

Using Anionic Polymerizable Surfactants in Ultrasonically Irradiated Emulsion Polymerization to Prepare Polymer Nanoparticles

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ABSTRACT: An ionic polymerizable surfactant, sodium sulfopropyl-lauryl maleate (M12), was synthesized and used as an emulsifier, an initiator, and a comonomer in ultrasonically irradiated emulsion polymerization. FTIR spectra and gravimetric method results indicated that copolymers P(Styrene-M12) and P(Butylacrylate-M12) were prepared successfully by ultrasonically irradiated emulsion polymerization and the composition of M12 elevated with the increasing concentration of M12 added. TEM photographs of P(St-M12) showed that the nanoparticles with small diameters (20–45 nm) were prepared. With the increase of M12 concentration, the particle size became

smaller and the size distribution became wider. The P(BA-M12) particles size was also small (<100 nm) but the size distribution was wide due to the high reactivity of BA. Because surfmer M12 was chemically bonded with the latex particles, the stability of the copolymer latex prepared by ultrasonically irradiated emulsion polymerization was much better than that of the homopolymer latex (PSt or PBA) prepared by the same way. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2022–2027, 2008

Key words: polymerizable surfactant; emulsion polymerization; ultrasonic irradiation; nanoparticle

INTRODUCTION

Emulsion polymerization is one of the most important techniques for preparing polymer nanoparticles. A general trend in emulsion polymerization is the search for ways to conduct the process more cheaply and with less negative effects on environment. However, the use of conventional surfactants such as sodium dodecyl sulfate (SDS) has adverse effects on product properties due to their physical adsorption on the polymer particle surfaces and their residuary in the latex. Surfactants can migrate to the surface of a latex coating and desorb from the latex particle surface under high shear, causing destabilization.^{1–3} There are also some disadvantages in the use of chemical initiators in an emulsion polymerization. It would affect the molecular weight, particle size distribution, and the stability of the latex production. In addition, the residual initiator present after polymerization may act as an undesirable contaminant and affects the purity and properties of the production.⁴ Moreover, the diameter of latex particles polymerized by conventional emulsion polymerizations is

usually between 70 and 500 nm. It is difficult to prepare latex particles with diameter below 100 nm.

Therefore, there is a great interest to find new ways to prepare polymer nanoparticles, especially new emulsifier systems and new polymerization techniques. Several methods can be used to eliminate the disadvantages caused by using conventional emulsifiers. In the surfactant-free emulsion polymerization, the latex particles are mainly stabilized by the sulfate groups and groups derived from the persulfate initiator.^{5,6} Because of the relatively low particle surface charge density, a significant amount of coagulum are formed during the reaction, particularly at high solid content. Some researchers find functional comonomers can copolymerize with the monomer and contribute the hydrophilic-lipophilic balance to the latex particles, replacing the surfactant.⁷ However, because of their high solubility in water, large amounts of water soluble oligomers are often formed, which is not desirable. A more promising method is to use polymerizable surfactants, which have reactive groups and can bind into the latex particles during the polymerization.^{8–16} Their incorporation into the polymer chains would not necessarily affect the molecular weight of products or the rate of polymerization; i.e., the main advantages of emulsion polymerization are not affected.¹⁵

Many previous work report that ultrasonically irradiated emulsion polymerization of some mono-

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mers can occur without chemical initiators. Under ultrasonic irradiation, radicals can be generated due to decomposition of solvent, monomers, surfactants, or rupture of polymer chains. These radicals can initiate further chemical reactions in the absence of any added chemical initiator.^{17–19} Our early study²⁰ proved that in ultrasonically irradiated emulsion polymerization the most radicals that could initiate monomers to react come from the decomposition of ionic surfactants. The ionic surfactants play a very important role in obtaining a high polymer yield in the ultrasonically irradiated emulsion polymerization, serving as not only the emulsifier but also the initiator. The most interesting aspect of ultrasonically irradiated emulsion polymerization was that it always resulted in smaller latex particles (i.e., <100 nm) due to the intense blast wave and shearing effect of ultrasound.^{21–23}

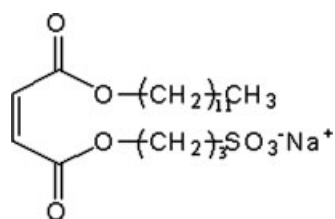
In this article, nanolatex with good stability was prepared by combining the use of an ionic polymerizable surfactant with ultrasonic irradiation. In ultrasonically irradiated emulsion polymerization, the ionic polymerizable surfactants served not only as an emulsifier, but also as an initiator. At the same time, they are comonomers and can copolymerize with other monomers, such as styrene and butyl acrylate. The manifold effects of polymerizable surfactants in ultrasonically irradiated emulsion polymerization were investigated in this article.

EXPERIMENTAL

Reagent

Butyl acrylate (BA, Chengdu Kelong Chemical Reagents Factory of China, CP) and styrene (St, Tianjin Chemical Reagents Institute of China, CP) were washed three times with 10% aqueous sodium hydroxide and distilled water to remove the inhibitor. Then they were dried with anhydrous sodium sulfate and vacuum distilled. SDS (AR, Wuhan Chemical Reagents, Wuhan, China) was used as supplied.

The ionic reactive surfactant sodium sulfopropyl-laurylmaleate (M12) was synthesized according to the preparation method reported in the literature.^{24,25} The molecular structure of M12 was shown in Scheme 1.



Scheme 1 The molecular structure of M12.

TABLE I
Basic Recipe and Reaction Conditions of Ultrasonically Irradiated Emulsion Polymerization

Feed	
Monomer (g/100 mL)	10
M12 (g/100 mL)	3
Total volume (mL)	80
Water (mL) = 80 - V_m - V_{M12}	
Conditions	
Acoustic intensity (W/cm^2)	9.54
Temperature ($^{\circ}C$)	30
Reaction time (min)	60
Velocity of N_2 flow (mL/min)	40

Apparatus

Ultrasound, with a frequency of 20 kHz, was produced with a Sonics and Materials 1500 Ultrasonic Generator (USA), with a standard titanium horn and a 1-in. replaceable flat titanium probe. The schematic diagram of the ultrasonic polymerization apparatus has been published previously.^{20,23} The height of probe to reaction vessel base is about 3 cm. The power output is adjustable. The acoustic energies varied between 14.4 and 56.6 W, and this corresponded to a range of acoustic intensity from 3.0 to 11.8 Wcm^{-2} . During polymerization, constant temperature bath water was circulated to maintain a constant temperature reaction condition.

Ultrasonically irradiated emulsion polymerization

Table I lists the basic recipe and conditions of ultrasonically irradiated polymerization studied in this article. All polymerization reactions were carried out at these conditions unless otherwise stated. The reaction mixture of St (or BA), M12 and water was introduced into the reaction vessel and deoxygenated by bubbling with oxygen-free nitrogen. The reaction vessel was kept cool by circulating 30 $^{\circ}C$ water through the water jacket surrounding the vessel. The system was subjected to ultrasonic irradiation for 1 h.

After reaction, the emulsion mixture was precipitated with ethanol and dried under vacuum. The final product was extracted with distilled water and methylbenzene for 48 h and dried under vacuum for FTIR analysis.

Ultrasonically irradiated polymerization of homopolymers polystyrene (PSt) and poly(butyl acrylate) (PBA) were carried out at same conditions listed in Table I except M12 was replaced by SDS.

Measurements

Monomer and M12 conversions were determined gravimetrically. They were calculated according to eqs. (1) and (2),

$$x = (W_2/W_1 - x_c)/x_m \times 100\% \quad (1)$$

$$x_s = (W_3 - W_4 \cdot x) / W_s \times 100\% \quad (2)$$

where x is monomer conversion, x_s is M12 conversion, x_c is mass percent of the nonvolatile matters in the system, x_m is mass percent of the monomer added, W_1 is mass of the latex sample, W_2 is mass of the latex sample after drying, W_3 is mass of the solid powder after extraction, and vacuum drying, W_4 is mass of the monomer added, and W_s is mass of M12 added.

The polymerization rate versus time curves of reactions were obtained by derivation of the conversion versus time curves.

FTIR spectra of polymers were recorded with a Nicolet 560 Spectrometer (USA). Each spectrum was an average of 20 scans recorded at a resolution of 4 cm.

Particle sizes of polymer latex were examined with transmission electron microscope (JEM100X, Japan). The diameters of over 200 particles were used in the calculation of the average sizes for the samples imaged by TEM. The number-average diameter (D_n), the volume-average diameter (D_v), weight-average diameter (D_w), and the polydispersion of particle size (PDI) were calculated according to eqs. (3)–(6), where N_i is the number of particles with diameter D_i (nm). The particle number (N_p) generated per milliliter of water was calculated from Eq. (7), where y is latex solid content (g/mL), D_v is volume-average diameter of the latex particle (m), and ρ is polymer density (g/mL).¹⁸

$$D_n = \sum N_i D_i / \sum N_i \quad (3)$$

$$D_v = \sum N_i D_i^3 / \sum N_i D_i^2 \quad (4)$$

$$D_w = \sum N_i D_i^4 / \sum N_i D_i^3 \quad (5)$$

$$\text{PDI} = D_w / D_n \quad (6)$$

$$N_p = 6y / \pi (D_v)^3 \rho \quad (7)$$

The stability of the polymer latices:

1. Storage stability: the copolymer and homopolymer latex were stored for 1 year under ambient conditions. Good storage stability means there is no precipitate in the emulsion.
2. Mechanical stability: 50 mL latex was introduced into a round bottom flask, stirring for 60 min under the rotational speed of 1500 rpm. The latex without floccule was considered to be stable.
3. High temperature stability: the latex in tubes was heated at 0.5°C/min in the water bath and observed the transition temperature at which the clear emulsion turned turbid.

4. Low temperature stability: the latex in tubes was cooled slowly in the ice salt-water bath and observed the transition temperature at which the clear emulsion turned turbid.
5. Dilution stability: All latices prepared by ultrasonically irradiated emulsion polymerization were diluted for 50 times and the latex with no floccules was considered to be stable.
6. pH stability: to observe the stability of the latices at different pH values. 1M HCl or 1M NaOH aqueous solution was dropped into the latex respectively.

RESULTS AND DISCUSSION

Ultrasonically initiated emulsion polymerization with M12

The ionic surfactant sodium sulfopropyl-laurylmaate (M12) is a kind of intermediate-type polymerizable surfactant. It has a polymerizable moiety between the hydrophilic group and the hydrophobic group in the molecular chain. M12 does not tend to homopolymerize but tend to copolymerize with other monomers.

Figure 1 shows monomer conversion versus reaction time in emulsion polymerization with M12 and without any surfactants under ultrasonic irradiation. No chemical initiator was added to the reaction system. It is obvious that the monomer conversions of systems without surfactants are nearly zero. Upon addition of M12, both BA and St conversions increase significantly. Especially for BA, it has a 90% monomer conversion under 1-h ultrasonic irradiation. Figures 2 and 3 show the conversions of BA and St versus reaction time at various M12 concentrations respectively. With the increasing amount of M12 added, the induction period of polymerization

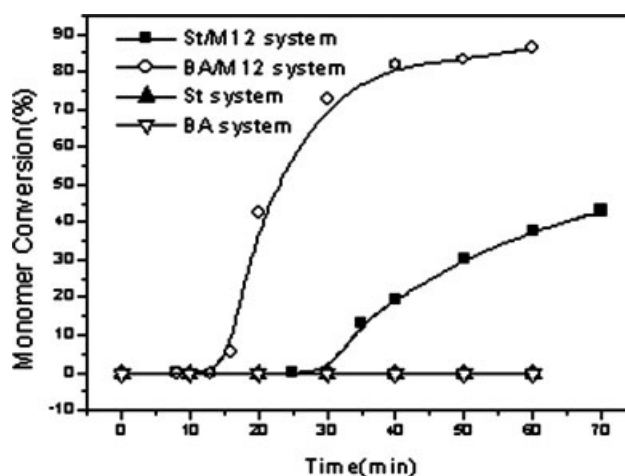


Figure 1 Monomer conversions versus reaction time curves in different systems.

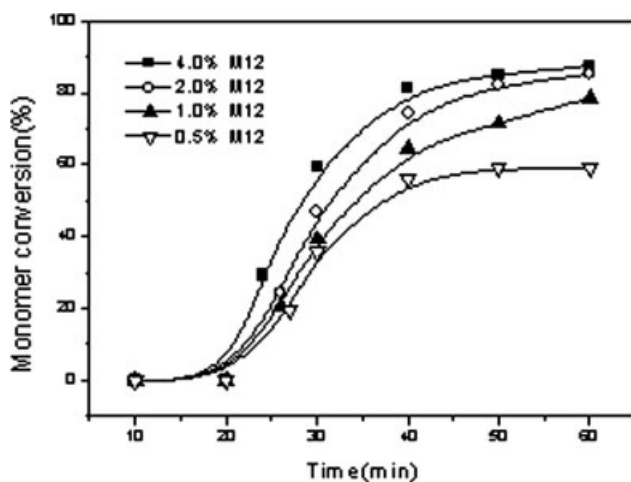


Figure 2 Monomer conversions versus time curves of BA with different M12 concentrations.

shortens and the conversion of monomer increases. These results indicate that the ionic surfmer M12 produces radicals to initiate the emulsion polymerization, in agreement with our previous studies.²⁰ M12 plays a very important role in obtaining a high polymer yield in the ultrasonically irradiated emulsion polymerization, serving as both the emulsifier and the initiator.

Copolymer structure and properties

FTIR spectra of the products prepared by ultrasonically irradiated emulsion polymerization of St with different M12 concentrations are shown in Figure 4. It can be seen that the spectra show both the vibration band of carbonyl units of M12 ($\nu_{\text{C=O}}$, 1734 cm^{-1}) and the vibration bands of styrene (754 , 696 , 1700 to 1400 cm^{-1}). So the products prepared are copolymers of styrene and M12 (P(St-M12)).

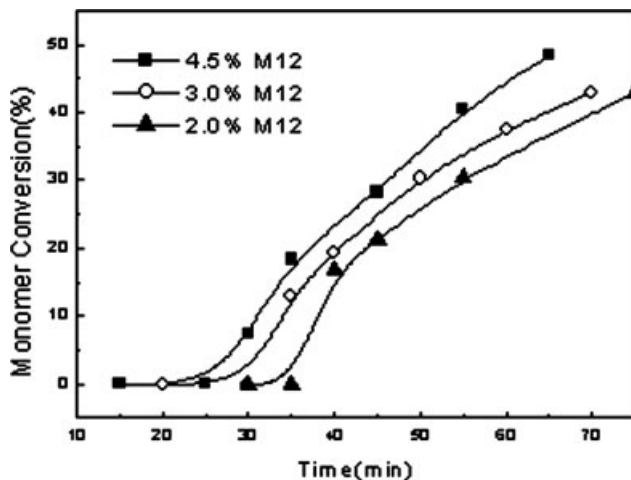


Figure 3 Monomer conversions versus time curves of St with different M12 concentrations.

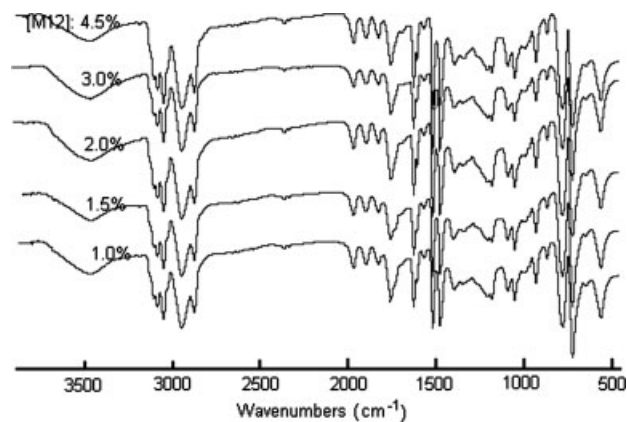


Figure 4 FTIR spectra of P(St-M12) prepared by ultrasonically irradiated emulsion polymerization with different M12 concentrations.

The ratio β , the integrated area of the C=O stretching band of the surfmer M12 at 1734 cm^{-1} to the area of C—H out-of-plane bending peak of the St aromatic ring at 754 cm^{-1} , is well suited for the determination of the relative surfmer composition in copolymers. The relative M12 composition in copolymer (β) versus the corresponding M12 added concentration is shown in Figure 5. It is found that the relative M12 composition increases with the concentration of M12 added.

The typical TEM photomicrograph of the P(St-M12) latex prepared by ultrasonically irradiated emulsion polymerization is shown in Figure 6. The diameter of the latex particles is in the range of 10–60 nm, which is much smaller than that prepared by conventional emulsion polymerization with the same emulsifier. The particle size distribution is shown in Figure 7. The number-average particle diameter is 33.2 nm and the polydispersity of particle size is 1.14. In ultrasonically irradiated emulsion polymer-

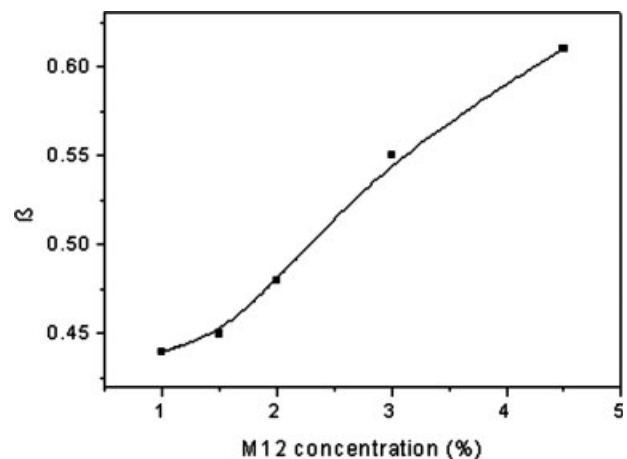


Figure 5 Effect of M12 concentrations on the relative surfmer composition in copolymers (β).

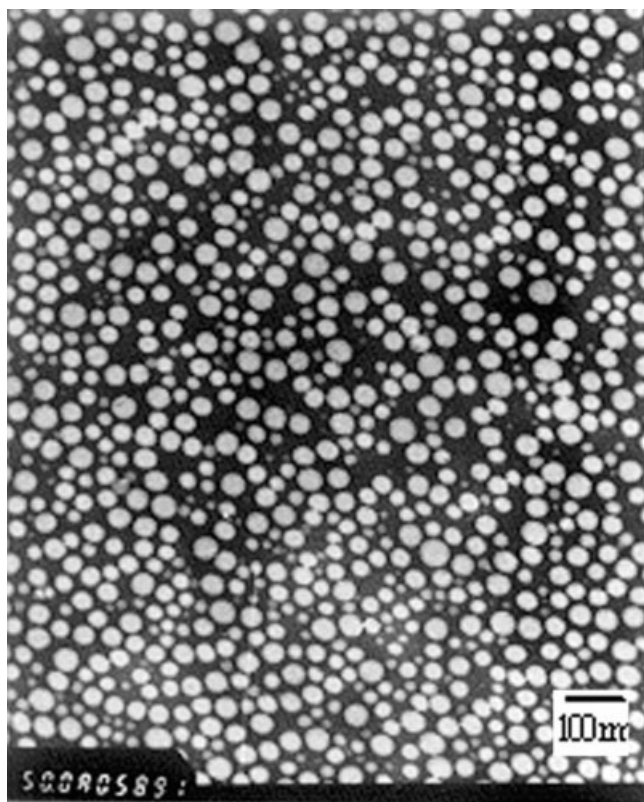


Figure 6 TEM of P(S-M12) latices prepared by ultrasonically irradiated emulsion polymerization ($\times 50,000$).

ization, a great number of small monomer droplets with large surface area are produced by the intense shearing effect of ultrasound. Surfactants added prevent these small droplets from aggregating. At the same time, a high concentration of radicals is pro-

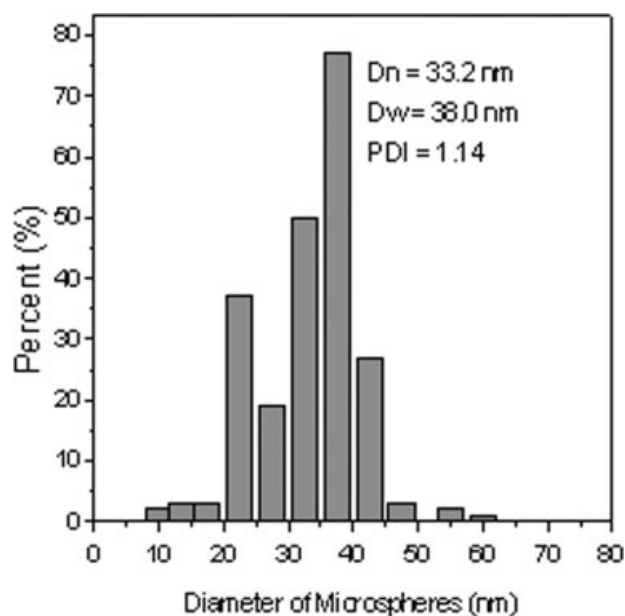


Figure 7 Particle size distribution of P(S-M12) latices prepared by ultrasonically irradiated emulsion polymerization.

TABLE II

Effect of M12 Concentrations on Latexes Properties

[M12] (g/mL)	y^a (g/100 mL)	D_v^b (nm)	N_p^c ($\times 10^{-15}$ /mL)
0.015	5.41	38.32	3.04
0.030	6.90	32.56	6.11
0.045	8.89	28.91	6.48

^a Latex solid content.

^b Volume-average diameter of the latex particle.

^c The particle number per mL.

duced by ultrasonic cavitations. The radicals are easy to be captured by the small monomer droplets because of their large surface areas. Most of the droplets will be nucleated. Thus, smaller latex particles will be produced. Because of this monomer droplets nucleation mechanism, it is believed that ultrasonically irradiated emulsion polymerization is a promising technique for preparing polymer nanoparticles.

The characteristics of the P(St-M12) latex obtained with different M12 concentrations are listed in Table II. With the increase of M12 concentration, a significantly large number of latex particles with smaller particle size are obtained. According to the mechanism of ultrasonically irradiated emulsion polymerization, elevating the surfactant concentration could increase the number of micelles formed or assist with the stabilization of small monomer droplets, both resulting in a decrease of particle size and an increase of particle number.

The typical TEM photomicrographs of the P(BA-M12) latex prepared by ultrasonically irradiated emulsion polymerization is shown in Figure 8. The average size of P(BA-M12) particles is also small (< 100 nm). Some particles are large and the size distribution is wide. It may result from PBA chains continue to react and tangle with each other due to the high reactivity of BA. Moreover, the PBA particles are soft and rubber-like because of the low glass

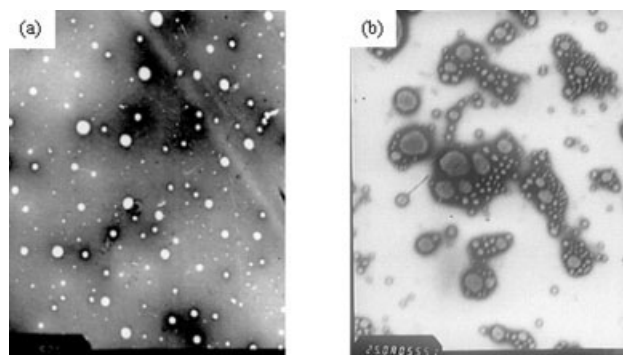


Figure 8 TEM photos of P(BA-M12) latices prepared by ultrasonically irradiated emulsion polymerization, take photo after reaction (a) at once; (b) a month later ($\times 25,000$).

TABLE III
The Stability of Copolymer and Homopolymer Latexes Prepared by Ultrasonically Irradiated Emulsion Polymerization

Property	P(St-M12)	PSt	P(BA-M12)	PBA
Storage stability	Good	Unstable	Good	Unstable
Mechanical stability	Good	Good	Good	Good
High temperature stability	$T_h > 100^\circ\text{C}$	$T_h \approx 94^\circ\text{C}$	$T_h > 100^\circ\text{C}$	$T_h \approx 95^\circ\text{C}$
Low temperature stability	$T_l < 0^\circ\text{C}$	$T_l \approx 4^\circ\text{C}$	$T_l < 0^\circ\text{C}$	$T_l \approx 4^\circ\text{C}$
Dilution stability	Good	Good	Good	Good
pH stability	pH = 1–14 (good)	pH > 7 (unstable)	pH = 1–14 (good)	pH > 7 (unstable)

transition temperature of PBA. One month later, they tend to adhere together and form bigger aggregates [Fig. 8(b)].

The latex prepared by ultrasonically irradiated emulsion polymerization is thermodynamically stable system. It can be stored for a long time. However, when conditions change, the stabilization of the latex may be damaged. The influencing factors on stabilization of the latex include mechanical force, temperature, pH value of the latex, and so on. Table III lists the stability of P(St-M12), P(BA-M12) latex, homopolymers PSt and PBA. The homopolymers prepared at the same reaction conditions are references (SDS (3 g/100 mL) as the emulsifier and initiator).

All results above show that the copolymer latices prepared by ultrasonically irradiated emulsion polymerization are more stable than the homopolymer latex. This is due to the chemical incorporation of the surfactant M12 into the copolymer latices during the course of the polymerization. They stabilize the latices when the storage conditions change.

CONCLUSIONS

An ionic polymerizable surfactant sodium sulfo-*n*-propyl-laurylmaleate (M12) was used as the emulsifier, the initiator, and comonomer in ultrasonically irradiated emulsion polymerization to prepare nanolatex. The copolymers P(St-M12) and P(BA-M12) and the nanoparticles with small diameters (<100 nm) were prepared.

In St-M12 system, the increasing amount of M12 added can shorten the induction period of polymerization and increase the conversion of monomer. More M12 also causes the smaller particle size and the wider size distribution. In BA-M12 system, the P(BA-M12) particles size is also small (<100 nm) but the size distribution is wide due to the high reactivity of BA. The stability of the copolymer latices prepared by ultrasonically irradiated emulsion polymerization are much better than that of the homopolymer latices prepared by the same way, resulting

from the stabilizing ability of M12 molecules bonded with the latex particles.

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