High Solid Content Multisized Emulsion Copolymerization of Styrene, Butyl Acrylate, and Methacrylic Acid

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ABSTRACT: Polymer lattices with a multimodal particle size distribution (PSD) polymer latex were prepared by introducing additional surfactants during the semicontinuous emulsion polymerization of styrene, butyl acrylate, and methacrylic acid. The polymerization was investigated by following the variation of the particle size, the size distribution, the number of particles, the T_{σ} of the different particle sizes, and the total conversion at different steps of the polymerization process. The results show that bimodal and trimodal PSD polymer lattices can be obtained by this method and that the secondary generation of particles is greatly influenced by the nature and the amount of additional surfactants, as well as the moment when they are introduced. When the amount of additional surfactants is increased, the diameters of both the small and large particles decrease and the number of particles in each of the populations increases. Earlier introduction of these surfactants favors the generation and the growth of the small particles and thereby leads to a reduction of the relative fraction of large particles in the final latex. On introduction of 7 wt % of additional surfactants, based on the total monomers, 100% of the monomers of the second-stage polymerization were consumed to form the small particles. This fraction decreases with a decreasing amount of the additional surfactants. These results were further demonstrated by measuring the T_{σ} 's of both the large and the small particles of two lattices, in which the T_{σ} 's of the copolymers produced in each of the stages were different. High solid content (>65%), low viscosity, and coagulum-free lattices have been obtained through secondary nucleation, and a minimum in viscosity was found when the weight fraction of the large particles was around 80%. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2667-2677, 1998

Key words: emulsion copolymerization; particle size distribution; multisized; high solid content; latex

INTRODUCTION

The preparation of polymer emulsions with multimodal particle size distributions (PSD) is an area of considerable industrial interest and importance. High solid content, good film-forming characteristics, and improved mechanical and rhelogical properties can be obtained with multisized polymer emulsion. Nevertheless, this area has received very little attention in the literature when compared to the vast amount of published work for monosized emulsions. However, in response to the growing interest expressed by industry, the amount of work in technical literature on multimodal PSD polymer lattices has been increased in recent

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	St	MA	BA	MAA	NaOH	MOS_{25}	HV25	APS	H_2O	Solid
Run	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	Content
A-1	65	0	33	2	0.28	0.26	1.36	0.67	104	49.5%
A-2	65	0	33	2	0.28	0.26	1.36	0.67	104	49.5%
A-3	65	0	33	2	0.28	0.26	1.36	0.67	104	49.5%
A-4	65	0	33	2	0.28	0.26	1.36	0.67	104	49.5%
B-1										
Stage I	52.5	0	16.1	1.4	0.2	0.15	0.98	0.47	76	52.5%
Stage II	0	6.9	22.5	0.6	0.08	0.06	0.3	0.2	16	52.5%
B-2										
Stage I	46.9	0	23.1	0	0	0.14	0.84	0.47	76	52.5%
Stage II	0	6.9	22.5	0.6	0.08	0.09	0.24	0.2	16	52.5%
IE	67	0	32	1	0.14	0.27	1.56	0.67	90.8	53%

Table I Recipes for the Seeded Semicontinuous Emulsion Polymerization

years.¹ Two-stage or multistage polymerizations are the most common techniques for the preparation of this type of latex.

Kuo and Chen² studied such a polymerization using polymeric emulsifiers, and the emulsions obtained were found to be a bimodal PSD, which was interpreted in terms of the formation of polymer aggregates. Masa et al.³ investigated a semicontinuous seeded emulsion polymerization and reported that secondary nucleation can occur when a large amount of emulsifier was used. Buckmann et al.⁴ prepared a bimodal latex by mixing two mono-sized lattices and studied the effect of the blend ratios on the rheology, the drying behavior, the MFT, and the water absorption of latex. Another approach for the realization of the multimodal latex is miniemulsion polymerization,^{5,6} in which a much longer nucleation period results in polydispersity of particles.

It is recognized that the concentration of surfactant in the system must be below the critical micelle concentration (cmc) for a seeded polymerization to prevent the formation of secondary particles.^{7,8} Although this is often the case in batch polymerizations with low monomer concentrations, in the commercial manufacture of polymer lattices, a relatively high concentration of surfactant (above cmc) is usually used to reduce the amount of coagulum. However, this does not always lead to a polydisperse PSD. This was pointed by Erickson et al.,9 who studied the seeded polymerization of styrene and styrene-acrylate and indicated that complete association can occur when the surfactant surface coverage exceeds 100%. Of course, it is obvious that secondary nucleation will occur when the concentration of free surfactant in polymerization system is high enough.

The purpose of this article is to provide a method for a secondary generation of particles by introducing some additional surfactants during polymerization, and to investigate the effect of these surfactants on particle size, size distribution, and overall polymerization features.

EXPERIMENTAL

Technical-grade monomers were used in this work. Styrene (St, Acros) contained 10–15 ppm *p-tert*-butylcatechol as inhibitor. Butyl acrylate (BA, Acros) and methyl acrylate (MA, Acros) contained 25–40 ppm *p-tert*-butylcatechol. Methacrylic acid (MAA, Acros) contained 250 ppm methyl hydroquinone. Ammonium persulfate (APS, Merck), sodium hydroxide (Prolabo), emulsifier HV25 (polyoxyethylene alkylphenyl ether from Schering), and NOS₂₅ (sodium salt of sulfated polyoxyethylene alkylphenyl ether from Schering) were also used as received. Deionized water was used throughout the work.

Polymerizations were carried out in a 1-L glass reactor equipped with a reflux condenser, anchor stirrer, sample device, nitrogen inlet, and two feed inlet tubes. Three series of experiment were carried out. Table I gives the recipes for the first and second series of polymerizations. In the first series, the monomer molar ratios and polymerization conditions (temperature, monomer feed rate, quantity of the initiator and stirring rate, etc.) were kept constant, but varying amounts of additional surfactants were introduced into the reactor by a shot process during the polymerization. The amount of these surfactants added and the corresponding percent of the monomer feed already introduced at the moment of the addition are presented in Table II.

	Additional Surfactants		Corresponding			
Run	$\overline{\mathrm{NOS}_{25}}$	HV25	Monomer Feed ^a (%)	Conversion ^b (%)	Ratio Calculated of Monomers (Stage I/Stage II) ^c	
A-1	3.5	3.5	50	88.9	44.5/55.5	
A-2	3.5	3.5	70	87.1	61/39	
A-3	1.75	1.75	70	88.0	61.6/38.4	
A-4	1.0	1.0	70	79.6	55.7/44.3	
B-1	2.5	2.5	Beginning of feed II	82.8	58/42	
B-2	2.5	2.5	Beginning of feed II	>99	70/30	
C-1	2	2	Beginning of feed	>99	70/30	
C-2	2	2	Beginning of feed	>99	60/40	
C-3	2	0.5	Beginning of feed	>99	60/40	
C-4	1	0.25	Beginning of feed	>99	60/40	
C-5	1.5	1.5	Beginning of feed	>99	50/50	

Table II Amount and Introducing Moment of the Additional Surfactants

^a The percent of the pre-emulsion that had already been introduced when the additional surfactant was added.

^b The overall conversion of the monomers when the additional surfactant was added.

^c The stage I and stage II of polymerization was separated by the moment when the additional surfactant was introduced.

The second series of polymerizations was designed for investigating the mechanism of the formation and growth of the particles. Two experiments were run in which the feed was divided into two stages. The monomers of the feed of the first stage lead to a high T_g copolymer, and those of the second have a low T_g , as shown in Table 1. For the two series of polymerizations, a seeded semicontinuous emulsion polymerization process was used. The seed (7.5% of the total monomers, initiator, and 25% of the total surfactant, as well as water) was charged into the reactor under nitrogen atmosphere, heated to 70°C, maintained at that temperature for 1.5 h, and then heated to 80°C, and the feed was started. The feed was divided into two streams; a pre-emulsion of the monomers, surfactant, and water and an 10% aqueous solution of the initiator. The flow rates of these streams were adjusted to finish the addition of both streams in 5 h. Then the polymerization was continued in batch for another 2 h.

In the third series of polymerizations, an intermediate emulsion (IE) was prepared using the same procedure as before. (The recipe of this emulsion was also presented in Table I.) This emulsion was taken as the seed (or the first-stage emulsion) for further polymerization, and some additional surfactant (Table II) was added under agitation. The mixture was then heated to 80°C, and the monomers and the solution of initiator were fed over 3 h. After that, the reactor was maintained at 80°C for another 2 h to complete the polymerization. Table III shows the recipes of these polymerizations.

Samples were withdrawn during the process, and the polymerization was stopped with hydroquinone. The overall conversion was determined gravimetrically. The particle sizes and size distributions were characterized by a method that combines centrifugation and quasi-elastic laser light scattering (QELS).¹⁰ The small and large particles were separated by centrifugation using a Beckman JA-21 centrifuge. The conditions of centrifugation were as follows: (1) the A and B series of latex [20 000 rpm, 0.5 h (to separate the large particles) and then 20 000 rpm, 16 h (to precipitate the small particles)]; (2) the C series of latex [7500 rpm, 45 min (to separate the large particles); 20 000 rpm, 1 h (to separate the middle particles); and finally 20 000 rpm, 16 h (to precipitate the small particles)]. To carry out these separations, the latex samples were diluted to a solid

Run	Emulsion IE (Solid Content 53%)	St	BA	MAA	APS	H ₂ 0	Solid Content
C-1	440.3	65	32	3	1.0	5	61%
C-2	283.0	65	32	3	1.0	5	64.5%
C-3	283.0	65	32	3	1.0	5	64.5%
C-4	283.0	65	32	3	1.0	5	64.5%
C-5	188.7	65	32	3	1.0	10	67%

 Table III
 Recipes Used in the Third Series of Polymerizations

content of 15–17% to eliminate the effect of viscosity and increase the precision of measurement. To calculate the concentrations of particles, the concentration of the small particles in the precipitate after centrifugation was assumed to be half of that in the upper layer solution.¹⁰ The diameters of the particles thus obtained were measured by a Brookhaven BI8000 QELS and checked by transmission electron microscopy. The mass fraction of particles was determined gravimetrically. Measurement of T_g was conducted in a Setaram differential scanning calorimetry (DSC) 101 at a heating rate of 10°C/ min. Viscosity of the latex was measured with a Rheometer System V10 at 21°C.

RESULTS AND DISCUSSION

Table II presents the amount of additional surfactants and the corresponding percent of the feed already introduced. For the first series of polymerizations, the additional surfactants were added in a shot process after 50 or 70% of the pre-emulsion was introduced. The polymerization was then divided into two stages before and after the addition of the surfactants. Figure 1 shows the time evolution of the overall conversion of run A-1. The conversion is 83% at the end of the seed polymerization and increases progressively during polymerization. Introduction of the additional surfactants does not have



Figure 1 Conversion-time curve of run A-1.

a significant effect on the rate of polymerization, even though a new group of particles has been formed.

The effect of the moment of introduction of the additional surfactants on the particle size and the particle number $(\times 10,^{15}$ in reactor using the recipe presented in Table I) is shown in Figure 2. In the two experiments (A-1 and A-2), the same amount of additional surfactants were added but in a different way. In both cases the introduction of additional surfactants decreases the growth rate of the large particles, because part of the monomers has been consumed by the secondary generation of particles. Comparing run A-1 to run A-2, it is clear that earlier introduction of the additional surfactants favors growth of the small particles and hence reduces the diameter of the large particles. The number of large particles in the reactor remains unchanged during the first step of polymerization but decreases slightly during the second step. This possibly can be interpreted by a limited flocculation of particles caused by the high solid content. It can also be seen from Figure 2 that the number of small particles decreases sharply during polymerization. This can be explained as follows: When the additional surfactants were added, an enormous amount of small particles were generated. When these particles grow, the surface of the particles increases. The amount of surfactant in the reactor is no longer sufficient to stabilize all the particles, and aggregation of the particles occurs. Because of their large numbers, the small particles aggregate more easily than the large ones. This can also explain why the final latex of run A-2 has more small particles than run A-1.

Before the introduction of the additional surfactants, no small particles (secondary nucleation) were found, even though the concentration of surfactant in the polymerization system was very high (Fig. 3). This may be explained by the



Figure 2 Effect of the introducing moment of the additional surfactants on the particle size and the particle number $(\times 10^{15})$.

incomplete surfactant surface coverage of the particles. As seen in Figure 4, the calculated surfactant surface coverage S was 78% at the end of the seed polymerization, assuming that all the surfactant molecules were absorbed on the surface of the particle, and it decreased progressively to 50% by the end of the first stage of the polymerization. At the end of the first stage of polymerization, the particle surface charge density was 5.0 μ eq/g for the SO_4^- and 1.0 μ eq/g for the COO⁻, corresponding to a surface coverage of about 6.5%. The carboxylic charge density seems to be rather low but is reasonable, because the methacrylic acid was partially neutralized, and the pH in the reactor was between $\sim 4.7-4.8$ during the polymerization. Consequently, most of the methacrylic acid was polymerized in the aqueous phase and remained in the serum. When the additional surfactants were introduced, the particles were overstabilized, and much of the surfactant remained in the serum, provoking the generation of new particles. The effect of the free surfactant concentration and surfactant surface coverage on secondary nucleation will be discussed in another article.

Figure 5 presents the effect of additional surfactants on particle size and particle number. As the amount of additional surfactants decreases, the diameter of both the large and the small particles increases and the number of these particles decreases. This behavior is to be expected. The sharp decrease in the number of small particles during polymerization is obviously due to the high solids content in the polymerization system and to the rapid decrease in surfactant surface coverage (see Fig. 4). Figure 6 shows the TEM micrographs of two final lattices. These micrographs clearly show that these lattices have a bimodal PSD. Table IV lists the sizes and size distributions of the final lattices for this group of experiments. Comparison with the size distributions and ratios of monomers of the two polymerization stages presented in Table II shows that 100% of the monomers in second stage of the polymerization form the small particles when 7 wt % (based on monomers) of the additional surfactants was used. This fraction was 82% when the amount of surfactants was reduced to 3.5 wt



Figure 3 Evolution of the total concentration of surfactants as a function of time (cmc = 0.11 g/L for HV25 and 0.6 g/L for NOS₂₅).



Figure 4 Evolution of the calculated surfactant surface coverage (S) as a function of time. S represents the area that can be covered by surfactant/surface area of particles. The molecular absorption area $A_p = 160 \text{ A}^2$ for NOS₂₅ and 110 A² for HV25.

% and 53% when it was reduced to 2 wt %. These results suggest that the additional surfactants play a important role on secondary nucleation and the growth of particles.

It was surprising to observe that no monomer contributed to the growth of large particles in second-stage polymerization of runs A-1 and A-2. This result was reasonable because when 7 wt % of the additional surfactants was introduced, numerous small particles were formed with a particle surface much higher than that of the large particles. There was little chance for the large particles to capture radicals or oligomers produced in the aqueous phase.



Figure 5 Effect of the amount of the additional surfactant on the particle size and the particle number $(\times 10^{15})$.



Figure 6 TEM microphotographs of the final lattices of run A-1 (left) and A-3 (right).

To follow the generation and growth of particles during the second stage of polymerization, two experiments were conducted in which the T_{σ} of the copolymer produced in each of the two stages were different. The recipes for these polymerizations were also presented in Table I, and 5 wt % of the additional surfactants based on monomers was used. At the end of the first stage of polymerization, run B-1 had an overall conversion of 82.8%. For run B-2, the polymerization was continued in batch at 80°C for another 2 h after finishing the feed of the first stage; then the additional surfactants were added, and the feed of the second stage was begun. Therefore, the overall conversion at the end of the first-stage polymerization was almost 100%. During the secondstage polymerization, the fractions of copolymer forming the small particles were 100% for run B-1 and 79% for run B-2. These results suggest that the large particles of latex B-1 are completely formed with the polymer of the first-stage monomers, whereas the small particles are composed of 21% of the first-stage monomers and 79% of the second-stage monomers. Because of the incompatibility between the polymers formed from the

monomers of the two different stages, the small particles of latex B-1 must show two T_g 's and the large particles only one T_g . But the small particles of latex B-2, which come only from the second-stage monomers, should have one T_g , whereas 91% of the large particles are composed of first-stage monomers and only 9% of second-stage monomers and thus should have two T_g 's. Figure 7 shows the DSC diagrams of different-sized particles, which corresponds exactly to the foregoing deduction.

The morphology of latex may be another indication of the foregoing observations. When the large particles of latex B-1 were coalesced to form a film, a transparent film was obtained that indicates a monophase morphology, whereas the large particles of the latex B-2 form a white film with multiphase morphology. On the other hand, the film of the small particles of latex B-1 shows a multiphase morphology and that of latex B-2 indicates a monophase. These morphologies closely agree with the measurements of T_g .

It is interesting to note that the two experiments use the same amount of additional surfactants but lead to a different small particles frac-

Latex	Particle	Size (nm)	Size Dist (large/	small)	Percent of Monomers Forming
	Small	Large	Weight	Number	Second Stage Polymerization
A-1	69	306	43.8/56.2	1/112	100
A-2	50	327	60.6/39.4	1/182	100
A-3	66	365	68.5/31.5	1/78	82
A-4	90	391	76.5/23.5	1/25	53
B-1	72	407	58.0/42.0	1/131	100
B-2	78	455	76.3/23.7	1/62	79

Table IV Particle Sizes and Size Distributions of the Final Lattices



Figure 7 DSC diagrams of the particles. 1, Large particles of latex B-1; 2, small particles of latex B-1; 3, large particles of latex B-2; 4, small particles of latex B-2.

tion. In run B-1, 100% of the monomers in the second-stage polymerization form the small particles, whereas in run B-2 only 79% do so. These results can be interpreted by the different levels of the free surfactant in serum in the two experiments. As can be seen in Table 1, the recipe of the first-stage polymerization of run B-1 contained 2 wt % of MAA, whereas no MAA was added in that of run B-2. At the end of the first-stage polymerization, the particles of run B-1 were better stabilized than those of B-2. When the additional surfactants were added, the particles of run B-2 absorbed more surfactant molecules, and, consequently, the concentration of the free surfactant in the serum is lower for run B-2 than for run B-1.

In the third series of experiments, an IE was used so that the first stages of polymerization are always the same for all the experiments. Table V presents the particle sizes and size distributions of the final lattices. Here a trimodal distribution was observed, which was clearly due to the polydispersity of the small particles. Compared to the first series of experiments, this series of experiments had a much higher solids content, and a longer period allowed secondary nucleation as well as particle growth to occur. The small particles in this series of experiments were thus much more polydisperse, and could be separated into two populations by centrifugation.

As seen in Figure 8 and Table V, the increased amount of additional surfactants causes the diameter of large particles, the diameter of medium particles, and the amount (weight) of large particles to decrease, but both the weight and number of the small and middle particles to increase. These trends show a reasonable agreement with the results obtained in the first series of experiments. Note that the number of the large particles seems to be constant (only 4–10% reduction) during the second-stage polymerization for this series of polymerizations, compared to the significant reduction in the number of large particles in the first series of polymerizations. This is probably caused by the high concentration (3 wt %based on monomers) of MAA in the monomers and the absence of neutralization in this series of polymerizations while 2% of MA was added and neutralized by NaOH in the first series of polymerization. As a result, the large particles of the series C lattices has a higher surface carboxylic charge density, which reduces the possibility of limited flocculation of the particles. This explanation can also account for why run C-2 shows a larger reduction in the number of large particles during the second-stage polymerization than runs C-3 and C-4, even though 4% of the additional

Latex	Р	article Size (ni	n)	Size Distributions small		
	Small	Middle	Large	Weight	Number ^a	Monomers to Smal Particles (%) ^b
C-1	26	91	507	89.1/0.9/10	0.96/2/753	36.3
C-2	38	91	531	82.1/5.7/12.2	0.90/13/365	44.8
C-3	36	121	538	88.7/4.2/7.1	0.93/4/248	28.3
C-4	36	130	549	93.3/3.5/3.2	0.93/3/113	16.8
C-5	55	101	549	80.5/9.0/10.5	0.96/17/125	39.0
IE	—	—	462	100/0/0	1/0/0	—

Table V Particle Sizes and Size Distributions of Final Lattices

^a The number of particles at the beginning of the second stage polymerization was taken as 1.

^b The percentage of monomers forming the small particle in the second stage polymerization.



Figure 8 Effect of the amount of additional surfactants on the properties of final lattices. (A) Diameters of the large particles (nm); (B) diameters of the middle particles (nm); (C) diameters of the small particles (nm); (D) percents of the large particles; (E) percents of the middle particles; (F) percents of the small particles.

surfactants were used. As can be seen in Table 5, for run C-2, only 55.2% of the second-stage monomers were used for the growth of the large particles, compared to 71.7% for run C-3 and 83.2% for run C-4. Consequently, the large particles of latex C-4 and latex C-3 would show a higher surface carboxylic charge density than those of latex C-2.

Figure 9 shows the effect of the ratio of monomers of the two polymerization stages in the third series of polymerizations on the properties of lattices. The diameters of all three groups of particles increase as the quantity of the monomers in the second stage increases. Due to the fact that the small particles have a larger surface than the large ones, the small particles grow faster than the large ones. As a result, the fraction of the large particles decreases with the increase in the ratio of monomers (stage II/stage I).

The viscosity of lattices is presented in Figure 10 as a function of the weight fraction of large particles. It is interesting to note that the viscosity of the lattices is closely related to the size distributions of particles. For a low fraction of large particles, the viscosity decreases with an increase of the fraction, but the reverse trend occurs when this fraction is beyond 80%. A minimum in the viscosity occurs when the weight fraction of the large particles is around 80%. This should correspond to the most efficient packing of particles. This optimal value has been confirmed by our study based on the blend of the monosized lattices,¹¹ and was also consistent with the observation of Buckmann et al.⁴

CONCLUSIONS

Lattices with the bimodal and trimodal size distributions were prepared by introducing additional surfactants during polymerization. The effects of the amount of the additional surfactants and the moment when they were introduced on the particle size, size distribution, and overall polymerization features were investigated. It was found that the secondary generation of particles is closely related to the amount of the additional surfactants and to the moment when they are introduced. The diameters of both the small and



Figure 9 Effect of the ratio of monomers of the two stages on the properties of final lattices. (A) Diameters of the large particles (nm); (B) diameters of the middle particles (nm); (C) diameters of the small particles (nm); (D) percents of the large particles; (E) percents of the middle particles; (F) percents of the small particles.

large particles decrease, and the number of these particles increase with the increase of the additional surfactants. When 7 wt % of the additional surfactants was used, all of the monomers formed small particles during the second stage of polymerization. This fraction decreases with a decreasing amount of additional surfactants. Earlier introduction of these surfactants favors the generation and the growth of the small particles, and then reduces the fraction of the large particles.



Figure 10 Viscosity of final lattices as a function of the weight fraction of large particles. Shear rate = 100 s^{-1} . The solid contents of A series lattices is ~ 48-48.5%, and those of the C series lattices were adjusted to be around 64.5% by either concentration or dilution.

The possibility of preparing high-solid-content lattices through secondary nucleation was also studied. The results show that low-viscosity, coagulum-free lattices with more than 65% solid content can be obtained, whereas the maximum solid content obtainable by means of the conventional emulsion polymerization was limited to 60%. This difference can be explained by the fact that the multisized latex exhibited better packing of particles than the monosized latex. A minimum viscosity was found when the weight fraction of

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the large particles was around 80%.

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