High-solids-content seeded semicontinuous emulsion terpolymerization of styrene, 2-ethylhexyl acrylate and methacrylic acid

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The effects of the type and amount of surfactant on the overall polymerization features and final product properties for the seeded semicontinuous emulsion terpolymerization of styrene, 2-ethylhexyl acrylate and methacrylic acid were investigated. The emulsifier systems studied included: (i) pure anionic emulsifier (sodium lauryl sulfate); (ii) anionic ethoxylated emulsifier (Alipal CO-436); and (iii) non-ionic emulsifiers of different ethylene oxide chain length (Myrj 45 and Myrj 52). The final latex properties considered were: latex viscosity both prior to and after neutralization, mechanical stability, chemical stability and freeze–thaw stability.

INTRODUCTION

Emulsion terpolymers have found use in a wide variety of applications. However, only limited attention has been paid to the study of emulsion terpolymerization in the open literature[1–9]. Ríos et al.[1] studied the batch emulsion terpolymerization of acrylonitrile, styrene and methyl acrylate, finding a significant polymer composition drift during the process owing to differences in monomer reactivity ratios. For the same system, Ríos and Guillot[2] tried to improve terpolymer homogeneity using a semicontinuous reactor. The authors reported that a rather heterogeneous terpolymer was obtained when a mixture of monomers of a composition equal to that desired for the terpolymer was fed into the reactor. On the other hand, the terpolymer homogeneity was significantly improved when the reactor was initially charged with both all of the acrylonitrile and all of the methyl acrylate, and the styrene feed was controlled based on the on-line gas chromatographic analysis of the unreacted monomers in the reactor. Jerman and Janovic[3] studied the terpolymer composition evolution in the emulsion terpolymerization of butadiene, acrylonitrile and methacrylic acid. Huo et al.[4] reported a preliminary investigation of the overall polymerization features of the 2-ethylhexyl acrylate/vinyl acetate/acrylic acid emulsion system, the effect of the semibatch policy, and the swelling that the latexes undergo on neutralization. Matejicek et al.[5] investigated the influence of agitation on the creation of coagulum in the seeded emulsion terpolymerization of styrene, butyl acrylate and acrylic acid. Storti et al.[6,7] studied the kinetics of emulsion terpolymerization of acrylonitrile, styrene and methyl methacrylate. López de Arbina and Asua[8] investigated the effect of the type and amount of surfactant, amount

of cosurfactant and sonication time on both the amount of coagulum and final latex properties in the high-solids-content batch miniemulsion terpolymerization of styrene, 2-ethylhexyl acrylate and methacrylic acid. Unzué and Asua[9] studied the effect of the solids content, initiator concentration, feed flow rate and amount of surfactant on the kinetics of the high-solids-content semicontinuous miniemulsion terpolymerization of butyl acrylate, methyl methacrylate and vinyl acetate. In addition, the effect of the operation variables on the feasibility of obtaining a 65 wt% solids-content latex with low amount of coagulum was investigated.

The purpose of this work is to investigate the effect of the type and amount of surfactant on the overall polymerization features and final product properties for the seeded semicontinuous emulsion terpolymerization of styrene, 2-ethylhexyl acrylate and methacrylic acid. The emulsifier systems studied included: (i) pure anionic emulsifier (SLS); (ii) anionic ethoxylated emulsifier (Alipal CO-436); and (iii) non-ionic emulsifiers of different ethylene oxide chain length (Myrj 45 and Myrj 52).

EXPERIMENTAL

Technical-grade monomers were used in this work. Styrene (St) contained 20 ppm of 4-t-butylcatechol as inhibitor. 2-Ethylhexyl acrylate (2EHA) and methacrylic acid (MAA) contained p-methoxyphenol (40 and 200 ppm, respectively). Potassium persulfate (KPS, Merck), sodium bicarbonate (Merck), sodium lauryl sulfate (SLS, Merck), Alipal CO-436 (ammonium salt of sulfated nonylphenoxy-poly(ethyleneoxy)ethanol(4-ethylene oxide), Rhône-Poulenc), A-103 (disodium salt of polyoxyethylenenated nonylphenol half ester of sulfosuccinic acid, Cyanamid), Myrj 45 (polyoxyethylene(8) stearate, ICI), and Myrj 52 (polyoxyethylene(40) stearate, ICI) were also used as received. Deionized water was used throughout the work.

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Polymerizations were carried out in a 1 litre glass unbaffled reactor equipped with a reflux condenser, stainless-steel stirrer, sampling device, nitrogen inlet and a feed inlet tube. Three different seeds (one for every anionic emulsifier, i.e. SLS, Alipal CO-436 and A-103) were prepared at 70°C by means of batch emulsion copolymerization of St and 2EHA using the recipes given in *Table 1*. After polymerization, the seeds were kept overnight at 90°C to decompose the initiator. The particle diameters of the seeds were: $d_p(S1) = 64$ nm, $d_p(S2) = 56$ nm, $d_p(S3) = 55$ nm.

The seeded semicontinuous emulsion terpolymerizations were carried out using the recipes given in *Table 2*. The seed (15 wt% of the total recipe) was charged into the reactor, heated to 80°C, and then the feed was started. The feed was divided into two streams. The first was a mixture of the monomers. The second was an aqueous solution of the initiator and emulsifier. The flow rates of these streams were adjusted to finish the addition of both streams in 6 h. Then, the polymerization was continued in batch for about 1 h. Four series of polymerizations were carried out to investigate the effect of the type and amount of surfactant on the overall polymerization features and final product properties. In the first, the seed prepared with SLS was used and the amount of SLS in the feed was varied. Also a polymerization using a feed

including a mixture of anionic (SLS) and non-ionic (Myrj 45) emulsifiers (SLS/Myrj 45 weight ratio 45/55) was carried out. The second series of polymerizations were carried out using the seed prepared with Alipal CO-436 and varying the amount of Alipal CO-436 in the feed. In one polymerization of this series a 45.8/54.2 weight ratio mixture of Alipal CO-436 and Myrj 45 was used in the feed. The third and fourth series of experiments were carried out using the seed prepared with A-103 and feeds including varying amounts of Myrj 45 and Myrj 52, respectively. In all cases, the final solids content of the latexes was 55 wt%.

Samples were withdrawn during the process and the polymerization was stopped with hydroquinone. The overall conversion was determined gravimetrically. The terpolymer composition was determined measuring the residual monomer by gas chromatography. In order to carry out these measurements, the latex samples were diluted in water, and injected into the gas chromatograph. A precolumn filled with glass wool was used to retain the polymer and avoid the clogging of the column. The particle size was measured by dynamic light scattering (d.l.s.) and transmission electron microscopy (TEM). The properties of the final latex studied were: latex viscosity both prior to and after neutralization, mechanical stability, chemical stability and freeze-thaw stability.

The viscosity of the final latex both prior to and after neutralization with ammonia was measured with a concentric-cylinder viscosimeter (UK ELV-8) using spindle no. 4 at 30 r.p.m. and 30°C.

Mechanical stabilities were determined at room temperature by means of a high-speed (about 10 000 r.p.m.) stirrer. The latex taken from the reactor at the end of the polymerization was subjected to high shear for 4 min. Then, the sample was filtered through a nylon cloth (63 mesh) and the retained solids washed with water. The dry weight of the coagulated material was determined as a measure of the mechanical stability. When no coagulated material was retained by the cloth, the particle

Table 1 Recipes used to prepare the seeds

	Seed		
	S1	S2	S3
Styrene (g)	125.0	125.0	125.0
2EHA (g)	125.0	125.0	125.0
Water (g)	750.0	750.0	750.0
Surfactant (g)	16.32 (A-103)	12.0 (SLS)	13.67 (Alipal CO-436)
KPS (g)	1.5	1.5	1.5
NaHCO₃ (g)	1.5	1.5	1.5

Table 2 Recipes used for the semicontinuous emulsion terpolymerizations

Run	Emulsifier in the seed	Emulsifier in the feed	Feed					
			Emulsifier[a] (g)	Styrene (g)	2EHA (g)	MAA (g)	KPS (g)	DI water (g)
A1	SLS	SLS	6.35	164.73	305.88	33.71	1.68	338.70
A2	SLS	SLS	12.00	163.12	302.80	33.37	1.68	338.70
A3	SLS	SLS	17.77	161.15	299.32	33.01	1.68	338.70
A4	SLS	SLS	27.11	158.02	293.78	32.43	1.68	338.70
A5	SLS	SLS/Myrj 45	8.0/9.77	161.15	299.32	33.01	1.68	338.70
B1	Alipal	Alipal	10.12	164.33	304.37	33.47	1.68	338.70
B2	Alipal	Alipal	18.80	160.78	298.62	32.93	1.68	338.70
B3	Alipal	Alipal	24.34	158.91	295.31	32.59	1.68	338.70
B4	Alipal	Alipal	33.43	155.82	289.85	32.02	1.68	338.70
B5	Alipal	Alipal/Myrj 45	11.16/13.18	158.91	295.31	32.59	1.68	338.70
C1	A-103	Myrj 45	6.34	165.88	306.88	33.68	1.68	338.70
C2	A-103	Myrj 45	9.45	164.80	305.00	33.49	1.68	338.70
C3	A-103	Myrj 45	12.50	163.62	303.02	33.30	1.68	338.70
D1	A-103	Myrj 52	19.84	161.14	298.50	32.81	1.68	338.70
D2	A-103	Myrj 52	29.19	156.96	292.01	32.26	1.68	338.70
D3	A-103	Myrj 52	46.59	152.11	282.65	31.18	1.68	338.70

[a] Based on active content

size of the stirred latex was measured by d.l.s. An increase of the particle size suggests limited coagulation and hence the relative increase of the latex diameter was taken as a measure of the mechanical stability.

Latex paints may employ ions as part of the pigment system or may be applied over new masonry where soluble calcium salts are present. Therefore, stability towards these ions is important. In order to measure the chemical stability of the latexes, a 10 g sample of the latex without any post-stabilization was mixed with 10 cm³ of salt solution. The salt solutions used were NaCl (0.1 M and 1 M), CaCl₂ (0.1 M and 1 M) and Al₂(SO₄)₃ (0.1 M and 0.5 M). The mixing between the latex and the salt solution was carried out slowly under agitation (titration-like) and kept at room temperature for 24 h. Then, the salt tolerance of the latex was determined by measuring either the amount of coagulum formed or the increase in particle diameter.

Latexes can freeze during storage, and therefore the resistance to freeze–thaw cycles is very important for commercialization. In order to measure the freeze–thaw stability, the latexes were subjected to cycles where the sample was frozen at −18°C for 12 h and then allowed to thaw at room temperature for 12 h. Both the amount of coagulum formed and the increase of the particle size were taken as a measure of the freeze–thaw stability.

RESULTS AND DISCUSSION

Overall polymerization features

Figures 1 and *2* present the effect of the amount of emulsifier in the feed on the time evolution of the weight fractional conversion for the series of polymerizations using SLS and Alipal, respectively. In these figures, weight instantaneous conversion is defined as follows:

$$X = \frac{\text{weight of polymer in the reactor}}{\text{weight of (polymer + monomer) in the reactor}} \quad (1)$$

Figures 1 and *2* show that neither the amount nor the type of emulsifier had a significant effect on the polymerization rate. In order to analyse these results, let us consider first the particle size distributions (*PSD*) of several final latexes presented in *Figures 3* and *4*. These figures show that, for both emulsifiers, a substantial secondary nucleation occurred when the amount of
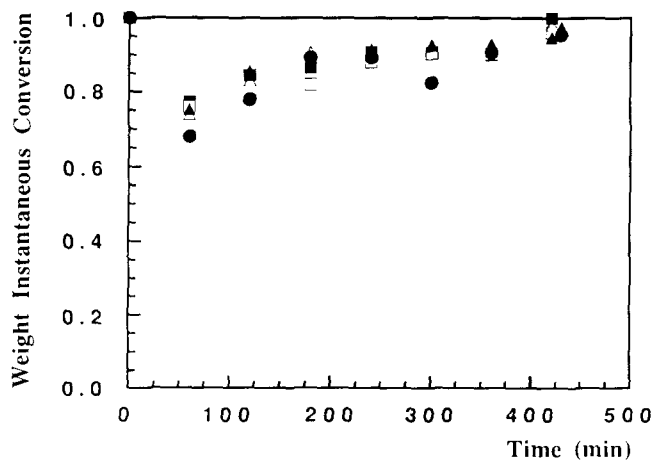
Figure 1 Time evolution of the weight instantaneous conversion for the series of semicontinuous emulsion polymerizations using SLS: (■) A1; (□) A2; (▲) A3; (△) A4; (●) A5
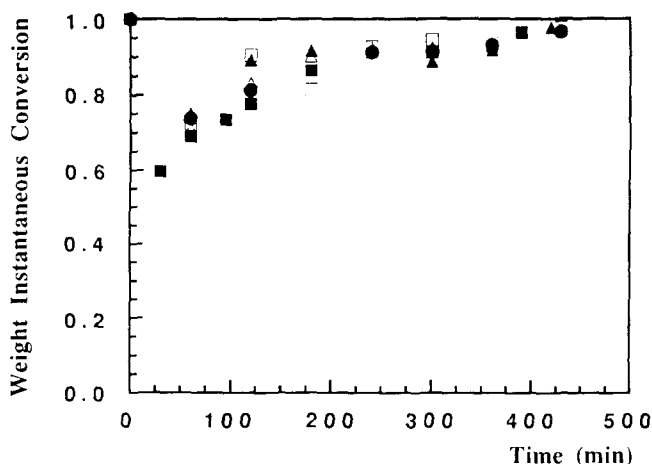
Figure 2 Time evolution of the weight instantaneous conversion for the series of semicontinuous emulsion polymerizations using Alipal CO-436: (■) B1; (□) B2; (▲) B3; (△) B4; (●) B5
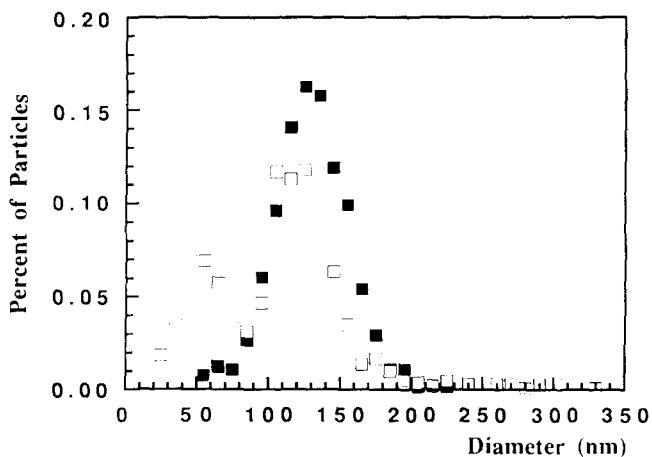
Figure 3 Particle size distributions of the final latexes obtained in the semicontinuous processes using SLS: (■) A2; (□) A4
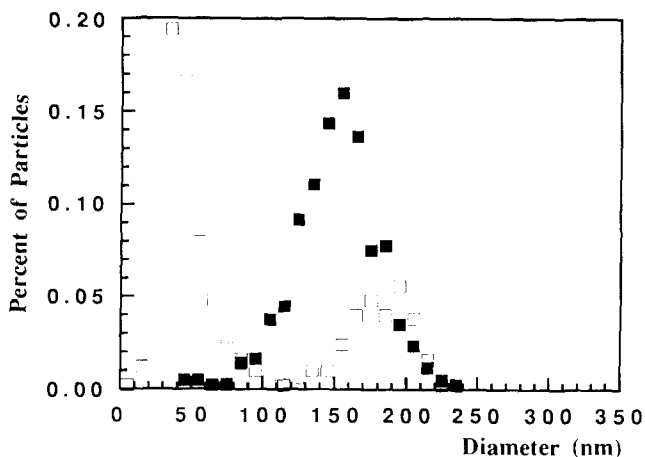
Figure 4 Particle size distributions of the final latexes obtained in the semicontinuous processes using Alipal CO-436: (■) B1; (□) B4

emulsifier increased. In a semicontinuous emulsion polymerization process with varying number of polymer particles, N_p, the polymerization rate would be rather insensitive to N_p under any of the following circumstances: (i) polymerization rate controlled by the addition rate (starved conditions); (ii) polymerization proceeding according to Smith–Ewart[10] case III kinetics ($\bar{n} \gg 0$); and (iii) polymerization proceeding according to Smith–Ewart case I kinetics ($\bar{n} \ll 0.5$).

Figures 1 and *2* show that a significant amount of monomer accumulated in the reactor. This means that the polymerizations did not proceed under starved conditions. Further evidence can be obtained by examining the terpolymer composition evolution presented in *Figure 5*. This figure shows that the terpolymer composition was different from that of the feed. This means that polymerization was not under starved conditions.

In order to discriminate between cases (ii) $\bar{n} \gg 0.5$ and (iii) $\bar{n} \ll 0.5$, the value of the average number of radicals per particle was calculated as described in the Appendix using the parameters given in *Table 3*. It was found that the calculated value of $\bar{n}$ ranged from 0.075 to 0.42. Even though this estimation may be subject to errors associated with the variability of the values of the parameters taken from the literature, this result suggests that the polymerization proceeded according to Smith–Ewart case I kinetics.

The polymerizations using Myrj 45 (polyoxyethylene(8) stearate) could not be completed because the latexes coagulated completely during the feeding period. The same occurred during experiment D1 carried out using the lowest amount of Myrj 52 (polyoxyethylene(40) stearate) in the feed. On the other hand, stable latexes with rather large particle size were obtained in experiments D2 and D3 where the amount of Myrj 52 was increased. The different performances of these emulsifiers indicate that a minimum polyoxyethylene chain length is required to provide steric stabilization.

Latex rheology

Figure 6 presents the effect of the amount of emulsifier on the latex viscosity for the latexes prepared with SLS and Alipal CO-436 both prior to and after neutralization with ammonia. The viscosity of the latex at low pH is
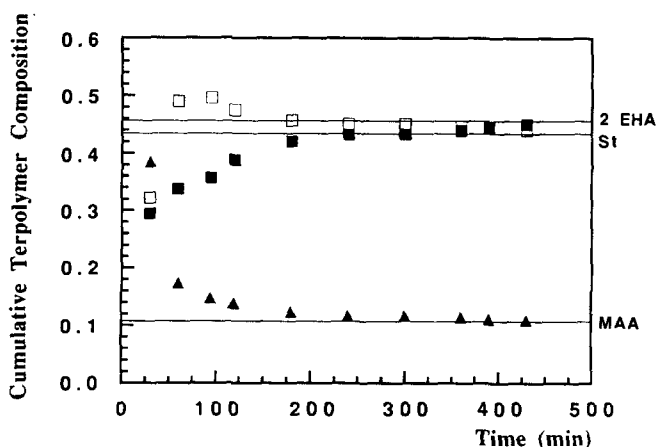

Figure 6 Effect of the amount of emulsifier on the latex viscosity. SLS latexes: ($\triangle$) acidic, ($\blacktriangle$) neutralized. Alipal CO-436 latexes: ($\bigcirc$) acidic, ($\bullet$) neutralized. SLS/Myrj 45 latexes: ($\square$) acidic, ($\blacksquare$) neutralized. Alipal CO-436/Myrj 45 latexes: ($\times$) acidic, ($+$) neutralized. Myrj 52 latexes: ($\diamond$) acidic, ($\blacklozenge$) neutralized. Emulsifier weight percentage is based on monomers

important because this is the viscosity of the latex in the reactor, which is critical for reactor performance. Thus, the maximum attainable solids content of a synthetic latex is limited by the viscosity of the reaction mixture. On the other hand, latexes are stored and used in a neutralized form, and therefore the latex viscosity after neutralization is important for latex applications. *Figure 6* shows that, in all cases, the viscosity of the latexes decreased when the amount of emulsifier in the feed increased. This can be explained by taking into account the results presented in *Figures 3* and *4*. These figures show that a significant secondary nucleation occurred when the amount of anionic emulsifier in the feed increased, giving a bimodal *PSD*. Polydisperse latexes have viscosities lower than those of monodisperse ones because the small polymer particles fit within the voids of the array of large particles.

Comparison between the viscosities of the latexes using SLS and those produced using Alipal CO-436 showed that the viscosities of the SLS latexes were lower than those produced with Alipal CO-436. These results suggest that the increase in viscosity observed for the Alipal CO-436 was due to an increase of the effective volume fraction of the polymer particles that resulted from the hydration of the ethoxy groups of the Alipal CO-436.

A significant increase of the emulsion viscosity was observed when the latexes were neutralized with ammonia. Acid-containing latexes swell upon addition of a base such as ammonia[15] and this results in an increase of the volume fraction of the polymer particles in the latex and hence in an increase of the viscosity.

Figure 6 also includes the viscosities of the latexes obtained using mixtures of anionic and non-ionic emulsifiers in the feed. It can be seen that a significant increase in the viscosity of the latex occurred when half of the SLS in the feed was substituted for Myrj 45. On the other hand, only a slight increase of the viscosity was observed when a 45.8/54.2 weight mixture of Alipal CO-436 and Myrj 45 was used instead of neat Alipal CO-436. In addition, the viscosity of the latex produced with the SLS/Myrj 45 mixture was similar to those of the latexes obtained with Alipal CO-436 and Alipal CO-436/Myrj 45. These results can be explained in terms of the contribution of the hydration of the ethoxy

Figure 5 Time evolution of the cumulative terpolymer composition for experiment B1: ($\blacktriangle$) MAA; ($\blacksquare$) 2EHA; ($\square$) St; (——) feed composition

Table 3 Values of the parameters used to estimate $\bar{n}$

	St (A)	2EHA (B)	MAA (C)
$k_{pii} \times 10^{-6}$ (cm^3 mol^{-1} s^{-1})	0.7[a]	0.6[a]	13.8[b]
r_{ij}	$r_{AB} = 0.94$[a]	$r_{BA} = 0.26$[a]	$r_{CA} = 0.70$[a]
	$r_{AC} = 0.15$[a]	$r_{BC}^c = 0.19$[a]	$r_{CB}^c = 4.8$[a]
$[i]_w/[i]_p$	5.9×10^{-4}[d]	1.9×10^{-4}[d]	0.57[e]

[a] Ref. 11
[b] Ref. 14
[c] Estimated using Q–e scheme
[d] Ref. 13
[e] Ref. 12

groups to the viscosity. When half of the SLS was substituted for Myrj 45, the hydration of the ethoxy groups of the Myrj 45 increased the effective volume of the particles and hence the latex viscosity. On the other hand, when the Alipal CO-436/Myrj 45 mixture was used instead of the neat Alipal CO-436, the increase of effective volume of the particles was much more modest because hydratable Alipal CO-436 (four ethoxy groups) was replaced by Myrj 45 (eight ethoxy groups).

The viscosities of the latexes obtained with Myrj 52 are also plotted in *Figure 6*. It can be seen that viscosities much lower than those of the anionic latexes were measured. The differences may be due to the large particle size of the latexes produced with Myrj 52.

Mechanical stability

Table 4 presents the results of the mechanical stability test. It can be seen that the latex formed with the smaller amount of SLS (run A1) coagulated during the test. The same occurred with the latex stabilized with the SLS/Myrj 45 mixture. The rest of the SLS latexes showed a good mechanical stability. The latexes stabilized with Alipal CO-436 (runs B1, B2, B3 and B4) also showed a good mechanical stability but the substitution of half of the Alipal CO-436 for Myrj 45 led to coagulation after the application of high shear. No increase in particle size was observed during the test for the latexes obtained with Myrj 52 (runs D2 and D3). However, the viscosity of the latex D2 (lowest amount of emulsifier) increased sharply during the test although no coagulum was observed. This suggests that latex D2 suffered reversible flocculation under high shear conditions.

Chemical stability

The salt tolerance of the latex without any post-stabilization was determined by measuring the relative increase of the particle size. The salt solutions were NaCl (0.1 M and 1 M), $CaCl_2$ (0.1 M and 1 M) and $Al_2(SO_4)_3$ (0.1 M and 0.5 M).

Figure 7 presents the variation of the particle diameter, d_p, for latexes obtained with SLS that did not coagulate upon salt addition. It can be seen that all latexes were stable when a 0.1 M solution of NaCl was added but a significant increase in d_p was observed upon addition of a 1 M NaCl solution. This increase in size, which suggests a limited coagulation, was less important when the amount of SLS in the feed increased. In addition, this latex coagulated completely when the ionic strength of
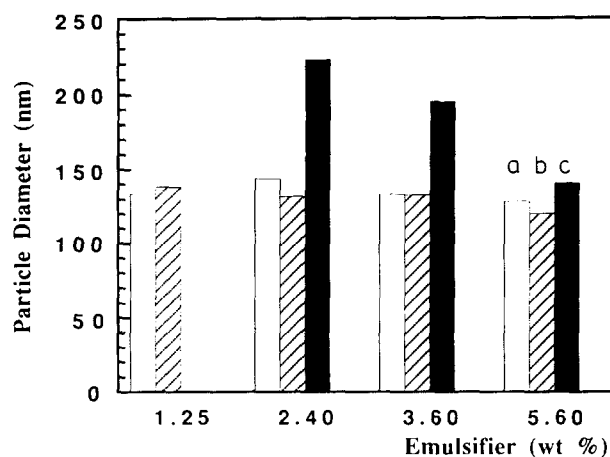

Figure 7 Effect of salt addition on the particle size of the latexes obtained with SLS: (a) original latex; (b) 0.1 M NaCl; (c) 1 M NaCl. Emulsifier weight percentage is based on monomers
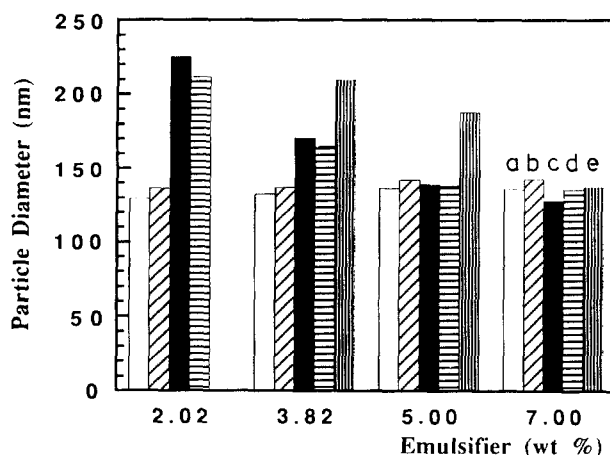

Figure 8 Effect of salt addition on the particle size of the latexes obtained with Alipal CO-436: (a) original latex; (b) 0.1 M NaCl; (c) 1 M NaCl; (d) 0.1 M $CaCl_2$; (e) 1 M $CaCl_2$. Emulsifier weight percentage is based on monomers

the salt solution was further increased and when $CaCl_2$ and $Al_2(SO_4)_3$ were used. This behaviour was due to the fact that SLS is an anionic emulsifier that promotes electrostatic stabilization of the latex particles, and hence the decrease of the double-layer thickness due to the increase in anionic strength of the aqueous phase resulted in a decrease in the stability of the latex particles.

Figure 8 presents the results obtained for latexes stabilized with Alipal CO-436. As expected, salt tolerance increased when the amount of surfactant in the feed increased. In addition, comparison between *Figures 7* and *8* shows that the latexes obtained with Alipal CO-436 were significantly more stable than those produced using SLS. This can be explained by taking into account the steric stabilization provided by the ethoxy groups of the Alipal CO-436.

Figure 9 presents a comparison between the latexes obtained using anionic emulsifiers and those produced with a mixture of anionic and non-ionic emulsifiers. Notice that the total amount of emulsifier was kept constant. It can be seen that the salt tolerance was significantly reduced when a mixture of emulsifiers was used. This means that the steric stabilization due to the addition of Myrj 45 did not compensate for the decrease of the electrostatic stabilization resulting from the decrease of the amount of anionic emulsifier in the recipe.

Table 4 Mechanical stability test

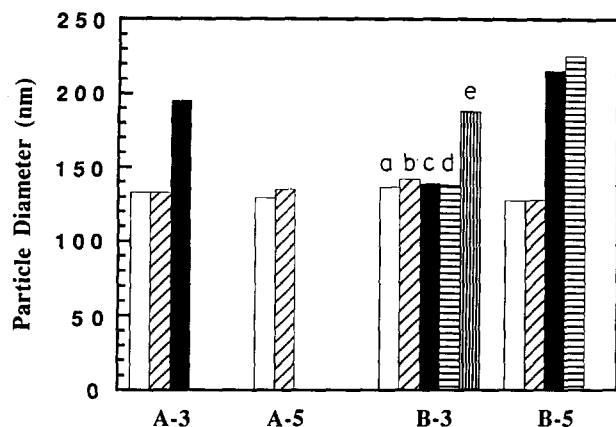|	Particle diameter, d.l.s. (nm)	
Run	Before test	After test
A1	134	Coagulum (7.20 wt%)
A2	144	148
A3	133	148
A4	128	121
A5	129	Coagulum (22.02 wt%)
B1	129	140
B2	132	141
B3	136	137
B4	136	135
B5	127	Coagulum (11.73 wt%)
D2	193	188
D3	242	255

Figure 9 Comparison between the chemical stability of latex obtained with anionic emulsifiers and that of those produced with a mixture of anionic and non-ionic emulsifiers: (a) original latexes; (b) 0.1 M NaCl; (c) 1 M NaCl; (d) 0.1 M CaCl$_2$; (e) 1 M CaCl$_2$
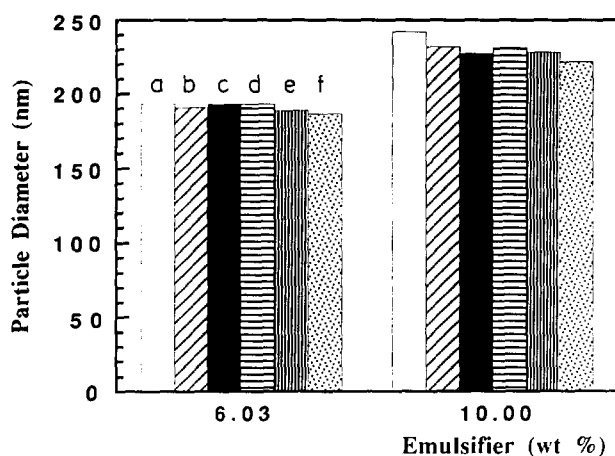

Figure 10 Salt tolerance of the latexes produced using Myrj 52: (a) original latex; (b) 0.1 M NaCl; (c) 1 M NaCl; (d) 0.1 M CaCl$_2$; (e) 1 M CaCl$_2$; (f) 0.1 M Al$_2$(SO$_4$)$_3$. Emulsifier weight percentage is based on monomers

Figure 10 shows that the latexes produced using the non-ionic emulsifier (Myrj 52) were very stable towards salt addition.

Freeze–thaw stability

All the latexes except those stabilized with the largest amount of Myrj 52 (run D3) coagulated after one freeze–thaw cycle. Nevertheless, D3 latex was stable to five freeze–thaw cycles. This was somehow expected, taking into account the process occurring during the freeze–thaw test. When freezing occurs, ice crystals separate from the unfrozen latex, reducing the volume of the continuous phase and increasing the ionic concentration of this phase. Therefore, the stability of the latex is reduced and the latex, which is subjected to high pressure, coagulates. On the other hand, non-ionic surfactants with long ethoxy chains can reduce coagulation during the freeze–thaw process[16].

CONCLUSIONS

The effects of the type and amount of surfactant on the overall polymerization features and final product properties for the seeded semicontinuous emulsion terpolymerization of styrene, 2-ethylhexyl acrylate and

methacrylic acid were investigated. The emulsifier systems studied included: (i) pure anionic emulsifier (SLS); (ii) anionic ethoxylated emulsifier (Alipal CO-436); and (iii) non-ionic emulsifiers of different ethylene oxide chain length (Myrj 45 and Myrj 52).

It was found that the type and amount of surfactant had no effect on the overall polymerization rate although they influenced the extent of secondary nucleation. In addition, the polymerizations did not proceed under starved conditions. These results suggest that polymerizations followed Smith–Ewart case I kinetics. Polymerizations carried out using Myrj 45 (short ethoxy chain) led to complete coagulation whereas stable latexes could be obtained using Myrj 52 (long ethoxy chain).

The viscosity of the latexes decreased as the amount of emulsifier increased because bimodal *PSD* were obtained using large amounts of emulsifier in the feed and polydisperse latexes have viscosities lower than those of monodisperse ones because the smaller polymer particles fit within the voids of the array of large particles. The viscosities of the Alipal CO-436 latexes were larger than those of the SLS latexes because of the increase of the effective volume fraction of the polymer particles that resulted from the hydration of the ethoxy groups. Most of the anionic latexes showed a good mechanical stability but this stability was substantially reduced when half of the anionic emulsifier was substituted by the short-ethoxy-chain non-ionic emulsifier (Myrj 45). Steric stabilized latexes showed a rather poor mechanical stability. Steric stabilized latexes had a better performance than the anionic latexes in the chemical stability and freeze–thaw stability tests.

ACKNOWLEDGEMENTS

APPENDIX

The weight instantaneous conversion is defined as the weight fraction of the monomer already charged into the reactor converted to polymer:

$$X = \frac{M_s + F_m t - M}{M_s + F_m t} \qquad (A.1)$$

where M_s is the seed weight, F_m the weight feed rate of the monomers, and M the weight of the unreacted monomers in the reactor at time t given by:

$$\frac{dM}{dt} = -R_p + F_m \qquad (A.2)$$

where R_p is the overall weight polymerization rate. Combining equations (A.1) and (A.2) the following equation for R_p can be obtained:

$$R_p = (M_s + F_m t)\frac{dX}{dt} + F_m X \qquad (A.3)$$

Equation (A.3) allows the calculation of the overall polymerization rate from the instantaneous conversion vs. time experimental curves. This calculation involves the difficulty of using differentials of data curves. These differentials were calculated from a low-order polynomial used to fit the data curves. High-order polynomials result in unstable values of the differentials. The values of R_p

calculated from equation (A.3) together with the values of the total number of polymer particles were used to estimate $\bar{n}$ from the following equation[17]:

$$R_{p} = \{(k_{pAA}P_{A} + k_{pBA}P_{B} + k_{pCA}P_{C})M_{A}[A]_{p}$$

$$+ (k_{pAB}P_{A} + k_{pBB}P_{B} + k_{pCB}P_{C})M_{B}[B]_{p}$$

$$+ (k_{pAC}P_{A} + k_{pBC}P_{B} + k_{pCC}P_{C})M_{C}[C]_{p}\} \times \frac{\bar{n}N_{p}}{N_{A}}$$

where k_{pij} are the propagation rate constants, $[i]_{p}$ the concentration of monomer i in the polymer particles, N_{p} the total number of polymer particles in the reactor, P_{i} the time-averaged probability of finding a growing chain with an ultimate unit of type i, and M_{i} the molecular weight of monomer i. Details for the calculation of P_{i} and $[i]_{p}$ are given in ref. 17.

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