Use of Styrene-Maleic Anhydride Copolymers (SMA Resins) in Emulsion Copolymerization

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ABSTRACT: The composition and quantity of styrene-maleic anhydride (SMA) copolymer resins were varied in emulsion copolymerizations of methyl methacrylate and *n*-butyl acrylate conducted by both batch and semicontinuous processes. The resulting particle sizes and levels of coagulum were measured to determine the optimum conditions for incorporation of the SMA resins into the resulting latexes. A semicontinuous process, in which no buffer was included and the SMA was added in a second stage comonomer emulsion, was found to produce coagulum-free latexes. These recipes, however, relied on nucleation of the polymer particles by conventional surfactants [nonyl phenol poly(ethylene) oxide and its corresponding sulfate salt] with a first-stage addition of a monomer emulsion prepared with these surfactants. SMA1000, having a 1/1 ratio of styrene to maleic anhydride in its copolymer, was determined to be the preferred resin (as opposed to SMA2000 and SMA3000, having SMA ratios of 2/1 and 3/1, respectively) because it interacted the least with conventional surfactants, which allowed its ready incorporation into coagulum-free recipes. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2729–2747, 1998

Key words: styrene-maleic anhydride copolymers; emulsion polymerization

INTRODUCTION

The development of latexes containing functional groups has been investigated over the last two decades as an important means of modifying the surface properties of latex particles. The preparation of such latexes has been achieved by emulsion polymerization using small amounts of functional comonomers^{1–10} that contribute to the colloidal stability of the particles and modification of the properties of the polymeric product. The incorporation of sulfonic acid groups, for instance, was found to lead to the production of latexes with exceptional stability, which are used for paints, paper coatings, leather treatment, foams, and adhesives.

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Additional approaches for incorporating functional groups onto or into the latex particles include the addition of functional polymers, such as costabilizers into the final latex as a postadditive, or by using these in the emulsion polymerization. The first approach, which seems to be simple, might present the disadvantage of migration of the functional polymers that are usually highly soluble in water during film formation. On the other hand, the use of functional costabilizers in an emulsion polymerization offers the possible advantage of grafting at the particle surface^{6,7} or providing additional particle stabilization during latex preparation.

Styrene-maleic anhydride (SMA) copolymers have been developed for a variety of possible applications, such as pigment dispersants, protective colloids, and thickeners for paint formulations, as well as in making adhesives.¹¹ These

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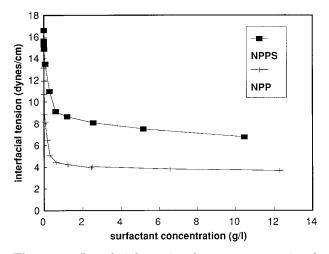


Figure 1 Interfacial tension between conventional surfactant solutions (NPP and NPPS) and MMA/BuA (50/50, wt ratio) as a function of surfactant concentration.

copolymers can also be fixed to wood, paper, ceramics, metals, or plastics leading to high water resistance materials. It can also be expected that latex films containing these copolymers would exhibit exceptional hydrophobicity. These copolymers are water insoluble and undergo reactions with bases, such as ammonium hydroxide, to form water-soluble salts that can have emulsifier properties and, therefore, can act as stabilizers in emulsion polymerizations. A patent¹² claims the aqueous solution dispersion of these copolymers for suspension and emulsion polymerizations leading to polymer dispersions used for paints, having excellent stability to shear and good pigment binding capacity.

Unfortunately, the literature does not provide further information on the extent of the use of SMA's in emulsion polymerization. The main goal of the present work was to study the role of SMA resins in emulsion polymerization. The specific objectives include: (1) comparison of the surfaceactive properties and the emulsification efficiencies of various SMA resins having varying SMA ratios to those of conventional surfactants; (2) determination of whether or not the different SMAs used as the sole surfactant or in combination with conventional surfactants can act as good stabilizers; (3) determination of how the SMAs affect the course of polymerization in terms of monomer conversion and particle size as a function of conversion, as well as their influence on the final latex characteristics, such as stability, particle size, and size distribution; and (4) investigation of the appropriate means and time (addition) to use the SMAs during emulsion polymerizations. In this respect, batch and semicontinuous emulsion polymerizations were used to study a number of parameters, such as the type of SMA, the amount of SMA when used as the sole surfactant, the SMA/conventional surfactant ratio, and the mode of addition of SMA.

EXPERIMENTAL

Materials

The monomers (Aldrich Chemical Co., Milwaukee, WI) used for the emulsion polymerizations were methyl methacrylate (MMA) and n-butyl acrylate (BuA). They were distilled and stored at -2°C until use. Conventional surfactants (Rhône Poulenc, France) represent a combination of nonionic nonyl phenol poly(ethylene oxide) (Igepal CO 880; 30 mol of ethylene oxide; referred to throughout the text as NPP) and its corresponding sulfate salt (ABEX EP 120; referred to as NPPS). Three types of SMA copolymers (Elf Atochem, France) were used: SMA1000, SMA2000, and SMA3000 having 1/1, 2/1, and 3/1 SMA ratios, respectively, and molecular weights reported in the range of 1200 to 2500. These were neutralized at 60°C by ammonium hydroxide (Fisher, Pittsburgh, PA) before use in emulsion polymerizations. Ammonium persulfate (Fisher), potassium metabisulfite (Fisher), sodium bicarbonate

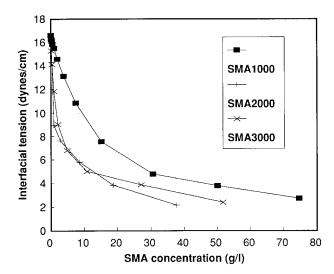


Figure 2 Interfacial tension of SMA ammonium salt solutions/(MMA/BuA) as a function of SMA concentration.

Surfactant	SMA1000	SMA2000	SMA3000	NPPS	NPP
$CMC (g L^{-1})$	30.4	0.93	6.4 - 7.4	0.64	0.42

Table I	Critical Micel	le Concentrations	(CMCs)

(Fisher), and hydroquinone (Fisher) were used as received.

Polymerization Process

Two types of polymerizations were conducted at 70°C: batch (bottle) and unseeded semicontinuous polymerizations. In the latter process, a jacketed glass reactor was equipped with a reflux condenser, a glass stirrer, and a nitrogen inlet, and sampling tube.

RESULTS AND DISCUSSION

Characterization of SMAs and Conventional Surfactants

Because the conventional surfactants (NPP and NPPS) can act as good emulsifiers in emulsion polymerizations, a comparative study of the surfaceactive properties of these and the ammonium salts of the SMA resins was conducted. This involved the comparison of the interfacial tensions between solutions of the different SMAs (SMA1000, SMA2000, and SMA3000), as well as the conventional surfactants, and the acrylic monomers (MMA and BuA) and the determination of their relative efficiencies in the preparation of stable pre-emulsions used in subsequent polymerizations.

Surfactant Solution/Monomer Interfacial Tensions

Interfacial tensions between the different surfactant solutions and a MMA/BuA monomer mixture (50/50 wt ratio), as used in the emulsion polymerizations, were determined using the drop volume method that is a fairly accurate and convenient means of measuring the interfacial tensions of liquid/liquid interfaces. The ammonium salt solutions of SMA1000, SMA2000, and SMA3000 were used, as well as the conventional surfactants, NPP and NPPS. The purpose of these measurements was to determine whether or not the SMAs form micelles and to compare their relative efficiencies at decreasing the interfacial tension between water and the MMA/BuA monomer mixture. Figures 1 and 2 report the interfacial tension as a function of surfactant concentration for the conventional surfactants, NPP/NPPS, and the SMAs, respectively. The break in the curves (change in slope), which represents the critical micelle concentration (CMC), is more obvious and easier to distinguish for the conventional surfactants than for the SMAs. This might be due to the heterogeneity in composition of the SMA copolymers. Nevertheless, by taking into account these breaks, one can estimate the CMC values as listed in Table I.

SMA1000 is less efficient in decreasing the interfacial tension of water/(MMA/BuA) than SMA2000 and SMA3000. Furthermore, the CMC of SMA1000 is the highest. One can, therefore, expect better stabilization of the latexes prepared in emulsion polymerizations using SMA2000 and SMA3000.

Surfactant Emulsification Efficiencies

The best way to prepare high solids content latexes is by semicontinuous emulsion polymerization, which includes the feed of a stable preemulsion prepared from a combination of the surfactants, monomers, and water. In this respect, preemulsions having various amounts of SMA were prepared, and their stability was studied under the conditions used in the polymerizations [i.e., unstirred at room temperature for 10 h (feed time)].

The recipe used for the preparation of different preemulsions is given in Table II. The water, surfactants, and monomers were mixed for 30 min with a magnetic bar, followed by a short period

Table IIRecipe for Preparationof Preemulsions

Ingredient	Amount (Parts)
Water	44
Surfactants (SMA/NPP/NPPS) ^a	2.7
MMA/BuA (50/50 wt ratio)	100

 $^{\rm a}$ NPP/NPPS ratio is 1/5 when conventional surfactants are used in the recipe.

%SMA ^a	100	88	75	60	50	33	20	0
1000	S	S	S	S	S	S	S	\mathbf{S}
2000	U	S	S	\mathbf{S}	\mathbf{S}	\mathbf{S}	\mathbf{S}	\mathbf{S}
3000	U	U	U	\mathbf{S}	\mathbf{S}	S	S	\mathbf{S}

Table IIIEmulsion Stability as a Function of the Amount and Type of SMA Used in Combinationwith Conventional Surfactants (NPP/NPPS)

S and U denote stable and unstable preemulsions, as judged by whether or not phase separation occurred at room temperature 10 h after preparation.

^a Amount of SMA is based on total surfactants (SMA, NPP/NPPS).

without mixing. Mixing a second time lead to a stable and viscous preemulsion. This mix-rest-mix procedure was found to be necessary to prepare stable emulsions. The addition of water to the stable preemulsion led to a homogeneous emulsion for a short period of time (~ 10 min), followed by phase separation between the added water and preemulsion. This result indicated that these were water-in-oil type preemulsions.

The results of the stability tests for the different preemulsions are given in Table III as a function of the SMA content in the surfactant mixture. It is interesting that SMA1000 alone was able to form a stable preemulsion in contrast to SMA2000 and SMA3000, which required the presence of some of the conventional surfactants to achieve stabilization. It should be noted that, if the SMAs were simply removed from the recipes that were just on the stable side of the results in Table III (i.e., 88% SMA2000 and 60% SMA3000), then the resulting emulsions were not stable. This is an indication that SMA2000 and SMA3000 indeed help in the emulsification, even if they are not able to form stable preemulsions alone.

By taking into account the results of Table III, preemulsions having various amounts of SMA could be used in emulsion polymerizations: up to 100%, 88%, and 60%, for SMA1000, SMA2000, and SMA3000, respectively.

Batch and semicontinuous emulsion polymerization processes were both used to prepare MMA/BuA copolymer latexes at 70°C.

Batch Emulsion Polymerizations

Batch emulsion polymerizations were conducted to prepare low solids content (10%) latexes using either the SMAs as the sole surfactant or in combination with the conventional surfactants, NPP and NPPS. The first objective of this study was to compare the relative efficiencies of the different SMAs in forming stable latexes when only SMA was involved in the stabilization and to determine their influence on the latex characteristics, such as the latex stability, and the particle size and size distribution. Secondly, it was of interest to probe and compare the interaction between the different SMAs (SMA1000, SMA2000, and SMA3000) and the conventional surfactants, over a wide range of SMA/conventional surfactant ratios and total surfactant concentration in the polymerizations. The last objective of this study was to determine the optimum recipe (in terms of the combination and amount of these surfactants) required to prepare stable latexes.

Bottle polymerizations were run at 70°C using the recipe given in Table IV. The time of polymerization was 8-10 h and the final conversions, determined by gas chromatography and gravimetry, were $\sim 100\%$.

Batch Emulsion Polymerizations Using SMA as the Sole Surfactant

Characteristics of the latexes prepared using varying amounts of SMA1000, SMA2000, and SMA3000 are listed in Tables V and VI. Table V also lists as a reference the characteristics of latexes prepared using the conventional surfac-

Table IV	Recipe	for	Bottle	Polymerizations
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Ingredient	Amount (g)
Water	40
Surfactant ^a	0.0222 - 2.44
MMA/BuA mixture	4.44
(50/50 wt % ratio)	
Ammonium persulfate	0.0254
Sodium bicarbonate	0.0254

 $^{\rm a}$ NPP/NPPS wt ratio = 1/5 when using conventional surfactants alone or in combination with SMA.

Sample Name	%SMA ^a 1000	$\operatorname{Stability^{b}}$	% Solids Content	% Coagulum	D_w (nm)	D_n (nm)	D_w/D_n
DTNBS2	3.8	\mathbf{S}	7.0	34	167	149	1.12
DTNBS26	8.0	S	6.5	43	147	116	1.27
DTNBS27	12.7	S	7.5	38	172	160	1.07
DTNBS33	20.0	S	8.9	30	161	128	1.26
DTNBS34	25.0	S	9.3	31	139	100	1.39
DTNBS41	30.0	\mathbf{S}	10.5	23	141	133	1.06
DTNBS42	35.0	S	11.3	19	110	95	1.16
DTNBS52	40.0	\mathbf{S}	12.7	9	103	85	1.21
DTNBS58	45.0	S	13.8	2	98	88	1.12
DTNBS59	50.0	S	14.2	2	90	73	1.24
DTNBS78	55.0	S	14.5	3	74	59	1.25
Sample	% NPP/						
Name	NPPS ^a	Stability ^b	% Solid Content	% Coagulum	D_w (nm)	$D_n (\mathrm{nm})$	D_w/D_n
DTNBS18 ^c	3.8	S	10.4	0	43.1	31.2	1.38
DTNBS61 ^c	8.0	S	10.8	0	27.0	14.7	1.84
DTNBS62 ^c	12.7	S	11.2	0	26.1	15.1	1.73
DTNBS51 ^c	20.0	S	11.9	0	21.9	10.8	2.02

Table VCharacteristics of MMA/BuA Copolymer Latexes Prepared Using Varying Amountsof SMA1000 or Conventional Surfactants (Based on Monomer)

^a Wt % based on monomer.

 $^{\rm b}$ S = stable; latex with or without a lump of coagulum at the bottom of the reaction flask.

^c These latexes appeared translucent; all others were milky white in appearance.

tants alone. Included in the characterization are the amounts of coagulum, determined by filtering the final latex through a $100-\mu$ m filter, and the weight and number average particle sizes, determined by dynamic light scattering (Nicomp), as a function of the amount of SMA (based on monomer). As expected, no coagulum was formed for polymerizations using only conventional surfactants. On the other hand, greater amounts of SMA2000 and SMA3000 (>8% based on monomer) were needed to prepare latexes without coagulum. However, the synthesis of coagulum-free latexes with a reasonable amount of SMA1000 was not achievable; coagulum was still produced even at a very high SMA1000 content (55%).

These results, obtained over a wide range of SMA concentrations, provide direct evidence that SMA1000 is less efficient in stabilizing latex particles and corroborate the interfacial tension measurements that indicated a poorer ability of the SMA1000 to reduce the interfacial tension, compared with the SMA2000 and SMA3000.

The smallest particle size was obtained for latexes prepared using only the conventional surfactants. Similar amounts of SMA resulted in larger particle sizes. The largest particle sizes were found for latexes prepared using SMA1000. This was probably due to limited aggregation occurring during the polymerization. For SMA2000 and SMA3000, the particles were stabilized better, agglomeration being less a factor, and therefore the particles were smaller. No recognizable trend can be seen in the results for SMA2000 and SMA3000, except that the particle size does not seem to be a strong function of the SMA content when it is > 8%.

The breadth of the particle size distribution, as indicated by the polydispersity index (D_w/D_n) , was lower when using the SMAs, compared with the conventional surfactants. For SMA1000 and low concentrations of SMA2000 or SMA3000 (up to 8% SMA based on monomer), the lower polydispersity might be due to the agglomeration phenomenon that removes a part of the particle population that can lead to a narrower distribution.

Batch Emulsion Polymerizations Using SMA in Combination with Conventional Surfactants

The recipe given previously in Table IV was used to carry out polymerizations using combinations of the different SMAs and the conventional sur-

Sample Name ^a	$\% \mathrm{SMA^{b}}$	Stability ^c	% Solids Content	% Coagulum	D_w (nm)	D_n (nm)	D_w/D_n
			SMA	2000			
DTNBS5	3.8	U	5.1	53	55.5	45.4	1.22
DTNBS37	8.0	\mathbf{S}	10.1	1	44.3	30.9	1.43
DTNBS38	12.7	S	11.2	0	46.1	31.6	1.46
DTNBS31	20.0	S	11.8	0	45.6	28.9	1.58
DTNBS35	25.0	S	12.3	0	28.9	14.2	2.03
DTNBS42	30.0	S	12.6	0	50.0	35.9	1.39
DTNBS44	35.0	S	13.2	0	42.6	26.2	1.63
			SMA	3000			
DTNBS8	3.8	U	3.1	73	61.0	47.0	1.30
DTNBS39	8.0	S	10.5	1	36.1	22.0	1.64
DTNBS40	12.7	S	11.2	0	44.1	31.1	1.42
DTNBS32	20.0	\mathbf{S}	11.9	0	43.4	35.9	1.21
DTNBS36	25.0	S	12.3	0	27.0	13.1	2.06
DTNBS45	30.0	S	12.9	0	32.3	15.2	2.13
DTNBS46	35.0	S	13.3	0	29.3	13.5	2.17

Table VICharacteristics of MMA/BuA Copolymer Latexes Prepared Using Varying Amountsof SMA2000 and SMA3000

^a All latexes were translucent.

 $^{\rm b}$ Wt % based on monomer.

 c S = stable; latex with or without a lump of coagulum at the bottom of the reaction flask. U = unstable; latex with suspension of coagulum.

factants (1/5 NPP/NPPS wt ratio in all cases) over a wide range of surfactant concentrations. In one series of experiments, the SMA/conventional surfactants ratio was kept constant at 50/50, with varying amounts of the total stabilizer between 3.8 and 35% based on monomer. In another series of experiments, the amount of the conventional surfactants based on monomer was held constant (1.9% or 4%), and the SMA/conventional surfactants ratio was varied from 0/1.9 to 0.1/1.9. Using this approach, a better understanding of the interaction between the two types of surfactants was expected.

Influence of the Type of SMA and Total Amount of Surfactant (SMA/Conventional Surfactant, 1/1 Wt Ratio)

Table VII gives the characteristics of the latexes prepared by replacing half of the conventional surfactants (NPP/NPPS, 1/5 wt ratio) with SMA1000, SMA2000, and SMA3000, and varying the total amount of added surfactant. Although no coagulum was obtained in latexes prepared using only the conventional surfactants at 2 wt % based on monomer, when polymerizations were run with 2 wt % of the conventional surfactants plus 2 wt % SMA, substantial amounts of coagulum were formed. The greatest amount of coagulum was obtained for SMA3000 (62% coagulum), whereas the lowest amount corresponded to SMA1000 (20% coagulum). These results strongly suggest that the SMA interacts in some manner with the conventional surfactants during the emulsion polymerization. This interaction could take place by hydrogen bonding between the nonneutralized SMA and the oxygen of the ethylene oxide unit of the conventional surfactants leading to the formation of a more hydrophobic stabilizer (complex), which could act to destabilize the latex particles. With greater amounts of surfactant (>8% for SMA1000 or 12% for SMA2000 and SMA3000), no coagulum was formed that might indicate that the amount of available surfactant (mostly the conventional surfactants) that was not involved in these interactions, was sufficient to stabilize the latex particles.

The amount of coagulum formed might be taken as an indication that the greatest interaction is between the SMA3000 and the conventional surfactants, because this system resulted

Sample Name ^a	% Surfactant ^b	$\operatorname{Stability^{c}}$	% Solids Content	% Coagulum	D_w (nm)	D_n (nm)	D_w/D_n
			50% SMA	1000			
DTNBS13	3.8	S	8.4	20	67.2	65.0	1.12
DTNBS53	8.0	S	10.8	0	48.8	36.6	1.33
DTNBS54	12.7	S	11.3	0	47.6	37.0	1.29
DTNBS49	20.0	S	11.9	0	42.8	31.9	1.34
DTNBS50	35.0	S	13.2	0	40.5	29.5	1.37
			50% SMA	2000			
DTNBS14	3.8	U	5.1	20	66.5	55.5	1.20
DTNBS55	8.0	S	10.6	2	55.1	43.2	1.28
DTNBS56	12.7	S	11.4	0	53.6	42.9	1.25
DTNBS47	20.0	S	11.9	0	46.9	36.4	1.29
			50% SMA	3000			
DTNBS15	3.8	U	4.2	62	66.2	51.7	1.28
DTNBS57	8.0	S	8.8	20	41.9	26.5	1.58
DTNBS60	12.7	S	11.4	0	39.4	26.9	1.46
DTNBS48	20.0	S	11.9	0	26.5	14.8	1.79

Table VIICharacteristics of MMA/BuA Copolymer Latexes Prepared Using Varying Amountsof SMA/Conventional Surfactant Mixture (50% SMA Based on Total Surfactants)

^a All latexes were translucent.

^b Wt % based on monomer.

 c S = stable; latex with or without a lump of coagulum at the bottom of the reaction flask. U = unstable; latex with suspension of coagulum.

in the greatest amount of coagulum. However, if the nature of this interaction is by hydrogen bonding, this interaction should have been more enhanced in the presence of the SMA1000, because it has the largest number of maleic anhydride units that can generate a greater number of complexed carboxyl groups. The relationship between the interaction of SMA with conventional surfactants and the destabilization of latex particles (occurrence of coagulum) could be explained in terms of the degree of hydrophobicity of the stabilizer resulting from this interaction. The hydrophobic nature of the interacting emulsifiers is the greatest when using SMA3000 due to greater quantity of polystyrene units in the SMA. The hydrophobic complex resulting from this interaction should be more strongly adsorbed at the particle surface leading to greater stability *via* steric repulsion. Therefore, the formation of more coagulum when using SMA3000 might be an indication that the conventional surfactants alone act as better stabilizers than the interacting emulsifiers unless the hydrophile/lypophile balance (HLB) of the resulting complex is shifted toward

lower values, making it a poor stabilizer for the aqueous dispersions.

Particle size results in Figure 3 show that larger particles were formed when using the SMA/conventional surfactant mixtures, compared with the conventional surfactants alone, even at the higher amounts of surfactant when no coagulation occurred. In contrast to the previous results where SMA was used as the sole surfactant, the difference in particle size between SMA1000 and the two other SMAs (2000 and 3000) was substantially decreased. When using SMA as the sole surfactant, an extremely large particle size difference between SMA1000 and SMA2000 or SMA3000 was obtained due to agglomeration resulting from the poorer stabilizing ability of SMA1000. This large difference in particle size is no longer apparent in the present case. This is attributed to the SMA1000/conventional surfactants interaction, which enhances the emulsifying properties compared with those for mixtures of SMA2000 or SMA3000 with the conventional surfactants.

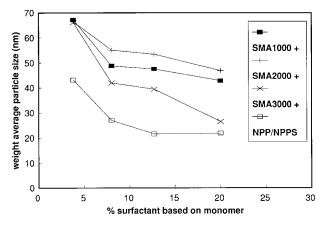


Figure 3 Weight average particle diameter of MMA/ BuA copolymer latexes prepared using the conventional surfactants (NPP/NPPS) alone and SMA/conventional surfactants mixtures (50/50) as a function of the total amount of surfactant.

Figure 4 shows a plot of the weight average particle size as a function of the concentration of surfactant for latexes prepared using SMA1000 alone, compared with those resulting from the SMA1000/ conventional surfactants mixtures. As might be expected, the particles sizes decreased with increasing surfactant levels, but again do not seem to be very

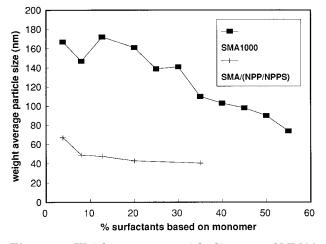


Figure 4 Weight average particle diameter of MMA/ BuA copolymer latexes prepared using 4 wt % conventional surfactants based on monomer in combination with an increasing amount of SMA.

sensitive at the higher concentrations. It appears that the use of SMA1000 in combination with the conventional surfactants results in a large decrease in the particle size, compared with polymerizations using SMA1000 as the sole surfactant. Again, this difference was probably due to agglomeration. SMA is a poor stabilizer, and these results show that,

Sample Name ^a	%SMA ^b	$Stability^{c}$	% Solids Content	% Coagulum	D_w (nm)	D_n (nm)	D_w/D_n
	,			,	- w ()	- n ()	-w - n
			SMA	1000			
DTNBS11	0	\mathbf{S}	10.4	0	43.1	31.2	1.38
DTNBS53	4	S	10.8	0	48.8	36.6	1.33
DTNBS73	8.7	S	10.3	9	41.9	26.6	1.58
DTNBS74	16	S	11.8	0	40.0	23.0	1.74
			SMA	2000			
DTNBS55	4	S	10.6	2	55.1	43.2	1.28
DTNBS68	8.7	\mathbf{S}	10.9	3	34.6	22.7	1.52
DTNBS69	16	S	11.9	0	33.4	20.4	1.6
			SMA	3000			
DTNBS57	4	S	8.8	20	41.9	26.5	1.58
DTNBS63	8.7	\mathbf{S}	10.2	10	21.8	10.1	2.16
DTNBS64	16	S	11.9	0	30.3	19.3	1.57

Table VIIICharacteristics of MMA/BuA Copolymer Latexes Prepared Using Varying Amountsof SMA and 4 Wt % NPP/NPPS (1/5 Wt Ratio) Based on Monomer

^a All latexes were translucent.

 $^{\rm b}$ Wt % based on monomer.

 $^{\rm c}$ S = stable; latex with or without a lump of coagulum at the bottom of the reaction flask. U = unstable; latex with suspension of coagulum.

Sample Name	% SMA ^a	$\operatorname{Stability}^{\mathrm{b}}$	% Solids Content	% Coagulum	D_w (nm)	D_n (nm)	D_w/D_n
			SN	IA1000			
DTNBS29	0	S	10.3	0	59.9	47.0	1.27
DTNBS13 ^c	1.9	S	8.4	20	67.2	65.0	1.12
DTNBS75°	6.1	\mathbf{S}	7.4	34	58.7	40.8	1.44
DTNBS76 ^c	10.8	S	8.2	31	58.0	40.3	1.44
DTNBS77 ^c	18.1	S	10.0	20	65.3	50.5	1.29
			SN	IA2000			
DTNBS14	1.9	U	5.1	53	66.5	55.5	1.20
DTNBS70	6.1	\mathbf{S}	7.2	36	26.3	13.1	2.01
DTNBS71	10.8	\mathbf{S}	10.3	9	18.9	9.0	2.10
DTNBS72	18.1	S	11.9	0	33.5	20.4	1.64
			SN	IA3000			
DTNBS15	1.9	U	4.2	62	66.2	51.7	1.28
DTNBS65	6.1	S	6.5	44	28.0	15.8	1.77
DTNBS66	10.8	S	9.7	15	36.7	20.5	1.78
DTNBS67	18.1	S	11.9	0	28.2	17.4	1.64

Table IXCharacteristics of MMA/BuA Copolymer Latexes Prepared Using Varying Amountsof SMA1000 and 1.9 Wt % NPP/NPPS (1/5 Wt Ratio) Based on Monomer

^a Wt % based on monomer.

 b S = stable; latex with or without a lump of coagulum at the bottom of the reaction flask. U = unstable; latex with suspension of coagulum.

^c These latexes were milky white.

even if some interaction occurs, the SMA1000/conventional surfactants mixture acts as a better stabilizer resulting in smaller particle sizes than the SMA1000 alone. This is in contrast to the SMA2000 and SMA3000 where a slight increase in the particle size took place (with the exception of the higher surfactant concentrations for SMA3000).

Influence of SMA/Conventional Surfactants Ratio (Fixed Amount of Conventional Surfactants)

Polymerizations were conducted using a constant amount of the conventional surfactants (NPP/ NPPS, 1/5 wt ratio) based on monomer in combination with an increasing amount of SMA. Characteristics of the resulting latexes prepared using SMA1000, SMA2000, and SMA3000 are listed in Table VIII. The amount of the conventional surfactants was fixed at 4 wt %, based on monomer. Table IX gives the values for latexes prepared using a constant 1.9 wt % (based on monomer) of the conventional surfactants in combination with SMA1000, SMA2000, and SMA3000. As indicated previously, by using 12.7 wt % SMA2000 or SMA3000 as the sole surfactant, no coagulum was formed. These results show that when part of the 12.7% SMA2000 or SMA3000 was replaced by the conventional surfactants [e.g., 4 wt % (based on monomer) of the conventional surfactants plus 8.7 wt % SMA (=12.7 wt %) or 1.9 wt % of the conventional surfactants plus 10.8 wt % SMA]that have a better stabilization efficiency-a substantial amount of coagulum was obtained. This provides strong support for the proposed interaction of SMA with conventional surfactants. In agreement with the previous results, the greatest amount of coagulum was formed when using SMA3000, with the exception of the higher levels of SMA in combination with 1.9% of the conventional surfactants where SMA1000 induced more coagulum. In fact, the amounts of SMA1000 used (10.8 and 18.1%) were not sufficient to avoid coagulum if SMA alone was used for particle stabilization in contrast with SMA2000 and SMA3000, where no coagulum was found at these concentrations.

The amount of coagulum systematically decreased when the amounts of SMA2000 and SMA3000 were increased from 1.9 to 18.1%. In the case of SMA1000, the decrease followed an increase in the coagulum at lower levels of SMA (0-6.1%), indicating that an increasing amount of SMA (above 6.1%) induces more interactions with the conventional surfactants until probably most or all of the conventional surfactants are involved in the interaction, thereby changing the HLB to lower values. Then, the excess SMA at the higher concentrations itself contributes to increasing the HLB value, resulting in better stabilization. Because SMA1000 by itself is a poor stabilizer, as demonstrated previously in Table V, more coagulum was induced with greater amounts of added SMA.

From the preceding results obtained in batch emulsion polymerizations, the following conclusions can be made:

- 1. The preparation of coagulum-free latexes requires relatively large amounts of the surfactants if only SMA or SMA/conventional surfactants mixtures are used in the preparation because of the relatively poor surface active properties of the SMAs and their interaction with conventional surfactants.
- 2. In using SMA as the sole surfactant, SMA2000 and SMA3000 act as better stabilizers and induce smaller particle sizes, compared with SMA1000, which is unable to form a latex without coagulum.
- 3. In using SMA in combination with the conventional surfactants, better stabilization of the latex particles, as well as smaller particle sizes, occurs in the presence of SMA1000 because of its weaker interaction with the conventional surfactants. SMA3000 has the greatest interaction, leading to the formation of the greatest amount of coagulum. It is proposed that the nature of this interaction is *via* hydrogen bonding of the carboxylic group with the oxygen ether of the ethylene oxide of the conventional surfactants.

Due to the large differences between SMA1000 and SMA3000 in stabilizing latex particles and their effect on the latex particle size, the following semicontinuous emulsion polymerizations were conducted using these in combination with conventional surfactants.

Semicontinuous Emulsion Polymerizations

The purpose of this study was to prepare latexes using a fixed total amount of the surfactants (3 wt %

Table XRecipe for Semicontinuous EmulsionPolymerizations

Phase	Ingredient	Amount (g)
Precharge	Water	85.10
0	Surfactant (NPP/	
	NPPS)	0.36
	Sodium bicarbonate ^a	0.36
	Potassium	
	$metabisulfite^{b}$	0.36
Preemulsion	Water	52.8
	Surfactant (SMA/	
	NPP/NPPS)	3.24
	MMA/BuA (50/50 wt	
	ratio)	120
Initiator solution	Water	125.3
	Ammonium	
	persulfate	0.36
	Sodium bicarbonate ^a	0.36

Reaction temperature = 70°C. NPP/NPPS wt ratio = 1/5. Feed rate of preemulsion = 42 mL h⁻¹. Feed rate of initiator solution = 28 mL h⁻¹. Polymerization is continued 2 h after the end of the feed time (4 h 30 min).

^a Use of sodium bicarbonate depends on the mode of addition described previously.

^b 0.36 g of potassium metabisulfite in 16.8 g of water is introduced in the precharge 10-15 min before the feed of the preemulsion and initiator solution.

based on monomer) by: (1) using only the conventional surfactants (NPP/NPPS); and (2) replacing a part of the conventional surfactants with varying amounts of SMA1000 and SMA3000. Using this approach, it was expected to determine how much SMA can be incorporated into the latex without inducing coagulum, simultaneously maintaining the particle size close to that of the conventional latex. It was also of interest to study the effect of the SMAs on the monomer conversion, particle size, and latex stability. The approach consisted first of preparing 33% solid content MMA/BuA copolymer latexes to determine the best conditions for using the SMAs and the appropriate time to feed SMA during emulsion polymerizations. The second step of this approach was to extend the investigation to 53% solid content MMA/BuA/AA latexes.

Semicontinuous Emulsion Polymerizations of MMA/BuA with Buffer

As stated previously, SMA forms a water-soluble salt in a basic medium giving it emulsifier properties. To maintain these properties in emulsion polymerization, the use of sodium bicarbonate is

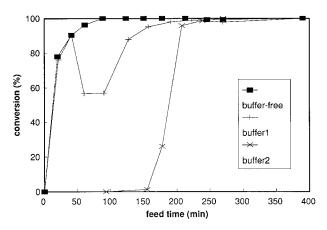


Figure 5 Monomer conversion *versus* time for semicontinuous emulsion polymerizations of MMA/BuA using only conventional surfactants (NPP/NPPS) and different modes of buffer addition: buffer 1 = bufferfree precharge and buffer fed continuously; buffer 2 = buffer in the precharge and fed continuously.

appropriate for two reasons: (1) to counter the effect of pH on the kinetics of polymerization to better determine the effect of SMA on the monomer conversion; and (2) to keep most of the carboxylic groups of the SMA neutralized to gain in electrostatic stability and to avoid the precipitation of the SMA due to the decrease in pH with decomposition of the persulfate. Due to the fact that the decomposition of the initiator and, therefore, the monomer consumption, can be strongly affected by the pH, the emulsion polymerization recipe given in Table X was adjusted by focusing on the mode of use of the sodium bicarbonate in the polymerizations. Three different modes of bicarbonate addition were tested in this study: (1)half of the buffer was used in the precharge and half was fed continuously; (2) no buffer was used in the precharge and the buffer was fed continuously; and (3) no buffer was used at all, neither in the precharge nor added continuously. These

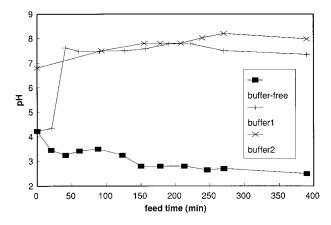


Figure 6 pH *versus* time for semicontinuous emulsion polymerizations of MMA/BuA using only the conventional surfactants (NPP/NPPS) and different modes of buffer addition: buffer 1 = buffer-free precharge and buffer fed continuously; buffer 2 = buffer in the precharge and fed continuously.

three variations were first used in semicontinuous emulsion polymerizations using the conventional surfactants (NPP/NPPS) as the sole surfactant (i.e., no SMA). The monomer conversion was determined by gravimetry and the particle size by capillary hydrodynamic fractionation (Matec Applied Sciences, Northborough, MA). Figure 5 shows the conversion *versus* time curves, and the resulting latex characteristics are listed in Table XI.

Figure 5 shows that the use of the buffer both in the precharge and fed continuously induced a substantial induction period (labeled "buffer 2"). If the precharge did not contain sodium bicarbonate, no induction period took place (labeled "buffer 1"). However, in this case, the monomer conversion, which was high at the beginning of the polymerization (80–90% conversion up to 40 min), rapidly dropped to $\sim 55\%$ conversion, and then increased again. It is interesting to point out that, when no

 Table XI
 Characteristics of MMA/BuA Copolymer Latexes Prepared Using Different Modes of Addition of Sodium Bicarbonate

Sample Name	Buffer Addition Mode	D_w	D_n	D_w/D_n	% Solids Content	pH
DTN41	Half of buffer in the precharge and half fed continuously	98.0	89.9	1.09	33.5	8.0
DTN33	Buffer-free precharge and all of the buffer fed continuously	122.7	114.6	1.07	33.9	7.4
DTN47	Buffer-free recipe	128.9	120.1	1.07	33.8	2.5

buffer was used at all in the recipe, high monomer conversions were obtained throughout polymerization.

Two factors can possibly explain the decrease in the monomer conversion after 40 min: (1) pH effect and (2) disappearance of potassium metabisulfite. In the buffer-free precharge recipe ("buffer 1"), before starting the feed of the preemulsion and initiator solution that contained bicarbonate, the precharge was acidic (pH 4.2) due to the presence of potassium metabisulfite. When the feed started, the amount of buffer in the reaction medium increased leading to an increase in the pH as shown in Figure 6 as a function of time for the three polymerizations. Decomposition of the initiator was faster at the beginning of the polymerization due to the acidic pH,¹³ producing more radicals, thus leading to a higher monomer conversion. Then, the decomposition rate of the persulfate decreased as the pH increased from 4.2 to 7.5-8, thus inducing the drop in monomer conversion.

In the buffer-free recipe, all of the polymerization took place in an acidic medium inducing a high production rate of radicals and therefore high conversions. If bicarbonate was used in the precharge and fed continuously, the pH of the medium was not acidic and increased from neutral to mildly basic. The rate of decomposition of the initiator was, therefore, relatively low leading to an induction period.

The second factor that can have the same effect on the monomer conversion is the disappearance of potassium metabisulfite. In fact, the reaction temperature of 70°C is rather high for the persulfate/metabisulfite redox system. The disappearance of metabisulfite might be so fast that, after 40 min, its concentration nears 0. The decomposition of metabisulfite can be accelerated also by the increase in pH. Consequently, the decomposition of persulfate might decrease. However, in the buffer-free precharge experiment, by feeding the metabisulfite continuously or by adding it at 35-40 min, just before the drop in the monomer conversion, there was no significant change in the shape of the conversion-time curve.

As seen in Table XI, the particle size of the latex prepared using the bicarbonate in the precharge was the smallest, whereas the other two modes of bicarbonate addition resulted in similar particle sizes. The reason for these differences is not clear.

The buffer-free recipe (Table X) was next modified to run polymerizations using a 10/90 SMA/ conventional surfactants ratio. Three modes of addition of SMA in the preemulsion were used: (1) the SMA was fed as a component of the preemulsion from the beginning to the end of the polymerization; (2) the SMA preemulsion was fed after first feeding half of the monomer as a preemulsion prepared using only the conventional surfactants; and (3) only the last 20% of the monomer was fed as a preemulsion prepared using SMA after feeding 80% of the monomers as a preemulsion prepared with the conventional surfactants.

Table XII lists the characteristics of the latexes prepared adding SMA1000 and SMA3000 via the various feed modes. When SMA1000 was used as part of the surfactant system, no coagulum was formed, with the exception of the polymerizations where SMA was used in the precharge (DTN39; feed mode 2). The formation of coagulum was found to take place during the first stage of the polymerization (0-30 min) due to the acidic medium that precipitated SMA. The corresponding particle size was also the highest. In addition, if the preemulsion containing SMA1000 was added from the beginning to the end (DTN35; feed mode 3), an increase in the particle size, compared with polymerization using conventional surfactants alone (DTN33; feed mode 1), was observed. Therefore, using this recipe, it is not recommended that SMA be used in the precharge or that the SMA preemulsion be fed in the first stage of the polymerization to avoid the formation of coagulum and subsequent increase in particle size.

Using SMA3000 as part of the surfactant system, coagulum was formed and a large increase in particle size was obtained no matter which mode of addition of SMA in the preemulsion was used, with the exception of the polymerization where SMA was added after feeding 80% of the preemulsion prepared using only the conventional surfactants (DTN46).

Table XII also shows that the particles were larger for latexes prepared using SMA3000 than those formed in polymerizations using SMA1000. The particle size was smaller if the SMA was added later in the polymerization, and the effect was more enhanced in the case of the SMA3000. Therefore, it is recommended that SMA, and especially SMA3000, be used no earlier than the second stage of the reaction (emulsion feed) and preferably in the later stages of polymerization.

Sample	${f SMA}$ Feed				% Solids	
Name	Mode ^a	D_w (nm)	$D_n \; ({\rm nm})$	D_w/D_n	Content	% Coagulum
			SMA1000			
DTN33	1	122.7	114.6	1.07	33.9	0
DTN39	2	174.5	170.2	1.03	32.4	4
DTN35	3	135.4	125.6	1.08	33.9	0
DTN29	4	115.0	104.6	1.10	32.2	0
DTN40	5	118.2	106.3	1.11	33.4	0
			SMA3000			
DTN33	1	122.7	114.6	1.07	33.9	0
DTN36	3	183.7	168.3	1.09	29.5	11
DTN30	4	142.3	135.2	1.05	30.1	8
DTN46	5	123.9	113.8	1.09	33.8	0

Table XII Characteristics of MMA/BuA Copolymer Latexes Prepared Using Only Conventional Surfactants and by Replacing 10 Wt % of Conventional Surfactants with SMA1000 and SMA3000 at Different Stages of Polymerizations

^a Mode of addition of SMA: 1, conventional surfactants only; 2 half of SMA used in the precharge and the second half fed continuously in the preemulsion from the beginning to the end of polymerization; 3 SMA free precharge and the SMA in the preemulsion added from the beginning to the end of polymerization; 4 SMA free precharge: the first half of the preemulsion containing only the conventional surfactants and the second half fed with the SMA; 5 SMA free precharge and only the last 20% of the preemulsion added using SMA.

Semicontinuous Emulsion Polymerizations of MMA/BuA without Buffer

As shown previously, the problem of the induction period or the drop in monomer conversion during the emulsion polymerization using only the conventional surfactants was overcome if no bicarbonate was used in the recipe. As a reminder, the role of the buffer was to prevent the precipitation of the SMA due to the drop in the pH induced by the persulfate decomposition and to counter the effect of pH to determine better the effect of SMA on the monomer conversion. A bicarbonate-free recipe was used for polymerizations using SMA in combination with the conventional surfactants to study the effect of the type of SMA, amount of SMA, and SMA feed mode on monomer conversion, latex stability, and resulting particle size. It was also of interest to follow the evolution of the pH of the medium that might affect the rate of decomposition of the initiator and the SMA stabilizing properties that would consequently have an influence on the monomer conversion and latex stability.

Influence of the Type and Amount of SMA

Polymerizations were conducted using the conventional surfactants alone and by replacing 2-40% and 2-20% of the conventional surfactants with SMA1000 and SMA3000, respectively. In all cases, the precharge contained only the conventional surfactants and the preemulsion prepared using SMA was added from the beginning to the end of the polymerization.

Figure 7 is a plot of the monomer conversion as a function of time for polymerizations using varying concentrations of SMA1000 (0-40%). Note that there was no induction period, no drop in the monomer conversion, and no major effect on the monomer conversion when using a low concentration of SMA ($\leq 27\%$). This can be explained by the effect of the pH of the medium. Figure 8 presents the evolution of pH against time, showing that it decreased until \sim 30 min due to the decomposition of persulfate, then increased as a consequence of the feed of the basic SMA solution. At a low concentration of SMA, all of the polymerization was conducted in an acidic medium (pH < 7), and the rate of decomposition of the persulfate was high leading to a high monomer conversion. At a high concentration of SMA, an increase in the pH of the medium occurred at the beginning of the polymerization, resulting in a mildly basic or nearly neutral medium (pH 7). Consequently, the lower rate of radical formation induced a drop in the monomer conversion for polymerizations

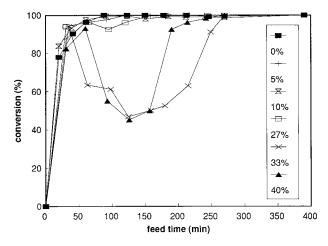


Figure 7 Monomer conversion *versus* time for semicontinuous emulsion polymerizations of MMA/BuA using varying concentrations of SMA1000 in combination with conventional surfactants (concentration based on total surfactants).

using the greater amounts of SMA1000, as shown in Fig. 7.

Table XIII gives characteristics of the latexes corresponding to polymerizations using varying concentrations of SMA1000 and SMA3000. In contrast to the previous latexes prepared using buffer in the initiator solution, the latexes prepared using 10 wt % SMA (especially SMA3000) and feeding the SMA preemulsion from the beginning to the end of polymerization were coagulumfree, and the particle sizes were not increased significantly. These results seem paradoxical if we take into account that, using the buffer, most of the carboxylic groups of the SMA are in the neutralized form and consequently can act as a better stabilizer. Formation of coagulum when using the buffer might be due to the accumulation of the monomer in the reaction medium induced by the drop in monomer conversion shown previously.

The preparation of coagulum-free latexes was achieved over a wide range of SMA1000 concentrations between 2 and 27%, based on the total surfactants (SMA + conventional surfactants), and there was little change in the particle size compared with the latexes prepared using only the conventional surfactants (SMA $\leq 27\%$). However, formation of coagulum, as well as an increase in the particle size, occurred at the higher concentrations of SMA1000 (33 and 40% SMA1000).

Preparation of latexes without coagulum in the presence of SMA3000 could be achieved only with the lower SMA concentrations (up to 10% SMA3000). Above 10% SMA3000, a substantial amount of coagulum was formed, and particle size was increased substantially. A larger particle size and more coagulum were formed for latexes prepared using SMA3000, compared with SMA1000—this being attributed to a stronger interaction between SMA3000 and conventional surfactants.

Influence of the Mode of Addition of SMA

Emulsion polymerizations were conducted by feeding the first half of the preemulsion, prepared using only the conventional surfactants, and the second half prepared with SMA1000 and SMA3000 in combination with conventional surfactants. Concentration of SMA in the surfactant mixture was between 5 and 20%. In Table XIV are listed the characteristics of the corresponding latexes, as well as those prepared by feeding the SMA preemulsion from the beginning to the end of the polymerization for both SMA3000 and SMA1000. From these results, it appears that the use of SMA in the second stage of polymerization allows the incorporation of more SMA into the latex without the formation of coagulum. Fifteen percent of the conventional surfactants could be replaced by SMA3000 during the second stage without inducing the formation of coagulum. When 20% (DTN60) and 15% (DTN58) SMA3000 were used in the second stage, the amount of coagulum dropped appreciably.

Besides the preparation of coagulum-free latexes, smaller particle sizes were formed when SMA was added in the second stage of polymerization,

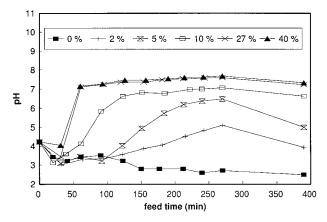


Figure 8 pH *versus* time for semicontinuous emulsion polymerizations of MMA/BuA using varying concentrations of SMA1000 in combination with conventional surfactants (concentration based on total surfactants).

Sample					% Solids		
Name	% SMA ^a	D_w (nm)	$D_n \; (\mathrm{nm})$	D_w/D_n	Content	% Coagulum	$_{\rm pH}$
			SMA1	000			
DTN47	0	128.9	120.1	1.07	33.8	0	2.5
DTN63	2	122.7	112.8	1.09	33.9	0	3.9
DTN55	5	127.8	117.3	1.09	34.6	0	5.0
DTN49	10	131.0	121.4	1.08	33.8	0	6.6
DTN53	15	136.6	128.8	1.06	33.5	0	6.6
DTN51	20	128.3	119.9	1.07	33.8	0	7.0
DTN57	27	140.7	131.4	1.07	33.8	0	7.2
DTN62	33	178.7	177.4	1.01	29.2	11	7.3
DTN59	40	179.0	173.5	1.03	29.1	11	7.3
			SMA3	000			
DTN64	2	126.3	116.7	1.08	33.7	0	3.9
DTN56	5	133.6	123.5	1.08	33.9	0	4.9
DTN50	10	131.0	119.3	1.10	33.9	0	6.7
DTN54	15	171.0	165.5	1.03	27.4	19	6.8
DTN52	20	179.3	173.6	1.03	28.1	19	6.8

Table XIII Characteristics of MMA/BuA Copolymer Latexes (33% Solids) Prepared Using Varying Amounts of SMA1000 and SMA3000 in Combination with Conventional Surfactants (3 Wt % Total Surfactant Based on Monomer)

^a Wt % based on total surfactant.

and these values are close to that of conventional surfactants. For example, particle size decreased from 171 nm to 131 nm when using 15% SMA3000 in combination with conventional surfactants.

At lower concentrations of SMA, no significant difference in particle size was noted by adjusting the SMA feed mode. The main advantage of the second stage addition was found at higher concentrations of SMA—especially SMA3000—where the particle size was similar to that of conventional latex (i.e., no SMA added), coagulum was avoided, and more SMA was incorporated into the latex.

Semicontinuous Emulsion Polymerizations of MMA/BuA/Acrylic Acid

Previous results dealing with the preparation of low solids content (10-33%) MMA/BuA copolymer latexes *via* batch and semicontinuous emulsion polymerizations showed that a substantial amount of SMA can be incorporated into the latex without inducing coagulum or a significant increase in the particle size. The second stage addition of SMA was found to be efficient in avoiding the formation of coagulum and an increase in the latex particle size. The goal of this study was to extend this type of investigation to the preparation and characteriza-

tion of MMA/BuA/acrylic acid copolymer latexes having 53% solids contents via semicontinuous emulsion polymerizations using SMA1000 and SMA3000 in combination with conventional surfactants. In addition, an esterified version of SMA1000 (termed SMA1440) was also used in some experiments.

Semicontinuous emulsion polymerizations were conducted by replacing varying amounts of the conventional surfactants: NPP/NPPS (1/5 wt ratio), with SMA1000, SMA1440, and SMA3000. The recipe is given in Table XV. Varying SMA/conventional surfactants ratios were used. Table XVI lists the characteristics of the resulting copolymer latexes. SMA preemulsions were fed either from the beginning to the end of polymerization or during the second stage after feeding the first half of the preemulsion prepared using only conventional surfactants. Substantial amounts of coagulum were formed above 10% SMA1000, in contrast with the 33% solid content latexes prepared without acrylic acid, where no coagulum was noted up to 27% SMA1000. Furthermore, unlike the latex prepared using 15% SMA1000 and acrylic acid, the one prepared with the same amount of SMA1000, but without acrylic acid, was coagulum-free. These results

Sample					% Solids		
Name	% SMA ^a	D_w (nm)	$D_n \; (\mathrm{nm})$	D_w/D_n	Content	% Coagulum	pН
			SMA1	000			
DTN47	0	128.9	120.1	1.07	33.8	0	2.5
DTN65	5^{b}	122.6	114.0	1.08	33.7	0	4.9
DTN45	$10^{ m b}$	128.7	117.8	1.09	34.0	0	6.6
DTN61	$15^{ m b}$	117.8	109.7	1.07	32.9	0	6.7
DTN55	5	127.8	117.3	1.09	34.6	0	5.0
DTN49	10	131.0	121.4	1.08	33.8	0	6.6
DTN53	15	136.6	128.8	1.06	33.5	0	6.6
			SMA3	000			
DTN66	5^{b}	128.3	121.0	1.06	33.6	0	5.6
DTN48	$10^{ m b}$	134.0	123.8	1.08	33.6	0	6.5
DTN58	$15^{ m b}$	131.7	122.8	1.07	33.5	0	6.4
DTN60	20^{b}	122.0	111.0	1.10	32.8	4	6.9
DTN56	5	133.6	123.5	1.08	33.9	0	4.9
DTN50	10	131.0	119.3	1.10	33.9	0	6.7
DTN54	15	171.0	165.5	1.03	27.4	19	6.8
DTN52	20	179.3	173.6	1.03	28.1	15	6.8

Table XIV Characteristics of MMA/BuA Copolymer Latexes (33% Solids) Prepared Using Different Modes of Addition of SMA in the Preemulsion with Varying Amounts of SMA1000 and SMA3000 in Combination with Conventional Surfactants

 $^{\rm a}$ Wt % based on total surfactant (3 wt % total surfactant based on monomer).

^b Second-stage addition of SMA: addition of the second half of the preemulsion prepared using SMA in combination with conventional surfactants after feeding the first half as a conventional preemulsion.

show that the use of acrylic acid in emulsion polymerizations with SMA as a part of the surfactant system in some manner induces coagulum. This might be due to the pH of the medium. In the presence of acrylic acid, the pH of the reaction medium is more acidic (4 < pH < 5), compared with the acrylic acid-free polymerization where the pH ranged from 4 to 7. The amount of nonneutralized carboxylic groups of the SMA1000 and, therefore, the SMA/conventional surfactants interaction by Hbonding, is the greatest when using acrylic acid, leading to the formation of substantial amounts of coagulum. In the same direction, it can be noted that using the esterified SMA1440-having fewer carboxylic groups, compared with SMA1000-led to a lower amount of coagulum and could be used to prepare coagulum-free latexes up to 15% SMA1440.

In contrast to the previous study, coagulum was formed when feeding the preemulsion prepared using SMA1000 or SMA1440 in the second stage of the reaction. However, it is interesting to point out that using 15% SMA based on the total surfactants in the second stage addition, only the latex prepared using SMA3000, having the lowest amount of carboxylic groups, was coagulum-free. Destabilization of particles when using SMA in the emulsion polymerizations seems to be due to concomitant factors that are the interaction of the SMA with conventional surfactants and the degree of hydrophobicity or the HLB of the emulsifier complex. Using acrylic acid, most of the carboxylic groups are not neutralized and the strongest interaction occurs. SMA1000, having the greatest amount of carboxylic groups, induces the largest amount of coagulum. Regarding the particle size, no increase in particle size was noted for coagulum-free latexes prepared using SMA (i.e., up to 10% SMA1000, 15% SMA1440, and 10% SMA3000) when feeding SMA in the early stage of the polymerizations or 15% SMA3000 when using the second-stage addition of SMA. At higher concentrations of SMA, an increase in the particle size took place due to agglomeration.

CONCLUSIONS

SMAs were found to be less efficient than the conventional surfactants in reducing the interfacial

Phase	Ingredients	Amount (g)	
Precharge	Water	80.0	
0	Surfactant		
	(NPP/NPPS,		
	1/5 wt ratio)	0.6	
	Potassium		
	metabisulfite ^a	0.6	
Preemulsion	Water	88.0	
	Surfactant		
	(SMA/NPP/		
	NPPS)	5.4	
	MMA/BuA/AA		
	(44/55/1 wt		
	ratio)	200.0	
Initiator solution	Water	22.0	
	Ammonium		
	persulfate	0.6	

Table XV	Recipe for Semicontinuous Emulsion				
Polymerizations of MMA/BuA/Acrylic					
Acid (AA;	53% Solids)				

Reaction temperature = 70°C. NPP/NPPS wt ratio = 1/5. Feed rate of preemulsion = 70 mL h⁻¹. Feed rate of initiator solution = 5 mL h⁻¹. Polymerizations were continued 2 h after the end of the feed time (4 h 30 min). Monomers are not distilled to resemble industrial reaction conditions.

 $^{\rm a}$ 0.6 g of potassium metabisulfite in 10 g of water is introduced in the precharge 10–15 min before the feed of the preemulsion and initiator solution.

tension between water and monomer (MMA/BuA). SMA1000 was found to be the only type of SMA studied that was able to form a stable monomer emulsion. By using combinations of SMA2000 and SMA3000 with conventional surfactants, it was possible to prepare stable emulsions over a wide range of SMA content.

Preparation of coagulum-free, stable latexes via batch emulsion polymerization of MMA/BuA was found to require greater concentrations of surfactant if SMA alone or SMA/conventional surfactant mixtures were used in polymerizations. This was considered to be a direct consequence of the lower surface-active properties of the SMAs and their interaction with conventional surfactants over a wide range of SMA concentrations.

Using SMA as the sole surfactant in batch emulsion polymerizations, SMA2000 and SMA3000, which were shown to have greater surface active efficiencies, acted as better stabilizers and resulted in smaller particles, compared with SMA1000 that was not able to form a stable latex without coagulum, even at very high concentrations. Using the SMAs in combination with conventional surfactants, better stabilization of the latexes and smaller particle sizes were produced in the presence of SMA1000, because of its weaker interaction with conventional surfactants and its lower degree of hydrophobicity in emulsifier complexes. The hydrophobic nature of these complexes was enhanced when using SMA3000, which induced a greater interaction leading to the formation of the greatest amount of coagulum and the largest particle size.

In semicontinuous polymerizations, the use of buffer in the precharge was found to result in an induction period due to the relatively high pH of the medium and the reaction between the bicarbonate and the metabisulfite leading to a lower decomposition rate of the initiator. This induction period was eliminated by simply removing the buffer in the precharge. In addition, the presence of the buffer in the added initiator solution was found to induce a drop in the monomer conversion during emulsion polymerizations for similar reasons. This problem was overcome by eliminating use of the buffer in all stages of polymerizations.

Semicontinuous emulsion polymerizations using no buffer were conducted over a complete range of SMA1000 and SMA3000 concentrations in combination with conventional surfactants. At lower concentrations of SMA, all of the polymerizations took place in an acidic medium, with no major effect on monomer conversion and particle size, compared with the results obtained for the conventional surfactants alone. However, a decrease in monomer conversion occurred at higher concentrations of SMA (above 27% based on the total surfactant) due to the increase in the pH caused by the feed of the basic SMA solution.

It was demonstrated that a considerable amount of SMA (2–27% SMA1000 and 2–10% SMA3000 based on the total surfactants) can be incorporated into the latex (at 33% solids) *via* the semicontinuous process without inducing coagulum or a significant increase in latex particle size. At higher concentrations of SMA, a substantial amount of coagulum was formed, as well as an increase in particle size. However, a second-stage addition of SMA in polymerization was found to be the best way to incorporate larger amounts of SMA in the latex without inducing coagulum while maintaining particle size close to that of the conventional latex.

SMA1000 was found to be the most suitable of the three SMA samples to use in combination with conventional surfactants for the following

Sample Name	% SMA ^a	D_n (nm)	D_w (nm)	D_w/D_n	% Solids Content	% Coagulum	pН
DTN70	0	132.6	139.2	1.05	53.6	0	2.4
			SMA	1000			
DTN71	10	139.5	146.0	1.05	53.0	0	4.8
DTN71 DTN75	10 15	133.4	140.0 152.1	$1.05 \\ 1.14$	53.0 53.1	6	4.0 5.0
DTN73	20	153.4 153.3	152.1 160.7	1.14	53.1 52.5	6	5.3
DTN69	$\frac{20}{27}$	155.5 164.7	179.5	1.05	52.3	12	5.5
DTN83	15^{b}	122.8	133.5	1.09	52.5 53.0	0	5.5 7.0
DTN85 DTN77	15°	122.8	135.5 137.0	1.09	53.0 53.2	$\frac{0}{2}$	7.0 5.1
DTN77 DTN80	15 27°	120.0 124.2	137.0	1.05	52.3	12	5.6
DINOU	21	124.2	130.1	1.05	02.0	12	5.6
			SMA	1440			
DTN79	10	134.7	139.1	1.03	53.9	0	5.1
DTN81	15	129.9	137.1	1.06	53.0	0	5.3
DTN84	20	146.4	152.1	1.04	52.3	5	5.5
DTN82	15°	118.7	124.9	1.05	51.3	14	5.2
			SMAS	3000			
DTN74	5	137.9	142.0	1.03	53.8	0	3.8
DTN76	10	134.2	138.1	1.03	53.4	0	4.1
DTN78	$15^{\rm c}$	127.5	136.4	1.07	54.7	0	4.4

Table XVI Characteristics of MMA/BuA/AA Copolymer Latexes (53% Solids) Prepared Using Varying						
Amounts of SMA1000, SMA1440, and SMA3000 in Combination with Conventional						
Surfactants (3 Wt % Total Surfactant Based on Monomer)						

^a Wt % based on total surfactant.

^b Latex prepared without acrylic acid (MMA/BuA, 45/55 wt ratio).

^c Second-stage addition of SMA.

reasons: (1) its weaker interaction with conventional surfactants; (2) its ability to form a stable coagulum-free latex, even at high concentrations; and (3) its ready incorporation into the latex and its insignificant effects on particle size.

Preparation of coagulum-free, stable MMA/ BuA/acrylic acid copolymer latexes having high solid contents (53%) *via* semicontinuous emulsion polymerization was found to require lower concentrations of SMA1000 in the SMA/conventional surfactant mixtures, compared with previous polymerizations conducted without added acrylic acid. The decrease in pH due to the use of acrylic acid was found to enhance the interaction between SMA and the conventional surfactants, leading to formation of greater amounts of coagulum and an increase in particle size. However, it was demonstrated that a reasonable amount of SMA (up to 10% SMA1000, 15% SMA1440, and 15% SMA3000 based on the total surfactants) can be incorporated into latexes without inducing coagulum and an increase in the particle size, compared with conventional latex.

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