Synthesis of New Acrylate-Based Nonionic Surfmers and Their Use in Heterophase Polymerization

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ABSTRACT: New acrylate-based nonionic reactive surfactants have been successfully designed, synthesized, and polymerized. Their homo- and copolymerization properties were studied, and while a low degree of homopolymerization was achieved, good copolymerization behavior with methyl methacrylate was observed. High solids content acrylic latexes were prepared using these new amphiphilic reactive molecules and were shown to have these reactive surfactants covalently incorporated. Well-defined latex particles with narrow particle size distributions were produced. Both scanning electron microscopy and atomic force microscopy (AFM) techniques were used to confirm the size and size distribution of the particles formed. AFM measurements conducted on the films formed from these latexes demonstrated their low degree of water sensitivity. This seems to indicate a low level of surfactant migration during the film formation and that the surfmers have been successfully incorporated into the final copolymers produced via heterophase polymerizations.

Introduction

Emulsion polymerization is one of the most important techniques for preparing polymers from an industrial point of view. In emulsion polymerization, carried out to obtain film-forming latexes (useful in waterborne coatings), it is necessary to introduce surfactants in the polymerization recipe in order to control both the size of the particles and the stability of the latexes. However, the presence of these species, which are generally low molecular weight compounds and are mainly associated with the polymeric particles through adsorption that involves weak associative bonds such as H or π bonding, may result in adverse effects on the latex stability and the final polymer properties. For instance, lack of stability under specific constraints, such as high shear, freezing, or high ionic strength, may arise from the use of conventional surfactants. Furthermore, these amphiphilic molecules may migrate through the matrix upon film formation[1−3] and affect the overall properties of the final polymeric material such as adhesion, water sensitivity, and gloss.[4−7] Migration of these molecules may also lead to their association and agglomeration leading to phase separation and an increase in the anisotropy in the final polymer that may affect its mechanical properties. The use of polymerizable surfactants can avoid these issues as they can deliver the amphiphilic properties of standard surfactants andcan also chemically interact (e.g., covalently bound) with the growing polymer chains. In doing so, the secondary effects on the final polymer are reduced as they are chemically bound to the matrix. Then, the surfactants cannot migrate in the same way as conventional surfactants and the risk of desorption is dramatically reduced. A reactive surfactant can participate in the polymerization process as an initiating moiety (*inisurf*), a moiety capable of chain transfer (*transurf*), or a group capable of copolymerization during the free-radical polymerization (*surfmer*).[8−16] Most of the work dealing with reactive surfactants involved surfmers as these molecules give the greatest potential molecular diversity. Anionic, cationic, and nonionic surfmers have been synthesized and applied in emulsion polymerizations.[17] The use of surfmers has been shown to improve the water resistance and surface adhesion in comparison to conventional emulsifiers.[18,19] Water and vapor permeability were also shown to be reduced when surfmers were used.[20]

The reactivity of the polymerizable surfactant and its adsorption characteristics are critical factors in defining its performance. To be effective, the surfmer must react such that, during the main part of the polymerization, its incorporation into the polymer being produced is low. This avoids the surfmer getting buried in the bulk of the polymeric particle and maximizes the amount of surfmer to be present at the surface. Thus, the surfactant activity is maximized and the quantities required are kept to a minimum. However, toward the end of the reaction, high surfmer incorporation should be achieved to avoid the presence of unreacted species in the final polymer, which may eventually migrate through the film during the final product formation (e.g., film formation).[21]

A wide range of surfmers have already been developed incorporating reactive groups such as acrylates, methacrylates, styrenyls, and maleates. The main limitation on surfmer use at the moment is related to the reactivity of the polymerizable unit. Traditionally, the reactivity of the functional groups has been restricted to prevent the "burying" phenomenon. Thus, the situations that they are applied to are niche opportunities.[22−40]

Here, we report the synthesis of new amphiphilic alkyl α-methylacrylate-based molecules and their incorporation as reactive surfactants in heterophase polymerizations. Hydroxymethylacrylate esters (RHMA) are vinyl monomers, which have a very high susceptibility to undergo radical polymerization. This high reactivity can be tailored by the nature of the functional groups present in the molecule. The polarity, resonance, and steric effects of the substituents all play an important role in defining the reactivity of RHMA monomers. For instance, conventional acrylate monomers having α-alkyl double bond substituents larger than a methyl group exhibit poor or no ability to polymerize under free-radical polymerization

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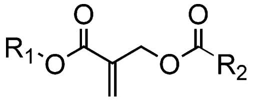
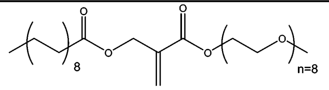
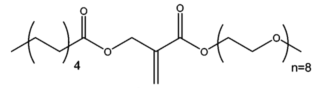
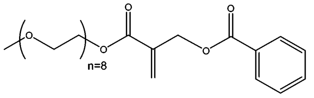
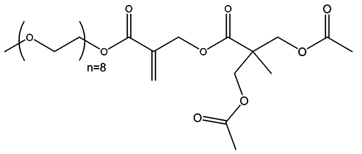
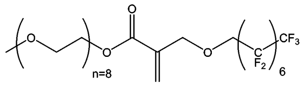


Figure 1. RHMA-based monomer.

Table 1. Structures of the Synthesized Acrylate-Based Reactive Surfactants

surfmer	structure	MW (g/mol)	purity (%)[a]
S1		700.55	98
S2		588.35	97
S3		538.2	96
S4		634.28	98
S5		816.17	97

[a] Evaluated by HPLC.

conditions due to steric effects.[41,42] In contrast, the substitution of an oxygen atom β to the double bond increases the reactivity of the monomer (a) by helping to overcome these steric effects and (b) due to a combination of hydrogen bonding and electronic effects from the ester group promoting propagation while decreasing chain transfer.[43,44] As a result, RHMA-based monomers as shown in Figure 1 present an excellent capability for polymerization, giving rise to very high molecular weight polymers. More importantly, when copolymerized with other acrylates or methacrylates, these monomers lead essentially to random copolymers, and good control of the final polymer composition can be achieved.

In this article, we report the synthesis of new RHMA-based reactive surfactants (Table 1) and their incorporation into high solids content acrylic latexes. The study of the surface of latex films incorporating these reactive surfactants by atomic force microscopy (AFM) is also reported, wherein the influence of the surfactants on the topographical features, roughness, and surface defects of the film is probed using this technique.

Experimental Section

Materials. The following reagents with the exception of methyl methacrylate (MMA) and 2,2′-azobis(2-methylpropionitrile) (AIBN) were used as received without further purification. MMA (Aldrich Chemical Co.) was redistilled over calcium hydride (Aldrich), and AIBN was recrystallized from methanol (Ficher Scientific). Poly(ethylene glycol) methyl ether (MPEG, $M_n = 350$ g/mol) and thionyl chloride were purchased from Acros Organics. *t*ert-Butyl acrylate, paraformaldehyde, 2,2-bis-(hydroxymethyl)-propionic acid, benzoic acid, stearic acid, decanoic acid, pentadecafluoro-1-octanol, triethylamine, 1,4-diaza[2.2.2]bicyclooctane, and sodium dodecyl sulfate (SDS) were purchased from Aldrich. Acetic anhydride, butyl acrylate (BuA, technical grade), potassium hydroxide, and acrylic acid (AA) were purchased from Fluka. Ammonium persulfate (APS, ACS reagent) was purchased from Acros Chemical Company. Toluene, tetrahydrofuran, and other solvents were obtained from Aldrich or Ficher. *tert*-Butyl α-hydroxymethylacrylate (t-BHMA) was prepared using previously published procedure.[45]

Instrumentation and Characterization. Molecular weights and molecular weight distributions of the polymers obtained by solution polymerization were measured using size exclusion chromatography on a system equipped with four styrene gel mixed-bed columns (American Polymer Standard Corporation, Mentor, OH) using THF as the eluent. Polystyrene standards (molecular weights ranging from 4630 to 400 000 g/mol) were used for calibration. Molecular weights and molecular weight distributions of the final latexes were determined by gel permeation chromatography (GPC) with THF as the eluent. Solution ^{1}H and ^{13}C NMR spectra were collected on a Varian Inova-500 MHz instrument. NMR spectra were recorded at room temperature in $CDCl_3$ with TMS as the internal reference. FT-IR spectra were obtained using a Bio-Rad FTS 6000 Digilab FT-IR spectrometer equipped with a Ge MIRacle single reflection using 32 co-added scans. The particle sizes and particle size distributions of latexes were measured by dynamic light scattering (Microtrac UPA 150).

Synthesis of α-(Chloromethyl)acryloyl Chloride (CMAC) A. t-BHMA (20 g, 0.126 mol) and excess of thionyl chloride were added to a 100 mL round-bottom flask and stirred at ambient temperature for 24 h. Most of the thionyl chloride was removed under vacuum. Vacuum distillation of the residue gave α-(chloromethyl)acryloyl chloride as a clear liquid in ca. 60% yield. FT-IR (cm^{-1}, NaCl): 3107, 2966, 1742, 1637, 1407, 1284, 967, 896. ^{1}H NMR ($CDCl_3$, δ): 4.26 (s, 2H, CH_2Cl), 6.41 and 6.74 (s, 2H, $CH_2{=}C$). ^{13}C NMR ($CDCl_3$, δ): 41.53 (CH_2Cl), 136.14 ($CH_2{=}C$), 141.14 ($C{=}CH_2$), 166.78 ($C{=}O$).

Synthesis of MPEG α-(Chloromethyl)methacrylate (MPCMA) B. In a 250 mL round-bottom flask, poly(ethylene glycol) methyl ether (20 g, 57.1 mmol) was added to 100 mL of dried THF. The solution was stirred at −10 °C for 30 min. CMAC (10.32 g, 74.3 mmol) diluted in 50 mL of dried THF was then added dropwise to the stirring mixture. The resulting mixture was stirred overnight at room temperature. The precipitate was filtered off, and the solvent was removed under reduced pressure. Excess CMAC was removed by washing the crude oil with aliquots (3×60 mL) of hexane to give MPCMA as a light brown oil in ca. 94% yield. FT-IR (cm^{-1}, NaCl): 3407, 1742, 1641, 1407, 1118, 812. ^{1}H NMR ($CDCl_3$, δ): 4.30 (s, 2H, CH_2Cl), 6.01 and 6.41 (s, 2H, $CH_2{=}C$), 4.35 (t, 2H, $CH_2C{=}CH_2$), 3.38 (s, 1H, CH_2OCH_3), 3.61 (s, 2H, CH_2CH_2O). ^{13}C NMR ($CDCl_3$, δ): 41.53 (CH_2Cl), 128.96 ($CH_2{=}C$), 136.74 ($C{=}CH_2$), 164.85 ($C{=}O$), 64.32 ($CH_2C{=}O$), 70.54 (CH_2O), 58.99 (CH_2OCH_3).

Synthesis of the Surfmers S1−S3. First, potassium salts of stearic acid, decanoic acid, and benzoic acid were obtained by mixing at room temperature in THF the corresponding acid (1 mol) and potassium hydroxide (1.05 mol) in slight excess. The salts were then collected by filtration of the crude mixture and dried overnight at 60 °C in a vacuum oven. In a 250 mL round-bottom flask, the corresponding acid potassium salt (26.1 mmol) was dispersed in THF. MPCMA was then added to the salt solution dropwise at room temperature. The resulting mixture was allowed to stir at room temperature for 24 h. The precipitate was filtered off and the solvent removed under reduced pressure to give the corresponding monomers in quantitative yields.

Surfmer S1. FT-IR (cm^{-1}, NaCl): 3492, 2871, 1730, 1641, 1118. ^{1}H NMR ($CDCl_3$, δ): 4.77 (s, 2H, CH_2O), 5.81 and 6.34 (s, 2H, $CH_2{=}C$), 4.30 (t, 2H, $CH_2C{=}CH_2$), 3.34 (s, 1H, CH_2OCH_3), 3.61 (s, 2H, CH_2CH_2O). ^{13}C NMR ($CDCl_3$, δ): 62.13 ($CH_2C{=}CH_2$), 127.42 ($CH_2{=}C$), 135.30 ($C{=}CH_2$), 165.09 ($C{=}O$), 173.13 ($C{=}O$), 64.09 ($CH_2C{=}O$), 70.56 (CH_2O), 59.01 (CH_2OCH_3), 14.13 (CH_3CH_2), 22.68 (CH_2CH_3), 24.91 ($CH_2CH_2C{=}O$), 29.68 (CH_2), 31.92 ($CH_2CH_2CH_3$), 34.19 ($CH_2C{=}O$).

Surfmer S2. FT-IR (cm^{-1}, NaCl): 3490, 2872, 1731, 1641, 1118. ^{1}H NMR ($CDCl_3$, δ): 4.78 (s, 2H, CH_2O), 5.82 and 6.32 (s, 2H, $CH_2{=}C$), 4.31 (t, 2H, $CH_2C{=}CH_2$), 3.32 (s, 1H, CH_2OCH_3), 3.61 (s, 2H, CH_2CH_2O). ^{13}C NMR ($CDCl_3$, δ): 62.10 ($CH_2C{=}CH_2$), 127.38 ($CH_2{=}C$), 135.28 ($C{=}CH_2$), 165.04 ($C{=}O$), 173.06 ($C{=}O$), 64.07 ($CH_2C{=}O$), 70.54 (CH_2O), 58.98 (CH_2OCH_3), 14.12 (CH_3CH_2), 22.66 (CH_2CH_3), 24.88 ($CH_2CH_2C{=}O$), 29.65 (CH_2), 31.89 ($CH_2CH_2CH_3$), 34.16 ($CH_2C{=}O$).

Surfmer S3. FT-IR (cm^{-1}, NaCl): 3492, 1740, 1641, 1622, 1118. ^1H NMR ($CDCl_3$, δ): 5.04 (s, 2H, $\mathrm{CH_2O}$), 5.93 and 6.42 (s, 2H, $\mathrm{CH_2{=}C}$), 4.33 (t, 2H, $\mathrm{CH_2C{=}CH_2}$), 3.34 (s, 1H, $\mathrm{CH_2OCH_3}$), 3.61 (s, 2H, $\mathrm{CH_2CH_2O}$), 8.04 (t, 1H, $\mathrm{CH{=}C}$), 7.44 (t, 1H, $\mathrm{CH{=}CH}$), 7.54 (t, 1H, $\mathrm{CH{=}CHCH}$). ^{13}C NMR ($CDCl_3$, δ): 62.77 ($\mathrm{CH_2C{=}CH_2}$), 127.73 ($\mathrm{CH_2{=}C}$), 135.18 ($\mathrm{C{=}CH_2}$), 165.07 ($\mathrm{C{=}O}$), 165.84 ($\mathrm{C{=}O}$), 64.14 ($\mathrm{CH_2C{=}O}$), 70.49 ($\mathrm{CH_2O}$), 58.96 ($\mathrm{CH_2OCH_3}$), 129.77 ($\mathrm{C{=}CO}$), 129.62 ($\mathrm{CH{=}C}$), 128.42 ($\mathrm{CH{=}CH}$), 133.17 ($\mathrm{CH{=}CHCH}$).

Synthesis of 2,2-Bis(acetoxymethyl)-propionic Acid. In a 250 mL Erlenmeyer flask, 2,2-bis(hydroxymethyl)-propionic acid (15 g, 0.11 mol) and acetic anhydride (23.79 g, 0.233 mol) in slight excess were mixed overnight . The excess acetic anhydride was removed by vacuum distillation of the crude residue to give 2,2-bis(acetoxymethyl)-propionic acid as a white solid in ca. 99% yield. FT-IR (cm^{-1}, KBr): 2929, 1745, 1376, 1234. ^1H NMR ($CDCl_3$, δ): 2.08 (s, 3H, $\mathrm{CH_3C{=}O}$), 1.29 (s, 3H, $\mathrm{CH_3C}$), 4.25 (s, 2H, $\mathrm{CH_2C{=}O}$), 11.58 (OH). ^{13}C NMR ($CDCl_3$, δ): 17.77 ($\mathrm{CH_3C}$), 20.76 ($\mathrm{CH_3C{=}O}$), 46.0 ($\mathrm{CCH_3}$), 65.29 ($\mathrm{CH_2C{=}O}$), 170.95 ($\mathrm{C{=}O}$), 178.44 ($\mathrm{C{=}O}$).

Synthesis of Surfmer S4. To a 250 mL round-bottom flask containing 75 mL of dry THF was added MPCMA (15 g, 33.1 mmol) and triethylamine (4.7 mL, 33.1 mmol). To the stirring solution was added 2,2-bis(acetoxymethyl)-propionic acid dropwise. The resulting mixture was allowed to stir overnight at room temperature. The precipitate was filtered off and the solvent removed under reduced pressure to give the surfmer S4 as a light brown oil in ca. 95% yield. FT-IR (cm^{-1}, NaCl): 2871, 2930, 1730, 1641, 1119. ^1H NMR ($CDCl_3$, δ): 1.27 (s, 3H, $\mathrm{CH_3C}$), 2.06 (s, 3H, $\mathrm{CH_3C{=}O}$), 3.38 (s, 3H, $\mathrm{CH_3O}$), 4.24 (s, 2H, $\mathrm{CH_2C}$), 4.34 (t, 2H, $\mathrm{CH_2OC{=}O}$), 4.87 (s, 2H, $\mathrm{CH_2C{=}O}$), 5.86 and 6.41 (s, 2H, $\mathrm{CH_2{=}C}$). ^{13}C NMR ($CDCl_3$, δ): 17.80 ($\mathrm{CH_3C}$), 20.71 ($\mathrm{CH_3C{=}O}$), 46.27 ($\mathrm{CCH_3}$), 63.03 ($\mathrm{CH_2C{=}CH_2}$), 58.99 ($\mathrm{CH_2OCH_3}$), 64.14 ($\mathrm{CH_2C{=}O}$), 65.35 ($\mathrm{CH_2C{=}O}$), 70.49 ($\mathrm{CH_2O}$), 127.73 ($\mathrm{CH_2{=}C}$), 134.83 ($\mathrm{C{=}CH_2}$), 164.82, 170.50, and 172.15 ($\mathrm{C{=}O}$).

Synthesis of Surfmer S5. In a 250 mL round-bottom flask, pentadecafluoro-1-octanol (10.42 g, 26.1 mmol) was mixed with potassium hydroxide (1.46 g, 26.1 mmol) in THF (100 mL) for 5 h. MPCMA (13 g, 19.9 mmol) diluted in 30 mL of dried THF was then added dropwise. The resulting mixture was allowed to stir at 60 °C for 24 h. The precipitate was filtered off and the solvent removed under reduced pressure to give surfmer S5 as a light brown oil in ca. 89% yield. FT-IR (cm^{-1}, NaCl): 3490, 1730, 1641, 1118, 936, 813. ^1H NMR ($CDCl_3$, δ): 3.32 (s, 3H, $\mathrm{CH_3O}$), 3.99 (m, 2H, $\mathrm{CH_2CF_2}$), 4.28 (t, 2H, $\mathrm{CH_2OC{=}O}$), 4.31 (s, 2H, $\mathrm{CH_2O}$), 5.86 and 6.33 (s, 2H, $\mathrm{CH_2{=}C}$). ^{13}C NMR ($CDCl_3$, δ): 58.85 ($\mathrm{CH_3O}$), 61.43 ($\mathrm{CH_2C{=}CH_2}$), 63.93 ($\mathrm{CH_2C{=}O}$), 67.64 ($\mathrm{CH_2CF_2}$), 72.54 ($\mathrm{CH_2O}$), 127.14 ($\mathrm{CH_2{=}C}$), 135.75 ($\mathrm{C{=}CH_2}$), 165.27 ($\mathrm{C{=}O}$).

Solution Free-Radical Homopolymerization of Surfmers 1−5. In a typical polymerization procedure, the surfmer (2 mmol) was dissolved in deionized water (20 mL) and stirred under nitrogen for 30 min in a 100 mL round-bottom flask. The temperature was gradually increased and stabilized at 70 °C. Ammonium persulfate (0.045 g, 0.2 mmol) was dissolved in water (1 mL) and added to the stirring solution in one portion. The solution was allowed to stir for 4 h under nitrogen atmosphere. The resulting polymer was filtered off and dried overnight in a vacuum oven to give the corresponding homopolymer.

Solution Free-Radical Copolymerization of Surfmers 1−5 and MMA. In a typical copolymerization procedure, the surfmer (1.97 mmol) and MMA (0.79 g, 7.91 mmol) were mixed in 10 mL of THF, under nitrogen, in a 50 mL three-neck round-bottom flask equipped with a condenser. The solution temperature was gradually brought to 60 °C. The resulting solution was allowed to stir for 30 min prior to addition of AIBN (0.031 g, 0.188 mmol) in one portion, which had been predissolved in THF. The flask was sealed, and the solution was stirred for 24 h under nitrogen atmosphere. The final copolymer was isolated by precipitating in hexane.

Latex Preparation. MMA/BuA/AA copolymer latexes were prepared by means of seeded semicontinuous emulsion polymerization. This polymerization technique has been chosen because it allows good control of the reaction batch temperature, particle nucleation, final particle size, and particle size distribution. The recipe for the seed is given in Table 2, and the recipe for the seeded reaction is given in Table 3. The reactions were carried out in a 500 mL glass reactor equipped with a reflux condenser, a stainless steel stirrer (200 rpm speed), a nitrogen inlet, and a water bath for temperature control. The seed was prepared by means of batch emulsion polymerization using the following procedure. The monomers, water, and the surfactant were mixed together, and the resulting mixture was poured into the reactor placed in a water bath, temperature controlled at 65 °C, and allowed to stir for 30 min under a nitrogen blanket. The initiator (APS) was dissolved in 2.5 mL of water and injected into the reactor. The reaction was carried out overnight to ensure complete monomer conversion. The final seed latex had a solids content of 30% and a final average particle size of 89 nm determined by dynamic light scattering (DLS) measurements. Two separated streams were used in the preparation of the final latex; one with the neat monomers and the other which contained the surfactant, initiator, and buffer. Feeding of the streams was achieved by use of two Masterflex diastolic pumps (Cole-Parmer Instrument Co.), one each for the monomer and the aqueous streams. The addition of both monomer and aqueous solution was controlled by a Camille 2000 data acquisition system (Dow, Camille Products, LLC) coupled to the Camille TG (v4.0.5) acquisition software. In these reactions, the initial charge was purged with nitrogen for 30 min, before starting the feeding. After the feeding period, the system was left to react overnight to ensure high monomer conversion.

Table 2. Recipe Used To Obtain the Seed (30% Solids)

compound	seed (g)
water	300
MMA	33.75
BuA	82.5
AA	4
surfactant (SDS)	2.3
initiator (APS)	1.15
total	323.7

Table 3. Recipe Used in the Semicontinuous Emulsion Polymerizations[a] (50% Solids)

compound	initial charge (g)	feed 1 (g)	feed 2 (g)
seed	52		
H_2O	100		50
MMA	1.88	20	
BuA	4.10	44	
AA		2	
surfactant			3
APS	0.02		0.30
$NaHCO_3$			0.70
Total	158	66	53

[a] Reaction conditions: $T = 65$ °C; stirring rate = 200 rpm; reaction time in semibatch = 2 h; reaction time in batch = 2 h; flow rate 1 = 0.55 g/min; flow rate 2 = 0.45 g/min.

Latex Characterizations. At the end of the reaction, samples were taken to determine the particle size via DLS measurements. The mean particle size was measured by light scattering (Microtrack UPA 150). The amount of coagulum was measured by collecting the coagulum on the reactor wall and stirrer and by filtering the latex. The result is presented as weight of coagulum per total weight of monomer added. Gravimetric analysis was performed to determine the percentage of solids in the final latex product and the percentage conversion for the corresponding emulsion polymerization. The latex (1 g) was poured into a preweighed vial. The polymer was precipitated by the addition of methanol. Methanol was decanted off, and the polymer was washed several times with aliquots of methanol to remove any unreacted monomer, surfmer, or initiator. The vial was then placed in a vacuum oven to remove the methanol. The resulting polymer weight was then compared to the original emulsion solids content to determine the overall monomer conversion. The latexes were centrifuged, and analysis

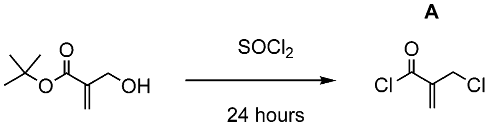


Figure 2. Synthesis of α-(chloromethyl)acryloyl chloride (CMAC).

via NMR spectroscopy of both the final serum after centrifugation and the recovered polymer allowed the evaluation of the final reactive surfactant incorporation.

Film Formation. Latexes were drawn down on a glass microslide substrate (carefully washed with acetone and deionized water prior to latex deposition) using a 3 mil draw-down bar and allowed to dry at room temperature overnight. The films formed were then used in the AFM measurements.

Latex Stability. The stability of the latexes synthesized was assessed by the following method. To 1 g of latex, the same amount of the electrolyte test solutions (0.1 M $MgSO_4$, 0.1 M NaCl, 0.5 M NaCl, and 1.0 M NaCl) was added and the time for flocculation to occur was assessed visually. For the freeze−thaw test, a small amount of the latex (2 mL) was kept at −20 °C for 24 h. After 24 h at room temperature, the flocculation of latex sample was assessed by visual observation.

Scanning Electron Microscopy (SEM). Particle morphology and particle distribution were visualized using SEM. In a typical sample preparation, the specimen was prepared by depositing a diluted latex onto a carbon adhesive tab, allowing it to dry, and then coating the dried residue with gold (5 nm) using a sputter coater Emitech K550X. The images were obtained with a FEI Quanta 200 SEM under high vacuum conditions.

Atomic Force Microscopy (AFM). Surface topography of the films formed by spreading on glass microslide the corresponding latex was investigated. The topography of the air−film surface was characterized using a Dimension 3000 scanning probe microscope (Digital Instruments, Santa Barbara, CA). The probe for surface topography was purchased from Veeco probes, CA. Surface topography and roughness were obtained in tapping mode using an etched silicon probe, 125 μm long with a resonant frequency of 275 kHz, nominal force constant of 40 N/m, and a nominal tip radius of 10 nm. Height and phase images were collected simultaneously on 5 μm × 5 μm scan size with an image resolution of 256 × 256 pixels at a scan rate of 1 Hz. Surface roughness and section analysis were performed on 5 μm × 5 μm scan area for all the samples using NanoScope v5.30 r2 image analysis software.

Results and Discussion

Synthesis and Characterization of the Surfmers. All the reactive surfactants synthesized are composed of a hydrophobic part, a polymerizable double bond, and a hydrophilic part. In this study, the hydrophobic part is either an aliphatic, aromatic, or perfluorinated moiety while the hydrophilic part in all cases is a poly(ethylene glycol) methyl ether moiety. Different hydrophobic moieties were incorporated in order to determine their effect on particle stability during the emulsion polymerization as well as the final polymer characteristics. A methacrylate group links both hydrophobic and hydrophilic moieties and constitutes the reactive site. This group will become involved in the emulsion copolymerization reactions with MMA, BuA, and AA. These macromonomers were all synthesized by functionalization of the α-(chloromethyl)acryloyl chloride (CMAC) intermediate A, which was synthesized according to the synthetic scheme presented in Figure 2. This compound allows two different functional groups to be incorporated on either side of the polymerizable double bond. The reactive surfactants shown in Table 1 were synthesized following the general synthetic routes presented in Figure 3.

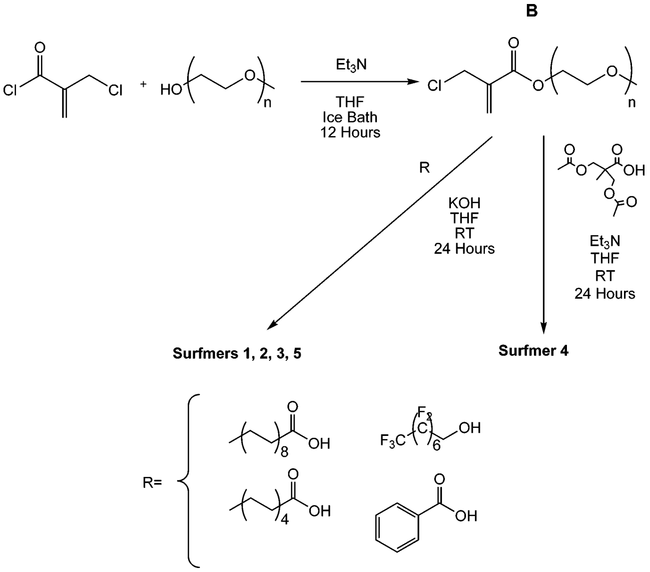


Figure 3. Synthesis of surfmers S1−S5.

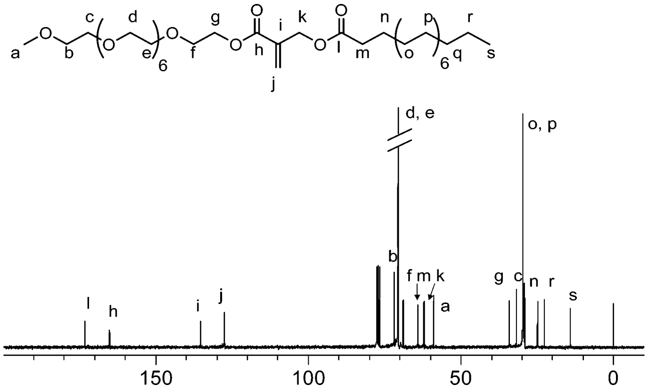


Figure 4. ^{13}C NMR spectrum of surfmer S1 ($CDCl_3$).

MPEG of molecular weight 350 g/mol, chosen to constitute the hydrophilic part of these molecules, was first reacted with CMAC to form the intermediate MPCMA (structure B in Figure 3) that was subsequently reacted with different carboxylic acids or alcohols in the presence of a base. To form surfmers S1, S2, and S3, MPCMA was reacted at room temperature with different aliphatic and aromatic carboxylic acid potassium salts. This mild procedure gave high purity products in high yields after filtration of the reaction mixture and evaporation of the solvent. ^{1}H NMR was used to follow the formation of the desired products by monitoring the appearance of the proton peaks at 4.78, 4.77, and 5.04 ppm corresponding to the α-methylene protons of the ester form of the respective monomers. The surfmer S4 was synthesized following the same procedure by reaction of MPCMA with the potassium salt of 2,2-bis(acetoxymethyl)-propionic acid; the acid was obtained by the reaction of 2,2-bis(hydroxymethyl)-propionic acid and an excess of acetic anhydride at room temperature. The fluorinated surfmer S5 was obtained by the reaction of MPCMA and pentadecafluoro-1-octanol in the presence of potassium hydroxide. The structures of the different intermediates and macromonomers were confirmed by ^{1}H and ^{13}C NMR and FT-IR, while their purity was evaluated by HPLC (Table 1). As an example, ^{13}C NMR and FT-IR spectra of S1 are shown in Figures 4and 5.

Homopolymerization of the Reactive Surfactants. In the first series of experiments, the homopolymerization of the reactive surfactants S1−S5 in water was investigated in order to determine their capacity to homopolymerize in an aqueous medium. The results of these experiments are given in Table 4. The monomers were all homopolymerized in deionized water

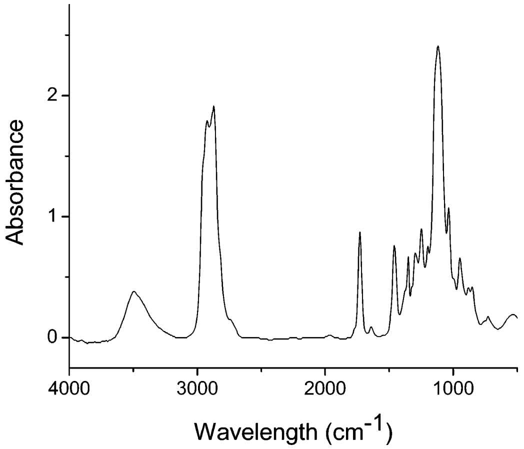


Figure 5. FT-IR spectrum of surfmer S1 (NaCl).

Table 4. Homopolymerization Characteristics of Surfmers S1−S5

sample	surfmer	solvent	M_n/1000 (g/mol)	PDI	conversion[a] (%)
H1	S1	water	3.9	1.23	62.3
H2	S2	water	6.7	1.4	54.2
H3	S3	water	5.3	1.32	40.3
H4	S4	water			*b*
H5	S5	water	6.8	1.5	70.1

[a] Determined by gravimetry. [b] No polymer was formed.

at 80 °C using ammonium persulfate as the water soluble initiator. Polymerizations were carried out for 24 h to ensure maximum conversions. As shown in Table 4, low yields and low molecular weights were obtained for all systems. All these polymers precipitated from the solution during polymerization due to agglomeration of the growing chains. Attempts to polymerize these monomers in organic solvents, for example, tetrahydrofuran, gave even lower molecular weight polymers. This suggests that preorganization of the amphiphilic molecules in water by the formation of micelles leads to higher degrees of polymerization in aqueous medium than in organic solvent. It is well-known that polymeric surfactants show generally lower values of critical micelle concentration (cmc) than those of small molecules. Thus, in aqueous medium, the amphiphilic molecules will be above their cmc and arranged into micelles. However, the critical concentration is continually decreasing during homopolymerization as the polymeric chain is growing. At the same time, the homopolymer has a vastly reduced degree of freedom in which to orientate themselves due to the steric restrictions placed on them by their neighboring monomers. Both of these factors restrict the ability of the surfmers to organize themselves into micelles, and their influence on the system continues to increase until the point when agglomeration occurs resulting in the precipitation of the polymer in water. It should be noticed that surfmer polymerization in the aqueous phase should be minimized because it can promote flocculation and wasting of the surfmer.

Copolymerization of the Reactive Surfactants. During the course of emulsion polymerization, the surfmer may be incorporated into the polymer backbone by both copolymerization and chain transfer to the surfmer. The extent of surfmer copolymerization depends on the reactivity ratios of the surfmer and the monomers. In the second series of experiments, copolymerization of the reactive surfactants S1−S5 in THF has been investigated in order to determine their capacity to copolymerize with a less bulky monomer, methyl methacrylate. The ^{13}C NMR spectra of a typical surfmer (S1) and the corresponding copolymer with methyl methacrylate are shown in Figures 4 and 6. The disappearance of the resonances corresponding to the vinyl carbons of the monomers and their appearance as backbone peaks is consistent with the surfmer having undergone vinyl polymerization. The copolymerization results shown in Table 5 suggest that these monomers have copolymerized well with the corresponding comonomer, with the surfmer incorporation being fairly close to the monomer feed ratio.

Earlier studies showed that hydroxymethylacrylate esters (RHMA)-based monomers lead essentially to random copolymers when copolymerized with MMA. Similar copolymerizations were carried out with *n*-butyl acrylate also showing high incorporation of the amphiphilic comonomer in the final copolymer. As mentioned earlier, the reactivity of the surfmer and its adsorption characteristics are critical in surfmer performance. The surfmer should not homopolymerize too efficiently in order to avoid destabilization of the latex particles as they are forming. Furthermore, to minimize the negative effects on the final material performance (a) the reactive surfactant conversion should be high at the end of the polymerization to ensure there is little or no free surfactant in the final polymer and (b) large amounts of surfmer homopolymerization should be avoided to minimize the presence of surface active, amphiphilic polymeric coproducts. It is believed that a competition between homopolymerization and copolymerization will take place during the emulsion polymerization, and the observed balance between the homo and copolymerization behavior of the surfmers reported in this study suggests that they have great potential for use in heterophase polymerization techniques. This is because their molecular structure has been demonstrated to lead to a preference toward efficient copolymerization with monomers such as MMA and BuA. Thus, during the course of the emulsion polymerization, they will not produce significant amounts of the homopolymer due to their relative bulkiness nor will they leave unreacted surfmer due to their high potential toward copolymerization.

Emulsion Polymerizations. High solids content MMA/BuA/AA (29/69/2) latexes were prepared via seeded semicontinuous emulsion polymerizations. Table 6 lists the percentage of coagulum and the particle size of the latexes investigated.

These data show that a high conversion of monomers was achieved as determined by gravimetry. No vinyl peak from the double bond of the reactive surfmers could be noticed in the ^1H NMR spectra (D_2O) of the latexes, suggesting high incorporation of the surfmer into the polymer. Further characterization of the centrifuged latexes was attempted using NMR spectroscopy. NMR-supported analysis of the final serum after centrifugation systematically showed that no surfmer was remaining. This result indicates either that complete incorporation occurred or that centrifugation was not effecient in eliminating the physically adsorbed species. Then, for all latexes, the recovered polymer was washed with hot methanol in order to remove the adsorbed species and was analyzed by ^1H NMR spectroscopy in $CDCl_3$ solution. ^1H NMR allowed determining the incorporation of surfmer in the final copolymer produced by heterophase polymerization. As an example, Figure 7 shows ^1H NMR spectra of both the surfmer S1 and the corresponding polymer recovered from latex L1. Proton peaks at 3.64 and 1.25 ppm were observed in the polymer spectrum corresponding to the MPEG and the hydrocarbon unit of S1, respectively. This attests to the efficient incorporation of the surfmer in the final polymeric matrix.

Although surfmers S1, S2, S3, and S5 lead to stable polymeric emulsions, coagulation occurred during the emulsion polymer-

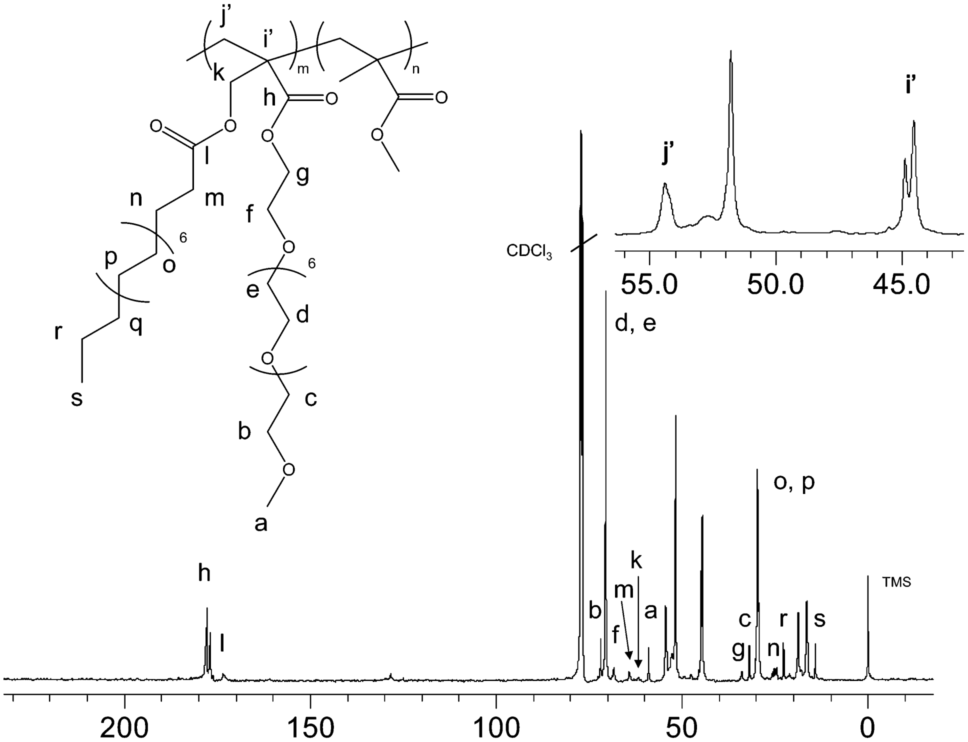


Figure 6. ^{13}C NMR spectrum of S1-*co*-MMA copolymer ($CDCl_3$).

Table 5. Copolymerizations Characteristics of Surfmers S1−S5

sample	surfmer−MMA molar feed ratio	solvent	temp (°C)	M_n/1000 (g/mol)	PDI	yield (%)	surfmer incorporation[a] (%)
P0	0	THF	65	20.52	1.22	98.0	
P1	1:4	THF	65	17.0	1.48	97.3	92.5
P2	1:4	THF	65	17.5	1.32	88.7	75.5
P3	1:4	THF	65	19.4	1.35	91.2	98
P4	1:4	THF	65	18.5	1.41	92.4	78
P5	1:4	THF	65	17.2	1.25	82.0	83

[a] Determined by analysis of ^{1}H NMR spectra of copolymers.

ization involving S4 and no stable latex could be formed. It is believed that the high degree of hydrophilicity of the surfmer S4 compared to the other surfactants resulted in an inability to efficiently stabilize the growing particles during the polymerization process, because too much surfmer was loaded into the aqueous phase. In all the emulsion polymerizations reported in this paper, the amount of surfmer added to form the latex was approximately 1 mol % as shown in Table 6. This value could be lowered as the critical micelle concentration (cmc) of some of these surfactants was much lower than the fixed surfactant concentration. For instance, the cmc for surfmer S1 was evaluated to 0.095 g/L.

Apparent molecular weights obtained for the corresponding surfmer latexes formed are summarized in Table 7. We observed a wide range of molecular weights for the latexes obtained. These differences may be attributed to some degree of secondary nucleation arising during the polymerization. For instance, the lower molecular weight observed for latex L3 may be due to the higher degree of hydrophilicy of this compound compared to those of other reactive surfactants investigated. It should be noticed that these data are based on polystyrene standards and that some degree of incertitude should be taken in account when considering these results. Nevertheless, we should expect some impact on the final molecular weight of the polymer as the hydrophilicity of the corresponding surfactant is increased.

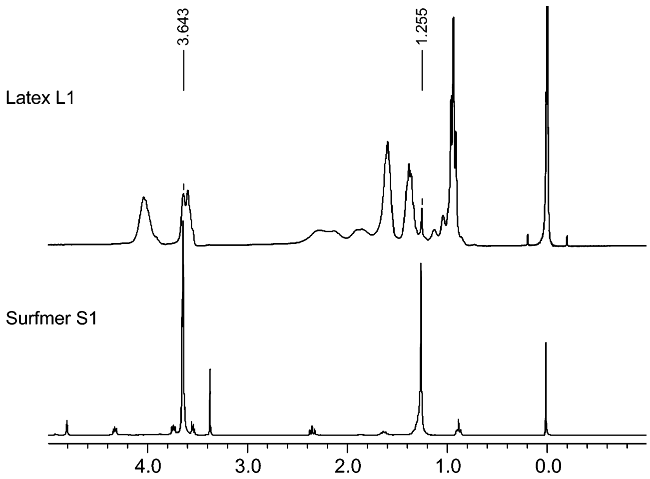


Figure 7. ^{1}H NMR spectra of latex L1 and surfmer S1 ($CDCl_3$).

Table 6. Characteristics of the Final Latexes

latex	surfactant	feed time (h)	Dp seed (nm)	surfactant concn (wt %/mol %)	initiator/ (g)	coagulum (%)	Dp (nm)	PDI (nm)[d]	appearance of latex
L0	SDS	2	89	1 mol %	APS/ 0.30	<1	151.3	43.2	*a*
L1	S1	2	89	4.16/1.00	APS/ 0.32	2.5	163.4	75.2	*a*
L2	S2	2	89	4.03/1.15	APS/ 0.34	1.5	171.5	65.7	*a*
L3	S3	2	89	4.04/1.26	APS/ 0.30	<1	190.3	67.5	*b*
L4	S4	2	89	4.10/1.08	APS/ 0.30				*c*
L5	S5	2	89	4.14/0.85	APS/ 0.31	1.7	164.5	54.6	*b*

[a] Typical latex appearance. [b] Very thick latex. [c] Emulsion polymerization was not successfully achieved. [d] Particle size polydispersity index.

Table 7. Molecular Weights of Latexes

latex	surfactant	M_n/1000 (g/mol)	M_w/1000 (g/mol)	PDI	conversion (%)[a]
L0	SDS	220.3	386.4	1.75	95
L1	S1	158.3	350.7	2.22	98
L2	S2	183.1	384.9	2.10	96
L3	S3	84.9	204.4	2.40	99
L5	S5	284.4	358.6	1.26	94

[a] Determined by gravimetry.

Evolution of the particle size during the polymerization reaction was followed for each system by withdrawing aliquots of the latex at different times and carrying out DLS measurements. The particle size evolution for each system is shown in Figure 8. It was found that the final particle size was obtained after 4 h by analysis of the data collected over a 24 h period. DLS measurements also showed that low particle size polydispersity indexes were obtained for all latexes investigated (Table 6). As an example, DLS distribution profile corresponding to latex L1 is shown in Figure 9. SEM allowed confirming this data as shown in Figure 10 (latex L5). The SEM pictures were taken in the high vacuum mode and the particle size and particle size distribution could be seen to be in good agreement with the DLS measurements.

As reported in Table 6, a low amount of the coagulum was noted, suggesting a low amount of destabilization during the heterophase polymerization. Unzué et al. reported that in a similar reaction at 50% solids with 1 mol % of nonionic methacrylate-based reactive surfactant a large amount of coagulum was obtained.[22] It was suggested that this behavior was a consequence of the homopolymerization of methacrylate surfmer in the aqueous phase, leading to the formation of a type of water soluble polymer capable of causing bridging flocculation. By comparison, while homopolymerization of the surfmers S1−S5 is certainly possible, as shown in the homopolymerizations reported earlier in this paper, the low amount of coagulum that was observed in the emulsion polymerizations detailed in this study suggests that these materials exhibit low amounts of homopolymerization and are able to copolymerize efficiently during the heterophase polymerization. Thus, it is concluded that the molecular design of the surfmers in this work has successfully influenced the balance between aqueous phase homopolymerization and heterophase copolymerization such that their performance is better tuned toward achieving a successful emulsion polymerization, which produces a high-quality final polymer than other reactive surfactants used in the past.

Film Surface Morphology. During setting and drying of a latex film, any surfactant that is only physically adsorbed (and not chemically bound) to the resulting polymer may either remain at the particle surface or phase separate with the polymer. If the surfactant undergoes phase separation, the water flux may carry it to the film surface. Alternatively, it may accumulate in the interstices between the particles. From there it will migrate to the film−air or film−substrate interface through a long-term exudation process. The surfactant may also segregate from the matrix and form aggregates and pockets that could affect the overall polymer properties. The mobility of surfactants during film formation has been widely studied using a wide range of different techniques such as attenuated total reflectance FT-IR, transmission electron microscopy, X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and AFM.[46−50] AFM is an attractive technique due to the fact that it is nondestructive.[48] In this study, AFM was used to observe the surface morphology of the films directly and also to evaluate the roughness of the tested film before and after exposing to water. This technique allowed the particle sizes previously determined via dynamic light scattering to be confirmed, as the AFM measurements of the particle sizes and particle size distributions for all latexes were in good agreement with DLS measurements. Figure 11 shows typical AFM pictures (height and phase) obtained under tapping mode conditions for the films studied where individual latex particles could be observed.

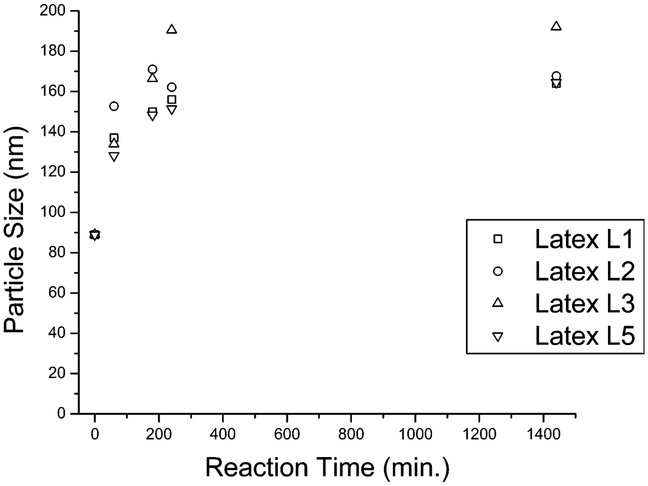


Figure 8. Particle size evolution for each latex.

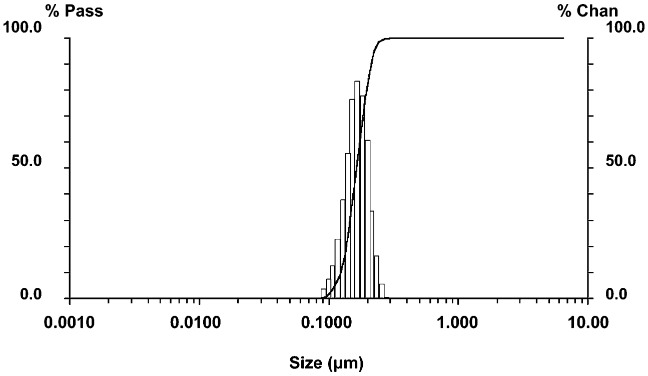


Figure 9. Particle size distribution profile of the final latex L1 determined by laser light scattering.

Asua and co-workers showed that the surface of a film incorporating conventional nonreactive surfactants such as sodium lauryl sulfate is totally covered with the surfactant, obscuring the individual particle identities. In our study, this behavior could be confirmed as no particle could be identified by AFM characterization of the film incorporating sodium dodecyl sulfate (SDS). However, the particles appeared well defined for all the other films by AFM measurements, attesting to low migration of the surfactant upon film formation. Furthermore, the narrow polydispersities previously reported by DLS measurements were also found to be in good agreement with the AFM results for all films formed. Differences in the root-mean-square surface roughness between the original film and the film washed with deionized water were determined by AFM for each system as reported in Table 8. The nonbonded and highly water soluble reactive surfactant should be washed away when rinsed with deionized water. The roughness of the remaining film is caused by disruption of the particle packing by the migrating surfactant phase, as described by Juhué, et al.[49] Very little difference could be observed in roughness measurements for these systems compared to the film incorporating SDS as the surfactant, which is consistent with the conclusion that surfactant migration has been minimized in these systems.

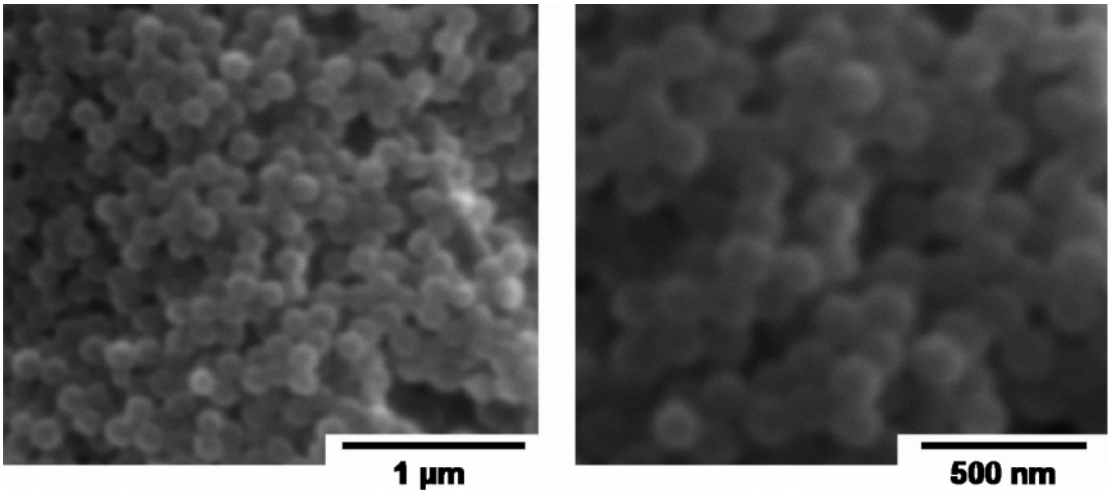


Figure 10. SEM micrographs of latex L5.

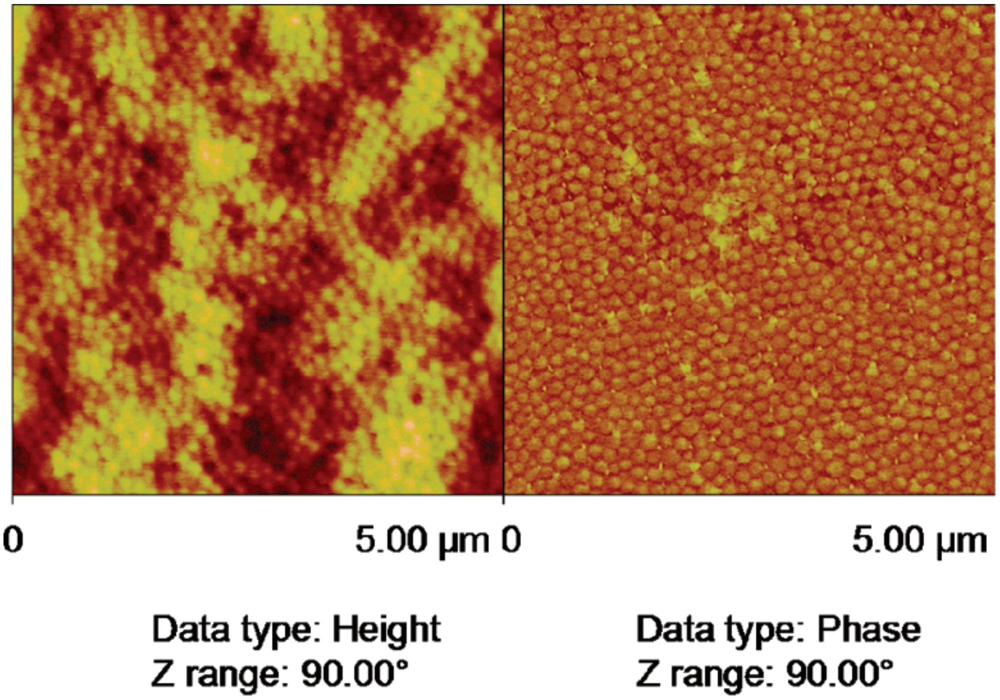


Figure 11. Height and phase images of the film obtained from latex L5 on glass substrate (5 μm × 5 μm).

Table 8. Roughness Analysis Results Conducted Using Atomic Force Microscopy of the Films Obtained from the Latexes

latex	roughness (nm)	Dp (nm)
L0 (neat)	5.14	n/a
L0 (washed)	14.32	
L1 (neat)	3.04	173.5
L1 (washed)	3.23	
L2 (neat)	3.44	162.5
L2 (washed)	3.23	
L3 (neat)	2.87	194.5
L3 (washed)	3.56	
L5 (neat)	2.08	166.7
L5 (washed)	2.10	

Table 9. Freeze−Thaw Test and Stability in Different Electrolyte Solutions[a]

latex	0.1 M NaCl	0.5 M NaCl	1.0 M NaCl	0.1 M $MgSO_4$	freezing −20 °C
L1	++	+++	+++	+++	+++
L2	+++	+++	++	+++	+++
L3	++	+	+	+	+++
L5	++	++	++	+	+++

[a] Legend: +++ immediate flocculation; ++ partly flocculated after 1 day; + complete flocculation after 1 month.

Latex Stability. The stability of the polymeric emulsions produced was assessed by addition of certain amount of electrolyte solution to the corresponding latexes. The results are summarized in Table 9. All latexes showed entire flocculation after 24 h at −20 °C. However, the latexes showed differences in flocculation behavior depending on the electrolyte solution used in the test. Latexes that incorporated surfmers S3 and S5 were found to be the most stable latexes. Structure−property relationship of the surfmers is currently in progress to better understand this behavior.

Conclusion

New acrylate-based, nonionic reactive surfactants were specifically designed to optimize the reactivity of the surfmer by balancing the bulkiness of the macromeric surfmers with the reactivity of the polymerizable double bond they contained. The aim of the design was to create species which had a more reactive double bond that is usually found in nonmigratory surfactants to maximize the incorporation into the emulsion polymer and thus reduce any secondary interfacial effects and leaching of the surfmer during the course of the polymerization. These target molecules were synthesized successfully and used in high solids content emulsion polymerization of butyl acrylate, methyl methacrylate, and acrylic acid. Analysis of the final polymers from these emulsion reactions via NMR supports the conclusion that a high level of surfmer incorporation into the emulsion polymer was achieved. Additionally, a low level of coagulum was observed in these reactions, suggesting a high stability of the emulsion during the reaction. Well-defined particles and narrow particle size distributions were observed by DLS and confirmed by other microscopic measurements (SEM and AFM). Homogeneous and transparent films were formed from the latexes which exhibited little difference in surface roughness values between the neat films and the films washed extensively with deionized water. This latter result suggests a very low degree of surfactant migration through the polymeric matrix during the film formation. Additionally, the AFM images clearly showed the presence of individual latex particles which again supports the conclusion that the macromeric surfmer is highly incorporated into the polymeric film. Thus, it is concluded that these surfmers impart very interesting and beneficial properties to the emulsion polymerizations conducted in this study. Thus, this strategy of attempting to optimize the balance between the reactivity of the double bond and the bulkiness of the molecules has delivered real benefit to the heterophase polymerization systems investigated. This balance of surfmer reactivity allows the amphiphilic surfmer molecules to stabilize the growing polymer particles and to be incorporated within the final copolymer. These factors lead to the production of films which present reduced water sensitivity compared to those made using conventional surfactants. These new acrylate-based reactive surfactants open up a new library of amphiphilic monomers that can stabilize efficiently the growing polymeric particles in acrylic emulsion polymerizations and confer higher stability of the final polymeric material.

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Supporting Information Available: ^{13}C NMR spectra of the reactive surfactants investigated and roughness measurements for the film made from latex L5 (surfmer S5). This material is available free of charge via Internet at http://pubs.acs.org.

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