LINOLEIC ACID FUNCTIONALIZED AMPHIPHILIC BLOCK COPOLYMERS APPLICATION IN WATERBORNE COATINGS

DISSERTATION

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on the authority of the rector magnificus,
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on account of the decision of the graduation committees,
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by

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born on 10 April 1975

in Klang, Selangor, Malaysia.

This dissertation has been approved by:

Promoters: **prof. dr. Jan Feijen**
prof. dr. Dirk W. Grijpma

dedicated to Ailing, my parents and family
for all the love and supports

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Linoleic Acid Functionalized Amphiphilic Block Copolymers Application in Waterborne Coatings

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"The essence of knowledge is, having it, to apply it." Confucius

Tan Boon-Hua
December 2006

Contents

CHAPTER 1

Introduction and Scope of the Thesis

INTRODUCTION

An important target of the paint industry nowadays is to decrease the emission of organic solvents in coating systems. By decreasing the use of organic solvents, the industry aims at protecting the environment and ensuring the safety of professional users.

Waterborne latex-based paints are attractive replacements for conventional organic solvent-based coating systems, as their processing properties are similar [1-2]. Most latices used in formulating these paints are prepared by emulsion polymerization. Surface active agents (surfactants) are required during the polymerization for particle nucleation and latex stability. However, during film formation the particles coalesce, and the surfactant migrates out of the bulk phase and concentrates at the film interface. High concentrations of water-soluble components at the film surfaces will adversely affect its adhesion properties to the substrate and its resistance to water [3-9].

In a pigmented paint formulation, the latex is combined with a pigment slurry, and competitive adsorption of surface active agents may give rise to poor dispersion stability and to unexpected rheological effects [9-10]. The physically adsorbed latex surfactant may have higher affinity for pigment than for polymer particles, a situation which often leads to latex instability. In addition, surfactants used to stabilize the latex are usually of a different type than those used to stabilize the pigment. The two surfactants will compete for the surfaces and in the equilibrium situation the coverage and composition of the latex and pigment surfaces may be very different from that before mixing [11-19].

Several approaches have been investigated to overcome these surfactant-related problems. A first approach employs reactive or polymerizable surfactants [6-9, 20-23] in the preparation of the latices. By copolymerizing with the monomer(s) during emulsion polymerization, the surfactant becomes covalently attached to the latex particle. Many of the problems encountered with conventional emulsifiers can be minimized and the performance of the latex can be improved significantly.

In another approach polymeric surfactants are used in the emulsion polymerization [24-27]. In this case surfactant migration is limited due to the high molecular weight of the surfactant. Moreover, as the particles are stabilized through steric effects, latices prepared with polymeric surfactants can possess other advantageous properties such as excellent mechanical- and freeze-thaw stability.

In the past decades much research has been carried out on the synthesis and properties of reactive surfactants. Nevertheless, several important issues still need to be addressed: How is particle coalescence and film formation of latex particles prepared with a reactive (polymeric) surfactant affected? And what will be the effect on the properties of the dried film even though surfactant migration is prevented?

AIM AND SCOPE OF THE THESIS

In this research program, novel amphiphilic block copolymers consisting of poly(ethylene oxide) (PEO) and poly(ε-caprolactone) (PCL) segments end-functionalized with linoleic acid (LA)) are described and applied as stabilizers in emulsion polymerization of acrylates and in waterborne acrylate coatings. The unsaturated double bonds present in the linoleic acid moiety can undergo autoxidative crosslinking upon exposure to air (or copolymerize with the monomer), thereby minimizing migration upon drying of the latex film. As controls, analogous surfactants containing stearic acid (SA) moieties are investigated. These compounds are saturated and cannot crosslink or copolymerize.

The properties of these surfactants with regard to the following subjects will be investigated:

1) latex preparation, latex film formation, surfactant migration and film properties
2) copolymerization of the surfactant with (meth)acrylate monomers during emulsion polymerization and autooxidation upon drying of the latex and
3) use as an additive to waterborne coating systems and performing as a pigment dispersant and rheological modifier.

This thesis is divided into three parts: In the first introductory part, an overview of the literature regarding the properties and application of surfactants as emulsifiers in emulsion polymerization, pigment dispersants in pigment paste preparation and rheological modifiers in formulating waterborne acrylic coatings is given (**Chapter 2**).

The second part describes the synthesis and properties of block copolymers based on PEO, PCL and end-functionalized with LA. These block copolymers are then applied as emulsifiers in acrylate emulsion polymerizations. This part is further subdivided:

1) **Chapter 3** describes the synthesis of PEO and PCL block copolymers by ring-opening polymerization and subsequent functionalization by esterification with LA. The obtained block copolymers are characterized and their surface active properties are investigated. Also their crosslinking behavior in air is examined. The potential of these block copolymers as stabilizer in emulsion polymerization of methyl methacrylate (MMA) at low solids contents is investigated.
2) To investigate the potential of this block copolymer in MMA emulsion polymerization at higher solids content, a comprehensive study was carried out in which emulsion polymerization reaction conditions were varied. The system was further optimized with regard to the nature of the surfactant, surfactant to monomer ratio, initiator system (thermolysis- or redox-initiating system), initiator concentration and reaction temperature. The results are presented in **Chapter 4**.
3) In **Chapter 5**, the effect of the purity of the raw materials and the polymerization conditions in the surfactant synthesis and its effect on poly(methyl methacrylate/n-butyl acrylate), P(MMA/BA) latex characteristics and film mechanical properties are described.
4) Film formation from P(MMA/BA) copolymer latices prepared with selected PEO-PCL-LA block copolymer surfactants, and surfactant migration, water-uptake and mechanical properties of the resulting films is described in **Chapter 6**. Also the effect of water and moisture on the tensile properties of the P(MMA/BA) latex films is addressed.

The third part of this thesis describes the potential of these block copolymers as pigment dispersants and rheological modifiers in waterborne paint formulations. Two commercially available pigment dispersants were used as references and their properties were compared to those of MPEO-CL block copolymers when preparing pigmented latices from different (commercially available) binders (**Chapter 7**). To assess the potential of this block copolymer as a rheological modifier in P(MMA/BA) latices, preliminary studies were carried out and described in **Appendix A**. In **Appendix B** a pigmented P(MMA/BA) latex and latex film was prepared with MPEO-CL and MPEO-CL-LA surfactants, showing the multifunctionality of these novel block copolymers.

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CHAPTER 2

Reactive Surfactants for Waterborne Acrylic Coating Systems

INTRODUCTION

In conventional solventborne paint and coating formulations, organic solvents are used to dissolve binders and additives and to disperse pigments and extenders in order to produce ready-for-use paints and coatings [1]. The use of organic solvents in these formulations is a major issue because exposure to these solvent vapors can result in a number of human health risks. Organic solvent vapors also can pose fire or explosion hazards, necessitating careful storage and handling procedures.

Due to the stringent/new environmental pollution acts (EPA), the use of volatile organic compounds (VOC) in commercial products has been reduced dramatically. The drive to reduce VOC emissions is also stimulated by the raising cost of organic solvents [2-5]. Numerous alternatives to reduce VOC emissions from paints and coatings have been developed in the foregoing 50 years and comprise [1-5]:

- water-soluble coatings
- waterborne coatings
- solventborne high solids coatings
- radiation-curing coatings (Ultra-Violet (UV) or electron beam (EB))
- powder coatings

Among these alternative coating systems, emulsion polymerized waterborne coating systems have attracted much attention in industry due to a number of advantages [4, 6]:

1) Low viscosity at high molecular mass and at high volume fraction of polymer.
2) Preparation process is simple and versatile.
3) Tunable final properties of polymer dispersion.
4) Easy to be formulated to match different applications.

5) Using water as the continuous liquid phase is inexpensive and safe.
6) Clean up of equipment is easier.

Waterborne coatings

With the aim to replace conventional organic solvents by water, which has the obvious advantages of being noncombustible and nontoxic, the first waterborne paints were developed in the 1950's. In the following years, new waterborne paints were formulated and nowadays such formulations can contain binders (polymer latices), pigments and extenders, solvents (in this case mainly water) and additives (emulsifiers, pigments dispersants, associative thickeners, defoaming agents, etc.) [1, 5, 7].

Latex

The majority of waterborne paints are latex paints: aqueous dispersions of water-insoluble polymers made by emulsion polymerization using free radical initiators (see below). The (co)polymers are prepared from monomers such as methyl methacrylate, butyl acrylate, styrene, vinyl acetate and butadiene. These polymers are known as emulsion polymers or latices. The latices can be prepared with a particle size diameter ranging from of 0.02–100 μm. Most of the latices are prepared with an average particle size of 100 to 500 nm [3, 4, 8, 9].

EMULSION POLYMERIZATION

Emulsion polymerization is the most common and widely used process in the production of dispersed polymers for different end-applications such as adhesives, paints, coatings, diagnostic tests, drug delivery systems, thermoplastics and synthetic rubbers [10, 11]. The advantages of emulsion polymerization are rapid polymerization and relatively low viscosities at high polymer molecular weight. In addition, the final product is readily applied, cheap, odourless, non-inflammable and environmentally friendly [10].

When compared to other polymerizations processes, emulsion polymerization allows the reaction to take place at high conversion rates with simultaneous formation of high molecular weigh polymer. Furthermore, although the polymerization of acrylic monomers is highly exothermic, it is easy to maintain isothermal reaction conditions because of efficient heat transfer through the aqueous phase [10, 12].

A typical emulsion polymerization reaction involves water, monomer, an initiator and an emulsifier. Water is the major ingredient in emulsion polymerizations. The main functions of water are to maintain a low viscosity and to act as a medium for heat transfer. Water-soluble initiators, redox initiators, and oil-soluble initiators are used to generate radicals for initiation of the polymerization. The role of the emulsifier is crucial and multifold. The emulsifier is important in particle nucleation and growth during the emulsion polymerization as well as in the stabilization of the final latex after the polymerization. A variety of chain transfer agents are primarily used to control the molar mass of the polymer [12, 13].

Emulsion polymerization

In general the emulsion polymerization can be divided into three stages as illustrated in Figure 1. In stage I, particles are formed; in stage II particles grow and in stage III monomer droplets have disappeared and complete polymerization is attained.

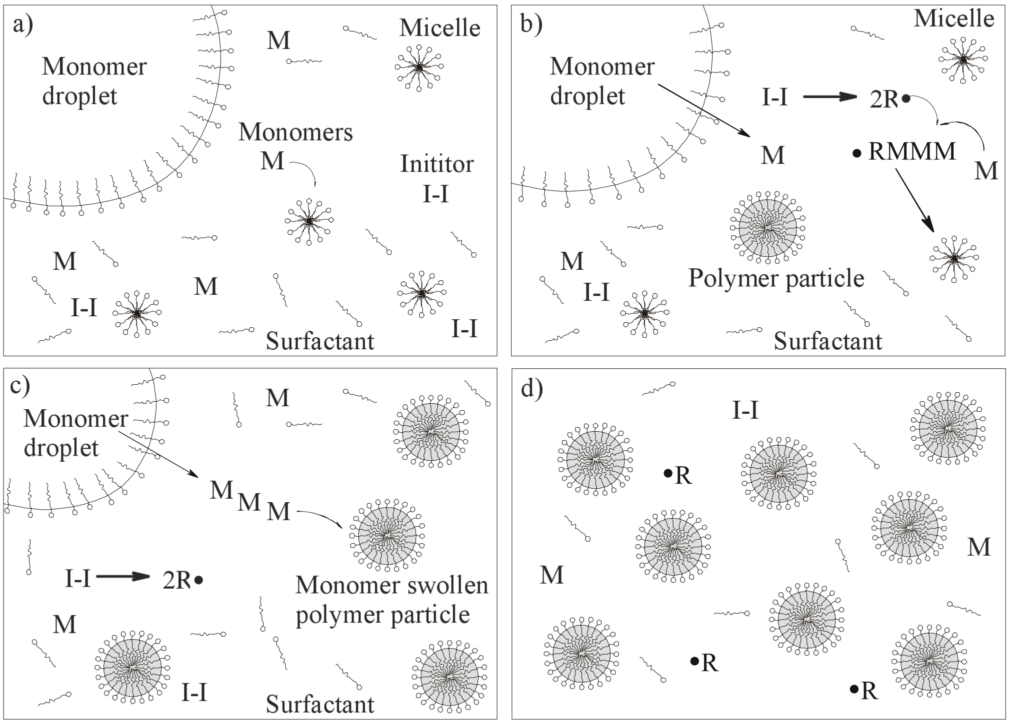

Figure 1: a) Initial situation b) Stage I c) stage II d) stage III of the emulsion polymerization process. (Simplified representation of an emulsion polymerization system)

In the initial phase, as the surfactant concentration is above the critical micelle concentration (CMC), micelles are formed. Added monomer(s) will also be emulsified by the surfactant, and monomer droplets are formed as well. At the beginning of the polymerization process, free radicals (from water-soluble initiators) are formed in the aqueous phase. Nucleation can take place by micellar nucleation and/or homogenous nucleation. In micellar nucleation, the entry of radicals (either primary radicals or oligomeric radicals formed by polymerization in solution) occurs from the aqueous phase into the micelles. Homogeneous nucleation, involves solution-polymerized oligomeric radicals becoming insoluble and precipitating, forming primary particles. By controlled coagulation, primary particles coalesce to determine the final particle number. The relative extents of micellar and homogeneous nucleation depend on the water-solubility of the monomer and on the surfactant concentration [10-12, 14].

In Stage II, the particles are swollen with monomer and subsequently these swollen particles become the loci of the polymerization. As polymerization proceeds, the monomer droplets (which act as reservoirs) are drained by diffusion of the monomer through the aqueous phase from the monomer droplets to the growing polymer particles.

The monomer concentration in the growing particles maintains a nearly constant dynamic equilibrium value [15]. The reaction mass now consists of a constant number of growing polymer particles and the monomer droplets, Stage II [15]. Polymerization will continue within the particle until either all of the monomer has been depleted or until another radical enters the particle and terminates the growing chain. If termination occurs, the particle will remain “dead” until another radical enters and initiates a new polymer chain. With polymerization taking place within a particle and new monomer continuously entering the particle, the particles will increase in size during the process. Stability is maintained by further adsorption of surfactant molecules at the surface [11, 12, 14].

Important monomers

A wide variety of monomers can be used in emulsion polymerization, either to give homopolymers or, more frequently, to yield copolymers (two different monomer units), terpolymers (three different monomer units) or polymers based on an even higher number of monomers. The different reactivities of the monomers can lead to an uneven distribution of the monomers throughout the polymer chains.

An important factor in the choice of a monomer is the glass transition temperature, Tg, of the homopolymers. This is the temperature at which the polymer changes from a glassy state to a rubbery material, a change that takes place over a relatively narrow temperature range. Table 1 lists a number of widely used monomers with their boiling point (b.p.) and the Tg of the homopolymers.

Table 1. Some important monomers used in emulsion polymerizations.

Monomer	Structure	Normal b.p.(^{o}C)	Tg of Homo-polymers (^{o}C)
Vinyl acetate	CH_2=CH-O-C(O)-CH_3	73	32
Vinyl chloride	CH_2=CH-Cl	-13	81
Acrylonitrile	CH_2=CH-CN	77	97
Styrene	CH_2=CH-(C_6H_5)	145	100
n-Butyl acrylate	CH_2=CH-C(O)-O-$(CH_2)_3$-CH_3	148	-56
2 Ethylhexyl acrylate	CH_2=CH-C(O)-O-CH_2- CH(CH_2CH_3)-$(CH_2)_3$-CH_3	216	-50
Methyl acrylate	CH_2=CH-C(O)-O-CH_3	80	10
Methyl methacrylate	CH_2=C(CH_3)-C(O)-O-CH_3	100	105

The Tg of copolymers prepared from mixtures of different monomers can be estimated by use of the Fox equation:

$$\frac{1}{T_g} = \frac{W_{m1}}{T_{g1}} + \frac{W_{m2}}{T_{g2}} + \ldots + \frac{W_{mn}}{T_{gn}}$$

where Tg refers to the copolymer, Tg1, Tg2… refer to the Tg of the individual homopolymers, and Wm1, Wm2… are the weight fractions of the different monomers that make up the final copolymer [14].

Initiator systems

Two major types of radical initiator systems are used, namely thermolysis systems in which free radicals are produced by thermal decomposition and redox systems in which free radicals are generated via redox reactions. Although light or radiation can be used to generate free radicals as well, this is not widely used in emulsion polymerization [10, 14].

By far the most often applied thermal systems are those based on peroxy compounds. Ammonium-, sodium- or potassium persulfate and a wide range of organic peroxides and hydroperoxides are most commonly applied. The rate of decomposition of these compounds is usually specified by their “half-life”, defined as the time at a particular temperature required reducing the concentration of the compound to half of its initial value. The three persulfates mentioned before have similar “half-lives” and therefore their effectiveness in emulsion polymerization is comparable as well.

At elevated temperatures, decomposition is usually too fast to give efficient use of the free radical polymerization due to radical recombination. While at low temperatures, persulfates are used in conjunction with a reducing agent such as sodium bisulfite. Persulfates generally display optimal decomposition rates in the temperature range of 60-95°C [10, 14].

Thermal decomposition of persulfate produces both sulfate and hydroxyl radicals, according to:

$$S_2O_8^{2-} \longrightarrow 2SO_4^{-\bullet}$$

$$SO_4^{-\bullet} + H_2O \longrightarrow HSO_4^{-} + HO^{\bullet}$$

$$2HO^{\bullet} \longrightarrow H_2O + \tfrac{1}{2}\,O_2$$

It is generally accepted that the primary initiating species in the emulsion polymerization is the sulfate anion radical, termination is predominantly caused by reaction with another sulfate-initiated radical species. For this reason, it is expected (and it has been verified) that most polymer chains will contain two sulfur atoms.

Persulfates are often chosen in preference to organic peroxides because of the increase in colloidal stability of the latex that results from the presence of sulfate end groups on the polymer chains. However, these sulfate groups also increase the water sensitivity of polymer films prepared by drying of the latex.

An organic peroxide decomposes as follows:

$$ROOR \longrightarrow 2RO^{\bullet}$$

At lower temperatures, peroxides or hydroperoxides can yield radicals upon reaction with reducing agents:

$$ROOH + Fe^{2+} \longrightarrow RO^{\bullet} + HO^{-} + Fe^{3+}$$

SURFACTANTS

Surface-active agents, more commonly known as surfactants, are substances that consist of hydrophilic and hydrophobic segments. Surfactants are added to waterborne coating formulations for different purposes. In the binder (latex) preparation, surfactants play important roles in emulsification of monomer droplets, forming micelles, stabilizing primary particles and stabilizing growing polymer particles. In formulating waterborne coatings, surfactants are added to enhance the application properties of the finished latex and its wetting properties by reducing the surface tension of the system [5, 7, 10, 11, 16, 17].

In general, surfactants can be subdivided into ionic (anionic, cationic and zwitter-ionic) and non-ionic surfactants. These two classes of surfactants stabilize growing particles in different ways during emulsion polymerization: ionic surfactants contribute to electrostatic repulsion, whereas non-ionic surfactants provide a steric stabilization effect [5, 10, 11, 17].

Low molecular weight conventional anionic and nonionic surfactants can be used in the binder (latex) preparations. However, conventional surfactants can cause adverse effects when the latex is used in a coating. These negative effects are mainly caused by desorption of surfactant from the surface of the latex particles. The unbound surfactant can migrate to the particle interfaces and increase percolation by water. The surfactant can also migrate to the air-film interface affecting gloss or to the film-substrate interface leading to poor adhesion of the coating. If the polymer is recovered via coagulation, the surfactant can adversely affects wastewater treatment processes [9-11, 14, 17-20].

To overcome these drawbacks, several approaches in preparing the latex have been investigated. The first method is carrying out emulsifier-free emulsion polymerization, this however is too costly. A second approach uses a polymeric surfactant in emulsion polymerization. Owing to its large molecular structure and strong adsorption, the polymeric surfactant is able to eliminate the disadvantages associated with surfactant migration. Moreover, due to its steric effect on particle repulsion, polymeric surfactants can give latices with excellent mechanical stability and freeze-thaw stability. The third method employs a reactive surfactant. This method improves the stability of the latex significantly by copolymerizing with the monomer thereby anchoring itself to the surface of the particles [20, 21].

Polymeric surfactants

Besides the classical ionic and non-ionic surfactants, polymeric surfactants can be used as stabilizers in emulsion polymerization. These polymeric surfactants can either be homopolymers or copolymers. The homopolymer is not so effective in stabilizing the particles, because the homopolymer can only associate with either the particle surface or with water. Hence, amphiphilic copolymer surfactants, which combine several polymeric components (blocks) in a single macromolecule, have gained the interest of researchers [3, 8, 22-25]. Amphiphilic copolymeric surfactants contain segments with different functionalities:

1) one or more segments of the surfactants (the anchoring group) adsorb strongly onto the particle surface and

2) segments or tails (the stabilizing moiety) dissolve in the continuous phase and extend into the dispersion medium thereby providing the steric barrier needed for stabilization.

This amphiphilic character can lead to the formation of aggregates, such as micelles [16, 26, 27].

Amphiphilic copolymers can be prepared either as block, random or graft copolymers. A variety of non-ionic amphiphilic block- and graft copolymers have been used in emulsion polymerization, these are summarized in Table 2. Among these copolymers, block copolymers have attracted most attention due to their good performance in emulsion polymerizations [28]. As stabilizers in emulsion polymerization, amphiphilic block copolymers can be used at lower concentrations than the analogous random block copolymers or the ionic surfactants [29, 30]. Moreover, their reduced mobility is advantageous in the coating industry, as a mobile emulsifier may weaken the polymer film properties, specifically with regard to adhesion.

Finally, recent publications have demonstrated that block copolymer micellar aggregates offer the unique property of acting as a seed for the creation of particles, provided that they are stable over sufficiently long periods of time [31].

Table 2. Polymeric Surfactants

Copolymer	Abbreviation	Reference
Block copolymers		
Diblock		
Poly(methyl methacrylate-*b*-sulfonated glycidyl methacrylate),	P(MMA-*b*-SGMA)	[32]
Polystyrene-*b*-polyoxyethylene	PS-PEO	[24, 33-35]
Poly(styrenesulfonate)-*b*-poly(ethyl-ethylene)	PSS-PEE	[36]
Poly(styrenesulfonate)-*b*-polystyrene	PSS-PS	[37]
Poly(acrylic acid)-*b*-poly(methyl methacrylate)	PAA-PMMA	[24, 31, 38]
Poly(methyl methacrylate)-*b*-poly(methacrylic acid)	PMMA-PMAA	[38-40]
Poly(methyl methacrylate)-*b*-poly(ethylene oxide)	PMMA-PEO	[24]
Poly(acrylic acid)-*b*-polystyrene	PAA-PS	[29, 30]
Poly(vinylbenzyltriethylammonium chloride)-*b*-polystyrene	PVBTC-PS	[29]
Polyisoprene-*b*-polybutadiene	PI-PB	[41]
Poly(isobutylene)-*b*-poly(methyl methacrylate)	PIB-PMMA	[38]
Poly(ethylene oxide)-*b*-polybutadiene	PEO-PB	[42]
Triblock		
Polyoxyethylene-*b*-polystyrene-*b*-polyoxyethylene	PEO-PS-PEO	[24, 34]
Polystyrene-*b*-polybutadiene-*b*-polystyrene	PS-PB-PS	[41]
Polystyrene-*b*-poly(acrylic acid)-*b*-polystyrene	PS-PAA-PS	[30]
Poly(acrylic acid)-*b*-polystyrene-*b*- poly(acrylic acid)	PAA-PS-PAA	[30]
Star-shaped		
(Poly(acrylic acid)-*b*-polystyrene)$_3$	(PAA-PS)$_3$	[30]
Graft copolymers		
Poly(lauryl methacrylate-*g*-ethylene oxide-*g*-2-hydroxy-ethyl methacrylate)	P(LMA-EO-HEMA)	[43]
Poly(stearyl methacrylate-*g*-ethylene oxide-*g*-2-hydroxy-ethyl methacrylate)	P(SMA-EO-HEMA)	[43]

Reactive surfactants

As an alternative to adsorption of polymeric surfactants to particle surfaces, reactive surfactants may be considered. Reactive surfactants are also known as polymerizable surfactants (surfmers) due to their ability to copolymerize. These surfactants will be incorporated in the polymer chain and particles during the polymerization process. Therefore, the reacted surfactant molecules cannot be desorbed like conventional non-reactive surfactants. It was shown that these surfactants offer good latex stability at high shear conditions [44].

From 1993 to 2001, in two successive European Community funded research projects, eight different academic laboratories and five industrial laboratories collaborated in the investigation of reactive surfactants. Excellent reviews and research articles from this work have been published, most studies dealt with anionic, cationic, non-ionic and zwitterionic surfactants and are summarized in Table 3 [20, 44-65].

Table 3. Reactive Surfactants.

Reactive Surfactant	Reference
Anionic	
Sodium 11-methacryloyl undecan-1-yl sulfate (MET)	[45-47]
Sodium 11-crotonoyl undecan-1-yl sulfate (CRO)	[45-47]
Sodium 3- sulfopropyl tetradodecyl maleate (M14)	[45-49]
Dodecyl sulfopropyl maleate (M12)	[45, 46, 48, 49]
Sodium monododecylmaleate (MDM)	[50]
2-(methacryloyloxy)ethyl maleate (MAEM)	[44, 51, 52]
Hexadecylester of maleic anhydride (HE16)	[53, 54]
Hexadecylamide of maleic acid (HA16)	[53]
4-(acroyloxy)butyl maleate (ABM)	[52]
1-(methacryloyl)-2-propyl maleate (MAPM)	[52]
4-vinylbenzyl maleate (VBM)	[52]
Cationic	
2-(N,N-diethylammonio)ethyl alkyl maleate chloride	[55, 56]
2-(N,N,N-triethylammonio)ethyl alkyl maleate iodide	[55, 56]
2-(N-allyl-N,N-diethylammonio)ethyl hexadecyl maleate bromide	[55, 56]
Alkyl pyridinium bromide maleate	[57, 58]
Nonionic	
2-(N,N-diethylamino)ethyl alkyl maleate	[55, 56]
Maleate nonionic (MALPEO)	[47]
Acrylated Poly(ethylene oxide)-*b*-poly(butylene oxide)	[62]
Styrenic functionalized poly(ethylene oxide)-*b*-poly(butylene oxide)	[54, 59-61]
Hexadecylmaleate N-(2-hydroxyethyl) amide	[63]
Hexadecylmaleate N-tris(hydroxymethyl) methylamide	[63]
Zwitterionic	
3-(N,N-dimethyl-N-(sulfopropyl)ammonio) propyl alkyl maleate	[55, 56]

The most important conclusions that could be drawn from the first European program on reactive surfactants [20, 44, 46, 64, 65] are:

1) Ideally the incorporation of a surfmer is low at the beginning of the emulsion polymerization process and high at later stages. In this way the surfactant will be mainly anchored at the particle surface and not buried within the particles.

2) To achieve this ideal behavior, two latex preparation procedures have been suggested:

a) tune monomer and surfmer reactivity (surfactants prepared using maleic anhydride were found to possess adequate reactivities)

b) add surfmer at the end of the polymerization process.

If after emulsion polymerization all surfactant molecules are covalently bound to the polymer, no surfactant molecules will be present in the aqueous phase. To lower the surface tension of the latex to allow application on a substrate, wetting agents will need to be added to the formulation. As a consequence, the films and coatings could still be sensitive to moisture.

Although use of a reactive surfactant can lead to improved colloidal stability, it cannot be excluded that the surfmer will be partly buried within the latex particle, even when semi-continuous processes are conducted. Therefore, in order to manufacture latices with a reactive surfactant that are comparable to latices prepared with conventional surfactants, latex producers will need to adjust the reactivity of the surfmer in comparison to that of the other monomers [20, 64, 65].

From the second European program, only a limited number of papers concerning reactive surfactants appeared. These papers mainly refer to studies on derivatives of isophthalic acid [19], the effects of carboxylic monomers on mini-emulsion polymerization [66] as well as on nucleation in mini-emulsion and behavior of new non-ionic surfactants [67].

FILM FORMATION FROM LATICES

Latices are widely used as binders in waterborne coatings. To acquire the necessary mechanical properties and be able to function as a protective and decorative coating, these binders must form a continuous film by coalescence of particles and polymer chain interdiffusion. Therefore, film formation is an important process that will determine the properties of waterborne coatings [68, 69].

Latex film formation is a complex process, it is generally regarded as a three-stage process although some authors describe the film formation as a four phase process. First, evaporation of water from the latex brings the latex particles into close packing (particle ordering). Second, as more water evaporates, deformation of the latex particles occurs to form a void free solid structure, which still is mechanically weak. Finally, coalescence of the latex particles and interdiffusion of polymer molecules occurs to give a mechanically strong film [13, 70-75]. This film formation mechanism is schematically depicted in Figure 2.

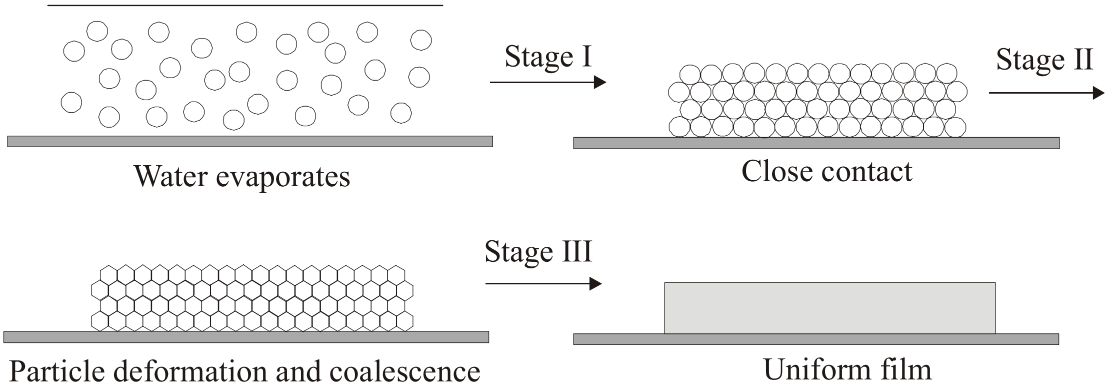

Figure 2: Film formation from latices

Stage I

In the initial stage, upon application of the latex, water is transported from the bulk of the film to the water-air interface. As evaporation of water from the surface of the latex proceeds, the concentration of the particles in the latex phase increases [72, 73] forcing the polymer particles closer together until the particles come into contact with each other [74]. As a consequence, close-packing of latex particles takes place. This stage ends when the polymer phase reaches a volume fraction, ϕ, of approximately 60-70 % (ϕ = 74 % for the closest spheres packing) or until the latex surface area at the liquid-air interface begins to decrease due to solid film formation [71, 75]. The effective particle volume (closely-packed volume) depends on the actual particle diameter and thickness of the stabilizing layer. This protective layer is generated by electrostatic repulsion when the particles surfaces bear identical electrical charges, by adsorbed ionic surface active moieties, or by hydrophilic polymer segments that have been copolymerized and attached to hydrophobic binder polymer [75].

Stage II

In this stage the overall rate of water evaporation decreases significantly, this is largely because the transport of water to the surface through a packed structure is slower than in the loose structure present in the first stage. Reduced rates of evaporation can lead to better quality films, as the particles have more time to arrange into an ordered closely packed structure before particle deformation [71].

As the remaining volatiles and water evaporate from the interstitial regions and the polymer particles, the polymer particles are forced to fill the formed voids. This particle migration is driven by capillary and interfacial forces which overcome the stabilizing (coulombic and steric) repulsions resulting in polymer-polymer contacts. The effect of capillary pressure is most pronounced for very small polymer particle sizes. Furthermore, surface tension increases with increasing particle curvature [74, 76].

Forces arising from the interfacial polymer-water tension can increase the pressure on the particles. The interfacial tension forces act in conjunction with capillary forces causing particle coalescence in the films [68, 72, 74, 76].

Stage III

At the end of stage II, the film is dry but interfaces between the particles still exist. A polyhedral-foam type structure is formed with the water contained in a network of bilayers. In stage III, the remaining water leaves the film initially via interparticle channels and then by diffusion through the fused polymer skin. The rate of evaporation eventually slows to approach that of diffusion. Impermeable or hydrophilic additives present in the film may decrease the rate of water removal [71]. In this stage, the latex particles coalesce and form a continuous film. The interface between particles disappears due to interdiffusion of macromolecular chains in the particles. This behavior is called auto-adhesion or further coalescence [68, 69].

As polymer chain interdiffusion occurs, coalescence of particles becomes complete and the cohesive strength of the film is significantly enhanced by increased chain entanglements and secondary bonding. Properties of the film, such as mechanical strength and chemical resistance, begin to develop [68, 69, 72]. Numerous models and mechanisms on the origin and extent of the coalescence forces have been proposed [76-79]. It is agreed that complete film formation in these systems requires diffusion of polymer molecules across particle boundaries in order to obtain the desired mechanical properties.

Minimum film formation temperature (MFFT)

The minimum film formation temperature (MFFT) is defined as the lowest temperature at which coalescence occurs sufficiently to form a continuous film. A major factor controlling MFFT is the glass transition temperature (T_g) of the polymer. The MFFT is normally very close to the Tg of the polymer [17, 70].

In order to apply waterborne coating systems on a substrate, the film formation temperature and MFFT of the emulsion need to be taken into account. To obtain a transparent film, the temperature at which the film is formed must be higher than the MFFT. The molecules in an individual particle should have enough freedom of movement to interpenetrate and entangle with molecules in an adjacent particle to form a coherent film. If the temperature of film formation is lower than the MFFT a brittle opaque film is formed in which voids scatter the light. However, if the MFFT of the system is too low, the film obtained can be soft and sticky. [14, 17, 70-72].

In waterborne coatings from high Tg polymers, the MFFT can be lowered by adding a plasticizing cosolvent (such as dipropylene glycol methyl ether) which depresses the MFFT during the drying but later evaporates. This will give a relatively hard (high Tg) coating that can be processed at ambient conditions.

PIGMENT DISPERSANTS

Pigments are important components in paints and coating formulations. Pigments are used in paints to give the desired color and optical properties to the coating. In addition, pigments often impart mechanical strength and protective properties to the paint. In many cases, the binders in waterborne paint systems cannot be used as stabilizing resins for the pigments, as is done in traditional solvent borne low-solids content paints. Also, in the process of replacing solventborne coating systems with waterborne coating systems, the additives used in the solventborne coatings are adapted to the new waterborne coating systems. The knowledge gained in working with the classical solventborne systems can only partially be transferred to the development of new dispersing agents for waterborne coatings [9, 17, 80, 81], and the use of tailored additives is required to allow dispersion of pigments in waterborne paint systems. The development of effective dispersing agents is one of the important issues in the waterborne coatings industry.

Pigments

Pigments are insoluble, fine-sized, particulate materials used in coatings for different purposes; such as to provide color, to hide substrate defects, to modify the application properties of a coating, to modify the performance properties of films, and/or to reduce hiding power. Pigments can be organic or inorganic and can be natural or synthetic. Pigments can be divided into four major classes: white, color, inert, and functional pigments [70, 82].

The pigments in a coating must have a high refractive index (larger than 2.0) to absorb light and a particle size of 200-400 nm to optimally scatter light. Titanium dioxide (TiO_2) has become a favoured white pigment for producing opacity in coatings. Rutile and anatase are two different crystal types of TiO_2 used in coatings. In practice, rutile is used in larger quantities because it gives about 20 % greater hiding power than anatase. The average refractive indices of rutile and anatase are 2.76 and 2.55, respectively. Rutile absorbs some violet light whereas anatase absorbs almost no light. Inorganic pigments with low refractive indices and poor opacity are termed extenders or fillers. These compounds are added to the paint to control mechanical- and rheological properties and to reduce costs [9, 70, 82].

The dispersion of pigments and fillers in a binding material has a significant effect on the quality and properties of the finished paints. Pigment volume concentration (PVC) in waterborne paints is a key parameter in adjusting application properties such as gloss, hiding power, rheology, scrub resistance, tensile strength and stability upon storage. PVC is referred to the volume percent of pigment in a dry film:

$$\mathrm{PVC} = \frac{V_{\mathrm{pigment}}}{(V_{\mathrm{pigment}} + V_{\mathrm{non\text{-}volatile\,binder}})} \cdot 100\%$$

The critical pigment volume concentration (CPVC) is defined as the minimum amount of binder which is needed to provide a complete adsorbed layer on the surface of the pigment particles and to fill all interstices between the particles in a closely-packed system [70, 83, 84].

Pigment dispersing process

An important parameter in determining the quality of coatings is the level of dispersion of the pigment particles in the binder. An optimal color development, good hiding power, high gloss and weather resistance will only be reached when dispersion of the pigment particles is optimized [5, 7, 17, 85].

Dispersion of pigments in aqueous media comprises three steps; wetting, grinding (mechanical break-up and separation of the pigment agglomerates and aggregates) and dispersion or stabilization of pigment particles in the paint. The purpose of these steps is to distribute and to stabilize the fine pigment particles in the (liquid) aqueous medium [5, 7, 17, 22, 70, 80, 82, 85-88].

Pigment particles tend to form aggregates or agglomerates especially in the liquid phase. To allow the wetting process to take place, the liquid phase must penetrate into these pigment aggregates or agglomerates. Depending on the hydrophilicity of the pigment surface, the pigment powder is covered with a thin layer of adsorbed water or air. This thin layer is replaced during the wetting process in the liquid phase [5, 7, 17, 70, 85, 87, 88].

In comparison with conventional solventborne systems, the wetting process in waterborne systems is more difficult due to the high surface tension of water. In order to accomplish this wetting process in waterborne systems, wetting agents are needed to lower the surface tension of the liquid phase. Multifunctional surfactants are commonly used wetting agents. In general, these types of surfactants consist of hydrophilic and hydrophobic groups that can completely wet surfaces of varying characteristics. Besides wetting agents, the viscosity of the liquid phase is a dominant factor influencing the wetting process; low viscosities lead to rapid wetting [70, 80, 85].

In the dispersing step, the wetted pigment aggregates or agglomerates are further broken down into smaller clusters or individual crystals and suspended in the liquid phase by applying external mechanical forces. The pigment dispersants aid wetting of newly formed surfaces and maintain the stability of the dispersion, thereby avoiding re-agglomeration of the pigment particles. To rapidly disrupt the aggregates, the millbase should have a high viscosity exerting the highest shear stresses on the pigment aggregates [5, 7, 22, 70, 88].

Pigment stabilization process

Stabilization is critical in manufacturing, storage and usage of pigments. Instability of dispersed pigment particles can result in flocculation, where larger pigment particles are formed in the coating system. With increased pigment particle size, light scattering and light absorption are reduced. Also, flocculation of pigment particles can change the CPVC of the coating films. Consequently, these affect the hiding power, color strength and gloss level of the final film [5, 70, 85].

There are several important attractive forces operating between the dispersed pigment particles [7, 17, 85, 87, 88]:

1) London-van der Waals forces;
2) Polymer bridging between adsorbed polymers;
3) Hydrogen-bonding and
4) Electrostatic attractive forces or Coulombic forces as a consequence of charge on the pigment surface.

In addition, pigment particles coarser than 1 μm are largely influenced by gravitation forces [7] as well. A pigment dispersant stabilizes the pigment dispersions either by providing steric (nonionic polymers), electrostatic, electrosteric or depletion stabilization mechanisms (polymers soluble in dispersion medium) [5, 7, 17, 24, 82, 88].

In steric stabilization mechanism, pigment dispersants are adsorbed on the particle surface, forming protective layers that prevent colliding particles from reaching a critical distance at which attractive forces become effective. The stabilization is dependent on the structure and the dimensions of the adsorbed polymer layer.

In electrostatic repulsion, the pigment particles are stabilized by Coulombic forces where the repulsive potential is created by interactions of diffused electrical double layers surrounding the particles. This stabilization mechanism is well described by the DLVO theory [5, 7, 9, 17, 70, 85, 88].

Electrosteric stabilization by ionic polymeric dispersing agent involves both electrostatic and steric mechanisms. Electrosteric stabilization is based on the formation of an electrically charged double layer at the interface of the pigment particle and the liquid as well as on steric effects due to adsorption of polyelectrolyte chains on the pigment particle surface [11,82].

For the depletion stabilization mechanism, at high polymer concentrations, the free polymer chains or non-adsorbed polymer chains present between colloidal particles generate repulsion forces and keep the pigment particles separated [89-91].

RHEOLOGICAL BEHAVIOR OF PAINTS

Definitions in rheology

Rheology is the study of deformation and flow behavior of matter under the influence of external forces [7, 17, 91-95]. Viscosity is defined as the force needed to compel two parallel liquid surfaces of unit area separated by a distance of one differential unit to slide past each other with a constant unit of velocity or as a measurement of its resistance to flow [7, 91, 93, 95]. Viscosity can also be defined as the shear stress, τ, exerted across an area when there is of velocity gradient normal to the area [7, 91, 95, 96].

$$\text{Shear stress, } \tau = \text{force/surface area (Pa)} \qquad (2.1)$$

$$\text{Shear rate, } D = \text{velocity/distance } (s^{-1}) \qquad (2.2)$$

$$\text{Viscosity, } \eta = \tau/D \text{ (mPa.s)} \qquad (2.3)$$

The rheological behavior of a liquid can be classified as Newtonian or non-Newtonian behavior.

In Newtonian liquids the properties are not dependent on time- and on shear rate. Non-Newtonian liquids can display behavior that is not time-dependent but dependent on shear rate (shear thinning or pseudoplastic and shear thickening or dilatant) as well as behavior that is time-dependent at a constant shear rate (thixotropic and rheopexic). These rheological characteristics are important in coatings and paints [7]. The different types of rheological behavior become apparent in plots of the shear stress (shear force per unit area; Pa or N/m^2) against shear rate (unit per second), see Figure 4. The slope of the curves is the viscosity (shear stress/shear rate) [7, 17, 91-97].

1. A Newtonian fluid is a fluid in which the flow is independent of shear rate. At all times, the shear rate is proportional to the shear stress and the viscosity remains constant.

2. A non-Newtonian fluid is a fluid where viscosity is a function of the shear rate and the time it is applied. The behavioral characteristics of non-Newtonian fluids consist of five major classes: pseudoplastic, dilatant, plastic, thixotropic, and rheopexic.
    - In pseudoplastic fluids viscosity decreases with increasing shear rate or shear stress.
    - The behavior of dilatant fluids is opposite to the behavior of pseudoplastic fluids: the viscosity increases with the increasing shear rate.
    - Plastic fluids only flow after the shearing force reaches a minimum threshold value τ_y (yield strength or yield value). The viscosity is then independent of shear rate. The slope is the coefficient of rigidity.
    - When a constant shear force is applied to a thixotropic fluid, its viscosity decreases in time to a limiting value. This behavior is reversible.
    - Rheopexic fluids behave in an opposite manner as thixotropic fluids; the viscosity of the fluid increases with increasing shear rate.

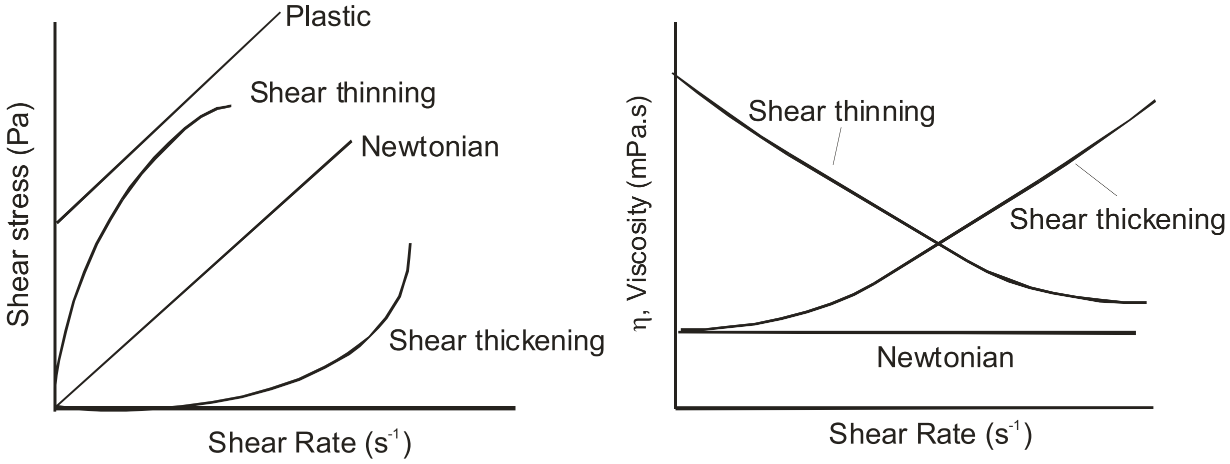

Figure 4. Rheological behavior of Newtonian and non-Newtonian liquids.

Rheological behavior of paints

The rheological behavior is an important property of waterborne latex paints because it influences the storage, processing and application performance of the paint. The rheology of paints can be significantly enhanced through use of rheology modifiers. Poor control of the rheology may lead to a variety of problems [7, 9, 17, 95].

A typical coating composition needs to perform adequately at different shear rates, as illustrated in Figure 5. The properties of a coating that depend on its viscosity at relatively low shear rates are sedimentation of pigments during storage and flowing and leveling of the paint after application. The higher the viscosity of the coating at low shear rates the lower tendency the coating show to run down and sag.

The appearance of the paint in the liquid state and its behavior during mixing is largely affected by its viscosity at medium shear rates. The viscosity at high shear rates affects the brushing, rolling and spraying properties of the paint. To achieve a good appearance of the film, brushing and rolling applications require higher viscosities while spraying applications require a much lower viscosity [9, 17, 98-100].

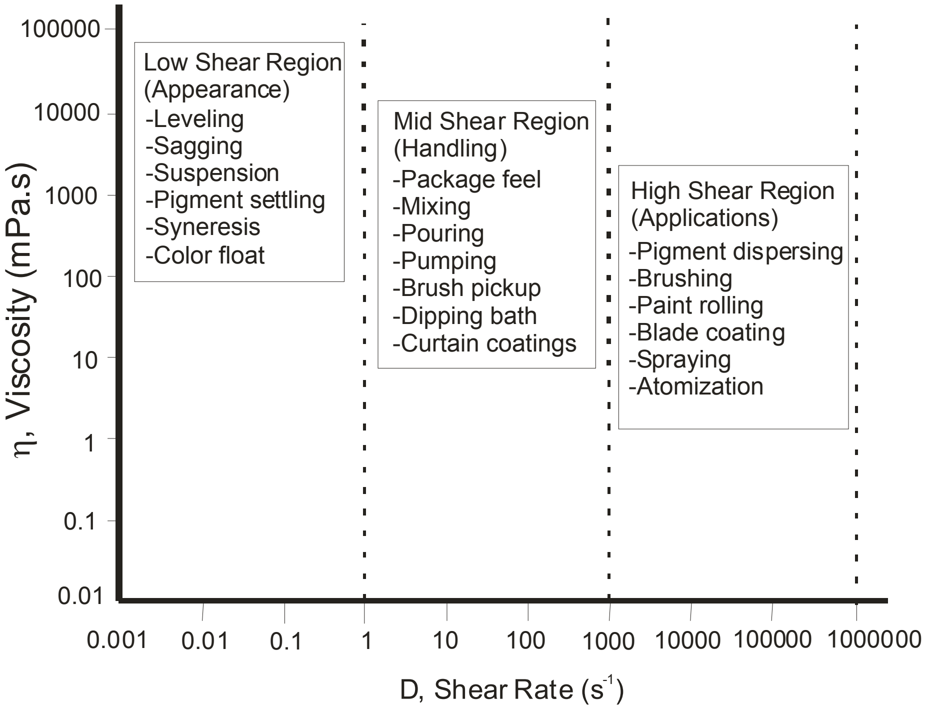

Figure 5. Viscosity and shear rate ranges required in the different processes during the production, handling and application of waterborne coatings

Rheological additives

Rheological additives play a major role in controlling the flow properties of liquid systems such as paints, inks, emulsions or pigment suspensions. In waterborne coatings, rheology modifiers affect key properties like vertical flow, leveling, gloss, film thickness, covering power, spattering tendency, brush and roll resistance, sedimentation tendency and pigment stabilization. The addition of a rheology modifier to provide the necessary processing (application and dispersion processes etc.) and performance (settling, sagging, leveling etc.) characteristics is typical of many formulations [7, 17].

CONCLUDING REMARKS AND PROSPECTS

Surfactants play widely differing, but essential, roles in the preparation of waterborne latex coatings. The use of a reactive surfactant has proven to be very effective in reducing migration of the surfactant towards the air-coating or substrate-coating interface. Only limited work has been performed on the incorporation of reactive groups into the surfactant molecule that crosslink during formation of the latex film. The design and application of multifunctional surfactants, that simultaneously can be used as emulsifiers, pigment dispersants, and rheological modifiers, is a field of research that largely remains to be explored.

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CHAPTER 3

Crosslinkable Surfactants based on Linoleic Acid-Functionalized Block Copolymers of Ethylene Oxide and ε-Caprolactone for the Preparation of Stable PMMA Latices

SUMMARY

Amphiphilic diblock and triblock copolymers consisting of poly(ethylene oxide) (PEO) as (central) hydrophilic segment and poly(ε-caprolactone) (PCL) as hydrophobic segment(s) were prepared by ring opening polymerization. The length of the PEO segment was kept constant ($\bar{x}_n$ = 45), whereas the length of the PCL block(s) was either 6 or 10 units for diblock copolymers and 3 or 5 units at each end for the triblock copolymers. These block copolymers were end-functionalized by esterification with linoleic acid (LA), which contains reactive double bonds. The autoxidative behavior of PEO_{45}-$(CL_3$-$LA)_2$ functionalized triblock copolymers was investigated by exposure of films to air at ambient conditions. Ninety percent of the double bonds had disappeared in 15 days and a crosslinked structure was obtained after 30 days. Critical micelle concentrations (CMC) of the crosslinkable surfactants were in the range of 0.08-0.19 mmol/l for the diblock copolymer and of 0.19 - 0.26 mmol/l for the triblock copolymer. The surface tension of aqueous surfactant solutions at the CMC (γ_{CMC}) (25 °C) varied from 47.1 - 51.4 mN/m for the diblock and from 45.6 - 48.1 mN/m for the triblock systems. For both systems CMC and γ_{CMC} increase with increasing HLB values. These surfactants were used in PMMA latex preparations. The latices of PMMA prepared with LA-functionalized diblock and triblock copolymers yielded narrow particle size distributions and particle sizes of 180 and 370 nm, respectively, whereas latices prepared with SDS had a particle size of 90 nm. After extraction of the latex particles with methanol, the amounts of the unextractable (either buried or copolymerized) LA-functionalized diblock and triblock copolymers

found in extracted PMMA latex particles were 10 % and 24 % of the initial amount of surfactant added respectively. Control experiments with a stearic acid (SA) containing diblock copolymer showed that the amount of buried surfactant in PMMA latices was 6.5 %. By comparing the overall latex characteristics and stability (shelf stability, freeze-thaw testing and addition of electrolyte solutions and ethanol) it was concluded that an LA-functionalized diblock copolymer (MPEO$_{45}$-CL$_{10}$-LA) gave better stabilization of PMMA latices than an LA-functionalized triblock copolymer of comparable composition and HLB value.

INTRODUCTION

Surface-active agents (surfactants) are essential in formulating low volatile organic compound (VOC) waterborne coating systems. Surfactants are added during the latex synthesis to ensure latex stability and to control particle size. Surfactants are also necessary to stabilize pigments and to allow appropriate wetting of the substrate [1-3].

In using conventional ionic or nonionic surfactants such as sodium dodecyl sulfate (SDS), alkylphenol ethoxylate (Triton X 405), two major problems arise. First, the amount of free surfactant needs to be limited to avoid migration towards the interfaces of the film during film formation. Secondly, competitive adsorption between the latex emulsifier and the pigment stabilizer can take place in pigmented latices. Surfactant migration can negatively influence the water sensitivity of the coating after film formation and the adhesion to the substrate [4-5]. Competitive adsorption between emulsifier and pigment stabilizer in an aqueous coating formulation often leads to latex instability and affects the rheology of the formulation in a negative way [6-8].

To prevent or minimize surfactant migration during film formation upon drying, the use of polymerizable surfactants that can covalently attach to the surface of the latex binder particles in heterophase polymerizations has been investigated [9]. Typical polymerizable surfactants used in the emulsion polymerization of styrene and (meth)acrylates are monomeric compounds with surface-active properties (anionic or cationic surfmers) [4, 10-11] or nonionic block copolymers (or oligomers) of polyethylene oxide (PEO) [4, 12-13, 15]. Both these surfactants contain polymerizable functionalities such as crotonic acid [10], styrene [12, 14-15], (meth)acrylic acid [5, 10, 12] and maleic acid [5, 10-13, 16].

However, there are still some difficulties with the use of polymerizable surfactants. These especially relate to the difference in reactivity of the polymerizable group in the surfactant molecule and the reactivity of the (binder) monomer. On the one hand, a too low reactivity will result in limited incorporation in or onto the latex particle or in homo-polymerization of the surfactant. This still can result in high rates of surfactant migration. On the other hand, a too high reactivity of the surfactant can lead to burying of the surfactant in the latex particles. In both cases a poor latex stability is obtained. Ideally, the reactivity of the polymerizable surfactant should be such that bound surfactant molecules are mainly located on the surface of the latex particle. In previous studies [5], several different surfactant molecules incorporating maleic acid structures were bound mostly on the surface of the latex particles. Although the formed latices are stable, the high surface tension of the latex system as a whole can impair wetting, leveling and formulation of the latex [17-18]. Therefore, the presence of free surfactant in the water phase is required as well.

In acrylic or styrenic emulsion polymerizations, the use of surfactants that can copolymerize with the binder monomer as well as form crosslinks by oxidative drying during or after the film formation process has not been investigated. Holmberg investigated the use of oxidatively drying surfactants based on fatty acid modified PEGs in the preparation of alkyd emulsions [7-8]. Such surfactants have reduced migration rates and can therefore lead to films with reduced water sensitivity that have good wetting and leveling properties during application to the substrate. In order to minimize competitive adsorption between binder and pigment, the ideal surfactant simultaneously has good pigment dispersion properties.

Also oxidatively drying alkyds have been employed to improve the properties of acrylic-based films. Hybrid systems were prepared by polymerizing acrylic monomers in the presence of colloidal alkyd droplets [19]. Fatty acid hydroperoxides that initiate the acrylic emulsion polymerization and simultaneously compatibilize the alkyd and acrylic components during emulsion polymerization were also employed [20-21]. The improved mechanical properties of these acrylic-based films show that the alkyd resins can oxidatively crosslink within the formed film.

In this study, crosslinkable diblock and triblock copolymers consisting of a fixed hydrophilic methoxy-polyethylene glycol (MPEG) or polyethylene glycol (PEG) length and different hydrophobic (poly(ε-caprolactone)) segment lengths will be prepared as nonionic polymeric surfactant. These nonionic polymeric surfactants are subsequently functionalized with linoleic acid, allowing oxidative drying during or after film formation.

The applicability of these surfactants in preparing stable methyl methacrylate (MMA) latices was investigated, and the amount of free crosslinkable surfactant in the aqueous phase was estimated.

EXPERIMENTAL

Materials

Poly(ethylene glycol (PEG_{45}) and methoxy-PEG ($MPEG_{45}$) with molecular weights of 2000 (this corresponds to 45 EO repeat units), monohydrated *para*-toluene sulfonic acid (*p*-TSA 99 %) and xylene (isomer mix, 98 %, bp = 140 °C) were obtained from Fluka, Switzerland and used without further purification. ε-Caprolactone, CL (Aldrich, United Kingdom) and stannous (II) octoate (SnOct) (Aldrich, USA) were used as received. Linoleic acid (LA) and stearic acid (SA) were supplied by Acros-Organic, USA.

Methyl methacrylate (MMA, Fluka, Switzerland, stabilized with 0.0025 % hydroquinone), potassium persulfate (KPS, Merck, Germany), sodium dodecyl sulfate (SDS, Fisher, UK) and Triton X 405 (octylphenol ethoxylate, Dow Chemical, Belgium) were used as supplied. Deionized water (Milipore Q, 18.2 MΩcm) was employed throughout the whole study.

Preparation of diblock and triblock copolymer surfactants

Block copolymers were prepared by ring opening polymerization of ε-caprolactone at 140 °C initiated by PEG_{45} or $MPEG_{45}$. Under a nitrogen atmosphere, *ε*-caprolactone was introduced into a flask containing a pre-weighted amount of MPEG or PEG. SnOct was added at a concentration of 0.010 to 0.015 wt% based on *ε*-caprolactone. After a reaction time of 24 hrs the resulting block copolymers were dissolved in chloroform and precipitated in an excess of cold hexane. After filtration, the polymers were dried at 40 °C under vacuum for 3 d. The diblock and triblock copolymers are respectively abbreviated as $MPEO_{45}$-CL_m or PEO_{45}-$(CL_m)_2$ [22-23].

Subsequent functionalization of the hydroxyl-terminated block copolymers with linoleic acid (LA) or stearic acid (SA) was carried out by esterification under a nitrogen atmosphere in refluxing xylene. The reaction was performed in a 250 ml reaction flask equipped with a mechanical stirrer (300 rpm) and a Dean-Stark trap. Typically, purified $MPEO_{45}$-CL_m or PEO_{45}-$(CL_m)_2$ (10 mmol) was reacted with a 10 to 20 mole-% excess of LA or SA using *p*-TSA as a catalyst (1.5 wt% with respect to LA or SA) in 30 ml of xylene during a reaction time of 4 hrs. The reaction products were dissolved in chloroform, precipitated in an excess of cold hexane and dried under vacuum for 3 d [24-25].

Batch emulsion polymerizations of MMA

Poly(methyl methacrylate) (PMMA) latices were prepared in batch emulsion polymerizations of MMA using LA-functionalized $MPEO_{45}$-CL_m or PEO_{45}-$(CL_m)_2$ block copolymers as surfactants. The formulation of the emulsion polymerizations carried out is given in Table 1.

Table 1. Formulation of PMMA batch emulsion polymerization.

Ingredient	
Deionized water	89.7 g
MMA	10.0 g
Surfactant	0.3 mmol
Initiator (KPS)	0.045 g
Total	≈ 100 g

The reactions were carried out at 80 °C in a 250 ml reactor equipped with a stainless steel impeller (300 rpm), nitrogen inlet and condenser. First the surfactant was dissolved in deionized water, then MMA was added and allowed to stir for 1 h under a bubbling nitrogen stream to remove dissolved oxygen. The contents were heated to 80 °C under nitrogen, and the polymerization was initiated by the addition of KPS. The reaction was continued for 4 hrs. As controls PMMA latices were prepared either without surfactant or with commercially available surfactants (SDS and Triton X 405) at an equal concentration.

Chemical and physical properties of the synthesized surfactants

To determine the molecular weight of the diblock and triblock copolymer surfactants, size exclusion chromatography (SEC) was carried out with chloroform as the eluent (1.5

mL/min). The experimental setup consisted of a Waters 510 pump, a HP Ti-Series 1050 auto sampler, four Waters Styragel columns (10^5, 10^4, 10^3, and 5 x 10^2 Å) placed in series, a Waters 410 differential refractometer and a Viscotek Viscometer Detector H502. Calibration was done with polystyrene standards with a narrow molecular weight distribution. Sample concentrations of approximately 0.5 wt/vol.% and injection volumes of 30 µl were used. All determinations were performed at 25 °C.

The composition of the block copolymers was determined by proton nuclear magnetic resonance (^{1}H-NMR) using a 300 MHz NMR spectrometer (Varian Inova). Furthermore, as $\overline{M}_n$ of MPEG and PEG are known as well, the CL_m block length can be readily determined. Deuterated chloroform was used as solvent.

From the determined compositions of the block copolymers, the approximate HLB value was calculated using the Griffin definition [26]:

$$HLB = \frac{W_H}{W_H + W_L} \times 20$$

Here W_H corresponds to the weight fraction of the hydrophilic components (EO) and W_L corresponds to the weight fraction of the lipophilic components (CL and LA).

Proton NMR was also employed to follow the conversion of double bonds in LA-functionalized surfactants upon reaction with oxygen. For this, the surfactants were spread on a glass slide and exposed to air. Periodically samples were taken from the glass slide and analyzed. Only after 30 days exposure to air, the surfactants did not dissolve in (deuterated) chloroform anymore.

Surface tension measurements were conducted using a microbalance surface tensiometer (Processor Tensiometer K12, Krüss, Germany) operating in the Wilhelmy plate mode at 25 ± 0.5 °C. The tensiometer was calibrated with deionized water before use. Critical micelle concentrations (CMC) of the surfactants were determined from surface tension versus concentration graphs after 30 min of equilibration. (For these block copolymers, equilibrium is already reached after 15 min).

PMMA latex properties

After a polymerization time of 4 hrs, the MMA monomer conversion and the latex solid content was determined gravimetrically after removal of unreacted monomer and water by application of vacuum and subsequent freeze-drying. The percentage of coagulum was determined gravimetrically after filtration of the latex through a 75 µm filter (Endecotts, UK). The molecular weight of the final polymer was determined by SEC as described above.

The latex particle size was determined by dynamic light scattering (DLS) (Zetasizer 4000, Malvern Instruments Ltd., Malvern, UK) at 25 ± 1 °C at an angle 90 °, taking the average of five measurements. The shape and morphology of the PMMA particles were determined by scanning electron microscopy (SEM). Diluted particle dispersions were placed on carbon grids, dried and viewed with a LEO1550 Gemini field emission SEM (LEO, Germany) operating at 0.70 kV.

SEC was used to determine the molecular weight of the PMMA latices in the same manner as described above.

To establish the presence of free surfactant in the latex and to get an indication of the wetting properties of the latex, the surface tension of the latices was determined as well in the same manner as described above. Also, The PMMA latices were centrifuged (20000 rpm, 1 hr), decanted and redispersed in deionized water twice, and subsequently extracted with methanol in a Soxhlet setup. The polymers were analyzed by ^{1}H-NMR before and after extraction, allowing quantification of the amount of surfactant copolymerized with MMA, buried in the latex particle or free in the water phase [13].

The stability of the latices prepared using different surfactants was determined by visual examination of the occurrence of phase separation [6, 15] upon freeze-thawing (the dispersions were kept at –20 °C for 24 hrs and subsequently at room temperature for another 24 hrs), addition of an equal volume of ethanol and addition of equal volumes of electrolytes (0.1 M $MgSO_4$, 0.1 M NaCl, 0.5 M NaCl or 1.0 M NaCl).

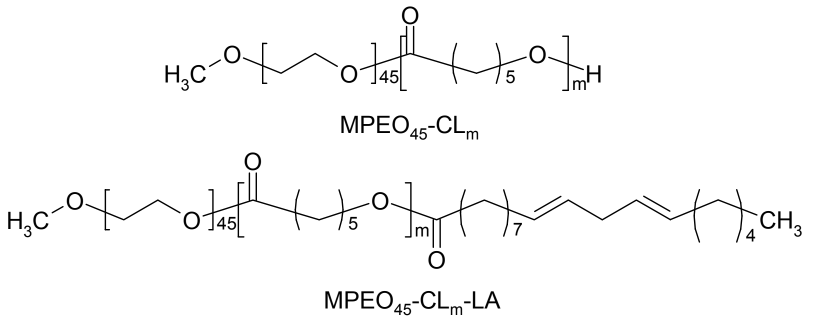
The shelf stability of the latices was evaluated upon standing at room temperature for two wks in the same manner.

RESULTS AND DISCUSSION

Properties of diblock and triblock copolymeric surfactants

Diblock and triblock copolymers based on hydrophilic PEO and hydrophobic PCL segments were prepared by ring opening polymerization of ε-caprolactone (CL) initiated with MPEG or PEG and SnOct. In a subsequent step, these copolymers can be functionalized with linoleic acid. The structures of these compounds are shown in Figure 1.

Diblock copolymers



Triblock copolymers

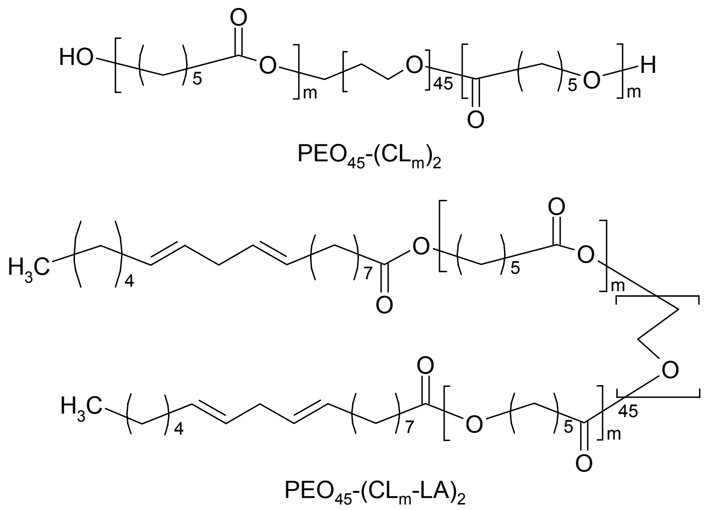


Figure 1. Chemical structure of diblock (MPEO$_{45}$*-CL*$_m$*-LA) and triblock (PEO*$_{45}$*-(CL*$_m$*-LA)*$_2$*) copolymer surfactants. The subscript m corresponds to the number of CL repeat units.*

In previous research [12], it was found that nonionic surfactants based on poly(ethylene oxide-*b*-butylene oxide) block copolymers showed good steric stabilization properties and high cloud point temperatures when the molecular weight of the PEO block was approximately 2000. High cloud point temperatures allow the emulsion polymerization to take place at elevated temperatures. Therefore, in our surfactant syntheses, we used MPEG and PEG with 45 repeating EO units in the initiation of the CL ring opening polymerization.

The length of the hydrophobic blocks of the diblock and triblock copolymers can be controlled by adjusting the MPEG or PEG macroinitiator to CL monomer ratio in the polymerization reaction. This will result in surfactants with different hydrophilic to lipophilic balance (HLB) values.

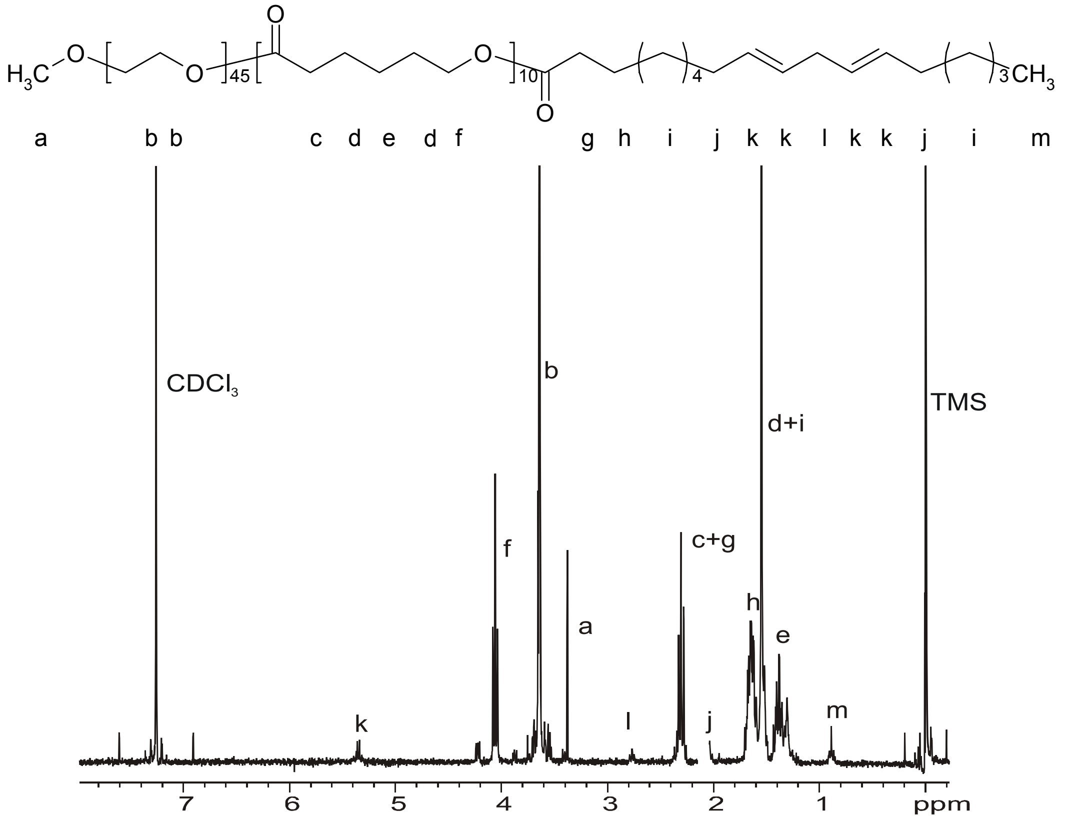


Figure 2. ^{1}*H-NMR of linoleic acid functionalized* $MPEO_{45}$-CL_{10}-*LA.*

After the ring opening polymerization and functionalization step, the prepared block copolymers are purified by precipitation in hexane. Figure 2 shows a proton NMR spectrum of MPEO-CL_5-LA. The sharp singlet at 3.65 ppm corresponds to the methylene protons of ethylene oxide in the MPEG. As MPEG does not precipitate under these conditions, the formation of a block copolymer is confirmed.

The peaks at 1.40, 1.55, 2.45 and 4.10 ppm can be assigned to the different methylene protons in the CL_m block. Similar spectra were obtained for the functionalized triblock copolymers. Proton resonances related to the unsaturations in the linoleic acid part can be observed at 5.4 ppm, other peaks from linoleic acid can be found at 0.88, 1.26, 2.10, 2.25 and 2.80 ppm. This indicates the successful functionalization of the block copolymers. By integration of the peak integral intensities, the chemical composition of the functionalized block copolymers can be determined.

Table 2. Characteristics of PEO_{45} and CL diblock and triblock copolymer surfactants before and after functionalization with linoleic acid (LA).

Block copolymer	Composition from NMR (units)			$\overline{M}_n$ expected [a] (g/mol)	$\overline{M}_n$ (H-NMR) (g/mol)	$\overline{M}_n$ (SEC) (g/mol)	HLB value
	EO	CL	LA				
$MPEO_{45}$-CL_6	45	5.8	0	2680	2670	5910	15.0
$MPEO_{45}$-CL_6-LA	45	5.8	0.5	2950	2770	4480	14.4
$MPEO_{45}$-CL_{10}	45	9.8	0	3140	3110	2420	12.8
$MPEO_{45}$-CL_{10}-LA	45	9.8	0.8	3400	3340	2570	12.0
PEO_{45}-$(CL_3)_2$	45	6.2	0	2680	2700	4480	14.9
PEO_{45}-$(CL_3$-$LA)_2$	45	6.2	1.6	3220	3150	5070	12.7
PEO_{45}-$(CL_5)_2$	45	9.7	0	3140	3110	-	12.9
PEO_{45}-$(CL_5$-$LA)_2$	45	9.7	1.8	3670	3620	4890	11.0

[a] $\overline{M}_n$ expected is calculated from the MPEG or PEG to CL molar ratio, assuming each terminal OH group initiates a (living) CL ring opening polymerization [28].

As the molecular weight of the used MPEG or PEG initiator is known and SEC chromatograms of the block copolymers are monomodal (data not shown), comparison of the integral values corresponding to the CL and PEO blocks allows the determination of the CL block lengths from the NMR data [22, 27]. The determined compositions and molecular weights of the synthesized block copolymers before and after functionalization with linoleic acid are summarized in Table 2. The degree of functionalization with LA is 0.5 - 0.8 and 1.6 - 1.8 for the diblock and triblock copolymers, respectively. This indicates, that a fraction of the diblock and triblock copolymers is not functionalized, and that part of the triblock copolymers is mono-functionalized.

The molecular weights of the block copolymers determined by NMR agree well with the expected values. Also, functionalization with LA at 180 ^{o}C does not lead to degradation. SEC determinations of the molecular weight of the block copolymers gave significantly different values than those derived from NMR. This has previously been observed for low molecular weight PEG-poly(lactide) block copolymers as well [29], and can most likely be related to the calibration procedure in which poly(styrene) standards were used instead of PEO standards. The determined polydispersities are very narrow

(1.05 - 1.08), indicating that extensive transesterification and/or backbiting reactions have not occurred during the ring opening polymerization or functionalization reaction [27-28].

Autoxidation of LA-functionalized polymeric surfactant (PEO_{45}-(CL_3-LA)$_2$)

Since NMR spectroscopy confirmed the presence of unsaturated double bonds in the linoleic acid derivatized surfactants after the esterification reaction at 180 °C, crosslinking of the surfactants at ambient conditions was evaluated. It is known that unsaturated fatty acids, such as linoleic acid, can crosslink via a radical mechanism involving oxygen from the surroundings [30-31]. The disappearance (conversion) of the double bonds in PEO_{45}-(CL_3-LA)$_2$ surfactant films exposed to air was determined by NMR from the change in time of the (normalized) integral values of the double bond signal at 5.4 ppm [30, 32].

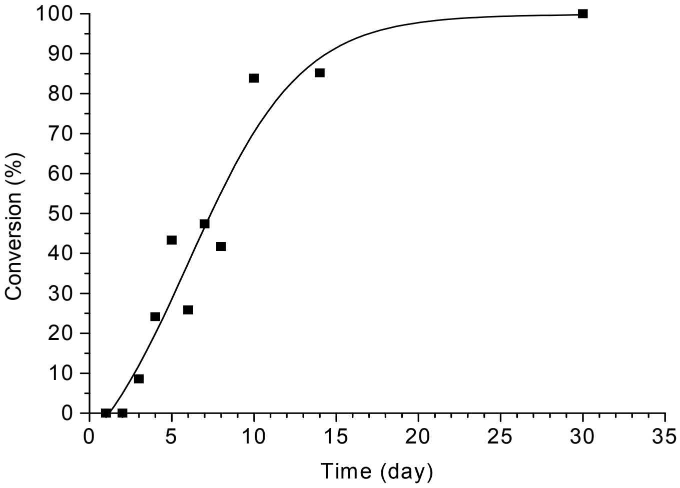


Figure 3. Disappearance (conversion) of the double bonds in PEO_{45}-(CL_3-LA)$_2$ films exposed to air as determined by NMR.

Figure 3 shows the conversion of double bonds as a function of time. Up to a period of 30 days, the surfactant films were found to be soluble in (deuterated) chloroform. In a period of 15 days, almost 90 % of the double bonds were converted and after 30 days full autoxidation was observed. Furthermore, after this time period, the surfactant film did not dissolve anymore, and a swollen, crosslinked structure had been obtained. The conversion of the unsaturated, non-conjugated double bonds in these LA-functionalized surfactants is analogous to the oxidation of unsaturated bonds in alkyl linoleates ($C_nH_{2n+1}OOC_{18}H_{31}$), which were used as model compounds in oxidatively drying alkyd systems. These compounds yield a crosslinked structure via a propagation-like reaction mechanism [30-

31]. From this it follows, that the block copolymeric surfactants used in this study can be referred to as being crosslinkable surfactants.

Surface active properties of (crosslinkable) diblock and triblock polymeric surfactants (MPEO$_{45}$-CL, PEO$_{45}$-(CL)$_2$, MPEO$_{45}$-CL-LA and PEO$_{45}$-(CL-LA)$_2$

The relation between surface tension and concentration of several crosslinkable surfactants is shown in Figure 4. The behavior of SDS and of Triton X 405, a commercially available nonionic surfactant, is shown as well. The surface tension decreased significantly as the concentration of surfactant increased.

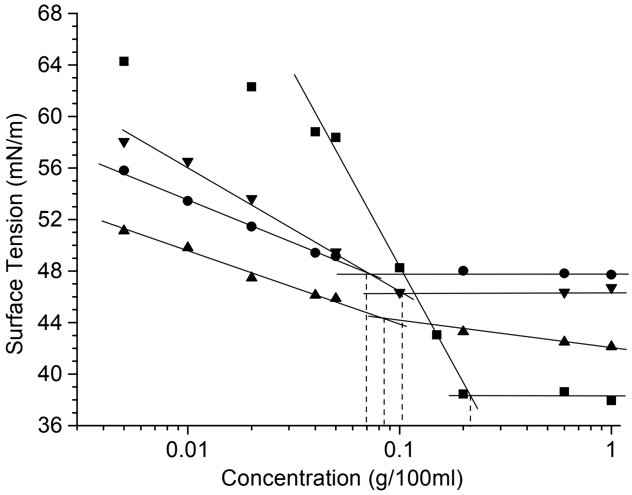


Figure 4. Surface tension versus concentration for PEO$_{45}$-(CL$_3$)$_2$ (●), PEO45-(CL$_3$-LA)$_2$ (▲), Triton X 405 (▼) and SDS (■) surfactant solutions in water. The dotted lines indicate the CMC.

The critical micelle concentration (CMC) is a characteristic parameter of a surfactant. At the CMC, a sudden change in surface tension of the solution with an increase in concentration can be observed due to the formation of micellar-like structures [33]. The CMC of LA-functionalized surfactants in water is less well defined than that of SDS and non-functionalized nonionic surfactant solutions. This behavior can be due to the variations in surfactant composition upon functionalization. Nevertheless, clear discontinuities in the surface tension curve can be discerned. With these surfactants, the surface tension of the micellar-like solutions can be reduced to approximately 42 mN/m at 25 °C.

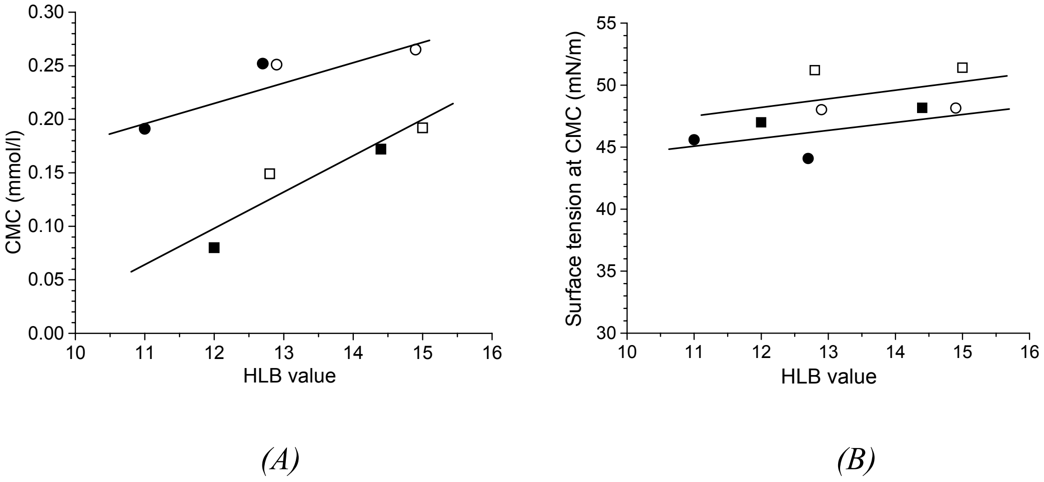
The determined CMC and surface tension values at the CMC (γ_{CMC}) are summarized in Table 3. The CMC values of the diblock and triblock copolymeric surfactants range between 0.02 and 0.09 g/100 ml.

Table 3: CMC and surface tensions at CMC (γ_{CMC}) of PEO_{45} and CL diblock and triblock copolymer surfactants and of reference ionic and nonionic surfactants

Surfactant	HLB	CMC (g/100 ml)	CMC[a] (mmol/l)	γ_{CMC} (mN/m)
Diblock copolymers				
$MPEO_{45}$-CL_6	15.0	0.05	0.19	51.4
$MPEO_{45}$-CL_{10}	12.8	0.05	0.15	51.2
$MPEO_{45}$-CL_6-LA	14.4	0.05	0.17	48.2
$MPEO_{45}$-CL_{10}-LA	12.0	0.03	0.08	47.0
Triblock copolymers				
PEO_{45}-$(CL_3)_2$	14.9	0.07	0.27	48.1
PEO_{45}-$(CL_5)_2$	12.9	0.08	0.25	48.0
PEO_{45}-$(CL_3\text{-}LA)_2$	12.7	0.08	0.25	44.1
PEO_{45}-$(CL_5\text{-}LA)_2$	11.0	0.07	0.19	45.6
Commercial surfactants				
Triton X 405	17.6	0.10	0.59	46.3
SDS	-	0.22	7.69	38.1

[a] based on molecular weights derived from NMR

Compared to the commercially available ionic and nonionic surfactants, the diblock and triblock copolymer surfactants form aggregates at a significantly lower concentration. The CMC and γ_{CMC} values decreased with increasing hydrophobic CL segment length and upon LA-functionalization of the block copolymers. When plotted in a graph, see Figure 5, it can be seen that for the different architectures (diblock copolymers and triblock copolymers) γ_{CMC} and CMC increased with an increase in HLB value. At comparable HLB values, the CMC values were higher for triblock copolymers than for diblock copolymers, while γ_{CMC} was slightly lower. These higher CMC values are due to reduced hydrophobic interactions of the CL-LA segments in the block copolymer, which are relatively shorter than in diblock copolymers. Functionalization with LA seems to only affect the HLB value. This implies that at low concentrations non-functionalized and LA-functionalized diblock copolymers can be most effectively used as stabilizers in emulsion polymerizations.



(A) *(B)*

Figure 5: CMC (A) and surface tension at CMC (B) as a function of HLB values for non-functionalized (□) and LA-functionalized diblock copolymers (■) and non-functionalized (○) and LA-functionalized triblock copolymers (●)

MMA emulsion polymerization

The crosslinkable block copolymeric surfactants were used in the batch emulsion polymerization of methyl methacrylate (MMA). To investigate the effect of molecular architecture of the LA-functionalized surfactants on the MMA polymerization behavior, different surfactants with comparable HLB values were used. From Table 2, $MPEO_{45}$-CL_{10}-LA (diblock) and PEO_{45}-$(CL_3$-$LA)_2$ (triblock) with HLB values after LA-functionalization close to 12 were chosen. As controls the commercially available ionic and nonionic surfactants were employed as well. The characteristics of the prepared PMMA latices are summarized in Table 4.

The conversions of MMA in the prepared latices varied between 74 and 90 %, this is most likely due to the non-optimized polymerization conditions employed. The latex prepared with the anionic SDS surfactant had the smallest particle size (90 nm), while the surfactant-free system produces the largest particles (430 nm) with the broadest distributions. The emulsifier-free latex was stabilized only by the initiator sulfate groups, but interfacial surface tension reduction was not as efficient as with a surfactant. Latices prepared with the nonionic Triton X 405 surfactant, had a particle size of 190 nm.

Table 4. PMMA latices prepared by batch emulsion polymerizations with different surfactants. Surfactant concentrations are 0.3 mmol/100 ml.

Latex	Surfactant	SC [a] (%)	MMA Conv.[b] (%)	$\overline{M}_w$ [c] (x 10^6)	PS [d] (nm)	PDI [e]	Coag.[f] (%)
1	$MPEO_{45}$-CL_{10}-LA	7.4	74.2	1.27	180	0.10	0.5
2	PEO_{45}-$(CL_3$-$LA)_2$	7.8	77.9	1.61	370	0.05	8.3
3	SDS	7.8	78.2	1.03	90	0.03	0.2
4	Triton X 405	9.3	93.3	-	190	0.10	0.2
5	No surfactant	9.0	89.7	0.80	430	0.26	1.0

[a] *SC = Solid content determined after removal of volatiles by freeze drying;*

[b] *Conv. = MMA conversion calculated from SC, corrected for surfactant content;*

[c] $\overline{M}_w$ *= weight average molecular weight of final polymer determined by SEC;*

[d] *PS = Particle size;*

[e] *PDI = polydispersity index of particle size distribution;*

[f] *Coag. = Coagulum based on SC.*

Latices prepared with the crosslinkable $MPEO_{45}$-CL_{10}-LA and PEO_{45}-$(CL_3$-$LA)_2$ surfactants yielded narrow particle size distributions with particle sizes of respectively 180 nm and 370 nm. The former particle sizes are comparable to the particle sizes of latices prepared with Triton X 405 (a commercially available nonionic surfactant) at the same molar concentration.

Triblock copolymer-stabilized latex particles (Latex 2) were approximately twice as large as the diblock copolymer stabilized latex particles, although the surfactants had similar HLB values. This could be due to bridging flocculation of the latex particle as a result of the hydrophobic-hydrophilic-hydrophobic architecture of the surfactant molecule. It should also be realized that monomer conversion was not complete. Although most latex preparations resulted in low contents of coagulum, less than 1 %, the (PEO_{45}-$(CL_3$-$LA)_2$) triblock copolymer stabilized latex contained 8.3 % of coagulum [17-18].

Figure 6 shows SEM images of the different latex particles prepared. It can be seen that the latex particles are reasonably uniform in size. The diameters of the particles observed in the SEM images are close to the sizes obtained from dynamic light scattering.

The particles are smooth and spherical, although in some cases (Figure 6a, 6c, 6d) the applied vacuum and electron beam has resulted in fusion of the particles.

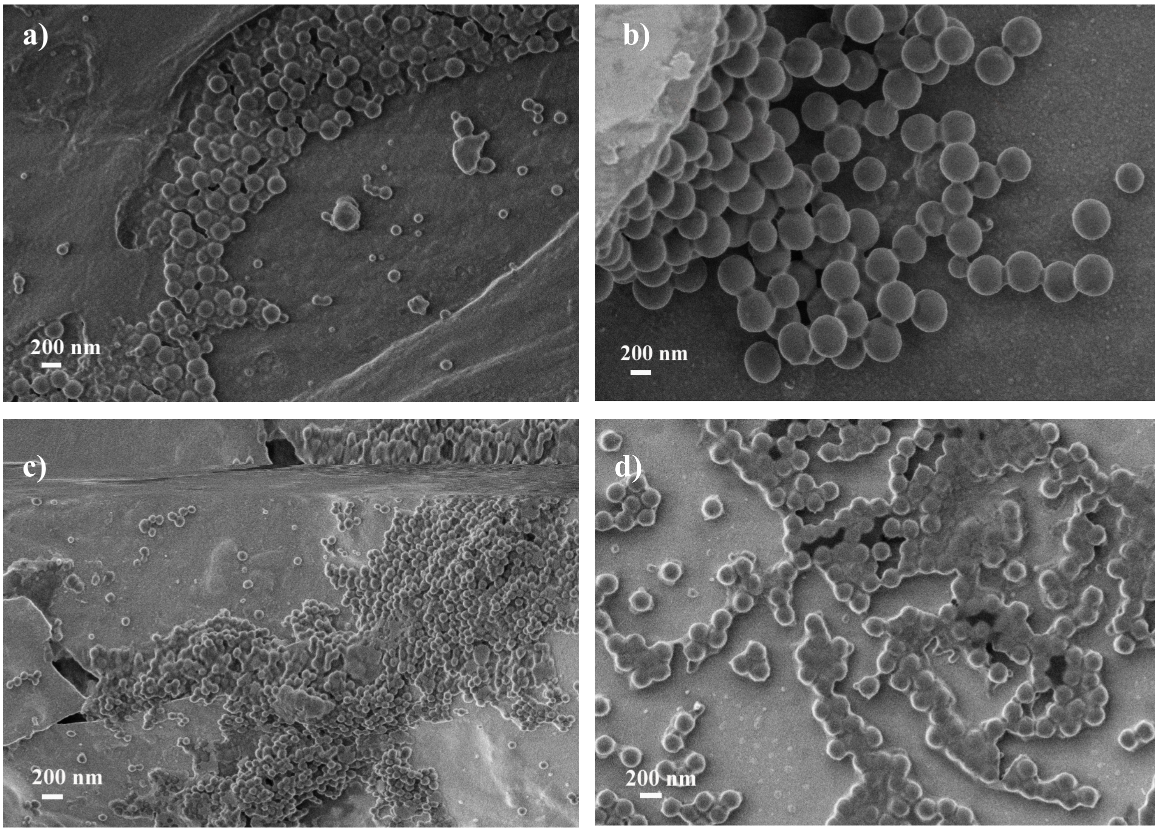


Figure 6. Scanning electron microscopy (SEM) images of PMMA latices prepared with linoleic acid functionalized surfactants: a) MPEO$_{45}$*-CL*$_{10}$*-LA; b) PEO*$_{45}$*-(CL*$_{3}$*-LA)*$_{2}$ *and commercial surfactants c) SDS and d) Triton X 405.*

Availability of free surfactant

The developed surfactants should stabilize the latex particles during and after the emulsion polymerization and provide good wetting properties during application of the latex. For this, free surfactant molecules, which can oxidatively crosslink during film formation, should remain available after the emulsion polymerization. Analyses of free surfactant were carried out by surface tension measurements of the prepared latices and are shown in Table 5.

Table 5. Surface tension of PMMA latices prepared in batch emulsion polymerizations with different surfactants. Surfactant concentrations are 0.3 mmol/100 ml.

Latex	Surfactant used	Surface tension of latex (mN/m)
1	$MPEO_{45}$-CL_{10}-LA	49.2
2	PEO_{45}-$(CL_3$-$LA)_2$	50.7
4	SDS	55.8
5	Triton X 405	50.5
6	No surfactant	64.5

The surface tensions of the latices prepared using crosslinkable block copolymeric surfactants are 49-52 mN/m. These values are lower than those of the SDS-stabilized latices (55.8 mN/m), emulsifier-free latex (64.5 mN/m) and water (72.5 mN/m). Also, similar surface tension values are obtained with Triton X 405- and $MPEO_{45}$-CL_{10}-SA- (non-crosslinkable diblock copolymeric surfactant analogous to LA) stabilized latices. This indicates that free crosslinkable polymeric surfactant molecules are available in the aqueous phase of the latex. This can promote wetting and spreading during application of the latex on a surface. With the surface tension data given in Table 5, a rough approximation of the free surfactant concentration in the latex can be determined by interpolation of Figure 4. The surfactant concentrations for $MPEO_{45}$-CL_{10}-LA and PEO_{45}-$(CL_3$-$LA)_2$ stabilized latices determined in this manner are 3.46×10^{-3} and 6.3×10^{-3} g/100 ml respectively.

The amount of surfactant either in the water phase, buried within the PMMA particles or copolymerized with MMA can be determined by NMR. After freeze drying of the PMMA latex prepared with $MPEO_{45}$-CL_{10}-LA (to remove unreacted MMA and water), the availability of unreacted double bonds originating from the surfactant can be illustrated by NMR, as shown in Figure 7.

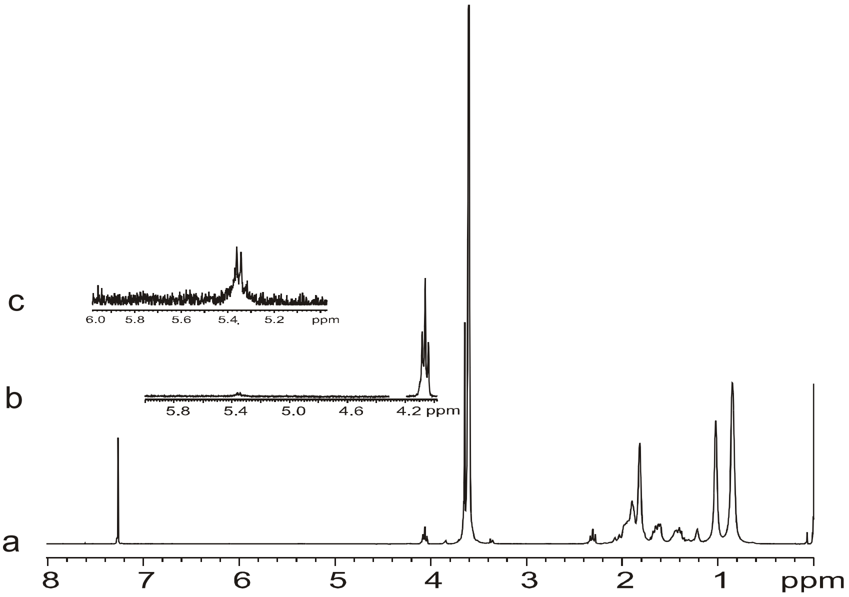


Figure 7. ^{1}H-NMR spectrum of a PMMA latex prepared with MPEO$_{45}$-CL$_{10}$-LA surfactant. a) Full spectrum b) Expansion of the spectrum illustrating the relative intensities of unreacted LA double bond protons and CL methylene protons. c) Further expansion of the spectrum illustrating the presence of unreacted LA double bond protons.

The signal at 5.35 ppm corresponds to the double bonds in LA. Signals at 3.6 ppm and 3.65 ppm are associated with the O-CH_3 of PMMA and the O-CH_2CH_2O of PEO, respectively. Peaks at 4.1 ppm correspond to CL methylene protons. The peaks at higher fields (0.88 ppm (syndiotactic), 1.02 ppm (atactic), 1.18 (isotactic) CH_3-C- of PMMA and at 1.82 -CH_2- of PMMA [34-35] overlap with resonances of the LA and CL components of the surfactant.

To quantify the amount of surfactant that is copolymerized with MMA or buried within the latex particle, and therefore not present in the water phase, Soxhlet-extractions of the latices with methanol were carried out. By comparing the ratio of the integrals at 3.65 ppm (MPEO or PEO) and at 3.6 ppm (PMMA) in NMR spectra of latex particles before extraction to those of particles after extraction, the amount of LA-functionalized diblock copolymer remaining in the latex particles was calculated to be 10 % of the amount of surfactant added. In the case of LA-functionalized triblock copolymers 24 % could not be extracted.

To differentiate between copolymerized surfactant and surfactant buried in the latex particles, diblock surfactants functionalized with SA were employed as well. Under the same reaction conditions it was shown that MPEO$_{45}$-CL$_{10}$-SA could be used to prepare

PMMA latices as well. Typical characteristics of these surfactants are HLB value: 12.1, CMC 0.064 g/100 ml (0.19 mmol/l), γ_{CMC}: 48.6 mN/m. The surface tension of a PMMA latex prepared with this surfactant at the given conditions had a surface tension of 48.9 mN/m, a particle size of 240 nm, and the amount of coagulum was 1.0 %.

SA is analogous to LA, but does not contain double bonds and cannot be copolymerized with MMA. For latices prepared with SA-functionalized diblock copolymers, NMR analysis showed that after the extraction experiments 6.5 % remained buried within the latex particles. By assuming that SA and LA-functionalized diblock copolymers have comparable compatibility and adsorption to the PMMA latex particles, the amount of buried LA-functionalized diblock copolymer surfactant can also be estimated at 6.5 %. Therefore, to a first approximation, it can be estimated that the amount of copolymerized LA-functionalized diblock copolymers in the PMMA latex particles is 3.5 % (10 % – 6.5 % = 3.5 %).

Stability of PMMA latices

Table 6 gives an overview of the stabilities of the PMMA latices prepared under comparable conditions with different surfactants. Although a PMMA latex can be prepared without a surfactant, these latices were not stable. When using SDS as a surfactant the latices were not stable in freeze-thaw tests, while the use of nonionic Triton X 405 and the functionalized block copolymeric surfactants described in this paper resulted in stable latices. This implies that in freeze-thawing cycles steric stabilization is necessary. In shelf life studies, the diblock copolymer $MPEO_{45}$-CL_{10}-LA was found to be more effective than the triblock copolymer PEO_{45}-$(CL_3\text{-}LA)_2$. This can be due to the higher incorporation of triblock copolymer into the latex particles, and therefore a lower amount present in the water phase (see above). Bridging flocculation can also have played a role. In the particle size analysis (dynamic light scattering (DLS)) (no figure was included here), no significant changes were observed of the latex particle size in most of the latices except for the surfactant-free latex system.

Table 6. Stability of PMMA latices prepared with different surfactants.

Latex	Surfactant used	Shelf stability (2 weeks)	Freeze-thaw test
1	$MPEO_{45}$-CL_{10}-LA	+	+
2	PEO_{45}-$(CL_3$-$LA)_2$	+-	+
3	SDS	+	-
4	Triton X 405	+	+
5	No surfactant	-	-

+ *stable, no macroscopic phase separation*

+- *slight macroscopic phase separation*

- *unstable, macroscopic phase separation*

The stabilities of the latices upon addition of salts and ethanol are summarized in Table 7. Equal volumes of NaCl (monovalent) salt solutions ranging from 0.1 M to 1.0 M in concentration and $MgSO_4$ (divalent) solutions of 0.1 M were added to the latices.

Table 7. Stability of PMMA latices prepared with different surfactants upon addition of electrolyte solutions and ethanol.

Latex	Surfactant used	0.1 M NaCl	0.5 M NaCl	1.0 M NaCl	0.1 M $MgSO_4$	Ethanol
1	$MPEO_{45}$-CL_{10}-LA	+	+	+	+	+
2	PEO_{45}-$(CL_3$-$LA)_2$	+	+-	+-	+-	+
3	SDS	+-	-	-	-	-
4	Triton X 405	+	+	+	+	+
5	No surfactant	-	-	-	-	-

+ *stable, no macroscopic phase separation*

+- *slight macroscopic phase separation*

- *unstable, macroscopic phase separation*

Again, the sterically stabilized latices (Latex 1, 2, and 4) are relatively resistant to the addition of electrolytes and ethanol. The ionic surfactants do not perform well, as can be expected [36]. At higher concentrations of NaCl and in the presence of $MgSO_4$, the $MPEO_{45}$-CL_{10}-LA diblock copolymer surfactant is more effective than the triblock copolymer. The stability of the nonionic surfactants towards ethanol is also indicative of strong adsorption of the surfactant to the particle surface [6].

Future work will address issues regarding the properties of waterborne acrylate coatings prepared with these surfactants; latex application to a substrate, surfactant migration during drying and film formation and pigment stabilization will be investigated.

CONCLUSIONS

Linoleic acid functionalized diblock and triblock copolymers based on poly(ethylene oxide) and ε-caprolactone segments have been prepared by ring opening polymerization and esterification. The double bonds in the LA-functionalized block copolymers can undergo oxidative crosslinking in the presence of air. Furthermore, these block copolymers display good surface activity. Both the diblock and the triblock copolymeric LA-functionalized surfactants can be used as surfactants in emulsion polymerizations of MMA. Compared to the triblock copolymeric surfactant (PEO_{45}-$(CL_3$-$LA)_2$), the diblock copolymer ($MPEO_{45}$-CL_{10}-LA) gives less coagulum, smaller particle size and more stable latices in PMMA emulsion polymerizations. After emulsion polymerization, the free surfactant present can help in wetting of a substrate during application of waterborne coating systems. Upon drying and film formation the surfactants can crosslink oxidatively.

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CHAPTER 4

Redox-initiated PMMA emulsion polymerizations stabilized with block copolymers based on poly(ethylene oxide), ε-caprolactone and linoleic acid.

SUMMARY

A redox initiating system, consisting of *t*-butyl hydroperoxide (tBHPO), iso-ascorbic acid (iAA) and ethylenediaminetetraacetic acid ferric-sodium salt (FeEDTA), was employed in emulsion polymerizations of methyl methacrylate (MMA) at 30 wt% in water. The system was stabilized using, linoleic acid (LA) functionalized and non-functionalized surfactants based on methoxy-PEG (MPEG) and ε-caprolactone (CL). To optimize reaction conditions and to avoid coagulation, the temperature, the amount of initiator, the chemical characteristics of the surfactant and the surfactant to monomer ratio were varied. $MPEO_{45}$-$CL_{6.5}$-LA was found to be the most suitable surfactant, as it performs adequately under sub-optimal reaction conditions. In the emulsion polymerization of MMA in water at approximately 30 wt%, best results were obtained at a reaction temperature of 60 ^{o}C, with an initiator system comprising tBHPO, iAA and FeEDTA, and a surfactant to monomer ratio of 10/90 or higher. Under these conditions, stable PMMA latices with average particle sizes of 200 to 300 nm were obtained at complete monomer conversion.

INTRODUCTION

High solids content latices are of much interest in industrial applications. In their preparation, a surfactant is needed to stabilize the particles during polymerization and storage. Conventional surfactants, such as sodium dodecyl sulfate, have been used in the preparation of high solids content latices. However, the use of these low molecular weight compounds is not ideal, as desorption of the physically bound surfactant from the latex particle can cause destabilization of the particles. Also, migration of the surfactant to film-air and film-substrate interfaces after application of the latex films can lead to water sensitivity and adhesion problems [1-2].

Several solutions have been investigated. In one method the surfactant is removed by extensive washing with water. This procedure is costly and time-consuming, while surfactant removal from the final product is incomplete [3]. In another method hydrophilic comonomers such as (meth)acrylic acid, (meth)acrylamide and their derivatives are employed. However, this can lead to a change in the overall polymer properties [4]. A more promising solution is the use of reactive surfactants (surfmers) which can participate in the polymerization reaction, covalently binding to the polymer chain and simultaneously stabilizing the formed particles [1-3, 5-8]. Most latices prepared using this type of surfactant have been latices with solids contents below 10 % [6-8]. Only a limited number of publications in which relatively high solids content latices (30-40 %) have been prepared with surfmers are available in the open literature [1-2, 5-6].

In previous work [9], we have shown that linoleic acid (LA) functionalized block copolymers can be used in stabilizing latex particles during emulsion polymerization and, as they are oxidatively crosslinkable during drying of the film when casted, migration will be minimized. These relatively low solids contents latices (10 wt%) were prepared using potassium persulfate (KPS) as initiator for methyl methacrylate (MMA) emulsion polymerizations. With this initiator a reaction temperature of 80 ^{o}C is generally required. At these elevated temperatures, the solubility of the PEO component in water is not very high due to the disruption of a structured water layer that at lower temperatures surrounds the PEO chains and increases solubility [10]. When increasing the solids content to 20 wt%, coagulation of the emulsion occurred, making it impossible to prepare stable MMA latices at higher solids contents.

To overcome the effects of decreased solubilities at high temperatures, we propose to use a redox initiator system based on *t*-butyl hydroperoxide (tBHPO), iso-ascorbic acid (iAA) and ethylenediaminetetraacetic acid ferric-sodium salt (FeEDTA) at lower temperatures. In this study, the reaction conditions of relatively high solids contents (30 wt%) MMA emulsion polymerizations with the aforementioned redox system were optimized, and the resultant latex characteristics were determined.

EXPERIMENTAL

Materials

Methoxy-poly(ethylene glycol) (MPEG) with a molecular weight of 2000 g/mol containing 45 ethylene oxide repeat units, monohydrated *para*-toluene sulfonic acid (*p*-TSA) and xylene (mixture of isomers) were obtained from Fluka, Switzerland. ε-Caprolactone (CL) from Aldrich, United Kingdom, linoleic acid (LA) from Acros-Organic, USA and stannous (II) octoate (SnOct) from Aldrich, USA. These materials were used as received. Deionized water (Milipore Q, 18.2 MΩcm) was used throughout the study.

Methyl methacrylate (MMA, stabilized with 0.0025 % hydroquinone) from Fluka, Switzerland was repeatedly washed with a 4 % aqueous solution of sodium hydroxide (NaOH, Fluka, Switzerland) to remove the hydroquinone and then washed with deionized water. The monomer was stored at + 4 ^{o}C.

As a redox radical initiating system, aqueous solutions of *tert*-butyl hydroperoxide (tBHPO, from a 70 % aqueous solution from Merck, Germany), iso-ascorbic acid (iAA, 5 % aqueous solution, Sigma, Germany) and ethylenediaminetetraacetic acid ferric-sodium salt (FeEDTA, 1 % aqueous solution, Sigma, Germany) were used and sequentially added to the MMA emulsion. As an initiating system, a standard amount ($[I]_{standard}$) for the polymerization of 14.6 g MMA in 33.1 ml water consisted of 0.32 g of a 30 w/w% tBHPO aqueous solution, 1.94 g of a 5 w/w% iAA aqueous solution and 0.10 g of a 1 w/w% FeEDTA aqueous solution was employed.

Synthesis and characterization of MPEO-CL and MPEO-CL-LA block copolymers

Surfactants based on MPEG and CL and on MPEG, CL and LA were prepared by ring-opening polymerization of *ε*-caprolactone using MPEG as a macroinitiator. Functionalization of the obtained diblock copolymer by esterification with linoleic acid results in the formation of an oligomer that in principle is crosslinkable and copolymerizable. Details of the experimental procedures are given elsewhere [9].

The non-functionalized diblock copolymers and the LA-functionalized block copolymers can be abbreviated as $MPEO_{45}$-CL_m and $MPEO_{45}$-CL_m-LA, respectively. Here, MPEO refers to the poly(ethylene oxide component and the subscript *m* to the number of CL repeating units present. The average composition of the obtained block copolymers was determined by proton nuclear magnetic resonance (^{1}H-NMR) using a

300 MHz NMR spectrometer (Varian Inova). Furthermore, as $\overline{M}_n$ of MPEO is known, the CL block length and the average molecular weight of the surfactant can readily be determined.

Surface tension measurements of aqueous solutions of the block copolymer surfactants were conducted using a microbalance surface tensiometer (Processor Tensiometer K12, Krüss, Germany) operating in the Wilhelmy plate mode at 25 ± 0.5 °C. The tensiometer was calibrated with deionized water. Critical aggregation concentrations (CAC) of the surfactants were determined from surface tension versus concentration graphs.

Emulsion polymerizations of MMA

Poly(methyl methacrylate) (PMMA) latices were prepared by emulsion polymerization of MMA using a redox initiating system and several $MPEO_{45}$-CL_m and $MPEO_{45}$-CL_m-LA copolymers as surfactant. The experiments were conducted at different temperatures, initiator solution concentrations, and surfactant to monomer ratios.

MMA polymerizations were carried out in a three-neck round-bottomed flask equipped with a condenser, a nitrogen gas inlet, magnetic stirrer and a rubber septum. The surfactant was dissolved in water, and purged with nitrogen for 30 min. Then, the temperature was set to the appropriate reaction temperature, monomer was added and equilibrated for another 30 min under stirring to emulsify the monomer and remove dissolved oxygen. First the aqueous tBHPO solution was added to the emulsified monomer, then the iAA solution, and the polymerization started immediately after the FeEDTA was added.

At different polymerization time points, a syringe was used to withdraw samples of the emulsion. A small amount of hydroquinone was added to these aliquots to quench the radical polymerization. From these samples the solids content, monomer conversion and particle size were determined.

Characterization of PMMA latices

The solids content of the latices was determined gravimetrically by evaporating the volatile components (water and MMA) by heating the specimens in an oven at 70 ^{o}C for 24 hrs. By taking into account the mass of the initiator and surfactant used, the MMA monomer conversion can be calculated. The percentage of coagulum was determined gravimetrically after filtration of the latex through a 75 µm filter (Endecotts, UK) and drying at 70 ^{o}C for 24 hrs. The relative error in the solids content and in the MMA monomer conversion determinations, derived from duplicate measurements, was approximately 2 %.

Size exclusion chromatography (SEC) was performed at 40 ^{o}C using an Alliance Separation Module (Waters 2690) equipped with three PL Mixed B columns (Polymer Laboratories) and a guard column. Tetrahydrofuran (THF) to which 1.0 vol% acetic acid was added and used as an eluent. The injection volume was 150 µl, the flow rate was 1.0 ml/min. and a temperature of 40 °C was applied. The detection was performed with a differential refractive index detector (Waters 410). Calibration was performed with eight polystyrene standards, ranging from 500 to 4,000,000 g/mol. The obtained molar masses are polystyrene equivalent molar masses (g/mol). The molecular weights and the molecular weight distribution of the obtained polymers were determined after purification by extraction and dissolution in chloroform and precipitation in methanol.

The size of the latex particles was determined by dynamic light scattering (DLS) (Zetasizer 4000, Malvern Instruments Ltd., Malvern, UK) at 25 ± 1 °C at an angle of 90 ° (633 nm), taking the average of five measurements. The number of particles N_p in the latex (expressed as the number of particles per ml) was then calculated according to [8]:

$$N_p = \frac{6\tau}{\pi \rho_P D^3},$$

where τ is the polymer content (g/ml), ρ_{p} is the polymer density (PMMA = 1.174 g/ml) and D is the diameter of the latex particle (m).

RESULTS AND DISCUSSION

Preparation of surfactants based on MPEG, CL and LA

A series of MPEO-CL and MPEO-CL-LA surfactants was prepared in which the chemical composition was varied. The length of the hydrophilic MPEO component was constant ($\overline{M}_n$ = 2000 g/mol, which corresponds to 45 EO repeating units) while the hydrophobic CL length was varied. This gives surfactants with different levels of surface activity. These diblock copolymers were prepared by ring opening polymerization of CL initiated with the hydroxyl group of MPEG. Subsequent functionalization with LA through an esterification reaction yielded a functionalized surfactant [9]. The chemical composition and the average molecular weights of these block copolymers are listed in Table 2. It should be realized, that the surfactant prepared in this study is a heterogeneous mixture of block copolymers, varying in composition and molecular weight. A more detailed analysis will be given in Chapter 6 of this thesis.

Table 2. Chemical composition of non-functionalized and of linoleic acid functionalized MPEO-CL diblock copolymers

Surfactant	Composition (repeating monomer units)			$\overline{M}_n$ calculated[a] (g/mol)	$\overline{M}_n$ ^{1}H-NMR[b] (g/mol)
	EO	CL	LA		
$MPEO_{45}$-CL_1	45	1.2	-	2110	2130
$MPEO_{45}$-$CL_{6.5}$	45	6.4	-	2680	2730
$MPEO_{45}$-CL_9	45	9.2	-	3140	3040
$MPEO_{45}$-CL_1-LA	45	1.2	1.0	2380	2390
$MPEO_{45}$-$CL_{6.5}$-LA	45	6.4	0.9	2940	2960
$MPEO_{45}$-CL_9-LA	45	9.2	0.9	3400	3280

[a] $\overline{M}_n$ was calculated from the MPEO to CL molar ratio in the polymerization mixture, assuming each terminal OH group initiates a CL ring opening polymerization [11]

[b] $\overline{M}_n$ was determined by ^{1}H-NMR

In our case, it is more appropriate to use the term critical aggregation concentration (CAC) than critical micelle concentration (CMC), as is used for conventional low molecular weight surfactants. The CAC and surface tension at CAC (γ_{CAC}) of the prepared block copolymers are summarized in Table 3. By varying the length of the hydrophobic CL segment as well as functionalizing with LA, surfactants with different HLB values are obtained. In general, the CAC decreased with a decrease in the HLB value, whereas for surface tension at CAC no clear relationship with the HLB value could be observed. At a same CL block length, CAC and γ_{CAC} values were lower for LA-functionalized diblock copolymers than for non-functionalized block copolymers. This is due to the LA component that further increases the hydrophobicity and favors formation of surfactant aggregates. The diblock surfactants in Table 3 form aggregates at a significantly lower concentration than commercially available ionic (SDS, critical micelle concentration, CMC = 8.0 mmol/l) and nonionic surfactants (Triton X 405, CMC = 0.6 mmol/l).

Table 3. CAC *and surface tension at* CAC *(γ_{CAC}) of $MPEO_{45}$-CL_n diblock copolymers non-functionalized and functionalized with linoleic acid functionalization.*

Block Copolymer	HLB[a]	CAC (mmol/l)	γ_{CAC} (mN/m)
$MPEO_{45}$-CL_1	19.0	0.31	48.2
$MPEO_{45}$-$CL_{6.5}$	14.9	0.19	51.4
$MPEO_{45}$-CL_9	12.7	0.15	51.2
$MPEO_{45}$-CL_1-LA	16.8	0.18	43.1
$MPEO_{45}$-$CL_{6.5}$-LA	13.7	0.15	43.9
$MPEO_{45}$-CL_9-LA	11.8	0.11	40.3

[a] Calculation based on the Griffin definition [12]

In prior work, stable 10 wt% solids content PMMA latices were prepared by emulsion polymerization of MMA at 80 ^{o}C using the same surfactants at a surfactant to monomer ratio of approximately 1:11 [9]. Potassium persulfate was used as an initiator, where radicals are formed by thermolysis at relatively high temperatures. However, when attempting to prepare latices of higher solids content (20 or 30 wt%) coagulation of the particles occurred. When increasing the monomer content, and keeping the surfactant to monomer ratio constant, the surfactant content is increased as well. As the solubility of PEO and PEO -containing block copolymers is limited at these elevated temperatures [10], not all surfactant will be available in solution to stabilize the growing particles.

To increase the surfactant solubility, the reaction temperature was reduced. In order to still maintain a good initiation rate at lower reaction temperatures, a redox initiating system based on *tert*-butyl hydroperoxide (tBHPO) and *iso*-ascorbic acid (iAA) was employed. Preliminary results using $MPEO_{45}$-$CL_{6.5}$-LA showed that stable PMMA latices could now be prepared at approximately 30 wt% solids contents at 60 ^{o}C (and indeed, when using this redox-initiating system in preparing a 30 wt% solids content latex at 80 ^{o}C complete coagulation occurred again).

The different surfactants, varying in composition as shown in Table 2, were now used to prepare PMMA latices in which the MMA content was approximately 30 wt% at a low temperature of 50 ^{o}C. Table 4 shows that most surfactants employed did not yield stable latices. In most cases MMA conversion was incomplete and the latices coagulated and solidified upon standing. The molecular weight of the resulting polymers was high, although it was observed that the molecular weight of the PMMA latices prepared with LA functionalized surfactants is lower than latices prepared with non-functionalized surfactants. The unsaturated double bonds present in the linoleic acid ester can lead to chain transfer reactions, which lead to decreased molecular weights. During the polymerization, the unsaturated groups in linoleic acid can abstract a radical resulting in chain termination and reduced molecular weights of polymer; the allylic radical is not active enough to propagate [13-16]. In previous work [9] we found that approximately 3.5 % of a similar surfactant was covalently attached to the PMMA chain.

Similar chain transfer reactions were observed in alkyd-acrylic systems [14]. When unsaturated alkyds are used in hybrid binder systems, the acrylate polymerization rates and the obtained molecular weights are significantly decreased due to strong degenerative chain transfer activity of the unsaturated groups present in the alkyd fatty acid. The exact fate of the resultant alkyd radicals, however, still needs to be accounted for: the radicals may either terminate by alkyd-alkyd crosslinking or by alkyd-acrylic combination, or they may reinitiate the acrylate polymerization. In comparison, when a fully saturated fatty acid alkyd was used in the hybrid emulsions, the polymerization of MMA proceeded very rapidly. Also, the MMA monomer conversion rates were higher than compared to the unsaturated system.

Also, Hudda *et. al.* have pointed out that grafting can take place either by addition to the double bonds in the alkyd molecule, or by abstraction of the allylic hydrogen [15,16]. With monomers like MMA, grafting takes place by abstraction of the allylic hydrogen. This chain transfer produces a relatively inactive radical which reduces the overall polymerization rate. When approached by a second MMA macroradical, it terminates with formation of a graft.

Only the $MPEO_{45}$-$CL_{6.5}$-LA surfactant gave stable latices under these non-optimized reaction conditions. Further analysis of this latex showed that a high molecular weight polymer was obtained, in which the average particle size was 225 nm, with a polydispersity index of 0.2 and the number of particles per ml was 3.86×10^{13}. Therefore, $MPEO_{45}$-$CL_{6.5}$-LA block copolymer was chosen for further optimization of the reaction conditions of the MMA emulsion polymerization.

Table 4: Emulsion polymerization of MMA prepared with linoleic acid functionalized and non-functionalized $MPEO_{45}$*-*CL_n *diblock copolymers.*

The reaction conditions [a] *were: T = 50* ^oC*, reaction time is 5 hrs (followed by storage at room temperature for 24 hrs), [I] = [I]*$_{standard}$*, S/M = 10/90*

Surfactant	% MMA conversion[b]	$\overline{M}_w$ [c] (10^3 g/mol)	$\overline{M}_n$ [c] (10^3 g/mol)	Appearance
Non-functionalized surfactants				
$MPEO_{45}$-CL_1	59	290	110	Solidified upon standing
$MPEO_{45}$-$CL_{6.5}$	39	660	160	Solidified upon standing
$MPEO_{45}$-CL_9	36	440	150	Solidified upon standing
LA-functionalized surfactants				
$MPEO_{45}$-CL_1-LA	20	270	70	Solidified upon standing
$MPEO_{45}$-$CL_{6.5}$-LA	86	330	95	Stable latex, average particle size = 225 nm
$MPEO_{45}$-CL_9-LA	11	290	80	Solidified upon standing

[a] *Reactions were carried out at 50* ^oC *and 29.4 wt% MMA (14.6 g MMA in 33.1 ml water). The amount of initiator employed was [I]*$_{standard}$ *and consisted of 0.32 g of a 30 w/w% tBHPO aqueous solution, 1.94 g of a 5 w/w% iAA aqueous solution and 0.10 g of a 1 w/w% FeEDTA aqueous solution. The surfactant to monomer ratio was 10/90 by weight.*

[b] *The MMA conversion is determined gravimetrically by removal of volatile components and correction for the surfactant content*

[c] $\overline{M}_w$ *and* $\overline{M}_n$ *are determined after precipitation of the PMMA polymer*

Optimization of MMA emulsion polymerizations using $MPEO_{45}$**-**$CL_{6.5}$**-LA as a surfactant**

To reach optimal emulsion polymerization conditions at a solids content of 30 wt% and obtain stable PMMA latices with high MMA conversions a series of polymerizations was carried out in which the reaction temperature and the concentrations of the initiator system were varied. The reactions were optimized using a constant $MPEO_{45}$-$CL_{6.5}$-LA surfactant to monomer ratio (S/M) of 10/90 by weight.

Effect of emulsion polymerization temperature on PMMA latex properties

The effect of the reaction temperature on MMA conversion is shown in Figure 1. The polymerization rate of MMA increased significantly with an increase in the reaction temperature. Also, at higher temperatures a higher monomer conversion was reached.

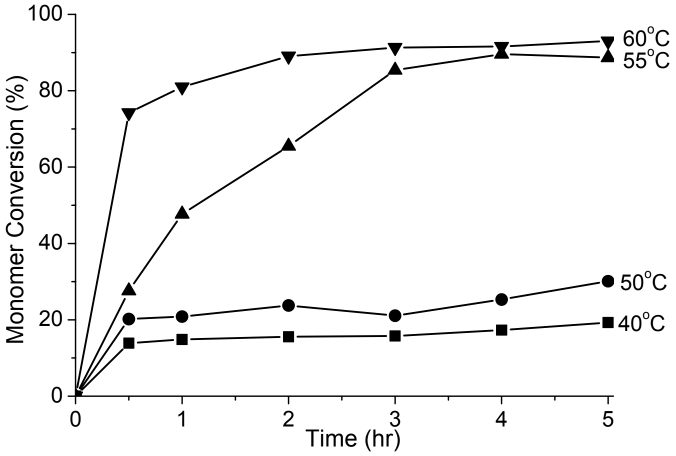

Figure 1: The effect of reaction temperature on monomer conversion in the emulsion polymerization of MMA (at 29.4 wt%) using MPEO$_{45}$-CL$_{6.5}$-LA as a surfactant. The other reaction conditions were: [I] = [I]$_{standard}$, S/M = 10/90

After 5 hrs the reactions were stopped by cooling to room temperature under stirring. After approximately 1 hr the latices were filtered and the resulting emulsions were stored for 24 hrs before further characterization. The properties of the resulting PMMA latices are summarized in Table 5. From the solids content of the obtained latices it can be seen that the reaction temperature has an important effect on the final MMA conversion, relatively high temperatures of 55 to 60 °C are required to reach appropriate monomer conversion.

High molecular weight polymers were obtained, with molecular weight distributions ranging from 2.98 to 3.90. The average particle sizes (PS) of latices prepared above 50 °C were in the range of 180 - 225 nm, the particle size distribution (or polydispersity index, PDI) was 0.16 - 0.21. For latices prepared at 40 °C larger average particle size were found, likely due to the influence of unreacted MMA monomer. Also a much broader particle size distribution can be seen. Likely due to the presence of micrometer sized monomer droplets and aggregation of particles.

Table 5: Effect of reaction temperature on the final properties of PMMA latices prepared using $MPEO_{45}$-$CL_{6.5}$-*LA as a surfactant. The other reaction conditions were: MMA content at 29.4 wt%,* $[I] = [I]_{standard}$, *S/M = 10/90*

Latex	T (^{o}C)	SC^{a} (wt%)	% MMA conversion^{a}	PS (nm)	PDI	N_p (10^{13} cm^{-3})	$\overline{M}_w$ (10^{3}g/mol)
1	40	5.8	17	1040	0.65	0.06	280
2	50	27.1	86	225	0.20	3.86	330
3	55	27.8	94	180	0.21	7.73	355
4	60	27.8	94	225	0.16	3.96	210

[a] *Final solids content (SC), MMA conversion determined after 5 hrs polymerization and 24 hrs storage at room temperature.*

The number of latex particles per unit volume, N_p, can be determined from the solids content, polymer density and the particle size. N_p is an important value in emulsion polymerization as it is a measure for the efficiency of the surfactant. According to the Smith-Ewart theory, at a low initiator concentration, the lifetime of the polymeric radical in the particles is high when the number of particles is large. With a large number of particles, overall reaction rates and polymer molecular weights increase [17, 18].

Effect of the amount of initiator used in the MMA emulsion polymerization on the PMMA latex properties

In further optimization experiments, in which we aimed at reaching complete conversion in the MMA batch emulsion polymerizations with $MPEO_{45}$-$CL_{6.5}$-LA as a surfactant, the amount of initiator used was varied between 0.5 to 2 times that of the standard initiator amount ($[I]_{standard}$). The reaction temperature and surfactant to monomer ratio (S/M) were fixed at 60 ^{o}C and 10/90, respectively. The effect on MMA monomer conversion can be seen in Figure 2.

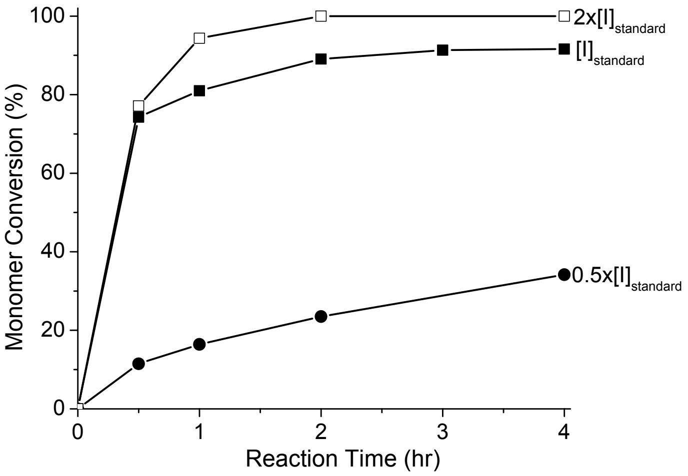

Figure 2. The effect of the amount of initiator used ([I] = 0.5 x [I]$_{standard}$, [I] = [I]$_{standard}$, [I] = 2 x [I]$_{standard}$) on monomer conversion in the emulsion polymerization of MMA at approximately 30 wt% stabilized with MPEO$_{45}$-CL$_{6.5}$-LA. The other reaction conditions were: T = 60 °C, S/M = 10/90)

Table 6: Effect of the amount of initiator on the final properties of PMMA latices prepared using MPEO$_{45}$-CL$_{6.5}$-LA as a surfactant. The other reaction conditions were: MMA content at approximately 30 wt%, T = 60 °C, S/M = 10/90

Latex	Amount of initiator	SC[a] maximum (wt%)	SC[b] (wt%)	% MMA conversion[a]	PS (nm)	PDI	$\overline{M}_w$ (10^3 g/mol)
5	0.5x[I]$_{standard}$	29.9	10.3	32	solidified	-	270
4	[I]$_{standard}$	29.4	27.8	94	225	0.16	210
6	2x[I]$_{standard}$	30.7	30.7	100.0	260	0.30	160

[a] *Maximum solids content that can be reached*

[b] *Final solids content (SC) and MMA conversion determined after 4 hrs polymerization and 24 hrs storage at room temperature.*

The MMA monomer conversion after 4 hrs of reaction was significantly increased as the amount of initiator increased from half the standard initiator amount [I]$_{standard}$ to twice [I]$_{standard}$. At the highest amounts of initiator, full conversion of MMA was achieved in 2 hrs. The properties of the PMMA latices after 24 hrs are summarized in Table 6.

The final conversion of MMA (i. e. after 4 hrs polymerization and 24 hrs storage) increased as the amount of initiator increased. At low initiator concentrations poor conversion and even solidification of the particles were observed. Full conversion of MMA was reached when the highest amounts of initiator were used. The average particle size and polydispersity index of the latices were in the range of 225 - 260 nm and of 0.16 - 0.30, respectively.

In general, the amount of initiator also has an effect on the weight average molecular weight of the latices. The increase in the amount of initiator led to a decrease in $\overline{M}_w$. This is due to the change in the rates of initiation and termination in the system as the amount of initiator increases [19]. Nevertheless, the molecular weights obtained were quite high in all cases.

From the foregoing experiments, we conclude that stable PMMA latices, with high monomer conversion, could be prepared at 30 wt% solids content with MPEO$_{45}$-CL$_{6.5}$-LA at a reaction temperature of 60 ^{o}C and an amount of initiator consisting of 0.64 g of a 30 w/w% tBHPO aqueous solution, 3.88 g of a 5 w/w% iAA aqueous solution and 0.20 g of a 1 w/w% FeEDTA aqueous solution was employed ($[I] = 2 \times [I]_{standard}$). Under these conditions we further investigated the effect of the nature of the surfactant and the surfactant to monomer ratio on the properties PMMA latices prepared with this type of block copolymeric surfactants.

Effect of the chemical composition of the MPEO-CL surfactant on the properties of PMMA latices prepared.

Although, first experiments to show the potential of these MPEO-CL surfactants in stabilizing PMMA latex preparations with a redox initiating system have already been conducted, see Table 4, the conditions chosen might have been suboptimal and only MPEO$_{45}$-CL$_{6.5}$-LA could be used to prepare stable latices. Therefore, we now set out to investigate the effect of surfactant composition and chemistry under more appropriate reaction conditions as derived in the foregoing part.

To prepare stable PMMA latices with a solids content of 30 wt% and high monomer conversion, we carried out comparative emulsion polymerization experiments in which the amount of initiator was two times the standard amount of initiator ($2 \times [I]_{standard}$) at a reaction temperature of 60 ^{o}C for 4 hrs. The results of these polymerizations are summarized in Table 7.

The table shows that in comparison to the previous (suboptimal) results presented in Table 4, the conversion of MMA monomer in the polymerizations was much higher in all cases. However, with only two of the employed surfactants, MPEO$_{45}$-CL$_1$-LA and MPEO$_{45}$-CL$_{6.5}$-LA, monomer conversion was complete and stable latices were obtained. The average particle size and the polydispersity index obtained were in range of 260 to 280 nm and 0.20 to 0.30, respectively. Surprisingly, non-functionalized surfactants did not give stable latices at all, although their HLB values were not much different from those of LA-functionalized surfactants. A latex prepared with MPEO$_{45}$-CL$_9$-LA block copolymer was not stable and solidified upon standing for 24 hrs.

Table 7: Final properties of PMMA latices prepared with different MPEO-CL surfactants. The reaction conditions were: MMA content = 30.7 wt%, T = 60 °C, and [I] = 2 x $[I]_{standard}$, S/M = 10/90

	Surfactant	SC[a] (wt%)	% MMA Conversion[a]	$\overline{M}_w$ (10^3 g/mol)	PS (nm)	PDI
Non-functionalized surfactants						
Latex 7	MPEO$_{45}$-CL$_1$	22.7	70	280	Solidified	-
Latex 8	MPEO$_{45}$-CL$_{6.5}$	25.6	81	280	Solidified	-
Latex 9	MPEO$_{45}$-CL$_9$	19.0	57	270	Solidified	-
LA-functionalized surfactants						
Latex 10	MPEO$_{45}$-CL$_1$-LA	30.1	100	140	280	0.10
Latex 6	MPEO$_{45}$-CL$_{6.5}$-LA	30.7	100	160	260	0.30
Latex 11	MPEO$_{45}$-CL$_9$-LA	19.3	58	180	Solidified	-

[a] *Final solids content (SC) and MMA conversion determined after 4 hrs polymerization and 24 hrs storage at room temperature.*

The molecular weights of PMMA polymers prepared with the LA-functionalized surfactants were again lower than those prepared with the non-functionalized surfactants. Chain transfer behavior of the functionalized surfactant, as mentioned earlier, might account for this. The molecular weight distribution (MWD) of the PMMA polymers varied between 2.5 and 4.3, and this value was not higher for polymerizations carried out with functionalized surfactants.

In addition to the surfactants given in Table 7, MPEG and LA-functionalized MPEO (which does not contain CL) were synthesized and used as surfactants in the preparation of PMMA emulsions. In these experiments it was not possible to obtain stable PMMA latices with $MPEG_{45}$ and a solidified mass was obtained. However, $MPEO_{45}$-LA did yield a stable PMMA latex, in which the MMA monomer conversion and solids content of were 97 % and 29.7 wt% respectively. The average particle size and the polydispersity index of particles in the latex were 230 nm and 0.02, respectively. Apparently, the amphiphilic character of $MPEO_{45}$-LA allows stabilization of the emulsion. This implies that LA is a key component in the surfactant.

The role of CL might still be important as it allows the tuning of the hydrophilic/hydrophobic balance. This could be required to simultaneously allow stabilization of the pigment dispersion and influence rheological behaviour of the paint formulation as well.

At short CL block lengths (1 to 6.5 units of CL), Table 7 shows that LA-functionalized MPEO-CL block copolymers are suitable as surfactants. For further investigation on the effect of surfactant to monomer ratio on latex particle characteristics in the emulsion polymerizations of MMA at a solids content of 30 wt%, $MPEO_{45}$-$CL_{6.5}$-LA was chosen as the surfactant in comparative experiments.

Effect of the surfactant to monomer ratio on the properties of PMMA latices prepared with $MPEO_{45}$-$CL_{6.5}$-LA as a surfactant.

The effect of the surfactant to monomer ratio on the PMMA latex and particle properties is shown in Table 8. The $MPEO_{45}$-$CL_{6.5}$-LA surfactant to MMA monomer ratio (S/M) in the preparation of PMMA latices at 30 wt% was varied from 1/99 to 20/80 (1/99, 5/95, 10/90, 15/85 and 20/80) The employed reaction conditions were: T = 60 ^{o}C, polymerization time = 4 hrs, $[I] = 2 \times [I]_{standard}$.

Monomer conversion was lowest when the surfactant to monomer ratio in the system was the lowest. This is because the rate of polymerization is proportional to the number of particles in a system which in turn depends on the surfactant to monomer ratio. Also, for latices in which MMA conversion was relatively high, the molecular weight of PMMA (determined after purification) increased as the amount of surfactant was increased. At a constant monomer concentration and initiation rate, the degree of polymerization will increase with an increase in the number of particles as illustrated in the following equation [23]:

$$\overline{X}_n = \frac{N_p k_p [M]}{R_i}$$

where $\overline{X}_n$ is the degree of polymerization, N_p is the number of particles, k_p is the rate constant for propagation, [M] is the monomer concentration and R_i is the rate of radical initiation. The reason for the relatively high molecular weight and broad molecular weight distribution of PMMA Latex 12 is not clear, although this sample had coagulated and solidified upon standing.

Table 8: The effect of surfactant to monomer ratio (S/M) on the PMMA latex properties prepared in batch emulsion polymerizations using $MPEO_{45}$-$CL_{6.5}$-LA as a surfactant. The employed reaction conditions were: MMA content approximately 30 wt%, T = 60 °C, polymerization time = 4 hrs, [I] = 2 x $[I]_{standard}$.

Latex	S/M[a] (g/g)	SC[b] maximum (wt%)	SC[c] (wt%)	% MMA Conversion[c]	$\overline{M}_w$ (10^3 g/mol)	MWD[d] (SEC)	PS (nm)	PDI	N_p (10^{13} cm^{-3})
12	1/99	28.8	17.4	59	270	3.02	Solidified	-	-
13	5/95	29.7	22.3	73	90	2.52	725	1.00	0.10
6	10/90	30.7	30.7	100	160	2.54	260	0.30	2.86
14	15/85	32.0	30.2	93	180	3.16	96	0.25	55.3
15	20/80	33.3	31.6	94	220	3.79	73	0.18	131.7

[a] *surfactant to monomer ratio used in the emulsion polymerizations*

[b] *Maximum solids content that can be reached*

[c] *Final solids content (SC) and MMA conversion determined after 4 hrs polymerization and 24 hrs storage at room temperature.*

[d] *MWD=polydispersity obtained from size exclusion chromatography (SEC)*

The influence of the relative amount of surfactant on the particle size, as determined by dynamic light scattering (DLS), is also presented in Figure 4. The average sizes of the latex particles decreased significantly with increasing surfactant to monomer ratio. As more polymeric surfactant is available to stabilize newly formed particles during the polymerization, a larger surface are and smaller particles can be stabilized under given conditions. The particle size and particle size distribution decreased from 725 nm to 73 nm and 1.00 to 0.18, respectively, as the surfactant to monomer ratio was increased from 1/99 to 20/80.

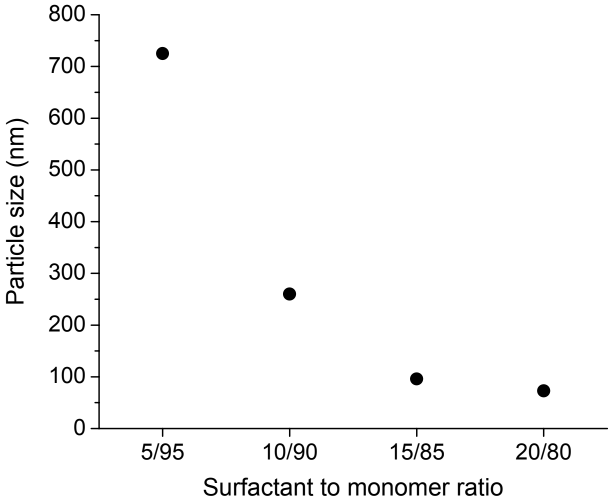

Figure 4: The effect of the surfactant to monomer ratio (S/M) on the latex particle size in MMA emulsion polymerizations using $MPEO_{45}$*-*$CL_{6.5}$*-LA. The employed reaction conditions were: MMA concentration = 30 wt%, T = 60* ^oC*, polymerization time = 4 hrs,* $[I] = 2 \times [I]_{standard}$.

CONCLUSIONS

This study shows that linoleic acid-functionalized based on MPEG, CL and LA, can be used in the emulsion polymerization of MMA at a relatively high monomer concentration. It is shown that especially the $MPEO_{45}$-$CL_{6.5}$-LA surfactant is suited for the latex preparations at approximately 30 wt% solids content, when a redox-initiating system based on tBHPO, iAA and FeEDTA is used and reactions are carried out at a relatively low temperature of 60 ^oC.

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Note: Surface coverage of latex particles with surfactant

To obtain an estimation of the surface coverage of the latex particles with $MPEO_{45}$-$CL_{6.5}$-LA surfactant at different surfactant to monomer (S/M) ratios, a rough calculation can be made. Assuming all surfactant is present at the surface, the area occupied per surfactant molecule (A_S) can be determined from plots of the surface tension of the surfactant solution versus the surfactant concentration using the Gibbs adsorption isotherm equation [20-22]:

$$\text{Surface excess concentration, } \Gamma = -\frac{1}{2.303RT} \times \frac{d\gamma}{d(\log c)} \qquad (1)$$

The surface excess concentration, Γ in mol/m^2, is the number of moles of surfactant that can be adsorbed per unit interfacial area (The surface excess concentration is defined as the excess, per unit area of interface, of the amount of component actually present in the system over that present in a reference system of the same volume in which the bulk concentration in the two phases remain uniform up to a hypothetical (Gibbs) dividing surface [24]). From Γ the surface area occupied by a single surfactant molecule (A_S; unit: Å^2/ molecule) can be determined:

$$\text{Area of a single surfactant molecule occupied, } A_S = \frac{10^{16}}{6.022\text{x}10^{23}\Gamma} \qquad (2)$$

In these equations Γ (mol/m^2) is the surface excess concentration, $d\gamma/d(\log c)$ (N/m) is the slope of the surface tension isotherm below CAC, R the gas constant (8.314 NmK^{-1}mol^{-1}) and T (K) the absolute temperature. N_A is Avogadro's number and equals 6.022 x 10^{23}.

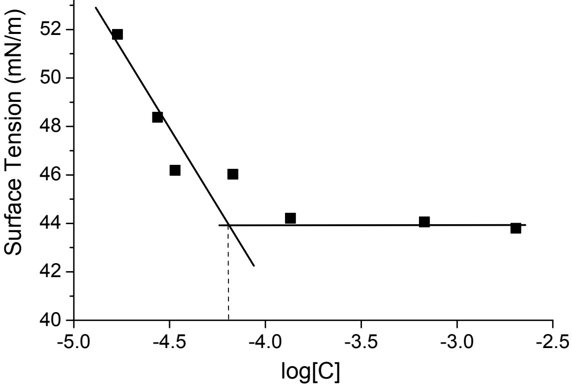


Figure 5. Surface tension versus surfactant concentration of MPEO$_{45}$-CL$_{6.5}$-LA surfactant solutions in water at room temperature.

For the MPEO$_{45}$-CL$_{6.5}$-LA block copolymer, the slope of the surface tension versus surfactant concentration yields $\frac{d\gamma}{d\log C}$ =-16.61 x 10^{-3} N/m. With this value, $\Gamma = 2.91$ x 10^{-8} mol/dm^2 and A$_S$= 0.57 nm^2/ molecule (57 Å^2/molecule) can be determined.

In a given volume, the total surface area covered by surfactant molecules (S$_S$) is then calculated from the following equation:

$$S_S = n\, N_A\, A_s \qquad (3)$$

Where n (mol) is the amount of surfactant present, N$_A$ is Avogadro's number (molecules per mol) and A$_S$ (57 Å^2/ molecule) is the area a single surfactant molecule occupies.

Assuming spherical particles with uniform diameters, the total surface area of the latex particles can be calculated using:

$$S_L = N\pi D^2 \qquad (4)$$

Where N is number of particles present and D is the particle diameter (see Table 8).

Then, by comparing the area occupied by surfactant molecules to the total area available on the latex particles, the latex particle surface coverage (S$_S$/S$_L$) can be estimated. The estimated maximum fraction surface coverage data for different S/M ratios is summarized in Table 9.

Table 9: Estimated maximum surface coverage (S$_S$/S$_L$) of PMMA latex particles prepared with MPEO$_{45}$-CL$_{6.5}$-LA at different S/M ratios. In the preparation of the PMMA emulsions, 14.6 g MMA emulsified in 33.1 ml water was used. The targeted solids content of the PMMA latices is 30 %.

Latex	S/M	Surfactant (g)	Surfactant n (mole)	N^a Present (10^{13})	D^b (nm)	S$_S$ (m^2)	S$_L$ (m^2)	Fraction surface coverage
13	5/95	0.77	2.60 x 10^{-4}	5.3	725	88	88	1.00
6	10/90	1.60	5.41 x 10^{-4}	154.7	260	186	328	0.57
14	15/85	2.58	8.72 x 10^{-4}	3042.6	96	299	881	0.34
15	20/80	3.65	1.24 x 10^{-3}	7387.1	73	423	1237	0.34

[a] N_p (expressed per ml) was obtained from Table 8. The number of particles present Np was calculated by multiplying with the volume of the emulsion: For S/M = 5/95, 10/90, 15/85 and 20/80 these volumes were 53.2 ml, 54.1 ml, 55.0 ml and 56.1 ml, respectively.

[b] The particle diameter, D, was obtained from Table 8.

The data in Table 9 show that the maximum surface coverage of PMMA latex particles decreases as the S/M ratio increases. Although the amount of surfactant present in the system increases, more latex particles (with a larger total surface area) are formed. As a result of this, the relative latex particle surface coverage decreases. The decrease in the fraction of PMMA latex particle surface that is covered with surfactant to 34 % does not affect the stability of the latex, even after several months of storage.

It should be realized that only a small amount (3.5 %) of the surfactant that was employed in the emulsion polymerization is actually covalently bound to the latex particles [9]. Therefore, the latex is mainly stabilized by surfactant that is physically adsorbed to the latex particles.

Chapter 5

MPEO-CL and MPEO-CL-LA block copolymers as surfactants in P(MMA/BA) latices. The effect of the purity of MPEG and CL used in the surfactant preparation on latex stabilization behaviour and latex film properties.

SUMMARY

Amphiphilic block copolymers comprising methoxy polyethylene oxide (MPEO) and ε-caprolactone (CL) segments were prepared by ring opening polymerization of CL initiated with methoxy polyethylene glycol (MPEG). Subsequent functionalization with linoleic acid (LA) was performed by esterification. The effect of the purity of the MPEG and CL used in the synthesis on the surfactant behaviour of the resulting block copolymers was investigated by carrying out comparative experiments in which the block copolymers were analyzed and their surface tension, poly(methyl methacrylate/n-butyl acrylate) (P(MMA/BA)) latex stabilization and film formation properties were investigated. In the syntheses, when using the purified starting materials, the reactions were carried out under well controlled, highly inert conditions. Compositional analyses of the block copolymers by nuclear magnetic resonance (NMR) and liquid chromatography/mass spectrometry (LC/MS) showed that in MPEO-CL block surfactants prepared from non-purified compounds small amounts of linear and cyclic PCL homopolymer were present. In water, these surfactants yielded turbid solutions. However, upon functionalization with linoleic acid the structures seem to be randomized to some extent, and no differences were observed between MPEO-CL-LA surfactants prepared from purified and from non-purified starting compounds. Surface tension measurements showed that all diblock copolymers were surface active. After LA functionalization their surface activity was comparable with CAC (critical aggregation concentration) values of approximately 0.16 mmol/l, and surface tension at CAC values of approximately 47 mN/m. These surfactants were used in the emulsion polymerization of P(MMA/BA) and the subsequent formation of films from these latices. The average particle size (130 - 140 nm), particle size distribution (0.03 - 0.06) and molecular weight (310 x 10^3 g/mol) of the latices were comparable and typical for acrylic latices prepared with conventional surfactants. These latices could readily be cast, and yielded films with a low water-uptake of 25 - 35 % upon immersion in water for 24 hrs. The films possessed good tensile properties: approximate values determined after a drying time of 1 month were: E modulus = 90 - 115 MPa, ultimate tensile strength = 8.0 - 8.5 MPa, yield strength = 3.5 - 4.5 MPa, elongation at break = 500 - 550 %. Here too, the properties of the films were not much dependent on the purity of the compounds used in the synthesis of the MPEO-CL-LA surfactants.

INTRODUCTION

In the preparation of waterborne coatings, large quantities of acrylic latices produced by emulsion polymerization processes are used. In emulsion polymerization, surfactants play an important role as they allow for fast particle nucleation during the polymerization and for stabilization of the latex during its shelf life. Upon application of the coating, however, the residual surfactant present in the film can lead to undesired effects. A major problem that can occur is surfactant migration out of the bulk of the film leading to concentration at the film interfaces, which can result in limited resistance to water and detachment of the film from the substrate [1-3].

In previous studies [4-6], we prepared reactive and crosslinkable surfactants by functionalizing block copolymers based on ethylene oxide (EO) and ε-caprolactone (CL) with linoleic acid, and used them as surfactants in acrylate emulsion polymerizations in an attempt to overcome these difficulties. These surfactants were prepared by ring-opening polymerization of ε-caprolactone (CL) using methoxy-poly(ethylene glycol) (MPEG) as a macroinitiator and tin (II) 2-ethylhexanoate (SnOct) as catalyst. Subsequent functionalization with linoleic acid (LA) by esterification yielded surfactants that oxidatively dry at ambient conditions.

In the ring-opening polymerization of lactones with SnOct, many reaction mechanisms have been proposed. These mechanisms can be divided into two categories, (a) direct catalyst type mechanisms and (b) coordination insertion type mechanisms [7]. Most likely are the coordination insertion type mechanisms, where a hydroxyl group is thought to be coordinated to SnOct forming the initiating tin-alkoxide species [8-11]. These mechanisms have been studied in depth by Penczek *et al.* [9, 10] and Kricheldorf *et al.* [11]. When in the preparation of the diblock copolymer surfactants the reaction mixture contains hydroxyl group containing impurities, such as water or hydroxyhexanoic acid, homo-polymeric poly(ε-caprolactone) can be formed as a side product. Also, inter- and intra-molecular transesterification reactions can lead to the formation of linear homo-polymeric and cyclic compounds [8-11]. Besides this, it should be realized that in the preparation of block copolymers, the statistical nature of the polymerization process will result in a distribution of poly(ε-caprolactone) block lengths.

Although the block copolymeric surfactants performed effectively in stabilizing the acrylate emulsions and reducing water sensitivity of the films [5, 6], they were prepared without stringent monomer purification procedures, and it is to be expected that these surfactants were a heterogeneous mixture consisting of block copolymers, homopolymers, and cyclic compounds of varying molecular weights and chemical composition. Also as a result of occurring transesterification reactions.

In this study we investigated the effect of carefully purifying the MPEG macroinitiator and the ε-caprolactone monomer on the MPEO-CL block copolymeric surfactant composition. Its effect on stabilizing methyl methacrylate/butyl acrylate (MMA/BA) latices and on the physical properties of films cast from these emulsions were investigated as well.

EXPERIMENTAL

Materials

Methoxy-PEG (MPEG) with a molecular weight of 2000 (45 ethylene oxide repeat units), *para*-toluene sulfonic acid monohydrate (*p*-TSA, 99 %) and xylene (mixture of isomers, 98 %, bp = 140 °C) were obtained from Fluka, Switzerland. ε-Caprolactone (CL) and stannous (II) octoate (SnOct) were obtained from Aldrich, United Kingdom. (SnOct contains approximately 0.5 wt% (9.5 mol%) water [9, 10]). Linoleic acid (LA) (high purity 99%) was supplied by Acros-Organic, USA.

The solvents used for liquid chromatography and mass spectrometry (LC/MS) experiments were a HPLC grade acetonitrile and a 20 mM aqueous ammonium formate bufferred (pH 3) (Biosolve LTD, The Netherlands). Formic acid (pro analytical grade) was obtained from Merck (Darmstadt, Germany). Ammonium formate (highest quality available) was purchased from Aldrich.

Methyl methacrylate (MMA, stabilized with hydroquinone) and n-butyl acrylate (BA, stabilized with hydroquinone) were obtained from Fluka, Switzerland. The monomers were washed repeatedly with a 4 wt% aqueous sodium hydroxide solution to remove the hydroquinone and further washed with deionized water. After purification, both monomers were stored at 4 ^{o}C before use.

A 70 % aqueous solution of *tert*-butyl hydroperoxide (tBHPO) from Merck (Germany) was diluted to a 30 % solution prior to use. A 5 wt% aqueous solution of iso-ascorbic acid (iAA) (Sigma, Germany) and a 1 wt% aqueous solution of ethylenediaminetetraacetic acid ferric-sodium salt (FeEDTA, Sigma, Germany) were freshly prepared before use. These aqueous solutions were used as redox-initiating system in the acrylate emulsion polymerization processes. Deionized water (Milipore Q, 18.2 MΩcm) was used throughout the study.

All chemicals were used as received unless stated otherwise.

Synthesis of MPEO-CL and functionalized MPEO-CL-LA block copolymers

MPEO-CL block copolymers based on methoxy polyethylene glycol and ε-caprolactone were prepared by initiating the ε-caprolactone ring opening polymerization with MPEG as a macroinitiator and stannous (II) octoate (SnOct) as a catalyst. Under a nitrogen stream, *ε*-caprolactone was introduced into a flask containing a pre-weighed amount of MPEG, then SnOct was added at a concentration of 0.010 to 0.015 wt% based on the amount of *ε*-caprolactone. After reaction at 140 °C for 4 hrs, the resulting block copolymers were dissolved in chloroform and precipitated into an excess of cold hexane. After filtration, the polymers were dried at 40 °C under vacuum for 3 days.

In the preparation of block copolymeric surfactants from purified starting materials the ring opening polymerizations were carried out analogously. However, purified starting materials were used and the handling of the chemicals was conducted under a strictly inert atmosphere (glove box or Schlenk line) at all times. ε-Caprolactone was purified by vacuum distillation over calcium hydride (CaH_2). The fraction distilling at 96

– 98 °C (at 5 mmHg) was collected and used in the polymerization experiments. Monomethoxy poly(ethylene glycol) (MPEG) was dried by first dissolving in dry toluene and subsequent azeotropic distillation of the toluene. Dry toluene was obtained by refluxing over sodium wire under argon and distilling. Traces of toluene in the MPEG were removed under reduced pressure.

Linoleic acid (LA) end group functionalization of the different block copolymers was carried out in the same manner. The esterification reactions were carried out in boiling xylene under a nitrogen atmosphere. Typically, MPEO-CL (10 mmol) was reacted with a 10 to 20 mol% excess of LA, using *p*-TSA as a catalyst (1.5 wt% with respect to LA) in 30 ml of boiling xylene for a duration of 4 hrs in a 100 ml reaction flask equipped with a Dean-Stark trap. After removal of the solvent, the reaction products were dissolved in chloroform and precipitated into an excess of cold hexane, filtered and dried under vacuum for 3 days.

Schematically, the synthesis procedures are given in Figure 1.

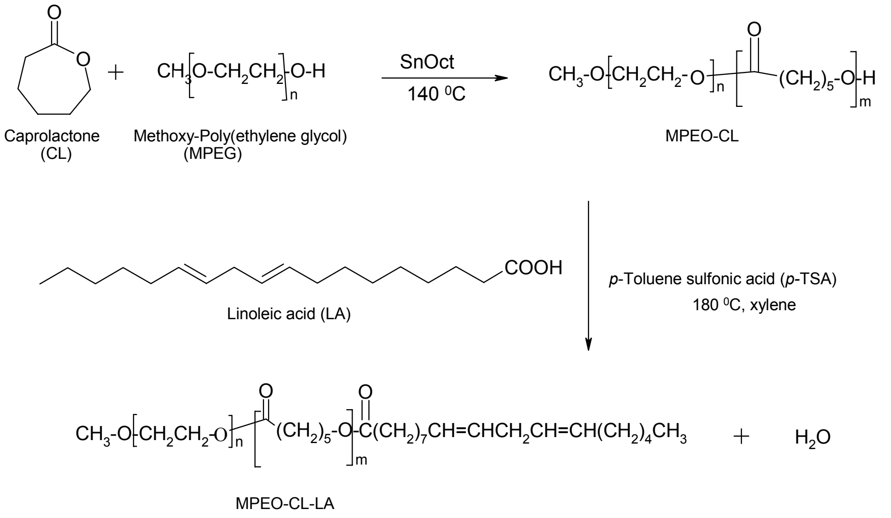


Figure 1. Synthesis of MPEO-CL and MPEO-CL-LA block copolymers by ring opening polymerization and subsequent esterification.

Characterization of MPEO-CL and MPEO-CL-LA block copolymers

The composition of the synthesized block copolymers was determined by nuclear magnetic resonance (^{1}H-NMR, $CDCl_3$) using a 300 MHz NMR spectrometer (Varian Inova). As $\overline{M}_n$ of the employed MPEG is known, ($\overline{M}_n$ of the MPEG used was 2000 g/mol as determined by NMR) the average CL block length in the block copolymer can be readily calculated as well.

From the composition of the block copolymers, an estimate of the hydrophilic to lipophilic balance (HLB) value was calculated using the Griffin definition [15]:

$$HLB = \frac{W_H}{W_H + W_L} \times 20$$

where W_H corresponds to the weight fraction of the hydrophilic components (EO) and W_L corresponds to the weight fraction of the lipophilic components (CL and LA).

Surface tension measurements were made using a microbalance surface tensiometer (Processor Tensiometer K12, Krüss, Germany) operating in the Wilhelmy plate mode at 25 ± 0.5 °C. The tensiometer was calibrated with deionized water before use, and each measurement was read after 30 min of equilibration. Critical aggregation concentrations (CAC) of the surfactants were determined from graphs of surface tension versus surfactant concentration.

For the LC/MS experiments, an Agilent Technologies (Germany) HP1100 liquid chromatograph, comprising of a binary gradient pump model G1312A, an autosampler model G1313A and a diode array detector model G1315B, was used. The chromatograph was coupled to an Esquire 3000*plus* ion trap mass spectrometer from Bruker Daltonics (Germany), and connected to either an electrospray ionization (ESI) interface or an atmospheric pressure chemical ionization (APCI) interface.

LC parameters: Reversed phase chromatographic separation was performed on a C-8 column (Macherey-Nagel, Düren, Germany), 2.1 x 150 mm. A gradient of acetonitrile (solvent B) in 20 mM aqueous ammonium formate buffer (pH ~ 3, solvent A) was applied, as listed below, at a flow rate of 300 µL/min. Injection volumes of sample or blank solutions were 5 µL. The elution gradient was as follows:

Time [min]	0	2	40	79	80	90
c(B) [v/v%]	10	10	95	95	10	Stop

MS parameters. The mass spectrometer was operated in both positive ion and negative ion mode. Full scan mass spectra were recorded in the range of m/z = 150 to m/z = 3000 with the mass focus on m/z = 1500, while accumulating 20000 or 5000 ions for each scan in the positive ion and the negative ion mode, respectively. Ion source parameters for the different interfaces and ion modes are listed below:

	Spray voltage (V)	Corona current (nA)	Nebulizer gas (N_2) (psi)	Nebulizer temperature (^{o}C)	Dry gas (N_2) (L/min)	Dry gas (N_2) temperature (^{o}C)
ESI(+)	4000	-	40.0	-	9.00	365
ESI(-)	4000	-	40.0	-	9.00	365
APCI(+)	1500	2500	50.0	375	4.00	350
APCI(-)	1500	3000	50.0	375	4.00	350

MMA/BA emulsion polymerizations

Table 1: Recipe of P(MMA/BA) copolymer emulsion polymerizations conducted at 60 ^{o}C for 4 hrs at surfactant to monomer ratio of 10/90 using MPEO-CL-LA surfactants.

Component	Amount (g)	wt%
Water	33.11	61.22
MPEO-CL-LA surfactant [a]	1.63	3.01
MMA monomer	7.30	13.50
BA monomer	7.30	13.50
TBHPO (30 w/w% aqueous solution)	0.65	1.20
iAA (5 w/w% aqueous solution)	3.89	7.20
FeEDTA (1 w/w% aqueous solution)	0.20	0.37
Total	54.08	100.00

[a] Different MPEO-CL-LA surfactants were used, either prepared from non-purified starting materials or from carefully purified starting materials.

Poly(methyl-methacrylate/n-butyl acrylate) (PMMA/BA) latices were prepared by emulsion copolymerization of MMA and BA using a redox initiating system, consisting of tBHPO (30 w/w%), iAA (5 w/w%) and FeEDTA (1 w/w%) aqueous solutions, and

MPEO-CL-LA copolymers as surfactant. The reaction conditions used for the emulsion copolymerization of MMA and BA were similar to the reaction conditions of MMA emulsion polymerizations reported previously [6]. At different polymerization time points, samples were withdrawn from the emulsion, and the solids content, monomer conversion and particle size were determined.

The recipe of the P(MMA/BA) emulsion copolymerizations is summarized in Table 1.

Characterization of P(MMA/BA) latices

The solids content of the latices was determined by evaporating the volatile components (water, MMA and BA monomers) in an oven at 70 °C for 24 hrs. By taking into account the mass of initiator and of surfactant, the total (MMA and BA) monomer conversion was calculated. The relative error in the solids content and monomer conversion, as derived from triplicate measurements, was approximately 2 %.

The latex particle size and particle size distribution were determined by dynamic light scattering (DLS) (Zetasizer 4000, Malvern Instruments Ltd., Malvern, UK) at 25 ± 1 °C at an angle of 90 ° (633 nm), taking the average of five measurements.

Size exclusion chromatography (SEC) was performed at 40 °C using an Alliance Separation Module (Waters 2690) equipped with three PL Mixed B (Polymer Laboratories) and a guard column. Tetrahydrofuran (THF) containing 1.0 vol% acetic acid was used as an eluent. The injection volume was 150 µl, the flow rate 1.0 ml/min and a temperature of 40 °C was applied. The detection was performed with a differential refractive index detector (Waters 410). Calibration was performed with eight polystyrene standards, ranging from 500 to 4,000,000 g/mol. The molecular weight and the molecular weight distribution of the polymers were determined after dissolution in chloroform and precipitation in methanol.

Formation of P(MMA/BA) latex films and measurement of their physical properties

Latex films were cast by pouring 15 g of the latex dispersion into a Petri dish (diameter = 15 cm) and subsequent drying at ambient conditions (temperature = 25 ± 2 °C, relative humidity = 50 ± 10%). After 3 d the polymer films were removed from the dish and further dried for different time periods. The final thickness of the films was 0.25 ± 0.05 mm.

The tensile properties of the latex films were determined in triplicate at room temperature using a Zwick Z020 (Germany) tensile testing machine. Standard tensile test specimens were cut from the latex films according to ISO 37 (type 2). A 500 N load cell was employed and the experiments were conducted at a crosshead speed of 50 mm/min using a 0.01 N pre-load. The tensile strength, yield stress, E-modulus and elongation at break of the films were determined. Typical standard deviations of the average values found were between 10 and 15 %.

Water uptake measurements were conducted on latex films dried for different time periods. Samples (1 cm x 1 cm) were weighed prior to being totally immersed in water at 25 ^{o}C. After 24 hrs, the samples were taken out of the water and wiped dry. The water uptake was calculated as: water uptake = $(W-W_0)/W_0$, where W_0 is the film weight before immersion in water and W is the weight after immersion in water.

RESULTS AND DISCUSSION

Synthesis and characterization of MPEO-CL and MPEO-CL-LA block copolymers

MPEO-CL and MPEO-CL-LA block copolymers, to be used as surfactants in the emulsion copolymerization of MMA and BA, were prepared by ring opening polymerization of CL using MPEG as an initiator and SnOct as a catalyst. As described, the ring opening polymerizations were carried out under different conditions. In one case MPEG and CL were used as supplied, without further purification, and polymerizations were conducted under a nitrogen flow. In a second case, careful purification of MPEG and CL was performed, and materials handling and polymerizations were conducted under highly inert conditions. Both block copolymers were then esterified with LA to yield functionalized surfactants that can polymerize and crosslink oxidatively. These block copolymers are respectively designated as:

MPEO-CL (non-purified MPEG, CL) and MPEO-CL-LA (non-purified MPEG, CL) and as MPEO-CL (purified MPEG, CL) and MPEO-CL-LA (purified MPEG, CL). The different block copolymers were analysed by NMR to determine their chemical composition and monomer block length. The results are summarized in Table 2.

Table 2: Composition and properties of MPEO-CL and MPEO-CL-LA surfactants prepared from purified and from non-purified starting materials.

Surfactant	Composition (repeating units)			$\overline{M}_n$ [a] expected	$\overline{M}_n$ (NMR)	HLB[b]
	EO	CL	LA			
$MPEO_{45}$-CL_6[c] non-purified MPEG, CL	45	5.8	-	2680	2660	15.0
$MPEO_{45}$-CL_6-LA[c] non-purified MPEG, CL	45	5.8	0.85	2940	2880	13.9
$MPEO_{45}$-CL_6[c] purified MPEG, CL	45	6.0	-	2680	2680	14.9
$MPEO_{45}$-CL_6-LA[c], purified MPEG, CL	45	6.0	0.89	2940	2910	13.7

[a] The expected value is based on the composition of the feed

[b] HLB value is calculated according to the Griffin definition

[c] The number of EO, CL and LA repeat units determined by NMR is used to indicate the composition of the surfactant

NMR allows the determination of the extent of ε-caprolactone monomer conversion, surfactant composition and (using the known molecular weight of the MPEG used as initiator and assuming each MPEG molecule initiates the ring opening polymerization of CL) the number average molecular weight and the average number of EO and CL repeating units in the respective blocks. However, the distribution of the CL block sequence lengths and the presence of (unreacted) MPEG and homo-polymeric poly(CL) cannot be discerned. Details of the peak assignments and the methods used to calculate the compositions of the surfactants have been reported elsewhere [5]).

Typical NMR spectra of the surfactants at different time points of the synthesis are given in Figure 2. The figures show that after ring opening polymerization of CL with MPEG as an initiator, CL conversion is essentially complete; the spectra of the crude block copolymers and of the block copolymers purified by precipitation are not essentially different. Upon esterification, the spectra of the purified, functionalized surfactants indeed show the presence of a linoleic acid moiety. From the spectra and the results of the calculations presented in Table 2, it can be seen that the composition of the block copolymers prepared with purified MPEG and CL is not different from those prepared with non-purified starting materials.

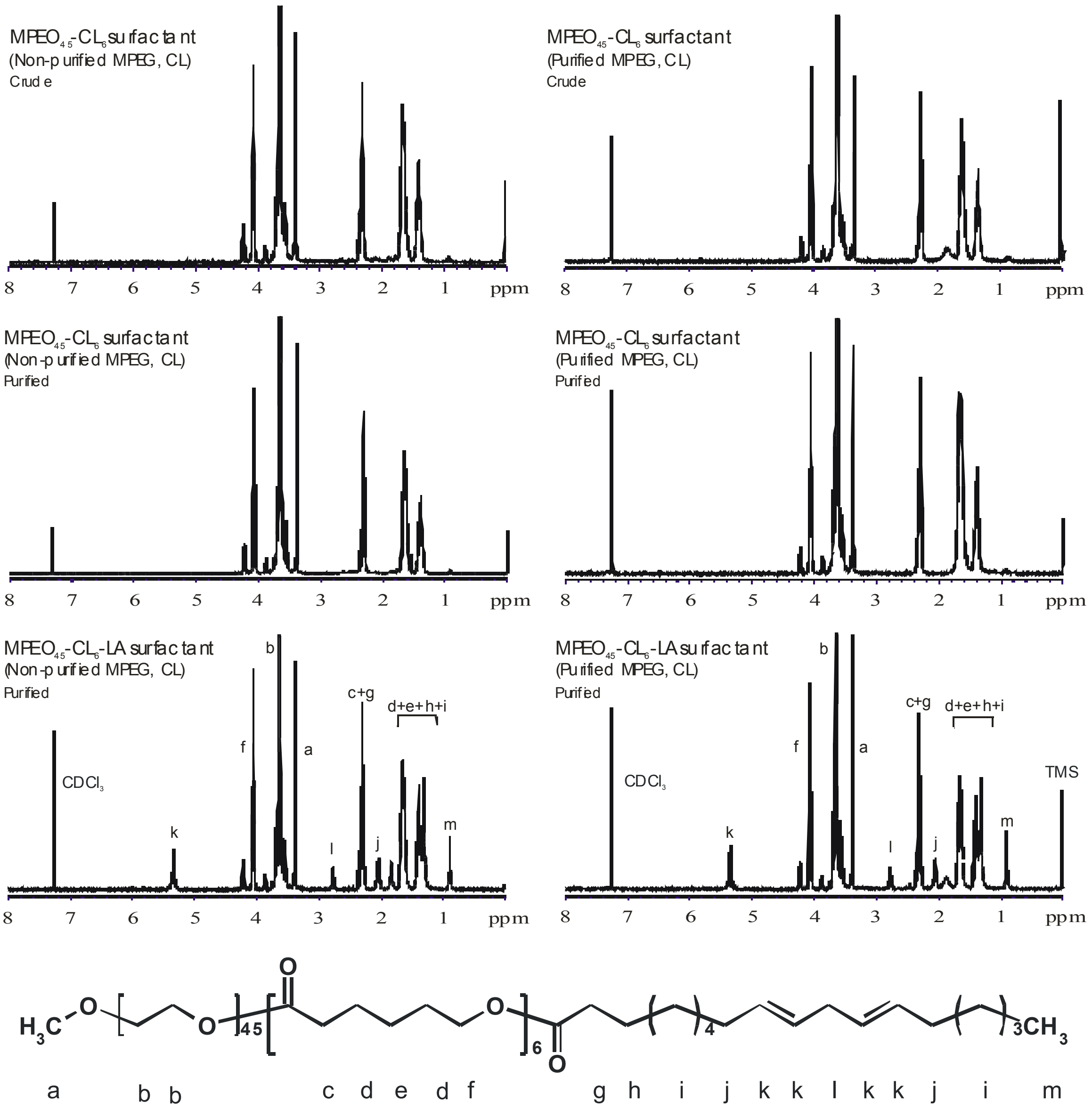


Figure 2. NMR spectra of MPEO-CL and MPEO-CL-LA surfactants prepared from non-purified and from purified MPEG and CL starting materials. Where indicated, the block copolymers were purified by precipitation.

For a more thorough analysis of the composition of the block copolymers upon ring opening polymerization and esterification, we employed liquid chromatography/mass spectrometry, LC/MS. Figure 3 shows LC/MS chromatograms (obtained with the positive ESI interface) of four different copolymer samples. Figures 3a and 3c respectively show the block copolymers formed after ring opening polymerization using non-purified CL and MPEG and after ring opening polymerization using purified CL and MPEG. The corresponding functionalized block copolymers, formed after esterification with LA, are shown in Figures 3b and 3d.

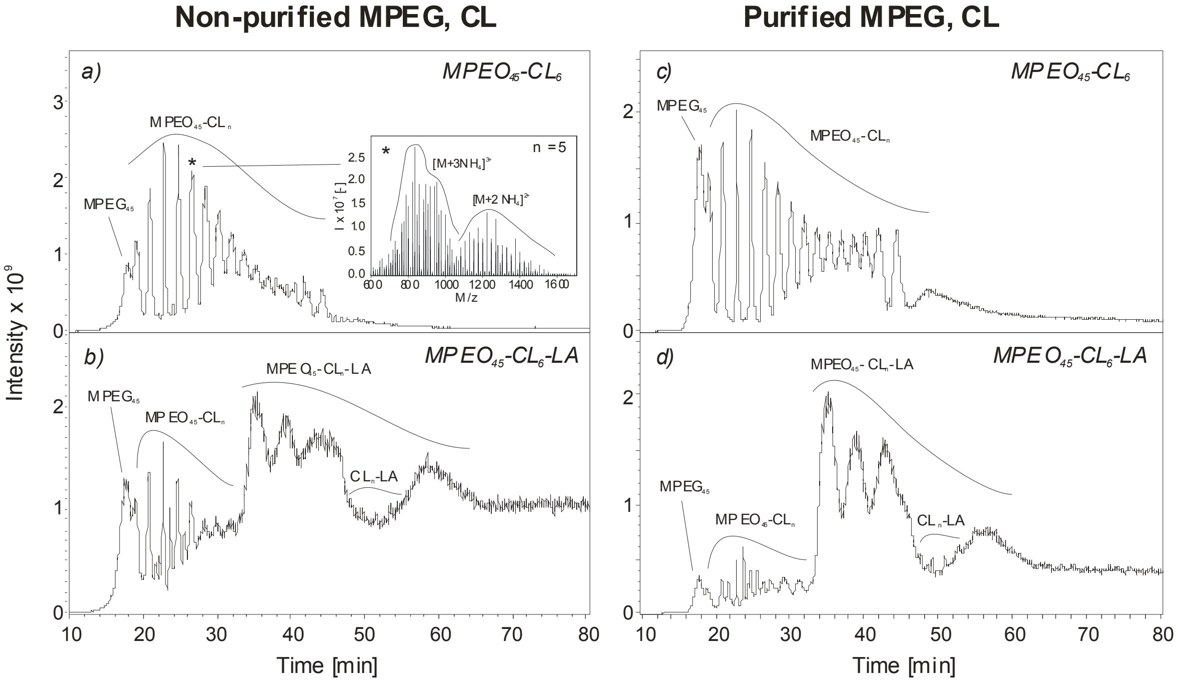


Figure. 3: LC/MS ESI(+)-chromatograms of MPEO-CL (a) and MPEO-CL-LA (b) block copolymers prepared using non-purified MPEG and CL and MPEO-CL (c) and MPEO-CL-LA (d) block copolymers prepared using purified MPEG and CL.

In the chromatograms, n refers to the number of repeating CL units in the block copolymers.

Insert in a: Mass spectrum corresponding to the marked elution peak. At n=5 repeating CL units, the molecular weight distribution of the MPEO-CL_5 block copolymers, due to the distribution of molecular weights of the starting MPEG, can be discerned. The molecules with mass M are detected as charged complexes (([M+2NH_4]$^{2+}$) and ([M+3NH_4]$^{3+}$).

In the chromatograms, a multitude of elution peaks can be distinguished. Based on molar mass data obtained from mass spectrometry, MPEO-CL_n copolymers of different (CL) sequence lengths could be identified in Figures 3a and 3c. Besides the presence of unreacted MPEG (which also shows a molar mass distribution), MPEO-CL_n with CL sequence lengths (n) ranging from 1 to 16 can be discerned. Comparison of the chromatograms of MPEO-CL block copolymers prepared from non-purified and from purified starting materials shows that at the same reaction time and temperature, block copolymers prepared from purified starting materials show higher amounts of block copolymers with longer CL blocks. Although NMR analysis did not show such a difference, in both cases average CL sequence lengths of n = 6 were determined, this could indicate that in this case side reactions that lead to homopolymer formation and cyclization have occurred to a lesser extent.

The insert in Figure 3a shows the mass spectrum of the elution peak of block copolymer composition corresponding to a CL sequence length of n = 5 (peak marked with an asterisk). Here the molecular weight distribution due to the distribution in molecular weights of the starting MPEG can clearly be discerned.

The spectra of the reaction products obtained after functionalization of the MPEO-CL prepared from non-purified and from purified starting materials with linoleic acid are respectively displayed in Figures 3b and 3d. The compounds are separated on the basis of the number of repeating CL units. Mass analysis shows that, although the different homologous series partially overlap, they can be identified. Elution peaks corresponding to unreacted MPEG initiator, non-functionalized $MPEO_{45}$-CL_n block copolymers, functionalized $MPEO_{45}$-CL_n-LA and CL_n-LA (LA functionalized polyCL sequences) can be discerned. Apparently in the latter case water, present as an impurity, has initiated the ring opening polymerization of CL which upon esterification with linoleic acid yields CL_n-LA.

Upon LA functionalization, $MPEO_{45}$-CL_n-LA block copolymers with n only ranging from 1 to 4 were found in the chromatograms. Apparently, the esterification conditions applied in the functionalization reaction have reduced the CL sequence length through transesterification reactions. By comparing the intensities of the compounds in the chromatograms in Figures 3b and 3d, it seems that in block copolymers prepared from purified MPEG and CL starting materials, the extent of LA functionalization is higher than in the case of non-purified starting materials.

Although in Figure 3a and 3c no signals due to homopolymeric CL sequences can be observed, these compounds are expected to be present in the reaction products. When using other ionization techniques, such as negative ESI or APCI, in the mass spectrometry such compounds can indeed be detected. In Figure 4 a spectrum of MPEO-CL showing the presence of polyCL (PCL_n) and cyclic-PCL_n) after ring opening polymerization of CL. It is likely that the cyclic PCL_n products are formed by backbiting and transesterification reactions.

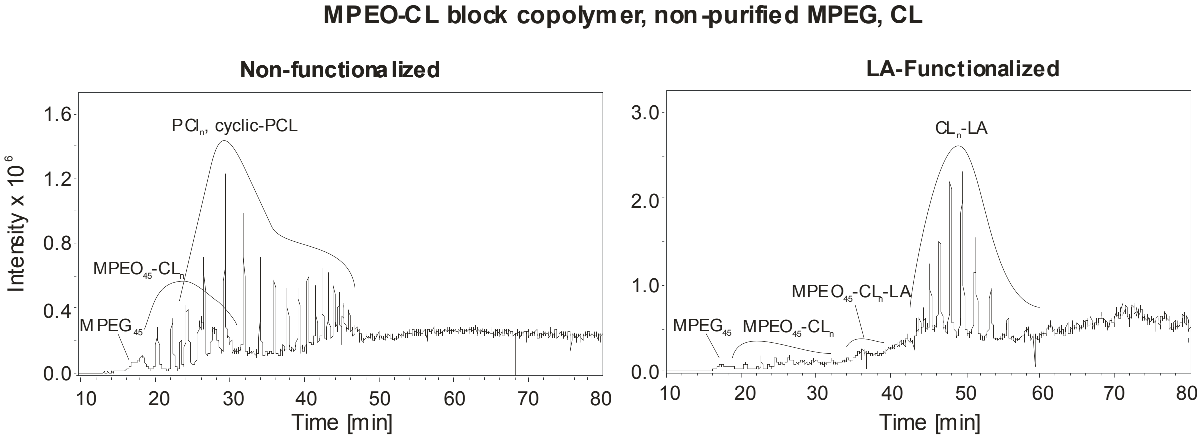
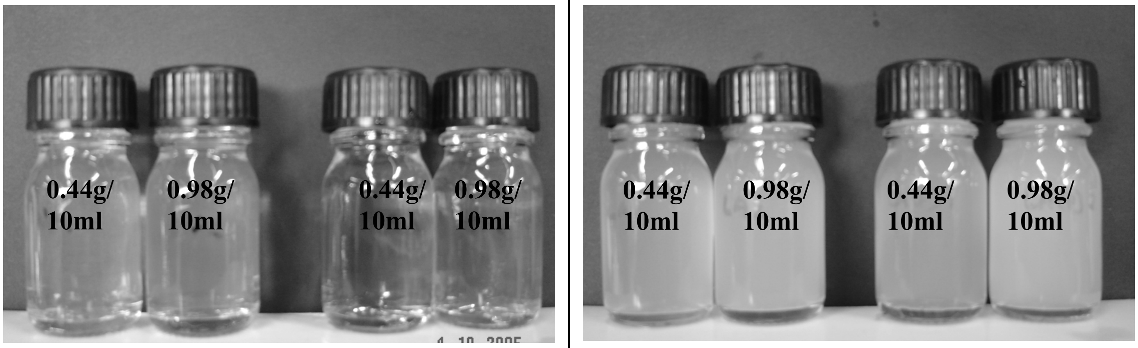


Figure 4. LC/MS APCI (-) chromatogram of $MPEO_{45}$-CL_6 block copolymer prepared using non-purified MPEG and CL.

The compounds present in the surfactant polymerization and functionalization reaction mixtures can be identified by LC/MS. However, it should be realized that their quantification is not straightforward, as the ionization efficiencies of the different compounds are not identical. A more detailed description of the analytical aspects of the analysis of the surfactants by LC/MS will be reported at a later time [19].

In preparing aqueous solutions of the different surfactants, it was observed that only turbid solutions could be obtained. As PCL is a hydrophobic polymer, the presence of (short) homopolymeric PCL chains in the surfactant could have a large effect on its solubility and appearance in water. Figure 5 shows a series of photos of MPEO-CL and MPEO-CL-LA surfactants in water at different concentrations and temperatures. The concentrations of 0.44 and 0.98 g/10 ml respectively correspond to the amount of surfactant used in the P(MMA/BA) latex preparation at S/M ratios of 10/90 (Table 1) and

20/80. The different temperatures correspond to room temperature (25 °C) and to the emulsion polymerization temperature (60 °C).



a) MPEO$_{45}$-CL$_6$ solutions at 25 °C

Non-purified MPEG, CL *Purified MPEG, CL*

c) MPEO$_{45}$-CL$_6$-LA solutions at 25 °C

Non-purified MPEG, CL *Purified MPEG, CL*

b) MPEO$_{45}$-CL$_6$ solutions at 60 °C

Non-purified MPEG, CL *Purified MPEG, CL*

d) MPEO$_{45}$-CL$_6$-LA solutions at 60 °C

Non-purified MPEG, CL *Purified MPEG, CL*

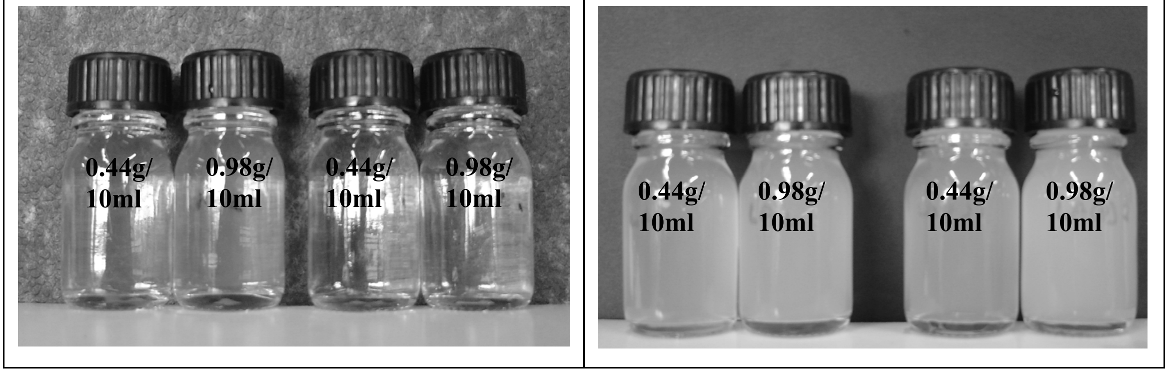


Figure 5. Aqueous MPEO-CL and MPEO-CL-LA surfactant solutions prepared with non-purified MPEG and CL, and prepared with purified MPEG and CL at different concentrations and temperatures.

It can be seen that before LA-functionalization of the surfactants, solutions of MPEO-CL block copolymer prepared from non-purified MPEG and CL were significantly more turbid than those of surfactants prepared using purified MPEG and CL. The presence of larger amounts of hydrophobic compounds is in agreement with the LC/MS results, which indicate that the occurrence of homopolymeric and cyclic PCL compounds is much higher when using non-purified starting materials.

Upon LA-functionalization the HLB value and the hydrophobicity of the surfactants increase (Table 2), and hence the turbidity of the surfactant solutions increases significantly as well (Figure 5). It is likely that surfactant aggregates were formed. However, Figure 5 shows no significant difference in turbidity between the different MPEO-CL-LA surfactants. Apparently, during the functionalization with linoleic acid at the elevated temperatures employed, randomization of the polymers through *e.g.* transesterification reactions has occurred.

This reduced solubility of the surfactants in water is not necessarily undesired. In general, for a surfactant to be used successfully in emulsion polymerizations, increased solubility could lead to decreased stabilization of the growing polymer particles [14].

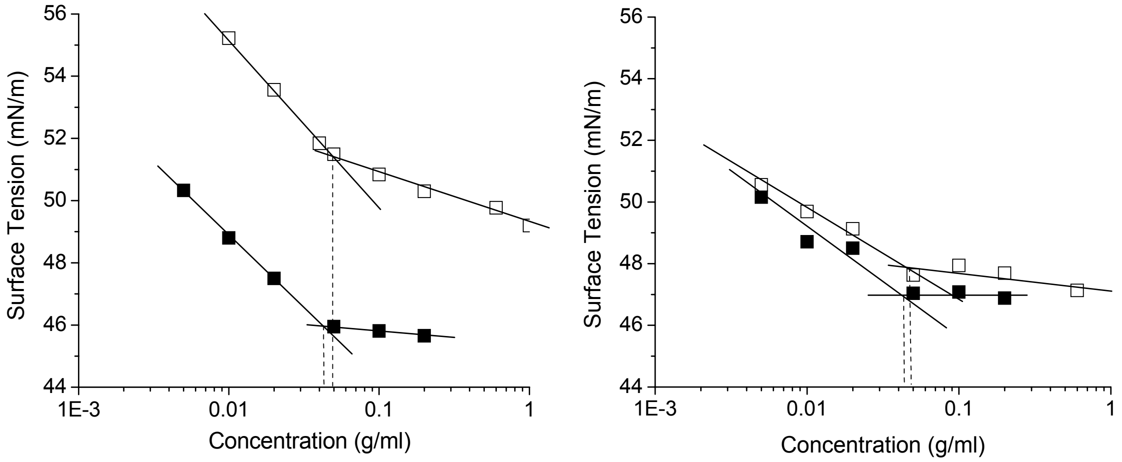
Temperature and surfactant concentration did not seem to have a major effect on the turbidity of the samples.

Surface activity of the non-pure and pure surfactants

To quantify an effect of the MPEG and CL purity used in the preparation of the MPEO-CL and MPEO-CL-LA surfactants on their surface activity, surface tension determinations at different concentrations were carried out.

Figure 6 shows that the different functionalized and non-functionalized block copolymers were obviously surface active substances. The surface tension reduced significantly as the block copolymer concentration was increased. At a certain surfactant concentration, the critical aggregation concentration (CAC), this effect leveled off. This reduction of the surface tension is due to the amphiphilic nature of the block copolymer molecule, allowing it to orientate at hydrophobic-hydrophilic interfaces [15].

When comparing the non-functionalized surfactants, block copolymers prepared from purified MPEG and CL exhibited a higher surface activity than block copolymers prepared from non-purified starting compounds. When using purified MPEG and CL, homopolymerization of CL was minimized and the hydrophobic character of MPEG-CL block copolymers increased.



a) MPEO$_{45}$-CL$_6$ *b) MPEO$_{45}$-CL$_6$-LA*

Figure 6. Surface tension versus concentration (a) MPEO$_{45}$-CL$_6$ (a) and (b) MPEO$_{45}$-CL$_6$-LA surfactant solutions in water. The dotted lines correspond to the CAC. The surfactants were synthesized using non-purified (□) and purified (■) MPEG and CL starting materials.

Upon LA functionalization, the block copolymers prepared from purified and from non-purified starting materials displayed similar surface activity. Capping the terminal hydroxyl group can lead to a significant reduction in the polarity of the surfactant head group [16]. The long aliphatic and hydrophobic hydrocarbon chain of the LA part reduces the solubility of the functionalized block copolymer in water. However, this can result in increased diffusion of the block copolymer towards the (latex) particle surface increasing the amount of surfactant present on that surface [17].

The critical aggregation concentration (CAC) values of the surfactants were determined from the inflection points in the surface tension versus concentration curves of the surfactants shown in Figure 6, and are presented in Table 3. Prior to functionalization both surfactants show clear surface active behaviour, although the inflection point was more pronounced in the case of surfactants prepared from purified compounds. MPEO-CL block copolymers prepared from non-purified MPEG and CL show slightly higher CAC and significantly higher surface tension at CAC than those prepared from purified MPEG and CL. The values for CAC and the surface tension at CMC were 0.18 mmol/l and 51 mN/m for MPEO-CL prepared from non-purified compounds, and 0.16 mmol/l and 46 mN/m for the block copolymer prepared from purified compounds.

In the MPEO-CL surfactant prepared from purified MPEG and CL, the hydrophobic CL block length in the block copolymer is expected to be larger and will thereby affect the CAC [18].

Table 3: CMC and surface tension at CMC (γ_{CMC}) of $MPEO_{45}$-CL_6 and $MPEO_{45}$-CL_6-LA diblock copolymer surfactants prepared from purified and from non-purified MPEG and CL.

Surfactant	CAC (g/l)	CAC[a] (mmol/l)	γ_{CAC} (mN/m)
$MPEO_{45}$-CL_6 non-purified MPEG, CL	0.49	0.18	51.4
$MPEO_{45}$-CL_6 purified MPEG, CL	0.43	0.16	46.0
$MPEO_{45}$-CL_6-LA non-purified MPEG, CL	0.48	0.16	47.9
$MPEO_{45}$-CL_6-LA purified MPEG, CL	0.44	0.15	47.0

[a] *based on molecular weights determined by NMR*

After LA-functionalization, the purity of the reactants used in the preparation of MPEO-CL-LA surfactants does not seem to significantly influence surface activity. In both cases, values of CAC were approximately 0.16 mmol/l, and surface tension at CMC values were approximately 47 mN/m. Apparently here too, the esterification at the employed reaction conditions led to randomized structures.

Characteristics of P(MMA/BA) Latices and Films

In previous work we prepared MPEO-CL-LA surfactants and effectively used them in emulsion polymerizations of acrylates [5-6]. In these investigations, the surfactants were prepared from non-purified MPEG and CL starting compounds. To investigate a possible effect of the purity of the MEPG and CL used in the preparation of the MPEO-CL-LA surfactants on the properties of P(MMA/BA) latices and films cast from these latices, comparative experiments were performed. Using the different surfactants, MMA and BA emulsion polymerizations were conducted at a solids content of approximately 30 wt%. The surfactant to monomer ratio was 10/90, and the polymerizations were conducted at 60 °C for 4 hrs. Characteristics of the resulting P(MMA/BA) latices are shown in Table 4.

From the table it follows that the properties of latices prepared with MPEO-CL-LA synthesized using purified starting materials were very much like those synthesized using non-purified starting materials. Solids contents, conversion of monomers, particle sizes and distributions were comparable, and typical latices prepared using more conventional surfactants such as sodium dodecyl sulfate (SDS), and sodium tetradecyl 3-sulfopropyl maleate [19] and propylene oxide-ethylene oxide [20] surfmers. Apparently, the similar surface active behaviour of the linoleic acid functionalized surfactants (see Figure 6 and Table 4) has lead to similar properties of the P(MMA/BA) latices.

Table 4: Characteristics of P(MMA/BA) latices prepared at 60°C using $MPEO_{45}$-CL_6-LA surfactants at a surfactant to monomer ratio of 10/90.

Surfactant	SC [a] (%)	Conv.[b] (%)	$\overline{M}_w$ [c] (10^3 g/mol)	PS [d] (nm)	PDI [e]
$MPEO_{45}$-CL_6-LA (non-purified MPEG, CL)	30.7	100	310	140	0.06
$MPEO_{45}$-CL_6-LA (purified MPEG, CL)	29.1	97	-	130	0.03

[a] *Solids content (SC) determined gravimetrically upon removal of volatiles;*

[b] *Conversion of MMA and BA monomer determined from the solids content;*

[c] *Weight average molecular weight ($\overline{M}_w$ determined by GPC);*

[d] *Average particle size (PS) as determined by DLS;*

[e] *Polydispersity index of the particle size distribution (PDI) as determined by DLS;*

From these latices, films can readily be prepared by casting and evaporation of the water. As the surfactant is linoleic acid functionalized, exposure to ambient surroundings will lead to (partial) crosslinking [5, 21, 22]. The mechanical properties of the latex films prepared with both MPEO-CL-LA surfactants are shown in Figures 7 and 8.

As can be observed in the figures, the E-modulus, yield strength, ultimate tensile strength and elongation at break of the latex films increase in time. This increase of the tensile properties of P(MMA/BA) latex films was previously observed, and could be due to polymer inter-diffusion and surfactant crosslinking [23, 24].

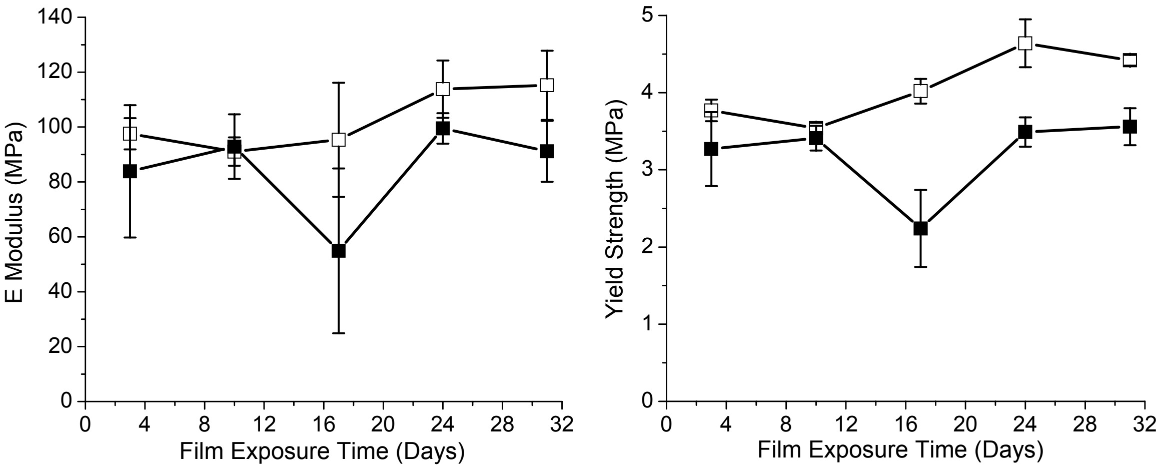


Figure 7. The E-modulus (left) and yield strength (right) of P(MMA/BA) latex films after drying at ambient conditions for different time periods. The MPEO-CL-LA surfactant used in the latex preparation was prepared from non-purified (□) and from purified (■) MPEG and CL starting materials.

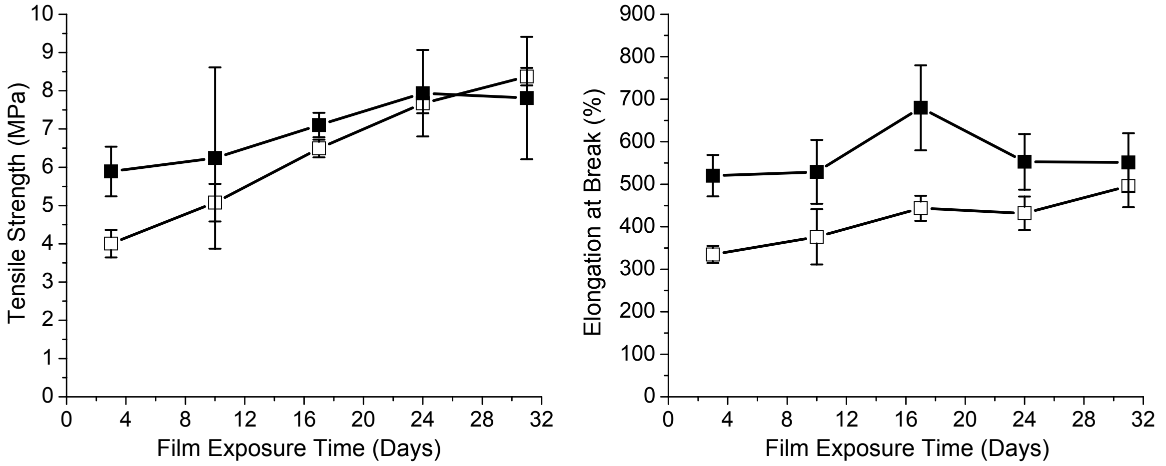


Figure 8. The tensile strength (left) and elongation at break (right) of P(MMA/BA) latex films after drying at ambient conditions for different time periods. The MPEO-CL-LA surfactant used in the latex preparation was prepared from non-purified (□) and from purified (■) MPEG and CL starting materials.

It does seem that the increase in tensile strength properties of latex films containing the MPEO-CL-LA synthesized from non-purified MPEG and CL is the largest. After approximately 1 month drying, the ultimate tensile strength and elongation at break of P(MMA/BA) latex films prepared with the different surfactants was comparable. However, the E-modulus and yield strength were somewhat higher for latex films containing MPEO-CL-LA synthesized from non-purified MPEG and CL.

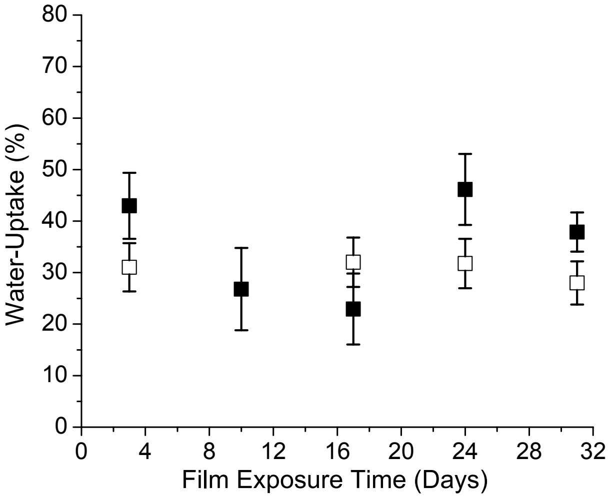


Figure 9. Water-uptake of P(MMA/BA) latex films after drying at ambient conditions for different time periods. The MPEO-CL-LA surfactant used in the latex preparation was prepared from non-purified (□) and from purified (■) MPEG and CL starting materials.

Similarly, the water-uptake behaviour of the P(MMA/BA) latex films was not significantly influenced by the purity of the MPEG and CL compounds used in the preparation of the surfactant, see Figure 9.

CONCLUSIONS

Polymeric MPEO-CL and MPEO-CL-LA surfactants were prepared from purified and from non-purified MPEG and CL starting materials. The properties of these (functionalized) amphiphilic block copolymers in displaying surface activity, P(MMA/BA) latex preparation and physical properties prepared by casting of these latices were compared.

In general, upon LA-functionalization, the performance of surfactants prepared from non-purified MPEG and CL starting materials is as good as that of surfactants prepared from purified starting compounds. As purification involves additional (costly) processing steps, it will be advantageous to apply the non-purified materials in the surfactant preparation procedures. Even though the composition of the surfactant itself might be less well defined, as LC/MS chromatography has shown.

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CHAPTER 6

Film Formation of P(MMA/BA) Latices Prepared Using Crosslinkable Poly(ethylene oxide) and ε-Caprolactone Block Copolymer Surfactants.

SUMMARY

In this study, linoleic acid (LA)-functionalized surfactants based on methoxy-poly(ethylene oxide) (MPEO) and ε-caprolactone (CL) were prepared for use as crosslinkable surfactants. These surfactants were used in the poly(methyl methacrylate/n-butyl acrylate), P(MMA/BA) emulsion copolymerization. Films were prepared by casting these latices and drying the films at ambient conditions. For comparison, latices and films were also prepared from analogous, non-crosslinkable stearic acid (SA) functionalized surfactants. The effect of the nature of the surfactant on the properties of the latex film was analyzed with regard to latex particle size, surfactant migration, water uptake and tensile properties. Films prepared using the crosslinkable LA-functionalized surfactant at a surfactant to monomer weight ratio (S/M) of 10/90 were already partly crosslinked after 10 days, and in tensile testing gave values of 115 MPa, 4.4 MPa, 8.4 MPa and 500 % for respectively the E-modulus, yield stress, tensile stress and elongation at break. In the wet state after equilibration with water, 30 wt% water was taken up, but similar tensile properties could be reached. An increase in the LA-functionalized surfactant to monomer ratio to 20/80 resulted in films (cast and dried for 31 days) with tensile properties at ambient conditions of E-modulus = 68 MPa, yield stress = 3.3 MPa, tensile strength = 5.5 MPa, elongation at break = 560 %. At these concentrations the surfactant apparently exhibited a plasticizing effect. Surprisingly, these films had the lowest water uptake: after 24 hrs immersion the water uptake was only 7 %. No change in hydrophilicity of the films in time as measured by contact angle measurements could be seen, implying that

migration of the surfactant was negligible. Films cast from latices prepared using the non-crosslinkable SA-functionalized surfactants were much more sensitive to water. Water uptake was now approximately 40% and in tensile testing values of 23 MPa, 0.6 MPa, 1.3 MPa and 215 % for respectively the E-modulus, yield stress, tensile stress and elongation at break were found for films in the wet state. When sodium dodecyl sulphate, an ionic surfactant, was employed at a much lower S/M ratio of 3/97 in the latex preparation, the water uptake of the films was significantly higher than that of films using the amphiphilic polymeric surfactants.

INTRODUCTION

In view of protecting the environment, waterborne coatings have attracted much industrial attention. In the formulation of a waterborne coating system, the acrylic latex is one of the main components. These latices are prepared by emulsion polymerization through a radical polymerization mechanism. In emulsion polymerization the use of surfactants is required to stabilize and to control the size of the particles.

The nature of these surfactants is the source of some potential problems as they are usually not strongly anchored (but only physically adsorbed) to the surface of the latex particles and can desorb. During film formation, the surfactant molecules can migrate to the surface of the film, causing poor adhesion of the film to the substrate. Moreover, as a result of phase separation within the film, surfactant molecules may concentrate in hydrophilic domains resulting in water sensitivity upon exposure of the film to water or a humid environment. This water sensitivity can have a detrimental effect on the mechanical properties of the polymeric film and impair its ability to act as a protective coating. Most of the ingredients of a latex coating system are either water-soluble or water-dispersible, and reducing the water sensitivity is a quite challenging goal [1-3].

One of the solutions to avoid these difficulties is to make use of reactive surfactants. The reactive surfactant can copolymerize with the acrylic monomer during the polymerization and thereby remain attached to the (surface of the) latex particle [4-6]. Although the formed latices are stable, a high surface tension of the latex itself can still impair the wetting properties of the latex [6]. Therefore, the use of crosslinkable block copolymers, which can act as a surfactant during the emulsion polymerization and can crosslink after application and during the film formation, was suggested as an alternative solution [7]. Crosslinkable surfactants based on methoxy-poly(ethylene oxide) (MPEO) and ε-caprolactone (CL) segments and functionalized with linoleic acid (LA) can undergo auto-oxidative crosslinking at ambient conditions [7]. In this way surfactant migration can be prevented and water sensitivity reduced.

In this study, we employed a crosslinkable, linoleic acid (LA)-functionalized surfactant in methyl methacrylate/n-butyl acrylate (MMA/BA) copolymer emulsion polymerization. The effect of water on the physical properties of films prepared from these latices was investigated. Analogous non-crosslinkable block copolymers (stearic acid (SA)-functionalized surfactant molecules which do not contain a reactive double bond) were used for comparison.

EXPERIMENTAL

Materials

Methoxy-poly(ethylene glycol) (MPEG) with a molecular weight of 2000 consisting of 45 ethylene oxide repeat units, *para*-toluene sulfonic acid monohydrate (*p*-TSA) and xylene (mixture of isomers) were obtained from Fluka, Switzerland. ε-Caprolactone (CL) from Aldrich, United Kingdom, linoleic acid (LA) from Acros-Organic, USA and stannous (II) octoate (SnOct) from Aldrich, USA were used as received. Deionized water (Milipore Q, 18.2 MΩcm) was used throughout the study. Methyl methacrylate (MMA, stabilized with hydroquinone) and n-butyl acrylate (BA, stabilized with hydroquinone) were obtained from Fluka, Switzerland. Sodium dodecyl sulfate (SDS) was used as received from Fisher, UK.

MMA and BA monomers were repeatedly washed with a 4 wt% aqueous sodium hydroxide solution to remove the hydroquinone and then repeatedly washed with deionized water. Both monomers were stored at + 4 ^{o}C.

A 70 % aqueous solution of *t*-butyl hydroperoxide (tBHPO) from Merck, Germany was diluted to a 30 % solution prior to use. A 5 wt% solution of L(+)-ascorbic acid (iAA) from Sigma, Germany and a 1 wt% solution of ethylenediaminetetraacetic acid ferric-sodium salt (FeEDTA) from Sigma, Germany were always freshly prepared. These aqueous solutions were used as a redox-initiating system in the emulsion polymerizations.

Surfactant Synthesis

Surfactants based on MPEG and CL and on MPEG, CL and LA or SA were prepared by first ring-opening polymerization of ε-caprolactone using MPEG as a macroinitiator. The obtained diblock copolymers were functionalized by esterification with linoleic acid (LA) or stearic acid (SA). In principle, the surfactant functionalized with LA is a crosslinkable and copolymerizable surfactant, whereas the $MPEO_{45}$-$CL_{6.5}$-SA copolymer is a non-crosslinkable surfactant. Details of the experimental procedures and surfactant properties are given elsewhere [7]. The non-functionalized diblock copolymers, and the LA- and SA-functionalized block copolymers are abbreviated as $MPEO_{45}$-$CL_{6.5}$, $MPEO_{45}$-$CL_{6.5}$-LA and $MPEO_{45}$-$CL_{6.5}$-SA, respectively. The chemical composition of the employed non-functionalized and fatty acid end-functionalized diblock copolymers are summarized in Table 1.

Table 1: Chemical composition of non-functionalized and fatty acid end-functionalized diblock copolymers

Surfactant	Composition (repeating units)			$\overline{M}_n$ calculated	$\overline{M}_n$ (H-NMR)	HLB
	EO	CL	FA			
$MPEO_{45}$-$CL_{6.5}$	45	6.4	-	2730	2730	14.7
$MPEO_{45}$-$CL_{6.5}$-SA	45	6.4	0.9	3000	2970	13.5
$MPEO_{45}$-$CL_{6.5}$-LA	45	6.4	0.9	2990	2960	13.5

SA = stearic acid; LA = linoleic acid

HLB = calculated hydrophilic to lipophilic balance.

Emulsion Copolymerizations of MMA and BA

Poly(methyl methacrylate/n-butyl acrylate) (PMMA/BA) latices were prepared by emulsion copolymerizations of MMA and BA using a standard redox initiating system, consisting of tBHPO (30 %), iAA (5 %) and FeEDTA (1 %) aqueous solutions, and employing $MPEO_{45}$-$CL_{6.5}$-LA or $MPEO_{45}$-$CL_{6.5}$-SA copolymers as the surfactants. The reaction conditions used for the MMA and BA emulsion copolymerizations were similar to the optimized reaction conditions determined previously for MMA emulsion polymerization [7]. The recipe (composition of the reaction mixture) used in the P(MMA/BA) emulsion copolymerizations is summarized in Table 2.

MMA/BA batch copolymerizations were carried out in a three-necked round-bottomed flask equipped with a condenser, a nitrogen gas inlet, magnetic stirrer and a rubber septum. The surfactant was added to water, and purged with nitrogen for 30 min. Then, the temperature was set to the appropriate reaction temperature, the monomers were added and the mixture was equilibrated for another 30 min under stirring to emulsify the monomer and remove dissolved oxygen. In successive steps, the aqueous tBHPO solution was added to the emulsified monomer, then the iAA solution, and finally the polymerization was started upon the addition of the FeEDTA solution.

Table 2: Recipe (composition of the reaction mixture) used in the MMA/BA emulsion copolymerizations at 60 ^{o}C for 4 hrs at a surfactant to monomer weight ratio (S/M) of 10/90.

Component	Amount (g)	wt%
Water	33.11	61.22
Surfactant	1.63	3.01
Monomers:		
MMA (50 %)	7.30	13.50
BA (50 %)	7.30	13.50
TBHPO (30 % aqueous solution)	0.65	1.20
iAA (5 % aqueous solution)	3.89	7.20
FeEDTA (1 % aqueous solution)	0.20	0.37
Total	54.08	100.00

At different polymerization time points, aliquots were withdrawn from the emulsion and a small amount of hydroquinone was added to quench the polymerization. From these samples the solids content, monomer conversion and particle size were determined.

Characterization of P(MMA/BA) latices

The solids content of the latices was determined by evaporating the volatile components (water, MMA and BA monomers) in an oven at 60 ^{o}C for 24 hrs. The total

(MMA and BA) monomer conversion was calculated, taking into account the mass of the initiator and surfactant used.

The molecular weights and the molecular weight distribution of the obtained polymers were determined after purification by dissolution in chloroform, precipitation in methanol and drying. Size exclusion chromatography (SEC) was performed at 40 ^{o}C using an Alliance Separation Module (Waters 2690) equipped with three PL Mixed B (Polymer Laboratories) and a guard column. Tetrahydrofuran (THF) containing 1.0 vol% acetic acid was used as eluent. The injection volume was 150 µl, the flow rate 1.0 ml/min and a temperature of 40 °C was applied. Detection was performed with a differential refractive index detector (Waters 410). Calibration was performed with eight polystyrene standards, ranging from 500 to 4,000,000 g/mol.

The latex particle size and particle size distribution were determined by dynamic light scattering (DLS) (Zetasizer 4000, Malvern Instruments Ltd., Malvern, UK) at 25 ± 1 °C at an angle of 90 ° (633 nm), taking the average of five measurements.

Film formation and physical properties

P(MMA/BA) latex films were prepared by pouring 15g of the latex dispersions into a glass Petri dish (diameter = 15 cm) and subsequent drying at 25 ± 2 ^{o}C (relative humidity = 50 ± 10 %). The polymer films were removed from the glass after 3 days and dried for different time intervals (1 to 4 wks) at ambient conditions (25 ± 2 ^{o}C; relative humidity, RH = 50 ± 10 %), unless mentioned otherwise. The final thickness of the films was 0.25 ± 0.05 mm.

The glass transition temperature (Tg) of latex films was determined by differential scanning calorimetry (DSC) (DSC 7, Perkin Elmer). The heating rate for all samples was 10 ^{o}C/min and the scanning temperature range was from -50 ^{o}C to 60 ^{o}C, a second scan was taken after rapid quenching. The Tg was taken as the midpoint of the inflection of the curve in the second heating scan.

The tensile properties of the latex films were determined using a Zwick Z020 (Germany) tensile testing machine at room temperature. Standard tensile test specimens were cut from the latex films according to ISO 037-2 Standard. The tests were conducted at a crosshead speed of 50 mm/min using a 500 N load cell and a 0.01 N pre-load. The tensile strength, yield stress, E-modulus and elongation at break were determined;

extensometers were not used in the strain measurements. At least three specimens were tested for each sample and the average values were determined. The relative errors in the measurements varied between 10 and 15 %.

To assess the effect of water, tensile tests were also conducted on wet, hydrated latex films and on stringently dried, moisture-free latex films. The wet films were prepared by casting the latex and drying under ambient conditions for 10 days and subsequent immersion in water for a period of 24 hrs at room temperature. Moisture-free films were prepared by casting the latex and drying for 14 days under ambient conditions followed by vacuum drying in the presence of silica gel for a further 3 days. Testing of these samples was performed immediately after conditioning.

The water uptake (WUT) of latex films (1 cm x 1 cm) was determined gravimetrically by immersing the specimens in water (25 ^{o}C) for 24 hrs. The wet mass was determined after blotting the surface dry. Water uptake is defined as WUT % = $(W-W_0)/W_0$ x100%, where W_0 is the weight before immersion and W is the weight after immersion [8].

Static contact angles of the latex films were measured using a Data Physics, OCA 15 plus apparatus, Millipore water was used as the probe liquid at room temperature. The static contact angles were measured 30 seconds after deposition of water on the latex film. Per sample, the average static contact angle measured in at least three different locations of the films was determined.

AFM analysis of film samples (in air and at room temperature) was conducted using a Nanoscope III (Digital Instruments) operating in tapping mode. Image analysis was performed with the Nanoscope software.

RESULTS AND DISCUSSION

In previous studies, LA-functionalized (crosslinkable) MPEO-CL block copolymers were successfully used as surfactants in the preparation of PMMA latices [7]. To further evaluate the applicability of this surfactant in formulating waterborne coatings, this surfactant was employed in P(MMA/BA) latex preparations. Due to their low Tg, P(MMA/BA) latices are often used as a film-forming binder in formulating waterborne coatings.

Several P(MMA/BA) latex batches containing MMA and BA in a ratio of 1:1 were prepared using $MPEO_{45}$-$CL_{6.5}$-LA as a surfactant. The conditions used for the emulsion copolymerizations of MMA and BA were similar to the optimized reaction conditions determined for MMA emulsion polymerizations reported previously [7].

The Tgs of PMMA and PBA homopolymers are 105 °C and -56 °C, respectively, accordingly the Tg of the P(MMA/BA) latex can be tuned by changing the ratio of the weight fraction of MMA to BA during the emulsion polymerizations.

Table 3: P(MMA/BA) latices prepared using $MPEO_{45}$-$CL_{6.5}$-LA (latex 1-3) or $MPEO_{45}$-$CL_{6.5}$-SA *(latex 4) block copolymers as a surfactant at a reaction temperature of 60 °C.*

Latex	**S/M**[a]	**SC**[b] **(%)**	**% MMA BA Conversion**[b]	**$\overline{M}_w$**[c] **(10^3 g/mol)**	**MWD**	**PS**[d] **(nm)**
Latex 1	5/95	29.6	100.0	360	2.88	230
Latex 2	10/90	30.7	100.0	310	3.74	140
Latex 3	20/80	32.9	98.4	390	1.77	110
Latex 4[f]	10/90	29.2	94.0	490	-	142

[a] *Surfactant to monomer weight ratio (S/M).*

[b] *Final solids content (SC) and MMA and BA conversion determined after 4 hrs polymerization and 24 hrs storage at room temperature.*

[c] *Weight average molecular weight of polymers determined by SEC;*

[d] *PS = particle size determined by DLS;*

[e] *PDI = polydispersity index of latex particle distribution by DLS*

[f] *$MPEO_{45}$-$CL_{6.5}$-SA surfactant*

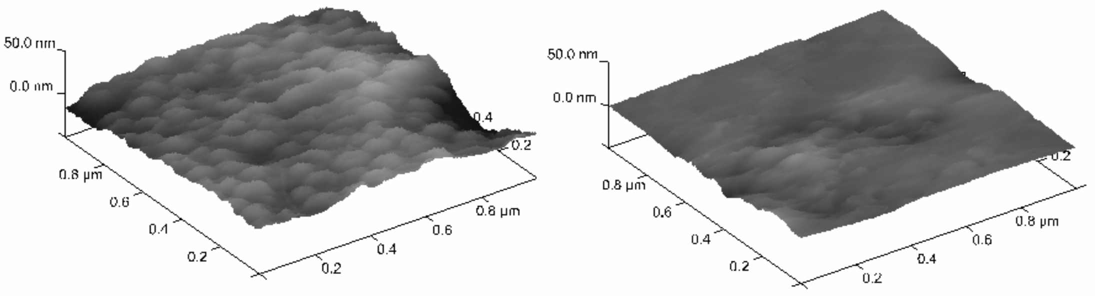
The properties of the P(MMA/BA) latices are listed in Table 3. Under these reaction conditions, the monomer conversion in all polymerizations was rather high (exceeding 98%). Also, the molecular weight of the polymers was relatively high, even though the presence of unsaturated groups in the $MPEO_{45}$-$CL_{6.5}$-LA surfactant could induce chain transfer either by the addition of radicals to the linoleic ester double bonds or by abstraction of allylic hydrogens of linoleic ester during the emulsion polymerization [7, 9].

The average particle size of the prepared latices ranged between 110 and 230 nm. The latex particle size decreased upon increasing surfactant to monomer ratio due to the increased number of micelles in a system containing high surfactant concentrations. The polydispersity index of the particle size distribution became broader as the S/M ratio increased. This could be due to secondary nucleation at higher surfactant concentrations [10].

Physical Properties of Cast P(MMA/BA) Latex Films

The film-forming ability of latices is largely dependent on the minimum film formation temperature (MFFT). This parameter describes the minimum temperature above which the drying of a latex produces transparent and crack-free films [11]. The MFFT is generally reduced with a decrease in Tg. DSC analyses showed that the Tg of the prepared MMA and BA copolymers varied between -15 and -13 ^{o}C. These values are well below room temperature, and easy film formation from the latices at ambient conditions was expected.

Upon casting and drying of a film, the latex particles coalesce and polymer interdiffusion occurs as water evaporates and film formation proceeds. This will result in the development of a coherent, transparent film with appreciable mechanical properties. After three days of drying at ambient conditions, individual particle-particle boundaries at the surface of the cast latex film still were observed by AFM (Figure 1a). At 31 days particle coalescence had resulted in a much smoother film (Figure 1b).



a) 3 days

b) 31days

Figure 1. AFM images of films prepared from P(MMA/BA) latices polymerized with MPEO$_{45}$-CL$_{6.5}$-LA *as a surfactant at S/M = 10/90. The films were dried at ambient conditions for a) 3 days and b) 31 days*

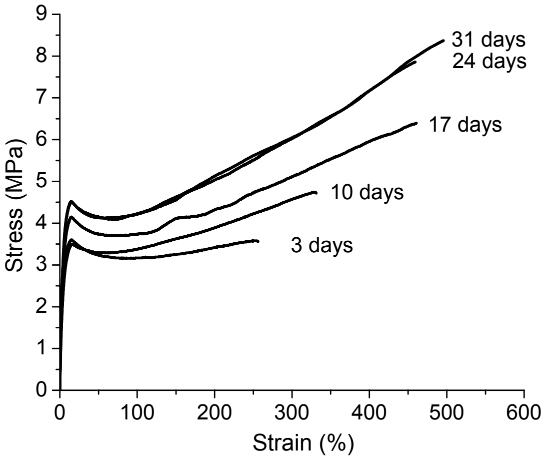


Figure 2: Typical stress-strain diagrams of films prepared from P(MMA/BA) latices polymerized with MPEO$_{45}$-CL$_{6.5}$-LA *as a surfactant at S/M = 10/90. The films were dried at ambient conditions for different time periods.*

Tensile testing of films prepared from P(MMA/BA) copolymer emulsions dried for different drying times revealed the effect of drying time on the mechanical properties of the films. Typical stress-strain curves of the P(MMA/BA) copolymer films prepared with the (crosslinkable) MPEO$_{45}$-CL$_{6.5}$-LA surfactant are shown in Figure 2. As can be observed in the figure, the mechanical properties of the latex film gradually increased with drying time. This improvement of the mechanical properties is due to particle coalescence and polymer interdiffusion in time, but also crosslinking of surfactant molecules through autoxidative crosslinking mechanisms, comparable to those previously reported for alkyd-based coating systems [12, 13], could be of influence.

The tensile properties of the P(MMA/BA) films are summarized in Table 4. In time, the values of the E-modulus, yield stress, maximum tensile strength and elongation at break increased. The values for the E-modulus and yield stress seemed to reach a plateau values after 24 days, while the maximum tensile strength and elongation at break continued to increase. Apparently, in this time period complete polymer interdiffusion was achieved [14]. During drying of the films under ambient conditions, where oxygen is present in the atmosphere, cross-linking reactions of the (covalently bound) surfactant molecules present in the films could have occurred [7].

Table 4. Tensile properties (E-modulus, yield stress, tensile strength and elongation at break) of P(MMA/BA) latex films dried under ambient conditions for varying time periods. The latices were prepared with MPEO$_{45}$-CL$_{6.5}$-LA as a surfactant at S/M =10/90.

Film drying time (days)	**E-modulus (MPa)**	**Yield stress (MPa)**	**Tensile strength (MPa)**	**Elongation at break (%)**
3	97 ± 6	3.77 ± 0.14	4.02 ± 0.36	335 ± 20
10	91 ± 5	3.54 ± 0.07	5.09 ± 0.49	375 ± 65
17	95 ± 20	4.02 ± 0.16	6.50 ± 0.23	440 ± 30
24	114 ± 10	4.64 ± 0.31	7.67 ± 0.26	430 ± 40
31	115 ± 15	4.42 ± 0.07	8.37 ± 0.23	500 ± 50

To illustrate that crosslinking had indeed occurred in these P(MMA/BA) latex films, a small piece of film, which had been dried for 31 days under ambient conditions, was immersed in chloroform for 24 hrs in a Petri dish. By carefully tilting the Petri dish insoluble gel fragments could be observed (see Figures 3a and 3b). A similar film was prepared from a P(MMA/BA) latex synthesized with a stearic acid (SA) surfactant that does not contain a reactive double bond. When this film was dried for 31 days and immersed in chloroform for 24 hrs, complete dissolution of the film was observed (Figure 3c). This implies that (to some extent) auto-oxidative crosslinking reactions had taken place only when the crosslinkable LA-containing surfactant was used during latex preparation.

This is in agreement with our previous studies [7], where nuclear magnetic resonance (NMR) was used to follow the conversion of double bonds in LA-containing surfactants. Here an insoluble, fully crosslinked surfactant film could be obtained after approximately 20 days exposure to air.

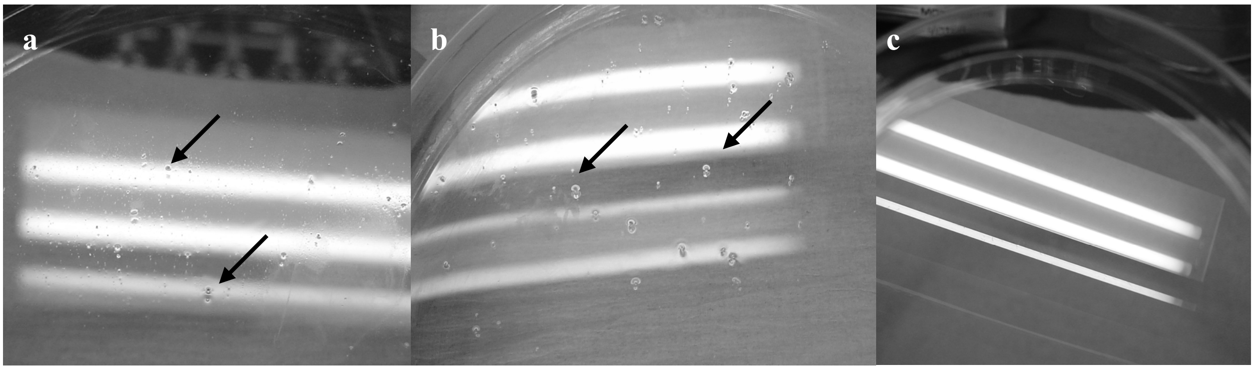


Figure 3. Photographs of P(MMA/BA) films prepared by casting and drying under ambient conditions. The films were immersed in chloroform for 24 hrs in a covered, 15 cm diameter Petri dish.

a) latex prepared with a LA-functionalized surfactant (S/M = 10/90) and dried for 10 days before the immersion in chloroform, insoluble gel particles can be observed (see arrows)

b) latex prepared with a LA-functionalized surfactant (S/M = 10/90) and dried for 31 days before the immersion in chloroform, insoluble gel particles can be observed (see arrows)

c) latex prepared with a SA-functionalized surfactant (S/M = 10/90) and dried for 31 days before the immersion in chloroform, note the absence of gel particles.

In addition, when an MMA/BA emulsion copolymerization was carried out with the LA-functionalized surfactant in a semi-continuous manner (where part of the reactants was first fed into the reactor, and then the rest of the monomers, surfactants and initiator solutions were fed continuously over a define period of time) under otherwise similar reaction conditions, a completely insoluble P(MMA/BA) latex film could be prepared. Indeed the crosslinkable groups present in the surfactant undergo auto-oxidative crosslinking in the latex film, yielding a crosslinked polymer film.

The effect of MPEO$_{45}$-CL$_{6.5}$-LA surfactant concentration on P(MMA/BA) latex film properties

In Figures 4 and 5, plots of the E-modulus, yield stress, tensile strength and elongation at break of P(MMA/BA) films at ambient conditions, in which the latex was prepared with crosslinkable LA-functionalized MPEO$_{45}$-CL$_{6.5}$-LA surfactant at different concentrations, are given as a function of the drying time at room temperature of the latex film.

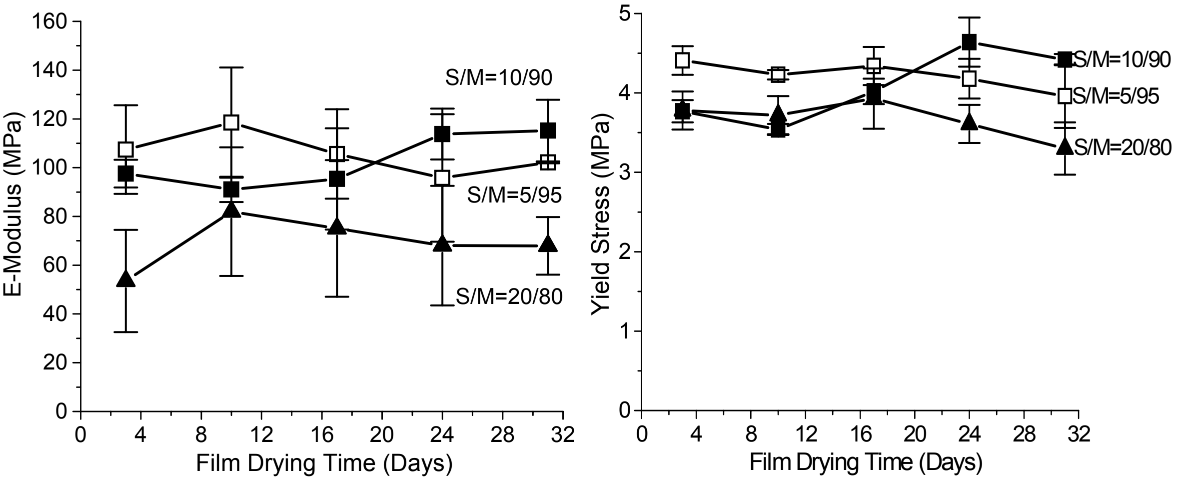


Figure 4: Effect of MPEO$_{45}$-CL$_{6.5}$-LA *surfactant concentration on E-modulus (left) and yield stress (right) of P(MMA/BA) latex films as a function of drying time.*

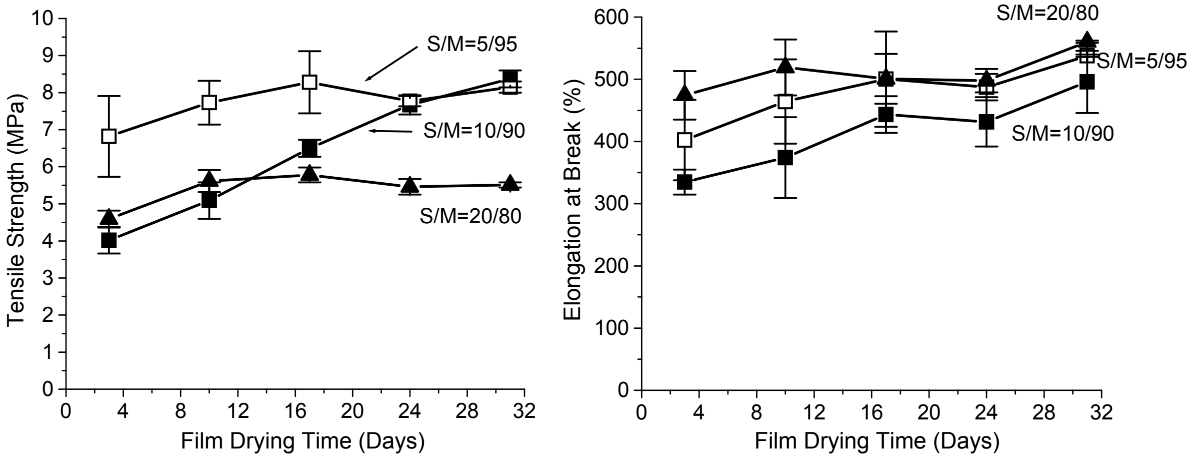


Figure 5: Effect of MPEO$_{45}$-CL$_{6.5}$-LA *surfactant concentration on tensile strength (left) and elongation at break (right) of P(MMA/BA) latex films as a function of drying time.*

At all surfactant concentrations the mechanical properties of the films improved in time: E-modulus, maximal tensile strength and elongation at break increase, the yield strength slightly decreased. With an increase in time, interdiffusion of the polymer chains between the latex particles can occur, thereby forming a continuous, flawless film. Also upon drying at ambient conditions, crosslinking of the linoleic acid moiety can result in improved mechanical properties. When comparing the different surfactant concentrations, it seems that in general the latices prepared at S/M = 5/95 and S/M = 10/90 reached similar levels of tensile properties. Latices with an S/M = 20/80 showed appreciably lower values of E-modulus, tensile (yield) stress and higher elongation at break. Under these conditions, it seems that the high amounts of surfactant also led to a plasticizing effect of the film [8, 15]. Also, PCL itself is a flexible polymer and exhibits a high elongation at break [16]. Although high crosslinking densities could lead to higher E-modulus values, at these crosslinkable surfactant concentrations this does not seem to be the case. In our case surfactant molecules will react with each other and it is not to be expected that overall crosslinking densities in the film are high.

Surfactant Migration

Contact angle measurements were used as an indirect, qualitative method to investigate changes in film surface hydrophilicity in time due to possible migration of the surfactant towards the polymer-air interface. A decrease in the contact angle implies an increase in hydrophilicity of the film surface. The results of the contact angle measurements for drying films of P(MMA/BA) latex prepared with different LA-functionalized surfactant concentrations (S/M between 5/95 and 20/80) are given in Figure 6. As the surfactant concentration increased, lower contact angles and more hydrophilic film surfaces were obtained. No significant changes in the contact angles of the latex films in time could be seen, indicating that surfactant migration could not be observed from contact angle measurements in time.

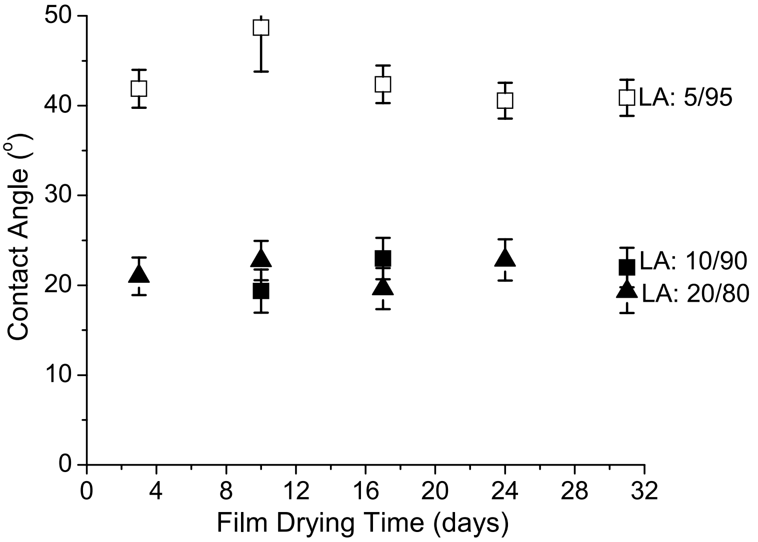


Figure 6. Contact angle measurements of P(MMA/BA) latex films as a function of drying time. The latices were prepared with (crosslinkable) MPEO$_{45}$-CL$_{6.5}$-LA surfactants at S/M = 5/95, 10/90 and 20/80.

Water uptake

The water uptake of latex copolymer films dried for different periods of time, where the latex was prepared with different surfactants and surfactant concentrations, is shown in Figure 7. As the LA-functionalized MPEO$_{45}$-CL$_{6.5}$-LA surfactant contains the most hydrophilic moiety in the system, it could be expected that as the surfactant to monomer ratio increased, the water uptake of the films would increase as well. However, the figure shows that films prepared from P(MMA/BA) latices with S/M ratios of 5/95 and 10/90 take up significantly more water than latices prepared with much higher surfactant concentrations (S/M = 20/80). Apparently the increased amount of surfactant can result in increased crosslinking reactions and a reduction of the mobility of the chains avoiding the formation of hydrophilic domains [17].

As a control, P(MMA/BA) latices were prepared with sodium dodecyl sulfate (SDS). Because SDS is not compatible with the redox-initiating system, potassium persulfate (KPS) was used in these polymerizations. The reaction was conducted at 80°C for 4 hr at a solids content of 30 wt%, and the surfactant to monomer ratio was S/M = 3/97.The monomer conversion and the latex particle size obtained were 95 % and 115 nm respectively (see also Chapter 3 of this thesis).

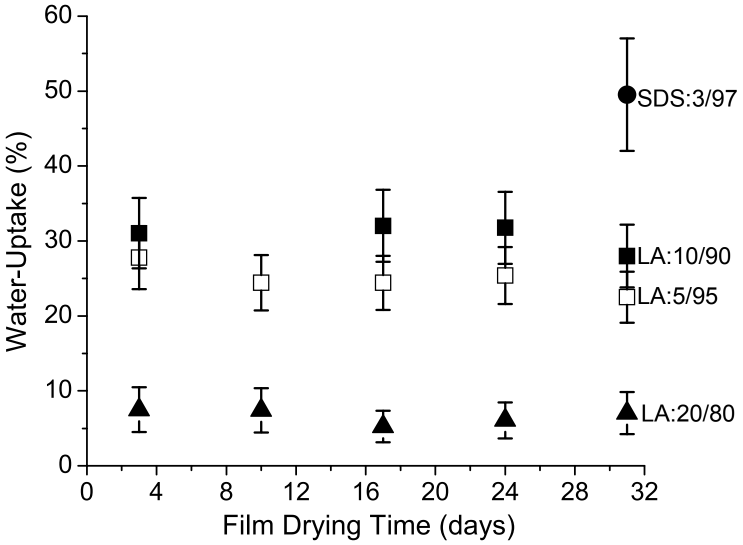


Figure 7. Water uptake of latex films prepared using a crosslinkable surfactant (MPEO$_{45}$-CL$_6$-LA) at different surfactant to monomer ratios (S/M = 5/95, 10/90 and 20/80) and using a conventional ionic surfactant (SDS; S/M = 3/97) at varying film drying times.

Films prepared from this SDS containing latex were found to be quite sensitive to water. Even at a much lower surfactant concentration water uptake of these films was significantly higher than that of the films prepared with a crosslinkable surfactant.

The effect of water on tensile properties of P(MMA/BA) latex films

Absorbed water and moisture can negatively affect the mechanical properties of the latex film. To assess this effect, tensile tests were performed on P(MMA/BA) latex films prepared with MPEO$_{45}$-CL$_{6.5}$-LA, at a S/M = 10/90 (Latex 2) as at this ratio water uptake was the highest. A cast film was first dried at ambient conditions for 10 days and then either tested directly or immersed in water for 24 hrs prior to tensile testing (giving a water uptake of 30 %). Another film was cast, dried for 17 days then vacuum dried in the presence of silica gel for another 3 days prior to testing. Figure 8 shows the stress-strain curves of the latex films equilibrated under the different conditions. The data is also presented in Table 5.

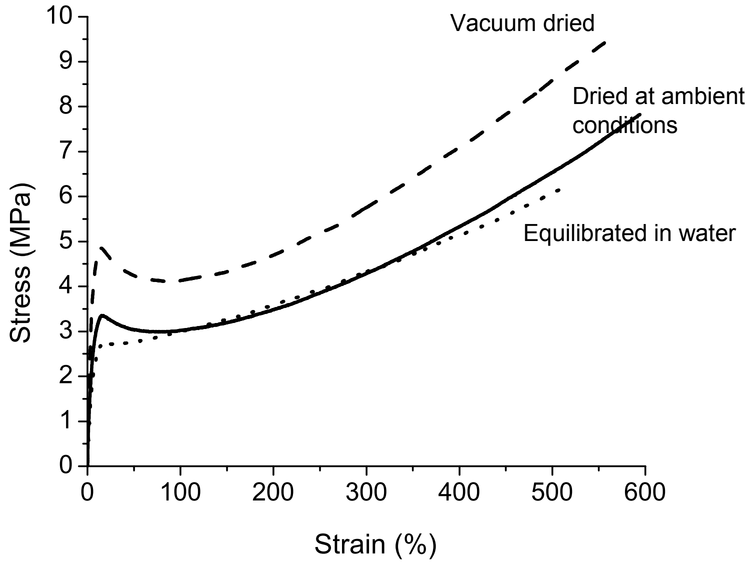


Figure 8. Typical stress-strain curves of films from a P(MMA/BA) *latex prepared with* $MPEO_{45}$-$CL_{6.5}$-*LA and dried at ambient conditions, and dried films equilibrated in water for 24 hrs or vacuum dried for 3 days in the presence of silica gel.*

Table 5. Tensile properties of films prepared from P(MMA/BA) latices using $MPEO_{45}$-$CL_{6.5}$-*LA as a surfactant and dried at ambient conditions for 17 days, and of dried films equilibrated in water for 24 hrs or vacuum dried for 3 days.*

	Dried at ambient conditions	**Equilibrated in water**[a]	**Vacuum dried** [b]
E-Modulus (MPa)	78 ± 12	60 ± 8	126 ± 4
Yield strength (MPa)	3.39 ± 0.34	2.66 ± 0.15	4.79 ± 0.11
Tensile strength (MPa)	7.17 ± 1.00	5.49 ± 0.78	9.51 ± 0.18
Elongation at break (%)	570 ± 90	450 ± 90	540 ± 20

[a] Water uptake: 40 w/w%. Samples were immediately tested after equilibration.

[b] Cast latex films were dried at ambient conditions for 14 days, then vacuum-dried in the presence of silica gel for 3 days. Samples were immediately tested.

It can be observed that in the wet state, the tensile properties of these latex films prepared with the LA-functionalized (crosslinkable) surfactant were comparable to those only cast and equilibrated at ambient conditions. Careful drying of the films, thereby removing most water, results in higher tensile (yield) strengths and elongations at break. Nevertheless, it is apparent that the water sensitivity of these films is apparently not so large that equilibration in water results in significantly reduced mechanical properties.

When a similar, but non-crosslinkable surfactant MPEO$_{45}$-CL$_{6.5}$-SA (which contains stearic acid instead of linoleic acid) was used to prepare a P(MMA/BA) latex at (Table 1, Latex 4) different behavior was observed. Although the latex itself had comparable properties to the previous one (Latex 2), its resistance to water was much lower. In this case the water uptake of the specimens was 40% and, as Table 6 shows, the mechanical properties were significantly influenced by water when the same experiments were performed. Although under moisture-free conditions, after vacuum drying, the mechanical properties were quite comparable to those of the latex films prepared with the linoleic acid-containing surfactant, the mechanical properties at ambient conditions were much affected. Further water uptake upon equilibration in water resulted in materials with even lower values of modulus and (yield) strength.

From this it follows that the moisture resistance of P(MMA/BA) latex films prepared with non-crosslinkable stearic acid surfactants is much lower than those of latex films prepared using linoleic acid functionalized surfactants.

Table 6. Tensile properties of films prepared from P(MMA/BA) latices using $MPEO_{45}$-$CL_{6.5}$-SA as a surfactant and dried at ambient condition for 10 days, and of dried films equilibrated in water for 24 hrs or vacuum dried for 3 days in the presence of silica gel.

	Dried at ambient conditions	**Equilibrated in water**[a]	**Vacuum dried**[b]
E-Modulus (MPa)	42 ± 8	23 ± 6	110 ± 20
Yield strength (MPa)	1.55 ± 0.19	0.62 ± 0.23	3.54 ± 0.38
Tensile strength (MPa)	1.73 ± 0.12	1.27 ± 0.17	2.03 ± 0.66
Elongation at break (%)	460 ± 60	215 ± 120	265 ± 130

[a] Water uptake: 40 w/w%. Samples were immediately tested after equilibration.

[b] Cast latex films were dried at ambient conditions for 14 days, or vacuum dried in the presence of silica gel for 3 days. Samples were immediately tested after equilibration.

CONCLUSIONS

This study shows that it is possible to prepare stable P(MMA/BA) latices at solids contents of 30 wt% using $MPEO_{45}$-$CL_{6.5}$-LA and $MPEO_{45}$-$CL_{6.5}$-SA surfactants in different concentrations. These latices can readily be cast to yield films at room temperature. Upon drying the latices prepared using the linoleic acid functionalized $MPEO_{45}$-$CL_{6.5}$-LA surfactant, crosslinked structures are formed. Films prepared from these latices showed good mechanical properties, in which the influence of water was limited. Surface contact angle measurements did not show migration of the surfactant to the surface of the latex films. Latex films prepared using $MPEO_{45}$-$CL_{6.5}$-SA showed a much higher sensitivity to water.

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CHAPTER 7

MPEO-CL and MPEO-CL-LA Block Copolymers as Pigment Dispersants for use in Waterborne Coatings

SUMMARY

In this study block copolymers, based on methoxy-poly(ethylene oxide) (MPEO) and ε-caprolactone (CL) were prepared. These MPEO-CL block copolymers were also functionalized with linoleic acid (LA). MPEO-CL and MPEO-CL-LA block copolymers were used in the preparation of TiO_2 pigment pastes. The properties of these pastes were compared to those of pastes prepared with two frequently used pigment dispersants (Disperbyk 190 (a block copolymer with pigment-affinic groups) and Surfynol 104E (a non-ionic acetylenic diol)). Viscosity measurements showed that all pastes are shear thinning. These pastes could readily be formulated with commercially available acrylic emulsions, yielding stable pigmented (shear thinning) latices that could readily be cast to form pigmented coatings. Upon drying, the waterborne coatings showed high levels of gloss and limited water uptake. The properties of pigmented films prepared with MPEO-CL and MPEO-CL-LA block copolymers compared favourably with those of films prepared using Disperbyk 190 and Surfynol 104E. The gloss levels of films prepared with MPEO-CL-LA was slightly higher than that of films prepared with MPEO-CL block copolymers, while water uptake was somewhat lower.

INTRODUCTION

Environmental concerns and legislation have required the reduction of the level of volatile organic solvents (VOC) in paint systems, and the production of waterborne coatings has increased significantly in the past decades. Substituting organic solvent-based paints with waterborne paints considerably complicates pigmentation. Only a thoroughly dispersed pigment will result in a high quality coating with high gloss and water resistance. Pigments are usually supplied as a powder that contains particles clustered into agglomerates. These agglomerates must be broken down into primary pigment particles. In traditional solventborne paints, the binder is used to disperse the pigment [1]. In waterborne paints, however, obtaining a high quality pigment dispersion remains a challenge. In waterborne coatings, the competitive adsorption between surfactant and pigment dispersant is also an important problem that can lead to instability of the paint formulations [2].

To disperse and stabilize the pigment, additives are used that absorb onto pigment particles. In general, the pigment particles can be stabilized by three mechanisms [2, 3]:
1) steric hindrance, 2) electrostatic repulsion and 3) electrosteric stabilization. (In the case of ionic polymeric stabilizers, electrostatic and steric stabilization mechanisms can occur simultaneously)

Polymeric pigment dispersants, which provide steric stabilization, have attracted the most attention, as they are insensitive to external parameters such as the presence of water, pH and ionic strength. With the development of binders for the aqueous coatings industry, new polymeric pigment dispersants are being investigated. Especially dispersants offering superior rheological performance, or products which can be applied in different pigment and coating systems are much researched [4-6]. Furthermore, finding substitutes for conventional pigment dispersants like nonyl ethoxylates, which cause ecological problems, is a major driving force for the development of novel polymeric dispersants [4].

Copolymers comprising methoxy-poly(ethylene oxide) (MPEO) and ε-caprolactone (CL) segments (MPEO-CL) and analogous block copolymers end-functionalized with linoleic acid (LA), (MPEO-CL-LA) have been prepared previously. These materials are non-toxic and have proven their effectiveness in stabilizing PMMA and P(MMA/BA) latex particles during emulsion polymerization [7]. It can be expected that by using the same compounds for the stabilization of the binder emulsion and dispersion of the pigment, competitive adsorption in the latex is minimized and more stable paint formulations are obtained.

To assess the potential of these block copolymers as pigment dispersants, these polymeric surfactants were employed in the preparation of pigment pastes. Titanium oxide (TiO_2) was used as model pigment, as it is widely used in waterborne paint systems. The pigment paste- and latex viscosity, and the gloss and water adsorption of cast latex films were investigated to examine the effectiveness of these block copolymers as a pigment dispersant. Two different commercially available pigment dispersants (Surfynol 104E (a non-ionic acetylenic diol) and Disperbyk 190 (a block copolymer with pigment-affinic groups)) were used as a reference. The compatibility of the polymeric pigment dispersants with binders in waterborne systems was investigated using three different commercially available acrylic emulsions.

EXPERIMENTAL

Materials

Latices: Neocryl XK-90 (an acrylic copolymer emulsion), Neocryl XK-98 (a self-crosslinking acrylic copolymer emulsion and Neocryl XK-188 (a styrene-acrylic copolymer emulsion) latices were received from DSM NeoResins, The Netherlands.

Additives: N,N'-dimethyl ethanol amine (AMP 90, BASF AG, Germany) was used to adjust the pH of the solutions. Dehydran 1293 (Cognis, France) was used as an antifoaming agent. Borchi Gel L75N (Borchers GmBH, Germany) was used as a thickening agent, and Drew S4386 (Ashland, The Netherlands) was used as a defoamer. Propylene glycol (PG), ethylene diglycol (EDG) and butylene diglycol (BDG) (Dow, The Netherlands) were used as coalescing aids.

Pigment and pigment dispersants: Titanium dioxide (Kronos 2190, Kronos Titan Inc., Dallas) was used as a pigment. Surfynol 104E (a non-ionic acetylenic diol from Air Products), Disperbyk 190 (a block copolymer with pigment-affinic groups from BYK Chemie GmbH, Germany) and NeoCryl BT-24 (an acrylic oligomer from DSM NeoResins, The Netherlands) were used as pigment dispersants.

All commercially available chemicals employed in pigment pastes and latex preparations were used as purchased. In several cases, details of the chemical composition of the materials are not available due to commercial interests.

MPEO-CL and MPEO-CL-LA block copolymeric dispersants were prepared by ring opening polymerization of CL using stannous octoate as a catalyst and MPEG as an initiator at 140 °C for 4 hrs. The block copolymers were purified by dissolution and precipitation. Subsequently, functionalization with linoleic acid was carried out by esterification in xylene at 180 °C for 4 hrs. Figure 1 gives an overview of the reactions involved, a more detailed description of the polymerization procedures is reported elsewhere [7].

The main characteristics of the MPEO-CL and MPEO-CL-LA block copolymers used in this study are listed in Table 1. The synthesized block copolymers are designated as $MPEO_{45}$-CL_6 and $MPEO_{45}$-CL_6-LA, referring to their composition as determined by NMR.

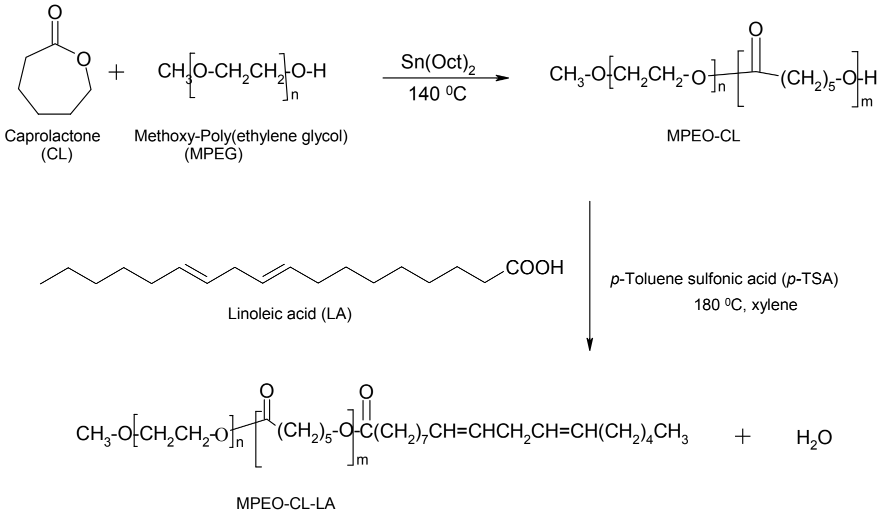

Figure 1: Synthesis of MPEO-CL and MPEO-CL-LA block copolymers by ring opening polymerization and subsequent esterification.

Table 1: Chemical composition and characteristics of non-functionalized MPEO-CL and linoleic acid end-functionalized MPEO-CL-LA block copolymers used in this study.

Surfactant	Composition (repeating units)			$\overline{M}_n$ calculated	$\overline{M}_n$ (H-NMR)	HLB
	EO	CL	LA			
MPEO$_{45}$-CL$_6$	45	6.0	-	2680	2690	14.9
MPEO$_{45}$-CL$_6$-LA	45	6.0	0.9	2940	2920	13.4

HLB= calculated hydrophilic to lipophilic balance.

For further use in the pigment and latex formulations, aqueous solutions (dispersions) of the MPEO$_{45}$-CL$_6$ and MPEO$_{45}$-CL$_6$-LA block copolymers were prepared by mixing with water. The concentration of the block copolymers was 18.1 wt%. The pH of the solutions (dispersions) was adjusted from 9.6 using minor amounts of AMP 90. The MPEO$_{45}$-CL$_6$ solution (dispersion) was milky, whereas the MPEO$_{45}$-CL$_6$-LA solution (dispersion) was transparent.

Preparation of Pigment Pastes

Table 2 shows the composition of the different aqueous pigment pastes prepared. The components were slowly added in the indicated order and thoroughly mixed using a Cowles mixer until a homogeneous solution was obtained. TiO$_2$ was then slowly added and dispersed into the mixture until the pigment particles in the pigment pastes were smaller than 10 μm. The fineness of the pigment paste was monitored and visualized by using a Hegmann grind gauge (according to ASTM D 1210-54).

Pigment pastes were prepared using MPEO$_{45}$-CL$_6$ and MPEO$_{45}$-CL$_6$-LA at different concentrations, as well as two commercially available pigment dispersants; Surfynol 104E (a non-ionic acetylenic pigment dispersant) and Disperbyk 190 (a polymeric pigment dispersant.

The viscosities of the pigment dispersions were measured using a Brookfield viscometer (Brookfield Digital Viscometer DV-I+) at 25 ± 0.2°C according to ISO 2555-89. The error in the viscosity measurements was less than 3 %. The pH of the pigment dispersions was measured at 25 ± 1°C using a pH meter (Schott) according to ISO 1148-80.

Table 2: Preparation of TiO_2 pigment pastes using (polymeric) dispersants. The compositions of pigment pastes prepared with commercial Surfynol 104E and Disperbyk 190 pigment dispersants are typical of those used in industry. $MPEO_{45}$-CL_6 and $MPEO_{45}$-CL_6-LA dispersants were employed at different concentrations.

	Pigment dispersant	Surfynol 104E	Disperbyk 190	$MPEO_{45}$-CL_6		$MPEO_{45}$-CL_6-LA	
	Ingredient	(Parts by weight)	(Parts by weight)	(Parts by weight)	(Parts by weight)	(Parts by weight)	(Parts by weight)
1	PG	2.2	2.1	2.2	2.3	2.2	2.3
2	Water	3.0	4.4	2.3	3.2	2.3	3.2
3	AMP 90	0.2	-	0.2	-	0.2	-
4	Dehydran 1293	0.5	0.4	0.5	0.4	0.5	0.4
5	Surfynol 104E	0.4	-	-	-	-	-
6	Dysperbyk 190	-	1.4	-	-	-	-
7	$MPEO_{45}$-CL_6 solution[a]	-	-	1.0	3.0	-	-
8	$MPEO_{45}$-CL_6-LA solution[a]	-	-	-	-	1.0	3.0
9	NeoCryl BT-24	2.8	-	2.8	-	2.8	-
10	Kronos 2190	21.7	19.7	21.7	21.1	21.7	21.1
	Total	30.0	30.0	30.0	30.0	30.0	30.0
	Viscosity at 6 rpm (mPa.s)	6500	300	25000	68000	25000	38700
	Viscosity at 60 rpm (mPa.s)	4500	140	5640	>10000	5120	5100
	pH	9.0	7.3	9.1	9.2	9.0	8.4

[a] $MPEO_{45}$-CL_6 and $MPEO_{45}$-CL_6-LA block copolymer pigment dispersants were introduced as 18.1 wt% solutions in water.

Pigmented waterborne latices

In the preparation of pigmented waterborne latices using the previously described pigment pastes, three different commercially available waterborne acrylic binder systems were selected: Neocryl XK-90 is an acrylic copolymer emulsion, with a solids content of 45 % by weight and an MFFT of below 0 ^{o}C. Neocryl XK-98 is a self-cross-linking acrylic copolymer emulsion, with a solids content of 44 % by weight and an MFFT of 7 ^{o}C. Neocryl XK-188 is a styrene-acrylic copolymer emulsion with a solids content of 44.5 % by weight and an MFFT of 6 ^{o}C. For commercial reasons, the precise composition and characteristics of the binders could not be disclosed.

The composition of the waterborne binder formulations as employed in pigmentation experiments is given in Table 3.

Table 3: Formulation of waterborne NeoCryl XK-90, NeoCryl XK-98 and NeoCryl XK-188 latices.

	Binder Ingredient	NeoCryl XK-90 (Parts by weight)	NeoCryl XK-98 (Parts by weight)	NeoCryl XK-188 (Parts by weight)
1	Binder	60.8 (27.4)	64.0 (28.2)	62.2 (27.7)
2	Water	4.9	3.2	-
3	EDG	3.0	-	6.8
4	BDG	-	1.6	-
5	Dehydran 1293	0.2	0.8	-
6	Drew S4386	-	-	0.5
7	Borchi Gel L75N:Water 1:1	1.2	0.7	0.5
	Total	70.0	70.0	70.0

The pigment pastes (30 parts by weight) were slowly added to the binder formulations (70 parts by weight) under continuous agitation. Homogeneous mixing was ensured by controlling the rate of pigment addition and stirring speed. The final pigment volume concentrations in the NeoCryl XK-90, NeoCryl XK-98 and NeoCryl XK-188 were 41.9 %, 42.8 % and 43.3 % respectively.

Preparation and characterization of pigmented waterborne latex films

Films of the pigmented waterborne latices were prepared by casting the latices on glass and drying at ambient conditions. The glossiness of the films was evaluated by measuring the gloss with a haze-gloss meter (BYK-Gardner 4601) at 20 °, 60 ° and 85 ° incident angle (according to DIN-67530), measurements were carried out in triplicate. Table 4 classifies the gloss levels at 20 °, 60 ° and 85 °.

Table 4. Classification of glossiness levels of paint films (polished glass = 100%).

Type of paint	20 ° gloss	60 ° gloss	85 ° gloss
Flat	-	0 - 10	0 - 15
Semi-glossy	5 - 45	25 - 75	-
Glossy	20 - 90	70 - 95+	-

To determine the water absorption of the pigmented latex films, 80 µm thick films measuring 100 x 100 mm were prepared. The films were immersed in deionized water for 24 hrs at room temperature. The films were then wiped to remove excess water present on the surface. The water absorption was calculated from:

Water absorption = $((W_1 - W_0)/ W_0) \times 100$ %

In which W_0 is the dry weight of the film and W_1 is the weight of the film after equilibration in water. All measurements were performed in duplicate.

RESULTS AND DISCUSSION

Preparation of pigmented latices

A pigment dispersant is an important additive in waterborne coatings [3]. The block copolymers, based on methoxy-poly(ethylene oxide) (MPEO), ε-caprolactone (CL) and end functionalized with linoleic acid (LA) described in Table 1, were evaluated as dispersants in TiO_2 pigment pastes. (The block copolymers were introduced as a 18.1 wt% solution/dispersion in water). To compare the behaviour of these block copolymers as pigment dispersants, two commercially available (polymeric) pigment dispersants, Disperbyk 190 and Surfynol 104E were evaluated as well.

In the preparation of TiO_2 pigment pastes (see Table 1), Disperbyk 190 is typically used at a higher concentration than Surfynol 104E. Therefore, pigment paste formulations with MPEO-CL and MPEO-CL-LA containing different amounts of block copolymer dispersant were prepared. For the comparison with the behaviour of Surfynol 104E, the pH was adjusted as well.

In all cases fine pigment pastes could be prepared, in which the fineness of the pigment was below 10 µm. From the table it follows that, especially at low shear rates, the viscosities of the pigment pastes prepared with MPEO-CL and MPEO-CL-LA dispersants increased with concentration, and that these were higher than of pastes prepared with the commercially available dispersants. When the speed at which the viscosity is measured was increased from 6 to 60 rpm, the viscosities of all pigment pastes prepared decreased somewhat. This implies shear thinning, which is desirable in paints formulations. Interestingly, it could be observed that upon standing the viscosities of the pigment pastes increased. This implies thixotropic behaviour of the pastes as well. At these shear rates, the viscosities of the pastes prepared with MPEO-CL and MPEO-CL-LA dispersants were comparable to those of pastes prepared with Surfynol 104E.

Different pigmented latices were prepared by slowly adding the pigment pastes (30 parts by weight) to the binder formulations (70 parts by weight) under continuous agitation. Table 3 gives an overview of the formulations of the different binders used. Homogeneous mixing was ensured by controlling the rate of pigment paste addition and stirring speed. In all cases stable, non-flocculating latices were obtained. Substituting the commercially available Surfynol 104E or Disperbyk 190 pigment dispersants with the MPEO-CL and MPEO-CL-LA block copolymers in the waterborne paint formulations did not negatively affect the paint properties (pigment paste stability, rheological behaviour and gloss)

Viscosities of the pigmented latices were measured and the results are summarized in Table 5. In all cases a slight decrease in viscosity was observed with respect to commercial systems. Nevertheless, all pigmented latices exhibited shear thinning and thixotropic behavior. (It was observed that upon standing, the viscosities of the pigment pastes increased significantly.) This behavior of the latex is an important characteristic regarding the storage, handling and final application of waterborne paints.

Table 5: Viscosities of pigmented waterborne latices. The pigment pastes were prepared with different pigment dispersants and added to the latex at a 30 to 70 pigment paste to latex ratio.

Latex [a]	**Pigment paste** [b]	**Viscosity (mPa.s)**	
		6 rpm	60 rpm
NeoCryl XK-90	Surfynol 104E	3400	2670
	Disperbyk 190	8200	6230
	MPEO-CL 1.0	2200	1840
	MPEO-CL-LA 1.0	2100	1790
	MPEO-CL 3.0	3600	3010
	MPEO-CL-LA 3.0	3700	2970
NeoCryl XK-98	Surfynol 104E	1600	1460
	Disperbyk 190	2000	1600
	MPEO-CL 1.0	1100	980
	MPEO-CL-LA 1.0	1000	920
	MPEO-CL 3.0	1600	1440
	MPEO-CL-LA 3.0	1600	1460
NeoCryl XK-188	Surfynol 104E	4400	3240
	Disperbyk 190	19000	9820
	MPEO-CL 1.0	4200	3300
	MPEO-CL-LA 1.0	3800	2740
	MPEO-CL 3.0	8600	5410
	MPEO-CL-LA 3.0	6800	4450

[a] The latex formulations are presented in Table 3

[b] The pigment paste formulations are presented in Table 2, here the paste is identified by the pigment dispersant used and the amount of its solution in the paste. (For example: an MPEO-CL-LA 3.0 pigment paste is a pigment paste prepared using 3.0 parts of an 18 wt% solution of MPEO-CL-LA in water)

Pigmented latex films

In the application of paint, it is important that the pigment is well dispersed in the latex and in the dry film as well. To minimize surface irregularities, agglomeration of the pigment during drying needs to be prevented. If the pigment is not adequately wetted in the pigment paste, it can be expected that agglomerates will form at the surface of the paint film reducing the glossiness of the film [3, 8, 9]. Pigment aggregation may also depend on the type of binder used in the latex. To avoid flocculation during the film formation process, and achieve highest gloss levels, the pigment dispersant used should be compatible with the binder. Gloss level measurements of dried latex films are a good indication for the effectiveness of a pigment dispersant in wetting and stabilizing pigment particles in a certain latex.

Pigmented latex films were prepared by casting the latex formulations and drying at ambient conditions as described, see Tables 3 and 5. The amount of TiO_2 in the films was approximately 20 wt%. Different commercially available binders and latexes (NeoCryl XK-90, NeoCryl XK98 and NeoCryl XK 188) were used tot prepare the pigmented latices. Glossiness tests were carried out on the pigmented films after thorough drying.

As pigment pastes prepared with Disperbyk 190 contain higher amounts of dispersant than those prepared with Surfynol 104E (Table 1), the properties of films prepared using Disperbyk 190 should be compared with those of films prepared with the higher amounts of MPEO-CL and MPEO-CL-LA in the pigment paste. Properties of films prepared using the lower amounts of MPEO-CL and MPEO-CL-LA should be compared with Surfynol 104E containing films.

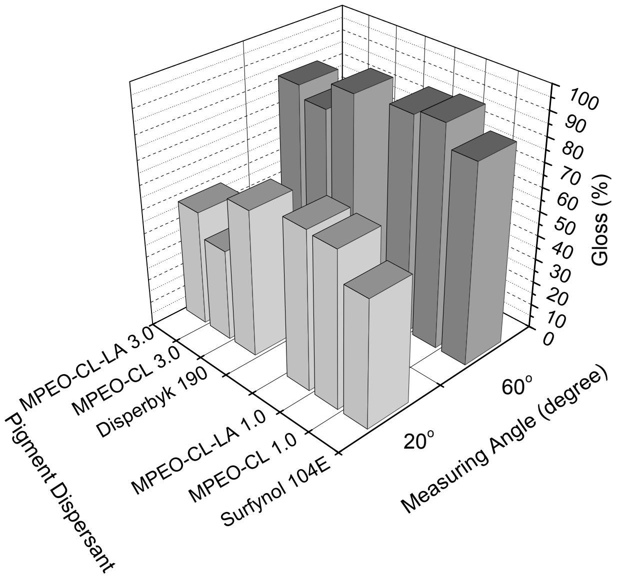

Figure 2. Gloss of pigmented NeoCryl XK-90 latex films. The pigment pastes used in pigmenting the latex were prepared with different pigment dispersants (see Tables 2, 3 and 5). The TiO$_2$ pigment content was approximately 20 wt%.

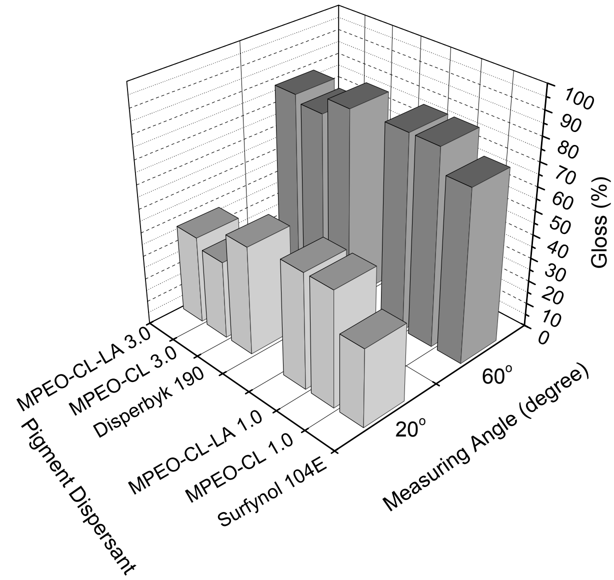

Figure 3. Gloss of pigmented NeoCryl XK-98 latex films. The pigment pastes used in pigmenting the latex were prepared with different pigment dispersants (see Tables 2, 3 and 5). The TiO$_2$ pigment content was approximately 20 wt%.

Figures 2 and 3 show the gloss at different angles of pigmented films, respectively prepared with a NeoCryl XK-90 or a NeoCryl XK-98 latex. It can be seen that in these latex films, the pigment dispersant used in the pigment paste and the concentration at which it is used have an effect on the glossiness of the dried films. When compared to NeoCryl XK-90 and NeoCryl XK-98 latex films formulated with Surfynol 104E, the MPEO-CL 1.0 and MPEO-CL-LA 1.0 (pigment paste prepared using 1.0 part of an 18 wt% solution) containing films yielded higher gloss at 20 ° and 60 °. In these latices Disperbyk 190 films also yielded a high gloss. Latex films formulated with MPEO-CL 3.0 and MPEO-CL-LA 3.0 (pigment paste prepared using 3.0 parts of an 18 wt% solution) gave lower gloss than Disperbyk 190 films. Nevertheless, at 60 ° their gloss levels were above 70 %, allowing them to still be classified as relatively glossy films (Table 5). At both concentrations MPEO-CL-LA seemed to perform better than MPEO-CL giving slightly glossier films.

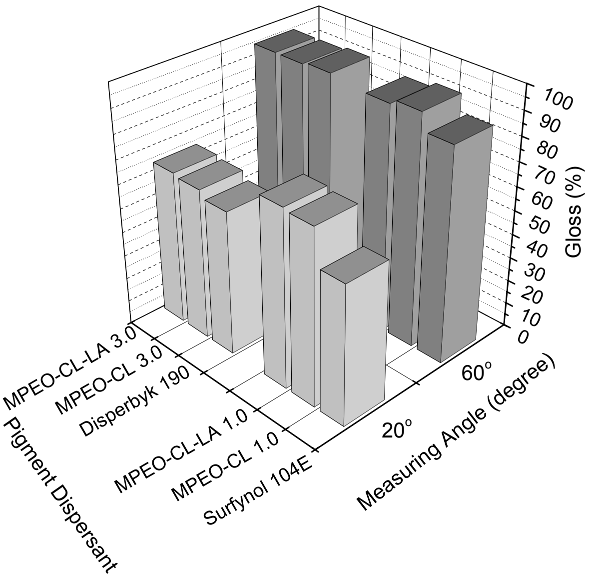

Figure 4. Gloss of pigmented NeoCryl XK-188 latex films. The pigment pastes used in pigmenting the latex were prepared with different pigment dispersants (see Tables 2, 3 and 5). The TiO_2 pigment content was approximately 20 wt%.

Using NeoCryl XK-188 binder formulations, the gloss levels of pigmented films was even higher, see Figure 4. At 20 ^{o}, the gloss levels of the films prepared with the MPEO-CL 1.0 and MPEO-CL-LA 1.0 pigment formulation and the MPEO-CL 3.0 and MPEO-CL-LA 3.0 were 73 % and 74 % and 63 % and 64 %, respectively. These values were higher than gloss values reached with Disperbyk 190 and Surfynol 104E pigment dispersants. At a measuring angle of 60 ^{o}, the gloss levels of films prepared with the MPEO-CL 1.0 and MPEO-CL-LA 1.0 pigment formulation and the MPEO-CL 3.0 and MPEO-CL-LA 3.0 were again higher than those reached with Disperbyk 190 and Surfynol 104E. Relative glossiness values were respectively 95 % and 95 % and 94 % and 96 %.

When used as pigment dispersants, both block copolymers led to latex films with high levels of gloss. This implies that MPEO-CL and MPEO-CL-LA block copolymers can prevent flocculation of the pigment particles during film formation [3] and therefore are capable of adequately stabilizing the TiO_2 pigment particles.

Water resistance of pigmented films can also give an indication of the distribution of pigment particles in a latex film. When pigment particles agglomerate, the distribution of the particles becomes less homogeneous and the diffusion and permeability of water through the film is enhanced. The water absorption of the different latex films prepared using different pigment dispersants is presented in Figure 5.

The results show that when compared to films in which the pigment paste was prepared with Surfynol 104E, the water uptake of latex films prepared with the MPEO-CL 1.0 and MPEO-CL-LA 1.0 pigment formulation was lower. This was the case for all latex formulations. At higher pigment dispersant concentrations, the films prepared with MPEO-CL 3.0 and MPEO-CL-LA 3.0 showed significantly higher water uptake. When comparing with Disperbyk 190 formulations, MPEO-CL 3.0 and MPEO-CL-LA 3.0 containing films only showed a higher water uptake than Disperbyk 190 films when NeoCryl XK-98 was used as a binder. As can be seen from the figure, the binder itself has a significant effect on water uptake of the film as well.

In general, these results show that MPEO-CL and MPEO-CL-LA can be effectively used to prepare glossy pigmented latex films with limited water uptake. It seems that MPEO-CL-LA gives slightly less water sensitive films than MPEO-CL containing films.

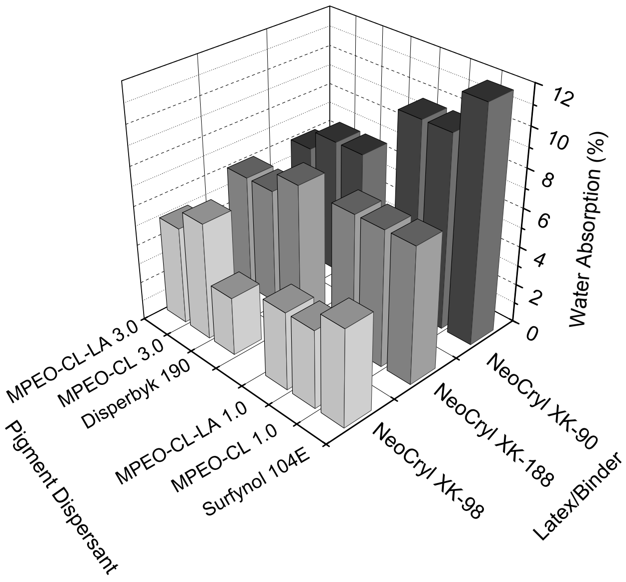

Figure 5. Water absorption of pigmented latex films prepared using different latex binder formulations. The pigment pastes used in pigmenting the latex were prepared with different pigment dispersants (see Tables 2, 3 and 5). The TiO_2 pigment content was approximately 20 wt%.

CONCLUSION

Block copolymeric dispersants based on MPEO, CL and LA can effectively be used to prepare TiO_2 pastes. These pastes can then be formulated with waterborne acrylic latices and used to prepare pigmented latex films. Glossy films containing approximately 20 wt% pigment could readily be prepared. In terms of glossiness and water uptake, these films compare favourably with films prepared using commercially available Disperbyk 190 and Surfynol 104E pigment dispersants. MPEO-CL-LA block copolymer formulations give slightly more glossy films with less water uptake than MPEO-CL containing films.

As these compounds can also be used as a surfactant in the latex preparation, see Chapters 3 to 6 of this thesis, it is to be expected that by using these multifunctional block copolymers competitive adsorption between emulsifier and pigment dispersant in a pigmented latex formulation is minimized. First experiments are described in Appendix B of this thesis.

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APPENDIX A

The Influence of Linoleic Acid-functionalized PEO-PCL Block Copolymers on the Rheological Behavior of P(MMA/BA) Latices

SUMMARY

A diblock copolymer consisting of methoxy-poly(ethylene oxide) (MPEO) and a poly(ε-caprolactone) block (PCL) end-capped with linoleic acid (LA) was used as a surfactant to prepare stable poly(methyl methacrylate) (PMMA) latices at 30 wt% solids contents. Surprisingly, shear thinning behavior of these PMMA latices was observed when the surfactant to monomer weight ratio (S/M) was 15 to 85 or 20 to 80. Shear thinning behavior is important in waterborne paints. In this study, the potential of $MPEO_{45}$-$CL_{6.5}$-LA as a rheological modifier was investigated. Using $MPEO_{45}$-$CL_{6.5}$-LA as surfactant, poly(methyl methacrylate/n-butyl acrylate) P(MMA/BA) latices at 30 wt% solids content were prepared, S/M was 10/90. In 33 ml water 1.63 g of surfactant were used to emulsify 14.6 g of the monomer mixture. The resulting average latex particle diameter and the particle size distribution obtained were 140 nm and 0.05 respectively. Then different amounts of the $MPEO_{45}$-$CL_{6.5}$-LA surfactant were added to 6 ml of this latex. The rheological behavior of these latices was studied by performing steady shear experiments. A latex to which an additional amount of surfactant was added (0.11 g in 6 ml of the P(MMA/BA) latex) exhibited thixotropic behavior. Other compositions were not as effective and only Newtonian behavior of the latex at a slightly increased viscosity was observed. These results show that besides acting as an emulsifier, the PEO-PCL block copolymer could act as a rheological modifier in waterborne paints as well.

INTRODUCTION

The reduction of the emission of volatile organic compounds (VOC) from paints remains an important issue. Nowadays, waterborne coatings, radiation cured coatings, powder coatings, and high solids coatings are available alternatives to solventborne paints. These coating systems significantly reduce the emission of organic solvents. Waterborne coatings turn out to be the most widely used systems due to their non-flammability and their ease of preparation and application.

Waterborne acrylic latices, which are generally used in formulating waterborne coating systems, are prepared by emulsion polymerization. A commercially attractive waterborne acrylic paint needs to have a high viscosity at low shear rates to avoid settling and sagging. On the other hand, however, the paint needs to have a low viscosity at relatively high shear rates present during application [1, 2]. Usually, waterborne latices do not sufficiently exhibit this rheological behavior. To impart the desired rheology to waterborne coatings, rheological modifiers, such as associative thickeners, are usually added to influence viscosity and at the same time improve vertical flow and leveling, film thickness, spattering tendency, brush and roll resistance, sedimentation tendency, pigment stabilization, hiding power and gloss development, [1-4]. In general, such compounds are low molecular weight amphiphilic linear or graft block copolymers. However, when using such modifiers in latex paint formulations, the interactions between the rheological modifier and other components of the paint like emulsifiers, pigment dispersants, latex- and pigment particles lead to competitive adsorption processes that can destabilize the latex [2-7].

A possible solution to prevent competitive adsorption is to use a single compound that simultaneously acts as an emulsifier, a rheological modifier and a pigment dispersant. To our knowledge, no studies have been reported on such multifunctional additives in literature. In previous studies, we synthesized block copolymers based on poly(ethylene oxide), ε-caprolactone and end-capped with linoleic acid and used them as emulsifiers in acrylic latices [9, 10] and as pigment dispersants [11]. Surprisingly, when preparing the latices at 30 % solids contents, it was observed that certain compositions of the latices were highly viscous. In this preliminary study, we assessed the potential of this block copolymer as a rheological modifier in P(MMA/BA) latices.

EXPERIMENTAL

Materials

Methoxy-poly(ethylene glycol) (MPEG) with a molecular weight of 2000 g/mol, monohydrated *para*-toluene sulfonic acid (*p*-TSA) and xylene (mixture of isomers) were obtained from Fluka, Switzerland. ε-Caprolactone (CL) was purchased from Aldrich, United Kingdom, linoleic acid (LA) from Acros-Organic, USA and stannous (II) octoate (SnOct) from Aldrich, USA and used as received. Deionized water (Milipore Q, 18.2 MΩcm) was used throughout the study.

Methyl methacrylate (MMA, stabilized with hydroquinone) and n-butyl acrylate (BA, stabilized with hydroquinone) were obtained from Fluka, Switzerland. MMA and BA monomers were repeatedly washed with a 4 % aqueous solution of sodium hydroxide (NaOH) to remove the hydroquinone and then washed with deionized water. The monomer was stored at + 4^{o}C.

As a redox radical initiating system for the MMA and BA emulsion copolymerizations, aqueous solutions of *tert*-butyl hydroperoxide (tBHPO, 70 % aqueous solution, Merck, Germany), iso-ascorbic acid (iAA, Sigma, Germany) and ethylenediaminetetraacetic acid ferric-sodium salt (FeEDTA, Sigma, Germany) were prepared and sequentially added to the MMA/BA emulsion.

Synthesis and characterization of MPEO-CL and MPEO-CL-LA block copolymers

Block copolymers based on MPEG and CL and end-capped with LA were prepared by ring-opening polymerization of *ε*-caprolactone using MPEG as a macroinitiator. Subsequently esterification with linoleic acid was carried out. Details of the experimental procedures are given elsewhere [8].

The non-functionalized diblock copolymers and the LA-functionalized block copolymers are abbreviated as $MPEO_{45}$-CL_{n} and $MPEO_{45}$-CL_{n}-LA, respectively. Here, MPEO refers to the methoxy-poly(ethylene oxide) block and the subscript n to the number of CL repeating units present. After purification by precipitation of solutions in chloroform into cold hexane, the average composition of the obtained block copolymers was determined by proton nuclear magnetic resonance (^{1}H-NMR) using a 300 MHz NMR spectrometer (Varian Inova). As $\overline{M}_n$ of the starting MPEG is known, the CL block length and the average molecular weight of the block copolymers can readily be determined. It should be realized, that the surfactant prepared in this study is a mixture of polymers of varying composition and molecular weight. A more detailed analysis on the characteristics of the surfactant is given in Chapter 5 of this thesis.

Table 1: Chemical composition of $MPEO_{45}$-$CL_{6.5}$ *before and after functionalization with linoleic acid*

Surfactant Type	Composition (repeating units)			$\overline{M}_n$ (expected)	$\overline{M}_n$[a] (^{1}H-NMR)	HLB[b]
	EO	CL	LA			
$MPEO_{45}$-$CL_{6.5}$	45	6.4	-	2730	2730	14.7
$MPEO_{45}$-$CL_{6.5}$-LA	45	6.4	0.9	2990	2960	13.5

[a] *based on molecular weights derived from* ^{1}*H-NMR*
[b] *hydrophilic to lipophilic balance (calculation based on the Griffin definition)* [12]

Emulsion copolymerizations of MMA and BA

Table 2: Recipe of MMA/BA emulsion copolymerizations at 60 °C for 4 hrs at a surfactant to monomer ratio (S/M) of 10/90.

Component	Amount (g)	% (of total weight)
Water	33.11	61.22
$MPEO_{45}$-$CL_{6.5}$-LA surfactant	1.63	3.01
MMA monomer	7.30	13.50
BA monomer	7.30	13.50
TBHPO (30 w/w% aqueous solution)	0.65	1.20
iAA (5 w/w% aqueous solution)	3.89	7.20
FeEDTA (1 w/w% aqueous solution)	0.20	0.37
Total	54.08	100.00

Poly(methyl methacrylate/n-butyl acrylate) (P(MMA/BA)) latices were prepared by emulsion copolymerization of MMA and BA using a redox initiating system and $MPEO_{45}$-$CL_{6.5}$-LA copolymer as a surfactant. MMA (7.3 g) and BA (7.3 g) were copolymerized in 33.1 ml water, the redox initiating system consisted of 0.64 g of a 30 w/w% tBHPO aqueous solution, 3.88 g of a 5 w/w% iAA aqueous solution and 0.20 g of a 1 w/w% FeEDTA aqueous solution, as shown in Table 2. The polymerizations were conducted using a surfactant to monomer weight ratio (S/M) of 10/90. The employed reaction conditions were: total solids content approximately 30 wt%, T = 60 °C, polymerization time = 4 hrs. Further details are given elsewhere [9].

After polymerization the solids content, monomer conversion and average particle size of the latex were determined.

Characterization of P(MMA/BA) latices

The solids content of the latices was determined gravimetrically by evaporating the volatile components (water, MMA and BA) in an oven at 70 °C for 24 hrs. By taking into account the mass of initiator and surfactant used, the conversion of the monomers was determined. The relative error in the values of the solids content and monomer conversion, as derived from triplicate measurements, was approximately 2 %.

The average size and size distribution of the latex particles was determined by dynamic light scattering (DLS) (Zetasizer 4000, Malvern Instruments Ltd., Malvern, UK) at 25 °C at an angle of 90 ° (633 nm), taking the average of five measurements.

The rheological properties of the $MPEO_{45}$-$CL_{6.5}$-LA surfactant in solution, of the P(MMA/BA) latex (as prepared in emulsion copolymerization at an S/M ratio of 10/90) and of the P(MMA/BA) latex upon further addition of $MPEO_{45}$-$CL_{6.5}$-LA surfactant at different concentrations were evaluated in steady shear experiments. Using a rheometer (UDS200, Anton Paar) equipped with a 25 mm diameter plate-and-plate sample holder, the shear rate was varied from low to high values ((0-1000 s^{-1}) and the viscosity and shear stress were determined. All experiments were performed at 25 °C. In experiments where additional surfactant was added to the latex, the mixtures were stirred at room temperature for 24 hrs before carrying out the rheological measurements.

RESULTS AND DISCUSSION

In first experiments, we observed that PMMA latices prepared using $MPEO_{45}$-$CL_{6.5}$-LA at 30 wt% solids contents, had thixotropic properties. These emulsions were prepared as described previously [9]. When the surfactant to monomer ratio (S/M) in the emulsion polymerization was 15/85 or 20/80, shear-thinning behavior occurred. This is a highly desired property in waterborne paints. Based on these findings we set out to investigate the use of this block copolymer as a rheological modifier in our waterborne P(MMA/BA) coating systems.

Therefore, in this study, a P(MMA/BA) latex was prepared using $MPEO_{45}$-$CL_{6.5}$-LA surfactant at a surfactant to monomer ratio (S/M) of 10/90, as previously reported [10]. MMA (7.3 g) and BA (7.3 g) were copolymerized in approximately 33 ml water using 1.63 g of surfactant, which corresponds to a solids content of 30.7 wt%. A stable latex with average particle diameter and particle size distribution of respectively 140 nm and 0.05 was obtained, and monomer conversion was complete.

To investigate a possible effect on rheology, different amounts of $MPEO_{45}$-$CL_{6.5}$-LA surfactant (0.11 g, 0.22 g, 0.36 g or 0.51 g) were added to 6 ml of the latex (this volume contains 1.62 g P(MMA/BA) and 0.18 g $MPEO_{45}$-$CL_{6.5}$-LA surfactant) as shown in Table 3. After equilibration at room temperature for 24 hrs, particle size and size distribution were measured. A small increase in the average latex particle size and particle sized distribution was observed. The increase in the average particle size is likely due to the adsorption of an additional amount of surfactant molecules to the particle surface. (In previous work, we estimated that the surface coverage of the prepared latex was approximately only 30 % [9].

Table 3: The effect of addition of $MPEO_{45}$-$CL_{6.5}$-LA on particle size and particle size distribution of a P(MMA/BA) latex prepared by emulsion copolymerization at S/M = 10/90 using $MPEO_{45}$-$CL_{6.5}$-LA as a surfactant. A latex quantity of 6 ml initially contained 14.6 g of MMA/BA and 1.63 g of surfactant

	amount of surfactant added to 6ml of latex (g)	total amount of surfactant present in 6ml of latex (g)	Average particle size (nm)	PDI
A	0	0.18	140	0.05
B	0.11	0.29	150	0.09
C	0.22	0.40	150	0.06
D	0.36	0.54	150	0.06
E	0.51	0.69	150	0.06

Of these latices, typical plots of the viscosity and shear stress versus the applied shear rate are shown in Figure 1. All latices showed an increase in the viscosity and the shear stress upon addition of extra surfactant. With the exception of composition B, the latex compositions showed that the viscosity is independent of shear rate and that shear stresses increased linearly with increasing shear rate. This behavior is typical of a Newtonian liquid.

Latex composition B, on the other hand, showed a pronounced shear thinning behavior; at very low shear rates the viscosity was very high, and decreased significantly with increasing shear rates. This behavior implies thixotropic behavior of latex B. Apparently, at this surfactant concentration, a physical network is formed in which the latex particles are bridged. The mechanism through which this occurs is not clear, although it can be expected that aggregations involving hydrophobic PCL sequences present in the heterogeneous surfactant composition play a role. The decrease in viscosity with increasing shear rates is due to disruption of these network junctions; the rate of junction disruption exceeds the rate at which hydrophobic associations can be re-formed [13-16].

In waterborne coatings, high viscosity in the medium shear rate region (10 - 200 s^{-1}) is required for storage stability and low viscosity in the high shear rate region (10^3 - 10^5 s^{-1}) is desired to give good application properties [4].

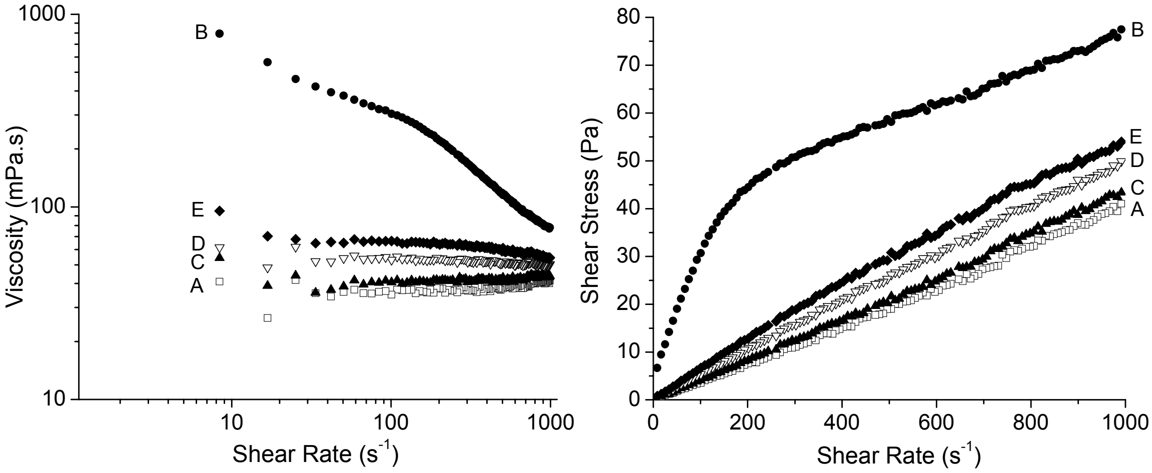

Figure 1. Plots of viscosity (left) and shear stress (right) as a function of the applied shear rate of P(MMA/BA) latex to which additional surfactant is added. Latex compositions are as given in Table 3.

The viscosities of the P(MMA/BA) latex at different shear rates upon further addition of different amounts of surfactant are plotted in Figure 2. With an increase of the amount of surfactant, the viscosities increase. At all shear rates, the viscosity of composition B was the highest. As the shear rate increases from 10 to 1000 s^{-1}, the viscosities decrease, which is typical of shear thinning.

In our case, our surfactants are a mixture of block copolymers with different compositions. Hypothetically, generally, more hydrophobic block copolymers will act as a rheological modifier which will help in viscosity build up while more hydrophilic block copolymers will act as a surfactant. As the concentration of block copolymer used in system increased, similar effect as shown in schematic could occur

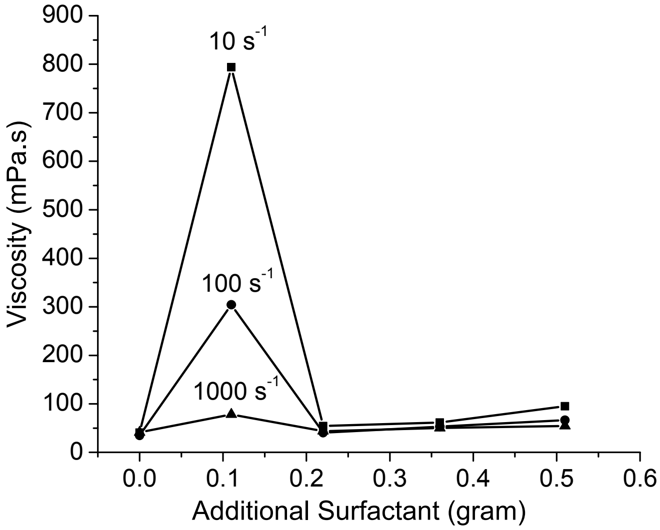

Figure 2. Viscosities at different shear rates of the P(MMA/BA) latices upon addition of $MPEO_{45}$-$CL_{6.5}$-LA *surfactant.*

To investigate the role of the $MPEO_{45}$-$CL_{6.5}$-LA surfactant itself, aqueous solutions were prepared at a concentration that corresponds to the amount of surfactant used in the emulsion polymerization of the initial latex, (0.18 g in 6 ml water), and one which corresponds to the final surfactant content in latex composition B, (0.29 g in 6 ml of water).

When analyzing the rheological properties of both surfactant solutions in water, the viscosity was higher than that of water, but only Newtonian behavior was observed for both solutions. Their viscosities were comparable with a value of approximately 40 mPa.s. Apparently, thixotropic behavior is only displayed in the presence of latex particles.

CONCLUSIONS

From the results obtained in this rheology study, it can be concluded that adding additional $MPEO_{45}$-$CL_{6.5}$-LA block copolymer surfactant to a P(MMA/BA) latex can result in thixotropic behavior of the latex. Therefore, this surfactant could also be used as a rheological modifier in formulating waterborne acrylic paints.

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APPENDIX B

MPEO-CL and MPEO-CL-LA Block Copolymers in Waterborne Paint Formulations. A Preliminary Study

SUMMARY

This appendix describes the use of MPEO-CL based block copolymers as multifunctional surfactants in waterborne acrylic coating systems. Their use as emulsifier, pigment dispersant and rheological modifier is described. First, a linoleic acid (LA) functionalized block copolymer MPEO-CL-LA was used as emulsifier in the preparation of poly(methyl methacrylate/n-butyl acrylate), P(MMA/BA) latices. Stable latices with a solids content and particle size of respectively 30 wt% and 140 nm could readily be prepared. Then TiO_2 pigment pastes were prepared using MPEO-CL or MPEO-CL-LA block copolymers. As references, NeoCryl XK-90 and a Disperbyk 190 pigment dispersant were used. A number of pigment latex formulations were prepared by thoroughly mixing the latex and pigment dispersions. Relevant properties of the waterborne paint formulations (viscosity) and of the cast films (gloss, water adsorption and appearance) were measured. All paint formulations were stable, and showed shear thinning behavior. In terms of viscosity of the pigmented latices and gloss and water uptake of the cast films, the performance of MPEO-CL and MPEO-CL-LA block copolymers was comparable to or even better than that of Disperbyk 190 formulations. Especially in P(MMA/BA) latices MPEO-CL-LA block copolymers performed well. However, the appearance of films containing MPEO-CL based block copolymers cast on glass were moderate to poor. Upon drying, the P(MMA/BA) latices showed poor wetting and extensive cratering on the glass surface. It should be emphasized, however, that these paint formulations were not optimized and that there is much room for improvement.

INTRODUCTION

Waterborne coating systems consist of a polymer emulsion, pigment, extenders, additives (emulsifiers, pigments dispersants, associative thickeners, de-foaming agents, etc…) and water. To be able to formulate waterborne coating systems, emulsifiers, rheological modifiers and pigment dispersants are essential. Emulsifiers play an important role in nucleation and stabilization during the binder (latex) preparation. In addition, emulsifiers enhance application properties of the finished latex by reducing the surface tension of the system. Rheological modifiers are added to adjust the viscosity and rheological behavior of paint formulations. Pigment dispersants are necessary for cluster size reduction and stabilization of pigment particles. However, the co-existence of these three compounds can lead to competitive adsorption that can result in destabilization of the latex or waterborne paint [1-6].

To overcome these difficulties, a single multifunctional surfactant was prepared that can perform as an emulsifier during emulsion polymerization, as a pigment dispersant during preparation of the pigment paste and as a rheological modifier in the paint formulation. These surfactants are copolymers based on methoxy-poly(ethylene oxide) (MPEO) and ε-caprolactone (CL) which can be end-functionalized with linoleic acid (LA). In previous studies, we have shown the potential of these surfactants as emulsifiers [7], pigment dispersants [8] and rheological modifiers [9]. The promising results obtained in these studies led us to prepare a poly(methyl methacrylate/n-butyl acrylate) (P(MMA/BA)) waterborne coating system based on the use of a single MPEO-CL or MPEO-CL-LA surfactant. Commercially available Disperbyk 190 pigment dispersant and NeoCryl XK-90 latex were used as references. The rheological behavior and viscosity of the pigment pastes and latices were evaluated. Also the water absorption and appearance of dried latex films was investigated.

EXPERIMENTAL

Materials

Methoxy-poly(ethylene glycol) (MPEG) with a molecular weight of 2000 g/mol, monohydrated *para*-toluene sulfonic acid (*p*-TSA) and xylene (mixture of isomers) were obtained from Fluka, Switzerland. ε-Caprolactone (CL) was purchased from Aldrich, United Kingdom, linoleic acid (LA) from Acros-Organic, USA and stannous (II) octoate

(SnOct) from Aldrich, USA and all the chemicals were used as received. Deionized water (Milipore Q, 18.2 MΩcm) was used throughout the study.

Methyl methacrylate (MMA, stabilized with hydroquinone) and n-butyl acrylate (BA, stabilized with hydroquinone) were obtained from Fluka, Switzerland. MMA and BA monomers were washed repeatedly with a 4 % aqueous solution of sodium hydroxide (NaOH), followed by a wash with deionized water, to remove the hydroquinone. The monomers were stored at + 4^{o}C before use.

As a redox initiating system, aqueous solutions of *tert*-butyl hydroperoxide (tBHPO, 70% aqueous solution, Merck, Germany), iso-ascorbic acid (iAA, Sigma, Germany) and ethylenediaminetetraacetic acid ferric-sodium salt (FeEDTA, Sigma, Germany) were prepared and sequentially added in the batch copolymerization of MMA and BA.

Titanium dioxide (Kronos 2190, Kronos Titan Inc., Dallas) was used as a pigment. Disperbyk 190 (a block copolymer with pigment-affinic groups from BYK Chemie GmbH, Germany) was used as pigment dispersants.

N,N'-dimethyl ethanol amine (AMP 90, BASF AG, Germany) and a 25 wt% ammonia solution were used as a base to adjust the pH. Dehydran 1293 (Cognis France) was used as an antifoaming agent. Borchi Gel L75N (Borchers GmBH, Germany) was used as a thickening agent.

Neocryl XK 90 (an acrylic copolymer emulsion with a solids content of 45 % and a minimal film formation temperature (MFFT) below 0 ^{o}C), was received from DSM NeoResins, The Netherlands. Propylene glycol (PG) (Dow, The Netherlands) was used as a coalescing aid.

All commercially available chemicals employed in pigment pastes and latex preparations were used as purchased. In several cases, details of the chemical composition of the materials are not available due to commercial interests.

Synthesis and characterization of MPEO-CL and MPEO-CL-LA block copolymers

MPEO-CL and MPEO-CL-LA block copolymeric dispersants were prepared by ring opening polymerization of CL using stannous octoate as a catalyst and MPEG as an initiator at 140 °C for 4 hrs. The block copolymers were purified by solution and precipitation. Subsequently, functionalization with linoleic acid was carried out by esterification in xylene at 180 °C for 4 hrs. A more detailed description of the polymerization procedures is reported elsewhere [7]. The main characteristics of the MPEO-CL and MPEO-CL-LA block copolymers used in this study are listed in Table 1.

Table 1: Chemical composition and characteristics of non-functionalized MPEO-CL and linoleic acid functionalized MPEO-CL-LA block copolymers used in this study

Surfactant	Composition (repeating units)			$\overline{M}_n$ calculated	$\overline{M}_n$ (H-NMR)	HLB[a]
	EO	CL	LA			
$MPEO_{45}$-CL_6	45	6.0	-	2680	2680	14.9
$MPEO_{45}$-CL_6-LA	45	6.0	0.8	2960	2910	13.8

[a] Hydrophilic to lipophilic balance (HLB) calculated according to the Griffin definition.

Emulsion copolymerizations of MMA and BA

Poly(methyl methacrylate/n-butyl acrylate) (P(MMA/BA)) latices were prepared by emulsion copolymerization of MMA and BA using a redox initiating system and $MPEO_{45}$-CL_6-LA copolymer as surfactant. A mixture of 7.3 g of MMA and 7.3 g of BA was copolymerized in 33.1 ml water. The redox initiating system consisted of 0.64 g of a 30 w/w% tBHPO aqueous solution, 3.88 g of a 5 w/w% iAA aqueous solution and 0.20 g of a 1 w/w% FeEDTA aqueous solution. The polymerizations were conducted at a surfactant to monomer ratio (S/M) of 10/90. The reaction conditions used were: total solids content approximately 30 wt%, a polymerization temperature of 60 °C, and a polymerization time of 4 hrs. Further experimental details are given elsewhere [10].

The solids content of the latices was determined gravimetrically by evaporating the volatile components (water, MMA and BA) in an oven at 70 °C for 24 hrs. Taking into account the mass of initiator and the surfactant used, the conversion of the monomers was determined. Measurements were performed in triplicate, the relative error in solids content and monomer conversion determinations was approximately 2 %.

The average size and size distribution of the latex particles were determined by dynamic light scattering (DLS) (Zetasizer 4000, Malvern Instruments Ltd., Malvern, UK) at 25 °C at an angle of 90 ° (633 nm) in five fold.

Preparation of Pigment Pastes

For further use in the pigment formulations, aqueous solutions (dispersions) of $MPEO_{45}$-CL_6 and $MPEO_{45}$-CL_6-LA were prepared by mixing with water. The concentration of the block copolymers was 18.1 wt%. The pH was adjusted to 8.9 using minor amounts of AMP 90. The appearance of the $MPEO_{45}$-CL_6 solution (dispersion) was milky, whereas the $MPEO_{45}$-CL_6-LA solution (dispersion) was transparent.

Table 2 shows the composition of the different aqueous pigment pastes prepared. A reference pigment paste formulation using Disperbyk 190 was prepared as well. The components were slowly added in the indicated order and thoroughly mixed using a Cowles mixer until a homogeneous solution was obtained. TiO_2 was then slowly added and dispersed into the mixture until the pigment particles in the pigment pastes were smaller than 10 μm. The fineness of the pigment paste was monitored and visualized by using a Hegmann grind gauge (according to ASTM D 1210-54).

The viscosity of the pigment dispersions was measured using a Brookfield viscometer (Brookfield Digital Viscometer DV-I+) at 25 ± 0.2 ^{o}C according to ISO 2555-89. The error in the viscosity measurements was less than 3 %. The pH was measured at 25 ± 1^{o}C using a pH meter (Schott) according to ISO 1148-80.

Table 2: Preparation of TiO_2 pigment pastes using Disperbyk 190, MPEO-CL or MPEO-CL-LA pigment dispersant.

	Ingredients:	Disperbyk 190 (Parts by weight)	$MPEO_{45}$-CL_6 (Parts by weight)	$MPEO_{45}$-CL_6-LA (Parts by weight)
1	PG	2.1	2.3	2.3
2	Water	4.4	3.2	3.2
3	Dehydran 1293	0.4	0.4	0.4
4	Disperbyk 190	1.4	-	-
5	$MPEO_{45}$-CL_6 solution [a]	-	3.0	-
6	$MPEO_{45}$-CL_6-LA solution [a]	-	-	3.0
7	Kronos 2190 (TiO_2)	19.7	21.1	21.1
	Total:	30.0	30.0	30.0
	Viscosity at 60 rpm (mPa.s)	200	>10000	5500
	pH	7.7	8.3	8.1

[a] $MPEO_{45}$-CL_6 *and* $MPEO_{45}$-CL_6-LA *block copolymer pigment dispersants were introduced as 18.1 wt% solutions in water*

Pigmented waterborne latices

The pigment pastes (30 parts by weight) were slowly added to the binder formulations (70 parts by weight) under continuous agitation. Homogeneous mixing was ensured by controlling the rate of pigment addition and stirring speed.

Preparation and characterization of pigmented waterborne latex films

Films of pigmented waterborne latex formulations were prepared by casting the formulations on glass and drying at ambient conditions. The specular gloss of the films was evaluated with a haze-gloss meter (BYK-Gardner 4601) according to DIN-67530. Measurements were carried out in triplicate.

To determine water absorption of the pigmented latex films, 80 μm thick films measuring 100 x 100 mm were prepared. The films were immersed in deionized water for 24 hrs at room temperature. The films were then wiped to remove excess water present on the surface. The water adsorption was calculated from:

Water absorption = $((W_1 - W_0)/ W_0) \times 100$ %

In which W_0 is the dry weight of the film and W_1 is the weight of the film after equilibration in water. All measurements were performed in duplicate.

RESULTS AND DISCUSSION

A P(MMA/BA) latex was prepared by emulsion copolymerization of MMA and BA using $MPEO_{45}$-CL_6-LA as an emulsifier and characterized as previously described [10]. The solids content, particle size and particle size distribution were approximately 30 wt%, 140 nm and 0.24, respectively.

This latex was formulated in a similar way as the reference latex NeoCryl XK-90. To the P(MMA/BA) latex, 0.2 wt% of Dehydran 1293, 1.2 wt% of Borchi Gel L75N in water at a ratio of 1:1 and an additional amount of 4.9 wt% water were added. The pH of the latex was 1.9 and its viscosity was 13 mPa.s. Upon adjustment of the pH to 8.2 with an ammonia solution, moderate sedimentation was observed. Although this was not further investigated, it could be due to interaction of the MPEO-CL based block copolymers with the other components in the formulation. (It should be emphasized that the formulation was typical of a NeoCryl XK-90 latex and had not been optimized).

Both latices, the P(MMA/BA) latex and the reference NeoCryl XK-90, were mixed with the different pigment pastes described in the experimental part in Table 2. In these pigment pastes TiO_2 was dispersed using Disperbyk 190, $MPEO_{45}$-CL_6 or $MPEO_{45}$-CL_6-LA as a pigment dispersant. The mixing ratio of clear latex to pigment paste was 7:3 by weight. The viscosity of the pigmented latex and the overall appearance, gloss and water adsorption of pigmented coatings obtained after casting and drying of the latices were determined. These results are summarized in Table 3.

Table 3 shows that all pigmented latex formulations displayed shear thinning behavior Shear thinning behavior is an important property of waterborne paints. The difference in viscosity between the NeoCryl XK-90 and the P(MMA/BA) latices is apparent; the viscosity of the former latex was much higher. In the pigmented P(MMA/BA) latices, the use of MPEO-CL-LA as pigment dispersant also results in quite high values of viscosity.

When comparing the appearance and gloss of 80 μm thick films cast on glass, films prepared from NeoCryl XK-90 latices perform better than the P(MMA/BA) latex films for all pigment dispersants. Nevertheless, in these non-optimized formulations, the

MPEO-CL and MPEO-CL-LA dispersants give satisfactory films with high gloss and relatively low uptake of water compared to the commercial systems.

In the experimental P(MMA/BA) latex films, the appearance (as determined by visual observation) of the cast films is rather poor and not as good as when using Disperbyk 190. In these formulations craters could be observed, indicating that the surface wetting properties of the latex are far from optimal. It can be expected that optimization of the formulation or addition of wetting agents will lead to enhanced properties. Besides this, the table shows that, when using MPEO-CL and especially MPEO-CL-LA surfactants, P(MMA/BA) films with high gloss levels can be prepared. As the surfactant used in the preparation of the P(MMA/BA) latex is the same as in the pigment dispersant used, issues of compatibility should not be relevant, and therefore the gloss levels are higher than when using Disperbyk 190.

Table 3: The viscosity of the latices and the appearance, gloss and water absorption of films prepared from NeoCryl XK-90 and P(MMA/BA) latices. The pigment dispersants used in the formulations were Disperbyk 190 and MPEO$_{45}$-CL$_6$ and MPEO$_{45}$-CL$_6$-LA.

		NeoCryl XK-90		
Pigment dispersant		Disperbyk 190	MPEO$_{45}$-CL$_6$	MPEO$_{45}$-CL$_6$-LA
Viscosity (mPa.s)	6 rpm	4600	2700	2400
	60 rpm	3650	1990	1810
Appearance on glass	80µ film	+	+/-	+/-
Gloss	20 °/60 °	55/83	34/70	43/78
Water absorption	(%)	9.7	10.6	9.5
		P(MMA/BA) latex		
Pigment dispersant		Disperbyk 190	MPEO$_{45}$-CL$_6$	MPEO$_{45}$-CL$_6$-LA
Viscosity (mPa.s)	6 rpm	600	2600	400
	60 rpm	490	1410	330
Appearance on glass	80µ film	+/-	-	-
Gloss	20 °/60 °	4/37	20/64	26/67
Water absorption	(%)	no data	7.7	10.6

Hard settlement (the settlement which can not be redispersed by agitation or stirring) was not observed in any of the formulations. This implies that the MPEO-CL and MPEO-CL-LA surfactants are indeed multifunctional and can potentially be of use in waterborne paint formulations.

CONCLUSIONS

The potential of $MPEO_{45}$-CL_6 and $MPEO_{45}$-CL_6-LA block copolymers as multifunctional surfactants has been shown. These compounds can be used as emulsifiers, pigment dispersants and rheological modifiers in the formulation of waterborne P(MMA/BA) coating systems. The properties of the latices and the latex films are satisfactory, and even without optimization, in several aspects comparable to those of commercially available systems.

OUTLOOK

MPEO-CL based block copolymers are novel, multifunctional polymeric surfactants. The potential of these block copolymers, as an emulsifier, a pigment dispersant and a rheological modifier has been proven in this preliminary study. However, more experimental work needs to be done on the rheology, the optimization of paint formulations and the assessment of the mechanical properties of the resultant films to assess the full potential of these compounds.

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7 Tan BH, Grijpma DW, Nabuurs T and Feijen J. *Polymer* 2005: 46, 1347-1358 (Chapter 3 of this thesis)
8 Chapter 7 of this thesis.
9 Appendix A of this thesis.
10 Chapter 5 of this thesis.

SUMMARY

Conventional organic solvent coating systems are a major concern in terms of safety, health and the environment and are therefore being replaced by waterborne coating systems. In the formulation of waterborne coating systems, surfactants play an important role, especially during the latex preparation where they influence particle nucleation and stabilization in emulsion polymerization. However, after application of the waterborne coating system on a substrate, the role of the surfactant becomes redundant.

During the film formation process the latex particles coalesce and the surfactant molecules migrate out of the bulk phase to concentrate at the interfaces. This build-up at the film surface adversely affects film properties like adhesion to the substrate and water resistance of the film. In addition, the presence of different surfactants, pigment dispersant and/or rheological modifiers in the system can lead to competitive adsorption phenomena and cause unexpected rheological effects and poor stability of the dispersion.

Although the use of polymeric and polymerizable surfactants is employed to solve these phenomena, these materials have their drawbacks. In this work, amphiphilic block copolymers consisting of poly(ethylene oxide) (PEO) and short poly(ε-caprolactone) (PCL) segments end-functionalized with linoleic acid (LA)) were synthesized to provide an alternative solution to the aforementioned phenomena. LA-functionalized block copolymers are crosslinkable, as the unsaturated double bonds can undergo autoxidative crosslinking upon exposure to air.

The aims of this work were:

1) to explore the potential of crosslinkable block copolymers based on PEO and PCL as surfactants in emulsion polymerizations of (meth)acrylates.

2) to study the influence of these block copolymers on the final properties of the acrylate latex films and

3) to explore the potential of the block copolymers as pigment dispersants and as rheological modifiers in waterborne paint formulations.

An overview of the state-of-art in the application of surfactants as emulsifiers in emulsion polymerization, of pigment dispersants in pigment pastes and of rheological modifiers in formulating waterborne acrylic coatings is presented (**Chapter 2**).

The first experimental part of this work describes the synthesis and characterization of di- and tri-block copolymers with and without LA end-groups. These block copolymers

have good surface activity (relatively low critical micelle concentration (CMC)) and surface tension at the CMC. In the crosslinking tests at ambient conditions, 90 percent of the double bonds had reacted in 15 d and a crosslinked structure was obtained after 30 d. The capability of this block copolymer to act as an emulsifier in emulsion polymerizations of methyl methacrylate (MMA) at 10wt% solids content utilizing a thermolysis initiator (**Chapter 3**) was proven. PMMA latices could readily be prepared with LA-functionalized di-block and tri-block copolymers. The respective particle sizes were 180 and 370 nm. The overall stability (stability during storage, freeze-thaw cycling and upon addition of electrolyte solutions and ethanol) of latices prepared with LA-functionalized di-block copolymers was higher than that of latices prepared with LA-functionalized tri-block copolymer of comparable compositions and HLB values.

The potential of these di-block copolymers in emulsion polymerizations of MMA at higher solids content was further investigated. Reaction parameters of the emulsion polymerization (initiator system (thermolysis- or redox-initiating system), initiator concentration, type of surfactant, surfactant to monomer ratio and reaction temperature) were varied to obtain a suitable surfactant and optimal reaction conditions (**Chapter 4)**. A redox initiating system, consisting of *t*-butyl hydroperoxide (tBHPO), iso-ascorbic acid (iAA) and ethylenediaminetetraacetic acid ferric-sodium salt (FeEDTA), could successfully be employed in emulsion polymerizations of MMA at 30 wt% solids in water. $MPEO_{45}$-$CL_{6.5}$-LA, was found to be a most suitable surfactant, as it performed adequately under sub-optimal reaction conditions. At full monomer conversion, stable PMMA latices having particle sizes ranging from 200 to 300 nm were obtained.

In **Chapter 5** the preparation of poly(methyl methacrylate/n-butyl acrylate) P(MMA/BA) latices under these optimal conditions is presented. The $MPEO_{45}$-$CL_{6.5}$-LA surfactants employed were prepared using either non-purified or carefully purified starting materials. The different block copolymers displayed comparable surface activities. Differences in the characteristics of the P(MMA/BA) latices and the mechanical properties of their films were not significant.

A detailed study on film formation, surfactant migration, water-uptake and mechanical properties of films prepared from these P(MMA/BA) latices, is described in **Chapter 6**. When using (crosslinkable) LA-functionalized surfactants at a surfactant to monomer ratio (S/M) of 10/90, an increase in the mechanical properties of the latex films in time could be observed. Films were also cast from P(MMA/BA) latices where the latex was stabilized with conventional sodium dodecyl sulphate (SDS) surfactant. It was found that the water-uptake of these films was noticeably higher than that of latex films cast from the latices where LA-functionalized surfactants were employed. And unexpectedly, at the highest surfactant to monomer ratios, the water-uptake of these films was the lowest.

Contact angle measurements showed that the hydrophilicity of latex films prepared from latices stabilized with LA-functionalized surfactants did not change after exposure to air for 1 month. This implies that migration of the surfactant to the surface of the film did not occur.

In a next part of this thesis, the use of these block copolymer surfactants as a pigment dispersant (**Chapter 7**) and as a rheological modifier (**Appendix A**) in the waterborne paint formulations is described. Two commercially available pigment dispersants (Surfynol 104E and Disperbyk 190) were used as reference materials and three different acrylic latices (NeoCryl XK-90, XK-98 and XK-188) were used as model binders. All pigment pastes and the pigmented latex dispersions prepared exhibited thixotropic behavior. The performance of $MPEO_{45}$-CL_6 and $MPEO_{45}$-CL_6-LA in gloss tests of the latex films was better than that of Surfynol 104E and comparable to that of Disperbyk 190. Water absorption of the latex films was also quite low. When comparing $MPEO_{45}$-CL_6-LA with $MPEO_{45}$-CL_6, the latter performed better in all cases.

The potential of this block copolymer as a rheological modifier in P(MMA/BA) latices is assessed in **Appendix A**. In these first experiments, shear thinning behavior of the latices was observed when $MPEO_{45}$-CL_6-LA was used. Upon further addition of this surfactant, the P(MMA/BA) latices exhibited thixotropic behavior. The other compositions were not as effective. From these results it can be concluded that, besides acting as an emulsifier, these block copolymer can act as rheological modifiers in the waterborne paints as well.

In **Appendix B**, $MPEO_{45}$-CL_6 and $MPEO_{45}$-CL_6-LA block copolymers were simultaneously used as emulsifier (in preparing P(MMA/BA) latices), pigment dispersant (in preparing a pigment paste) and rheological modifier in a single waterborne paint formulation. NeoCryl XK-90 latex and Disperbyk 190 pigment dispersant were used as references. First, stable P(MMA/BA) latices with a solids content, particle size and particle distribution of respectively 30 wt%, 140 nm and 0.24 were prepared using $MPEO_{45}$-CL_6-LA as emulsifier. Then TiO_2 pigment pastes were prepared using both

$MPEO_{45}$-CL_6 and $MPEO_{45}$-CL_6-LA block copolymers. A number of pigmented latex formulations were prepared by thorough mixing. All paint formulations were stable, and showed shear thinning behavior.

In terms of viscosity of the pigmented latices and gloss and water uptake of cast films, the performance of MPEO-PCL and MPEO-PCL-LA block copolymers was comparable to or better than that of Disperbyk 190 formulations. MPEO-PCL-LA block copolymers performed especially well in P(MMA/BA) latices. However, the appearance of cast films containing MPEO-PCL based block copolymers was rated moderate to poor. The films showed poor wetting and extensive cratering when applied on glass surfaces. It should be emphasized, though, that these were exploratory experiments and that optimization of the paint formulations is required.

Samenvatting

Conventionele, vluchtige organische oplosmiddelhoudende, coatings hebben een nadelige invloed op het mileu en op de veiligheid en gezondheid van de gebruiker. Daarom worden deze steeds meer vervangen door coatings met water als oplosmiddel. In de samenstelling van watergedragen coatings spelen de oppervlakte actieve stoffen (surfactants) een belangrijke rol, vooral tijdens de latex bereiding door middel van emulsie polymerisatie waar het de vorming en stabiliteit van de latex deeltjes beinvloed. Na het aanbrengen van de coating op een substraat wordt de surfactant echter overbodig.

Tijdens het vormen van een film coaguleren de latex deeltjes en migreren de surfactant moleculen naar de grensvlakken. De ophoping van surfactant aan de buitenkant van de latex film heeft een negatief effect op de adhesie en water afstotende eigenschappen van de coating. Bovendien kan de interactie met eventuele andere toevoegingen zoals pigmenten, dispergeermiddelen en vloeimiddelen, er toe leiden de coating minder stabiel wordt.

Door het gebruik van polymere en polymeriseerbare surfactants wordt geprobeerd deze problemen op te lossen. Deze surfactants hebben echter nog nadelen. In dit proefschrift wordt de synthese van amfifiele blokcopolymeren gebaseerd op poly(ethyleen oxide) (PEO) met korte poly(ε-caprolacton) (PCL) segmenten en linolzuur (LA) beschreven. De LA-gefunctionaliseerde blokcopolymeren kunnen crosslinken door oxidatie van de onverzadigde dubbele binding. Deze netwerk-vormende polymeren moeten een beter alternatief vormen voor de eerder genoemde conventionele surfactants.

Het doel van dit werk was:

1) het onderzoeken van crosslinkbare blokcopolymeren gebaseerd op PEO en PCL als surfactants tijdens de emulsie polymerisatie van (meth)acrylaten,
2) de invloed van deze blokcopolymeren op de eigenschappen van de acrylaat latex film te evalueren, en
3) de invloed van deze blokcopolymeren op het dispergeren van pigmenten en op de rheologische eigenschappen bestuderen.

De stand van zaken op het gebied van surfactants in emulsie polymerisatie, pigment dispersie en rheologie beinvloeding wordt in **hoofdstuk 2** gepresenteerd.

Het eerste experimentele hoofdstuk beschrijft de synthese en karakterisatie van di- en tri-blokcopolymeren met en zonder LA eindgroepen. Deze blokcopolymeren hebben een

goede oppervlakte activiteit (relatief lage kritische micel concentratie (CMC)) met een goede oppervlaktespanning bij de CMC. In de crosslink tests bij omgevingscondities reageerde 90% van de dubbele bindingen binnen 15 d en een netwerk was gevormd na 30 d. Het is aangetoond dat deze blokcopolymeren kunnen functioneren als surfactant voor emulsiepolymerisatie van methyl (meth)acrylaat (MMA) met 10 % vaste stof en een thermolytische initiator (**hoofdstuk 3**). PMMA latexen werden gemaakt met LA-gefunctionaliseerde di- en tri-blokcopolymeren als surfactant. De gemiddelde deeltjesgrootte was respectievelijk 180 en 370 nm. De stabiliteit (tijdens opslag, tijdens bevries-ontdooi cycli en na toevoeging van electrolietoplossingen en ethanol) van de latexen van LA gefunctionaliseerde di-blokcopolymeren was beter dan de stabiliteit van latexen van LA gefunctionaliseerde tri-blokcopolyermen met een verder vergelijkbare samenstelling en hydrofiel tot lipofiel balans (HLB-waarde).

De toepasbaarheid van deze di-blokcopolymeren bij het emulsiepolymeriseren van MMA met een grotere hoeveelheid vaste stof in de samenstelling was verder onderzocht. De reactie parameters werden geoptimaliseerd om de geschikte surfactant met bijbehordende reactie condities te vinden (**hoofdstuk 4**). Hiertoe werden onderzocht: het initiator mechanisme (thermolyse of redox-initiatie), de initiator concentratie, het type surfactant, de hoeveelheid surfactant ten opzichte van de hoeveelheid monomeer en de reactietemperatuur. Een redox initiatiesysteem, bestaande uit *t*-butyl hydroperoxide (tBHPO), iso-ascorbine zuur (iAA) en het ijzerzout van ethyleendiaminetetraacetaatzuur (FeEDTA), was geschikt voor de emulsiepolymerisatie van MMA met 30 % vaste stof in water. $MPEO_{45}$-$CL_{6.5}$-LA was de meest geschikte surfactant, zelfs onder niet optimale omstandigheden. Bij volledige conversie van de monomeren, werden stabiele PMMA latexen met een deetjesgrootte van 200 tot 300 nm verkregen.

Poly(n-butyl acrylaat) (PBA) en PMMA latexen werden gemaakt bij de optimale omstandigheden (**hoofdstuk 5**). $MPEO_{45}$-$CL_{6.5}$-LA surfactants zijn zowel met gezuiverde als ongezuiverde monomeren gemaakt. Deze surfactants vertoonden vergelijkbare opppervlakte actieve eigenschappen. De verschillen in eigenchappen tussen de hiermee gemaakte PBA/PMMA latexen en films waren niet significant.

De film vorming, surfactant migratie, water opname en mechanische eigenschappen van de PBA/PMMA films werd onderzocht (**hoofdstuk 6**). Het gebruik van LA-gefunctionaliseerde blokcopolymeer surfactants bij een surfactant tot monomeer (S/M) ratio van 10/90 gaf betere mechanische eigenschappen bij langere polymerisatietijden.

Films gemaakt met conventionele natrium dodecylsulfaat (SDS) gestabiliseerde PMMA/PBA latexen namen meer water op dan films van PMMA/PBA latexen gestabiliseerd met LA-gefunctionaliseerde bockcopolymeersurfactants. Verrassenderwijs was de wateropname was het laagst bij de hoogste S/M ratio.

Met contacthoekmetingen werd aangetoond dat de hydrofiliteit van films gemaakt met latexen gestabiliseerd met LA-gefunctionaliseerde blokcopolymeer surfactants niet veranderde gedurende een maand bij blootstelling aan lucht. Dit betekent dat er geen migratie van surfactant naar het oppervlak plaats vond.

In de volgende delen van dit proefschrift wordt het gebruik van deze blokcopolymeren voor pigmentstabilisatie (**hoofdstuk 7**) en als vloeimiddel (appendix A) in watergedragen coatings beschreven. Twee commercieel verkrijgbare pigmentstabilisatoren (Surfynol 104E en Disperbyk 190) werden gebruikt als referentie. Drie acryl latexen (NeoCryl XK-90, XK-98 en XK-188) werden gebruikt als modelbindmiddel. De pigment pasta's en latexdispersies met pigment vertoonden thixotroop gedrag. In glans-testen presteerden zowel $MPEO_{45}$-CL_6 en $MPEO_{45}$-CL_6-LA beter dan Surfynol 104E en vergelijkbaar met Disperbyk 190. De water-opname van de latex films was ook laag. In al deze gevallen presteerde $MPEO_{45}$-CL_6-LA beter dan $MPEO_{45}$-CL_6.

Het gebruik van de blokcopolymeren als vloeimiddel in the PBA/PMAA latex wordt in **appendix A** beschreven. Voorlopige experimenten lieten zien dat de latexen met $MPEO_{45}$-CL_6-LA afschuifverdunning (shear thinning) vertonen. Als meer van deze surfactant toegevoegd werd vertoonden de PBA/PMMA latexen thixotroop gedrag. De andere samenstellingen waren niet zo effectief. Uit deze resulaten kan geconcludeerd worden dat deze blokcopolymeren ook als vloeimiddel voor watergedragen coatings gebruikt kunnen worden.

In **appendix B** wordt het gebruik van de blokcopolymeren voor alle stappen in de bereiding van een coating beschreven. Tijdens dit proces functioneerden de blokcopolymeren achtereenvolgens als: surfactant (bij het maken van de PBA/PMMA latex), als stabilisator (van de pigmenten) en als vloeimiddel. De PBA/PMMA systemen met de beschreven blokcopolymeren als stabilisator werden vergeleken met een systeem met NeoCryl XK-90 latex en Disperbyk 190 als stabilisator. Een stabiele latex met 30% vaste stof, een deeltjesgrootte van 140 nm en een verdeling van de deeltjesgrootte van 0.24 werd bereid met $MPEO_{45}$-CL_6-LA als surfactant. Vervolgens werden TiO_2 (pigment) pasta's bereid met zowel $MPEO_{45}$-CL_6 en $MPEO_{45}$-CL_6-LA blokcopolymeren. De pigmentpasta's en latexen werden gemixt en leverden stabiele mengsels op die afschuifverdunning vertoonden.

De viscositeit van de gepigmenteerde latexen en de glans en wateropname van de daarmee gemaakte films waren vergelijkbaar of beter dan het referentiemateriaal. MPEO-CL-LA blokcopolymeren leverden de beste latexen. De films gemaakt van latexen met MPEO-CL blokcopolymeren waren minder goed, met name de waterafstotende eigenschappen en het ontstaan van gaten in de film als deze op glas aangebracht is. Het moet echter benadrukt worden dat dit slechts voorlopige resultaten zijn en het systeem nog geoptimaliserd moet worden.

Curriculum Vitae

BoonHua Tan was born on April 10th, 1975 in Klang, Malaysia. In the year of 1996, he entered the University Science Malaysia located in Penang, Malaysia. Soon after he obtained his BTech Degree (majoring in wood, paper and coating technology), he started his master 2 years research program in developing non-aqueous and aqueous UV curable coatings systems. After the completion of his master, he worked as research officer in developing UV curable coatings using modified renewable resource as raw materials in the same university. In 2001, he furthers his PhD study in University of Twente, Enschede, The Netherlands under the supervision of Prof. Dr. Dirk W. Grijpma in Polymer Chemistry and Biomaterials group (Prof. Dr. Jan Feijen's group). In 2005, he worked as head of research and development department in a wood coatings company for approximately six months before he moved to KMC oiltools. Currently, he is working as research scientist (KMC oiltools) in charge for synthesizing and developing surfactants for the applications in drilling fluids.