Effect of Surfactant Systems on the Water Sensitivity of Latex Films

Lauren N. Butler, Christopher M. Fellows, Robert G. Gilbert

Key Centre for Polymer Colloids, Chemistry School F11, University of Sydney, NSW 2006, Australia

ABSTRACT: The effects of three different types of surfactant systems (ionic, polymeric, and electrosteric stabilizers) on the water sensitivity of poly(butyl acrylate-*co*-methyl methacrylate) latex films was examined. The water sensitivity was found to be strongly dependent on the surfactant system used in their preparation. A number of factors, such as the surfactant mobility and crystallinity and surfactant/polymer polarity appeared to affect the water uptake of the films. Highly mobile and crystallizable surfactants yielded high water sensitivity for films containing ionic surfactants, whereas the surfactant polarity had a greater effect on latices stabilized by polymeric surfactants, with the more hydrophilic systems providing greater water uptake. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1813–1823, 2004

Key words: films; swelling; surfactants; emulsion polymerization

INTRODUCTION

Surfactants are used during emulsion polymerization to produce stable polymer particles dispersed in an aqueous environment. These latices are often used directly in applications such as paints, adhesives, and other coating applications. The use of surfactants enhances latex properties, such as shelf-life stability, freeze–thaw stability, and mechanical stability. However, the addition of surfactants can have a negative effect on the properties of the final product, such as the resistance of a coating to water.

The aim of this article is to examine the effects of different surfactant systems on the water sensitivity of cast films. For the sake of uniform conditions, all the latices used were grown to the same size by emulsion polymerization, and the surfactant was added after synthesis to eliminate the effects of the surfactant on variables such as the particle size and number concentration.

The surfactants used in this study were the ionic surfactants sodium dodecyl sulfate (SDS) and Aerosol MA (2-ethylhexyl sulfosuccinate), nonyl phenyl ethoxylates (NPEs) with ethoxylate lengths of 30 and 50, and *in situ* electrosteric stabilizers formed via the incorporation of water-soluble monomers such as acrylic acid (AA) and methacrylic acid (MAA) into

entering radicals during the emulsion polymerization of methyl methacrylate and butyl acrylate (Fig. 1).

Water sensitivity can be defined in a number of ways:

1. Permeability of a wet film to water and oxygen.
2. Loss of adhesion of a film to a substrate.
3. Loss of mechanical properties of a film during and after exposure to water.

The permeability of a latex-based film is affected by several factors, such as the particle size distribution, the molecular weight distribution, the type and hydrophobicity of the comonomers, the sequence distribution, the extent of crosslinking, and the concentrations and types of various additives used during emulsion polymerization, such as surfactants and salts.[1–3] Any voids or defects in the film structure will result in a higher diffusion rate of water through the film.

Water can disrupt the hydrogen bonding between a film and a polar substrate, leading to a loss of adhesion. If the surface tension of the substrate is too high, then the surfactant molecules will tend to order themselves at the film–substrate interface to lower the interfacial tension. This phenomenon, though desirable in terms of substrate wetting, can promote the diffusion of water through the film via osmotic forces. Once the water gathers at the substrate–film interface, it has no means of leaving and will have a tendency to disrupt the adhesion forces present as most of the adhesion forces are dependent on hydrogen bonding.

The absorption of water into a latex film can have detrimental effects on the mechanical properties of the
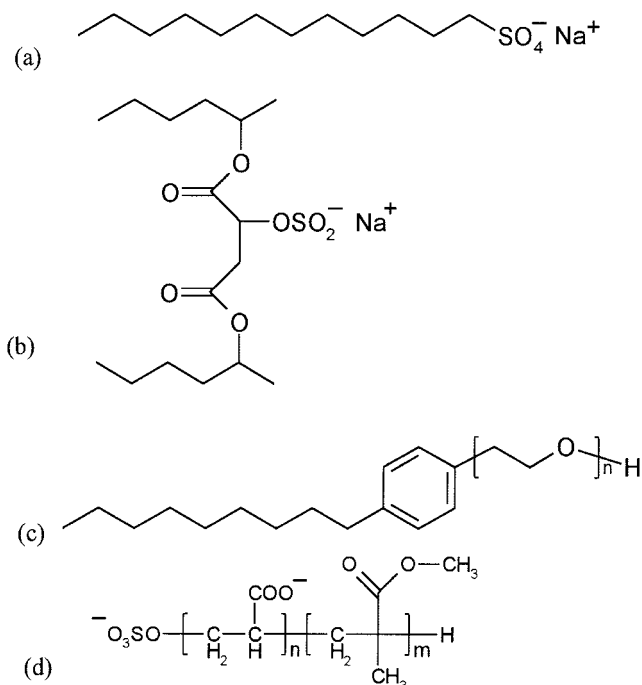
Figure 1 Structures of (a) SDS, (b) Aerosol MA, (c) NPEs [n = 50 (Igepal CO977, or NPE 50) or 30 (Igepal CO887, or NPE 30)], and (d) an ideal *in situ* electrosteric stabilizer.

polymeric film and impair its ability to act as a protective coating.[4] Because most of the ingredients of a latex coating are either water-soluble or water-dispersible,[5] reducing the water sensitivity is a challenging goal.

The water sensitivity depends on the distributions of hydrophilic and hydrophobic species in the final film, which in turn are dictated by the mechanisms governing film formation. The current model for latex film formation[1–3] is that it occurs in four steps: the

concentration of the latex, the sintering or deformation of the particle, the coalescence and rupture of interparticle membranes, and the interdiffusion of polymer chains to form a coherent film (Fig. 2).

During the first stage of film formation, the ordering of the particles in the film occurs. If a latex is monodisperse, then the most efficient arrangement of particles, a face-centered cubic structure, can occur. Bimodality and polydispersity will disrupt this packing arrangement, resulting in a greater number of voids in the film.[6,7] These voids are regions in which water, salts, and surfactants can build up in the film.

The presence of ionic species in films increases the water sensitivity as the major driving force of water absorption, osmotic pressure, is increased. During the sintering and coalescence stages of film formation, species that are incompatible with the film can be expelled from the film with the water. However, not all of the ionic species are extruded from the film, and some may reside in small pockets or voids throughout the film. As water is drawn into the film by osmotic forces, these concentrations of ionic species can result in localized defects such as discoloration and blistering.

The diffusion of water into a polymeric film is influenced by the solubility of water in the polymer; the more water is present, the more readily additional water will be able to diffuse through the matrix. The water sensitivity is influenced greatly by the hydrophobicity of the comonomers used, with more hydrophilic polymers normally showing greater permeability. Water sensitivity has been found to be strongly positively correlated with the oxygen content for a series of branched vinyl esters.[8]

Surfactants in a latex are distributed between the particle–water interface, the aqueous phase, and the other interfaces present, with the majority of the mol-
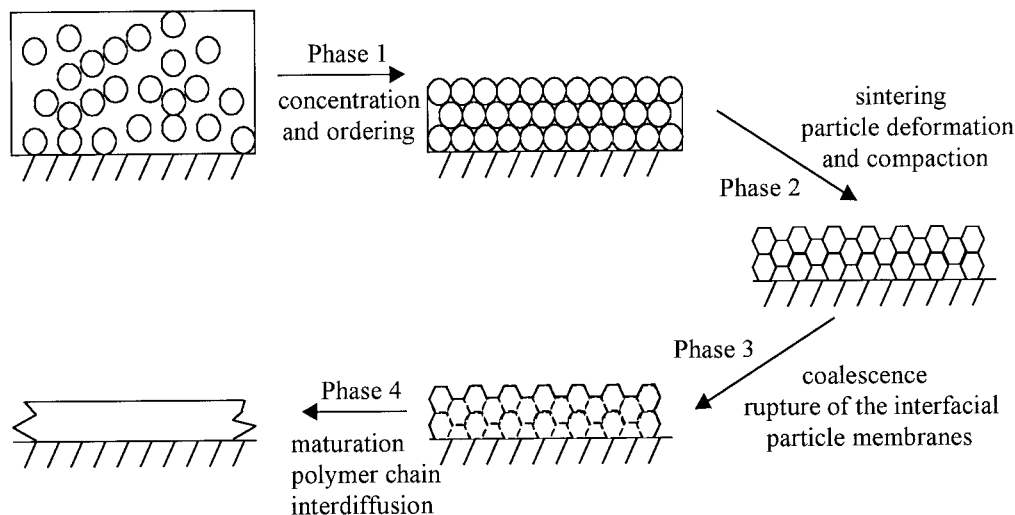

Figure 2 Film formation.

TABLE I
Composition of the Seed Latex

	Initial charge (g)	Initiator charge (g)	Feed 1 (g)[a]	Feed 2 (g)[b]
Butyl acrylate	28.14	—	211.1	—
Methyl methacrylate	28.88	—	211.3	—
Styrene sulfate	—	—	—	5.62
Potassium persulfate	—	1.23	—	—
Sodium carbonate	1.03	—	—	—
Water	564.80	27.07	—	35.19
Aerosol MA 80	16.47	—	—	—

[a] The flow rate for feed 1 was 0.7 mL/min from 10 to 70 min from the commencement of nucleation, 1.1 mL/min from 70 to 170 min, 1.6 mL/min from 170 to 270 min, and 2.1 mL/min from 270 to 310 min.
[b] The flow rate for feed 2 was 0.19 mL/min from 125 to 315 min from the commencement of nucleation.

ecules located at the particle–water interface. During film formation, the aqueous phase and the particle–water interface disappear, and the surfactant will be redistributed, depending on its compatibility with the polymer. If the surfactant is incompatible with the polymer, it will remain an independent mobile entity at the interfaces between coalesced particles, in pockets within the polymer matrix, or it will be extruded from the film to the air–film and substrate–film interfaces. A surfactant that is highly compatible with the latex may dissolve within the polymer particles, whereas in the intermediate case, the surfactant and polymer may exist in an interpenetrating network, in which some diffusion between the two phases and a degree of inhomogeneity both exist.[9]

The distribution of the surfactant in a film will depend on the surface tension of the substrate, the molecular weight of the surfactant, and the hydrophilicity of the surfactant.[10,11] If the surface tension of the substrate is too high, then the surfactant molecules will tend to order themselves at the film–substrate interface to lower the interfacial tension.

In most cases, for a homologous series of surfactants, the higher the molecular weight is of the surfactant, the more hydrophobic it tends to be. This leads to the surfactant being slightly soluble in the polymeric film. The solubilization of the surfactant in the polymeric film can have both positive and negative effects. The positive effect is that the surfactant can act as a plasticizer and accelerate the aging process.[12] The dissolved surfactant can also, however, increase the hydrophilicity of the film, increasing the water permeability of the film.

The greater the hydrophilicity is of the surfactant, the more unlikely it is that it will be soluble in the film. If trapped in pockets in the film, it will provide a strong osmotic driving force for the diffusion of water through the film. Furthermore, such pockets of the surfactant throughout the film can lead to haze and inconsistent coloring of the film.

Recent work in this area has been directed toward the study of water absorption in polymeric films and the study of polymer diffusion in films during the aging process. Experimental methods used over the last 20 years include Fourier transform infrared/attenuated total reflectance,[4,9–11,13–15] atomic force microscopy,[12,16,17] fluorescence,[18] capacitance measurement,[19] and gravimetric analysis.[5,20,21] The aim of this article is to achieve an improved understanding of the mechanism of film formation with respect to the role of the surfactants to design better coating systems. Each prepared latex had the same number concentration of particles and average diameter (to within ±5%) and was characterized by the determination of the critical coagulation concentration (CCC), the water gain on immersion of the formed film, and the proportion of water-extractable material.

EXPERIMENTAL

Seed synthesis

The monomers methyl methacrylate, butyl acrylate, and 4-styrenesulfonic acid sodium salt hydrate (Sigma–Aldrich, Sydney, Australia) were used as purchased. Potassium persulfate (Merck, Darmstadt, Germany), Aerosol MA (Cytec, Rotterdam, The Netherlands), and sodium carbonate (Ajax Chemicals, Sydney, Australia) were used as the initiator, surfactant, and buffer, respectively. The water used was Milli-RO water (passed through a single ion-exchange column), and it was equivalent to distilled water. The recipe used for the production of the seed is given in Table I.

The polymerization was carried out in a 1.3-L computer-controlled reactor (Moore Products, Melbourne, Australia) with a high-shear impeller-type agitator (Aldrich). The initial reactor charge was purged with nitrogen for 30 min to remove dissolved oxygen while the temperature was brought up to 60°C, after which the initiator solution was added. The reactor was placed

TABLE II
Preparation of the Electrosterically Stabilized Latices

	Charge (g)	Initiator (g)
Dialyzed seed	200.0	—
Butyl acrylate	55.6	—
Methyl methacrylate	60.0 g	—
MAA or AA	1.2–11.6	—
Potassium persulfate	—	0.58
Sodium carbonate	0.16	—
Aerosol MA 80	4.24	—
Water	140.76	40.62

TABLE III
Amounts of the Surfactants Added for Sample Preparation

Mass of surfactant per 100 g of seed latex (g)				
Aerosol MA 80	SDS	NPE 50	NPE 30	50/50 mixture of NPE 50/NPE 30
0.934	0.654	—	—	—
1.868	1.306	0.544	1.458	1.088
2.802	1.960	0.816	2.186	1.632
—	—	1.630	4.374	3.264

under positive nitrogen pressure during the reaction. The reaction time was taken from the commencement of nucleation (indicated by an exotherm or a blue hue) 2–8 min after the initiator solution was added. The monomer streams were added with a Waters 501 high-performance liquid chromatography pump (Milford, MA) for the feed 1 stream and with a syringe pump for the feed 2 stream. The reaction mixture was kept at 60°C for an additional 10–12 h after the completion of monomer addition.

For the removal of the surfactant, the resultant latex was dialyzed for 4–5 weeks against distilled water with dialysis membranes with 25-Å pores (Selby-Biolab, Melbourne, Australia) until the conductivity of the distilled water remained constant. The average radius of the resultant latex particles was between 50 and 55 nm.

Electrosteric stabilizer synthesis

An electrosteric stabilizer was added through polymerization onto the dialyzed seed with either glacial AA (Sumaika, Singapore) or MAA (Aldrich), which was used as purchased. The feed composition for each synthesis is given in Table II.

Polymerization was carried out in a 500-mL glass reactor equipped with a semicircular blade turbine agitator and a thermometer. The initial reactor charge was purged with nitrogen for 30 min to remove dissolved oxygen while the temperature was brought up to 60°C. The reaction was placed under positive nitrogen pressure during the reaction. The polymerization was stopped by the cooling of the latex and its exposure to air; this minimized the particle size difference between the seed and modified latex. The resultant latex was dialyzed for 4–5 weeks as previously described.

Surfactant addition

Further polymerization was carried out on the seed used for surfactant addition so that it was essentially the same size as those latices with the electrosteric stabilizers. The same procedure used for the electrosteric stabilizer synthesis was followed, with the exception that no acid was added.

The surfactants SDS (Merck), Aerosol MA 80 (Cytec), Igepal CO977 (NPE 50, Rhone Poulenc, Brookvale, Australia), and Igepal CO887 (NPE 30) were added individually to the dialyzed seed latex and stirred overnight before testing to ensure complete surfactant adsorption (Table III).

Characterization

CCC

In a typical experiment, a 1.5-mL aliquot of the latex dispersion (number concentration $\sim 10^{10}$ mL^{-1}) was placed in an ultraviolet–visible spectrometer cell. A given electrolyte solution (NaCl; 1.5 mL) was added and mixed by rapid syringe injection. The pH of the latex dispersion was adjusted to 6.0, the electrosterically stabilized latices being adjusted to 9.0 with hydrochloric acid (Sigma–Aldrich) or ammonia (Sigma–Aldrich) solutions. The time variation of the turbidity (seen through changes in absorbance) upon the addition of the electrolyte was followed in a Cary 4.0 ultraviolet–visible spectrometer (Varian, Cary, NC) at a wavelength of 520 nm.

The initial slopes of the turbidity curves were equivalent to the rate of the particle–particle collisions. These initial slopes of the turbidity curves slowly increased with increasing salt concentration until they reached a limiting value, defined as the rate of fast coagulation.

TABLE IV
CCC Determination for Latices Containing Ionic Surfactants at pH 6.0

Latex		CCC (mM NaCl)
Aerosol MA 80 (mM)	50	560
	70	680
	90	780
	140	820
SDS (mM)	50	1250
	70	1380
	90	1320
	140	1450

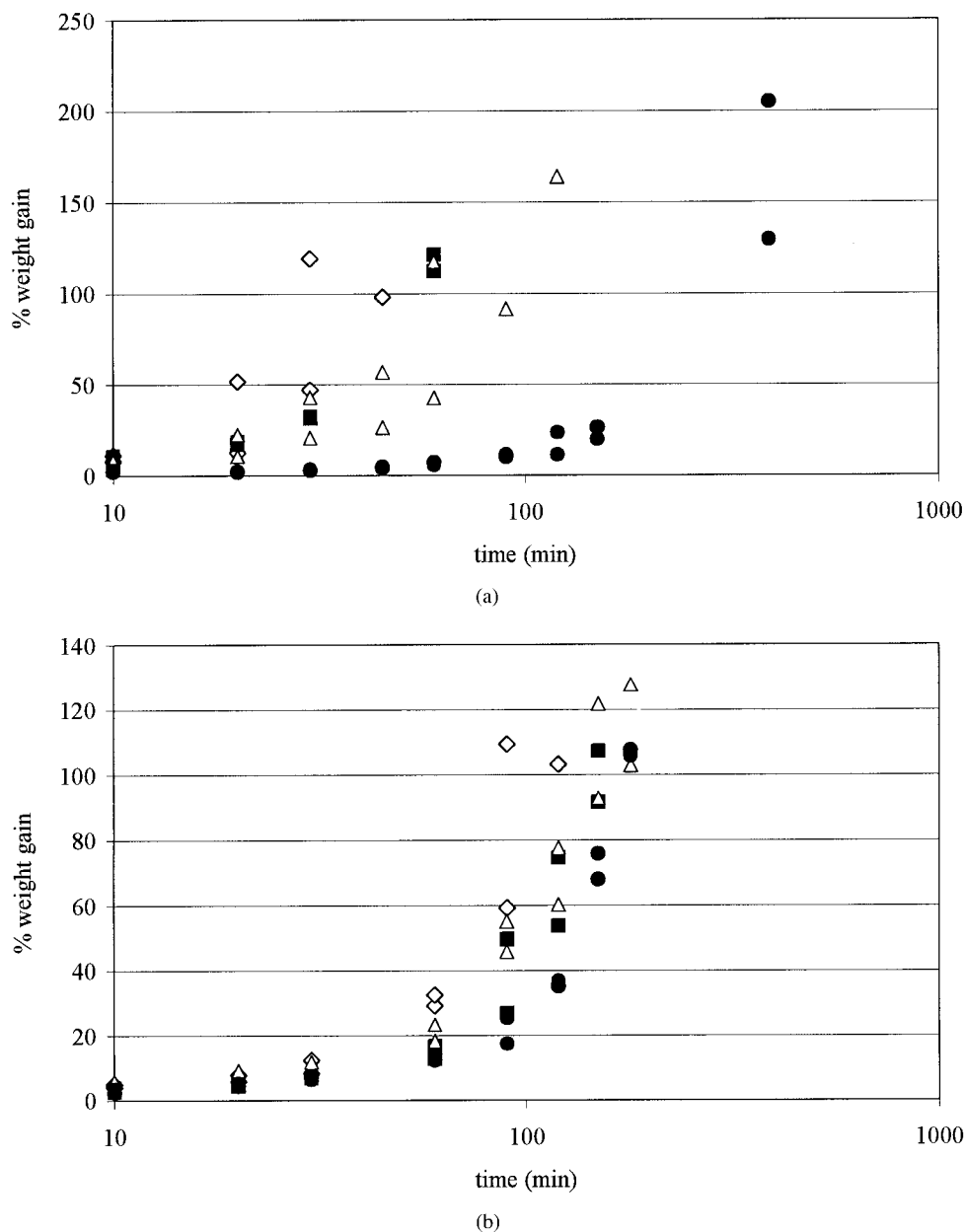**Figure 3** Weight gain on immersion for films 0.08 mm thick when wet: (a) from latices containing ($\diamond$) 140, ($\blacksquare$) 90, ($\triangle$) 70, or ($\bullet$) 50 mM SDS and (b) from latices containing ($\diamond$) 140, ($\blacksquare$) 90, ($\triangle$) 70, or ($\bullet$) 50 mM Aerosol MA.

The stability ratio (W) for each electrolyte concentration was calculated from the ratios of the initial slopes of the slow coagulation runs to those of the fast coagulation runs:[22]

$$W = \frac{\dfrac{dA}{dt}\text{fast}}{\dfrac{dA}{dt}\text{slow}} \qquad (1)$$

ln(W) was plotted against ln(C), where C is the salt concentration, and CCC was calculated from the intersection of two lines of differing slopes.

A requirement of latex paint systems is that the binder latex be stable with the addition of cosolvents and salts. The practical experimental upper limit of this method of measuring latex stability, approximately 2500 mM NaCl, is considered to be the level required for a latex to be able to withstand the paint formulation environment.

Weight gain on immersion

Latex films were prepared on panels of soda glass (16 cm × 12 cm) cleaned with acetone. The films were applied with a 0.08-mm doctor blade/applicator and

TABLE V
Water-Extractable Material from Latices Containing Ionic Surfactants

Latex		Amount extracted (wt %)
Aerosol MA 80 (mM)	50	0.6–1.1
	70	1.2–1.5
	90	2.0–3.2
	140	5.7–6.0
SDS (mM)	50	0.1–0.4
	70	0.9
	90	0.9–1.1
	140	2.7–3.0

TABLE VII
Water-Extractable Material from Latices Containing Polymeric Surfactants

Latex		Amount extracted (wt %)
NPE 30 (mM)	7	0.3
	10	0.5
	21	2.5
NPE 50 (mM)	12	0.3–0.4
	18	0.3–0.5
	36	0.5

RESULTS AND DISCUSSION

Ionic surfactants

Latices prepared with Aerosol MA and SDS were relatively unstable toward the addition of an electrolyte (Table IV). The addition of more surfactant had a marginal effect on increasing the stability of the latices, and all CCC values were well below the criterion limit of 2500 mM NaCl. The variation of CCC with pH for the ionic surfactants was small because the range covered was insufficient to protonate the surfactants at any stage and the change in pH only affected the CCC slightly by changing the ionic strength of the solution.

Latices containing ionic surfactants were found to be fairly water-sensitive by the measurement of the weight gain on immersion (Fig. 3). All failed by loss of adhesion of the film to the substrate within 3–5 h of immersion, at a weight gain of approximately 100%. The increase in the water sensitivity was correlated strongly with the amount of the surfactant in the latex.

The poor water resistance of the films prepared from the ionic surfactants could be explained by two factors: the poor packing structure of the film lattice and the mobility of the surfactant.

During the first stage of film formation, the latex is concentrated, and this results in an increase in the ionic strength as the result of the evaporation of water. Increasing the ionic strength of the latex results in a reduction in the electrical double layer around the particles. A critical limit was observed to which the latices containing an ionic surfactant could be concentrated before large amounts of coagulum were seen. This limit was around 40–43% solids. It can be concluded that these latices will coagulate at the end of the concentrating stage of film formation and that this will result in a structure with numerous voids in the lattice structure. This will make the film more permeable and provide sites on which the surfactant can crystallize in the later stages of film drying.

Because ionic surfactants are generally incompatible with polymers, the surfactant remaining within the film will reside either in interparticle voids or in regions in which particle interfaces exist. It has been
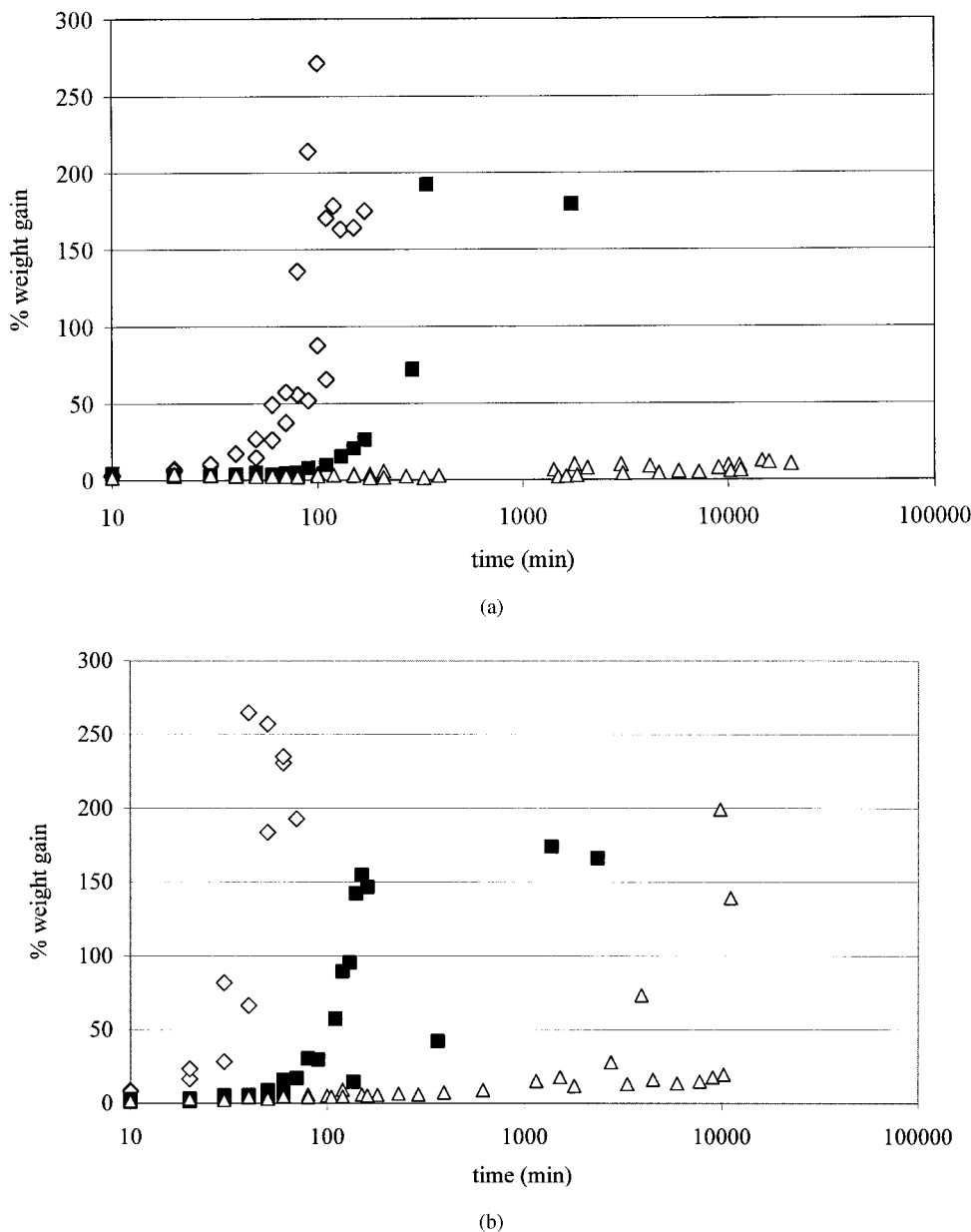
were dried in a fan-forced oven at 60°C for 24 h. The films and panels were weighed and placed in a water bath at room temperature for 14 days or until the weight gain of the film was greater than 100% of the original film mass, whichever came first. At variable intervals and after careful blotting of the surface liquid with paper, the samples were weighed as quickly as possible.

Water extractables

The latices were adjusted to pH 9.0 with ammonia (Sigma–Aldrich) and dried for 24 h at 60°C with a polyethylene container for easy removal and reduced surfactant adsorption to the substrate. A 4-g sample of the dry film was weighed into a cellulose-extraction thimble (Bonnet, Sydney, Australia), and the top of the thimble was plugged with facial tissue. The thimble was placed in Soxhlet equipment and extracted with 120 mL of deionized water under reflux. The extraction was performed continuously for 24 h. The extract was transferred to a container and evaporated to dryness. A blank thimble was run concurrently with each polymer sample, and the amount of water-extractable material was calculated as follows:

Water extractables (wt %) =

$$\frac{[\text{Sample extract (g)}] - [\text{Blank extract (g)}] \times 100}{\text{Sample weight (g)}}$$

$$(2)$$

TABLE VI
CCC Determination for Latices Containing Polymeric Surfactants at pH 6.0

Latex		CCC (mM NaCl)
NPE 30 (mM)	7	766
	10	1704
	21	>2500
NPE 50 (mM)	12–36	>2500

(a)

(b)

Figure 4 Weight gain on immersion for films 0.08 mm thick when wet: (a) from latices containing ($\Diamond$) 21, ($\blacksquare$) 11, or ($\triangle$) 7 mM NPE 30 and (b) from latices containing ($\Diamond$) 36, ($\blacksquare$) 18, or ($\triangle$) 12 mM NPE 50.

previously shown that SDS phase-separates in cellulose acetate films and is distributed heterogeneously.[23]

Ionic surfactants are smaller than the polymeric and electrosteric stabilizers used in this study and can readily desorb from the particles. Ionic surfactants are also more hydrophilic and less compatible with the polymer. These two factors result in ionic surfactants being more likely to be exuded from the film or aggregate in voids throughout the film. The exudation of SDS from latex films has been qualitatively reported during film formation by methods such as attenuated total reflectance/infrared spectroscopy[11,14] and atomic force microscopy.[17,24] Similar results have been seen for surfactants similar to Aerosol MA.[10]

The driving force for water absorption in the film is believed to be the osmotic pressure.[25] This would imply that samples containing greater amounts of the surfactant would experience greater water sensitivity because of greater osmotic pressure in the film. Water-extraction data for films prepared with ionic surfactants are consistent with the higher mobility and extractability of these species (Table V).

Accounting for the differences in the molecular weights of Aerosol MA and SDS (1.5:1), we find that a greater amount of Aerosol MA is extracted from the films than SDS (2–2.5 times more on average). This implies that a greater amount of SDS is trapped inside the film in voids. Higher levels of trapped surfactant

may result in the greater water sensitivity of SDS over Aerosol MA, as shown in Figure 3.

Polymeric surfactants

Polymeric surfactants have been shown to be more compatible with polymeric films than ionic surfactants as polymeric surfactants have a higher solubility in such films, often acting as plasticizers.[12,26] The compatibility of the NPEs in polymeric films depends on the length of the polyethoxylate portion of the surfactant: the larger this portion, the less compatible the surfactant. Odrobina et al.[27] found that once an NPE has more than 10 ethoxylate groups, the rate of interparticle diffusion is retarded; that is, the aging process during many film properties improve is impeded.

Most of the latices prepared with polymeric surfactants meet the criterion of having a CCC greater than 2500 mM NaCl (Table VI). The samples containing the two lower amounts of NPE 30 show lower stabilities, presumably as the surface coverage of the surfactant is below a critical limit for the optimal steric repulsion between the latex particles. These polymeric surfactants behave differently than the ionic surfactants because of their reduced mobility and increased compatibility with the polymer. This means that this type of surfactant is more likely to remain in the film than be exuded, and this could explain the smaller amounts of water-extractable material collected from these latices (Table VII). These polymeric surfactants are capable of supporting water-in-oil emulsions and oil-in-water emulsions.[28] As the water content increases in the film, it is possible that surfactant molecules could invert particle interfaces to stabilize some water droplets in the film. This would most likely occur at higher surfactant concentrations and may be responsible for the high water sensitivity of the films prepared with higher levels of polymeric surfactants (Fig. 4).

The results of the water-extractable determinations indicate that the less hydrophilic surfactant, NPE 30, is more readily extracted from the latex film (Table VII), and that the quantity of the material extracted increases with the amount of the surfactant added. A similar trend was not seen with the other polymeric surfactant, NPE 50, with minimal material being extracted from the films at all concentrations. This difference cannot be due to an increased compatibility of NPE 50 with the polymer matrix, as it is the more hydrophilic species; this suggests that the mobility of the surfactant through the film is a greater factor.

The low water sensitivity of films made from latices stabilized by NPE surfactants (at the lowest concentration, a weight gain remaining below 17% over a 2-week period) may be attributable to the enhanced latex stability, which should result in a better packing structure in the film. As seen in the ionic surfactant samples, the water sensitivity increases when the amount of the surfactant is increased. As high concentrations of a nonionic surfactant cannot cause aggregation upon concentration and lead to poor film formation, the increased sensitivity must be attributable to the retention of the surfactant within the polymer matrix. As the latices prepared with the more hydrophilic surfactant (NPE50) have higher water sensitivity, a phase transition from an oil-in-water emulsion to a water-in-oil emulsion at a low mass fraction of water is a possible mechanism for surfactant incorporation.

Electrosteric stabilizers

CCC measurements of the latices prepared with aqueous-phase monomers confirm that the particles are stabilized electrosterically (Table VIII). Anionic electrosteric stabilizers generally have poor stability at low pHs because of the protonation of the extended chains from the particle. This effect is greater with samples that contain shorter hairs on the surfaces of the particles. With long anionic hairs, steric stabilization is still present at low pH values.

Not all the acid-functionalized monomer is necessarily anchored to the particle surface as hairs. Some may be buried in the particle, especially in the systems containing MAA, whereas some may have formed a water-soluble polyelectrolyte. This polyelectrolyte will affect all the results in question, as a (meth)acrylic acid rich aqueous-phase polymer may act as a flocculating agent, leading to aggregation and poor particle packing.

The polyelectrolyte may be responsible for the large change in the water sensitivity above 6% AA levels seen in the data for the weight gain on immersion (Fig. 5). The amount of the polyelectrolyte is difficult to

TABLE VIII
CCC Determination for Latices Stabilized
Electrosterically at pH 6.0 and pH 9.0

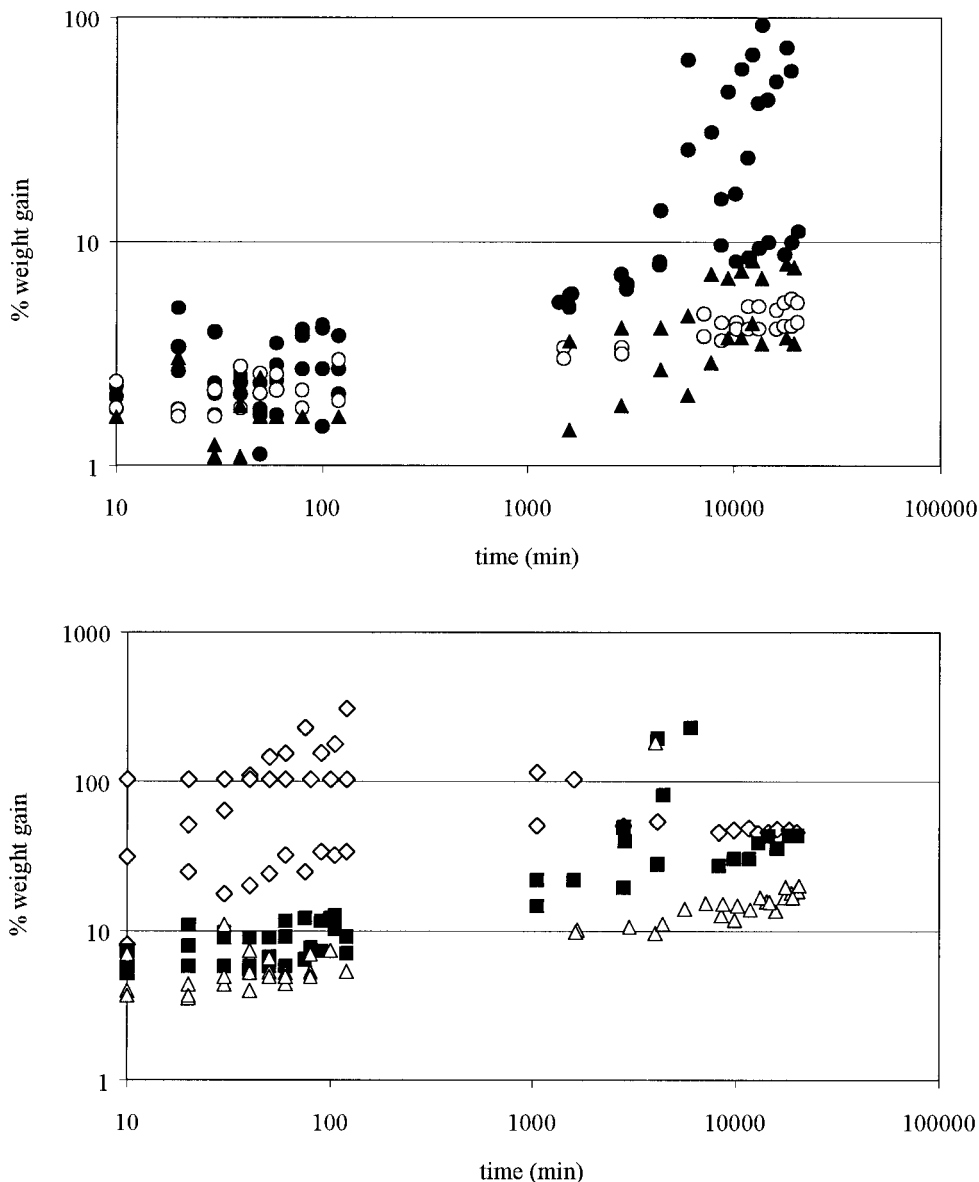| Latex	CCC (mM NaCl)	
	pH 6.0	pH 9.0
MAA (%)		
1	447	740
2	586	1000
4	1199	2539
6	1340	>2500
8	1549	>2500
10	>2500	>2500
AA (%)		
1	392	744
2	1749	2075
4	>2500	>2500
6	>2500	>2500
8	>2500	>2500
10	>2500	>2500
No hairy layer	730	778

Figure 5 Weight gain on immersion for films 0.08 mm thick when wet prepared from latices polymerized at AA concentrations of (◇) 12.0, (■) 8.1, (△) 6.1, (●) 4.4, (○) 3.1, and (▲) 1.5%.

estimate, but it is clearly more likely to form at higher concentrations of acid in the polymerization. The level of the polyelectrolyte may be estimated from the water-extractable data (Table IX).

The results for the weight gain on immersion show a complex relationship between the hydrophilic monomer content and water sensitivity (Fig. 5). For systems containing AA, there is a trend of increasing water sensitivity with increasing AA. This is not a linear relationship: films prepared with less than 6% AA absorb a relatively small amount of water and retain adhesion, whereas films with 6% or greater AA lose adhesion with relative rapidity. The presence of unequal amounts of the AA-containing polyelectrolyte from system to system is likely to be a major

TABLE IX
Water-Extractable Material from Latices Containing Electrosteric Stabilizers

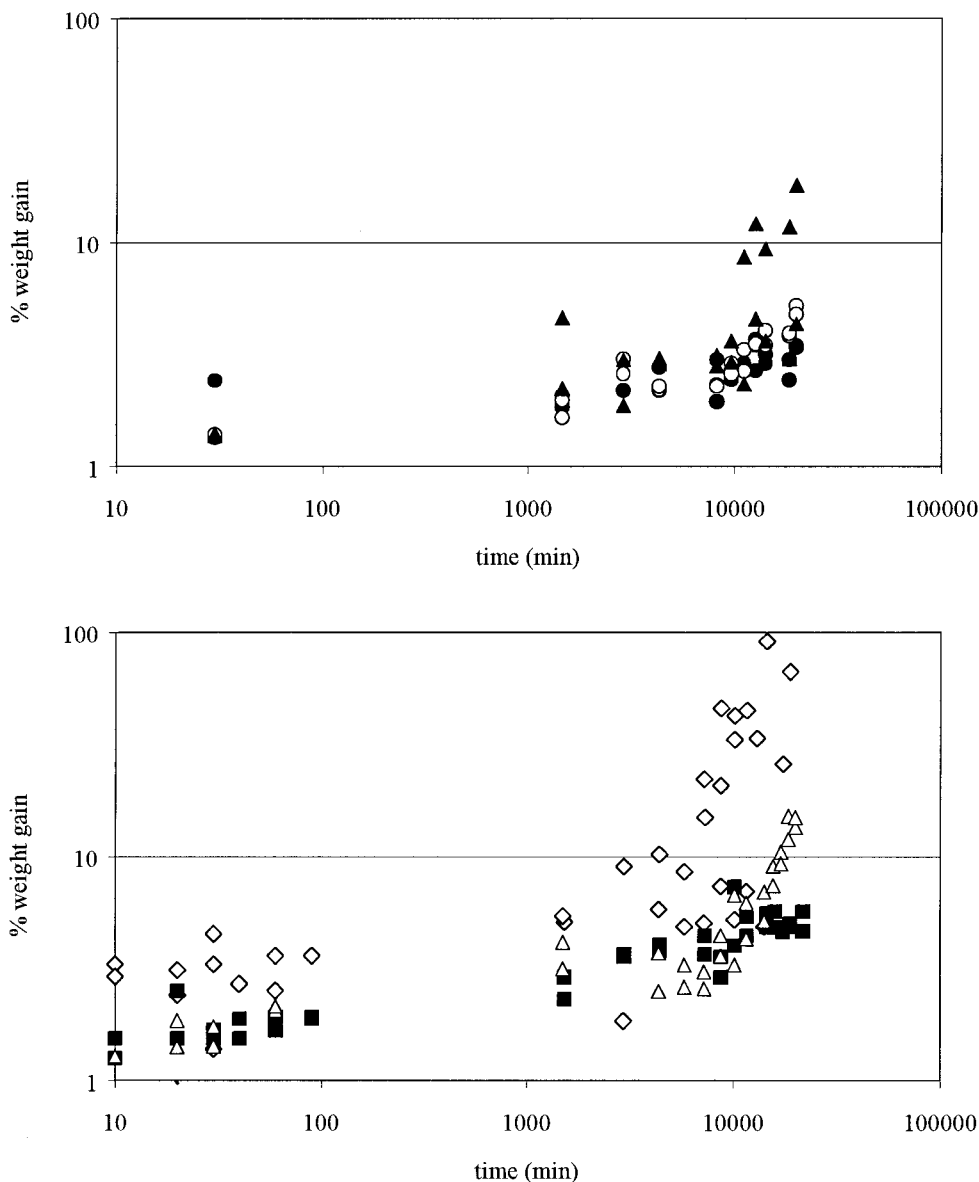| Latex		Amount extracted (%)
MAA (wt %)	1.1	0.1
	2.3	0.2
	5.0	0.4
	6.2	0.3
	8.3	0.1
	11.2	0.3
AA (wt %)	1.5	0.2
	3.1	0.3
	4.4	0.3
	6.1	1.5
	8.1	2.2
	12.9	3.1

Figure 6 Weight gain on immersion for films 0.08 mm thick when wet prepared from latices polymerized at MAA concentrations of ($\diamond$) 11.2, ($\blacksquare$) 8.3, ($\triangle$) 6.2, ($\bullet$) 5.0, ($\bigcirc$) 2.3, and ($\blacktriangle$) 1.1%.

complicating factor. For systems containing MAA, the trend of increasing water sensitivity with increasing MAA concentration is not as marked (Fig. 6), although significant swelling and the loss of adhesion are again only seen in latices with high MAA contents.

The electrosteric system used is expected to exhibit complex behavior during film formation. Estimated aqueous-phase polymer compositions suggest that the shell of the particle should be relatively hard (methyl methacrylate and AA/MAA have high values of the glass-transition temperature[29]). This hairy layer will be plasticized with water while in solution, but when most of the water has left the film during the initial stages of film formation, the hairy layer may act as a hard shell. This means that a pseudo-core–shell mor-

phology may exist during the sintering and aging stages of film formation. This will also retard the aging process, in which many film properties such as the water sensitivity are improved. A further disadvantage of having a hydrophilic shell is that water will act as a plasticizer for the shell when the latex film is exposed to moisture.

Despite the high glass-transition temperatures of AA- and MAA-containing copolymers, the latices considered in this study are all globally rubbery at the temperatures and likely water contents at which film formation takes place (glass-transition temperature ~ 5–10°C, with film formation at 60°C). We have suggested previously that under these conditions phase inversion may occur as the ratio of water to the

organic phase is reduced, giving a continuous polymer phase in which small droplets of water are dispersed. This would be expected to be less likely as the length of the hydrophilic tail of the electrosteric stabilizer increases, this resulting in a greater proportion of the hydrophilic monomer on the particle surfaces, on which it will be maximally effective in reducing adhesion and promoting the movement of water through the film matrix.[30]

In contrast to the steady increase in the water sensitivity with increasing AA or MAA seen in this work, previous work[21] performed on poly(butyl acrylate-*co*-acrylic acid-*co*-butyl methacrylate) systems has shown that the water sensitivity increases as the acid concentration decreases. The justification for this is that the latices are more stable with higher acid levels and hence form a better film structure. Such a trend cannot be found in the results presented here.

There is a sharp change in the amount of water-extractable material at the 4% AA concentration level, whereas a sharp increase in the water sensitivity of this series of latices only occurs at higher concentrations of AA in the feed (Table IX). This is consistent with a model in which the water sensitivity is due to a pseudo-core–shell morphology or to the failure of phase inversion to occur, as the length of the hydrophilic hairy layer reaches a certain dimension, but not with a model in which water sensitivity is a function of the amount of unincorporated polyelectrolyte.[30] The same is true for the MAA series, in which only small amounts of water extractables can be seen under all conditions (Table IX).

CONCLUSIONS

The water sensitivity of poly(butyl acrylate-*co*-methacrylic acid) films has been found to be overwhelmingly dependent on the surfactant system used in their preparation. A number of factors, such as the surfactant mobility and compatibility with the latex polymer, latex stability, and surfactant/polymer polarity, appear to affect the water uptake of a film. The results for ionic, polymeric, and electrosteric polymeric surfactants suggest that the stability of the source latex has little direct effect on the water stability of the formed film. Highly mobile and crystallizable surfactants provide water sensitivity for films containing ionic surfactants, whereas the surfactant polarity has a greater effect on latices stabilized by polymeric surfactants, with the more hydrophilic systems (NPE 50 and AA) providing greater water uptake. For electrosteric stabilizers, no linear relationship between the hydrophilic content and water sensitivity has been observed, but a discontinuity has been observed that suggests participation in some manner of a discrete hydrophilic phase.

Systems containing ionic surfactants are more water-sensitive and produce greater amounts of water-extractable materials. This is due to the greater absolute amounts of surfactant required to gain suitable particle stability. Polymeric and electrosterically stabilized systems containing low levels of stabilizers are the least water-sensitive and form latex films that lose little material upon extraction. This suggests that it is possible to formulate electrosterically stabilized latices with stability and water resistance similar to or better than those of conventional coating formulations.

References

1. Dobler, F.; Holl, Y. Trends Polym Sci 1996, 4, 145.
2. Eckersley, S. T.; Rudin, A. J Appl Polym Sci 1994, 53, 1139.
3. Steward, P. A.; Hearn, J.; Wilkinson, M. C. Adv Colloid Interface Sci 2000, 86, 195.
4. Nguyen, T.; Bentz, D.; Byrd, E. J Coat Technol 1995, 67, 37.
5. Snuparek, J.; Bidman, A.; Hanus, J.; Hajkova, B. J Appl Polym Sci 1983, 28, 1421.
6. Peters, A.; Overbeek, G. C.; Buckmann, A. J. P.; Padget, J. C.; Annable, T. Prog Org Coat 1996, 29, 183.
7. Geurts, J. M.; Lammers, M.; German, A. L. Colloids Surf A 1996, 108, 295.
8. Bassett, D. R. J Coat Technol 2001, 73, 43.
9. Kientz, E.; Holl, Y. Colloids Surf A 1993, 78, 255.
10. Niu, B. J.; Urban, M. W. J Appl Polym Sci 1998, 70, 1321.
11. Evanson, K.; Urban, M. J Appl Polym Sci 1991, 42, 2309.
12. Eckersley, S. T.; Rudin, A. J Appl Polym Sci 1993, 48, 1369.
13. Nguyen, T.; Bentz, D.; Byrd, E. J Coat Technol 1994, 66, 39.
14. Amalvy, J. I.; Soria, D. B. Prog Org Coat 1996, 28, 279.
15. Thorstenson, T. A.; Tebelius, L. K.; Urban, M. W. J Appl Polym Sci 1993, 50, 1207.
16. Juhue, D.; Lang, J. Colloids Surf A 1994, 87, 177.
17. Juhue, D.; Wang, Y. C.; Lang, J.; Leung, O. M.; Goh, M. C.; Winnik, M. A. J Polym Sci Part B: Polym Phys 1995, 33, 1123.
18. Miller, K. E.; Krueger, R. H.; Torkelson, J. M. J Polym Sci Part B: Polym Phys 1995, 33, 2343.
19. Kolek, Z. Prog Org Coat 1997, 30, 287.
20. Amalvy, J. I. Pigment Resin Technol 1998, 27, 20.
21. Paul, S. Prog Org Coat 1977, 5, 79.
22. Ottewill, R. H.; Shaw, J. N. Discuss Faraday Soc 1966, 42, 154.
23. Bindschaedler, C.; Gurny, R.; Doelker, E. J Appl Polym Sci 1987, 34, 2631.
24. Lam, S.; Hellgren, A. C.; Sjoberg, M.; Holmberg, K.; Schoonbrood, H. A. S.; Unzue, M. J.; Asua, J. M.; Tauer, K.; Sherrington, D. C.; Goni, A. M. J Appl Polym Sci 1997, 66, 187.
25. Eckersley, S. T.; Rudin, A. J Appl Polym Sci 1994, 53, 1139.
26. Kawaguchi, S.; Odrobina, E.; Winnik, M. A. Macromol Rapid Commun 1995, 16, 861.
27. Odrobina, E.; Feng, J. R.; Kawaguchi, S.; Winnik, M. A.; Neag, M.; Meyer, E. F. Macromolecules 1998, 31, 7239.
28. Marszall, L. In Nonionic Surfactants: Physical Chemistry; Schick, M. J., Ed.; Marcel Dekker: New York, 1987.
29. Polymer Handbook; Brandrup, A.; Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989.
30. Butler, L. N.; Fellows, C. M.; Gilbert, R. G. Ind Eng Chem Res 2003, 42, 456.