

Soap-Free Cationic Emulsion Copolymerization of Styrene and Butyl Acrylate with Comonomer in the Presence of Alcohols

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ABSTRACT: Preparation of a cationic polymer latex of styrene and butyl acrylate with comonomer *N,N*-dimethyl, *N*-butyl, *N*-methacryloyloxyethyl ammonium bromide (DBMEA) was carried out by soap-free emulsion polymerization. The effect of reaction conditions such as the ratio of methanol to water, DBMEA concentration, AIBA concentration and ionic strength on properties of copolymer particles was studied. The results showed that the average diameter (D_w) decreased with increasing of AIBA and DBMEA concentration; D_w decreased first then increased with increasing of methanol content; variation of the ionic strength led to a variation in the particle number (N_p) and

D_w because of the competition of two kinds of nucleation mechanisms. The same trend was found in the polymerization taking in pure water. The MWD was bimodal during the particle growth period. These results suggest that the particles can be generated through two particle-formation mechanisms, micelle nucleation and homogeneous nucleation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2791–2797, 2003

Key words: cationic polymerization; latices; particle nucleation; CH₃OH solvent; GPC

INTRODUCTION

Latices prepared through soap-free emulsion polymerization have many desirable qualities such as a narrow particle size distribution and a clean surface. Thus, they can be used in a variety of areas and have become the focus of much recent research in, for example, the study of model colloid dispersions, protein adsorption, immobilization supports of catalysis, colloidal stability, calibrating instruments for ultracentrifuges, and light-scattering units, and in the field of diagnostics, used as antibodies and so on.^{1–6} In fact, each technique has its own advantages and its own drawbacks. In the conventional emulsifier-containing method, the removal of emulsifiers is often quite difficult and destabilizes the latex after polymerization. Emulsifier-free lattices, on the other hand, have low solid content, slow conversion rates, and low surface charge densities. To improve the particle stability and enhance solid content, soap-free emulsion polymerization carried out by the addition of comonomer and latent solvent (e.g., methanol, ethanol, or acetone) can increase the monomer solubility. They are infinitely miscible with water and with styrene/butyl acrylate monomer and are a nonsolvent for polymer.

McCracken⁷ first reported soap-free emulsion polymerization of styrene in the presence of methanol, and Homola⁸ reported a preliminary study on the effect of methanol as cosolvent in soap-free emulsion polymerization of styrene in the literature.^{9–11} Although some studies have reported the effect of methanol, acetone, ethanol, and the like as cosolvent on soap-free emulsion polymerization, thus far there have been very few studies on soap-free cationic emulsion in the presence of organic solvent. In this study we report the soap-free polymerization of styrene/butyl acrylate (St/BA) with dimethylaminoethyl methacrylate (DMAEMA) as comonomer, using azobis(isobutyramidine hydrochloride) (AIBA) as initiator. The effects of reaction conditions, such as methanol/water ratio, AIBA concentration, *N,N*-dimethyl, *N*-butyl, *N*-methacryloyloxyethyl ammonium bromide (DBMEA) concentration, and ionic strength on the conversion, particle size, particle number, and surface charge density were also reported. Stable monodisperse latex systems with high surface charge density were obtained on the basis of the results of these experiments. The nucleation mechanism of the latex particle was proposed.

EXPERIMENTAL

Materials

Styrene and butyl acrylate purified by distillation under reduced pressure were stored in a refrigerator; AIBA was kindly supplied by the Institute of Chemical Engineering in Beijing; and DMAEMA was pur-

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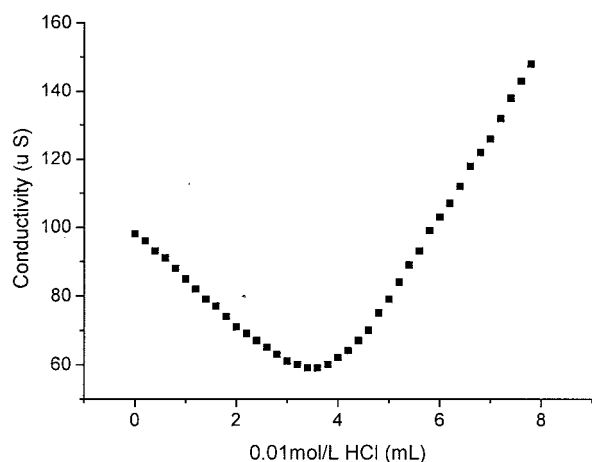


Figure 1 Conductivity as a function of the amount of acid added to latex. $[\text{HCl}] = 0.01 \text{ mol/L}$.

chased from Japan MARK lot. AIBA and DBMEA were used directly without further purification. *N,N*-Dimethyl,*N*-butyl,*N*-methacryloyloxyethyl ammonium bromide $[\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{C}_4\text{H}_9\text{Br}^-]$ (DBMEA) was synthesized before use according to the method described in the literature¹² (yield 92.51%; $T_f = 108\text{--}108.5^\circ\text{C}$).

Preparation of cationic polymer latex

All polymerization reactions were carried out in a 250-mL glass reactor equipped with nitrogen purging tube, a reflux condenser, a mechanical stirrer, and thermometer. St and BA were weighed into the reaction bottles, heated to 65°C , and purged with nitrogen for 20 min. The DBMEA and AIBA solution was injected into the reactor to start polymerization; samples (1 g) were removed from the reactor with syringes at intervals for gravimetric conversion analysis. The capped vials for collecting samples contained a small amount of 0.5 wt % hydroxyanisole solution to quench the polymerization in the samples. Here we note that the effect of temperature on the experimental results was significant; in this study, the temperature of reaction was controlled at $65 \pm 2^\circ\text{C}$.

Latex particle size and number

Particle diameter (D_w) was determined by dynamic light scattering by use of a Malvern Autosizer Lo-c (Poole, UK) at room temperature. The particle number (N_p) was calculated from the following equation: $WX = (1/6)\rho\pi D_w^3 VN_p$, where W is the monomer weight, ρ is the polymer density, and V is the volume of water.

Characterization of surface groups and surface charge density

Latices were diluted to 3–5% solid content with deionized water and purified by the ion-exchange method

with a mixed bed (1/1 weight ratio) of anionic 717 resins and cationic 732 resins. The latices were stirred at room temperature to a constant pH value and the conductance value was observed; the latices were then filtered and the solid contents were determined gravimetrically.

The latices were titrated conductometrically with standard 0.01 mol/L HCl. Typical conductometric titration curves of the ion-exchange cationic P(St/BA/DBMEA) copolymer latices are shown in Figure 1. Although the chains of cationic polymer contain amidino groups and amino groups as surface basic groups, Figure 1 shows only the equivalence point corresponding to both surface amidino groups and surface amino groups. This means that a separate determination of both groups is impossible by this method. Because both surface amidino groups and surface amino groups function as weak bases, they cannot be determined separately by this method. Thus in this study the surface group content and charge density of latex particles represent the total of amidino groups and surface amino groups. The surface charge density was calculated from latex solid contents and from the intersection of these two lines.

Molecular weight and its distribution

Latices were precipitated by methanol and NaOH solution, washed with water, and dried at room temperature. The MWD and the average molecular weight of polymer were determined by GPC with THF as carrier solvent at a rate of 1 mL/min at room temperature.

RESULTS AND DISCUSSION

Influence of methanol concentration

The effect of methanol concentration on particle diameter (D_w) and the final particle surface charge density

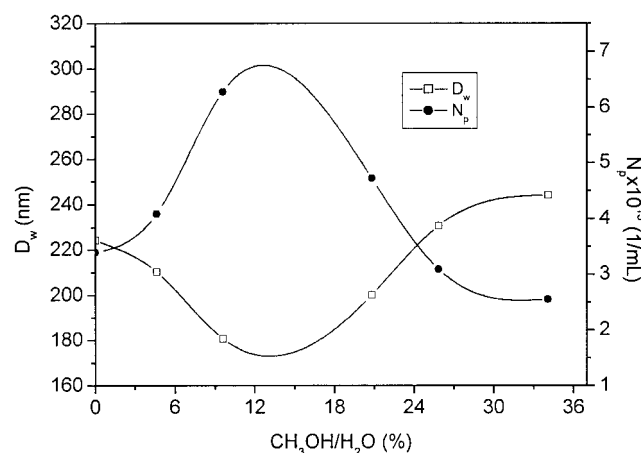


Figure 2 Effect of ratio of methanol/water (%) on D_w and N_p .

TABLE I
Effect of CH₃OH Concentration on Particle Surface Properties^a

Run no.	CH ₃ OH H ₂ O (ν %)	X (%)	<i>D_w</i> (nm)	<i>N_p</i> × 10 ¹³ (1/mL)	N ⁺ and C ⁺ (NH ₂) ₂ Groups	
					Surface (equiv/g)	Aqueous (equiv/g)
M-41	0.0	99.32	224.2	3.39	15.18	65.23
M-42	4.63	98.65	210.3	4.08	15.79	56.39
M-43	9.62	96.32	180.8	6.27	16.08	49.85
M-44	20.83	98.22	200.1	4.72	16.46	34.59
M-45	25.86	98.59	230.6	3.09	16.77	30.57
M-46	34.09	96.22	244.1	2.55	16.92	27.15

^a Polymerization recipe: St/BA = 10 mL/20 mL; concentration of DBMEA: 2.91×10^{-2} mol/L; concentration of AIBA: 5.69×10^{-3} mol/L; polymerization temperature: 65°C.

was studied at constant concentrations of styrene, BA, DBMEA, AIBA, and ionic strength. At lower concentrations of methanol, with increases in methanol concentration (<9.62%), the particle size decreased with a corresponding increase in particle number (*N_p*) (Fig. 2); The same tendency was observed in anionic emulsifier-free emulsion polymerization of styrene in methanol–water by Homola et al.⁸ and in acetone–water by Okubo et al.¹⁰ However, Chonde reported that the particle size and uniformity increased with methanol content in anionic St/NaVBS soap-free emulsion polymerization.⁹ Our results showed that with increasing methanol concentration (>9.62%), the particle size increased and the number of particles decreased; increasing the methanol content results in increased solubility of St and BA, catalyzing the decomposition of AIBA initiator through chain transfer and increasing St, BA, and DBMEA incorporation into the water-soluble oligomeric radicals. Thus, the rate of polymerization increased and, further, the number of particles increased (e.g., methanol < 9.62%).

However, the presence of methanol may have other effects (e.g., changes in the dielectric constant of the medium and reduction in the ability of water molecules to form sequence structures), which may lead to a decrease in the rate of polymerization and particles would likely coagulate. When polymer particles become larger and the particle size distribution becomes broader, the *N_p* decreases. Meanwhile, when the methanol content is increased, the polarity of aqueous me-

dium decreases, which may lead to increased solubility of oligomers at the early stages of polymerization; before reaching critical size, the oligomer molecule chains increased in length and became more hydrophobic, thus increasing *D_w*. The results in Table I show the effect of methanol content on particle surface properties. When the methanol content was increased, the content of surface groups increased slightly, but the polyelectrolyte content decreased.

Influence of initiator concentration

The effect of varying the AIBA concentration from 4.27×10^{-3} mol/L to 6.40×10^{-3} mol/L on the particle size (*D_w*) and number of particles (*N_p*) was investigated in the presence of methanol at 65°C and at constant St/BA ratio, DBMEA content, methanol content, and ionic strength, which was maintained by addition of the appropriate quantity of sodium chloride. The results in Table II and Figure 3 indicate that the higher initiator concentration, the smaller the *D_w* and the larger the *N_p*. These results are similar to those obtained without methanol soap-free emulsion polymerization¹³ and similar to anionic emulsifier-free emulsion polymerization of styrene in acetone–water¹⁰ and St/NaVBS emulsifier-free emulsion in methanol–water at a lower concentration of persulfate.^{9,10} As the AIBA concentrations increased, the polymerization rate and the rate of polymer particle nucleation increased and the particle size decreased. The effect of

TABLE II
Effect of AIBA Concentration on Particle Surface Properties^a

Run no.	AIBA × 10 ⁻³ (mol/L)	X (%)	<i>D_w</i> (nm)	<i>N_p</i> × 10 ¹³ (1/mL)	N ⁺ and C ⁺ (NH ₂) ₂ groups (surface)	
					(equiv/g)	surface charge density (mol/m ²)
A-41	4.27	91.12	278.5	1.62	14.18	0.658
A-42	4.98	93.31	243.1	2.50	15.78	0.619
A-43	5.69	98.22	200.1	4.72	16.37	0.546
A-44	6.40	99.32	198.5	4.89	16.52	0.477

^a Polymerization recipe: St/BA = 10 mL/20 mL; concentration of DBMEA: 2.91×10^{-2} mol/L; CH₃OH/H₂O = 20.83%; polymerization temperature: 65°C.

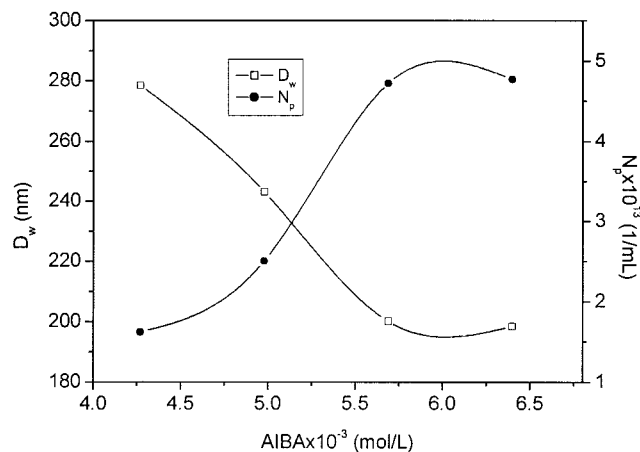


Figure 3 Effect of AIBA concentration on D_w and N_p .

AIBA concentration on particle surface properties in Table II also showed that the cationic group contents of latex particles increased slightly and the surface charge density decreased with increasing AIBA concentration. Because AIBA concentrations increased, which also corresponded to the increase in the number of particles and the total surface areas (S_a) of particles, the surface functional group content/ S_a decreased, that is, the surface charge density of particles decreased. The results were comparable to those obtained in aqueous medium under similar experimental conditions and the same AIBA concentration conditions.¹³

Influence of DBMEA concentration

In the presence of methanol, the effect of changing the comonomer DBMEA concentration over the range from 2.19×10^{-2} mol/L to 2.91×10^{-2} mol/L on the final particle number and average particle diameter was examined at constant St/BA ratio, AIBA content, methanol content, and ionic strength by the addition of the appropriate quantity of sodium sulfate. As shown in Figure 4 and Table III, increasing the DBMEA content increased the N_p , decreased final particle size, and increased the surface group contents; in addition, the surface density varied slightly. The re-

sults compared with St/NaVBS and MMA/BA/NaAS emulsifier-free emulsion in the presence of latent solvent were not the same.^{9,10} At a low concentration of NaVBS ($< 2 \times 10^{-3}$ mol/L), the particle size decreased sharply, followed by a slow, linear decrease with increasing concentrations of NaVBS. However, in the MMA/BA/NaAS system, D_w and N_p versus NaAS concentration show a minimum and maximum, respectively. In the present system, we supposed that when DBMEA concentration increased, the particle surface density of $-N^+$ groups increased, both accelerating the conversion rate of monomer (R_c) and enhancing the rate of polymerization (R_p). Because R_p affected the number of particles and increased the R_c , the R_p and N_p values increased, and the D_w value decreased.

In the St/BA/DBMEA copolymerization process, DBMEA produced polyelectrolytes in addition to copolymerization with St and BA. The results from Table III and Figure 4 were comparable to those of the system without methanol. After the addition of methanol, however, DBMEA may enhance the particle surface group contents (the function of which was not significant), and production of poly(DBMEA) was inevitable in the water phase, thus demonstrating the presence of an excess of DBMEA.

TABLE III
Effect of DBMEA Concentration on Particle Surface Properties^a

Run no.	DBMEA $\times 10^{-2}$ (mol/L)	X (%)	D_w (nm)	$N_p \times 10^{13}$ (l/mL)	N^+ and C^+ (NH_2) ₂ groups (surface) (equiv/g)	N^+ and C^+ (NH_2) ₂ surface charge density (mol/m ²)
D-41	2.19	97.10	275.9	1.78	14.29	0.657
D-42	2.42	97.25	224.3	3.32	15.47	0.578
D-43	2.61	97.65	218.2	3.68	16.07	0.584
D-44	2.91	98.22	200.1	4.72	16.37	0.546

^a Polymerization recipe: St/BA = 10 mL/20 mL; concentration of AIBA: 5.69×10^{-3} mol/L; CH₃OH/H₂O = 20.83%; polymerization temperature: 65°C.

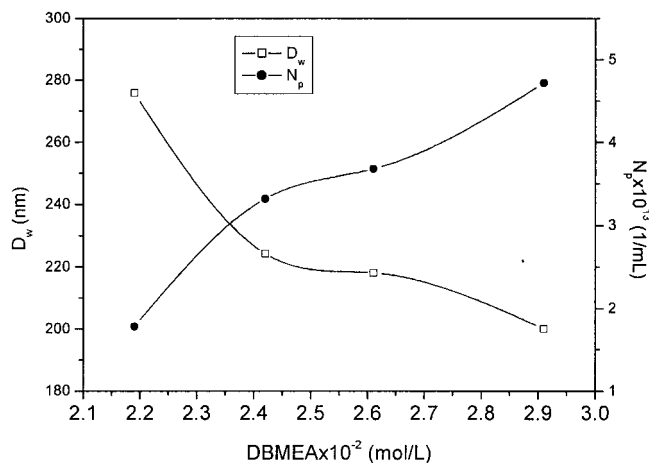


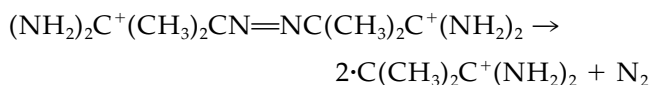
Figure 4 Effect of DBMEA concentration on D_w and N_p .

Effect of ionic strength

The effect of Na_2SO_4 concentration on the particle surface properties is as shown in Figure 5 and Table IV. The results were similar to those obtained without methanol and the anionic MMA/BA/NaAS soap-free emulsion with methanol^{11,14}: by increasing the concentration of Na_2SO_4 (i.e., increasing ionic strength in the water phase), D_w underwent a process of increasing/decreasing/increasing, but N_p underwent a process of decreasing/increasing/decreasing, whereas the concentration of surface groups and the surface charge density underwent a double variations course. Because at the start of polymerization there was no surfactant in the St/BA/DBMEA system, D_w increased and N_p decreased with the ionic strengths attributed to the shielding effect. When the ionic strength was high enough to allow the critical micelle concentration (cmc) value of DBMEA to decrease to the concentration of DBMEA, D_w decreased and N_p increased with the ionic strength because of the production of greater numbers of micelles; as the ionic strength increased further, the surface charge density decreased, the emulsion stability deteriorated, and D_w increased with ionic strength because of the shielding effect. Compared with results obtained in the absence of methanol, particles were similarly generated by a combination of the dual mechanisms of homogeneous nucleation and micelle nucleation.^{11,15}

Nucleation mechanism of particles

In the St/BA/DBMEA copolymerization process in the presence of CH_3OH , first the AIBA thermally decomposes to form primary radicals, $\cdot\text{C}(\text{CH}_3)_2\text{C}^+(\text{NH}_2)_2$, as follows:



$\cdot\text{C}(\text{CH}_3)_2\text{C}^+(\text{NH}_2)_2$ radicals react when dissolved in water, St, BA monomer, and ionic comonomer units to form oligomeric free radicals in the water/ CH_3OH phase. Initially, however, the DBMEA concentration is below its cmc (= 0.112 mol/L).¹³ Thus the DBMEA comonomer is soluble in the water phase and does not form micelles. Moreover, there are also no micelles in this system to capture the oligomeric free radicals; therefore they will continue to grow to form oligomeric free-radical chains and become increasingly hydrophobic. On the one hand, they will precipitate out to form primary particles at a critical degree of polymerization. Primary particles are unstable and coagulation will occur until the particles are sufficiently stabilized by the localization of amidino and amino end groups of polymers on the surface of the particles. Growing radicals, newly formed in water, will coil up and precipitate out to form new primary particles. That is, the polymer particles were generated through the homogeneous nucleation mechanism. On the other hand, the oligomers, which are visualized as having surfactant properties, grow until they reach a critical chain length, after which they will precipitate to form primary particles. The concentration of oligomers increased to levels sufficiently high enough to exceed its cmc and micelles were formed; therefore, the particles were also formed through the micelle mechanism in addition to the homogeneous nucleation mechanism.

Figure 6 and Figure 7 compare the results obtained in the presence and absence of CH_3OH , respectively. The results show that the D_w of both conditions increased with time, although in the presence of CH_3OH , D_w is smaller and N_p is greater because the addition of methanol increased the solubility of monomer and improved the compatibility of oligomer and copolymer with the media and decreased cmc. Therefore, more nuclei were produced and more particles were obtained; that is, the N_p was greater with than without methanol. In addition, in the absence of

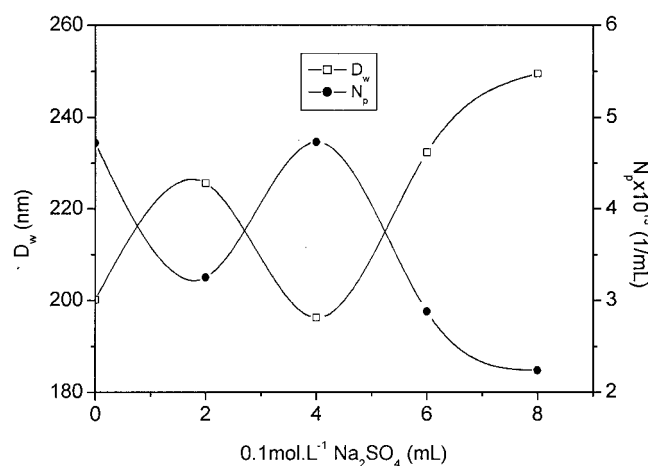


Figure 5 Effect of Na_2SO_4 concentration on D_w and N_p .

TABLE IV
Effect of Electrolyte on Particle Surface Properties^a

Run no.	0.1 mol/L Na ₂ SO ₄ (mL)	X (%)	D _w (nm)	N _p × 10 ¹³ (1/mL)	N ⁺ and C ⁺ (NH ₂) ₂ groups (surface) (equiv/g)	N ⁺ and C ⁺ (NH ₂) ₂ surface charge density (mol/L)
I-41	0.0	98.22	200.1	4.72	16.47	0.546
I-42	2.0	98.86	225.6	3.25	14.28	0.537
I-43	4.0	92.72	196.2	4.73	16.96	0.554
I-44	6.0	93.64	232.3	2.88	15.69	0.530
I-45	8.0	90.21	249.5	2.24	15.33	0.510

^a Polymerization recipe: St/BA = 10 mL/20 mL; concentration of DBMEA: 2.91×10^{-2} mol/L; concentration of AIBA: 5.69×10^{-3} mol/L; CH₃OH/H₂O = 20.83%; polymerization temperature: 65°C.

CH₃OH, N_p remained constant after 20 min of the final reaction; however, in the presence of CH₃OH, during the early stages of reaction N_p gradually decreased with reaction time and finally reached a steady value. This shows the period of particle nucleation is prolonged by use of methanol, although methanol did not change particle nucleation mechanisms. The results were further confirmed by GPC.

Figure 8 shows that the variations of MWD from 8.94% conversion at 20 min to 98.22% conversion at 240 min. Bimodal distributions are observed in the earlier period and with the peak of low molecular weight at about 3×10^3 at 20 min. This lower molecular weight peak gradually shifts toward the higher molecular weight region for samples taken at longer reaction times. The phenomenon that many molecules of low molecular weight exist in the early stages of reaction was also mentioned by Goodwin et al.,¹⁶ who reported that oligomers of molecule chain length of about 1000 behave as an emulsifier; furthermore, they form micelles during the induction period. Therefore we considered that polymer particles were generated through the micelle nucleation mechanism as well as through the homogeneous nucleation mechanism. This indicates that the two particle-formation mechanisms, micelle nucleation and homogeneous nucle-

ation, coexist in the emulsion copolymerization and two kinds of mechanisms are in competition with each other in the present systems with the addition of cationic $\cdot C(CH_3)_2C^+(NH_2)_2$ radicals. Thereafter, the primary particles continue to grow until they become unstable and coagulate to form more stable and larger particles. Furthermore, the effect of ionic strength on D_w, N_p, and the surface charge density in the presence of methanol was that, with an increase in ionic strength, the D_w, N_p, surface groups, and the surface charge density underwent a double variations course. This further indicates there are two kinds of mechanisms in the present systems.¹⁵

CONCLUSIONS

When latent solvent methanol was added to the St/BA/DBMEA system, compared with emulsifier-free cationic emulsion without methanol, the content of surface groups increased slightly and the polyelectrolyte content decreased, although formation of polyelectrolytes in the water phase still occurred.

DBMEA is an effective cationic comonomer for preparation of stable St/BA emulsifier-free lattices, and methanol did not influence the functions of AIBA initiator, DBMEA comonomer, and electrolytes: D_w

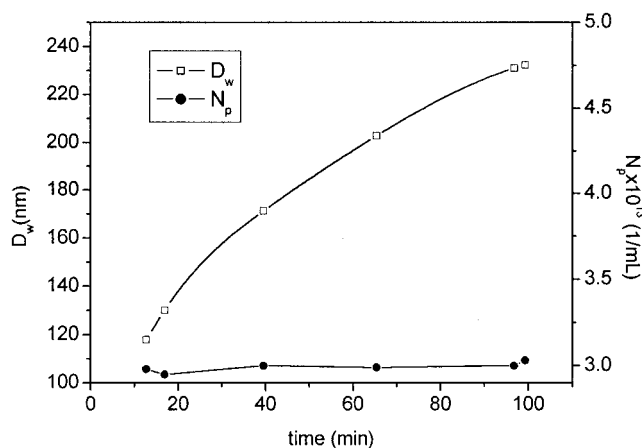


Figure 6 Course of particle nucleation and growth in the absence of methanol.

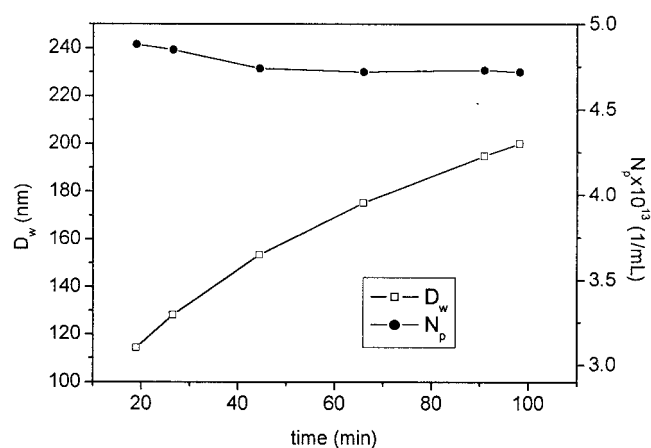


Figure 7 Course of particle nucleation and growth in the presence of methanol.

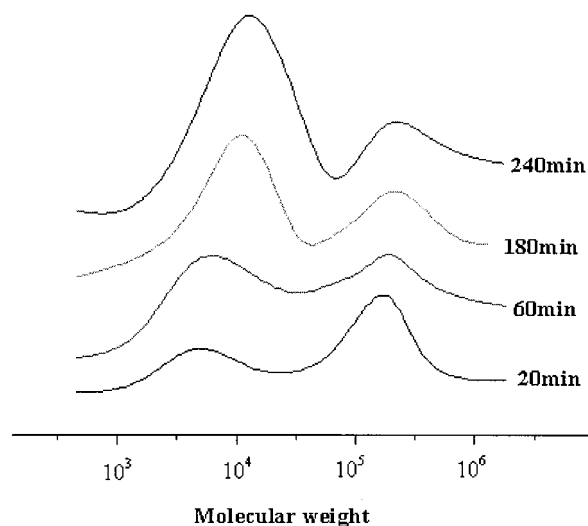


Figure 8 Molecular weight distributions at different reaction times.

decreased, N_p increased, the cationic group contents of latex particles increased, and the surface charge density varied slightly with the concentrations of AIBA and DBMEA. However, by increasing the ionic strength concentration, D_w , N_p , the surface group contents, and the surface charge density underwent a double variations course. The double variations effect of ionic strength on the latex particle surface proper-

ties and bimodal distributions of MWD proved that particles of polymer are generated through two particle-formation mechanisms, micelle nucleation and homogeneous nucleation. The two mechanisms coexisted in the emulsion copolymerization.

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