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Crosslinkable surfactants based on linoleic acid-functionalized block copolymers of ethylene oxide and ε-caprolactone for the preparation of stable PMMA latices

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Abstract

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 d and a crosslinked structure was obtained after 30 d. 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 to 51.4 mN/m for the diblock and from 45.6 to 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.

Keywords: Crosslinkable surfactants; Block copolymers; Emulsion polymerization

1. 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 X405), 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

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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) lattices was investigated, and the amount of free crosslinkable surfactant in the aqueous phase was estimated.

2. Experimental

2.1. 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 MΩ cm) was employed throughout the whole study.

2.2. 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 0.010–0.015 wt% based on ε-caprolactone. After a reaction time of 24 h 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 10–20 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 h. The reaction products were dissolved in chloroform, precipitated in an excess of cold hexane and dried under vacuum for 3 d [24–25].

2.3. 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.

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 h. As controls PMMA latices were prepared either without surfactant or with commercially available surfactants (SDS and Triton X 405) at an equal concentration.

2.4. 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 5×10^2 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 w/v% and injection volumes of 30 μl were used. All determinations were performed at 25 °C.

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 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 $\bar{M}_n$ 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]:

$$\mathrm{HLB} = \frac{W_\mathrm{H}}{W_\mathrm{H} + W_\mathrm{L}} \times 20$$

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 d 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).

2.5. PMMA latex properties

After a polymerization time of 4 h, 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 (20,000 rpm, 1 h), 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 h and subsequently at room temperature for another 24 h), 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 2 weeks in the same manner.

3. Results and discussions

3.1. 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 Fig. 1.

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.

After the ring opening polymerization and functionalization step, the prepared block copolymers are purified by precipitation in hexane. Fig. 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.

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 monofunctionalized.

The molecular weights of the block copolymers determined by NMR agree well with the expected values. Also, functionalization with LA at 180 °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].

3.1.1. 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].

Fig. 3 shows the conversion of double bonds as a

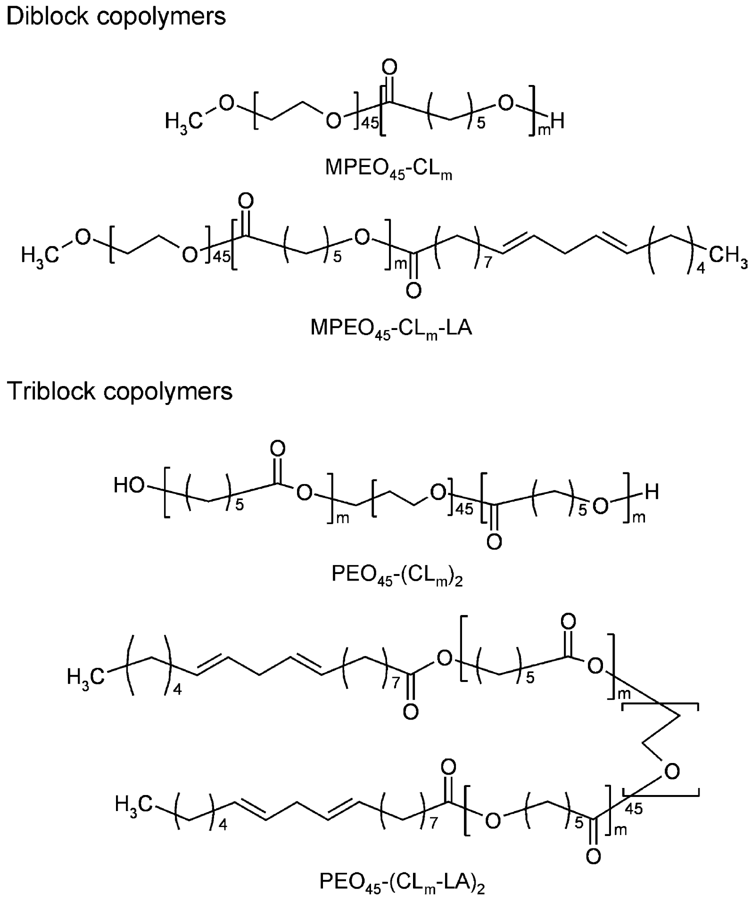

Fig. 1. Chemical structure of diblock ($MPEO_{45}$-CL_m-LA) and triblock (PEO_{45}-$(CL_m$-$LA)_2$) copolymer surfactants. The subscript *m* corresponds to the number of CL repeat units.

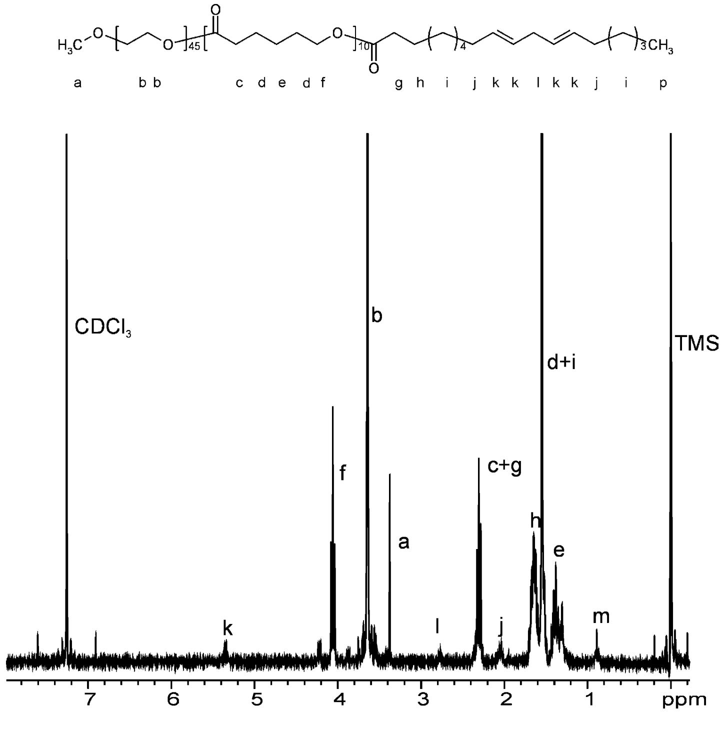

Fig. 2. ^{1}H-NMR of linoleic acid functionalized $MPEO_{45}$-CL_{10}-LA.

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)			$\bar{M}_n$ expected[a] (g/mol)	$\bar{M}_n$ (H-NMR) (g/mol)	$\bar{M}_n$ (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}-$(CL_3\text{-}LA)_2$	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}-$(CL_5\text{-}LA)_2$	45	9.7	1.8	3670	3620	4890	11.0

[a] $\bar{M}_n$ 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]

function of time. Up to a period of 30 d, the surfactant films were found to be soluble in (deuterated) chloroform. In a period of 15 d, almost 90% of the double bonds were converted and after 30 d 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.

3.1.2. Surface active properties of (crosslinkable) diblock and triblock polymeric surfactants ($MPEO_{45}$-CL, PEO_{45}-$(CL)_2$, $MPEO_{45}$-CL-LA and PEO_{45}-$(CL\text{-}LA)_2$

The relation between surface tension and concentration of several crosslinkable surfactants is shown in Fig. 4. The behavior of SDS and of Triton X405, a commercially available nonionic surfactant, is shown as well. The surface tension decreased significantly as the concentration of surfactant increased.

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.

Compared to the commercially available ionic and nonionic surfactants, the diblock and triblock copolymer

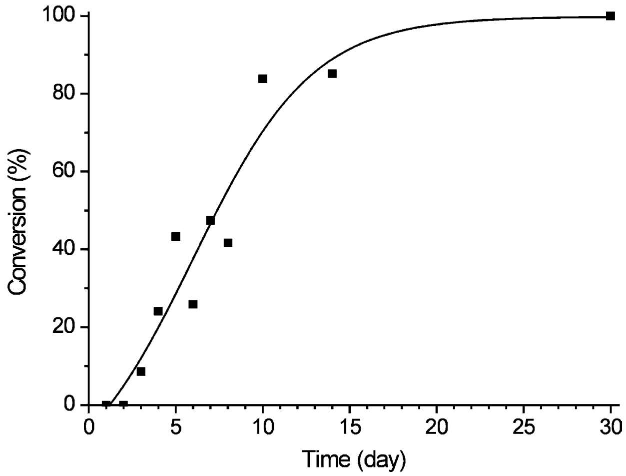

Fig. 3. Disappearance (conversion) of the double bonds in PEO_{45}-$(CL_3\text{-}LA)_2$ films exposed to air as determined by NMR.

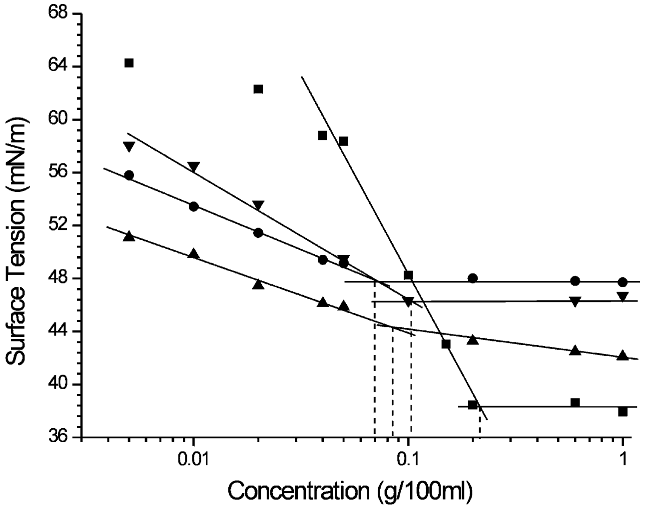

Fig. 4. Surface tension versus concentration for PEO_{45}-$(CL_3)_2$ (●), PEO45-$(CL_3\text{-}LA)_2$ (▲), Triton X 405 (▼) and SDS (■) surfactant solutions in water. The dotted lines indicate the CMC.

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 Fig. 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.

3.2. 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}-$(CL_3\text{-}LA)_2$ (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.

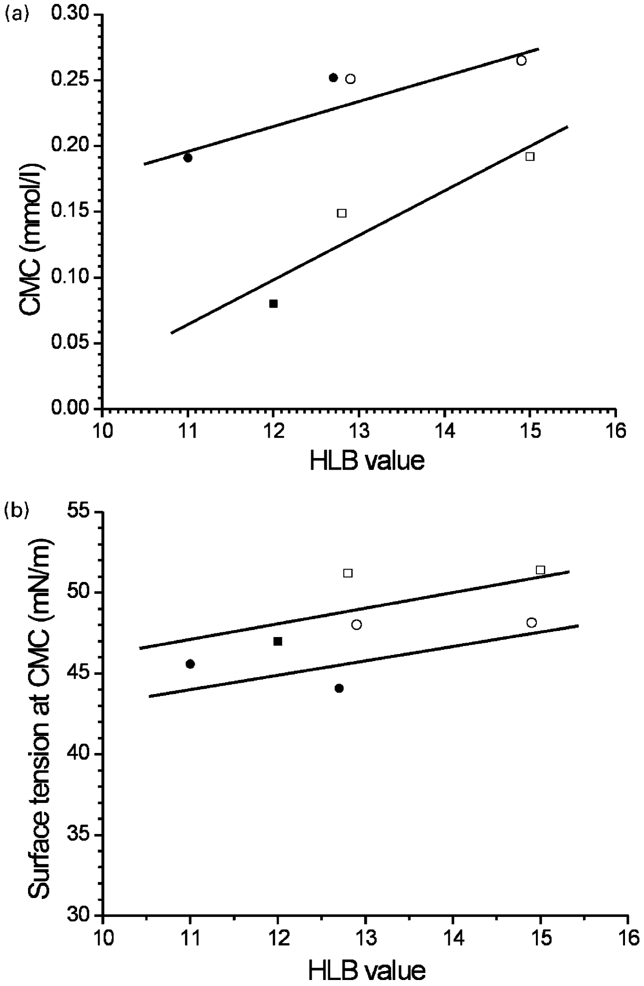

Fig. 5. CMC (a) and surface tension at CMC (b) as a function of HLB values for non-functionalized (□) and LA-functionalized diblock copolymers (■) and non-functionalized (○) and LA-functionalized triblock copolymers (●).

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 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 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.

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 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].

Fig. 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 (Fig. 6(a)–(d)) the applied vacuum and electron beam has resulted in fusion of the particles.

3.2.1. 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.

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 Fig. 4. The surfactant concentrations for $MPEO_{45}$-CL_{10}-LA and PEO_{45}-$(CL_3$-$LA)_2$ stabilized lattices 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 Fig. 7.

The signal at 5.35 ppm corresponds to the double bonds in LA. Signals at 3.6 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

Table 4
PMMA latices prepared by batch emulsion polymerizations with different surfactants

Latex	Surfactant	SC[a] (%)	MMA Conv.[b] (%)	$\bar{M}_w$[c] ($\times10^6$)	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

Surfactant concentrations are 0.3 mmol/100 ml.

[a] SC, solid content determined after removal of volatiles by freeze drying.

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

[c] $\bar{M}_w$, 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.

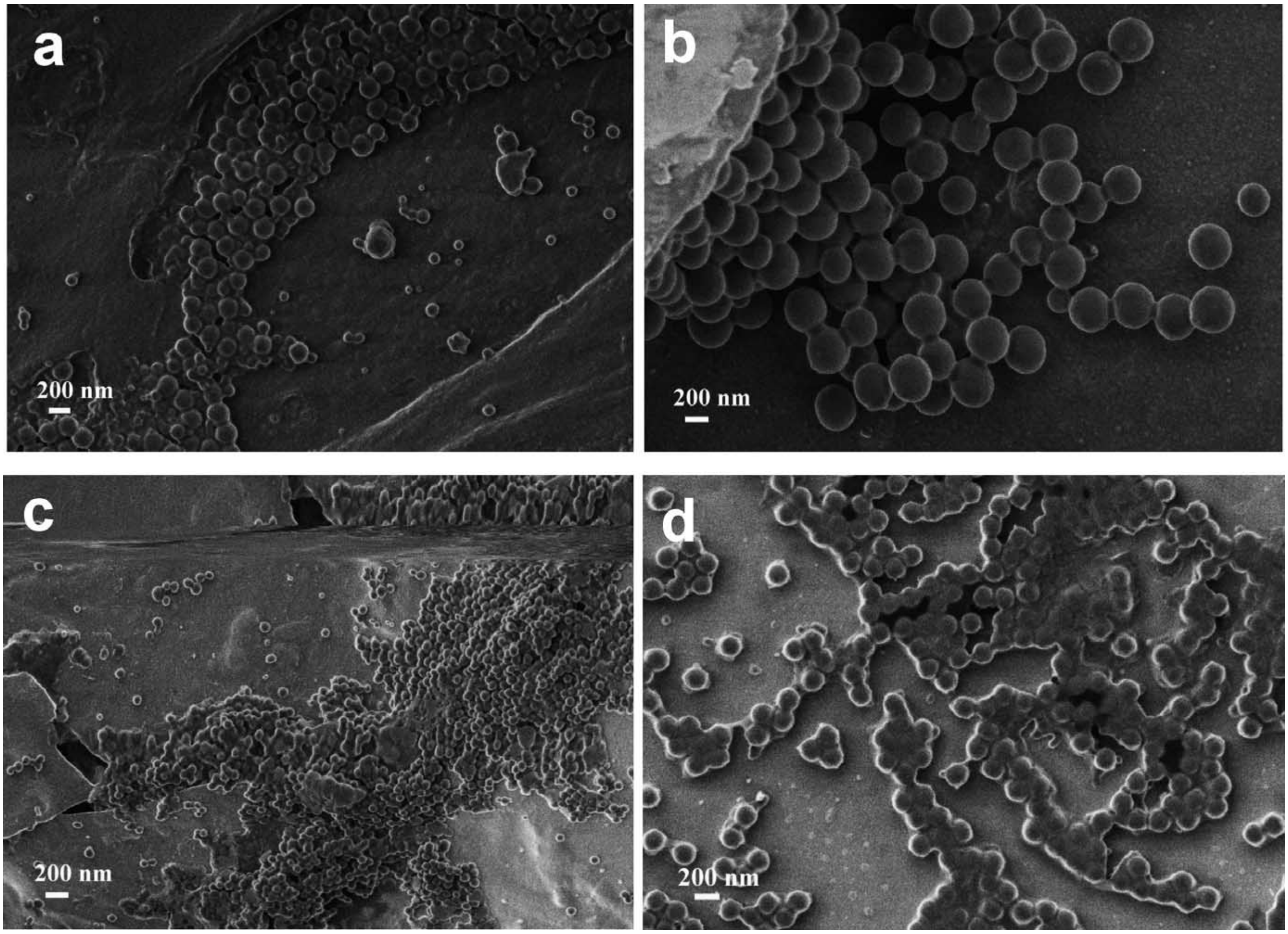

Fig. 6. Scanning electron microscopy (SEM) images of PMMA latices prepared with linoleic acid functionalized surfactants: (a) $MPEO_{45}$-CL_{10}-LA; (b) PEO_{45}-$(CL_3$-$LA)_2$ and commercial surfactants (c) SDS and (d) Triton X 405.

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 latexes 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% ($10-6.5\%=3.5\%$).

Table 5
Surface tension of PMMA latices prepared in batch emulsion polymerizations with different surfactants

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

Surfactant concentrations are 0.3 mmol/100 ml.

3.2.2. 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

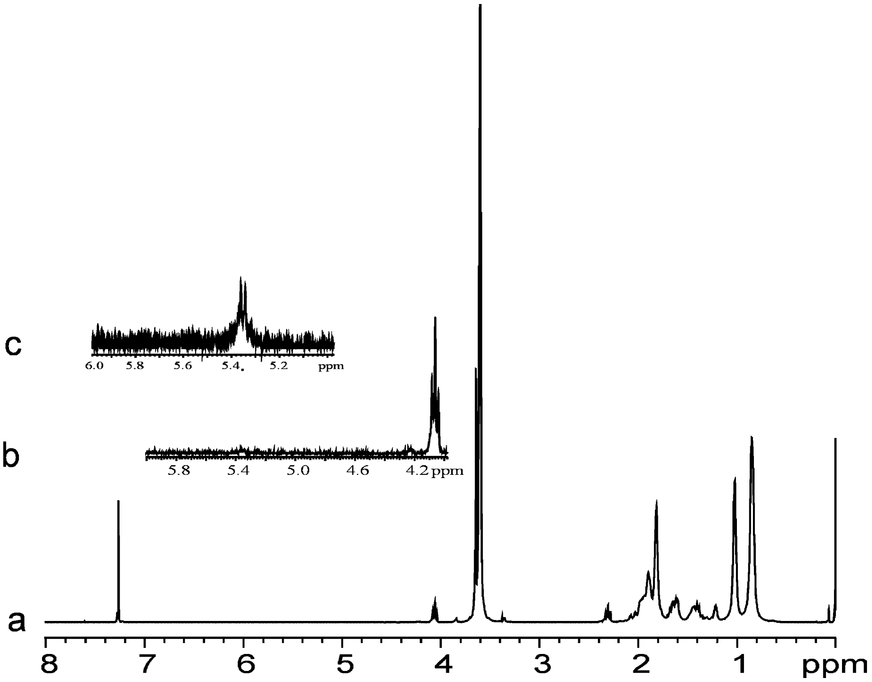

Fig. 7. ^{1}H-NMR spectrum of a PMMA latex prepared with MPEO$_{45}$-CL$_{10}$-LA surfactant. (a) Full spectrum; (b) expansion of the spectrum illustrating the relative intensities of unreacted LA double bond protons and CL methylene protons; (c) further expansion of the spectrum illustrating the presence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

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$_3$-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 of the latex particle size in most of the latices except surfactant-free latex system.

The stability 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 to 1.0 M in concentration and MgSO$_4$ (divalent) solutions of 0.1 M were added to the latices.

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.

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.

4. 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

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.

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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