistry courses. Students gain a more complete picture of modern chemistry that includes both small and large molecules, providing an introduction to natural and synthetic polymers they are likely to encounter in further study and their careers.

## Introduction

The POLYED National Information Center for Polymer Education was founded in 1989 to serve as a clearinghouse for educators interested in including polymer topics in their courses (*1*). This was the first center of its kind in the United States dedicated to materials science education (*2*). The Center is supported with funding from POLYED, the joint education committee of the American Chemical Society Divisions of Polymer Chemistry (POLY) and Polymeric Materials: Science and Engineering (PMSE). The initial focus of the Center was to provide resources to college and university faculty interested in incorporating polymer topics in their courses. With funding from the National Science Foundation, workshops were offered in the early 1990s to college and university faculty. With additional funding from NSF, the MaTR Institute (pronounced “matter” for **Ma**cromolecular **T**eacher **R**esource Institute) opened in 1995, which offered three-week, polymer-related summer workshops for K-12 teachers. These workshops led to the development of many hands-on activities that are available for courses at all levels, K-post-graduate (*3*). In the nearly twenty-five years since the POLYED Center first opened, the Center has received

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch005

requests for information from many college and university chemistry faculty, as well as K-12 faculty. Regardless of the level taught, the questions from faculty have been remarkably similar: Many faculty have not had formal coursework in polymers and thus, have limited background knowledge about them. Faculty typically are aware that the majority of the substances around them – besides air, water, and metals – are polymeric. They are aware that their clothes, desk, chair, computer, smart phone, shoes, windows, and paint on the walls, are natural and synthetic polymers. They also know that their hair, fingernails, and skin are all biopolymers. However, they want additional background information so that they can comfortably *teach their students* about polymers. Faculty who contact the POLYED Center already know about polymers, but they want to know more. They feel strongly that polymers/macromolecules are important and that they belong in the curriculum, but they sometimes have concerns about teaching about polymers due to their own limited backgrounds. Some have worked with polymers and others have had some coursework in polymers, but many have not. Nearly all note that there are generally few resources for learning about polymers and it is difficult to connect with others who are knowledgeable about them. This is especially true today as the field of polymer chemistry has grown and has become widely dispersed into biological, material science, engineering, and other areas. Faculty are very curious about how other faculty integrate polymer concepts and they especially want to know about lab experiments. Because they may be the only person at their campus who is responsible for polymer coursework, faculty seem especially pleased/validated when they learn that something they do is also being done at other institutions.

One question that is asked over and over, is how to incorporate polymer topics into a curriculum that is already too full. The following addresses this by suggesting some examples that integrate polymer topics with existing topics. The focus here is undergraduate organic chemistry courses, but many of these examples can be integrated across the curriculum.

## Day One of Organic Chemistry

Students are generally aware that polymers are all around them. Many have had some exposure to macromolecular concepts in high school and they may be surprised that they probably were not discussed in detail in their introductory college/university chemistry courses. The *Polymer Ambassadors* are an active group of master K-12 teachers who have offered workshops for many years for other K-12 teachers (*4*). Many of these presentations have been to filled rooms at National Science Teachers Association (NSTA) meetings or other regional meetings throughout the country.

Students certainly have heard about polyethylene, nylon, DNA, and proteins, and they want to have a better understanding of these materials. In my experience, students are receptive and expect to hear about polymers/macromolecules in chemistry courses. Including polymers does not have to take time away from other topics and it is easy to integrate them with concepts that are already discussed.

Macromolecules can be incorporated at the very beginning of the semester when fundamental aspects of the course are being introduced. In an organic chemistry course, it is common on the first day of the semester to include some examples to illustrate the prevalence of organic molecules. This is usually done to reinforce why two semesters are typically required to adequately introduce the fundamentals of organic chemistry. Students quickly understand when they learn that greater than 90% of all known compounds contain carbon. This is a perfect opportunity to introduce macromolecules into organic chemistry. They can be introduced simply by giving examples of small organic compounds, such as methane ($CH_4$), ethane($C_2H_6$), and carbon dioxide ($CO_2$), as well as giant macromolecules, such as polyethylene (e.g., $C_{20000}H_{40002}$ but pointing out that the molecular formula is not this exact with synthetic polymers, but is an average of many different-sized PE macromolecules), polystyrene, and polyethylene terephthalate (i.e., PET or PETE). It also can be emphasized that even though polymers/macromolecules are large to a chemist, they still are exceptionally small. A simple calculation using density, average molecular weight of a polymer, and Avogadro's number can affirm this by having students determine the cm3/molecule. All of this takes only a few minutes at the beginning of the semester or in an assigned problem set, yet students already will see that macromolecules are an important part of organic chemistry and that all molecules are very, very small (it probably is best to leave crosslinked materials for another time since some of them can actually be quite large). If another two or three minutes can be permitted, this also may be an opportune time to introduce natural and synthetic macromolecules (see Figure 1). Students find it interesting that Nylon was discovered in an effort to synthesize industrially important natural materials, such as silk and wool.

| Biopolymers | Synthetic Polymers |
|---|---|
| • DNA, RNA | • Polyethylene |
| • Starches | • Polystyrene |
| • Cellulose | • Polyethylene terephthalate |
| cotton, paper | • Polycarbonate |
| • Proteins | • Nylon |
| silk, wool | • Polylactic acid |
| • Natural rubber | • SBR rubber |

*Figure 1. Natural (biopolymers) and Synthetic Polymers*

Regarding the inclusion of polymer topics, students may ask "Is this on the test?" If material is deemed important enough to include in lecture, then the answer probably should be "YES!" But, the degree of emphasis on the exam should be commensurate with the time spent on the topic in class. This is especially important since the material covered may not be reinforced in the text. A single question on the first exam often is sufficient to have students pay attention to this "extra" material. Making it a bonus question is another option and one that students may especially like.

## Hydrocarbons

While there are viable alternatives, the homologous series of hydrocarbons is still often used to illustrate structure-property relationships early in the first semester of organic chemistry. As shown in Figure 2, the boiling points of low molecular weight linear hydrocarbons increases regularly with additional methylene units. Correlating boiling points with molecular structure provides an opportunity to discuss Van der Waal's interactions and their effect on both submicroscopic (i.e., molecular) and macroscopic properties. If students have been introduced to macromolecules early in the semester (as described in "Day One" above), it is straightforward to include polyethylene (PE), a polymer comprised of a large number of concatenated methylene units. While polyethylene can have different molecular weights (and the MW's are averages of chains of varying lengths), a number like n = 20000 is representative. It is informative to present only some of the data in Figure 2 and then ask the class to predict boiling points that have been omitted or hidden. Their predictions are likely to be quite good at relatively low molecular weights, but values they are likely to propose for high MW hydrocarbons would be inconsistent with known combustion properties, i.e., polymeric hydrocarbons will burn well before the expected boiling points would be reached. Real-life experiences can be drawn on to reinforce this point, i.e., asking if anyone has ever seen boiling polyethylene! It also is interesting to ask students if they can smell polymers. They may have a different perspective on this after estimating the vapor pressure of a high molecular weight polymer at room temperature (of course it is negligible). The odors associated with most polymers certainly must be due to residual monomers or additives and not high molecular weight polymer.

$C_nH_{2n+2}$

| n | bp (°C) |
|---|---|
| 1 | -164 |
| 2 | -89 |
| 3 | -42 |
| 4 | -1 |
| 5 | 36 |
| 6 | 69 |
| 10 | 174 |
| 20,000 | ? |

*Figure 2. Boiling points for homologous series of linear hydrocarbons.*

Depending on available time, this now presents several options for further introducing macromolecular topics. If polymers do not exhibit boiling points, what kind of thermal transitions do they have? A major difference between HDPE and LDPE is that the former can crystallize to a greater extent (typically >80% to about 40%, respectively). The close packing of the chains in the crystalline domains greatly increases the strength of HDPE compared to LDPE. This further reinforces the importance of Van der Waal's forces in both the submicroscopic and macroscopic properties of hydrocarbons. The temperature at which the crystalline domains undergo translational motion is the melt transition ($T_m$). This transition is analogous to the melting point of low molecular weight compounds. But, unlike most small molecules, even highly crystalline polymers exhibit some amorphous character due to entropic frustration during nucleation (*5*). While it can be exceptionally low in some types of HDPE (5% or less), most polymers exhibit a high degree of amorphous character. It is interesting that amorphous character is important in everyday materials, yet very little or no time is spent discussing amorphous materials in most chemistry curricula. If students use molecular models to construct a chain of about ten methylene units and then rotate these units freely about each C – C bond, it is quite easy for students to see why high molecular weight hydrocarbons tend to be amorphous. The rotated groups will quickly "ball-up" if the rotations are unrestricted. If the motion is slowed, the chain can unravel and take on an extended "all-trans" conformation that is characteristic of crystalline HDPE. Students may enjoy the challenge "if VSEPR predicts that $CH_4$ will be tetrahedral, what is the likely shape of polyethylene?" This is certainly not an easy question to answer, until students realize that a ball of yarn provides a pretty good approximation. Students typically have had some introduction to crystalline domains and it is straightforward to then present amorphous character, especially if the above examples are used when discussing conformational isomers. If $T_m$ has already been introduced as the dominant thermal transition for crystalline domains, a second-order transition, known as the glass transition temperature ($T_g$), can be presented as the important thermal transition for amorphous materials (Note: both high and low MW compounds can exhibit $T_g$. For example, some sugar candies exhibit $T_g$.) The glass transition can be demonstrated very easily by placing a piece of clear laboratory tubing in liquid nitrogen and then breaking it – behind a clear safety shield – with a hammer. As the resulting shards warm, they will pass through $T_g$ and will change from a hard solid to a flexible material. Most clear laboratory tubing is poly(vinyl chloride) that contains a plasticizer (i.e., low molecular weight additive). The $T_g$ of poly(vinyl chloride) is well above room temperature (~ 80°C), but the addition of plasticizer (typically bis(2-ethylhexylphthalate)) lowers the $T_g$ causing the tubing to be flexible at room temperature. The presence of the plasticizer can be demonstrated by placing a small piece of tubing in an organic solvent such as acetone or petroleum ether. After the plasticizer has been removed (this takes several hours and is best done using a Soxhlet extractor), the resulting tubing will be hard and its $T_g$ will again be above room temperature.

Fully amorphous polymers exhibit only $T_g$, while semi-crystalline polymers have both $T_g$ and $T_m$. These thermal transitions are characteristic of the amorphous and crystalline regions, respectively. It is interesting that amorphous polymers that are stereoregular may crystallize *upon heating*. Students that are familiar with crystallization from organic lab typically expect materials in solution to be cooled to form crystals. But, neat amorphous polymers must be heated above $T_g$ in order to have the translational motion necessary for segments to orient and form crystallites. Energy is released at the crystallization temperature ($T_c$), which lies between $T_g$ and $T_m$.

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Another key macromolecular principle may be introduced using PE as the example. That is, macromolecules exhibit unique properties because of their *size*. For example, it is not possible to construct a helix or a layered graphite structure with only three or four atoms. It is only possible with macromolecular structures. One of the key features of amorphous polymers is that the chains *entangle*. Small molecules cannot do this and these entanglements become a dominant characteristic of polymeric materials. If the molecules are entangled, translational motion – even just of segments – requires the motion of another molecule. The evaluation of the physical properties of macromolecules with increasing molecular weight clearly shows the importance of chain entanglements. At the point where the molecular weight is sufficient for chain entanglements (sometimes called the critical chain length), most physical properties level off and additional changes in molecular weight have little effect on the properties of the material (see Figure 3).

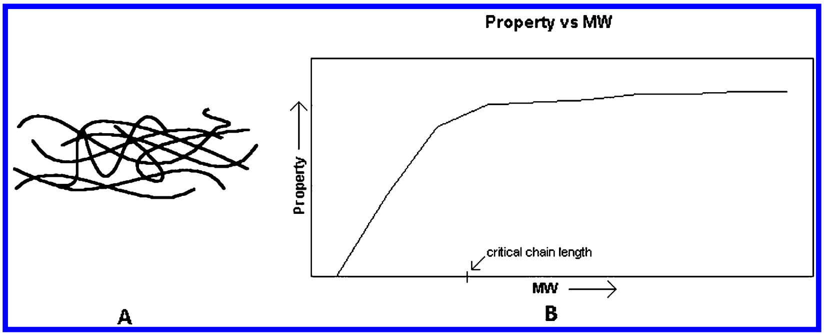

*Figure 3. A) Cartoon depiction of chain entanglements. B) Generalization of physical properties vs molecular weight.*

## Stereochemistry and Conformational Isomers

Polymers can be used as examples when stereochemistry is discussed. Polypropylene is especially well-suited for this, as its structure differs from polyethylene only by the inclusion of a methyl group in the repeat unit. However, with the methyl group, the macromolecule can now exhibit *tacticity*. It is easiest to see the tacticity if a segment of the chain is viewed in the *all-trans* conformation (Figure 4A shows a segment of isotactic polypropylene). If all of the methyl groups are on the same side, this is the *isotactic* form. If the methyl groups alternate sides, it is *syndiotactic*. A random arrangement is *atactic*.

If a ten carbon segment of an isotactic polypropylene chain is constructed using molecular models (students may need to combine kits), students can use it to understand the formation of helices. As mentioned earlier, helices are important macromolecular structures that are usually first encountered, in detail, in biochemistry courses. The structures of biologically important molecules typically are very complex and visualization of the helices can be very challenging. Isotactic polypropylene provides an accessible introduction to the study of these complex helices. Using the ten-segment model of isotactic polypropylene mentioned above, students can readily visualize the formation of

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a helix. After an introduction to conformational isomers and steric repulsion, students will predict that the adjacent methyl groups in isotactic PP will repel each other. If they sight down the main axis of their model and move the methyl groups to a gauche conformation to relieve the interactions, it is easy to see that the chain will begin to take on a helical structure. It has been established that isotactic polypropylene forms a 3/1 helix, i.e., three repeat units per turn of the helix, to relieve interaction of the methyl groups (*6*).

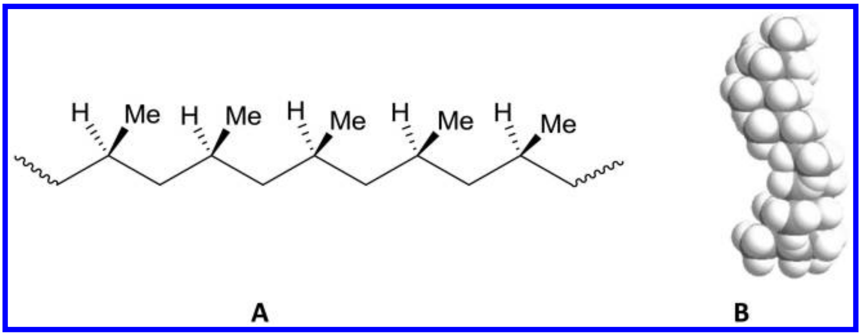

*Figure 4. A) Segment of isotactic polypropylene. B) 3-d perspective of same polymer.*

## Nomenclature

Naming organic compounds can be somewhat uninspiring and many courses no longer include detailed training in organic nomenclature. Part of the reason for this may be that tools are readily available for naming organic compounds. For example, structure drawing programs often include an option for obtaining the name of a compound from a chemical structure. For courses that do include a discussion of nomenclature, polymers may provide alternative examples. The naming of simple, single-strand, linear polymers can be summarized as follows: 1) identify the CRU (constitutional repeat unit), 2) orient the CRU from left to right using appropriate priorities, and 3) name the compound by starting with "poly" followed by usual IUPAC naming of the CRU (from left to right). Details for naming single-strand, linear polymers have been published (*7*).

## Reactions

Polymerization reactions provide a rich source of examples to illustrate how organic reactions may be used in a practical setting. They can be used to illustrate chain-growth processes, such as radical, anionic, cationic, and coordination-catalyzed olefinic polymerization. Polymers also provide examples of step-growth polymerization via nucleophilic acyl addition and substitution reactions. Most current organic textbooks include information on these reactions. Unfortunately, these reactions often are in one of the last chapters in the book. Integrating the reactions throughout the text is likely to be much more effective and accessible to students than combining all of the reactions into one chapter.

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## Summary

Providing students with an introduction to polymer topics early in the semester allows macromolecular topics to be integrated throughout the course and then presented whenever appropriate. This introduction could take as little as two to three minutes per week for the first several weeks of the semester. Employing this approach, students see polymers as a normal and integral part of organic chemistry, with some molecules being very small and others being extremely large (at least to a chemist!) This is consistent with our modern understanding of chemistry. Integration of macromolecular topics requires very little lecture time and it can be done with minimal change to the existing content of a course. Most importantly, it provides students with the information and skills necessary for their future work.

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch006

## Chapter 6

# Polymers Offer the Opportunity To Discover Foundational Principles of Organic Chemistry

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Polymers of all categories and the monomers necessary for their syntheses offer numerous opportunities for beginning students of organic chemistry to be exposed to and learn the details of foundational principles of organic chemistry. This view on polymer chemistry is the focus of three chapters in a new book, “Organic Chemistry Principles in Context: A Story Telling Historical Approach.” The chapter to follow is based on information from this book focused only on radicals and not on condensation polymers, which are also discussed in the book. The discussion on radicals yields information normally presented in undergraduate organic chemistry courses but in the context of the importance of polymers. In this manner polymer yield insight into the addition of radicals to double bonds, the reactivity of polymers in hydrogen abstraction, the beta-scission reactions of radicals and how resonance stabilization of radicals blocks the radical polymerization of propylene.

## Polyethylene

Polyethylene in its various forms is produced world-wide in the range of billions of pounds each year and finds it way into our lives in many ways. The beginning of the story of polyethylene is told in Herbert Morawetz’s wonderful book “Polymers the Origins and Growth of a Science.” Here is a quote from this book:

"Just as DuPont decided in 1928 to hire Carothers to "work on problems of his own selections," so at about the same time Imperial Chemical Industries (ICI) sent two of their research scientists to Amsterdam to gain experience in A. Michels' laboratory in the study of reactions under high pressure.*"*

DuPont's decision led to nylon, while ICI's decision led to polyethylene, which arose from a series of misunderstandings and errors demonstrating a famous statement by Louis Pasteur:

"In the fields of observation, chance favors only the mind that is prepared.*"*

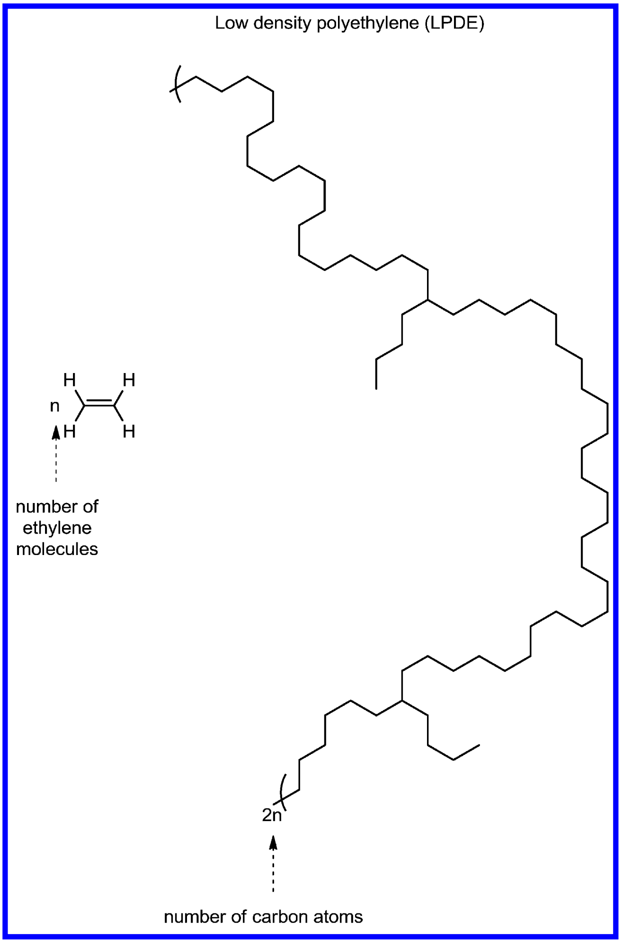
The ICI decision to look into high pressure arose from academic research that showed high pressure to cause unusual changes in chemical reactivity and phase and because engineering advances in the early years of the twentieth century in combination with new kinds of materials created during the first half of that century allowed remarkable advances in the ability to attain high pressure. The leader in this field was Percy W. Bridgman, who won the Nobel Prize in physics in 1946 for his high pressure work, which he began around 1905. Bridgman's most advanced high pressure apparatuses attained unbelievable pressures, in the range of 50,000 atmospheres! Imagine though that the pressure at the center of the earth is estimated to be in the range of four million atmospheres and the sun ten thousand times greater than that - plenty of room for advances in this field.

The scientists who returned from Amsterdam to ICI decided to try a high pressure experiment. Ethylene ($H_2C=CH_2$) was becoming increasingly available as the major product of thermal cracking, which later evolved to become steam cracking of certain petroleum fractions. Cracking technologies for converting petroleum fractions into small molecule alkenes, which was an important boost for the chemical industry's need for a reliable source of starting chemicals for a wide range of products, were developed before the development of the catalytic cracking process that involves carbocations and leads to the branched hydrocarbons necessary for production of high octane gasoline.

Starting in 1933, the ICI chemists tried mixing ethylene, the most abundant product of steam cracking, with various chemicals under high pressure, in the range of 1400 atmospheres, and high temperature. We now know that the reactions they were trying to accomplish are not possible, and, in fact, nothing came of their attempts except that when they opened the high pressure apparatus they found a small amount of a waxy solid, which analyzed as having the same composition as ethylene, two hydrogen atoms for each carbon atom, $CH_2$.

Realizing from the atomic composition that the waxy solid was a polymer of ethylene, the ICI chemists tried to improve its yield, by raising the pressure and probably the temperature as well. Their work was rewarded with an explosion, which closed down their research in this area for a couple of years. But eventually the experiments were begun again and through trial and error ICI was able, in 1939, to patent the production of polyethylene from ethylene producing a material for which they thought there might be a use but at the time had no idea of what that use might be.

But a use for polyethylene quickly arose as war came upon the world. Cables for radar had to be exceptionally well insulated against dielectric loss and the side with the best radar detection had a great advantage in "seeing" movement of the enemy from great distances. The polyethylene made by the ICI process, called now low density polyethylene (LDPE) (Figure1), turned out to be an excellent material for this insulation.



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## The Nature of Radicals

Let's look into the detail of the chemistry behind the production of LDPE, a chemistry that reveals much about the nature of radicals.

All introductory chemistry courses introduce the fact that $O_2$ is a ground state triplet, which means that the normal oxygen in the air we breathe is a diradical. The common reactivity patterns of $O_2$ in abstracting hydrogen atoms from hydrocarbons to form peroxides and carbon based radicals follows from this triplet state.

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Two important reactive characteristics of radicals are the abstraction of carbon bound hydrogen atoms, reactions **1**, **4** and **5** in Figure 2. In addition, there is the combination of two radicals to reform a bond, reaction **2** and the reverse of reaction **3**.

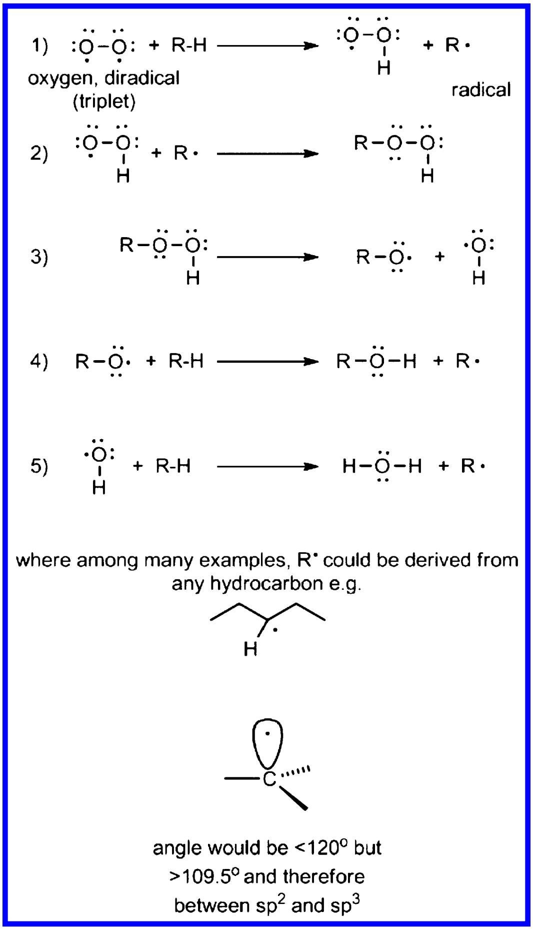

*Figure 2. Reproduced with permission from: Green, M.; Organic Chemistry Principles in Context: A Story Telling Historical Approach. Copyright 2012, ScienceFromAway Publishing.*

Reaction **3**, in the forward direction, which is the favored direction, is an exception to the general rule that at moderate temperatures covalent bonds do not break to form radicals. Bond breaking leading to two radicals is called homolytic cleavage in contrast to bond breaking that leads to a separation of charge, which is heterolytic cleavage. When chemical bonds are quite weak, even temperatures near to room temperature may be adequate to supply enough energy

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to homolytically break the bond. Peroxides, which are characterized by a single bond between two oxygen atoms, R-O-O-R, are such bonds and reaction **3** is an example of homolytic cleavage of this functional group.

Carbon based radicals (R·) are less electron deficient than carbocations and as well differ from carbocations, which do not obey the octet rule. The difference is the empty p orbital in the carbocation, therefore causing the carbocation to be $sp^2$ hybridized so that the three atoms bonded to the positively charged carbon atom exist in a plane.

In a radical the necessary placement of a single electron in what would be an empty orbital in a carbocation, causes some mixing of the 2s orbital into that p orbital leading to the hybridization picture presented in the above figure. The hybridization is neither $sp^2$ nor $sp^3$ but somewhere in between. In the $sp^3$ hybridization the four hybrid orbitals contain 25% s and 75% p, while in the $sp^2$ hybridization each of the three hybrid orbitals contain 1/3 s and 2/3 p and there is one empty p orbital. The three atoms bonded to the central carbon atom in the radical no longer exist in a plane associated with $sp^2$ hybridization nor do the three atoms bonded to the central carbon atom take a tetrahedral geometry. The three atoms bonded to the central carbon atom in the radical are bent by several degrees from a plane as shown in Figure 2.

In organic chemistry there is considerable focus on the reactive nature of carbanions, which together with carbocations and carbon-based radicals make up the most important, but not all the reactive intermediates in organic chemistry.

Let's take a moment to step back to understand the hybridization and geometric pictures of these three reactive intermediates. There is an interesting change in angular geometry in moving from the empty p orbital in a carbocation (120° for the three bonds – a planar arrangement), to having an orbital that can hold an electron in the radical (about 115° for the three bonds – deviation from planarity) to having an orbital that can hold two electrons in a carbanion. The bond angle between the three groups bonded to the negatively charged carbon atom is now even smaller, in the range of 105°.

Not withstanding the differences between carbocations and radicals, there are similarities. Just as carbocations are reactive with a source of electrons, a characteristic used to advantage in the industrial synthesis of the high octane gasoline, radicals also react rapidly with double bonds. The consequence of this reactivity with ethylene allows understanding of the formation of polyethylene, as shown in Figure 3, which shows the consequences of the addition of a radical to an ethylene molecule in the presence of a large number of ethylene molecules as in the high pressure apparatus used by ICI. The reactions shown follow the sequence: initiation, propagation and termination, which is the definition of a chain process, a mechanistic path encountered widely in organic chemistry.

"Passing the buck" is a characteristic of reactive intermediates responsible for many reactions in organic chemistry and we see this at work again here in the polymerization of ethylene. The initiating radical, R·, in adding to the double bond of ethylene, passes the radical to one of the $CH_2$ groups of this ethylene molecule. The $CH_2$ group, which now bears the burden as the site of the radical, reaction **1**, passes the radical site onto the $CH_2$ group of the next ethylene molecule (reaction **2**) and so on in reaction **3**.

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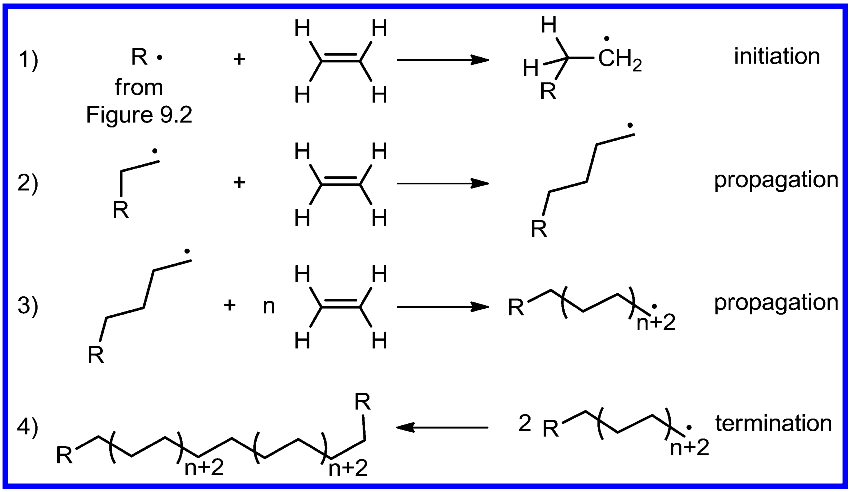

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As long as these propagation reactions go on (reactions **2** and **3**) the polymer chain will grow longer and longer, that is, the molecular weight of the polymer will grow larger and larger, and therefore the degree of polymerization will become a larger number. One limit to the chain growth would be a reduction in the number of molecules of ethylene available for reaction. For this reason the molecular weight is related to the pressure, as is well known to the industry.

However, all chain process are limited by termination reactions, that is, those reactions which eliminate radicals. Reaction **4** is a prominent example of a termination reaction (certainly not the only one) in the radical polymerization of ethylene. In reaction **4** two growing chains combine so that the radical sites on the $CH_2$ groups at the chains' ends combine to form a covalent bond. There is no radical left to continue the propagation reactions.

The probability of two chains, with radicals at their ends, finding each other (termination) is low as long as the population of ethylene molecules is high. The ethylene molecules capture the radicals causing extension of the chains – the process of polymerization. Toward the end of the polymerization process, when few ethylene molecules are left, the termination reaction becomes competitive.

The chain process presented in the above figure can not be the entire story because it does not account for the four carbon branches on the polyethylene chain shown in the structure of polyethylene (Figure 1). How are those structural features explained by the mechanism? The answer can be found in the fact that although abstraction of a carbon bound hydrogen atom occurs if the radical site is on oxygen as in reactions **1**, **4** and **5** (Figure 2) abstraction also occurs if the radical site is on carbon as: $R. + R'H \rightarrow RH + R'.$

Let's discover how a variation of the abstraction of a hydrogen atom by a carbon based radical from another carbon atom is responsible for the four carbon atom branches on the polyethylene chain (Figure 4).

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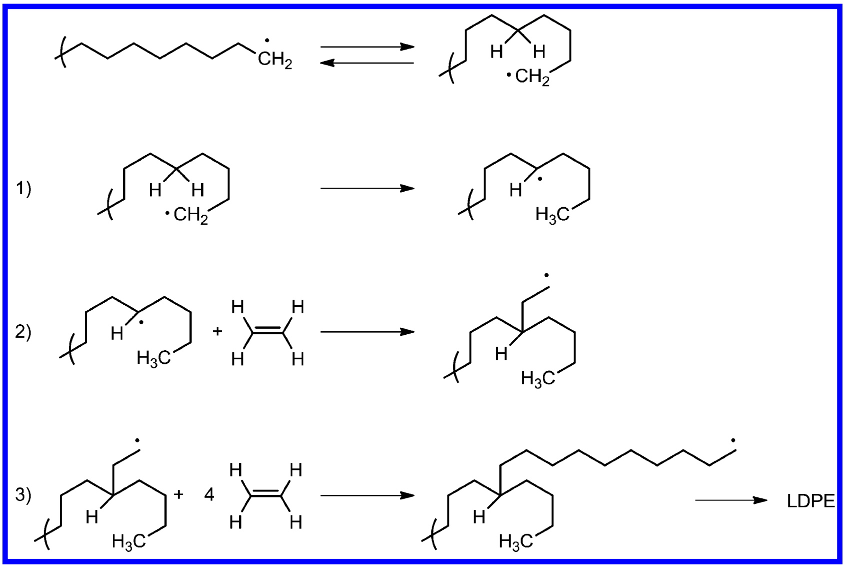

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Imagine the indescribably large number of conformations accessible to a long chain of $CH_2$ groups in polyethylene while the chain is growing or in its final state. Polymer science deals with this complexity using the power of statistical physics and some describe the array of conformations among the many chains in a sample of polyethylene as analogous to a plate of very long just cooked spaghetti. These rapid conformational motions along the growing polyethylene chain can occasionally bring the terminal $–CH_2$ radical site on the growing end of the chain in the vicinity of a carbon-bound hydrogen atom within the chain such as shown in the conformational motion in Figure 4.

Organic molecules “love” six-membered rings, which is a statement about structure. But six-membered rings are also favored in many reactions of organic chemistry. Although we can’t go into the details here, this fact brings up a reaction named after Derek Barton. In the Barton reaction, a radical is generated by converting an -OH group to a functional group with the structure –ONO. Loss of NO·, results in formation of –O·, which abstracts a hydrogen atom from a carbon atom in the same molecule so that the abstracted hydrogen atom, the oxygen and the intervening carbon atoms make up a six-membered ring. In other words, the activated complex of the reaction is constructed of four carbon atoms with the oxygen atom and the hydrogen atom. All this takes place in a molecule with a steroid structure and was the method by which an early version of birth control pills were first synthesized.

There are many other examples in organic chemistry of chemical reactions taking place via six membered activated complexes, which transfers (passes the buck) the radical site from which the chain is growing, a $CH_2$ group, to a site five carbons within the chain. Ethylene molecules, following the same mechanistic path leading to the growth of the chain as discussed above, then grow from this new radical site, leaving the four carbon branch seen in the structure of LDPE (Figure 1). The site transfer is an intramolecular rearrangement, and happens in a random fashion so that the numbers and placements of the four carbon branches are not predictable, except on a statistical basis. In fact, the same intramolecular process then allows formation of branches on the branches yielding a quite complex structure for LDPE.

In the above discussion we've seen two kinds of reactions of radicals, addition to double bonds and hydrogen abstraction from $sp^3$ hybridized carbon, in addition to studying the geometric and hybridization differences between radicals and carbocations and carbanions.

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## Where Does Ethylene Come From? The Answer to This Question Reveals More about the Chemistry of Radicals – Steam Cracking

The chemical industry needs starting materials with precisely predictable chemical reactivity. This means functional groups are necessary, and the simplest functional groups contain only carbon and hydrogen, which limits the family to triple bonds and double bonds. Early on, the favored starting material was acetylene. But acetylene, $C_2H_2$, H-C≡C-H, is too unstable and may unexpectedly explode with devastating consequences. Ethylene has a valuable and predictable reactive nature and is much safer, so that when it was discovered that petroleum fractions could be heated to high temperatures to yield large quantities of small molecule alkenes, predominately ethylene, the chemical industry increasingly switched to the double bond and substantially abandoned the triple bond.

Some of the steps that initiate the chemical processes in steam cracking of petroleum fractions are identical to those initiating polymerization of ethylene, that is, involve oxygen. However, there are other sources of the initiating radicals responsible for steam cracking arising from the exceptionally high temperature, in the range of 800° C, substantially higher than used for polymerization of ethylene. Figure 5 below outlines some of the important steps in steam cracking of a typical molecule found in the naphtha fraction of petroleum, n-decane.

As seen for formation of polyethylene, we encounter again in steam cracking, a chain process. The detailed initiation, propagation and termination steps may differ but the overall mechanistic paths are parallel to each other.

The bond breaking propagation steps, reactions **2**, **3** and **4**, show another example of a class of reaction found in carbon-bound radicals, β-cleavage. The name β-cleavage arises from the bond broken in this reaction, as shown in Figure 6, which also points out the overlapping electrons and orbitals leading to the formation of the π- bond resulting from this cleavage.

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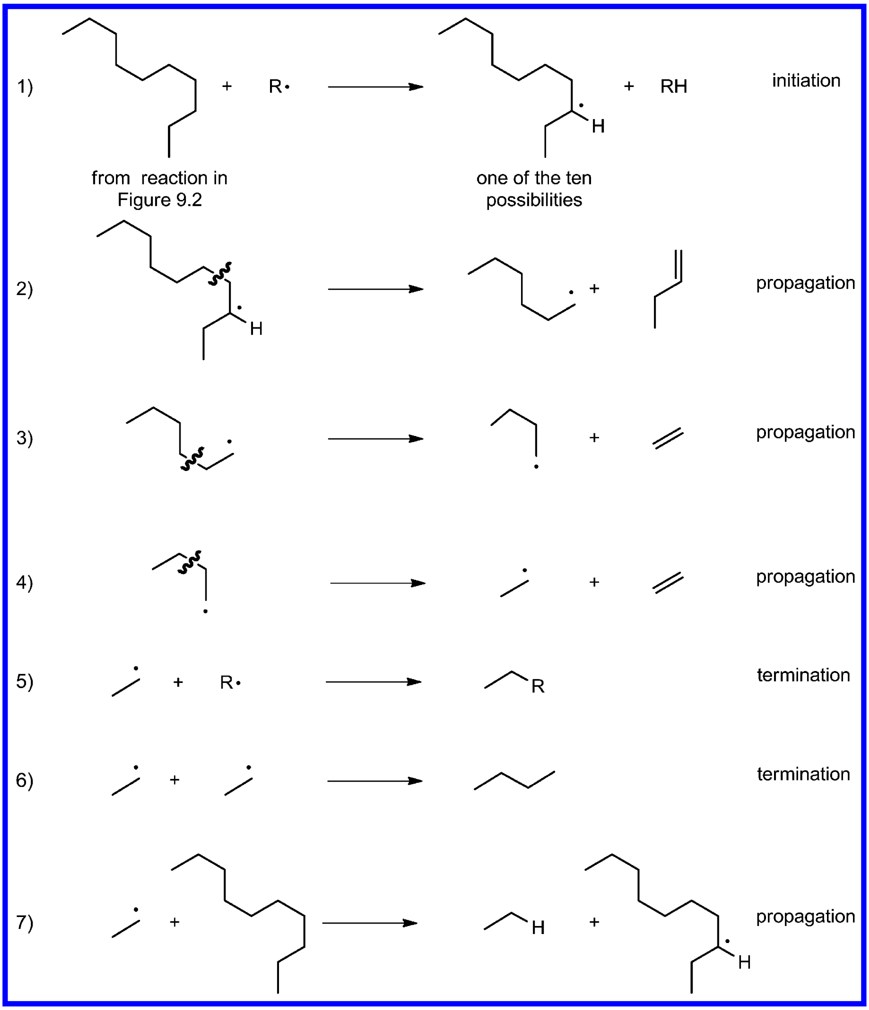

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The β-cleavage steps shown lead to two of the three most abundant alkenes formed in the steam cracking process (Figure 5), 1-butene (reaction **2**) and ethylene (reactions **3** and **4**). The orbital changes arising in β-cleavage (Figure 6) are chosen to demonstrate how the other most abundant alkene, propylene, would be formed as a consequence of the chance formation of the initiating radical at a different decane carbon atom.

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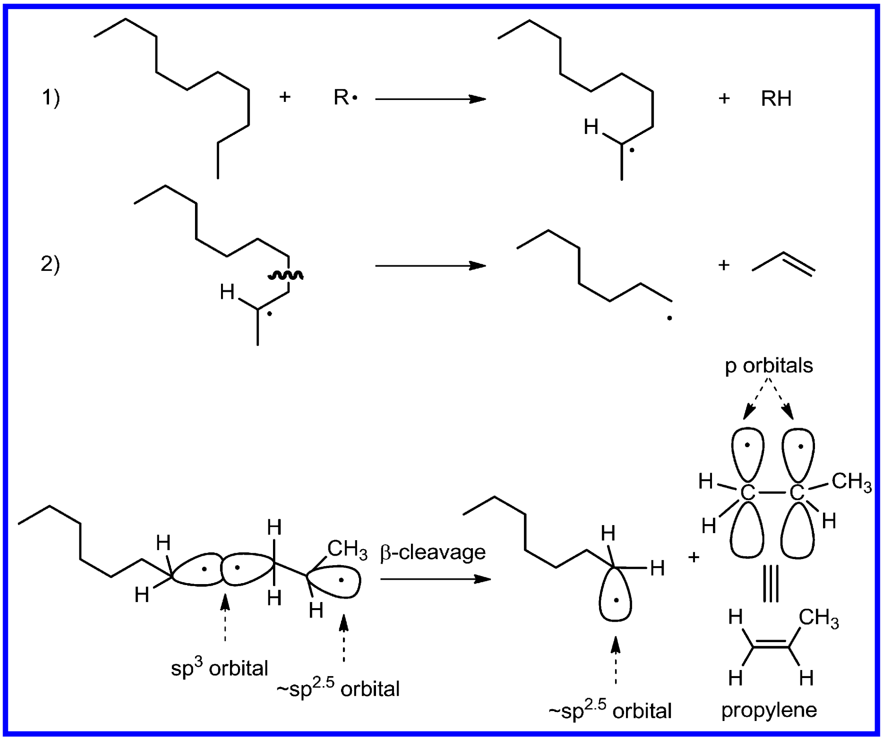

*Figure 6. Reproduced with permission from: Green, M.; Organic Chemistry Principles in Context: A Story Telling Historical Approach. Copyright 2012, ScienceFromAway Publishing.*

Many other initiation, propagation and termination steps can be imagined in addition to those shown and many other of these steps do, in fact, occur during the extremely short time, in the range of small fractions of a second, that the molecules in the petroleum fraction are exposed to the super heated steam. Steam cracking is big business.

The reactions shown occur for a range of linear hydrocarbons in the naphtha fractions of petroleum and produce huge amounts of alkenes. For one example, within the last ten years a steam cracking unit constructed in the United States by the European companies BASF and Fina produces per year 1.7 billion kilograms of ethylene, propylene and the isomeric butenes, 1-butene and cis and trans 2- butene. Of this 1.7 billion kilograms, about 0.9 billion kilograms of ethylene are produced. Much of this ethylene is used to synthesize the various forms of polyethylene.

## The Properties of Ethylene Polymerization and Steam Cracking Offer an Opportunity To Emphasize Foundational Principles of Thermodynamics

Steam cracking requires exceptionally high temperatures while polymerization of ethylene must be conducted at far lower temperatures and, in fact, cooling equipment has to be involved to keep the temperature from getting out of control leading to what engineers call a “runaway” process. An out of control polymerization of ethylene has the potential to explode as the temperature may reach values in which ethylene can explosively decompose.

The different temperature characteristics necessary for steam cracking and ethylene polymerization offer a lesson in fundamental aspects of thermodynamics.

There is a large difference in the strength of σ (sigma) versus π (pi) bonds. The difference arises from the linear overlap of the two $sp^3$ orbitals in a sigma bond versus the weaker overlap of the two p orbitals in the π bond. Conversion, therefore, of σ to π bond, as is the situation in steam cracking is an endothermic reaction. Energy must be added to the system to compensate for the formation of weaker bonds from stronger bonds, which translates to higher temperature favoring the cracking process.

Looking at steam cracking from another point of view, few molecules are converted to large numbers of small molecules, the large linear hydrocarbons in the naphtha fractions of petroleum are converted to alkene molecules. This increase in disorder translates to an increase in entropy in going from starting materials to products. Steam cracking is characterized by a positive, that is a $+\Delta S$ change in entropy. Because the entropy term contributing to the free energy change is $-T\Delta S$, an increase in temperature associated with a reaction with a $+\Delta S$ will move $\Delta G$ to a larger negative number, therefore increasing the equilibrium constant, K, ($-\Delta G = -RT\ln K$). The product alkenes in steam cracking will be favored, therefore, by increased temperature considering both the entropy and the enthalpy change. Here we find in this simple thermodynamic analysis of steam cracking, one of the important contributing reasons for conducting steam cracking near 800° C.

In the polymerization of ethylene a π bond is converted to a σ bond – a weaker bond is converted to a stronger bond, precisely the opposite of the situation in steam cracking. The enthalpic change must therefore be exothermic since energy will be released. Removing energy, that is, lowering the temperature will favor the process.

The polymerization also differs in terms of entropy from steam cracking. Instead of many small molecules produced from a large molecule, rather, very many small molecules, thousands in fact, are combined to form a very large molecule, a macromolecule – order from disorder, and therefore a negative change in entropy, $-\Delta S$. The entropy term therefore pushes the free energy change to more positive values, a less favorable reaction, a factor that is diminished as the temperature decreases.

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Considering both the enthalpic and entropic changes in the polymerization of ethylene, an increase in temperature will therefore act to push ΔG toward more positive values and therefore disfavor the polymerization. In fact, in the synthesis of polymers, there is a temperature called the "ceiling temperature," above which no net polymerization will take place.

Therefore, for thermodynamic reasons and also to avoid the danger of an out of control reaction, heat must be continuously removed in the industrial reactors producing polyethylene – the temperature must be held below about 200° C.

The discussion above finds parallel in the hydrogenation of benzene and, as is the nature of thermodynamic arguments, can be applied to all chemical reactions.

## Foundational Ideas about Conjugative Stabilization Can Also Be Found in the Study of the Attempted Radical Polymerization of Propylene

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I can't find a record of who might have tried to polymerize propylene ($H_2C=CH(CH_3)$) using the method ICI had developed for ethylene. Perhaps it was the ICI chemists. It would make sense to try it. I do know that chemists at Monsanto Corporation in Texas in 1963 tried it and failed to obtain a polymer. Instead they observed the formation of a gooey liquid indicating a molecular weight far below that of a polymer. Long before that, in 1953, Italian chemists in the group of Giulio Natta using a catalyst developed in Germany by Karl Ziegler had successfully polymerized propylene to polypropylene. Let's hold that Nobel-Prize-winning story and first discover what the problem is with radical polymerization of propylene, the basis of the attempt made by the Monsanto group.

No attempted polymerization of propylene using radicals has ever been successful, in contrast to the success with ethylene. Oligomers, which are small polymers, do form, the beginning of polymerization, but the process is always aborted after several propylene molecules have added.

An analogous initiation step to the step occurring in the radical polymerization of ethylene begins the path toward what would be polymerization in propylene (step **1** in Figure 7). And the propagation steps, **2** and **3**, continue the usual chain process. However, step **4**, terminates the growing chain before many propylene molecules have added. Why?

The problem is that the C-H bonds in the $CH_3$ group of propylene are weak bonds (high energy bonds) as a consequence of the conjugative stabilization of a radical formed at that position when the C-H bond is homolytically broken. The weakness of this carbon-hydrogen bond offers an opportunity to the carbon radical at the growing end of an oligopropylene chain to abstract this hydrogen atom in competition with adding to the π bond of another propylene molecule as shown in step **4**.

The ease of abstraction of a hydrogen atom from the methyl group of propylene arises from the conjugative stabilization of the product allyl radical as shown in Figure 7.

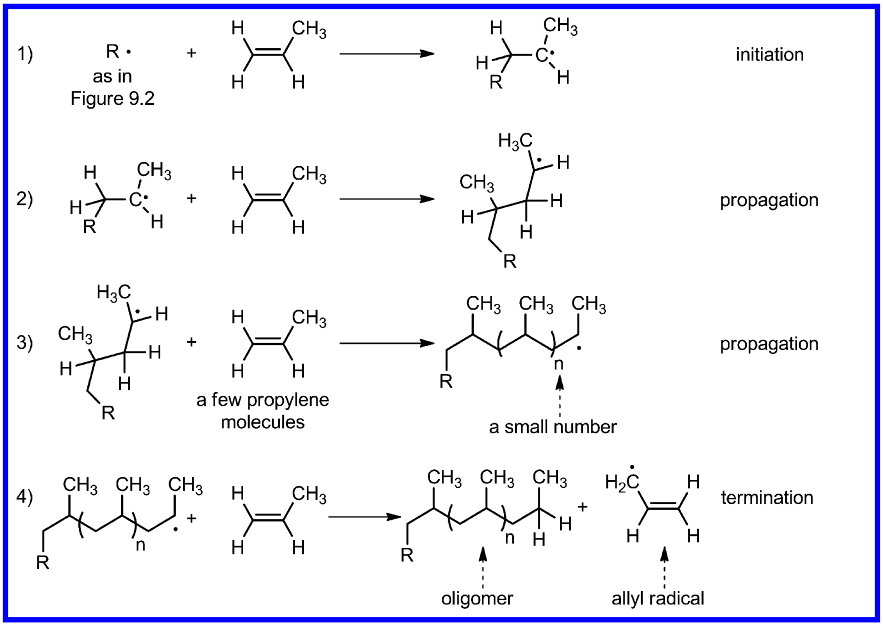

*Figure 7. Reproduced with permission from: Green, M.; Organic Chemistry Principles in Context: A Story Telling Historical Approach. Copyright 2012, ScienceFromAway Publishing.*

A lower energy of activation of reaction, **4** as discussed here, makes this reaction more competitive with other possible reactive choices in the system, **2** and **3**. So instead of the reaction path following **2** and **3** to propagate the macromolecule, polypropylene, the reaction path follows **4**, generating an aborted chain.

But there is an additional part to the story of the aborted polymerization of propylene. Why does the radical formed by loss of a hydrogen atom from the methyl group of a propylene molecule (designated allyl radical in Figure 8) not add to another propylene molecule π bond and start a new polymer chain growing? This possibility is evaluated in a graphical answer to this question using a reaction coordinate diagram.

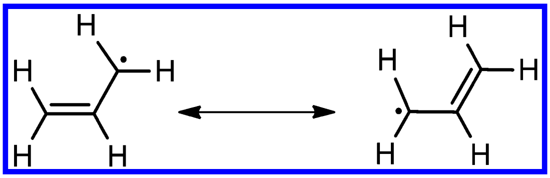

*Figure 8. Reproduced with permission from: Green, M.; Organic Chemistry Principles in Context: A Story Telling Historical Approach. Copyright 2012, ScienceFromAway Publishing.*

As shown in Figure 9, a conjugative-stabilized radical is lower energy than a comparable radical that is not delocalized, that is, R· versus the allyl radical in the reaction coordinate diagram. However, the addition of either radical to propylene will produce a new radical that is almost identical in energy. This means that the path for the allyl radical to add to a propylene π bond has a higher energy of activation than that for addition of R·. In fact, the energy of activation for addition of R· is accessible and so, as it has been put earlier in the discussion around Figure 3, a passing of the buck occurs. However, the energy of activation of addition of the allyl radical to the π bond of a propylene molecule is far larger, translating to a smaller rate constant. Therefore the buck is not passed, so-to-speak, and a new polymer chain is not begun.

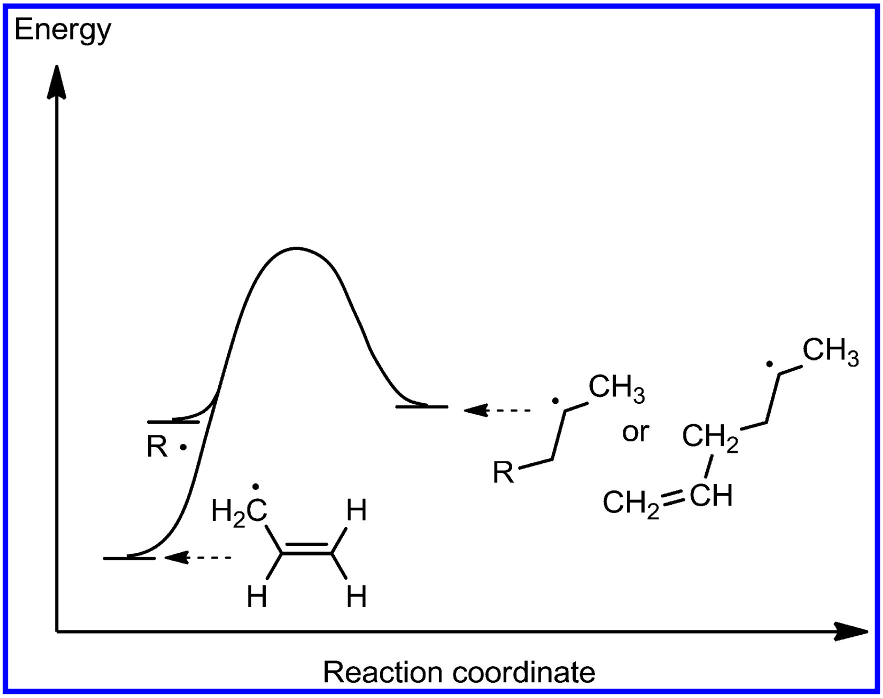

*Figure 9. Reproduced with permission from: Green, M.; Organic Chemistry Principles in Context: A Story Telling Historical Approach. Copyright 2012, ScienceFromAway Publishing.*

## Conclusions

The foundational organic chemistry course can be enhanced in many ways through the incorporation of some discussion of polymeric materials. Most importantly, it enhances student interest–it makes the course relevant to the everyday activities of students and permits the introduction of important concepts in a way that has practical significance for students.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch006

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch007

## Chapter 7

# Polymer Concepts Illustrated in the Context of Biopolymers

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In this chapter, we describe the treatment of polymers and polymer properties that has been integrated into a foundational biochemistry course at the University of Memphis. This course was first offered in the Spring of 2010 as part of a major curricular change we initiated in response to the added flexibility provided by the 2008 ACS Guidelines and Evaluation Procedures for Bachelor's Degree Programs. The course is thematically organized around the structure and function of biomolecules, many of which are natural polymers. This theme naturally lends itself to the discussion of many principles of polymer chemistry, from the solid-phase synthetic methods that are used for the laboratory production of nucleic acids and proteins to the relationship between polymer architecture and polymer properties.

## Introduction

A representative sample of books introducing polymer chemistry (*1–3*) treat a common set of topics including synthetic approaches to polymers, separation and characterization of polymers, polymer properties in solution and in bulk, and polymer structures. Given the prevalence of polymers in modern society, all of these topics should hold a place, and potentially more ubiquitous treatment, in any chemistry curriculum. The ACS Guidelines and Evaluation Procedures for Bachelor's Degree Programs, published in 2008, in fact states, "Students should be exposed to the principles of macromolecules across foundation areas, which could then serve as the basis for deeper exploration through in-depth course work or degree tracks." A quick internet search for "polymer chemistry syllabus" using the Google search engine (*4*) results in over 100,000 results, indicating that a specialized course is a very common way to include polymer chemistry topics in university and college curricula, although such courses are often upper division electives that may only be required of students in specific degree concentrations. Representative organic chemistry textbooks (*5–7*) also include treatment of polymers, often integrated as subsections within chapters on radical reactions, alkenes, or dienes (*6*, *7*) as well as in stand-alone chapters (*5*, *7*). Specific examples of integrating polymer chemistry into foundation-level organic chemistry coursework are provided throughout this volume, and certainly provide a more ubiquitous exposure to polymer concepts than would be achieved using an elective course that only a sampling of chemistry majors will complete. This chapter describes the integration of polymer chemistry topics into our Foundations of Bioorganic Chemistry course, which was created in 2009 to serve as the foundation-level biochemistry course in our curriculum. Continued treatment of macromolecular principles in the foundation-level biochemistry course is consistent with the recommendation in the ACS guidelines.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch007

## Curricular Context

The American Chemical Society (ACS) undertook a major revision of their guidelines for undergraduate chemistry programs, and published the new guidelines in the spring of 2008. One goal of these revised guidelines was to offer greater flexibility in chemistry degree programs. While the new guidelines were structured so that most accredited programs would not be required to utilize this flexibility, The Department of Chemistry at the University of Memphis elected to use the new guidelines as an opportunity to perform a thorough review and restructuring of our curriculum. One finding from the review of our pre-2009 curriculum was that none of our existing courses was suitable to be designated a foundation biochemistry course. Our Biochemistry I course was offered to advanced undergraduates and graduate students, and required completion of a sequence of four semesters of prior coursework (General Chemistry I & II, Organic Chemistry I & II). The content of this course was best classified as in-depth, rather than foundational. We therefore decided to create a new course to serve as our foundation-level treatment of biochemistry. We defined several overarching goals for our restructured curriculum, three of which are of particular relevance to the creation of this course. First, we elected to limit foundation-level courses to using either general chemistry or a single other foundation-level course as the primary prerequisites. Thus our foundation-level biochemistry course would follow the first organic chemistry course. As a result, we also developed a new organic chemistry course, designed to provide students with a strong foundation in organic chemistry suitable as a prerequisite for both the foundation-level biochemistry course and for in-depth courses building on the organic chemistry foundation. This course illustrates organic reactivity using the most common biochemical functional groups (aldehydes, ketones, carboxylic acids and derivatives, and amines) to a greater extent than is typical

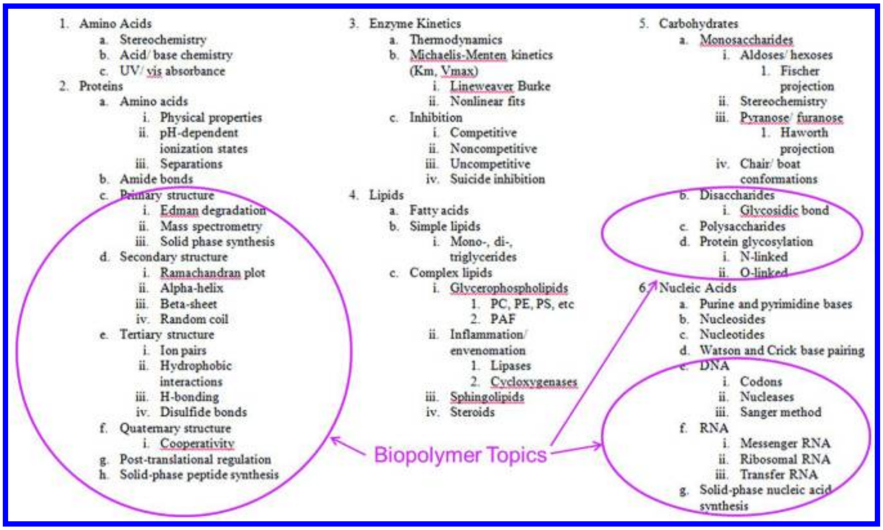
In Introduction of Macromolecular Science/Polymeric Materials into the Foundational Course in Organic Chemistry; Howell, B.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch007

in the first course of a two-semester sequence. Second, we elected to emphasize computational chemistry and principles of macromolecules throughout our foundation-level courses. Thus our foundation-level biochemistry course includes both hands-on computational chemistry, and introduces students to the structure, properties, and synthetic approaches to biological macromolecules. Finally, we aimed to produce a restructured curriculum that supported both the training of chemistry professionals and the preparation of students aiming toward the health science professions. We therefore discussed draft curricula with graduate health science program administrators in the region. The consensus was very positive that the proposed changes would provide excellent preparation for graduate health science programs, with the caveat that we must demonstrate our students still meet the entrance requirements defined by their accrediting bodies. In particular, we accommodated the pre-dental accreditation requirement that students admitted to their program complete a two-semester organic chemistry sequence with laboratories by emphasizing the organic perspective in our foundation-level biochemistry course as reflected in the final course title, “Foundations of Bioorganic Chemistry”.

## Polymer Concepts Illustrated Through Study of Biomolecules

The Foundations of Bioorganic Chemistry course focuses on the structure and function of the four major categories of biomolecules: proteins, lipids, carbohydrates, and nucleic acids. Figure 1 shows an outline of the course content, highlighting biopolymer topics. In the following sections, we give examples of specific polymer principles and how they have been integrated into the content of this course.



- 1. Amino Acids
  - a. Stereochemistry
  - b. Acid/ base chemistry
  - c. UV/ vis absorbance
- 2. Proteins
  - a. Amino acids
    - i. Physical properties
    - ii. pH-dependent ionization states
    - iii. Separations
  - b. Amide bonds
  - c. Primary structure
    - i. Edman degradation
    - ii. Mass spectrometry
    - iii. Solid phase synthesis
  - d. Secondary structure
    - i. Ramachandran plot
    - ii. Alpha-helix
    - iii. Beta-sheet
    - iv. Random coil
  - e. Tertiary structure
    - i. Ion pairs
    - ii. Hydrophobic interactions
    - iii. H-bonding
    - iv. Disulfide bonds
  - f. Quaternary structure
    - i. Cooperativity
  - g. Post-translational regulation
  - h. Solid-phase peptide synthesis
- 3. Enzyme Kinetics
  - a. Thermodynamics
  - b. Michaelis-Menten kinetics (Km, Vmax)
    - i. Lineweaver Burke
    - ii. Nonlinear fits
  - c. Inhibition
    - i. Competitive
    - ii. Noncompetitive
    - iii. Uncompetitive
    - iv. Suicide inhibition
- 4. Lipids
  - a. Fatty acids
  - b. Simple lipids
    - i. Mono-, di-, triglycerides
  - c. Complex lipids
    - i. Glycerophospholipids
      - 1. PC, PE, PS, etc
      - 2. PAF
    - ii. Inflammation/ envenomation
      - 1. Lipases
      - 2. Cycloxygenases
    - iii. Sphingolipids
    - iv. Steroids
- 5. Carbohydrates
  - a. Monosaccharides
    - i. Aldoses/ hexoses
      - 1. Fischer projection
    - ii. Stereochemistry
    - iii. Pyranose/ furanose
      - 1. Haworth projection
    - iv. Chair/ boat conformations
  - b. Disaccharides
    - i. Glycosidic bond
  - c. Polysaccharides
  - d. Protein glycosylation
    - i. N-linked
    - ii. O-linked
- 6. Nucleic Acids
  - a. Purine and pyrimidine bases
  - b. Nucleosides
  - c. Nucleotides
  - d. Watson and Crick base pairing
  - e. DNA
    - i. Codons
    - ii. Nucleases
    - iii. Sanger method
  - f. RNA
    - i. Messenger RNA
    - ii. Ribosomal RNA
    - iii. Transfer RNA
  - g. Solid-phase nucleic acid synthesis

*Figure 1. Foundations of Bioorganic Chemistry Course Outline.*

## Synthesis

Synthetic yield is an important consideration in any synthetic plan, but rises to prominence in the laboratory synthesis of biopolymers due to the essential relationship between sequence, monodispersity and function. To illustrate this point, students are tasked with calculating the overall yield in the synthesis of a 100-residue biopolymer if each individual coupling step has a yield that varies from 80% to 99%. Given the 99 individual coupling steps required to link 100 units, the calculated overall yields range from a stunningly low $2 \times 10^{-8}\%$ ($0.8^{99}*100$) to a still underwhelming 40% ($0.99^{99}*100$) overall yield. These yields are in stark contrast to expected overall yields of 64% to 98% for the synthesis of trimers using the same coupling step yields. These yield calculations clearly demonstrate that every operation included repetitively in the synthetic plan, including protection/deprotection steps, coupling steps, and purification steps, must be performed with nearly quantitative yield and recovery. Solid phase synthesis allows rapid and quantitative removal of reagents between synthetic steps by simple filtration, and has become the norm in the laboratory synthesis of both nucleotides and peptides. Additional polymer concepts that are integrated into the Foundations of Bioorganic Chemistry course in the context of solid-phase synthesis include classification by polymerization process (condensation polymers) and molecular weight distributions (monodispersity and its functional relevance in biopolymers).

## Structure

Biopolymer structure can be described with varying detail ranging from simple linear sequence of monomer units (primary structure) to the complex three-dimensional association of multiple polymer chains into a complex assembly (quaternary structure). The investigation of structure at these varying levels of detail provides a context for common polymer chemistry topics. Two of these topics are thermal transitions (melting temperature or glass transition temperature) and the relationship between crosslinking and mechanical strength. Crosslinking in proteins occurs through the oxidation of pairs of thiol groups in cysteine to form disulfide bridges. These can occur either intrastrand to stabilize the tertiary structure of a single protein chain or interstrand to stabilize the quaternary structure of an assembly of protein chains. Intrastrand disulfide bonds generally lead to increases in the melting temperature. Interstrand disulfide bonds lead to higher mechanical strength of materials made from highly cross-linked proteins such as keratin (horn, hair, tortoise shells wool) and glutenin (provides elastic strength in breads and other wheat products). A recent crystal structure of a heteromeric assembly of two types of keratin shows an interstrand cross-link (Figure 2) and illustrates cross-linking within keratin fibers.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch007

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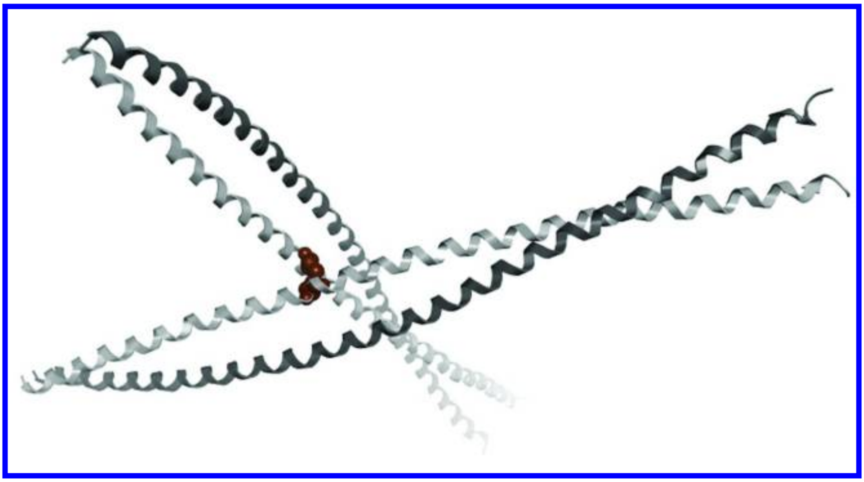

*Figure 2. Crystallographic structure of the keratin 5 (dark grey ribbons) complex with keratin 14 (light grey ribbons) showing an interstrand disulfide cross-link as spacefilling atoms (Protein Data Bank (8) entry 3TNU (9)).*

Although cross-linking has dramatic impact on macroscopic properties such as mechanical strength, polymer architectures play an equally important role. Polysaccharides exemplify the differences in macroscopic properties that derive from simply linking monomers together differently. Glycogen and cellulose are common examples used since both are condensation polymers formed from glucose monomers (Figure 3). Glycogen is a branched polymer of α-glucopyranose units connected by their anomeric positions to either the 4 or 6 positions of other glucose monomers. This architecture is analogous to synthetic star polymers. This highly branched structure is beneficial for energy storage. In contrast, cellulose is a linear polymer of β-glucopyranose that is utilized as a major structural component in plants and serves as the major chemical species by mass in cotton fiber.

## Analytical Characterization

Analytical methods serve as important tools to characterize biopolymer structure, purity, concentration, and function. These topics are incorporated into the class from both historical and modern perspectives. X-ray crystallography, in particular, affords an opportunity to highlight the pioneering work that defined the double-helical structure of DNA in 1953 (*10–12*) and the structure of myoglobin in 1958 (*13*). These are early examples of studies defining biomolecular tertiary structures. X-ray crystallography is still an essential tool for the characterization of tertiary and quaternary structures.

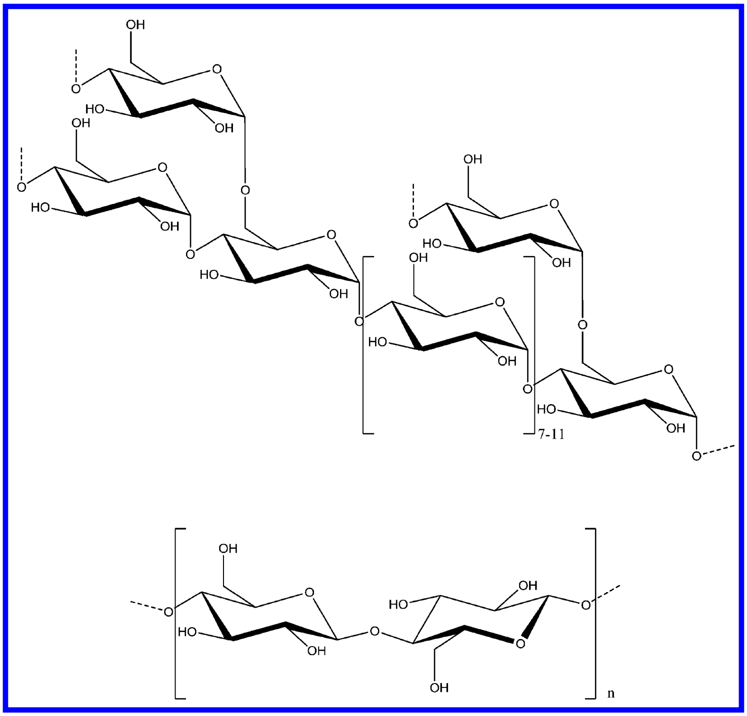

*Figure 3. Polysaccharide architectures of glycogen (top) and cellulose (bottom).*

A nice contrast between historical analytical methods and modern analytical methods is offered by comparison of methods that characterize protein primary structure. Chemical methods to derivatize the amino-terminal ends of protein chains were developed in the 1940's by both Pehr Edman and Fred Sanger. Edman's method is the basis of many modern automated protein sequencing instruments. Protein sequencing by mass spectrometry (MS) can be performed either by tandem MS or by peptide ladder sequencing. Figure 4 illustrates the locations of fragmentation along a peptide backbone and fragmentation mechanisms in tandem MS that allow sequences to be defined. Figure 5 shows an example used to illustrate the data actually collected and analyzed to define protein sequence by tandem mass spectrometry. Tandem MS is a powerful modern tool to characterize protein primary sequences.

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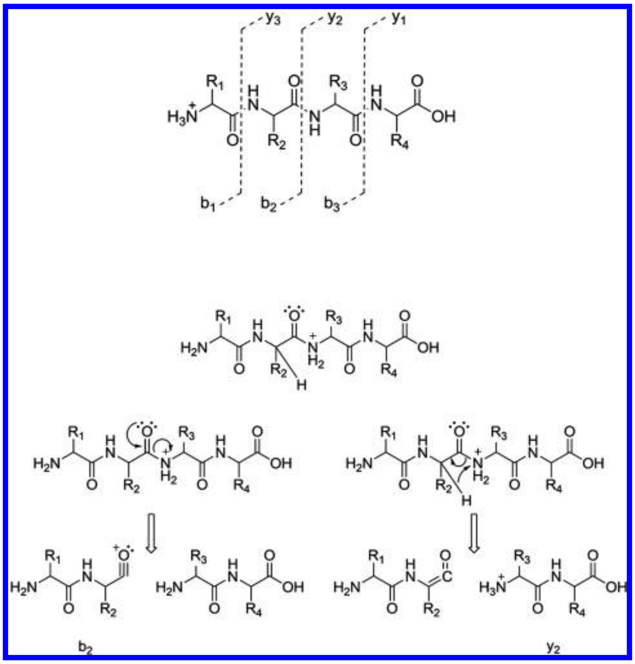

*Figure 4. Tandem-MS fragmentations (top) and fragmentation mechanisms (bottom) that provide protein sequence information.*

## Separations

Isolation of biopolymers from either their natural sources or from heterologous expression systems is an essential step that must precede many biochemical studies. Separations are routinely performed in biochemistry labs on both the analytical scale and the preparative scale. Methods to perform separations on both of these scales are illustrated in the unit on proteins and amino acids. Many of the predominant analytical-scale separation methods are electrophoretic in nature, and include sodium dodecylsulfate-polyacrylamide gel electrophoresis (SDS-PAGE), isoelectric focusing (IEF), and two-dimensional gel electrophoresis (2D-GE). Preparative scale separation methods discussed are typically chromatographic methods, and include gel filtration, anti-FLAG affinity, anti-myc affinity, cation exchange, and anion exchange chromatographies. Students are typically expected to be able to make predictions regarding the order of elution in the chromatographic methods and the appearance of electrophoretic results given a table of properties for proteins in a mixture such as Table 1.

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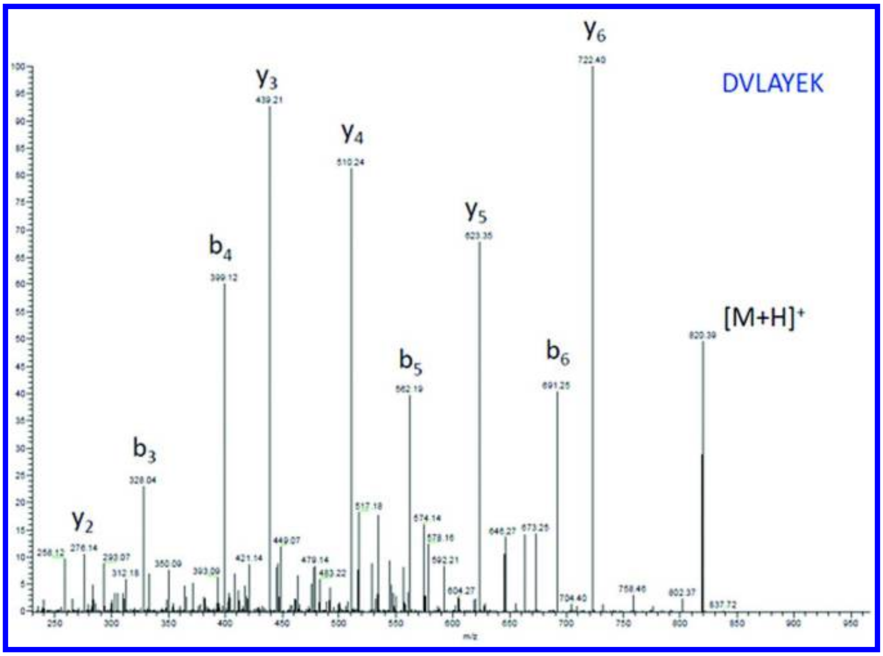

*Figure 5. Tandem-MS spectrum of a singly-charged peptide of length seven (primary amino acid sequence DVLAYEK) showing the b and y ions that allow determination of sequence.*

**Table 1. Table of protein properties to accompany the problems in which students predict elution order or electrophoretic mobility differences by a variety of analytical separation methods.**

| *Protein* | *MW (kDa)* | *pI* | *Affinity Tag* |
|---|---|---|---|
| 1 | 100 | 7 | None |
| 2 | 10 | 8 | FLAG |
| 3 | 50 | 4 | Myc |
| 4 | 85 | 5 | None |
| 5 | 75 | 9 | None |

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch007

## Perspectives

The foundational course in biochemistry offers a rich context within which to discuss the principles of polymer chemistry, as so many natural biomolecules are polymers. Inclusion of macromolecular topics in such a course is consistent with recommendations of the American Chemical Society Committee on Professional Training to provide exposure to macromolecular principles throughout the foundational curriculum. The Foundations of Bioorganic Chemistry course at the University of Memphis has a thematic emphasis on the structure and function of biomolecules. Discussion of polymer principles ranging from biopolymer synthesis to analysis fits nicely within this overarching theme, and complements the polymer principles introduced in the context of synthetic polymers in the preceeding foundational organic chemistry course.

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## Chapter 8

# Enhancement of the Laboratory Component of the First Course in Organic Chemistry through Incorporation of Polymeric Materials

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There are many good polymer experiments that may be utilized to illustrate the principles of organic synthesis, structure and spectroscopy. A popular experiment that serves to generate student interest, illustrate interfacial synthesis, and provide an opportunity to discuss the development of “synthetic silk” is the synthesis of nylon 6,10. In this case the product is removed from the interface between an aqueous basic solution of hexamethylenediamine and a methylene chloride solution of sebacoyl chloride as it is formed. It may be conveniently rolled onto an empty paper towel roller. This is the most remembered experiment when students are surveyed years after the course has been completed. The polymerization of lactide using tin octanoate as initiator and benzyl alcohol as initiator, provides a great opportunity to introduce the generation of materials from a renewable biosource, to discuss acid catalysis, and to illustrate nucleophilic addition-elimination at acyl carbon. However, the strongest feature of this experiment is the determination of structure using spectroscopy. Proton NMR spectroscopy can be used to determine the number average molecular weight by end-group analysis. Comparison of the peak area for the phenyl protons of the initiator fragment with that of the methylene protons of the polymer mainchain readily provides the number of mer units in the chain. The preparation of poly(aspartic acid) provides an example of a truly green experiment. No organic solvents are used. The monomer, an edible amino acid, is simply heated in a beaker. After hydrolysis (by warming in aqueous base) of the poly(succinimide) initially formed, polymer molecular weight may be determined by titration with standard aqueous hydrochloric acid solution. Poly(aspartic) acid is used commercially as a biodegradable scale inhibitor in steam lines. Its synthesis provides a ready bridge to a discussion of naturally-occuring poly(amino acid)s.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch008

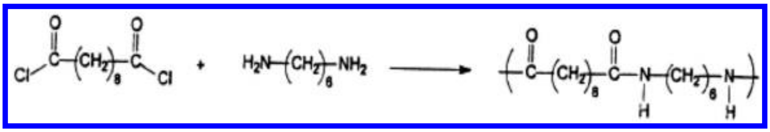
## Introduction

Some understanding of polymeric materials is essential for all chemistry graduates. Most will ultimately work in a polymer or polymer-related area. In addition, such understanding is essential to the functioning of graduates as aware, knowledgable citizens and consumers. This is acknowledged by the ACS Committee on Professional Training. Current guidelines assert that polymeric materials should be included in all foundational chemistry courses for approved programs. Polymeric materials may be readily incorporated into the first organic chemistry laboratory course. Inclusion of polymer experiments may be used to illustrate important organic reactions and to emphasize the utilization of spectroscopic and chromatographic methods (IR, NMR, MALDI-MS, SEC (GPC), DSC, TGA) in structure determination. Such experiments serve to facilitate interest in the course, student awareness of their surroundings, and intelligent Wal-Mart shopping. Inclusion of such experiments serves to illustrate the centrality of organic chemistry in the daily lives of citizens of the developed world and permits a discussion of green chemistry, materials from biosources, and sustainability.

## Results and Discussion

There are many good polymer experiments that may readily be incorporated into the first organic laboratory course to good effect. Three that are instructive, that serve to illustrate green chemistry considerations, and that have a lasting effect on students are described here. A listing of several more is also provided.

Nylong 6,10 is a representative of a very important and useful class of polymeric materials. It may be produced by interfacial polymerization using very simple glassware and reagents. This affords an opportunity to discuss interfacial reactions in general and the advantages that they may provide in the synthesis of sensitive compounds. Nylon 6,10 is prepared from sebacoyl chloride and hexamethylenediamine (Scheme 1).



*Scheme 1. Preparation of Nylon 6,10.*

Reaction occurs at the interface between a solution of sebacoyl chloride in methylene chloride (or other suitable solvent) and hexamethylenediamine in aqueous sodium hydroxide solution (Figure 1). The aqueous solution is carefully poured into a beaker containing the methylene chloride solution of sebacoyl chloride such that the solutions do not mix. The polymer starts to form almost immediately and can be pulled from the interface and collected by rolling onto a paper towel roller as illustrated in the series of photographs below (Figure 2).

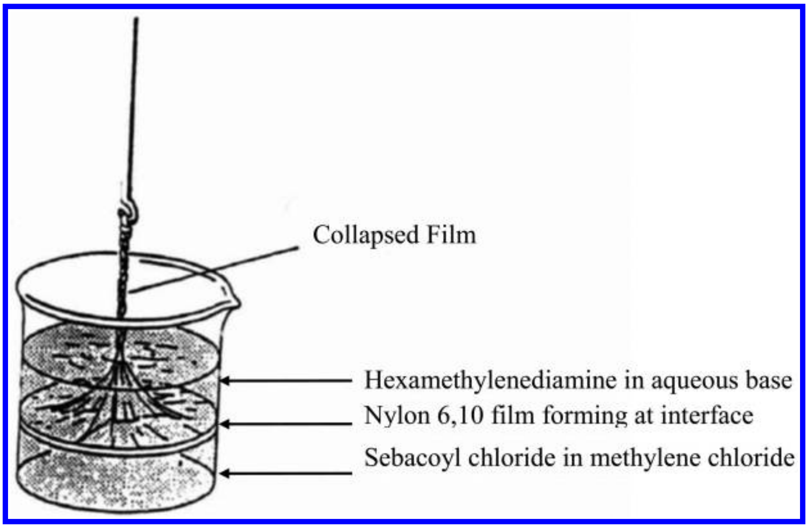


*Figure 1. Nylon 6,10 Forming at the Interface of Noncompatible Solutions*

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch008

Students are very impressed by the amount of material that can be removed from a mixture containing a few grams of reactants [this is the most remembered experiment from the organic lab when students are encountered years after graduating]. The polymer can be rinsed in a beaker of methanol, dried, and characterized by infrared spectroscopy (Figure 3).

Of course, many nylons may be generated in this way. Nylon 6,10 is attractive because of the moderate cost of reactants.

A discussion of nylon structure presents an opportunity to compare it to natural poly(amide)s, particularly silk, the material which it largely replaced. This can facilitate the introduction of biopolymers generally.

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*Figure 2. Student Preparing Nylon 6,10.*

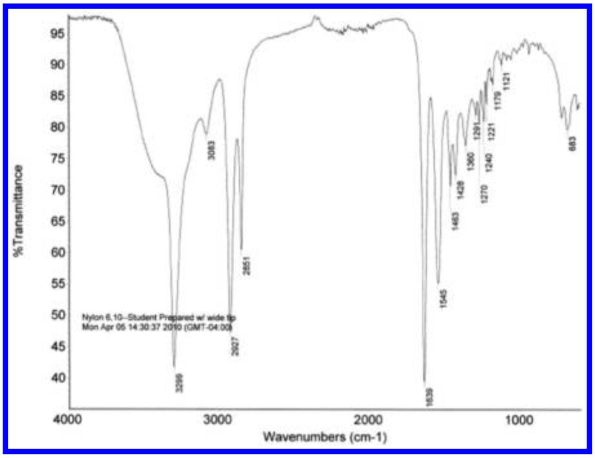


*Figure 3. Infared Spectrum of Student Prep Nylon 6,10.*

The inclusion of a nylon experiment provides an opportunity to discuss the discovery, development and societal impact of the nylons – “the nylon story” (*1*–*5*). The hiring of Wallace Carothers and the transformation of the DuPont Company is a great story in the development of the modern US chemical industry and one that enhances student interest and appreciation for “simple” organic reactions. Students are also intrigued by Carothers’ personal life- his struggles to get an education, his mentoring by Roger Adams and Carl Marvel at the University of Illinoios, his being hired away from Harvard by DuPont, his massive accomplishments and, of course, his bouts of depression. Carothers was a brilliant scientist (certainly among the greatest of the past century) who put polymer science on a firm experimental footing and made major contributions to both science and socetiy. Students are surprised that he did not receive a Nobel Prize. Had he lived long enough, he almost certainly would have. However, he suffered from severe bouts of depression. He dealt with these episodes by going to a major city and spending several days going to plays. During one such occurance in Philadelphia he drank orange juice containing potassium cyanide and died, age 41. The irony of this situation is not lost on the students – with today’s medical understanding and drugs, his condition could have been managed such that he could have continued to function for many years.

DuPont settled on nylon 6,6 for commercialization, not because it had the best properties of those prepared, but because the monomers could be generated from cyclohexane which could be obtained in high purity by hydrogenation of benzene. Nylon stockings were unveiled at the 1939 world’s fair in New York and were a sensation. They looked and felt like silk stockings but were affordale for everyone.

Every lady wanted a pair of nylons. Very soon nylon stockings disappeared from the market. Every bit of available nylon was required for the war effort. Betty Grable, a prominent movie star at the time, auctioned her nylons and raised $20,000 for the war effort.

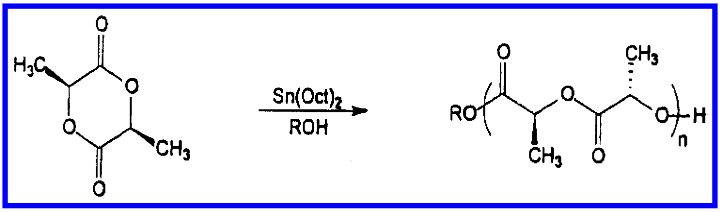
In fact, the Normandy invasion would have not been possible without the availability of nylon for the construction of parachutes (Figure 4). The Normandy invasion was the largest amphibious landing in military history. It was tremendously important. If successful, the Allies would gain a foothold on the continent which would lead to a libration of France and the defeat of Germany. If unsuccessful, Germany would have at least one more year to bolster its flagging military force, drive off the Soviet offensive and perfect new weapons (V1,V2 rockets, more powerful intercontinental ballistic missles, transcontinental aircraft).

- 101st Airborne Division
- 82nd Airborne Division
    - To secure exits from the beaches
    - To capture critical river crossings, bridges, railroad lines, roads, airfields

*Figure 4. Landing of US Paratroopers in Normandy*

This undertaking was, of course, successful and the war was ultimately brought to a satificatory conclusion. From this discussion students gain an appreciation for the impact of basic organic reactions and polymeric materials on the war effort. Perhaps, as importantly, they come to appreciate that the war was a near thing. There was no certainty that the Allies would prevail.

The preparation of poly(lactide) [PLA, Ingeo] is an experiment that works well, illustrates the generation of a useful material from a renewable biosource, and demonstrates the utility of proton NMR spectroscopy for the determination of molecular weight by end-group analysis (Scheme 2).



*Scheme 2. Preparation of Poly(lactide)*

It is conveniently prepared using tin octanoate as a catalyst and benzyl alcohol as an initiator (*6*). The preparation provides an opportunity to review the utility of acid catalysis in transesterification, i.e., reaction of a relatively poor nucleophile with an electrophile. The reaction can be carried out in common glassware found in the undergraduate organic chemistry laboratory in refluxing toluene. It may be isolated by precipitation in heptane. After drying, a sample is dissolved in deuterochloroform, the spectrum recorded and the number average molecular weight of the polyer determined as illustrated below (Figure 5). The integral area for the phenyl protons of the end group may be compared with that for the methylene protons of the polymer to determine the number of repeat units in the polymer This number times the molar mass of the repeat unit plus the molar mass of the initiator fragment provides the molecular weight. This illustrates the utilization of NMR spectroscopy for something other than structure determination.

Poly(lactide) [PLA] was initially prepared by Carothers in 1932 but it wasn't until 1954 that high molecular weight polymer was patented by DuPont. It remained for Cargill to develop PLA as an item of commerce. Cargill as a grain/food company has access to a ready source of starch from plant sources which serves as a source of glucose. In the future, the necessary glucose will come from cellulosic raw materials (crop waste, wood residues, etc.). Fermentation of glucose may produce lactic acid. Cargill is a large company with the financial reserves required to support a successful new startup. That company is NatureWorks LLC which opened a plant in Blair, Nebraska, in 2002, to manufacture PLA as Ingeo biopolymer.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch008

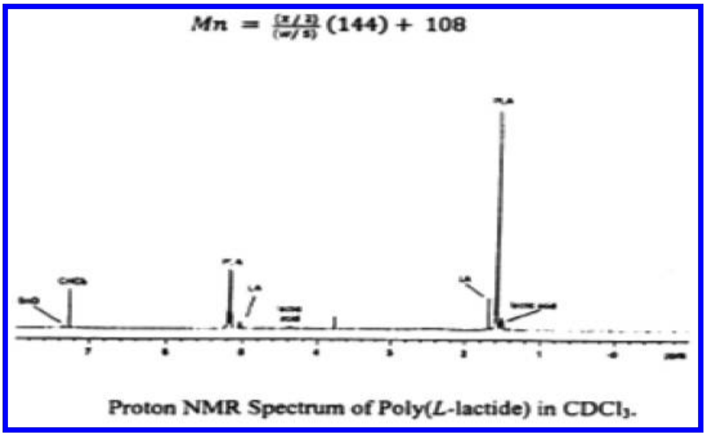


*Figure 5. Proton NMR Spectrum of Poly(lactide)*

Ingeo offers properties (high barrier, toughness, transparency) which makes it attractive for packagaing applications and it is replacing more traditional materials, principally poly(styrene) and poly(ethylene terephthalate) [PET]), for some uses. It may be formulated as either a plastic or a fiber. It is fully recyclable and is compostable but does not degrade at an appreciable rate in a landfill.

Aspartic acid is a naturally-ocurring amino acid. The Donlar Corporation (now NanoChem) developed thermal polymerization of this material to generate poly(aspartate), a biodegradable alternative to poly(acrylic acid) as an anti-scaling agent for steam lines. This polymerization can readily be carried out in the organic chemistry laboratory (*7*). The synthesis occurs in two steps 1. polymerization to form poly(succinimide) and 2. hydrolysis of the succinimide units (Scheme 3). The equipment required for this preparation is extremely simple.

Both polymerization and hydrolysis are carried out in a beaker. This is a truly green experiment. No organic solvents are used. The starting material is readily available, biodegradable and renewable. All the waste can go into the laboratory drain. Further, the molecular weight of the polymer may be determined by titration of an aqueous solution of poly(aspartate) with standard aqueous hydrochloric acid solution. This experiment demonstrates step-growth polymerization which can be related to the formation of many polymers that students encounter in their daily lives. It illustrates the relevance and applicability of organic chemistry to the solution of real problems as well as the principles of green chemistry. It also serves as a bridge to a discussion of naturally-occurring polymers. Although a poly(amino acid), poly(aspartate) is not a protein. The contrast can promote a discussion of intermolecular interactions and protein structure.

Three experiments that can easily be incorporated into the organic chemistry laboratory experience have been presented. There are, of course, many more. A partial listing of these may be found below.

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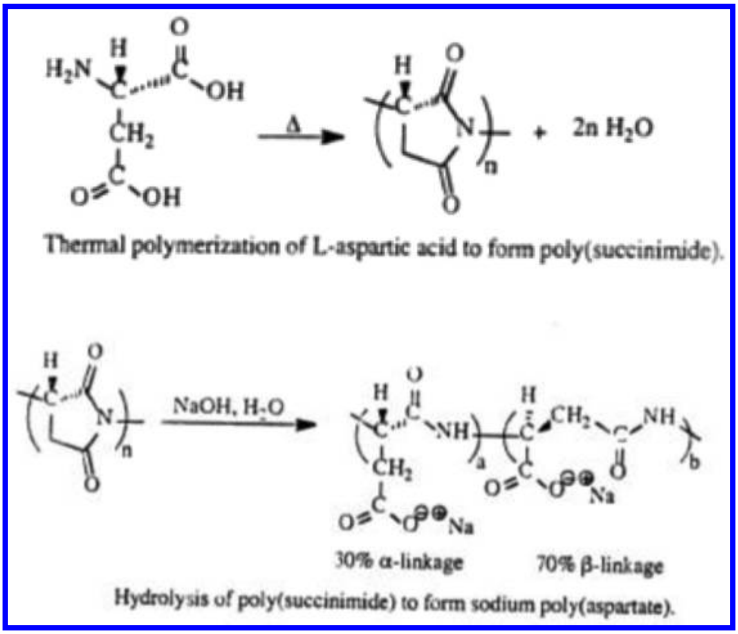

*Scheme 3. Synthesis of Poly(aspartate)*

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## Conclusions

The inclusion of polymer experiments in the first organic chemistry laboratory course facilitates

- The introduction of key chemical principles
- Illustration of spectroscopic and chromatographic methods for structure determination
- Awareness of surroundings, development of society, importance of materials (organic/polymer chemistry) in daily life
- Integrative thinking
- Discussion of sustainability issues
    - Green chemistry principles
    - Materials from biosources
    - Recycling
    - Degradability

These experiments generate student interest, promote better performance, and illustrate connectivity to the real world and the everyday lives of students.

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch008

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch009

## Chapter 9

# Radical Chain Reactions in Foundational Organic Chemistry

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In the foundational organic chemistry course radical chain reactions are introduced via the chlorination of alkanes. The mechanism of a chain reaction and its selectivity based on the homolytic C-H bond dissociation energies leading to methyl, primary, secondary, tertiary, allylic, and benzylic alkyl radicals are vital to understanding of material covered later in the course. Radical chain polymerization introduces polystyrene and poly(vinyl chloride) which, due to their everyday use, are more interesting to students than chloroalkanes. The polymerizations further support the importance of radical chain reactions, and the head-to-tail structures of the polymers reinforce the importance of selectivity of radical formation. Radical chain autoxidation of ethers and lipids and inhibition of both polymerization and autoxidation of foods by hindered phenols complete the discussion of radical reactions. The additional time devoted to polymerization and autoxidation is compensated by omitting topics such as radical addition of HBr to alkenes and multistep syntheses.

## Introduction

Radical chain reactions are fundamental to organic chemistry, although not as widely used in organic synthesis as heterolytic bond-breaking and metal-coordinated reactions. Most textbooks devote one chapter to radical chain reactions during the first term and then return to a few more specific examples in later chapters. The early chapter generally includes the mechanism of chlorination of methane and higher alkanes, homolytic bond dissociation energies in terms of reactivity and selectivity of chlorination, the greater selectivity of bromination than of chlorination, the planar structure of alkyl radicals that prevents enantioselective reactions, the anti-Markovnikov radical addition of HBr to alkenes, and multistep syntheses that include radical chain halogenation. Some texts cover radical reactions of biologically important compounds. Some texts include a section on radical chain polymerization. Others defer polymerization to a separate special topics section or to a separate chapter near the end of the book.

This article shows how polymerization can be incorporated into the radical chain reaction section of first term organic chemistry without devoting more than the usual amount of time to radical reactions. Of course this requires deletion of some of the standard topics in the radical reactions chapter. Students gain from the inclusion of polymerization because the familiarity with polymeric materials in everyday life arouses their interest and because understanding basic polymer chemistry prepares them for their future careers in chemistry, chemical engineering, molecular biosciences, and the health professions.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch009

## Organic Chemistry I

This article is based on the course taught at Oklahoma State University Fall semester 2010. The textbook was Solomons and Fryhle, *Organic Chemistry*, tenth edition (*1*). Two fifty-minute class periods and part of a review period preceding an exam were devoted to radical chain reactions. For out-of-class study students were assigned selected sections of the text, a two-page handout supplement on polymers, some of the text exercises for which answers were available in the accompanying study guide, and a short weekly problem set to be graded.

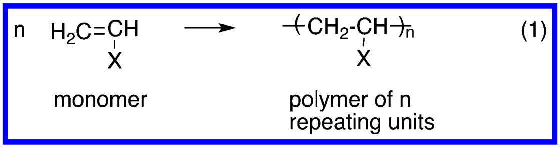
The mechanism of a radical chain reaction via initiation, propagation, and termination steps was introduced with the chlorination of methane. Experimental product distributions from monochlorination of propane and 2-methylpropane were compared with statistical distributions to illustrate selectivity of reaction of tertiary > secondary > primary C-H bonds. Using the large table of homolytic bond dissociation energies (DH°) in the text students calculated enthalpy changes of the overall reactions and of the individual propagation steps in the radical chain mechanism. The practical importance of alkanes from petroleum and natural gas and of the chlorination of alkanes in industrial organic synthesis were mentioned briefly in class.

Industrial organic synthesis and nature produce polymers, the materials we know as plastics, elastomers, and fibers. Students were told to look around them to see examples, and then materials that they identified from each class of polymeric materials such as cotton, wool, nylon, and polyester clothing, polyethylene, polystyrene, and poly(vinyl chloride) plastics, and synthetic and natural rubber were discussed briefly. The word "polymer" refers both to a material comprised of long chain molecules and to those long chain molecules, which also are called macromolecules. Thus "polymer" may refer either to a material or to a macromolecule. Common names were used because of familiarity. The systematic names of polymers are rarely used.

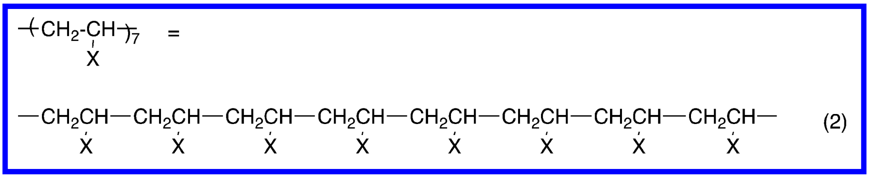
In Introduction of Macromolecular Science/Polymeric Materials into the Foundational Course in Organic Chemistry; Howell, B.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

## Relation of Polymer Structure to Monomer Structure

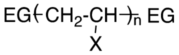
The handout material introduced the structural relations of alkene polymers to their monomers. It is essential at this point to understand the concept of a polymer repeat unit. Not all textbooks do this well. For structures we use monosubstituted alkenes and their polymers (eq 1). Polyethylene (X = H), poly(vinyl chloride) (X = Cl), and polystyrene (X = $C_6H_5$) are examples.


$$n\ H_2C{=}\underset{X}{CH} \longrightarrow \left(CH_2\text{-}\underset{X}{CH}\right)_n \qquad (1)$$

The empirical formula of the repeat unit of an addition polymer is identical to that of the monomer. The subscript *n* after the repeat unit is an integer that denotes the average number of repeat units in a chain. The average number of carbon atoms in the polymer chain is 2*n*. As a specific example let *n* = 8 and write out the 16-carbon atom structure (eq 2).


$$\left(CH_2\text{-}\underset{X}{CH}\right)_7 = -CH_2\underset{X}{CH}-CH_2\underset{X}{CH}-CH_2\underset{X}{CH}-CH_2\underset{X}{CH}-CH_2\underset{X}{CH}-CH_2\underset{X}{CH}-CH_2\underset{X}{CH}-CH_2\underset{X}{CH}- \qquad (2)$$

Polyethylene must have average lengths *n* of thousands, and polystyrene must have average lengths of hundreds to be a practical plastic. The dangling bonds at the ends of the repeat unit structure must be explained. Of course the polymer structure has end groups (EG in structure **1**), but the end groups are not usually shown because when *n* is very large, the two end groups cannot be identified in the presence of hundreds or thousands of repeat units. Moreover the structures of the end groups generally have no effect on the important properties of the polymer as a hard plastic, a thin film packaging material, or a fiber.


$$EG\left(CH_2\text{-}\underset{X}{CH}\right)_n EG$$

**1**

Even though it is the simplest alkene polymer, polyethylene was not discussed because it is no longer produced by radical chain reactions. New polyethylene manufacturing plants for decades have been based on metal coordination polymerizations that produce linear high density polyethylene and branched lower density polyethylene from mixtures of ethylene and 1-butene or 1-hexene. Although radical chain polymerization of ethylene is of historical interest and is instructive, its branched structures require additional discussion of chain transfer steps in radical chain reactions. Polypropylene, like polyethylene, is produced by coordination polymerization, so only the structure was mentioned.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch009

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## Mechanism of Radical Chain Polymerization

Why does polymerization occur at all? A reaction proceeds only if the free energy of the products is less than the free energy of the reactants ($\Delta G < 0$). Comparing monomer to polymer structure the net result of polymerization is conversion of a π-bond of the monomer to a σ-bond of the polymer chain. Because C-C single bonds are stronger (~335 kJ/mol) than C=C π-bonds (~250 kJ/mol) polymerization is exothermic. Polymerization also results in a loss of entropy, but the entropy ($\Delta S$) contribution is much less than the enthalpy ($\Delta H$) contribution to the net free energy change ($\Delta G = \Delta H - T\Delta S$). The mechanism of polymerization of styrene is shown in shown in Scheme 1.

### Initiation

Most radical chain polymerizations are initiated by thermal decomposition of an initiator that forms radicals at a convenient temperature, such as dibenzoyl peroxide at 80 °C. Initiation is endothermic because it breaks an O-O bond and forms two electron deficient radicals. The O-O bond of peroxides is weak (for dibenzoyl peroxide DH° = 139 kJ $mol^{-1}$). The value is given in the table of homolytic bond dissociation energies in the textbook (*1*). A benzoyloxy radical then adds to the C=C bond of styrene to form a benzylic styryl radical. Radicals are electron deficient. The Lewis structures have only 7 electrons in the valence shell of one oxygen atom of the benzoyloxy radical (**2** in Scheme 1) and only 7 electrons in the valence shell of the benzoyloxystyryl radical (**3**). As in chlorination of methane in which a chlorine atom and an alkyl radical have 7 electrons in the valence shell, radicals are reactive intermediates, not stable compounds. The electron deficient styryl radical has an average lifetime on the order of a microsecond before it reacts by propagation or termination.

### Propagation

In the first propagation step the styryl radical adds to another molecule of styrene to form a new, longer styryl radical. Propagation is exothermic; a π-bond breaks and a σ-bond forms. This process continues to form longer and longer styryl radicals until the chain reaction terminates. Propagation occurs only "head-to-tail" by addition of the styryl radical to the less hindered $CH_2$ end of the styrene double bond to form the benzylic radical, which is considerably more stable than the alternative primary alkyl radical because of delocalization of unpaired electron density into the phenyl ring. The regioselectivity of polymerization is based on the same principles of DH° and radical stability as the selectivity of radical chain substitution of Cl for H of alkanes. For a methyl C-H bond of toluene DH° = 375 kJ $mol^{-1}$ to form a benzylic radical vs. DH° = 421 kJ $mol^{-1}$ for a C-H bond of ethane to form a primary alkyl radical.

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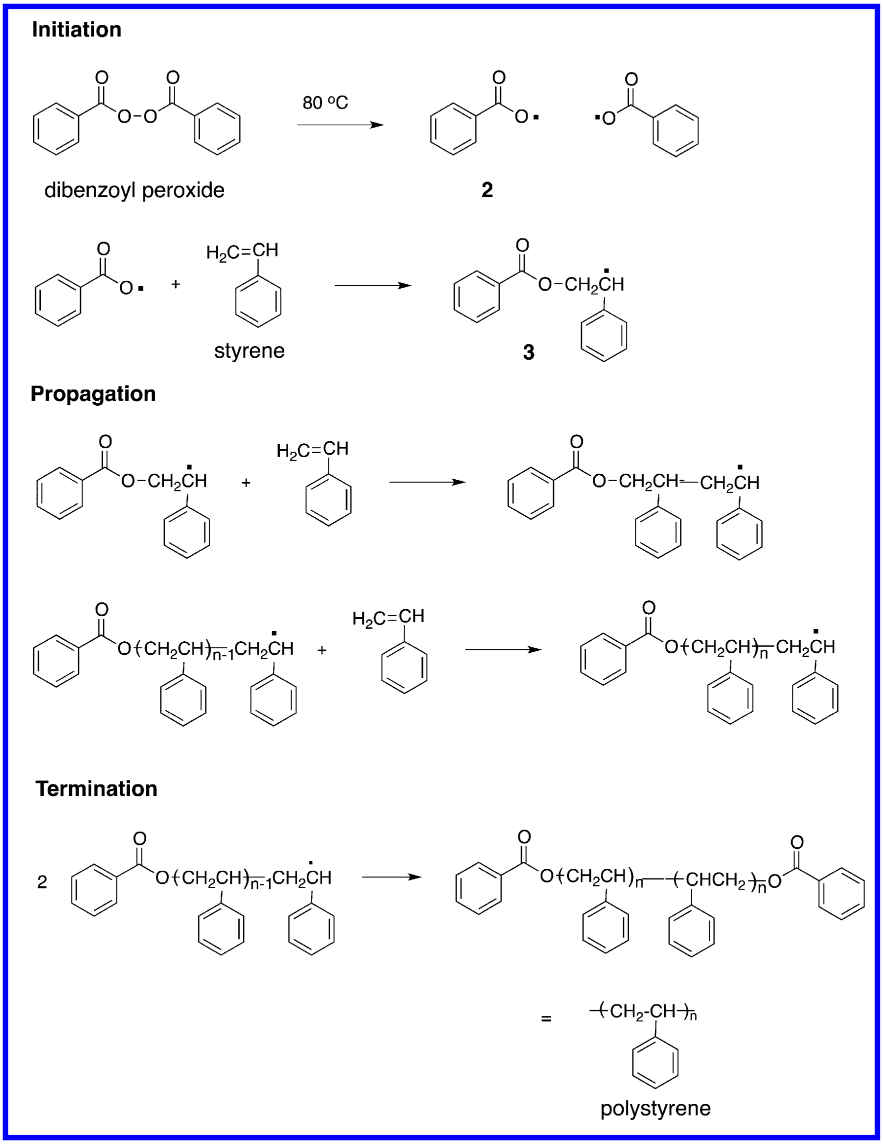

*Scheme 1. Mechanism of Polymerization of Styrene*

## Termination

Termination converts two radicals to stable molecules having completely filled valence shells of electrons. In the beginning class only termination by combination is shown, which is analogous to the combination of two methyl radicals to form ethane during the chlorination of methane. Combination of two polystyryl radicals having an average of *n* repeat units forms a polymer having *2n* repeat units. Other termination mechanisms give polymer chain lengths of *n*

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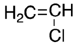
repeat units and different end group structures. Termination is highly exothermic because it forms a C-C single bond from two electron deficient radicals, but the probability of termination is much less than the probability of propagation because the concentration of styrene in the polymerizing mixture is more than a million times higher than the concentration of styryl radicals. A styryl radical collides more than a million times more often with a styrene molecule than with another styryl radical.

## Problem Assignment

To help the students learn by repetition and by analogous structures, the problem set they submitted asked questions such as those in Scheme 2.

1. Write initiation, propagation, and termination steps for polymerization of vinyl chloride initiated by dibenzoyl peroxide. The polymer is the plastic poly(vinyl chloride), also known as PVC, which has applications ranging from rigid pipes to "vinyl" raincoats.



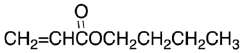
$H_2C{=}\underset{\displaystyle Cl}{CH}$

vinyl chloride

2. Draw the structures of the polymers that are made from the monomers.

$CF_2{=}CF_2$

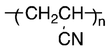
tetrafluoroethylene (makes Teflon)



$CH_2{=}CH\overset{\displaystyle O}{\overset{\|}{C}}OCH_2CH_2CH_2CH_3$

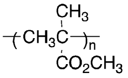
butyl acrylate (in many acrylic paints)

3. Draw the structures of the monomers that are used to make the polymers.



$-\!\!(CH_2\underset{\displaystyle CN}{CH}\!-\!)_n$

polyacrylonitrile (acrylic fiber)



$-\!\!(CH_3\underset{\displaystyle CO_2CH_3}{\overset{\displaystyle CH_3}{C}}\!-\!)_n$

poly(methyl methacrylate) (Plexiglas)

*Scheme 2. Problem Assignment*

In order to limit the time devoted to the radical chain reaction section of the course, other alkene polymers were not covered at this time. Polyethylene and polypropylene were not discussed because they are made by metal-coordination polymerization. The 1,2- vs. 1,4-repeat units of poly(1,3-butadiene) from the propagation polybutadienyl radicals was covered in the chapter on dienes after electrophilic 1,2- vs. 1,4-addition of HBr. Poly(isobutylene) is made by cationic polymerization and was covered in the section on substitution and addition reactions that proceed via carbocations.

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## Autoxidation and Antioxidants

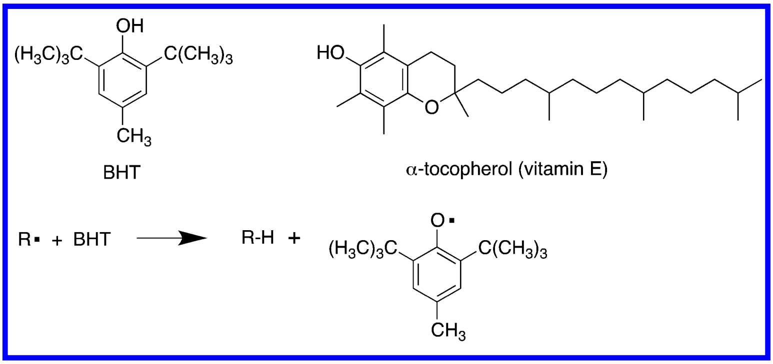
The radical chain reaction section of the course concluded with radical chain autoxidation and antioxidants. The mechanism of autoxidation was the third example of radical chain reactions. Radical chain autoxidation is important in the degradation of organic materials ranging from solvents such as diethyl ether, to plastics (which account for some of the reputation of plastics as cheap materials), to food as in the degradation of unsaturated lipids (butter turns rancid) during storage. The propagation steps are shown in Scheme 3. R-H represents a compound or polymer with an aliphatic C-H bond. In the first propagation step ground state triplet dioxygen adds to a carbon radical to form a new C-O bond of an alkylperoxy radical ($ROO\cdot$). In the second propagation step a hydrogen atom transfers from a C-H bond of another molecule of diethyl ether, a polymer, or a lipid to the peroxy oxygen atom to form an alkyl hydroperoxide (ROOH) and a new carbon radical. The topic of autoxidation of lipids appears again near the end of the two-semester course.

$$R\cdot + \cdot O\text{-}O\cdot \longrightarrow R\text{-}O\text{-}O\cdot$$

$$R\text{-}O\text{-}O\cdot + R\text{-}H \longrightarrow R\text{-}O\text{-}O\text{-}H + R\cdot$$

*Scheme 3. Propagation Steps of Autoxidaton*

Antioxidants were discussed also. Students were asked to look for BHT (butylated hydroxytoluene) and “mixed tocopherols” (which also are phenols; α-tocopherol is Vitamin E) in the lists of ingredients on packages of preserved foods such as breakfast cereals and bread. See Scheme 4. BHT and tocopherols inhibit both autoxidation and radical chain polymerization by transferring a phenolic hydrogen atom to a propagating radical, which stops the radical chain reaction because the hindered phenoxy radical does not propagate further. Antioxidants inhibit the formation of explosive peroxides in ether solvents during storage, the spoilage of foods, and the polymerization of monomers during storage in the laboratory and in railroad tank cars before use.



*Scheme 4. Inhibitors of Autoxidation and Polymerization*

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch009

## Omissions

How can radical chain polymerization and autoxidation be included without lengthening the radical reaction of the course? Several of the standard topics in the radical reaction chapter of the textbook are omitted, including selectivity of bromination of alkanes, lack of enantioselectivity at chiral centers formed by radical chain halogenation, radical addition of HBr to alkenes, and multi-step synthesis of small molecules that involve alkane halogenation. Which is more important to the world as we know it – polymerization of alkenes or anti-Markovnikov addition of HBr to alkenes? Which topic holds student interest better? Multi-step organic synthesis may captivate the instructor and students who are future organic chemists, who comprise less than 5% of the class, but synthesis is neither as important nor as interesting as polymerization and autoxidation to the vast majority of pre-health profession and engineering students.

## Acknowledgments

Both Chemistry 3053 and 3153 students and faculty colleagues at Oklahoma State University, who set high standards for research and teaching, have unknowingly contributed to my thinking about this article and the teaching of foundational organic chemistry.

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## Chapter 10

# Polymer Chemistry in an Undergraduate Curriculum

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch010

The multi-disciplinary applications that polymers have in biology, chemistry, medicine, and materials science make them ideal vehicles for teaching. They serve as familiar, real-world examples and help to reinforce concepts and reaction mechanisms while introducing developments in current chemical research. Examples of polymer-related topics and concepts are presented for use in introductory and intermediate organic courses.

## Introduction

Polymer science has burgeoned into a vibrant field that combines the disciplines of chemistry, biology, and physics to generate new materials. Polymers, be they synthetic or natural, are just about everywhere we look: clothing (rayon, nylon-6,6, spandex), toys (polyethylene, acrylonitrile-butadiene-styrene copolymers), and organisms (proteins, DNA, RNA, carbohydrates) to name a few. Since the first Nobel Prize in Chemistry was awarded in 1901, seven prizes have been given for advances in polymer science, and at least one per decade for the past 60 years. The effects of polymer science on today's world are far reaching.

At the heart of polymer science is chemistry – the ability to produce new materials based on small molecule monomers. The synthesis of monomers and polymers is often rather simple. The complexity of a polymeric material is attributed to the intrinsic molecular weight properties or subsequent engineering in addition to the structure of the polymer itself. As such, the basis for many monomer syntheses and polymerization strategies are covered in some form within the two-semester sequence of introductory organic chemistry.

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Underscoring the importance of polymers in society, many introductory textbooks contain a chapter or highlight sections that describe the chemistry of polymers. As many instructors would agree, the semester is always shorter than we would like, and few of us manage to cover all of the chapters within our chosen textbook. Table I lists some of the major organic chemistry textbooks currently in publication (*1–11*). Despite its importance, polymer chemistry is often the last chapter in the book, if it is included at all. The practical result is that polymer chemistry is often excluded from the introductory organic chemistry sequence simply due to the constraints of teaching within the two-semester framework. Highlighting this sentiment, a recent review of subjects in organic textbooks failed to even consider polymer chemistry as a topic of interest (*12*). In order to cover principles in polymer chemistry, instructors may need to introduce examples throughout the course as part of either the lecture or laboratory component. What follows are examples of polymer-related topics and concepts that can be incorporated into an introductory organic course.

**Table I. Polymers in organic chemistry textbooks**

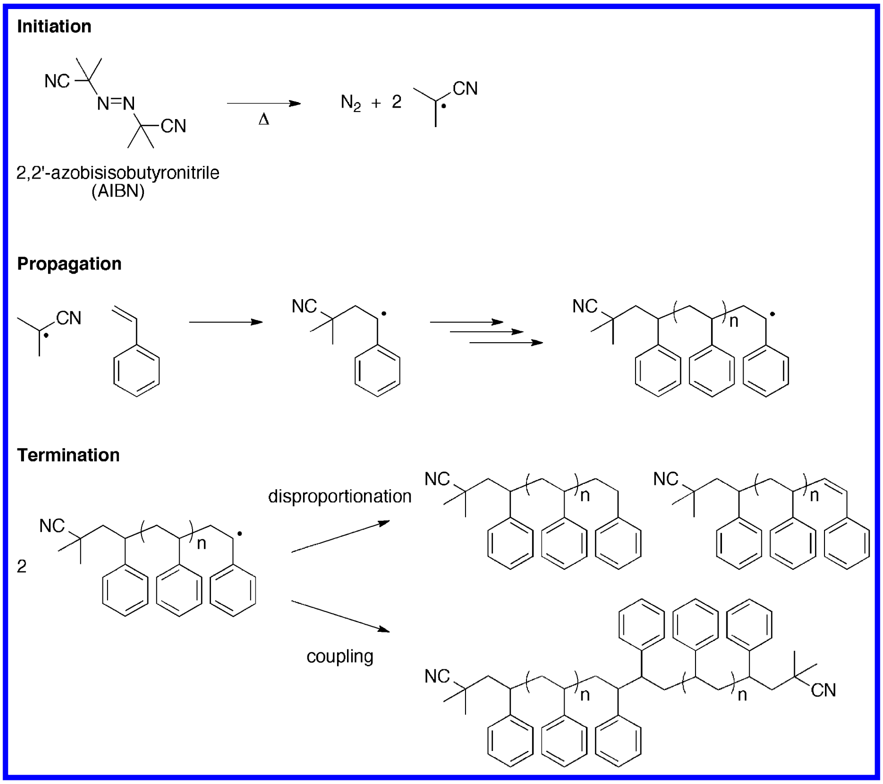
| *Author* | *# of chapters* | *Polymer Chapter* |
|---|---|---|
| Brown, Foote, Iverson, Anslyn (*1*) | 29 | 29 |
| Bruice (*2*) | 28 | 27 |
| Carey (*3*) | 27 | 27 |
| Jones (*4*) | 23 | 0 |
| Klein (*5*) | 27 | 27 |
| Loudon (*6*) | 27 | 0 |
| McMurry (*7*) | 31 | 31 |
| Smith (*8*) | 30 | 30 |
| Solomons, Fryhle (*9*) | 25 | 0 |
| Sorrell (*10*) | 28 | 26 |
| Vollhardt, Schore (*11*) | 26 | 0 |

# Radical Chemistry of Polymers

## General Mechanisms and Reactivity

Radical chemistry for alkenes is presented in organic textbooks as steps of initiation, propagation, and termination. These are the same processes that occur in radical polymerizations, thus allowing polymer chemistry to be easily integrated into an organic curriculum. Azonitrile and peroxide initiators, such as 2,2′-azobisisobutyronitrile (AIBN) and benzoyl peroxide

(BPO), are valid initiators for both alkene addition and polymerization strategies (Scheme 1). Addition across the vinyl group of olefin monomers (unsaturated hydrocarbons) occurs so as to preferentially generate the more stable radical. Polymerization is the result of multiple propagation steps. In uncontrolled systems, disproportionation and coupling mechanisms are responsible for many of the termination events. Chain transfer reactions are also examples of termination, where the active polymer chain end undergoes hydrogen abstraction, usually with solvent or monomer, to produce a dead chain end.



*Scheme 1. Steps in radical polymerzation. Shown is an AIBN thermally initiated polymerization of styrene.*

Many monomers can be polymerized using radical techniques (Figure 1). In general, these monomers possess alkenyl or other conjugatively-delocalizing groups groups to assist in stabilizing the active radical chain end. Concepts of resonance and hyperconjugation may be used to reinforce the head-to-tail mode of addition across the double bond.

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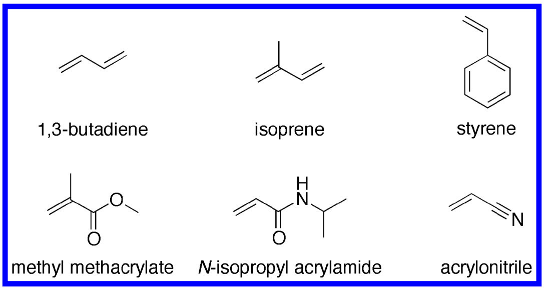

*Figure 1. Examples of common monomers that undergo radical polymerization.*

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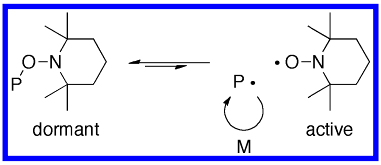
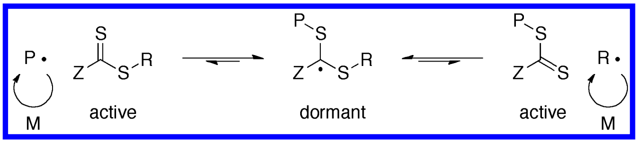
More recent advances in radical polymerization techniques include the development of controlled methods, such as nitroxide (*13*, *14*), atom transfer (*15–18*), and reversible addition-fragmentation chain transfer methods (*19*, *20*), as well as greener conditions of room temperature and aqueous solutions (*21*, *22*). Controlled or living methods of polymerization regulate chain growth and therefore molecular weight by suppressing or eliminating termination and unwanted chain transfer reactions.

Nitroxide mediated polymerization (NMP) uses a stable radical species such as 2,2,6,6-tetramethyl-1-piperidinoxyl radical (TEMPO) to mediate the radical concentration (Scheme 2). Initiation by AIBN or BPO and a few propagation steps generate the active polymer chain P•. The TEMPO radical couples with P• to make the polymerization dormant. This recombination is reversible, and homolytic cleavage of the C-O bond regenerates the active polymer chain end. Reaction conditions are chosen so as to favor the dormant state of this equilibrium, limiting the concentration of reactive radical species and thereby suppressing termination reactions to control the polymerization. Polymerization still occurs, as the equilibrium is not completely driven to the dormant state.



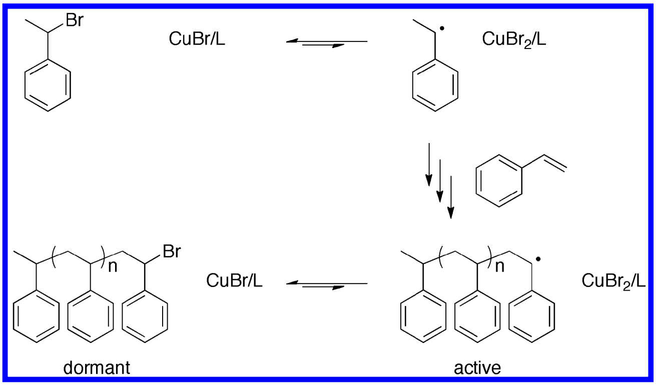
*Scheme 2. Chain transfer step in NMP using TEMPO that controls the concentration of growing polymer radical P•. In the dormant state, polymerization is shutdown. In the active state, monomer (M) adds to the active chain end, and the polymer chain grows.*

Reversible addition-fragmentation chain transfer (RAFT) polymerizations proceed much the same way as for NMP. Thermal initiation and propagation lead to a growing polymer radical P•. The addition of a chain transfer agent (CTA) traps the polymer radical (Scheme 3). The Z group of the CTA is chosen so as to stabilize the dormant species. Typical Z group are aryl or heteroatom derivatives (N, O, S) (*19*). The R group can also be cleaved from the dormant radical and is therefore designed to have fast reinitiation with the monomer to produce an alternate propagating chain. A much smaller amount of AIBN initiator is used in the reaction (AIBN:CTA typically 1:5 or 1:10) such that the two propagating chains equalize as part of a chain equilibration step. As with NMP, RAFT polymerization controls the concentration of active radical in solution.



*Scheme 3. Chain transfer step in RAFT polymerization. The Z group stabilizes the dormant radical. The CTA leaving group R• and the active polymer chain P• both undergo polymerization.*

Atom transfer radical polymerization (ATRP) is a method that also limits the concentration of active radicals. It does so by using a halide exchange between the growing polymer chain and a metal complex, with the concomitant redox reaction of the metal (Scheme 4) (*16*). Common exampes are copper complexes with ligands such as tris[2-(dimethylamino)ethyl]amine ($Me_6$TREN) or derivatives of 2,2′-bipyridine. The chain end undergoes propagation when the catalyst accepts a bromine and is oxidized. The active chain end abstracts bromine to return to the dormant state and the reduced copper species.



*Scheme 4. ATRP with styrene. The terminal halogen is shuttled between metal species and the polymer to produce dormant and active polymer chains (L = ligand to solubilize Cu).*

Although these topics may include slightly more complicated reaction mechanisms than would otherwise be covered in the introductory organic sequence, the research that employs these techniques offers a wealth of examples for applications of polymers in nanotechnology, biomedical applications, surface modifications and coatings, electronics, and more.

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Numerous laboratory experiments for radical polymerization have been have been reported. In addition to those referenced above, experiments that also demonstrate polymer properties or processing are available. For example, principles of microlithography are demonstrated using UV-initiated polymerization of 1,6-hexamethylene diacrylate (*23*). By conducting the polymerization on a movable stage, layers of crosslinked polymer can be successively built up to generate 3-D structures. Examples shown in Figure 2 were produced during an undergraduate laboratory period. More elaborate examples and templates are also available (*24*).

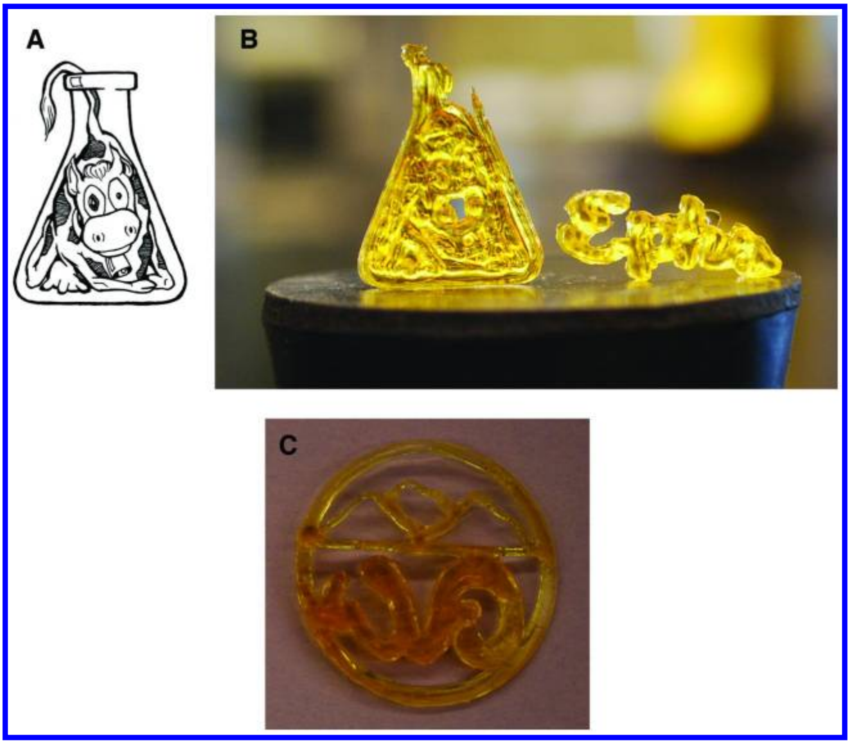

*Figure 2. Examples of 3-D structures built using microlithography and polymerization of 1,6-hexamethylene diacrylate. (A) Erlenmeyer template; (B) printed Williams Purple Cow in an Erlenmeyer flask and Williams "Ephs" (courtesy of Peter L. Clement); and (C) Williams Ultimate Frisbee (WFO) team logo (courtesy of Cameron R. Rogers). Objects are roughly 2 cm in length and/or width. (see color insert)*

A second example that illustrates polymer properties is an investigation of environmentally responsive hydrogels. Hydrogels are cross-linked, three-dimensional networks consisting of predominantly hydrophilic groups that can swell upon exposure to water, yet they maintain their physical shape. These "smart" gels can undergo volume changes that are dictated by a balance of the free

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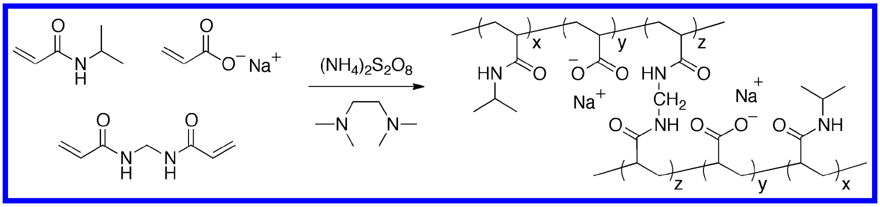
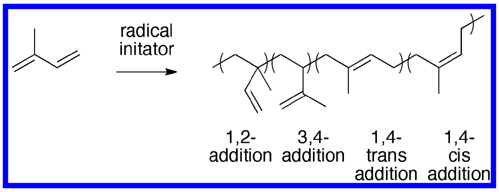
energy of the network and their surrounding medium in response to external stimuli (*e.g.* pH, temperature, ionic change). This volume change can be quite dramatic. It is often referred to as a volume collapse or transition and has been applied in a variety of areas ranging from pharmaceutics to biotechnology. By copolymerizing *N*-isopropylacrylamide (NIPAM) and the sodium salt of acrylic acid in the presence of the crosslinker *N*,*N′*-methylene-bis-acrylamide, temperature and pH responsive hydrogels are prepared (Scheme 5). Poly(*N*-isopropylacrylamide) (PNIPAM) exhibits a lower critical solution temperature (LCST) around 32 °C. As the polymer is heated, sidechain-sidechain interactions are more favorable than sidechain-solvent interactions, and the polymer precipitates out of solution. Incorporating PNIPAM into a hydrogel results in volume shrinkage above the LCST. Depending upon the pH and monomer composition, the diameter of these hydrogels can shrink up to 60% (data not shown). Their loading and swelling may be investigated under various conditions (T, pH) to illustrate the therapeutic potential of these materials. These hydrogels can be used as lecture or laboratory examples to demonstrate not only principles of organic reactivity through polymer synthesis, but also the function and use of these materials.



*Scheme 5. Synthesis of "smart" hydrogels using NIPAM (T sensitivity), sodium acrylate (pH sensitivity), and crosslinker N,N′-methylene-bis-acrylamide.*

## Dienes in Radical Polymerizations

Poly(isoprene), as a bifunctional monomer, presents an interesting example. Polymerization of this asymmetric diene results in 1,2-, 3,4- and 1,4- additions (Scheme 6). An instructor can ask students to identify the conjugative stability of the propagating radical for each of these additions. As well, students can predict the relative composition of the polymer product based on alkene stability. Under radical conditions, the *trans* 1,4- adduct predominates (>60%), followed by the *cis* 1,4-stereochemistry (<30%). The 1,2- and 3,4-additions are found in nearly the same ratio for radical polymerizations (~5%), except at higher temperatures, where the 3,4- structure is observed in a slightly higher amount (*28*). Thus, radical polymerization examples can be used to highlight topics of homolytic bond cleavage and radical mechanisms, resonance, and alkene stability.



*Scheme 6. Synthesis of poly(isoprene). Radical polymerization results in either 1,2-, 1,4-, or 3,4-addition.*

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## Polymers of Carboxylic Acid Derivatives

Carbonyl chemistry dominates much of the discussion in the second semester of the introductory organic sequence. In addition to the oxidation and reduction reactions of alcohols, aldehydes, and ketones, a significant portion of the course is devoted to studying carboxylic acid derivatives. There are a host of polymer examples, usually polyesters and polyamides, that may be developed in the course.

### Condensation Polymerizations

Amidation and esterification reactions with multifunctional reactants result in polymer formation (Scheme 7). Polyamides and polyesters are commonly synthesized through condensation reactions. The nylon rope trick (Flinn Scientific #AP2088) is a great demonstration of this condensation through an interfacial polymerization. Nylon-6,6 is produced by layering an aqueous solution of 1,6-hexadiamine and one of adipoyl chloride in hexane (Scheme 7A). The polymer forms at the interface of the two liquids and can be removed by pulling the solid polymer from solution. As the rope grows, polymer is removed and the reactant concentrations are refreshed, leading to further polymer growth.

While any carboxylic acid derivative can be used for amide formation, the efficiency of the reaction is improved by using the more reactive acid chloride. Commercial syntheses, though, use less reactive derivatives as the monomers are more stable when stored. The commercial synthesis of nylon-6,6 proceeds through the condensation polymerization of adipic acid and 1,6-hexanediamine, with water removed as the byproduct (Scheme 7B). The structure and properties of nylon-6 are similar to nylon-6,6. Nylon-6 has only one amide backbone per repeat unit and is made from either the condensation of 6-aminohexanoic acid or the ring opening polymerization of ε-caprolactam (Scheme 7C).

In addition to polyamide chemistry, it is worth noting the effect of the hydrocarbon spacers. Long alkyl chains, as in nylon-6,6, generate polymers that are flexible with low glass transition temperatures ($T_g$). By using more rigid spacers like aromatic rings, the $T_g$ increases, as does the toughness of the material to make polyamides such as Kevlar® (Scheme 7C).

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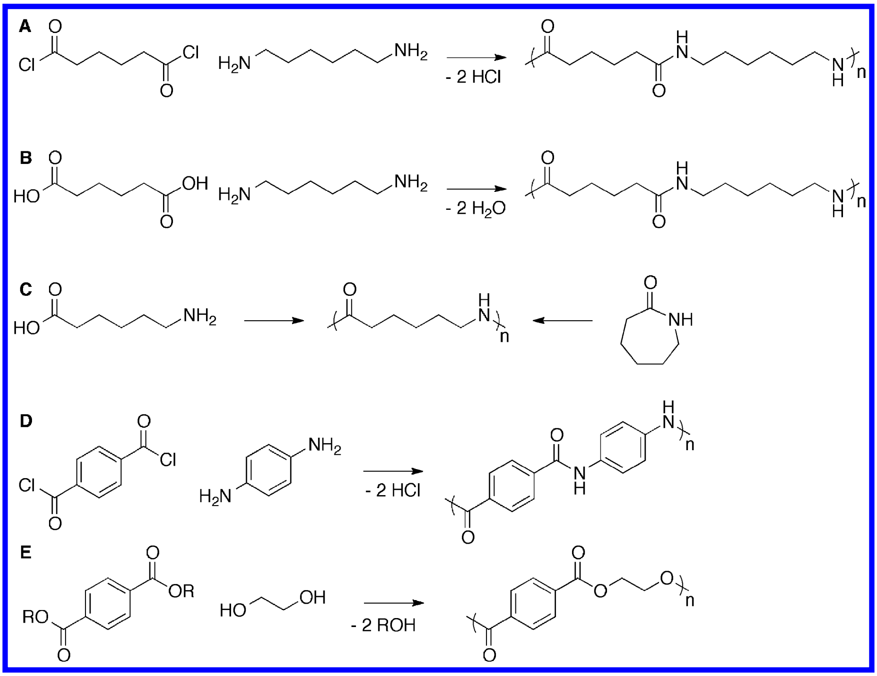


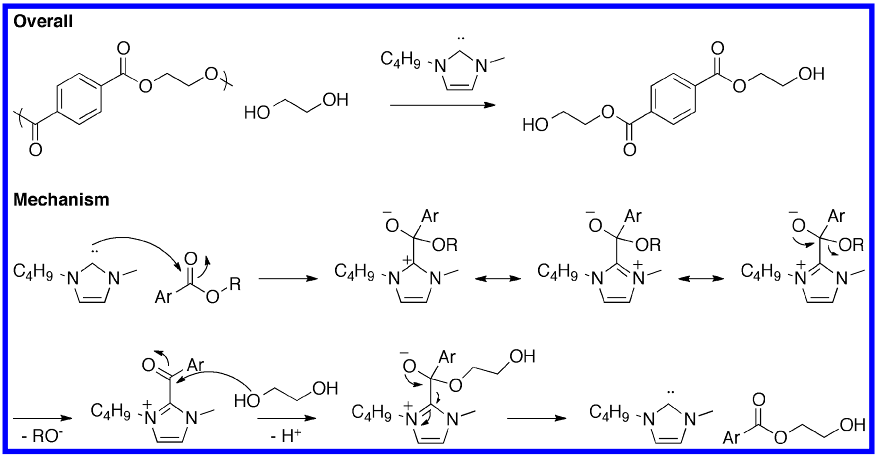
*Scheme 7. Examples of polyester and polyamide syntheses. (A) nylon-6,6; (B) commercial synthesis of nylon-6,6; (C) condensation of 6-aminohexanoic acid and ring opening polymerization of ε-caprolactam to form nylon-6; (D) Kevlar®; and (E) poly(ethylene) terephthalate (PET).*

Poly(ethylene terephthalate) (PET or PETE) is made through the condensation of ethylene glycol and a terephthalic acid derivative, typically dimethyl terephthalate (Scheme 7D). While PET is recyclable (#1), it can also be synthesized through plant-based materials rather than the more traditional petroleum feedstocks. Coca-Cola’s PlantBottleTM uses ethylene glycol derived from sugarcane. Pepsico has also introduced the EcoGreenTM bottle made from 100% plant sources. These bottles have the same components as traditional PET and can be sorted into the same recycle stream.

## Depolymerization of Polyamides and Polyesters

Acid and base-catalyzed hydrolysis mechanisms can be extended to discussions of polymer recycling through depolymerization. Although nylon exhibits good thermal stability, depolymerization can occur through acid catalyzed hydrolysis at elevated temperatures (*29*). Neutralization of the small molecule byproduct regenerates 1,6-hexanediamine and adipic acid, which can be reused.

PET can also be depolymerized via hydrolysis. Neutralization affords the original starting materials, which can be recycled to create new plastics. In addition to acid- or base-catalyzed methods, depolymerization also occurs using carbenes. *N*-heterocyclic carbene transesterification with ethylene glycol results in bis(2-hydroxyethyl)terephthalate, which can be used in subsequent transesterification polymerizations (Scheme 8) (*30*, *31*). This mechanism involves attack of the nucleophilic carbene on the electrophilic ester. The resonance stabilized intermediate breaks down to cleave the polymer chain. Addition of ethylene glycol regenerates the carbene catalyst and small molecule product. While carbenes are not covered as extensively as carbonyl derivatives, *N*-heterocyclic carbenes provide a nice example to reinforce the reactivity of neutral carbon nucleophiles.



*Scheme 8. N-heterocyclic carbene catalyzed PET depolymerization.*

## Ring Opening Polymerization

In addition to condensation polymerization methods, polyesters and polyamides can be synthesized using ring opening polymerization (ROP) techniques, as seen with nylon-6 and the ROP of ε-caprolactam (Scheme 7C). To produce polyesters or polyamides, monofunctional amines or alcohols, respectively, are typically used as small molecule initiators. A few examples of monomers used in ROPs are shown in Figure 3.

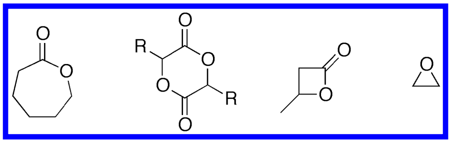


*Figure 3. Common monomers for ring opening polymerization. Left to right: ε-caprolactone, lactide (R=$CH_3$) and glycolide (R=H), γ-butyrolactone, and ethylene oxide.*

Poly(ε-caprolactone) is relatively hydrophobic, and poly(lactide) and poly(glycolide) hydrophilic. Block copolymers of these polyesters self-assemble

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into micelles and have been investigated for use as drug delivery vehicles (*32*, *33*). Hydrophobic drugs can be encapsulated into the micellar core, and the micelle serves to protect the drug from degradation or premature elimination. The esters are biodegradable and hydrolyze *in vivo*, releasing the drug and degrading the polymeric scaffold. γ-Butyrolactone, a more sterically strained cyclic ester, undergoes ROP to yield poly(3-hydroxybutyrate) (PHB) (*34*). PHB can also be synthesized by bacteria, and an undergraduate laboratory experiment has been developed using *C. necator* (*35*). Students can thus use their knowledge of transesterification and ring strain to understand reactivity and trends in ROP.

Poly(ethylene oxide) (PEO), also known as poly(ethylene glycol) (PEG), is synthesized by opening the highly strained epoxide ring using an alkoxide initiator (*e.g.* potassium *tert*-butoxide). Like the polyesters described above, PEO has been widely investigated for its therapeutic uses. The chain ends can be functionalized with a variety of molecules, including biomolecules, therapeutic and theranostic agents, or other types of polymers to generate block copolymers. Numerous PEO drug- and protein-conjugates are FDA approved and available for use (*36*, *37*). For example, the covalent attachment of PEO to interferon α-2a is sold as PEGasys®, a treatment for hepatitis B.

Poly(α-amino acids) are produced through ring opening *N*-carboxyanhydrides (NCAs). The NCA starting material is made by reaction of the appropriate amino acid with a phosgene equivalent to make the five membered ring monomer. Ring opening with an amine initiator occurs through either a nucleophilic initiator mechanism or an activated monomer mechanism (Scheme 9) (*38*). Chain length is controlled by tuning the monomer:initiator ratio. This technique has been used successfully to polymerize a variety of amino acids, most often protected lysine ($R=(CH_2)_4NH_2$) and aspartic acid ($R=CH_2CO_2H$) derivatives.

Both the nucleophilic amine and activated monomer mechanisms are possible during the course of polymerization. In either case, the nucleophilic species attacks the amino acid carbonyl. This selectivity can be explained through discussions of leaving group abilities. When the nucleophile attacks, the ring opens and the urethane acts as a leaving group. Subsequent loss of $CO_2$ drives the reaction forward, making attack at the amino acid carbonyl more favorable than attack at the urethane carbonyl.

Condensation and ring opening polymerizations using carboxylic acid derivatives make up an important class of polymer chemistry. More recent advances in polymerization strategies complement the traditional methods and can be easily incorporated into organic chemistry discussions.

## Olefin Metathesis Polymerization

Although organometallic chemistry is not regularly covered in introductory organic textbooks, its synthetic utility has prompted its inclusion in more recent textbook editions (*2*, *3*, *6*, *8*, *11*). One example of organometallic chemistry is olefin metathesis, for which Chauvin, Grubbs, and Schrock were awarded the Nobel Prize in Chemistry in 2005. Olefin metathesis is used in polymerization and small molecule syntheses for the exchange of double bonds.

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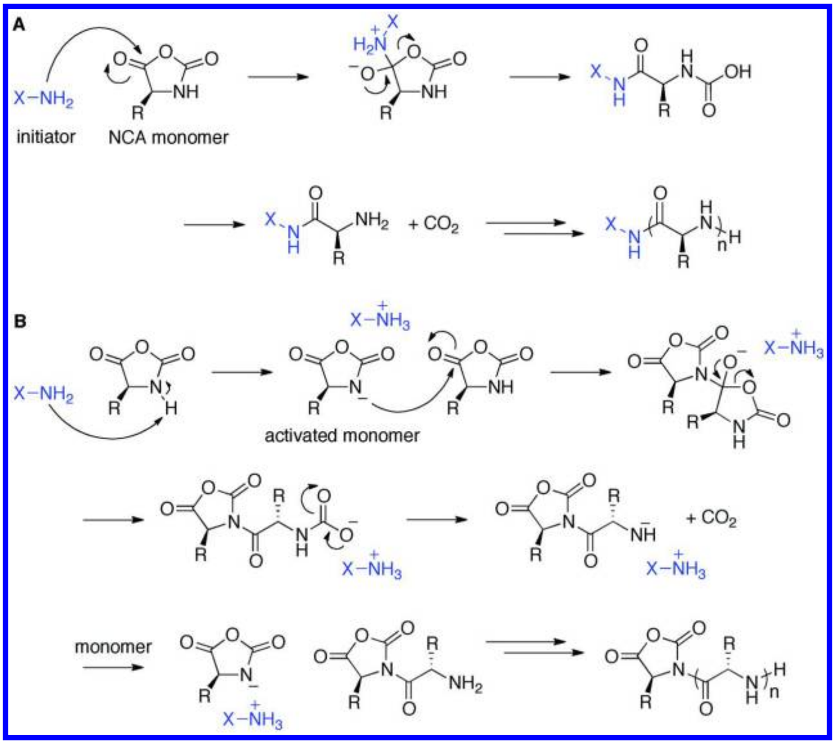


*Scheme 9. Mechanisms of NCA polymerization via nucleophilic amine (A) or activated monomer (B) pathways. R = amino acid side chain. (see color insert)*

Metal-carbene catalysts of the form M=CHR, most frequently comprised of ruthenium, tungsten, and molybdenum, catalyze the polymerization (Figure 4). Many of these catalysts are now commercially available through Sigma-Aldrich, Strem, and other suppliers.

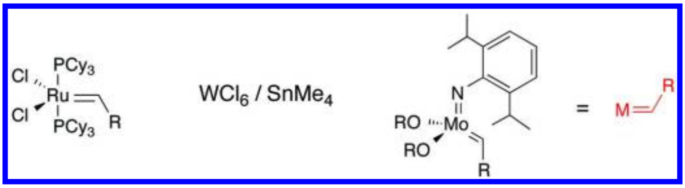
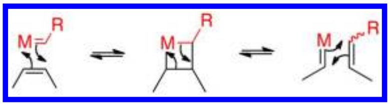


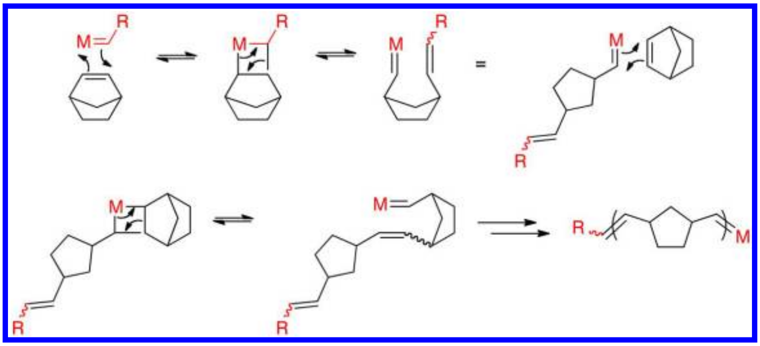
*Figure 4. Examples of metathesis catalysts. R = alkyl or aryl. (see color insert)*

The metathesis reaction scrambles the π-bonds of olefins using these transition metal catalysts (Scheme 10). The monomer alkene is cut through two four-membered ring activated complexes, similar to that for the Wittig mechanism. The driving force for the equilibrium is usually loss of small molecule byproduct, such as ethylene gas or relief of ring strain. Thus, olefin metathesis can be considered a form of step polymerization, as with acyclic diene metathesis (ADMET), or ring opening polymerization.



*Scheme 10. General reaction scheme of olefin metathesis. (see color insert)*

Metathesis reactions can be used in small molecule chemistry to combine two ends of a diene in a ring closing reaction to form generally from 5- to >30-membered rings. Alternatively, ADMET occurs when the alkenes dimerize not in a cyclic fashion but in a linear geometry to form a polymer (*39*). Ring opening metathesis polymerization (ROMP) exploits the metathesis equilibrium by using the relief of ring strain to drive the formation of, often *trans*, double bonds (Scheme 11). Typical monomers are cyclooctene, cyclooctadiene, norbornene, and norbornadiene derivatives (*40–46*). Monomers with functional groups, *e.g.* carboxylic acid derivatives, alcohols, and amines, can be used in metathesis polymerizations. The internal double can be further functionalized using electrophilic addition, for example, to generate new materials.



*Scheme 11. Olefin metathesis polymerization of norbornene. (see color insert)*

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## Conclusion

ACS guidelines for an undergraduate degree suggest polymer chemistry as an advanced elective (*47*). Additionally, the Committee on Professional Training recommends introducing students to concepts in polymer chemistry throughout the foundation courses. Within an introductory organic curriculum, there are several aspects of reaction mechanisms that can be illustrated using polymerization methods. Examples of radical polymerization, step and ring opening polymerizations of carboxylic acids derivatives, and polymerization with organometallic catalysts are easily incorporated in a lecture or laboratory setting. By engaging students in the study of polymer chemistry, an instructor broadens their understanding of the role that polymer chemistry plays in their everyday lives.

## Acknowledgments

Financial support from the National Science Foundation (RUI-DMR-080444) is gratefully acknowledged, as well as undergraduate students from the spring 2011 Williams College Polymer Chemistry course (CHEM 348).

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch010

## Chapter 11

# Use of Historical Events and Personalities To Facilitate the Incorporation of Polymeric Materials into the Beginning Organic Chemistry Course

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch011

The incorporation of polymeric materials into the foundational course in organic chemistry may be utilized to broaden the perspective of the student, to generate student interest in organic chemistry and its central role in the development of society, to place major developments in the field in historical context and to enhance general enthusiasm for the course. Polymeric materials have a tremendous impact on the daily lives of students. All aspects of their lives – from housing, transportation, clothing, personal care, palatable food, entertainment, etc. – are enhanced by the presence of polymeric materials. How these materials came to be and the individuals responsible for their creation are of interest to the student and serve to provide a thread for the course.

## Introduction

The prominence of polymeric materials may be traced to antiquity (*1*). Long before recorded history poly(amide)s were being used for clothing, shelter and inks. Man early learned to use animal skins, in various forms of refinement, for clothing, and blood was used as a naturally-pigmented ink for the generation of cave drawings. Poly(saccharide)s were used for the production of cords and components of clothing. Cellulosics were used in the construction of shelters, weapons, and utensils. A more general use of polymeric materials was slow in

In Introduction of Macromolecular Science/Polymeric Materials into the Foundational Course in Organic Chemistry; Howell, B.; ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch011

coming (*2*). An early material was poly(isoprene) derived from plants. It was discovered in South America in 1736. It's name "rubber" was coined by Jospeh Priestley who discovered its effectiveness in removing pencil marks from paper. A first major use was in the production of a waterproof coat, commonly referred to as a Mackintosh after the name of the inventor. These coats were popular with outdoorsmen and seafarers for several decades. It wasn't until 1884 that the correct structural formula for the polymer was established (Figure 1).

**Poly(isoprene) Natural rubber**

Discovered, 1736, South America
Charles Marie de la Condamine

Joseph Priestley, 1770
Discovered its use in removing pencil marks from paper, hence the name "rubber"

Charles Mackintosh, about 1800
Waterproof coats
Solution of poly(isoprene) in naphtha applied to cloth; two pieces pressed together

Charles Goodyear
Nathaniel Hayward, US 1090, 1838
Vulcanization

William A. Tilden, 1884
Correct Structural Formula

*Figure 1. History of Natural Rubber*

The history of modern organic chemistry begins with the rise of the German dye industry in latter half of the 19th century (*2*). This development was spurred by the efforts of two individuals, Justus Liebig and August Wilhelm Hoffman. Liebig was responsible for training several first-class chemists. Hoffmann who was the director of the Royal College of Chemistry in London returned to Germany. A student of Hoffmann in London was William Perkin who produced the first aniline dye (Perkin's mauve). This development formed the foundation for Imperial Chemical Industries (ICI) which became a major international company. The influence of Liebig and Hoffmann on the development of organic chemistry in Germany was huge, particularly in the training of students who could support new enterprises. In 1863, Friedrich Bayer set up a company for making dyes from aniline at Wuppertal (this company just celebrated the 150th anniversary of its founding (*3*)). In Hoechst, a small town near Frankfurt, a company was founded to make fuchsine red from aniline. In 1897 Badische Anilin and Soda-Fabrik (now BASF, the world's largest chemical company) achieved the first successful commercial synthesis of indigo. During this time an appreciation for macromolecules was developing but there was little understanding of their structure or properites (Figures 1 and 2). It remained for Hermann Staudinger to properly discern the structure of these materials (*4–6*).

German dye industry, 1850-1900

Adolph von Baeyer (Nobel prize, 1905)
Arthur Michael
Studied the reactions of phenol and aldehydes

Leo H. Baekeland, 1909
Phenol-formaldehyde resin, Bakelite

Carbohydrates
Poly(saccharide)s
Widely utilized
Later modified
Understanding of structure gained slowly

The first Nobel Prize associated with macromolecules was awarded to Walter N. Haworth in 1937

*Figure 2. Early Developments in Organic/Polymer Chemistry*

It had widely thought that large molecules could not exist and that polymers were colloids. Staudinger correctly perceived that this could not be the case. Staudinger's ideas were placed on a firm experimental base by Wallace Carothers (Figure 3), then at the DuPont Company in the US. Carothers demonstrated that polymeric materials could be generated from simple starting materials using well-accepted and understood reactions (*7*, *8*).

The acceptance of the Staudinger proposal for polymer structure was strongly supported by the work of Herman Mark and Kurt Meyer who demonstrated the semicrystalline nature of certain polymers (*9*). Julian Hill worked with Carothers at DuPont and was responsible for first observing "cold drawing" of nylon to produce fiber. Paul Flory was hired by DuPont to develop a theoretical basis for Carother's work. This led to an extraordinary career (at several locations) and provided a basis for understanding polymerization, polymer structure and morphology, and much more. Several of Flory's books are classic texts still in use today. In 1974, Flory was awarded the Nobel Prize "for his fundamental achievements, both theoretical and experimental, in the physical chemistry of macromolecules" (*10*, *11*). Despite the fundamental significance of Staudinger's work, it was not readily accepted in the chemistry community (the traditional view was maintained by many despite growing evidence to the contrary) and it was not until 1953 (see Figure 4) that he received the Nobel Prize (*12*, *13*).

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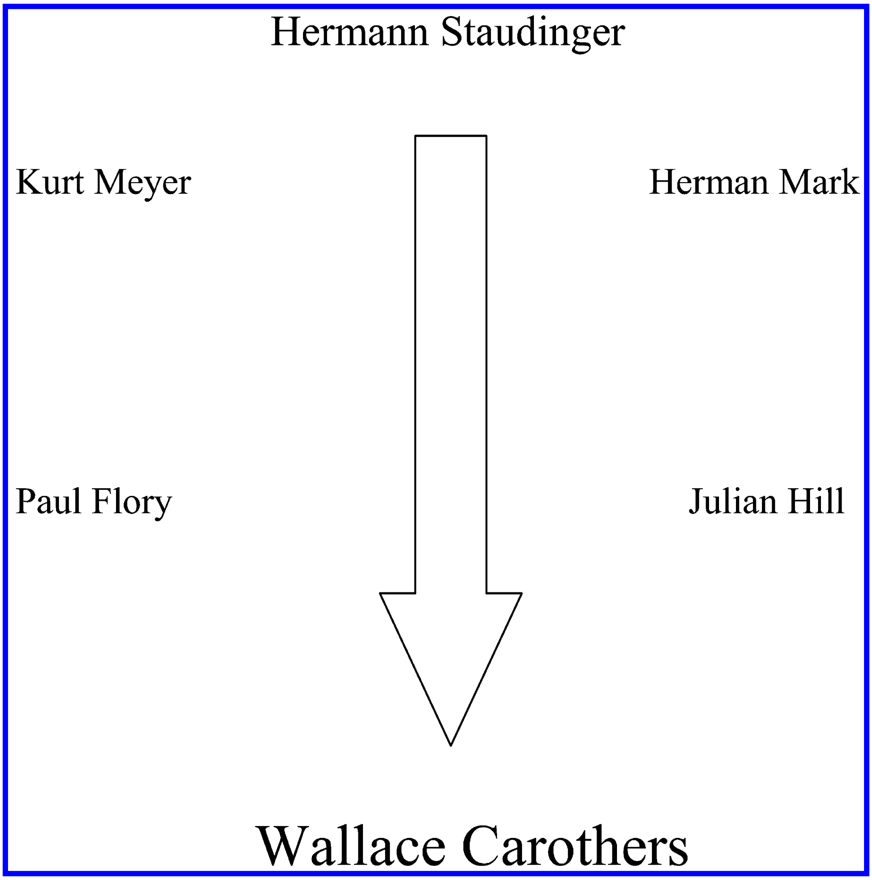

*Figure 3. Evolution of an Understanding of Macromolecular Structure*

**Hermann Staudinger**

- Born in Worms, Germany, 23 March 1881
- Educated as a chemist
- In 1910 began work on poly(isoprene) for BASF – beginning of a long, fruitful association with polymers
  - > Recognized that the prevailing views about macromolecules was incorrect

    1920, published “Uber Polymerisation”

    Nobel Prize, 1953

*Figure 4. Milestones in the Life of Hermann Staudinger*

Wallace Carothers was a remarkable scientist with great accomplishments (Figure 5). Not only did he lay the foundation for significant commercial advances but firmly established polymer science as a major component of organic chemistry. His work transformed DuPont from a powder company to a textile entity. It initiated dramatic changes in the well-being, first of US citizens and then for people around the world. Students are captivated by several aspects of his life – his early struggles to get an education, his interaction with Roger Adams and Carl Marvel as a graduate student at the University of Illinois, his enticement out of academia to initiate a research program at DuPont, his meticulous attention to detail, his significant accomplishmetns in founding polymer science and, of course, his long and ultimately unsuccessful struggle with depression.

**Wallace Hume Carothers**

Born, Burlington, Iowa, 27 April 1896

Entered Capital City Commercial College in Des Moines in 1914. Graduated a year later with a degree in accountancy and secretarial administration.

B.S. in Chemistry, Tarkio College, 1920

M.S. Chemistry, University of Illinois, 1921

Faculty appointment at the University of South Dakota, 1921

Returned to the University of Illinois to work with Roger Adams, 1922 (mentored by Adams and Carl Marvel)

Ph.D. Organic Chemistry, University of Illinois, 1924

Recruited by Harvard
Lured away by DuPont

- ➢ Anxious to find the best organic chemist in the country to head a new research effort

Established a firm basis for Staudinger's ideas based on simple organic reactions that everyone understood and accepted [1929, key paper in the Journal of the American Chemical Society]

- Many fundamental advances
- Neoprene [Poly(chloroprene)]
  - Poly(ester)s
  - Poly(amide)s
  - Nylons (Synthetic silk)
  - Apparel revolution

*Figure 5. Milestones in the Life of Wallace Carothers*

Of course, the development of greatest impact during this period was the synthesis and commercialization of nylon 6,6. The nylon story (see Chapter 9) is notable in several respects (*14–17*). Of all the possible poly(amide) structures examined, nylon 6,6 was selected for commercialization for several practical reasons. Both monomers, adipic acid and hexamethylenediamine could be produced from cyclohexane which could be obtained in relatively high purity

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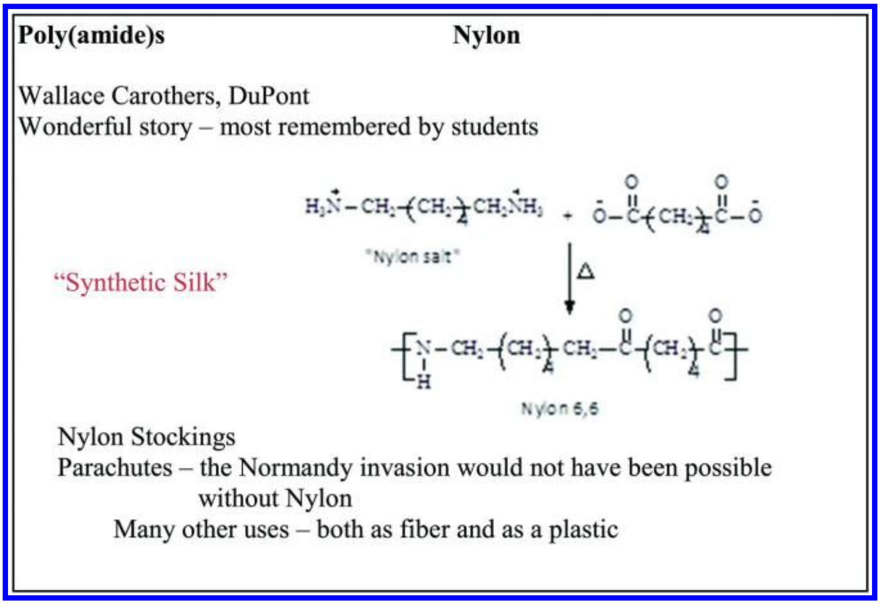
by hydrogenation of benzene. Secondly, the 1:1 salt from adipic acid and hexamethylenediamine, “nylon salt”, could be purified by crystallization. This assured that the monomers were present in pure form and in 1:1 stochiometry for polymerization (Figure 6).



**Poly(amide)s** **Nylon**

Wallace Carothers, DuPont
Wonderful story – most remembered by students

“Synthetic Silk”

Nylon Stockings
Parachutes – the Normandy invasion would not have been possible without Nylon
Many other uses – both as fiber and as a plastic

*Figure 6. Production and Applications of Nylon 6,6.*

The commercialization of nylon 6,6 had a dramatic and immediate influence on the fashion world. At the time, the most prized fiber for ladies stockings was silk. However silk is produced by an organism that must be maintained in a carefully controlled environment (both temperature and humidity must be controlled) and fed a special diet. As a consequence, silk was not available in large amounts and was expensive. Only the elite could have silk stockings. Stockings made from nylon 6,6 fiber were unveiled at the 1939 World’s Fair and were an instant sensation. Demand for these new stockings was immense – stores limited sales to one pair per person but were constantly sold out. Within a few months, nylon stockings were no longer available. Every bit of nylon available was required for the war effort. The landing of paratroopers at Normandy would not have been possible without the availability of nylon for the construction of the parachutes. After the war was over nylon stockings again became available - in initially limited supply but to an enthusiastic audience. So popular were the new stockings that the term “nylons” largely replaced stockings in the vocabulary of the consuming public (*18*). Nylon was so popular that after the war wedding dresses were often made from nylon cut from parachutes purchased from military surplus.

Much later poly(amide)s derived from aromatic diacids and aromatic diamines were also developed at the DuPont company (Figure 7). In this case, the development can largely be attributed to Stephanie Kwolek, a woman of small stature but large accomplishment. These materials were termed “aramids” to distinguish them from the more traditional nylons. These polymers are specialty materials with unique properties.

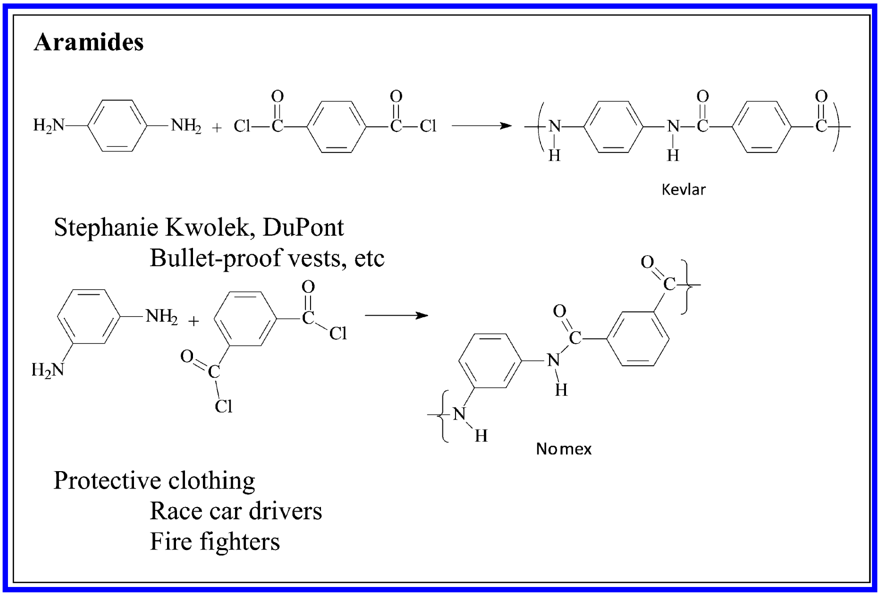


Figure 7. Development of Aramids

The polymer generated from the symmetrical monomers is known as Kevlar. Kevlar fibers are used for the production of bullet-proof vests used by the police and military personnel. Because of its great strength, it is also used as reinforcing fiber in the production of high-tech polymer composites used in the construction of railroad tank cars and other structures for which sturdiness is required. The polymer from the unsymmetrical monomers is known as Nomex and is resisitant to ignition. It is used for the manufacture of clothing used by fire fighters and race car drivers.

The war years were a period of enormous growth for organic chemistry and for the development of polymeric materials, in particular (Figure 8). In the United States, Carl Marvel (Figure 9) was a principal participant in much of this (*19*). Many new materials were developed during this period. Perhaps, most notable was the development of new materials for the production of tires needed for trucks and aircraft to support the war effort.

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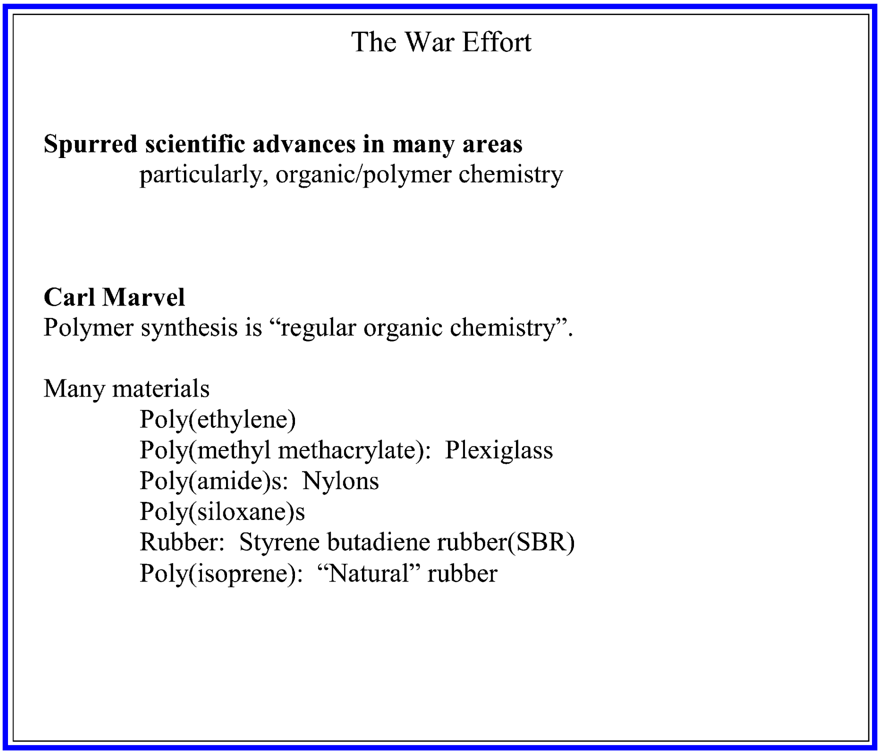

The War Effort

**Spurred scientific advances in many areas**
particularly, organic/polymer chemistry

**Carl Marvel**
Polymer synthesis is “regular organic chemistry”.

Many materials
Poly(ethylene)
Poly(methyl methacrylate): Plexiglass
Poly(amide)s: Nylons
Poly(siloxane)s
Rubber: Styrene butadiene rubber(SBR)
Poly(isoprene): “Natural” rubber

*Figure 8. Materials Development During World War II*

Prior to the war the need for rubber was met by importation of natural rubber from the far East. With the Japanese occupation of this area, rubber was no longer available to the United States. This presented a very precarious situation. To deal with this emergency, the Rubber Reserve Company was formed to bring together scientists from the rubber companies, several academic institutions and the government to develop elastomer substitutes for rubber that could no longer be imported (*20*).

This was no easy task but much progress was made and the crisis resolved (Figure 10). Marvel was a leader in this effort and was a member of the team sent to Germany after the war to assess progress made by that country during the war.

Marvel was remarkable in other ways as well. He completed a distinguished career at the University of Illinois, retired there, and moved to the University of Arizona where he had a second career and made significant contributions to the development of thermally stable polymers. While at the University of Illinois, Marvel served as a mentor to a young Wallace Carothers. Marvel, of course, strongly influenced Carother’s development as a chemist but, perhaps, more importantly he would often suggest a trip to an outdoor location when a bout of depression would begin to descend on Carothers. This was usually effective in bringing Carothers back to his normally functional state. Marvel also became an avid bird watcher. On consulting trips he would often stop suddenly as he caught sight of a bird that he hadn’t seen before.

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**Carl Marvel**

- Born, 11 September 1894, on a farm in Illinois
- B.S. Chemistry, Illinois Wesleyan University, 1915
- Entered the graduate program at the University of Illinois with a stipend of \$250/year, 1915. Earned the nickname “speed”.
- Ph.D. Organic Chemistry, University of Illinois, 1920.
- Joined the chemistry faculty at the University of Illinois, 1920.
- Major contributions to *Organic Synthesis*.
- Became a consultant to DuPont, 1928: continued for 60 years
- Served as a mentor to a young Wallace Carothers
- Full Professor, 1930; retirement in 1961
- Joined the faculty at the University of Arizona: began a second career – high temperature polymers [polybenzimidazole]s.
- Formal retirement from the University of Arizona, 1978; continued to work for several more years.
- Many honors including the Priestley Medal, 1956.
- Membership in ACS for 74 years; president, 1945.
- Founder of the High Polymer Forum that became the ACS Division of Polymer Chemistry; Chairman, 1950-1951.
- Both the universities of Arizona and Illinois have annual Marvel Lectureships and Marvel Scholarships.
- A major ACS award is named in his honor
- The Carl Shipp Marvel Laboratories of Chemistry at the University of Arizona and Marvel Hall at ACS headquarters in Washington, DC, named in his honor.

>>> US Synthetic Rubber Program, 1942-1955.
Headed a group of over 100 chemists.
Coordinated the efforts of many universities and industrial laboratories.
Member of the technical intelligence team that surveyed German polymerization efforts during the war.

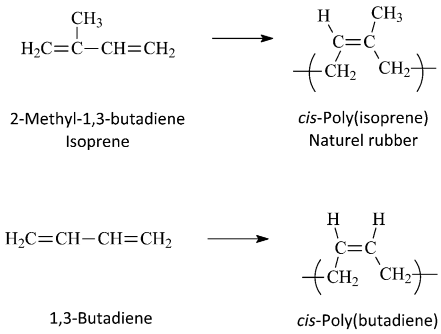
*Figure 9. Milestones in the Life of Carl Marvel*

**Diene Polymers : Elastomers**

War effort
Rubber Reserve Company (RRC)
cis-Poly(isoprene)
B. F. Goodrich (Gulf Oil)
1954 Ziegler catalyst
Firestone 1955
Shell

Styrene – butadiene Rubber (SBR)

Poly(isobutylene) Butyl Rubber



$H_2C{=}C(CH_3){-}CH{=}CH_2$

2-Methyl-1,3-butadiene
Isoprene

*cis*-Poly(isoprene)
Naturel rubber

$H_2C{=}CH{-}CH{=}CH_2$

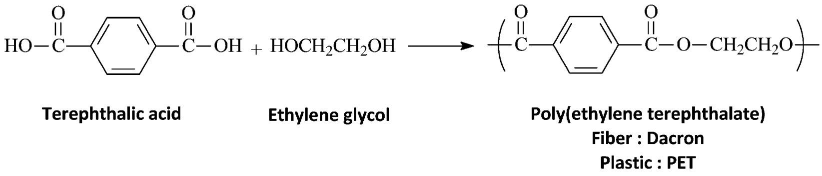
1,3-Butadiene

*cis*-Poly(butadiene)

*Figure 10. Development of New Elastomeric Materials During World War II*

Other major developments which occurred during this period include the synthesis of poly(ethylene terephthalate) (PET) by Whinfield and Dickson at the Calico Printers Association (Figure 11). This technology was licensed to ICI and DuPont. The polymer, PET, has found a large variety of uses as both a plastic and a fiber. Much of the clothing produced today contains PET fiber. The inclusion of PET fiber enhances wearability and appearance of articles of clothing. Many items are produced from blends of PET and cotton, a natural polymer. The PET provides durability while the cotton provides warmth of feel by hydrogen bonding a monolayer of water at the surface. As evidenced by observing an old tee-shirt, the cotton is subject to deteoration while the PET is not to leave a mesh of PET fiber.

**Poly(ester)**
**Poly(ethylene terephthalate)**



J. R. Whinfield and J. P. Dickson
Calico Printers Association
Patent applied for July, 1941 ; granted 1946.

Patent sold to ICI for outside US (1947)
to DuPont for inside US (1946).

Fiber
Clothing, carpeting, uphostery, curtains

Plastic
Trays, milk jugs

*Figure 11. Development and Uses of Poly(ethylene terephthalate)*

Poly(carbonate) is a useful material generated commercially from phosgene and bisphenol A. It is used in many applications in which impact strength is important (Figure 12). Students are impressed that their automobile bumper is made from poly(carbonate) and that it readily passes the 5 mph crash test mandated by the government.

Poly(urethane)s are generated from an isocyanate [toluene diisocyanate (TDI) is the traditional isocyanate used; methylenediphenyl diisocyanate (MDI) is also widely used] and a diol. The size of the diol may vary depending on the particular properties desired for the polymer. Often the diol is an oligomeric material derived from ethylene or propylene oxide (Figure 13).

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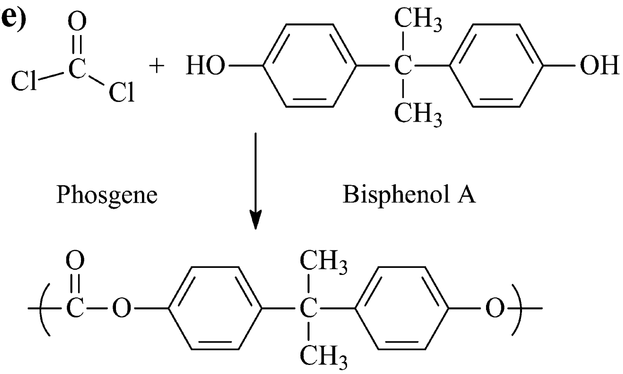
**Poly(carbonate)**



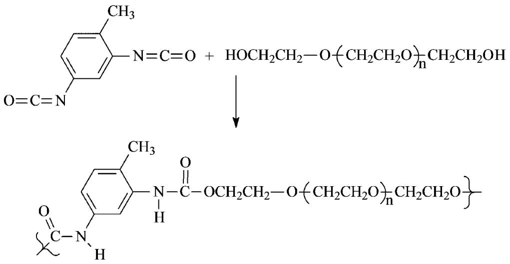
Fox, General Electric

Poly(carbonate) Lexan

Helmets, automobile bumpers
Many others

*Figure 12. Preparation and Uses of Poly(carbonate)*

**Poly(urethane)s**



Otto Bayer, I. G. Farben, 1937

Range of structures, properties
- Insulation
- Automobile seats
- Many other

*Figure 13. Preparation and Uses of Poly(urethane)*

Poly(urethane)s have a wide range of uses from adhesives and tough coatings to foamed materials for insulation, automobile construction, manufacture of running shoes, etc. Expansion of poly(urethane) to generate a foamed material may be achieved by addition of water to the polymerization mixture. Water reacts with the isocyanate to generate a carboxylic acid which readily decarboxylates to generate carbon dioxide which promotes expansion and the formation of cavities within the material. The density of the prodeuct is determined by the amount of water added and consequently, the volume of blowing agent generated. The modern automobile seat represents a marvelous application of this technology. The density of the matetrial decreases as the height from the floor increases, i.e., near the floor the density of the material is quite high to provide support but decreases gradually and is low at the top to provide comfort.

Epoxy resins represent another important class of materials with a variety of uses particularly in the electronics industry (circuit boards, etc.) and as adhesives (Figure 14). Most students have experience with simple epoxy adhesives and appreciate learning the chemistry involved.

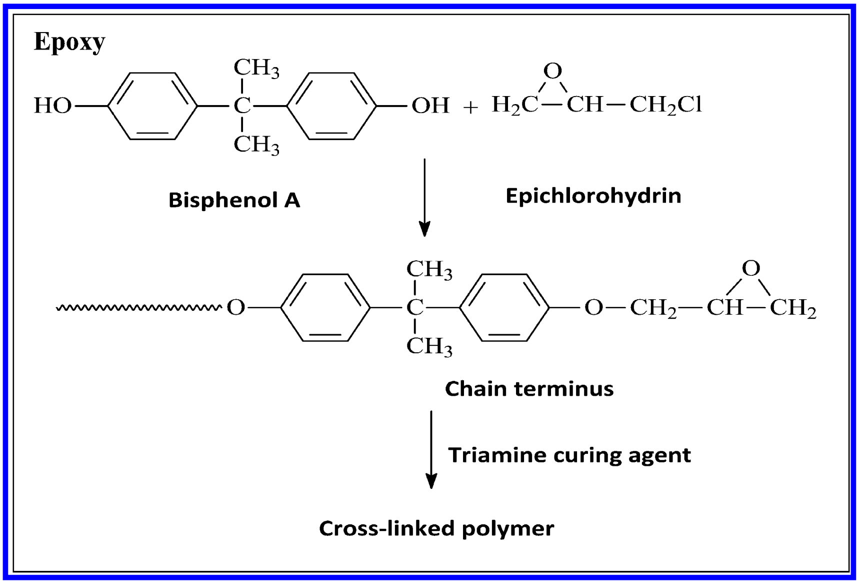


*Figure 14. Formation and Crosslinking of Epoxy Resin*

## Conclusions

The incorporation of polymeric materials into the beginning course in organic chemistry generates student appreciation for the practical value of organic chemistry and its impact on their lives. Students are impressed to learn that virtually every aspect of their daily lives are, in some way, enhacnced by polymeric materials. Providing a bit of historical context for the development of these materials and a discussion of some of the interesting personalities involved enhances student interest, generates enthusiasm, and leads to better course outcomes.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch011

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch011

## Chapter 12

# Why Should Anyone Want To Teach Polymers in a Chemistry Class?

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch012

This chapter describes the Nobel Prizes awarded to people studying polymers. Emphasis below is on the synthesis and structure of polymers, with examples.

## Introduction

The purpose of this chapter will be to illustrate several reasons why the teaching of polymers in a chemistry setting is important in the 21st century. Since probably all of the readers know and respect the Nobel Prizes, this chapter will start there.

## Nobel Prizes Awarded for Polymer Advances

1. Sir Norman Haworth, 1937, Chemistry, studied the structure of starch and cellulose, both natural saccharide polymers, and closely related in structure. While starch is well known as being in foods, cellulose is noted as being a 90+ percent component of cotton, and a 50+ percent component of wood. He worked out the structure of both, and in addition to determining the structure of the sugar mer, he determined how they are linked together.

2. Hermann Staudinger, 1953, Chemistry, published the "Macromolecular Hypothesis," which described the chain structure that makes a chemical a polymer (*1*). For the first time, a highly respected chemist described the difference between colloids and polymers. At that time, many academic professors thought that all of these compounds would really be shown to be colloids. (More on this topic below.)

3. Karl Ziegler and Giulio Natta, 1963, Chemistry, developed a series of catalysts that produced stereospecific polymers like isotactic polypropylene. In

In Introduction of Macromolecular Science/Polymeric Materials into the Foundational Course in Organic Chemistry; Howell, B.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

isotactic polymers, all the side groups, one per mer, were lined up on the same side of the polymer chain. This new class of polymers were more easily crystallized, and produced stronger fibers, etc.

4. Paul J. Flory, 1974, Chemistry, described the "random coil" and organization of polymer chains. Most of his early work was in dilute solutions. He showed that the chain "random coil" resembled a long piece of string in water of the same density. The string was randomly coiled, in the sense that one part of the string did not know where the other parts beyond being attached were. The only major correction was that one piece of the string could not go through another part. However, in a dilute solution that probability was low, so the correction was small and ignored for many calculations.

5. Pierre G. de Gennes, 1991, Physics, described the reptation of polymers and polymer structures at interfaces. The "reptation" motion somewhat resembles what one sees looking into a can of healthy earth worms on a fishing trip. That is, that small segments of the chain moved randomly in one direction or the other under thermal forces. The collection of these small motions served to move the whole chain. De Gennes was the only physicist, so far, to earn the Nobel prize for polymer work. His work was really at the interface between chemistry and physics, but he was a physicist, and got the physics prize.

6. Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock, 2005, Chemistry, for the development of the metathesis method in organic synthesis, leading to novel polymers. This is a novel synthetic method and has made new classes of polymers.

Thus, six Nobel prizes have been awarded to date for advances that led to the modern science of polymer chemistry.

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## How Did Polymers Come to America?

In the 19th century and early in the 20th century, there was a "struggle" going on between chemists in Europe, those primarily believing in polymers, and those thinking they were colloids. The polymer view went to industry first in Europe, while the academics thought it was all nonsense, and that the truth was in colloids. The polymer view went to industry first in America also. In America, Carothers, working at du Pont undertook research resulting in Nylon. He got his information reading advances in European industries.

What? Polymers were nonsense??? See for example, the book by H. Morawetz, "Polymers: From the early 1920's The Origins and Growth of a Science" (*2*). In Ch. 10, for example, he quoted H. Wieland: "Drop the idea of large molecules, organic molecules with a molecular weight higher than 5000 do not exist..." etc. etc. Morawetz had first hand information on this topic, having been raised and educated in Europe.

A few others, polymer people such as Herman Mark, came to America (in 1941 for Mark) (*3*) as refugees, seeing what was taking place in Europe. Mark became a professor at Brooklyn Polytechnic University, and was perhaps the strongest single person in America to champion the idea that there was a class of "colloids" that were really long chained materials known as polymers.

To a significant extent, it seems, the industrial people accepted polymers first, because the use of polymeric ideas led to the easier solution of industrial chemical problems and the synthesis of new, exciting materials. The academics in Europe resisted longer. At that time, if young American scientists wanted a "better position", they went to Europe to get their Ph.D. or do a post-doc. This gave them a stamp of approval greater than equivalent studies in America. (Note that this reversed entirely after World War II ended: Now, getting an advanced degree in America is the stamp of approval for a better position when foreign students return home.) However, since the European academics didn't believe in the polymer chain structures, their students carried those ideas back into American academics to a significant extent.

## A Few Synthesis Examples

Now, it is time to integrate polymers into both textbooks and day-to-day lectures, so that students will be better prepared. Note that somewhere between a quarter and a third of all chemists are active in polymer research in America right now! We must prepare them better while they are still students! Below, please find a few example syntheses that ought to attract some attention in text books as well as in the classroom:

One of the most common plastics, and one with the simplest chemical structure is polyethylene, a plastic film widely used for wrapping store-bought objects, etc. It requires a source of free radicals, R·, and the monomer ethylene *(4a)*:

$$R\cdot + \; nH_2C{=\!=}CH_2 \;\text{------>}\; (-CH_2-CH_2-)_n \qquad (1)$$

This indicates that n-mers are attached end on end. While termination can take place by several mechanisms, the meeting of two free radicals to make the polymer chain the total length of both of them is one important mechanism.

Another kind of polymerization involves condensation, an example being Nylon. The ordinary Nylon is a polyamide synthesized as follows *(4b)*:

$$nNH_2\text{-}(CH_2)_6\text{-}NH_2 + nCO_2H\text{-}(CH_2)_4\text{-}CO_2H \;\text{----->}\; NH_2\text{-}(CH_2)_4\text{-}CO\text{-})_n + (2n-1)H_2O \qquad (2)$$

Nylon was first used for lady's stockings, but is now used for many clothing items, and also parachutes, etc. The Nylon described above is frequently termed 6,6-Nylon, because both mers have six carbon atoms. Many other versions have been synthesized, and many are commercial as well.

This illustrates two of the more important routes to synthesize polymers. The polyethylene is a free radical reaction, while the polyamide reaction is a condensation reaction. The two reactions above were selected because everyone of college age has probably handled both of these many times. While both of these polymers are crystalline as ordinarily used, many others are amorphous, such as polystyrene, $(-CH_2-CH(C_6H_5)-)_n$, the major component of soda drinking cup tops in restaurants, etc. Should anyone become highly interested in drinking cup tops, the slightly cloudy appearance is caused by a few percent of a rubbery (also polymeric) material being added, which makes the material much tougher.

Try bending one of these tops back and forth: they don't break easily! There are several books on polymer structures and synthesis.

The reader has already been introduced to Odian's book (*4*). Other books illustrating polymer syntheses and structures include Carraher's book (*5*) and Gnanou and Fontanille's book (*6*).

Besides the ordinary synthetic polymers described above, there are many natural polymers, such as the proteins and DNA, as well as the cellulose and starch described above.

## Applications and Current Research

According to the American Chemistry Council, 75.7 billion pounds of plastics were produced in the United States in 2012 (*7*). Polymers include plastics, rubber, adhesives, coatings, fibers, and films. Some of these have been mentioned above. New polymers are being synthesized in many laboratories, many with an interest in bio applications. For examples, contact lenses and bone and joint replacements are in wide use, and are constantly being improved.

In addition, proteins and DNA are natural polymers, with more complex structures than the usually repetitive structures of the synthetic material. A huge amount of effort is being extended to better understand the biopolymers. The reader should also note that there are several polymer oriented journals, Journal of Polymer Science, Macromolecules, Journal of Applied Polymer Science, Biomacromolecules, Macromolecular Chemistry and Physics, Polymer, as well as others.

## Conclusions

While there are several routes to making polymers, the two oldest, and most widely used, are described above, along with some historical events illustrating how the field of polymers came to be. The field is growing very rapidly, and every B.S. or above chemist should understand how they are made and what kinds of structures will have the physical properties to produce polymers for new purposes. While many aspects of polymers are "practical", there are also huge advances being made in theory, new syntheses, and new properties (*5*, *6*).

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch012

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch013

## Chapter 13

# Computational Modeling of Anionic Block Copolymerization Kinetics for Organic Chemistry Pedagogy

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A computational algorithm was created using system dynamics software in order to model the kinetics of sequential addition anionic living *multi*-block copolymerization for vinyl monomers initiated by alkyl lithium reagents for organic chemistry pedagogy. The number average degree of polymerization and polydispersity index were computed over time as a function of reaction temperature as well as impurity concentration and compared to previously reported data. The temperature dependence of the rate constants for initiation and propagation were modeled using the Arrhenius equation. Interactive modeling during the foundational course in organic chemistry causes the student to forge a valuable link between proposed reaction mechanisms and laboratory kinetics. Students must consider p$K_a$ differences with regard to anionic intermediate species concerning initiation, proposed block sequences, and overall polymer structure-property-processing relationships.

## Introduction

Foundational undergraduate organic chemistry lecture exercises are conventionally aimed at applying a variety of learned fundamental mechanisms in order to predict the reaction products for archetypical systems stemming directly from well established laboratory data. In most circumstances, these exercises focus student attention on merely identifying the proposed reactive intermediate and/or product by directly applying mechanistic reasoning. Within a physical chemistry class, the link between the molecularity of each proposed elementary mechanistic step, possessing a single activated complex, is routinely emphasized (*1*). In contrast, the connection between observed reaction kinetic data with mechanistic reasoning is not routinely accentuated throughout a conventional foundational course in organic chemistry (*2*). Utilizing the junction between proposed mechanism and laboratory kinetic data where applicable causes organic chemistry to be less of a series of required functional group transformations and concomitant reaction conditions than a fundamental mechanistic reasoning approach garnered *via* laboratory reaction kinetics and spectroscopic techniques. Hence, modeling is used herein to pedagogically reinforce the bond between kinetic laboratory data and mechanistic organic chemistry learning.

Polymerization chemistry, due to its clearly defined set of elementary kinetic steps, provides an excellent instructional archetype for synthetic mechanistic pedagogy *via* kinetic observation (*3*, *4*). Nevertheless, polymer chemistry is routinely isolated within the conventional organic lecture course sequence and furthermore routinely relegated to the end of the organic chemistry textbook (*2*, *5–10*) if covered at all (*11*, *12*). Hence, polymerization customarily plays a small role in the fundamental organic chemistry lecture course sequence although it is arguably among the most vital areas of industrial chemistry (*13*, *14*). Although pedagogical anionic polymerization laboratory exercises have been published to date (*15–21*), interactive polymerization modeling exercises (*22–26*) to accompany organic chemistry lectures are not nearly as plentiful wherein no pedagogical exercises particular to sequential monomer addition anionic living block copolymerization models exist.

The kinetic modeling depicted herein was generated by undergraduate physical chemistry students studying organic reaction kinetics and thermodynamics. The models were used for the instruction of organic chemistry students studying reaction mechanisms following conventional functional group themes (*2*, *5–10*). The type of practical and interactive polymerization kinetic models presented herein allow Organic Chemistry I/II students to begin to investigate and better understand the governing reaction kinetics and rate determining steps used to rationalize the plethora of mechanisms which they are routinely asked to learn (*27*). The model herein utilizes a graphical interface differential equation problem solver to specifically map the anionic polymerization of olefins such as styrenic and alkyl esters of acrylic acid monomers as well as diene molecules. Given their Arrhenius energetics for propagation, the kinetic model can also incorporate monomers which are anionically polymerizable in a living manner possessing labile functionalities other than alkenes such as *n*-alkyl *mono*isocyanates for backbone rigidity (*28*). Styrene ($C_6H_5$-CH=$CH_2$) was chosen as a model system here primarily due to the plethora of available physical and reactivity data for this particular monomer (*29*). This project allows organic chemistry students to depict the influences of physical variables, such as temperature and impurity concentration as well as monomer identity, on the rate of propagation *via* Arrhenius rate constants. The kinetic model flowcharts tend to be challenging to initially envisage by a

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch013

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physical chemistry student but relatively facile to diagram and encode within the Berkeley Madonna® program (*30*). Nevertheless, the models tend to be highly user-friendly for a foundational organic chemistry student routinely producing coherent results represented in a concise, graphical manner.

Introducing individual polymerization mechanisms within the context of analogous small molecular weight organic mechanisms is highly advantageous. Anionic polymerization is conventionally introduced within the latter stages of an elementary organic chemistry course sequence as an isolated topic within a chapter on polymer chemistry (*2*, *5–10*). However, anionic polymerization can be most appropriately introduced within the section covering carbonyl compounds reacting at the α-carbon atom and more specifically as a corollary to the carbonyl condensation Michael reactions (*2*). A classic Michael reaction involves the conjugate (1,4-) addition of a resonance stabilized enolate (Michael donor) to the β-carbon atom of an α,β-unsaturated carbonyl system (Michael acceptor). Analogously, in anionic polymerization a carbanion nucleophile (Michael donor) attacks the π-bond of a vinyl monomer (Michael acceptor) creating a covalent C-C single bond as well as a new carbanion in a merely repetitive fashion thereby monotonically increasing the chain length (*i.e.* degree of polymerization) and molecular weight. Furthermore, alkenes possessing pendant electron withdrawing groups capable of resonance delocalization, such as the styrenic aromatic ring system, tend to greatly stabilize the growing carbanionic vinyl chain end moiety and significantly enhance anionic polymerizability. For monomers which undergo anionic polymerization, propagation tends to continue (*i.e.* remain living) until all monomer molecules have been consumed in the absence of adventitious acid (water) or an electrophile ($CO_2$) to terminate the living chain end.

Hence, the anionic living polymerization of appropriate vinyl monomers can be introduced during discussions of Michael reactions as a mere repetitive conjugate addition with the important capability of producing *multi*-block copolymer architectures *via* sequential addition (*31–33*). Block copolymers (*34*) routinely undergo a fascinating composition dependent microphase separation (*35*) and domain formation (*36*) due to a thermodynamic driving force. Furthermore, mismatch between the block chain stiffness (*i.e.* rod-coil) leads to *self*-assembly (*37–39*) and novel model morphologies (*40*, *41*). Due to their inherent microphase separation, ABA *tri*-block copolymer sequences with alternating hard and soft segments conventionally serve industrially as thermoplastic elastomers (*32*, *42*, *43*), whereas one particularly advantageous practical utility of AB diblock copolymer architectures lies in the area of compatibilizers for *homo*polymer blends (*44–46*). Herein we offer a novel pedagogical model individually detailing the kinetics of anionic living *multi*-block copolymerization possessing flexibility in monomer identity and block sequence (*47*).

## Theoretical Basis

Anionic polymerization of an appropriate monomer (*M*) is initiated in the presence of a highly reactive nucleophilic organometallic compound (*I*) such as an alkyl lithium (RLi) reagent as governed by the second order rate constant for initiation, $k_\mathrm{i}$, wherein the rate of initiation ($R_\mathrm{i}$) = $\{k_\mathrm{i}\ [I]\ [M]\}$. As general rule, the p$K_\mathrm{a}$ value for the conjugate acid of the anionic propagating intermediate formed from the monomer should lie below the corresponding p$K_\mathrm{a}$ of the initiator ($I$). For a monomer such as methyl-α-cyanoacrylate (p$K_\mathrm{a} \approx 11$) possessing two electron withdrawing substituents, relatively mild nucleophilic initiators (cyanide, bromide, amines, bicarbonate, water, and phosphines) can be used. However, for styrenic monomers (p$K_\mathrm{a} \approx 43$), relatively strong nucleophilic initiators such as alkyl lithium reagents (p$K_\mathrm{a} > 50$) must be employed. The rate of styrene initiation by *n*-butyl lithium is assumed to be both efficient and much faster than propagation for anionic polymerization allowing the assumption that $[\mathrm{M}^-] \approx [I]_\mathrm{o}$ as well as a steady state approximation for the reactive intermediate anionic chain end, $[\mathrm{M}^-]$ (*29*). The living carbanion ($\mathrm{M}^-$) functions as a nucleophile and attacks the π-bond of another alkene monomer ($M$), thereby creating a new carbanion on the monomer's more highly substituted carbon atom (C-2) in a consistent head-to-tail manner. Propagation is governed by an apparent second-order rate constant, $k_{p,app}$, wherein block copolymerization reactions tend to be first order in $[M]$, first order in $[\mathrm{M}^-]$, and second-order overall. Hence the rate of propagation ($R_p$) = $-d[M]/dt$ = $\{[k_{p,app}[M][\mathrm{M}^-]\}$ = $-J_i$, with the $i^\mathrm{th}$ monomer's initial molar concentration $[M]_{o,i}$ set by the program user. Nevertheless, each rate constant ($k$) modeled herein has an associated activation energy ($E_\mathrm{a}$) and *pre*-exponential factor ($A$), such that $k = \{A exp(-E_\mathrm{a}/RT)\}$ according to the Arrhenius equation, where $R$ is the gas constant and $T$ represents the temperature in Kelvin.

The apparent rate constant for propagation ($k_\mathrm{p,app}$) is actually the sum of the rate constants for propagating free anions ($k_\mathrm{p}^-$) and solvent separated ion pairs ($k_\mathrm{p}^\pm$), which are in equilibrium as governed by a temperature dependent equilibrium constant for dissociation, $K_\mathrm{d}$ (*48–50*). The propagation rate constant for solvent separated ion pairs ($k_\mathrm{p}^\pm$) is further fractionated into a rate constant for contact ion pairs ($k_\mathrm{c}$) and solvent-separated ion pairs ($k_\mathrm{s}$) *via* a temperature dependent equilibrium constant, $K_\mathrm{cs}$ (*51*, *52*). Both $K_\mathrm{d}$ and $K_\mathrm{cs}$ have been shown to vary with temperature ($T$) according to the thermodynamic equation for a reaction isotherm $\{ln\ K = -\Delta H/RT + \Delta S/R\}$ given both the enthalpic ($\Delta H$) and entropic ($\Delta S$) changes for the dissociative ionic and contact ion-solvent separation processes respectively (*29*). Hence, for a polymerization reaction $K_\mathrm{d}$ and $K_\mathrm{cs}$ can be estimated as a function of $T$ using the van't Hoff equation assuming a constant enthalpy change ($\Delta H$) over the temperature range of interest. Nevertheless, a very narrow range of anionic polymerization systems are available which report accurate values of both $k_\mathrm{p}^+$ and $k_\mathrm{p}^\pm$ for modeling (*29*, *53*). Hence, the operative apparent rate constant for anionic propagation of each monomer ($k_{p,app,i}$) (*54–60*) was used for pedagogical modeling reported herein. Anionic *homo*polymerization was merely amplified to model sequential addition *multi*-block copolymerization kinetics set initially at standard ambient temperature and pressure (SATP), where temperature ($T$) = 298 K and pressure ($P$) ≈ 1 atm.

Sequential addition of the $i^\mathrm{th}$ monomer within a *m*-block copolymer sequence was modeled utilizing a total delay time ($t_{d,i}$) set as the functional sum of all the preceding monomer's propagation half-lives ($t_{1/2,p,i}$) = $\{1/(k_{p,app,i}\ [M]_{o,i})\}$, such that $\{(t_{d,i}) = \sum_1^{i-1}\ [10(t_{1/2,p,i}]\}$, wherein $\{[M]_{i-1}(t)/[M]_{o,i-1} \leq 10^{-3}\}$ at the time of

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch013

the subsequent addition of the $i^{th}$ monomer. Hence, the increase in concentration for each polymer block was simply set as $\{d[Block_i]/dt = +J_i\}$, where initially $\{[Block_i]_o = 0\}$. For the block concentrations delayed by time ($t_{d,i}$) *via* subsequent addition, $\{d[Block_iDelayed]/dt = +J_1 + \sum_2{}^i J_{i,delayed}\}$ with $\{[Block_iDelayed]_o = 0\}$. Given the starting initiator concentration $\{[I]_o\}$ and the initial concentration for each monomer $\{[M]_{o,i}\}$ by the user, the effect of impurity fraction ($f_i$) within each monomer addition on the number average degree of polymerization for each block ($X_{n,block,i}$) was calculated by the model assuming immediate reaction of the anionic chain end with the adventitious impurity. The extent of reaction for the $i^{th}$ monomer, $\{p_i(t)\} = \{([M]_{i,o} - [M]_i(t)) / [M]_{i,o}\}$ and as such the total number average degree of polymerization, $\{X_{n,total}(t)\} = \sum_i{}^m{}_{=1} X_{n,block,i}(t) = \sum_i{}^{m=1} \{(p_i(t)[M]_{i,o})/([I]_o-(\sum_i f_i))\}$. Hence, the modeled effect of system impurities on molecular weight was cumulative upon each subsequent monomer addition. The impurity effect was observed merely as an increasing overshoot of the target number average degree of polymerization for each block ($X_{n,block,i}$) and ultimately the total number average degree of polymerization ($X_{n,total}$) for the block copolymer as $i \rightarrow m$.

Modeling was accomplished using Berkeley Madonna® version 8.3.18 system dynamics software (*30*) which possessed a graphical interface differential equation solver (GIDES). Berkeley Madonna® was used to solve systems of both ordinary differential equations (ODE)s as well as more simple linear and polynomial difference equations (Appendix). Modeling was done using Dell® Vostro 1520 and Dell® Latitude personal laptop microcomputers running the Windows® 7 version 6.1 graphical operating system by Microsoft®. The Berkeley Madonna® equation window required the Java Runtime Environment (JRE 7u6) download. A set of equations including reservoirs, reaction rates, and reagent (reactant, product) flows ($J_i$) as well as a series of physical and thermodynamic constants ($T$, $R$, $E_a$, *etc.*) were utilized (*29*, *54–60*). The RK4 (4th Order Runge-Kutta) fixed step-size method for the approximation of ordinary differential equations (ODE) solutions was used for all modeling herein. A start time, stop time, and incremental step-size time interval ($\Delta t$) were also set as user-defined for input. The Berkeley Madonna® DTOUT command was used throughout the modeling herein to record merely every $x^{th}$ data point in order to significantly reduce computational cost and merely garner kinetic trends for foundational organic chemistry pedagogy.

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## Results and Discussion

For the student, Figure 1 depicts a prospective laboratory apparatus for gram scale, low temperature anionic living AB *di*block copolymerization under an inert atmosphere (*61*) in contrast to the more cumbersome break-seal methods (*62*). *Multi*-block copolymerization would be prospectively accomplished by replacing monomers A and B in addition funnels 1 and 2 by monomers C and D respectively using air-sensitive techniques (*63*, *64*).

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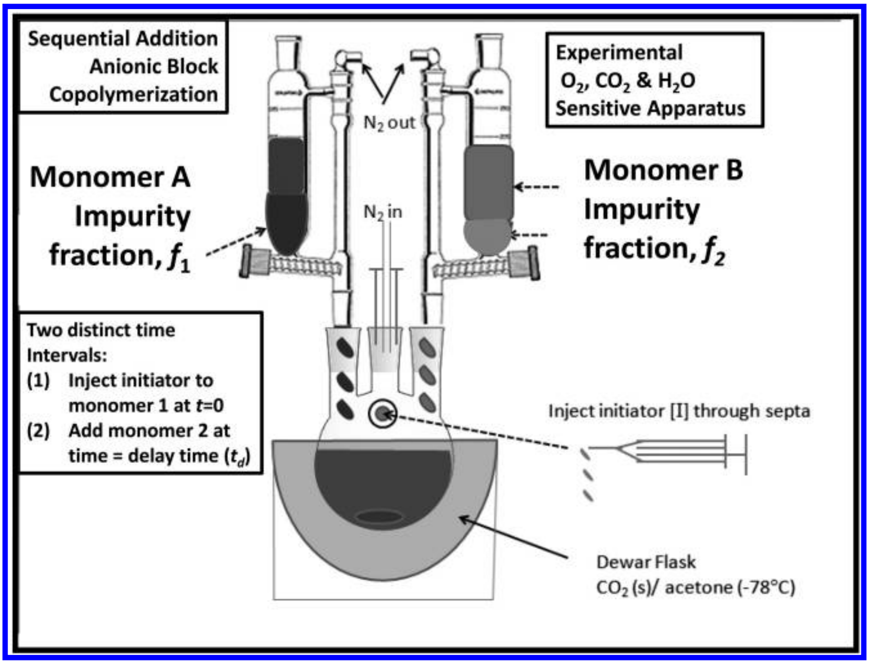

*Figure 1. Research laboratory apparatus and procedure for inert atmosphere anionic diblock copolymerization on the gram scale.*

Figure 2 depicts a flow chart for conversion of monomer A to living *homo*polymer ($PA^-$) and ultimately to living *di*block copolymer $\{PAB^-\}$ upon subsequent addition of monomer B to the living $\{PA^-\}$ solution in the absence of any adventitious impurities (*i.e.* $f_i$ =0 or an ideal reaction case). Hence, the preceding anionic living polymer block is used as the initiator for each subsequent monomer to ultimately create an ABC… *multi*-block copolymer chain sequence.

The initial monomer concentration $[M]_{o,i}$ and impurity fraction ($f_i$) for each addition were set to be controlled by the model program user. The effect of impurity fraction ($f_i$) on molecular weight distribution $\{X_w/X_n\}$ or polydispersity index (PDI) was modeled (*65*) given both $[M]_{o,i}$ and $[I]_o$ as $\{X_w/X_n\} = \{2 [[I]_o / f_i[M]_i(t)]^2 [(f_i[M]_i(t)/[I]_o) + (1 - [f_i [M]_i(t)/[I]_o])\, ln(1 - [f_i[M]_i(t)/[I]_o])]\} = \{(2/u^2)[ u + (1 - u) \ln(u)\}$, where $\{u = (f_i[M]_i(t)/[I]_o)\}$. Hence, the polydispersity index for each block ($PDI_{block,i,f}$) provided a link between experimental gel permeation chromatography (GPC) laboratory data on the polymer and the impurity fraction ($f_i$) for model input. Although it is not facile to solve for the impurity fraction explicitly, $f_i$ can be extracted herein from a simple *x*-*y* plot of $\{f_i(1 – [M]_i(t))/[M^-]_{i-1}\}$ versus $PDI_{block,i,f}$ with a best-fit cubic polynomial trend line such as $\{y\} = \{0.9914x^3 - 5.671x^2 + 11.061x - 6.3689\}$, with a resulting statistical coefficient of determination $\{R^2\}$ value of 0.9996. The impurity fraction ($f_i$) for each monomer addition can be calculated from PDI measured using either GPC or matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) techniques assuming complete extent of reaction ($p_{t\to\infty} = 1$) and hence total monomer conversion ($[M]_{t\to\infty} = 0$) as indicated in Figure 3 below.

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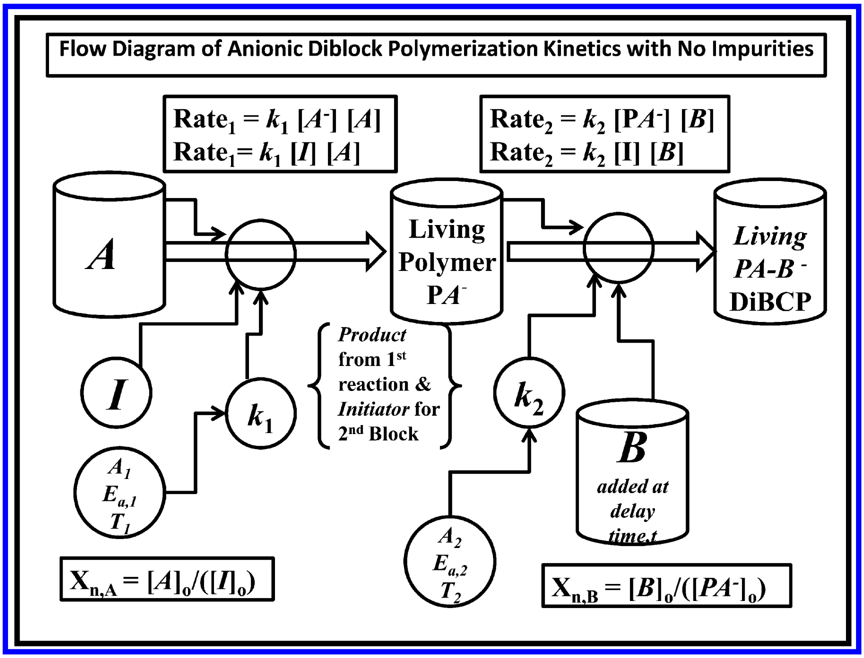

*Figure 2. Flow chart for anionic diblock copolymerization with no impurities.*

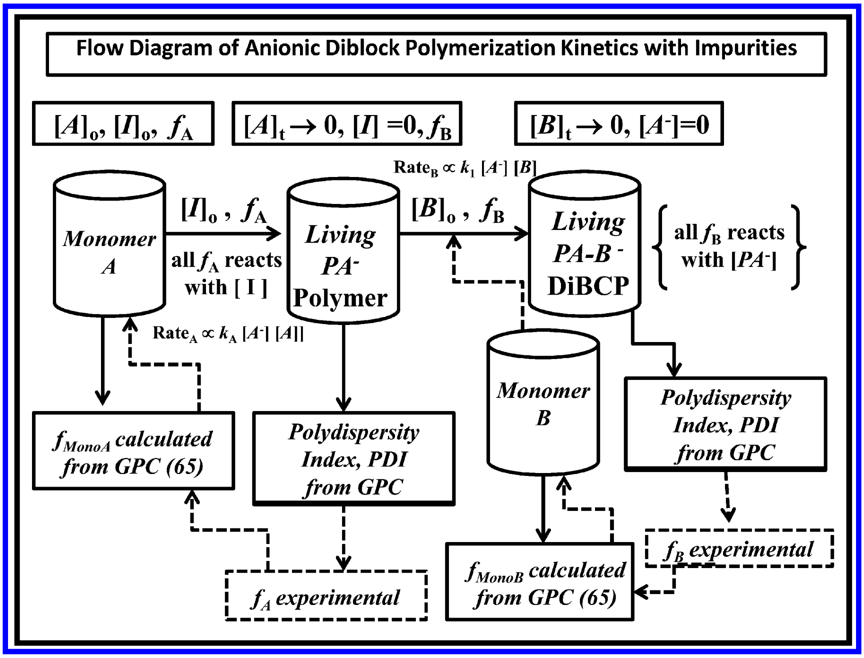

*Figure 3. Flow chart for anionic diblock copolymerization with impurity fraction, $f_i$.*

In order to initially examine the Berkeley Madonna® anionic propagation algorithm, the model parameters were set in accordance with parameters previously reported for the *homo*polymerization of styrene (*66*) with initial monomer concentration ($[M]_o$= 0.288 M) and *sec*-butyl lithium initiator concentration ($[I]_o$= 2.4x$10^{-4}$ M) in cyclohexane solvent at $T$ = 45°C and a second order propagation rate constant, $k_{p,app}$ = 64 L $mol^{-1}$ $min^{-1}$ (*25*, *41*, *42*, *49*). The number average degree of polymerization ($X_n$) was calculated versus time ($t$, minutes) and compared to previously reported data (*66*) as shown in Figure 4.

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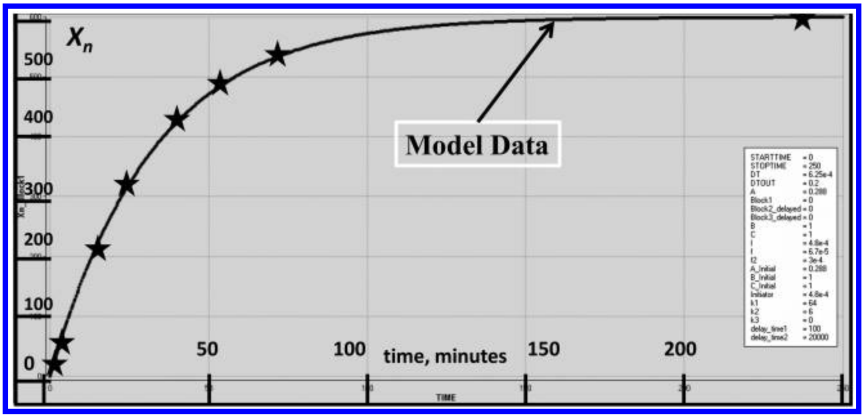


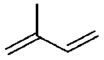
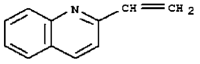
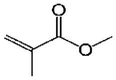
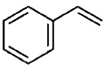
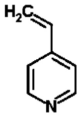
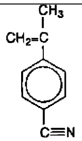
```
STARTTIME       = 0
STOPTIME        = 250
DT              = 6.25e-4
DTOUT           = 0.2
A               = 0.288
Block1          = 0
Block2_delayed  = 0
Block3_delayed  = 0
B               = 1
C               = 1
I               = 4.8e-4
I               = 6.7e-5
I2              = 3e-4
A_Initial       = 0.288
B_Initial       = 1
C_Initial       = 1
Initiator       = 4.8e-4
k1              = 64
k2              = 6
k3              = 0
delay_time1     = 100
delay_time2     = 20000
```

*Figure 4. Number average degree of polymerization for styrene initiated anionically by sec-butyl lithium in cyclohexane solvent at T = 45 °C. Stars represent data taken at finite intervals (66) whereas the line represents data from the Berkeley Madonna® model.*

From the experimental PDI calculated from GPC data measurements (*66*), an impurity fraction ($f_i$) for the styrene *homo*polymerization was calculated to be 6.7x$10^{-5}$ using the $\{(X_w/X_n)_i - f_i\}$ relationship (*65*), wherein ($X_w$) is the weight average molecular weight. Utilizing the calculated ($f_i$) impurity fraction parameter for the $i^{th}$ monomer, excellent agreement was observed throughout the anionic styrene *homo*polymerization between the experimental number average degree of polymerization ($X_n$) (*66*) and the theoretical $X_n$ values calculated using the Berkeley Madonna® model (Figure 4) thereby initially validating the model.

For the Berkeley Madonna® model herein, it is imperative to garner kinetic data for monomers in the same solvent system and counter cation (*gegenion*) conditions. The propagation *pre*-exponential factor ($A_i$) and Arrhenius activation energy ($E_{a,i}$) for a series of vinyl and diene monomers in tetrahydrofuran (THF) solvent with a lithium ($Li^+$) counter cation are listed in Table I.

**Table I. Arrhenius kinetic propagation parameters for selected monomers in THF solvent and $Li^+$ counter cation.**

| *Monomer* | *Structure* | $A_{p,i}$ | $E_{a,p,i}$, *cal mol*$^{-1}$ | *Reference* |
|---|---|---|---|---|
| Butadiene |  | 43,000 | 6100 | 54 |
| Isoprene |  | 10,000 | 6800 | 54 |
| 2-vinyl quinoline |  | $9.6 \times 10^8$ | 7900 | 55 |
| Methyl methacryalte |  | 7.4 | 4700 | 56 |
| Styrene |  | 2980 | 860 | 57 |
| 4-vinyl pyridine |  | $3.65 \times 10^8$ | 12,700 | 58, 59 |
| 4-cyano-α-methylstyrene |  | 14,400 | 3600 | 60 |

From the data in Table I, the apparent (*app*) propagation rate constant ($k_{p,app,i}$) = $\{A_{p,i}\, exp(E_{a,p,i}/RT)\}$, and second order half-life ($t_{1/2,i}$) = $\{1/(k_{p,app,i}\,[M]_o)\}$ of each monomer were calculated for Berkeley Madonna® program input.

Using the kinetic parameters in Table I, anionic living butadiene-isoprene (B-*block*-I) diblock copolymerization was simulated using the Berkeley Madonna® model (*54*). For modeling purposes, the initial monomer concentration $[M]_{o,i}$ = 1.0 M and initiator concentration $[I]_o$ = 0.001 M were user-defined. The data calculated using the Berkeley Madonna® model for monomer concentration $\{[M]_i(t)\}$ and block number average degree of polymerization $\{X_{n,i}(t)\}$ as a function of time for the poly(butadiene-*block*-isoprene) synthesis are shown in Figures 5 and 6 respectively. In Figure 7 the cumulative number average degree of polymerization ($X_{n,total}$) = $\{\sum_i (X_{n,i})\}$ was calculated for a butadiene-*block*-isoprene anionic living diblock copolymerization reaction with no impurities ($f_B = f_I = 0$) compared to the same reaction with a total impurity fraction ($f_{total}$) = 0.0003 ($f_B$ = 0.0001, $f_I$ = 0.0002). A nearly 25% overshoot in $X_n$ was observed over the target total number average degree of polymerization for the adventitious impurity case. Overshoot was due to premature termination of the living chain end at both the beginning of the polymerization as well as immediately upon

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sequential addition of the second (*i.e.* isoprene) monomer. Hence, the student would conclude that in order to reach the target block copolymer composition and overall molecular weight, the chemist would clearly have to account for the minimized yet highly important adventitious impurity concentration ($f_i$) within his/her initial calculations.

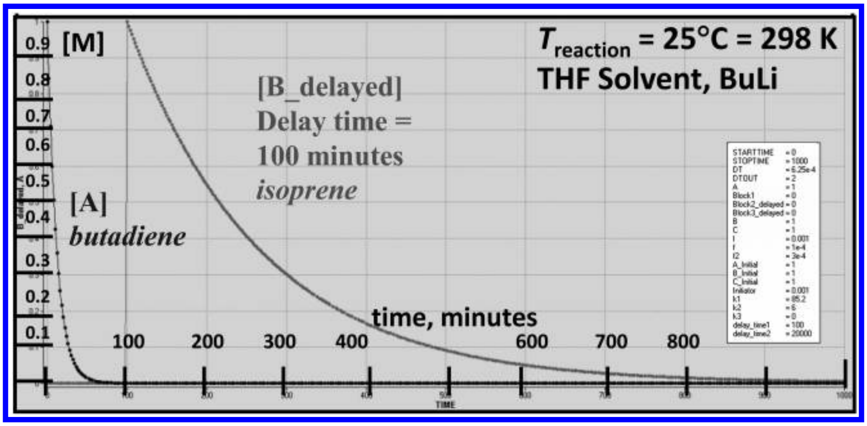

*Figure 5. Model data for monomer concentration $[M]_i(t)$ of poly(butadiene-block-isoprene) initiated anionically by butyl lithium in THF solvent at T = 25 °C.*

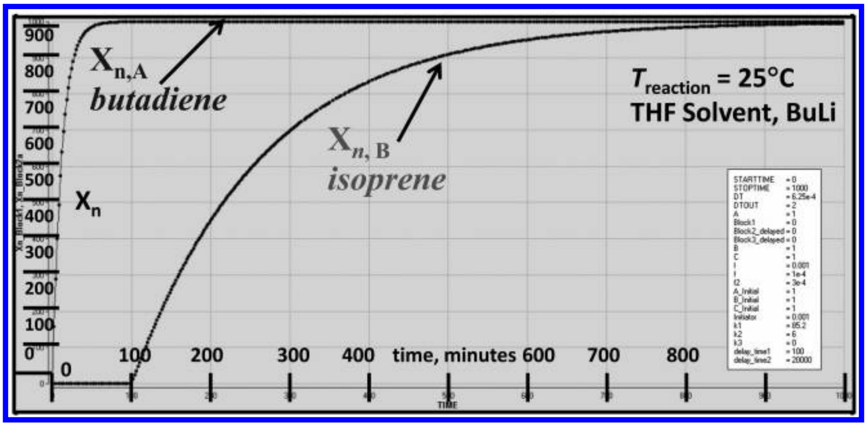

*Figure 6. Model data for block number average degree of polymerization ($X_{n,i}(t)$) of poly(butadiene-block-isoprene) initiated anionically by butyl lithium in THF solvent at T = 25 °C.*

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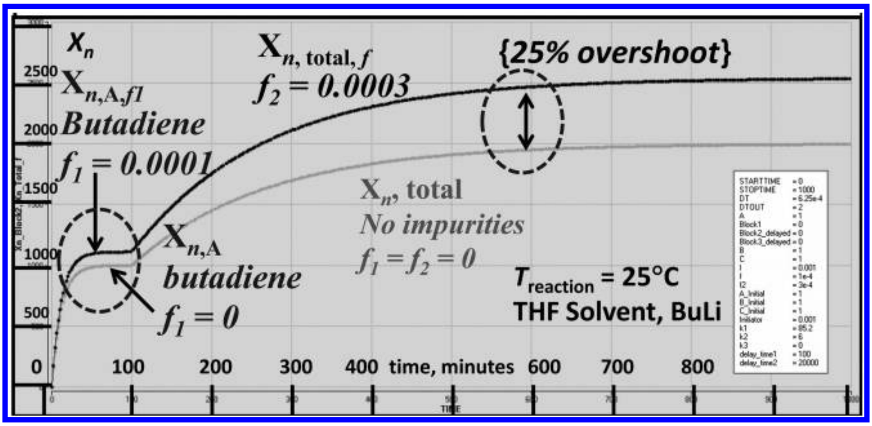

*Figure 7. Cumulative number average degree of polymerization ($X_{n,total}(t)$) for poly(butadiene-block-isoprene) initiated anionically by butyl lithium in THF solvent at T = 25 °C.*

The pedagogical models herein include the option of varying the reaction temperature (*T*) and thereby utilizing each monomer's Arrhenius energetics for propagation (Table I). Figure 8 models an alternating (ABAB) sequential addition living anionic *tetra*-block copolymerization reaction of 4-vinylpyridine (*58*, *59*) and 4-cyano-α-methylstyrene (*60*) at different reaction temperatures (*T*). It is clear to the student that at lower temperatures the delay time for subsequent monomer addition must be significantly raised compared to higher reaction temperatures notwithstanding the increased reaction control at low *T*. For *sub*-ambient anionic diblock copolymerization of 4-vinyl pyridine (4VPy) and 4-cyano-α-methylstyrene (4CMS) in particular, $t_{d,4CMS}$ must be significantly lengthened compared to the room temperature reaction as shown in Figure 8. If ($t_{d,4CMS}$) is not lengthened at -10°C relative to a room temperature reaction, a *tapered* poly(4VPy-*co*-4CMS) interface or gradient copolymer will be effectively created, which may not microphase separate similar to the singular covalent poly(4VPy-*block*-4CMS) AB interface (*53*).

Organic chemistry student modeling was amplified to synthesize a hypothetical *penta*-block (*ABCDE*) copolymer of butadiene-*block*-isoprene-*block*-2-vinylquinoline-*block*-methyl methacrylate-*block*-styrene as initiated by butyl lithium (BuLi) in THF solvent. The apparent rate constants for each monomer were calculated using the Arrhenius energetics (*54–57*) listed in Table I. The monomer concentration $\{[M]_i(t)\}$ and cumulative number average degree of polymerization $\{X_{n,total}(t)\}$ over time for the sequential addition *penta*-block copolymerization of butadiene (*B*), isoprene (*I*), 2-vinylquinoline (*VQ*), methyl methacrylate (*MMA*), and styrene (*S*) with no impurities ($f_i = 0$) are shown in Figures 9 and 10 respectively. Furthermore, the effect of reaction temperature (*T*) with no impurities and the effect of impurity concentration ($f_i$) at constant temperature (*T*) on the anionic living *B-I-VQ-MMA-S penta*-block copolymerization reaction are depicted in Figures 11 and 12 respectively.

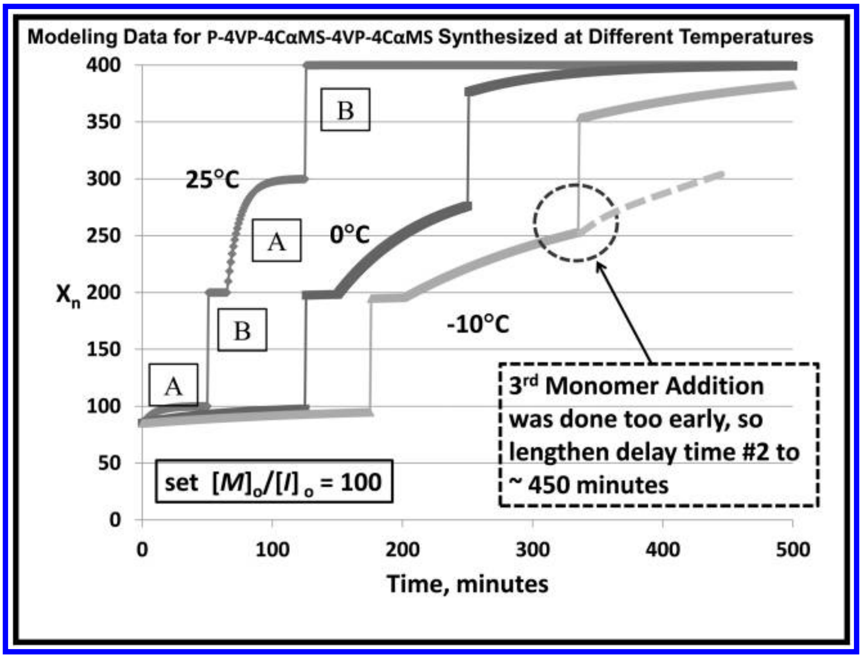

*Figure 8. Cumulative number average degree of polymerization {$X_{n,total}(t)$} for poly(4-vinyl pyridine-block-4-cyano-α-methylstyrene-block-4-vinyl pyridine-block-4-cyano-α-methylstyrene) initiated anionically by butyl lithium in THF solvent at varying reaction temperature (T) = -10 °C, 0 °C, and 25 °C.*

The effect of the distinctly low *pre*-exponential factor ($A_{p,MMA}$) for methyl methacrylate (MMA) monomer from Table I (*56*) was observed in the low rate of reaction for the MMA block in Figures 9 and 10. The time inefficiency by the polymer chemist was clearly evident to the student in raising the reaction temperature ($T$) by a mere 35°C, while keeping the delay time ($t_{d,i}$) for subsequent monomer additions constant in Figure 11. For MMA alone, the delay time used ($t_{d,MMA}$) was hundreds of minutes too long thereby wasting energy and potentially severely limiting industrial block copolymer production capacity *per* time. Hence, from the model herein the student has learned to concurrently adjust the delay time {$t_{d,i}$} with reaction temperature changes in order to begin to optimize industrial efficiency.

Student discussion can include the molecular explanation for the relatively low value of {$A_{p,MMA}$} due to an *intra*molecular solvation of the counter cation by the penultimate MMA ester group of the living polymer chain (*56*).

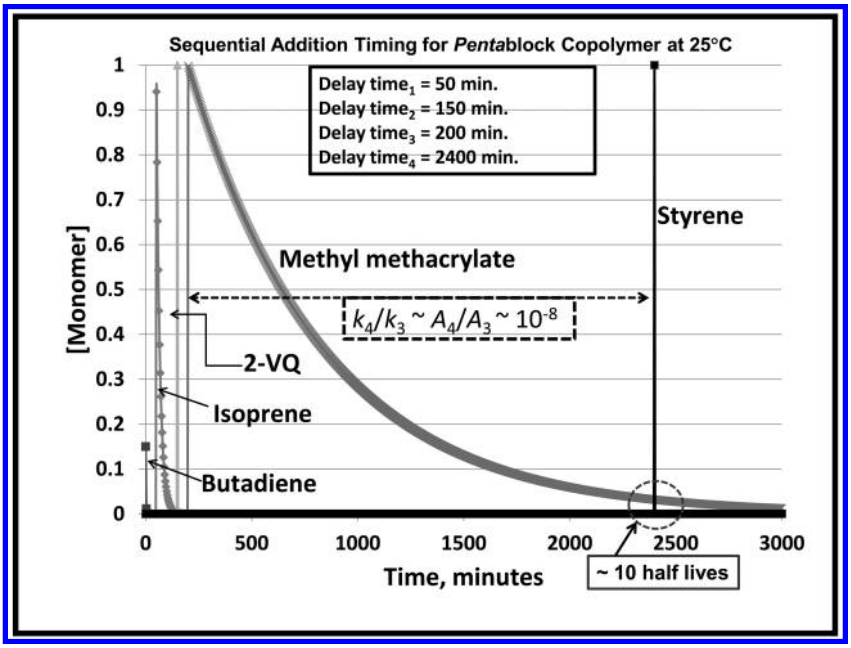

*Figure 9. Modeled monomer concentration {$[M]_i(t)$} for the anionic synthesis of a hypothetical poly(butadiene-block-isoprene-block-2-vinylquinoline-block-methyl methacrylate-block-styrene) penta-block copolymer by sequential addition with no impurities ($f_i = 0$), $[M]_o = 1.0$ M, and $[I]_o$=0.01 M as initiated by butyl lithium in THF solvent at T = 25 °C.*

Using the Berkeley Madonna® model, the organic chemistry student was allowed to clearly observe a cumulative 11% overshoot compared to the target molecular weight due to a consistent yet relatively miniscule adventitious impurity concentration ($f_i$ = 0.0002) upon each subsequent monomer addition (Figure 12). Hence, the student has learned that he/she must remove impurities to the best of their ability (*63*, *64*) in order to ultimately minimize the block copolymer polydispersity index (PDI). The student has also learned to concomitantly adjust the initial monomer concentration $[M]_{o,i}$ for each block with respect to the known impurity concentration ($f_i$) data in order to achieve the target *multi*-block copolymer composition and molecular weight.

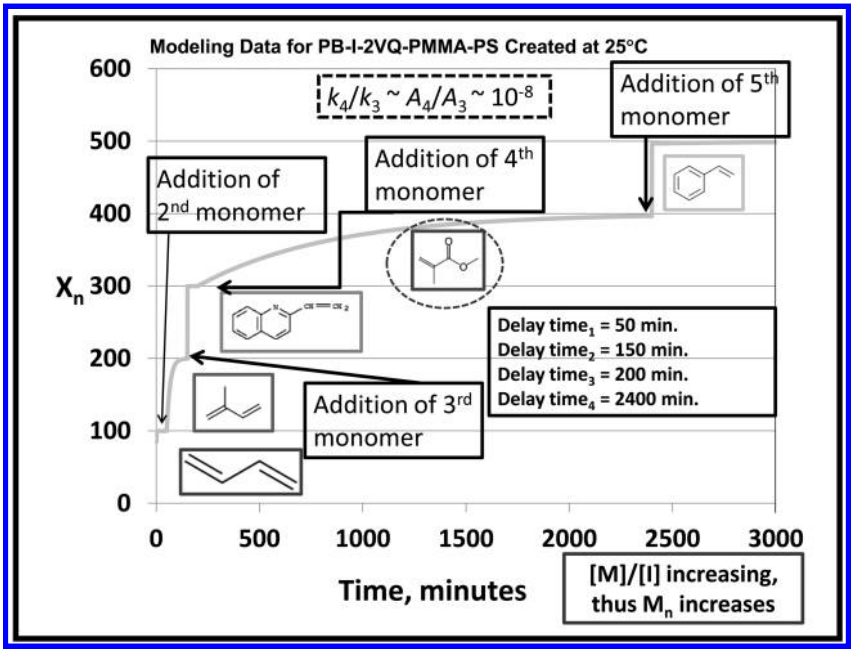

*Figure 10. Cumulative number average degree of polymerization {$X_n(t)$} for the anionic synthesis of a hypothetical poly(butadiene-block-isoprene-block-2-vinylquinoline-block-methyl methacrylate-block-styrene) penta-block copolymer by sequential addition as modeled with no impurities ($f_i = 0$), $[M]_o = 1.0$ M and $[I]_o = 0.01$ M as initiated by butyl lithium in THF solvent at T = 25 °C.*

Hence, student modeling of sequential addition block copolymerization was accomplished herein for a *hypothetical penta*-block copolymerization of butadiene (*B*), isoprene (*I*), 2-vinylquinoline (2-*VQ*), methyl methacrylate (*MMA*), and styrene (*S*). (Appendix) Many different block sequences (ABC, ACB, *etc.*) can be modeled using the Berkeley Madonna® algorithm. Within the organic chemistry classroom, it can be emphasized that although theoretically plausible, unfortunately all block copolymer sequences (*ABCDE* …) are not feasible *via* sequential addition anionic living polymerization methods within the organic polymer chemistry laboratory setting. The least reactive monomers have the largest p$K_a$ values for the corresponding conjugate acid of the propagating anionic intermediate species and thus require a more reactive (*i.e.* higher p$K_a$) initiating carbanion from the preceding block's chain end. For example, anionic living poly(methyl methacrylate) (p$K_a \approx$ 30-31) chain ends cannot routinely initiate styrenic monomers (p$K_a \approx$ 43 - 44) (*29*, *33*, *53*). Thus, Berkeley Madonna® modeling for the poly(butadiene-*block*-isoprene-*block*-2-vinylquinoline-*block*-methylmethacrylate-*block*-styrene) *penta*-block copolymer depicted in Figures 9-12 herein is *hypothetical* and not actually feasible due to imperative carbanion p$K_a$ differences within the polymer chemistry laboratory setting. Using the Berkeley Madonna® model (*30*) and chemical literature in tandem causes the student to

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become increasingly sensitive to functional group reactivity. For example, even in the case of polystyryl lithium nucleophilic attack on MMA, termination can result due to undesirable attack at the carbonyl carbon atom of MMA rather than at the desired less-substituted vinyl C-2 carbon. Diphenylethylene has been routinely employed to circumvent this apparent impasse to the synthesis of poly(styrene-*block*-MMA) macromolecular architectures (*33*, *53*).

Appreciation of these archetypical limitations to anionic block copolymerization can lead directly to a more in-depth look at block sequence effects and catalyze an increasingly comprehensive organic chemistry student discussion of polymer structure-property-processing relationships with respect to material selection. These topics provide a natural segue toward discussion of professional level communication as organic chemists with material scientists and chemical engineers with respect to industrial polymeric material production. Hence, the sequential addition block copolymerization model can be utilized pedagogically to significantly improve learning depth within the foundational course in organic chemistry and help guide the organic chemistry student concerning quantitatively maximizing industrial productivity.

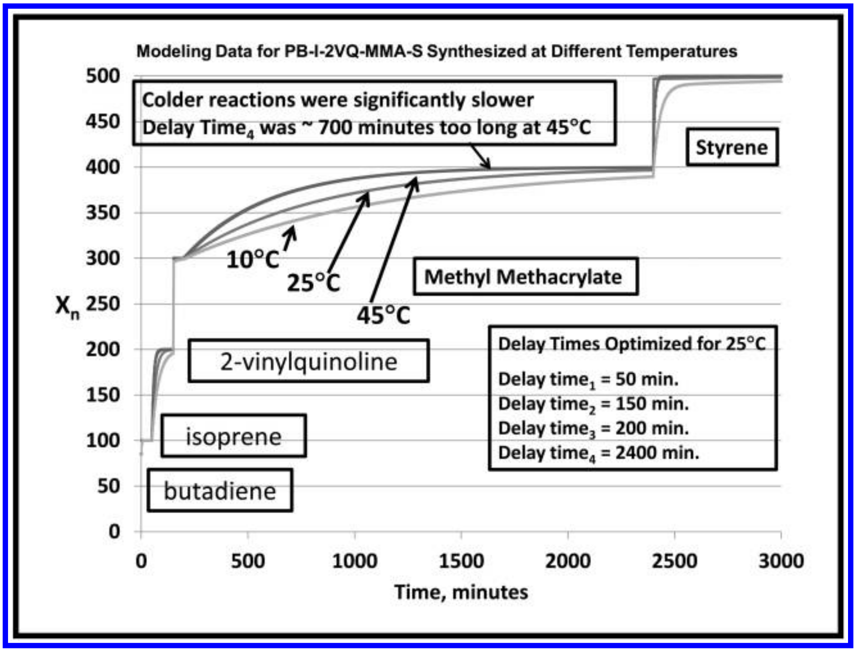

*Figure 11. Cumulative number average degree of polymerization {$X_n(t)$} for the anionic synthesis of a hypothetical poly(butadiene-block-isoprene-block-2-vinylquinoline-block-methyl methacrylate-block-styrene) penta-block copolymer by sequential addition as modeled with no impurities ($f_i = 0$), $[M]_o = 1.0$ M and $[I]_o=0.01$ M as initiated by butyl lithium in THF solvent varying reaction temperature (T) = 10 °C, 25 °C, and 45 °C.*

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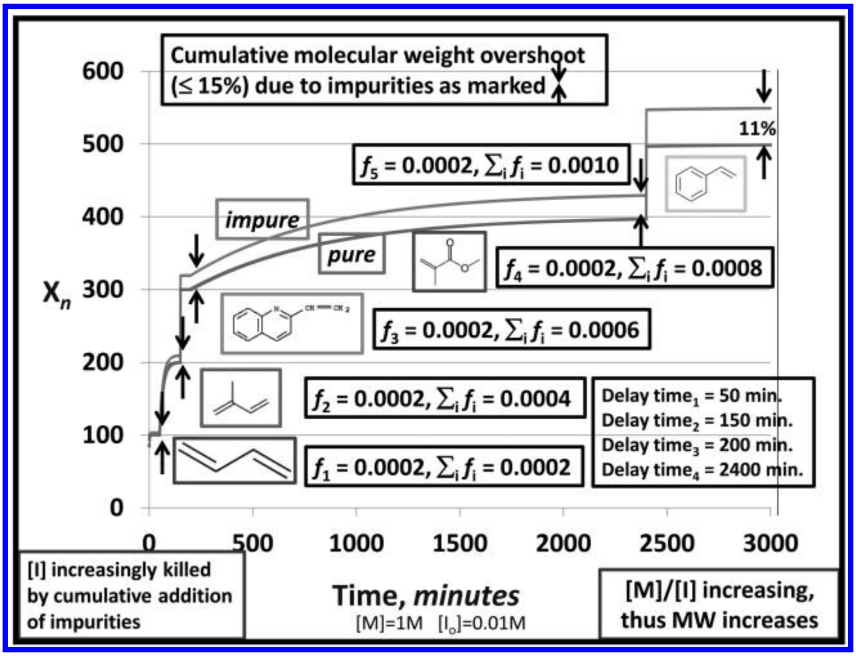

*Figure 12. Cumulative number average degree of polymerization {$X_n(t)$} for the anionic synthesis of a hypothetical poly(butadiene-block-isoprene-block-2-vinylquinoline-block-methyl methacrylate-block-styrene) penta-block copolymer by sequential addition initiated by butyl lithium in THF solvent as modeled varying reaction temperature (T) = 10 °C, 25 °C, and 45 °C with $[M]_o$ = 1.0 M, $[I]_o$=0.01 M, and block impurity fraction ($f_i$ =0.0002).*

## Conclusions

An adaptable computational algorithm was created by physical chemistry students using Berkeley Madonna® system dynamics software (*30*) for organic chemistry pedagogy. The user-friendly and interactive program for foundational organic chemistry students successfully modeled the kinetics of sequential addition anionic living *multi*-block copolymerization for vinyl and alkadiene monomers as initiated by alkyl lithium reagents. (Appendix) This expandable model successfully allows for flexibility in the number of blocks as well as monomer sequence based merely on Arrhenius rate constant kinetic parameters. By initially setting the reaction temperature ($T$) and initiator concentration {$[I]_o$} as well as the impurity fraction ($f_i$) and initial concentration for each ($i^{th}$) monomer {$[M]_{o,i}$}, the total number average degree of polymerization ($X_{n,total}$) as well as the number average degree of polymerization for each block ($X_{n,i}$) was computed as a function of time ($t$). Monomers for each block were identified merely by their Arrhenius energetics for propagation ($A_{i,p}$, $E_{a,p,i}$) and block copolymerization was modeled as a function of reaction temperature ($T$).

The computational kinetics model herein incorporated a delay time for the $i^{th}$ monomer, based on the preceding ($i$ -1) monomer's propagation half-life denoted as $\{t_{1/2,\ i\text{-}1}\}$ for sequential monomer addition anionic living *multi*-block copolymerization. The model's output can be optimally used to graphically guide the student to the appropriate time for subsequent monomer addition wherein the previous reactant had been effectively exhausted $\{e.g.\ [M]_i(t)/[M]_{i,o} \leq 10^{-3}\}$. The model showed a realistic cumulative molecular weight overshoot as observed experimentally due to an adventitious impurity fraction ($f_{\rm i}$) within both the monomers and solvent far below the mere detection limit of conventional organic chemistry gas chromatography (GC) laboratory techniques (*63*, *64*). Feedback from the model helps adjust subsequent monomer addition delay times $\{t_{d,i}\}$ as well as block molecular weights ($X_{n,i}$) while utilizing experimental molecular weight distribution data to both quantify and adjust for impurity concentration ($f_i$). Hence, an interplay exists between experimental gel permeation chromatography (GPC) data and the model with regard to taking adventitious impurities ($f_i$) into account. These models ultimately allow for adjustment of physical variables, such as reaction temperature ($T$), initiator concentration $[I]_{\rm o}$, and initial concentration of each monomer $[M]_{i,\rm o}$, in order to successfully achieve target composition and block molecular weights. The facile, user-friendly models can be used by organic chemistry students to effectively simulate control of a polymerization plant while facilitating foundational organic chemistry classroom discussion of nucleophilic attack-anionic reactivity, block copolymer sequence, organic polymeric material selection, and polymer structure-property-processing relationships with respect to crucial acid-base (p$K_{\rm a}$) differences within the laboratory. Hence, the sequential addition block copolymerization model can be utilized pedagogically to guide the foundational organic chemistry student toward optimized productivity with respect to industrial data.

Foundational organic chemistry student responses to the computational kinetics exercises herein are limited to date due to the recent introduction of these pedagogical methods into the classroom. Nevertheless, preliminary qualitative student feedback to the computational polymerization kinetics presented within has been collectively positive. Students have routinely termed the model as user-friendly and coherent wherein the model's graphical output appears clear, concise, and comprehensible with respect to the plethora of physical variables incorporated. However, foundational organic chemistry students have uniformly indicated that a significantly increased level of instruction and study beyond the treatment usually found in a conventional organic chemistry textbook is required in order to fully understand the intricacies of the underlying kinetics and accompanying computational subroutine. Beyond providing a tangential entree into polymerization chemistry, the mechanistic-kinetics interplay alluded to here appears to provide a break from the potentially perfunctory set of organic transformations and accompanying mechanisms routinely presented throughout an introductory organic chemistry text and conventional foundational organic chemistry lecture sequence. Furthermore, the interactive computational kinetics algorithms appear ideal for the type of modern foundational organic chemistry lecture classes being blended increasingly with world wide web-based assignment and assessment platforms. Algorithmic encoding herein was accomplished by

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undergraduate physical chemistry students studying phenomenological chemical kinetics. The student creators have indicated a significant increase to their own understanding of the kinetics of complex chemical reactions *via* programming both the molecularity and concomitant ordinary differential equation rate law for each elementary reaction step in addition to the requisite delay times for sequential addition anionic block copolymerization. The physical chemistry students did tend to recommend the pedagogical computational anionic living block copolymerization kinetic exercises as a learning technique to students within the foundational course in organic chemistry.

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## Acknowledgments

The authors wish to thank the Northeastern State University College of Science and Health Professions for their generous ongoing support of the research herein as well as travel for CLA to the 22nd Biennial Conference on Chemical Education in 2012. CLA wishes to thank Dr. Dale J. Meier (*36*, *44*) of the Michigan Molecular Institute, Dr. S. Packirisamy of the Indian Vikram Sarabhai Space Centre (*61*), Dr. Robert Zand of The University of Michigan-Ann Arbor, and Dr. David C. Martin of the University of Delaware College of Engineering for their tutelage during the early stages of his academic training concerning the elegance of anionic living polymerization and its capability for creating novel macromolecular architectures for tailored engineering applications. CLA wishes to thank his colleagues Dr. Michael T. Huggins and Dr. Jerome E. Gurst for their collaboration on this research while a 2005-2008 visiting faculty associate within the Department of Chemistry at the University of West Florida, Pensacola. CLA also wishes to thank Dr. Clyde R. Metz and Dr. Shawn C. Sendlinger of the National Computational Science Institute for their rigorous training and guidance during the 2004 Computational Chemistry for Chemistry Educators (CCCE) workshop at Wittenberg University and the 2005 Advanced CCCE workshop at the University of Northern Colorado (*67*).

## Appendix

Berkeley Madonna® example algorithm code which can be used to simulate anionic living *penta*-block copolymerization.

```
METHOD RK4

STARTTIME = 0
STOPTIME=3000
DT = 0.02
DTOUT = 3

{Top model}

  {Reservoirs}
  d/dt (A) = - J1
    INIT A = 0.15
  d/dt (Block1) = + J1
    INIT Block1 = 0
  d/dt (Block2_delayed) = + J1 + J2_delayed
    INIT Block2_delayed = 0
  d/dt (Block3_delayed) = + J1 + J2_delayed + J3_delayed
    INIT Block3_delayed = 0
   d/dt (Block4_delayed) = + J1 + J2_delayed + J3_delayed +
J4_delayed
    INIT Block4_delayed = 0
d/dt (Block5_delayed) = + J1 + J2_delayed + J3_delayed + J4_delayed+
J5_delayed
    INIT Block5_delayed = 0
  d/dt (B) = - J2
    INIT B = 1
  d/dt (C) = - J3
    INIT C = 1
d/dt (D) = - J4
    INIT D = 1
d/dt (E) = - J5
    INIT E = 1

B_delayed = delay(B, delay_time1, 1)
C_delayed = delay(C, delay_time2, 1)
D_delayed = delay(D, delay_time3, 1)
E_delayed = delay(E, delay_time4, 1)
```

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```
{Flows}
  J1 = A*I*k1
  J2 =B*I*k2
  J3 =C*I*k3
  J4 =D*I*k4
  J5 =E*I*k5
  J2_delayed = B_delayed*I*k2
  J3_delayed = C_delayed*I*k3
  J4_delayed = D_delayed*I*k4
  J5_delayed = E_delayed*I*k5
  pA = (A_Initial - A)/A_Initial
  Xn_Block1 = (pA*A_Initial)/Initiator
  Xn_Block1_f =  (pA*A_Initial)/(Initiator-f)
  FN = (Xn_Block1 +1)^2
  PDI_Block1 = 1 + (Xn_Block1/FN)
  pB = (B_Initial - B_delayed)/B_Initial
  Xn_Block2 = Xn_Block1 + (pB*B_Initial)/Initiator
  Xn_Block2a = (pB*B_Initial)/Initiator
  Xn_Block2_f = (pB*B_Initial)/(Initiator-f2)
  Xn_Total = Xn_Block1 + (pB*B_Initial)/(Initiator)
  Xn_Total_f = Xn_Block1_f + (pB*B_Initial)/(Initiator-f2)
  FN_Block2 = (Xn_Block2 +1)^2
  FNA_Block2 = (Xn_Block2a +1)^2
  PDI_Block2 =  1 + (Xn_Block2/FN_Block2)
  PDI_Block2A  = 1 + (Xn_Block2a/FNA_Block2)
  FN_Block2_f =  (Xn_Block2_f +1)^2
  PDI_Block2_f =  1 + (Xn_Block2_f/FN_Block2_f)
  pC = (C_Initial - C_delayed)/C_Initial
  pD = (D_Initial - D_delayed)/D_Initial
  pE = (E_Initial - E_delayed)/E_Initial

  Xn_Block3 = Xn_Block2+ (pC*C_Initial)/Initiator
 Xn_Block4 = Xn_Block3+ (pD*D_Initial)/Initiator
 Xn_Block5 = Xn_Block4+ (pE*E_Initial)/Initiator
  Ao = 1.001 - A
  FN1 = (I/(f*Ao))^2
  FN2 = f*Ao/I
  FN3 = 1 - (f*Ao/I)
  FN4 = LOGN(1-(f*Ao/I))
  FN5 = FN3*FN4
```

```
PDIf = 2*FN1*(FN2+FN5)
  Bo = 1.001 - B_delayed
  FN11 = (I/(f2*Bo))^2
  FN22 = f2*Bo/I
  FN33 = 1 - (f2*Bo/I)
  FN44 = LOGN(1-(f2*Bo/I))
  FN55 = FN33*FN44
  PDIf_Block2 = 2*FN11*(FN22+FN55)
  PDI_Total = 1+ (.25*(PDI_Block1 -1)+0.25*(PDI_Block2A-1))
  PDI_Total_f = 1+ (.25*(PDIf-1) +0.25*(PDIf_Block2-1))
  PDI_Total_f_alt = (.25*(PDIf) +0.25*(PDIf_Block2))

  Fract =  2*((PDI_Total -1)^0.5)
  Fract_f = 2*((PDI_Total_f -1)^0.5)

{Functions}
  I = 0.01
  f = 0.0001
  f2 = 0.0003
  f3 = 0.0001
  f4 = 0.0003
  A_Initial = 1
  B_Initial = 1
  C_Initial = 1
  D_Initial = 1
  E_Initial = 1
Initiator = 0.01
  k1 = 85.7
  k2 = 6.1
  k3= 91270
  k4 = 0.157
  k5 = 4180
{Globals}
delay_time1 = 50
delay_time2 = 150
delay_time3 = 200
delay_time4 = 2400
{End Globals}
```

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ch013

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Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ix002

In Introduction of Macromolecular Science/Polymeric Materials into the Foundational Course in Organic Chemistry; Howell, B.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ix002

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ix002

In Introduction of Macromolecular Science/Polymeric Materials into the Foundational Course in Organic Chemistry; Howell, B.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Publication Date (Web): November 22, 2013 | doi: 10.1021/bk-2013-1151.ix002