

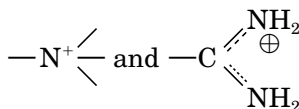
Emulsifier-Free Emulsion Copolymerization of Styrene and Butyl Acrylate with Cationic Comonomer

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ABSTRACT: Emulsifier-free emulsion copolymerization of styrene (St) and butyl acrylate (BA) in the presence of a cationic functional comonomer, *N*-dimethyl, *N*-butyl, *N*-ethyl methacrylate ammonium bromine (DBMA) was carried out using azobis(isobutylamidine hydrochloride) (AIBA) as an initiator. The surface properties of particles were studied by testing the actual value of



on the surface of the particles and the surface charge density. The copolymer particles were characterized using transmission electron microscopy (TEM). The effects of reaction temperature, DBMA content, AIBA content, ionic strength, etc., on the conversion of the monomer and the average diameter (\bar{D}_w) and number (N_p) of copolymer particles were investigated. Under constant ionic strength, the average diameter of copolymer particles (\bar{D}_w) decreased with increasing AIBA and DBMA concentrations and decreased with increasing reaction temperature also. Moreover, it increased with increasing St content in the monomer feeding. Under a constant concentration of the comonomer and initiator as well as the constant monomer composition, \bar{D}_w shows a change process of increase–decrease–increase in the ionic strength plot. The polymerization reaction rate increased with increasing the DBMA content, AIBA content, and increasing temperature. The surface charge properties of the particles were mainly decided by the DBMA content, AIBA content, ionic strength, etc. The methods of feeding the monomer affects the morphology, structure, size, and surface charge density of the particles. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1–9, 1997

INTRODUCTION

In a conventional emulsion polymerization, latices are stabilized by surfactants. The removal of a stabilizer after polymerization is difficult and coagulation may result.¹ Functional latexes suitable for fundamental research on colloid coagula-

tion and stability and electrokinetic and rheological properties are usually prepared in the absence of an emulsifier to ensure the formation of monodisperse particles; however, the particles being characterized by a low surface charge density exhibit a poor stability, so that this technique is successful only at polymer volume fractions below 10%. Furthermore, it is difficult to produce particles smaller than 0.4 μm in this way. To improve the particle stability and obtain a small particle diameter at a high solid content, emulsifier-free

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emulsion polymerizations were carried out in the presence of ionic or ionogenic functional comonomers.

In the case of surfactant-free emulsion polymerization, particles are stabilized by ionic initiator residues. Potassium as an initiator has been studied extensively and was found to give sulfate stabilized latices.² To obtain a better control of both particle size and surface charge density, ionogenic comonomers can be used. Most studies have been concerned with the stabilization by anionic groups³ introduced by sulfonate-containing monomers, other types of ionogenic monomer carboxyl groups,⁴ and nonionic hydrophilic monomers like acrylamide and acrylamide derivatives.⁵ Surprisingly, the use of cationic comonomers is less common.⁶ The use of surfactantlike monomers has also been reported.⁷ In recent years, much more attention has been paid to cationic emulsion.^{8,9}

During the last decades, attention has been paid to the emulsion copolymerization of hydrophobic with hydrophilic monomers.¹⁰ In almost all cases, emphasis was placed on the copolymerization kinetics, which appeared to deviate from ordinary emulsion homopolymerizations, often because the water-soluble comonomers polymerized first, thus forming stabilizers for the more hydrophobic polymer particles. Several studies^{6,11} have appeared describing the copolymerization of styrene and cationic comonomers, but so far a study comprising a thorough characterization of the particle surface of permanently charged copolymer latices prepared over a wide range of comonomer compositions has been lacking.¹²

Our goal was to prepare stable cationic latices with high surface charge density. The mechanism for particle nucleation and polymerization kinetics were also of interest. In this article, we report the use of *N*-dimethyl, *N*-butyl, *N*-ethyl methacrylate ammonium bromide (DBMA) as a comonomer and azobis(isobutylamidine hydrochloride) (AIBA) as an initiator in the emulsifier-free emulsion copolymerization of styrene (St) and butyl acrylate (BA), and the effects of comonomer concentration, initiator content, and ionic strength on particle size, polymerization rate, and surface charge density were also studied.

EXPERIMENTAL

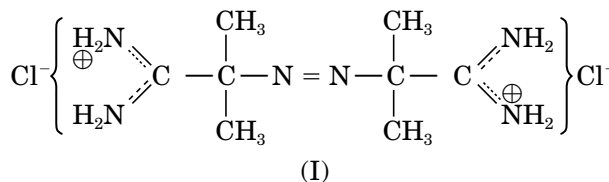
Material

Monomers such as St and BA were distilled in a stream of inert gas at a reduced pressure and

Table I Recipe for Preparation of Copolymer Emulsion by Batch Emulsion Polymerization

Ingredients	Amount
St	20
BA	40
DBMA	3
AIBA	0.65
0.1 <i>N</i> NaCl (mL)	0–20
Water	360

stored in a refrigerator, DBMA was synthesized, and AIBA(I) was of analytical grade and was recrystallized. The aqueous phase was prepared with redistilled water and all the polymerizations were conducted in a nitrogen atmosphere:



Preparation of DBMA

In a flask equipped with a stirrer, thermometer, and reflux condenser, 1 mol *N*-dimethyl aminoethyl methacrylate (DMA) was mixed with the solvent, and from a dropping funnel, 1.5 mol *n*-C₄H₉Br was slowly added with vigorous stirring. The temperature was kept below 40°C. Two hours after the addition of *n*-C₄H₉Br, the mixture was cooled in an ice bath without stirring; subsequently, the white crystals were filtered and washed several times with cold acetone. The white crystals were dried under a vacuum below 30°C to a constant weight. Yield: 92%. The purity of DBMA, which is refined, is 99.2%.

Preparation of Copolymer Emulsion

Polymerizations were carried out in a 0.5 L reactor equipped with stirrer, reflux condenser, sampling device, and inlet system for nitrogen. Copolymer emulsions were prepared in a batch process using the recipes given in Table I and the polymerizations were carried out at 70°C for 3 h; then, the latexes were heated to 80°C and this temperature was maintained for 3 h. Copolymer emulsions were prepared in a seeded process using the

Table II Recipe for Preparation of Copolymer Emulsion by Seeded Emulsion Polymerization

Ingredients	Amount	
	Stage 1	Stage 2
St	20	
BA		40
DBMA	3	
AIBA	0.65	
0.1 <i>N</i> NaCl	0–20	
Water	360	

recipes given in Table II. The first stage of seeded emulsion polymerization was processed at 70°C for 3 h; in the second stage, BA was added to the reactor by dripping. Then, the latexes were heated to 80°C and this temperature was maintained for 3 h after completing the addition of BA.

Determination of Conversion

A latex sample withdrawn from the reactor was added with hydroquinone solution to stop the polymerization. The contents were dried in an oven to constant weight. Conversion of this sample can be determined from the original monomer content and polymer weight obtained.

Latex Particle Size and Number

Particle size, i.e., particle median diameter (\bar{D}_w), was determined by dynamic light scattering, using a Malvern Autosizer Lo-c; polydispersity index values were obtained. The particle number (N_p) was calculated from the following equation: $W \cdot X = \frac{1}{6}\rho\pi\bar{D}_w^3VN_p$, where W is the monomer weight; ρ , the polymer density; and V , the volume of water.

Transmission Electron Microscopy

Latex particle morphologies were determined by transmission electron microscopy (TEM) using a 100-sx TEM. Internal particle morphologies were examined by drying samples of each latex, and the sections were stained with a phosphotungstic acid aqueous solution.

Characterization of Surface Groups

The number and type of functional groups on the latex particles were determined by conductimetric

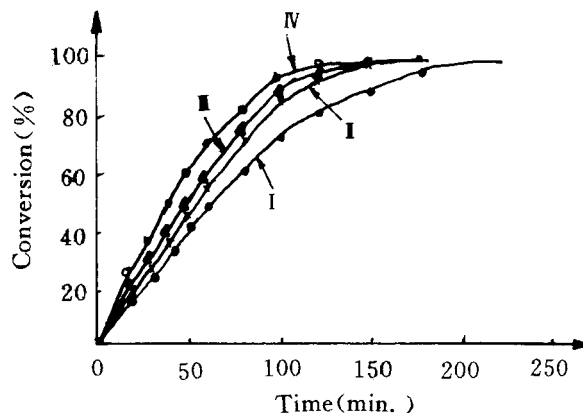


Figure 1 Conversion vs. time at various DBMA concentrations; $[\text{DBMA}] \times 10^2$ (mol L⁻¹): (I) 1.99; (II) 2.91; (III) 3.64; (IV) 4.01.

titration using 0.01*M* HCl and a DDS-II conductimeter after cleaning the latexes by ion-exchange with a mixed bed (1/1 weight) of anionic 717 resin (Cl form) and cationic 732 resin (Na form) which were purified in the H. L. Van Den Hul procedure and diluted to 3–5% solid content with deionized water.

Molecular Weight and Its Distribution

Latexes were precipitated by methanol, washed with water, and dried at room temperature. The purified samples were subjected to MWD measurement using SN-01A Gel-permeation chromatography with THF as the carrier solvent.

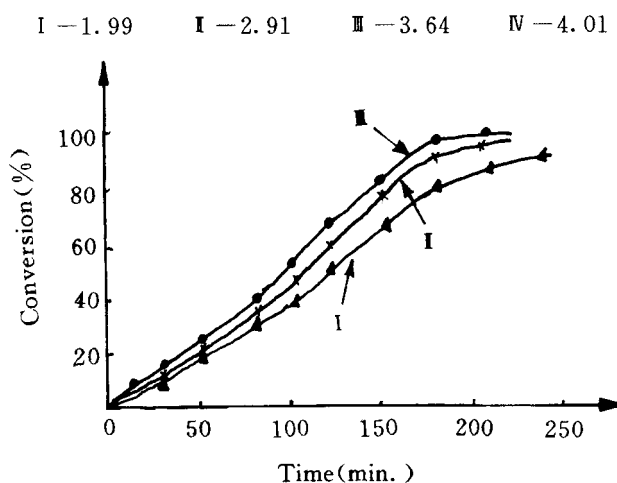


Figure 2 Conversion vs. time at various AIBA concentrations; $[\text{AIBA}] \times 10^3$ (mol L⁻¹): (I) 4.27; (II) 4.98; (III) 5.69.

Table III Effects of DBMA Concentration on R_p

[DBMA] $\times 10^2$ (mol L ⁻¹)	$dc/dt \times 10^3$ (min ⁻¹)	R_p (mol L ⁻¹ h ⁻¹)	$\ln R_p + 1$
1.99	7.17	0.698	0.64
3.01	8.98	0.874	0.865
3.64	9.48	0.923	0.920
4.01	12.03	1.171	1.158

RESULTS AND DISCUSSION

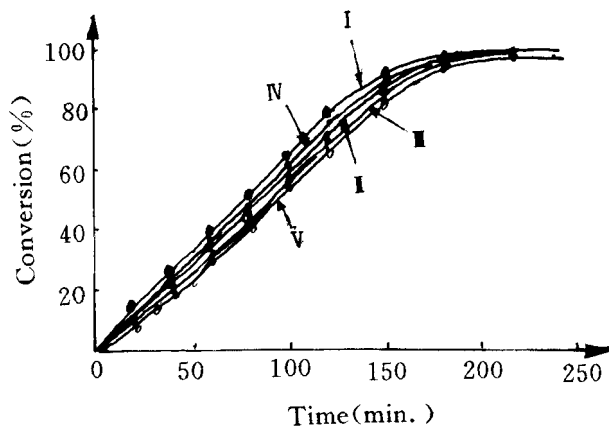
Kinetics of Emulsion Polymerization

In the kinetic studies, no salts were added to maintain constant ionic strength. Conversion vs. time curves at different DBMA and AIBA contents are shown in Figures 1 and 2, respectively. Figures 1 and 2 indicate that the conversion rate of the monomer increases with increasing comonomer DBMA and AIBA concentration, respectively. With increasing DBMA and AIBA concentration, the number of oligomeric radicals increases and results in an increasing polymerization rate R_p . From Tables III and IV we can obtain an R_p of $\alpha[\text{DBMA}]^{0.64} [\text{AIBA}]^{0.67}$. Figure 3 shows the effects of ionic strength on the polymerization rate. As can be seen, the rate of polymerization R_p reduces at first as ionic strength is increased by the addition of a NaCl solution. When ionic strength is high enough, the R_p increases, but as ionic strength increases further, the R_p decreases again.

The MWD curves during the polymerization process are shown in Figure 4. As can be seen, the MWD obtained in the earlier period was unimodal but became bimodal when conversion was over 3.5%. Furthermore, the area of the high MW peak increased gradually and its position shifted to the high MW side, while the area of the low MW peak decreased slightly and its position shifted slightly to the high MW side with conversion.

Table IV Effects of AIBA Concentration on R_p

[AIBA] $\times 10^3$ (mol L ⁻¹)	$dc/dt \times 10^3$ (min ⁻¹)	R_p (mol L ⁻¹ h ⁻¹)	$\ln R_p + 1$
4.27	4.74	0.462	0.227
4.98	5.53	0.538	0.381
5.69	5.93	0.577	0.451
6.40	6.26	0.609	0.505

**Figure 3** Conversion vs. time at various ionic strengths of 0.1N NaCl (mL): (I) 0; (II) 4; (III) 8; (IV) 12; (V) 16.

Surfactant-free emulsion copolymerization with ionogenic comonomers is different from conventional emulsion polymerization. In a classical emulsion polymerization, i.e., the polymerization of a scarcely water-soluble monomer in the presence of a water-soluble initiator and a surfactant, the kinetics may be described by the Smith-Ewart theory.⁷ The most important mechanistic difference between the emulsifier-free emulsion process and conventional emulsion polymerization is the nucleation period of the polymerization. At the start of the emulsifier-free emulsion polymerization, no monomer-swollen micelles are present to absorb the radicals formed by dissociation of the water-soluble initiator. For copolymer-

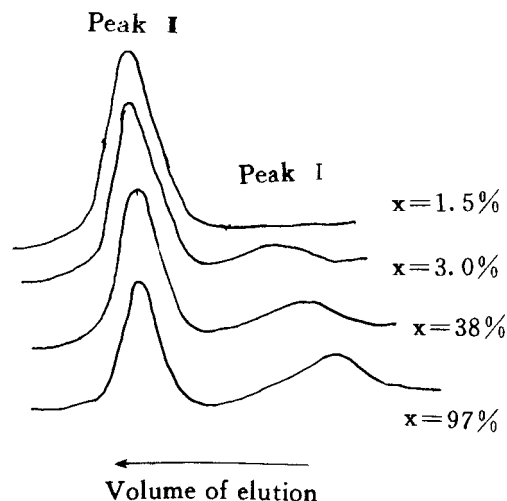
**Figure 4** GPC curves at different conversions.

Table V Effect of DBMA Concentration on the Properties of Emulsion Particles

Sample	[DBMA] × 10 ² (mol L ⁻¹)	N _p × 10 ⁻¹³	\bar{D}_w (nm)	Surface Groups	
				—N ⁺ and C	Surface Charge Density (μmol/m ²)
D ₁₁	2.19	2.69	241.9	13.69	0.569
D ₁₂	2.42	2.92	229.9	14.70	0.583
D ₁₃	2.67	3.10	229.8	14.88	0.588
D ₁₄	2.91	3.42	224.2	15.47	0.59

ization of hydrophilic comonomers, a homogeneous nucleation mechanism was proposed.¹³

In the case of a surfactant-free emulsion polymerization, e.g., copolymerization of St and BA with DBMA, the homogeneous nucleation mechanism and micelle nucleation mechanism are likely to occur. For the case in which the DBMA content was below its CMC, the comonomer was soluble in the water phase and no micelles formed. AIBA thermally decomposed to form cationic radicals and then reacted with the comonomer, St, and BA in the aqueous phase to form oligomeric free-radical chains which had a lower CMC than that of DBMA. These oligomers reacted continuously in the water phase to coil-up and formed primary particles which could absorb the monomer and grew when their chains length increased to a critical value (this is what is called the homogeneous nucleation process) or they aggregated to form micelle and absorbed the monomers and reacted through a micelle nucleation mechanism. In the very beginning of polymerization, the concentration of oligomers was too low to form micelles, the particles were formed through homogeneous

mechanism, and the MWD curve was unimodal. As the polymerization went on further, the concentration of oligomers increased high enough to exceed its CMC and micelles were formed, so the particles were also formed through the micelle mechanism in addition to the homogeneous nucleation mechanism. The MWD curves were bimodal, in which the low MW peak was the polymer formed through the homogeneous mechanism and the high MW peak was the polymer formed through the micelle mechanism.¹⁴ This might result from a higher monomer concentration at the interior of the micelle than that of the primary particle which formed through the homogeneous mechanism; the polymerization rate is faster. Increasing DBMA content led to more oligomers and micelles formed, and the probability of micelle nucleation increased as a result.

In conventional emulsion polymerization systems, the reactions take place in micelles formed by emulsifiers. Increasing the ionic strength of the aqueous could decrease the emulsifiers CMC and increase the micelle number *N_p* and *R_p* increased as a result, but if the ionic strength increased to

Table VI Effect of AIBA Concentration on the Properties of Emulsion Particles

Sample	[AIBA] × 10 ³ (mol L ⁻¹)	N _p × 10 ⁻¹³	\bar{D}_w (nm)	Surface Groups	
				—N ⁺ and C	Surface Charge Density (μmol/m ²)
B ₁₁	4.27	1.95	270	13.68	0.742
B ₁₂	4.98	2.24	258	14.87	0.662
B ₁₃	5.69	3.10	230	16.96	0.667
B ₁₄	6.40	4.22	210	19.35	0.685

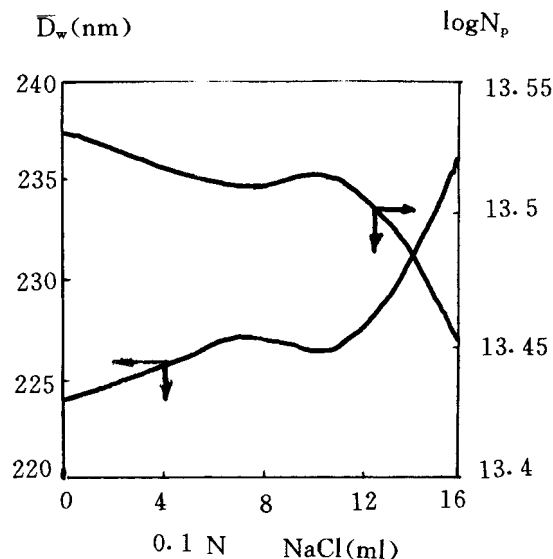


Figure 5 The effect of ionic strength on \bar{D}_w and N_p of the particles.

a too high level, the polymerization system would lose its stability and aggregation among particles would occur, which would lead to lower N_p and R_p . As can be seen, the results of the present system were different from those of conventional emulsion polymerization; two-particle formation mechanisms, micelle and homogeneous nucleation, coexisted and were in competition with conversion, DBMA content, and ionic strength. With addition of NaCl, the electrostatic repulsion force among particle surfaces decreased on account of the "shielding effect"; the aggregation of particles which caused an increase for \bar{D}_w and decrease for N_p and R_p took place. As ionic strength increased further, the CMC of oligomers dropped, causing the micelle number to increase. At same time, the

CMC of DBMA dropped to that below its content; probably, micelles are also generated in this way. All these would make for an increase in the high MW peak fraction, which implied a high micelle nucleation probability. The so-formed particles would be more stable and be less likely to coagulate with other particles after collision in comparison to the self-nucleated particles just formed.¹⁵

Particle Size, Number, and Surface Properties

To understand how each of the polymerization situations such as DBMA and AIBA concentration, ionic strength, and St/BA ratio affected the particle average diameter (\bar{D}_w), number (N_p), and its surface functional groups while other factors remained constant, a series of polymerizations was carried out. In variations of comonomer and initiator concentration, NaCl was added to maintain the solution at a constant ionic strength.

Effect of DBMA

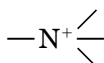
The essential role of the ionic comonomer in the emulsifier-free emulsion polymerization is that it can be chemically bonded onto the particle surfaces to provide a better stability, but different comonomers will provide different reactivities and hydrophilic properties leading to different polymerization behaviors in the aqueous phase and, therefore, the nucleation behaviors. At constant ionic strength, AIBA concentration, and St/BA ratio, \bar{D}_w decreased but N_p increased with increasing DBMA content, Table V shows the effect of DBMA on particle surface properties. When the comonomer content increased, the

Table VII Effect of Ionic Strength on the Properties of the Emulsion Particle

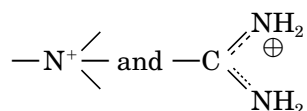
Sample	0.1N NaCl (mL)	Surface Groups —N ⁺ and C(NH ₂) ₂ ($\mu\text{equiv/g Polymer}$)	Surface Charge Density ($\mu\text{mol/m}^2$)
I ₁₁	0	15.18	0.584
I ₁₂	4	17.85	0.698
I ₁₃	8	12.49	0.491
I ₁₄	12	13.09	0.509
I ₁₅	16	11.90	0.493

Table VIII Effect of BA/St Ratio on the Properties of Emulsion Particles

Sample	BA/St	$N_p \times 10^{-13}$	\bar{D}_w (nm)	Surface Groups		Surface Charge Density ($\mu\text{mol}/\text{m}^2$)
				$-\text{N}^+$	$\text{C} \begin{matrix} \text{NH}_2 \\ \oplus \\ \text{NH}_2 \end{matrix}$	
M ₁₁	15/15	4.26	207.3	16.56		0.602
M ₁₂	17/13	4.0	211.2	16.34		0.598
M ₁₃	20/10	3.42	224.2	15.47		0.590



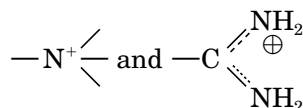
groups chemically bonded on particle surface increased, explaining the relationship among \bar{D}_w , N_p , and DBMA content, and the surface charge density increased slightly with increasing DBMA concentration. Because the ionogenic comonomer reacted with the initiator to form many oligomer radicals,¹⁶ the primary particle formation was accelerated with increasing DBMA concentration and resulted in decreasing \bar{D}_w and increasing N_p . Moreover, DBMA is a soluble-water monomer; the



groups were at the surface of the latex particle as far as possible after DBMA copolymerized with St and BA.¹⁷

Effect of AIBA

Table VI shows the particle size and number as a function of initiator concentration at constant DBMA content, ionic strength, and St/BA ratio. The results indicate that the higher initiator concentration results in a smaller particle size and a larger number, being similar to some reference. Table VI also shows that with increasing AIBA concentration the



groups of the latex particle increase and the surface charge density increases.

Effect of Ionic Strength

The ionic strength in the aqueous phase will cause a "shielding effect" to decrease the electrostatic

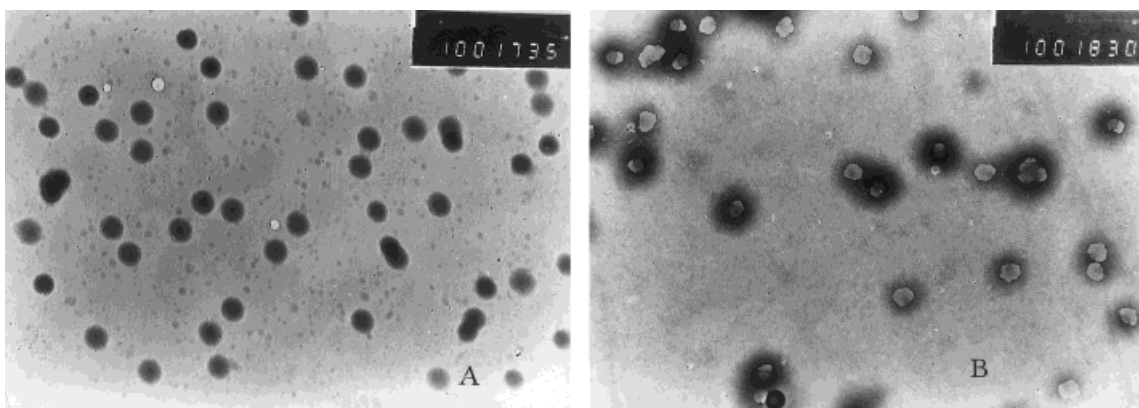
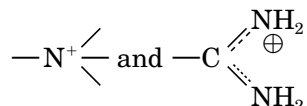


Figure 6 Transmission electron micrograph of emulsion particles prepared by different methods: (A) batch; (B) core/shell.

Table IX Effect of Emulsion Preparation Methods on the Properties of Emulsion Particles

Methods	$\bar{D}w$ (nm)	$Np \times 10^{-13}$	Surface Groups ($\mu\text{equiv/g Polymer}$)	Surface Charge Density ($\mu\text{mol/m}^2$)
Batch	224.2	3.42	15.47	0.590
Core/shell	205.4	4.35	11.32	0.408

repulsion force among the surfaces of the particles and therefore the particles' stability, leading to an increase and decrease in the average particle diameter and the number, respectively. In the present system, however, $\bar{D}w$ and Np were found to increase and decrease, respectively, at first with increasing ionic strength, then tended to decrease and increase, respectively. Finally, they tended to increase and decrease, respectively, again when the NaCl concentration was high enough (Fig. 5). To understand the effects of ionic strength clearly, particle surface properties at various NaCl concentrations were characterized (Table VII). Obviously, the particle surface properties were intimately tied to NaCl concentration: The variations of surface groups

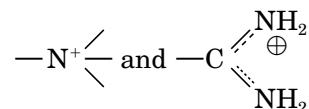


and surface charge density with ionic strength were all similar to that of Np ; they all had the process of decreasing–increasing–decreasing.

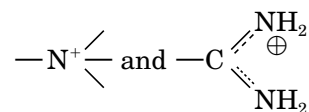
Effect of Monomer Composition

The polymerization mechanisms are bound up with monomers' solubilities in the emulsifier-free emulsion polymerization system; the fundamental difference of homogeneous and oligomer micelle nucleation mechanisms are based on the monomers' solubilities. Table VIII shows the effect of monomer composition on particle size, number, and the properties of the emulsion particle. From the results, we can say that $\bar{D}w$ and Np vs. the BA content in the monomer feed drastically increased and decreased, respectively. Rp in-

creased with increasing BA content. Corresponding to these, the



groups chemically bound on the particle surface and surface charge density were obviously dropped. These were caused by the different reactivity and solubility of St and BA; BA had the tendency to bind on the particle surface to compete with



groups due to its higher solubility.

Effect of Emulsion Preparation Methods

In the same conditions, only varying the feeding methods of the monomer, the particle size, the micromorphology, and the properties of the emulsion particles are affected. Figure 6 shows the composite particles prepared by different methods. As can be seen, the micromorphology of particles prepared by batch methods is uniform and has a narrow-size distribution. The micromorphology of particles prepared by core/shell methods is of a core–shell structure; moreover, the particle size, number, and the properties of emulsion particles are different with the emulsion preparation method used (Table IX).

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