

# Ultrasonically Irradiated Emulsion Copolymerization of Styrene and Surfmer

Jingzhi Zhang, Ya Cao

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

Received 31 July 2003; accepted 24 February 2004

DOI 10.1002/app.20722

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The nonionic surfmer AREO7 was first used in the ultrasonically irradiated emulsion polymerization of styrene. The added AREO7 could improve the emulsion solid content. Through FTIR, GC-MS, and DSC studies, it was found that the polymer produced was the copolymer of styrene and AREO7. The copolymer latices polymerized in proper conditions displayed nanoparticles. When AREO7 concentration increased, there were more nanostructured copolymer gels, in which AREO7 molecules form an amphiphilic network, whereas polystyrene was located in hydrophobic droplet. The latices had a structured morphology

that the AREO7 units were mainly on the surface of particles. The glass transition temperature ( $T_g$ ) of copolymers decreased with the increase of AREO7 composition in copolymers. Freeze-thaw test showed that the freeze-thaw stability of the copolymer emulsion was improved greatly because of the increasing composition of AREO7 in copolymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2356–2362, 2004

**Key words:** surfmer; nanoparticles; ultrasonically irradiation; emulsion polymerization; styrene

## INTRODUCTION

Recently, ultrasonically irradiated emulsion polymerization has attracted much research interest. Ultrasonic irradiation was shown to accelerate the conventional emulsion polymerization. The acceleration was thought to be due to the nonchemical effect of ultrasonic irradiation in early study,<sup>1</sup> for example, preventing monomer droplet from aggregation and degassing effect. In fact, the more important effect of ultrasonic irradiation on emulsion polymerization is a chemical effect. When an ultrasound passes through a liquid medium, a large number of microbubbles (called cavitated bobbles) form and grow, and then collapse. The collapsing of the cavitated bobbles can generate high local temperatures up to 5000 K and high local pressures up to 500 atm, which make possible the special chemical reactions.<sup>2</sup> Under such conditions, radicals can be generated by decomposition of solvent, monomers, surfactants, or rupture of polymer chains; these radicals can initiate further chemical reactions.<sup>3–5</sup> Stoffer et al. and Biggs et al.<sup>5–11</sup> did research on ultrasonically irradiated emulsion. Stoffer et al.<sup>5</sup> studied the initiation mechanics of ultrasonically irradiated emul-

sion polymerization by using a radical capture experiment. They confirmed that the radical in ultrasonically irradiated emulsion polymerization came mainly from surfactant. Biggs et al.<sup>9</sup> prepared polystyrene latex with ultrasonic initiation. The size distribution of latices was wide, and long reaction time was needed to obtain high monomer conversion.

Therefore, ultrasonically irradiated emulsion polymerization could be performed in the absence of any added chemical initiator because of ultrasonic cavitation. Because of the vivid blast wave and shearing action, the size of latex prepared by ultrasonically irradiated emulsion polymerization may be smaller than 100 nm, which is different from conventional emulsion polymerization. However, the nanolatices require more stability because of nanoparticle size. In ultrasonically irradiated emulsion polymerization, low molar mass surfactants were normally used. The use of low molar mass surfactants could not meet the stability of nanolatex because of their migration. A more promising method is to use polymerizable surfactants, which contain reactive group and ensure the chemical incorporation of surfactant into the latex particles during the course of the polymerization. The application of polymerizable surfactants and their copolymerization was presented.<sup>12–17</sup> Few studies of polymerizable surfactants in ultrasonically irradiated emulsion polymerization were reported. In this article, a polymerizable surfactant, dodecyl poly(ethoxy) acrylate, which is also called surfmer, was used in ultrasonically irradiated emulsion polymerization of styrene.

Correspondence to: Y. Cao (caoya@mail.sc.cninfo.net).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50303013.

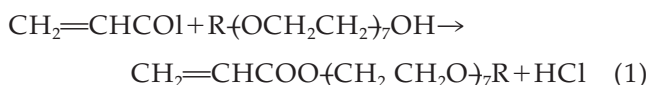
**TABLE I**  
Basic Recipe and Reaction Conditions of Emulsion Polymerization

| Feed                      |      | Conditions                 |            |
|---------------------------|------|----------------------------|------------|
| St, % (v/v)               | 5    | Ultrasonic power output, W | 600        |
| AREO7, $\times 10^3$ g/mL | 6.6  | Temperature, °C            | $30 \pm 2$ |
| SDS, g/mL                 | 0.02 | Time, min                  | 30         |

## EXPERIMENTAL

### Materials

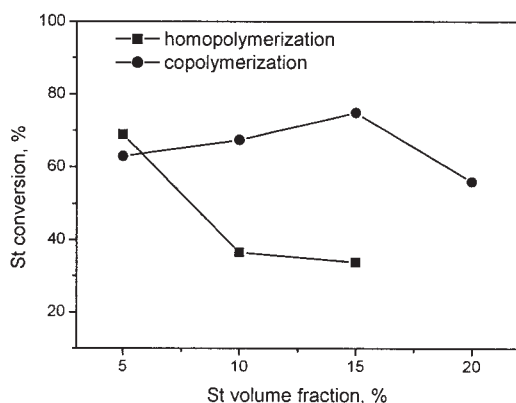
Styrene (St; Xilong Chemical Plant, Chengdu, China, CP,  $\rho = 0.906-0.909$ ) was washed with 10 wt % aqueous NaOH and deionized water and distilled under vacuum prior to use. Surface active surfmer, dodecyl poly(ethoxy) acrylate (AREO7), was synthesized by reaction of acryloyl chloride with dodecyl poly(ethoxy) ether (Beijing Synthetic Chemical Plant) according to the preparation method reported in the literature<sup>18</sup>



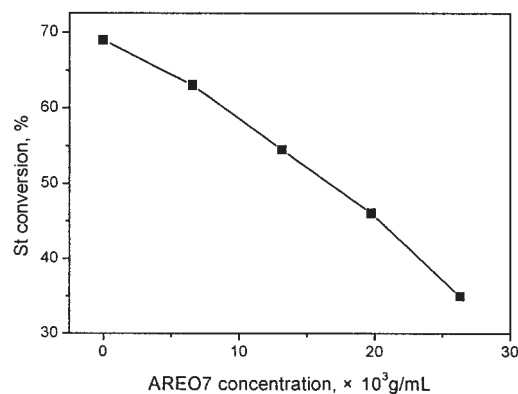
Sodium dodecyl sulfate (SDS) (Wuhan Chemical Reagents Corp., Wuhan, China) and solvents (tetrahydrofuran, ethanol) were used as supplied.

### Ultrasonically irradiated emulsion polymerization

The ultrasonically irradiated polymerization apparatus was reported.<sup>18</sup> The probe of the ultrasonic horn was immersed directly in the emulsion. A mixture of St, AREO7, SDS, and water (see Table I for recipe) was deoxygenated by using bubbling with nitrogen gas and then was subjected to ultrasonic irradiation. The flow of nitrogen gas and ultrasonic power output were



**Figure 1** Effect of St volume fractions on St conversion of the ultrasonically irradiated emulsion polymerization.



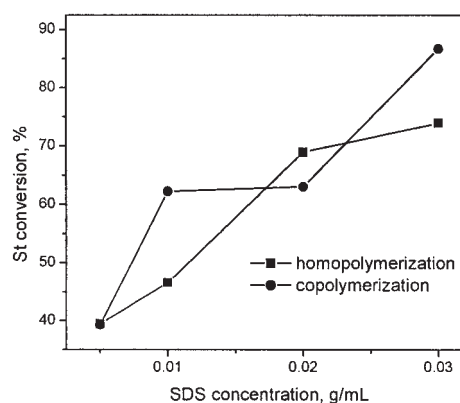
**Figure 2** Effect of AREO7 concentrations on St conversion of the ultrasonically irradiated emulsion polymerization.

kept constant. During the reactions, a syringe was used to withdraw polymerized emulsion. The latex sample was used directly for determination of monomer conversion and particle size by transmission electron microscopy (TEM). The dried latex was washed with water until it was free of surfactant SDS and the unreacted surfmer. The purified polymer sample was used for characterization by FTIR, gas chromatography-mass spectroscopy (GC-MS), and DSC.

### Measurements

Monomer conversions were determined gravimetrically. The polymerization rate versus time curves of reactions were obtained by derivation of the conversion versus time curves.

FTIR spectra of polymer were recorded with a Nicolet Model 560 spectrometer (USA). The samples were prepared by mixing the polymer with KBr and pressing the mixture into a compact pellet. Each spectrum was recorded in double precision at a resolution of  $4 \text{ cm}^{-1}$  with a total of 20 scans. The copolymer composition was also determined by GC-MS by using a



**Figure 3** Effect of SDS concentrations on St conversion of the ultrasonically irradiated emulsion polymerization.

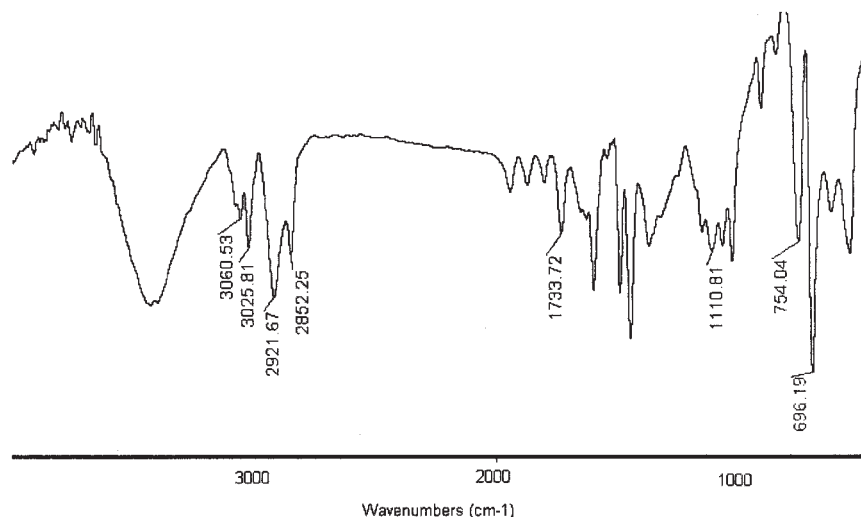


Figure 4 FTIR spectrum of St-AREO7 copolymer.

model HP5890A gas-phase chromatograph (Hewlett-Packard Co., USA), which was equipped with a pyrolysis oven and a model 5972 mass spectra (Hewlett-Packard).

Intrinsic viscosity  $[\eta]$  of the polymer was measured with viscometer. The polymer was dissolved in THF and its intrinsic viscosity was determined by using a Ubbelohde viscometer at  $24 \pm 0.1^\circ\text{C}$ .

Particle sizes of polystyrene latex were examined with TEM (JEM 100X, Japan). A drop of a diluted polymer emulsion was put on a carbon film supported by a copper grid and placed in the vacuum of the electron microscope after air-drying. The diameters of over 200 particles were used in the calculation of the average sizes for the samples imaged by TEM.

DSC spectra were obtained from a Perkin-Elmer DSC-2C at a heating rate of  $20^\circ\text{C}/\text{min}$  from  $-40$  to  $200^\circ\text{C}$ .

Freeze-thaw test was carried out according to ISO1147-1975 (E). The polymer emulsion was exposed at  $-10 \pm 2^\circ\text{C}$  for 16 h and then was rested under ambient conditions for 8 h. If there was no flocculation, the freeze-thaw test continued until flocculation. The stability of emulsion was expressed by the recycle time of the freeze-thaw test, which was no more than 5 times.

## RESULTS AND DISCUSSION

### Ultrasonically irradiated emulsion polymerization

Surfmer, AREO7, is a so-called head-type polymerizable surfactant, which has its polymerizable moiety near to the hydrophilic head group. The molecular structure was shown as formula (1). AREO7 is more likely to react with other monomers, because the reactivity of its double bond is relative low compared the low molecular monomer. Ultrasonically irradiated

emulsion polymerization of St could not be carried out if only using AREO7 as emulsifier. However, when SDS was added into the reaction system, the polymerization performed successfully. So in this article, AREO7 and SDS were used together as emulsifier. Most of the polymerization was carried out in ultrasonic reactor with 600 W ultrasonic power output at  $30^\circ\text{C}$ . Table I presents the basic recipe of ultrasonically irradiated emulsion polymerization.

Figure 1 shows the effect of St concentration on St conversion by using the recipe in Table I. We also carried out ultrasonically irradiated emulsion polymerization of St without AREO7 (homopolymerization) as a reference. It can be seen that the change of St conversion in copolymerization is not obvious with the increase of St content, while St conversion in homopolymerization decreases. In ultrasonically irradiated emulsion polymerization, the increase of oil phase would weaken the ultrasonic cavitation, which

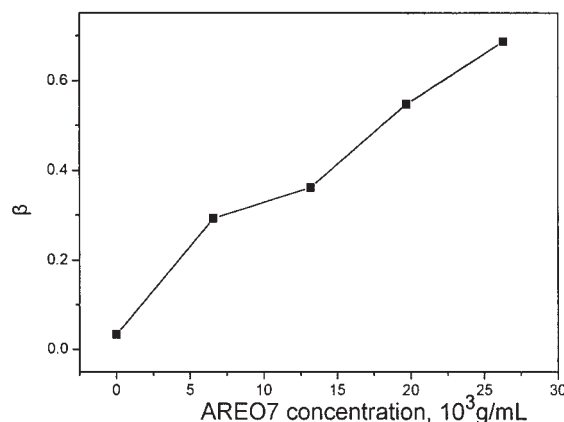


Figure 5 Effect of AREO7 concentrations on  $\beta$ .

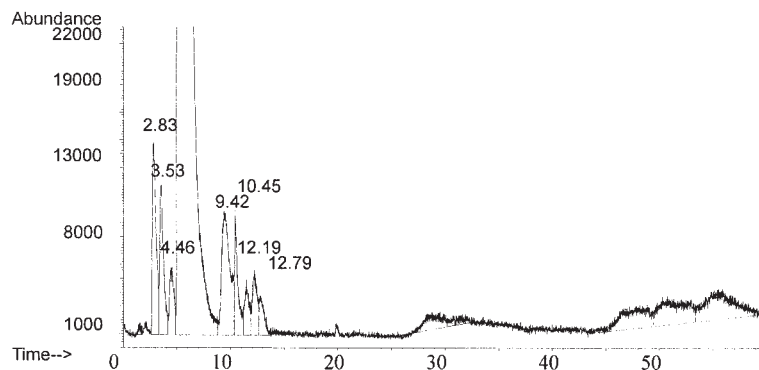


Figure 6 GC spectrum of PS polymerized by ultrasonically irradiated emulsion polymerization without AREO7.

produces fewer radicals. On the other hand, with an increase in St concentration, the ratio of surfactant and monomer decreases and the number of micelles formed in the medium decreases, leading to a decrease in nucleation rate. So, the conversion of St decreases with St concentration. When AREO7 was added to the polymerization, the excellent surface-active surfactant AREO7 gave rise to smaller micelle diameter and a larger number of micelles, leading to more polymerization loci and a higher polymerization rate. So, more St was converted into polymer. The improvement of emulsion solid content is important for application of ultrasonically irradiated emulsion polymerization.

In Figure 2, a St conversion versus AREO7 concentration is shown for the ultrasonically irradiated emulsion polymerizations, which were polymerized at an ultrasonic power output 600 W and in 60 min. It is obvious that the conversion of St drops gradually with the increase of AREO7 concentration. This behavior could be attributed to the reaction of St with AREO7 and the low activity of AREO7. The molecular structure of the h-type polymerizable surfactant AREO7, with reactive acrylate unit, is less favorable for the polymerization compared to a little monomer such as St. When more AREO7 was added, more AREO7 reacted, which made less reactivity of long-chain radi-

cals. Thus, the polymerization rate fell and St conversion decreased.

Figure 3 shows that St conversion increased with SDS concentration, suggesting that SDS is important in ultrasonically irradiated emulsion polymerization. Similarly to conventional emulsion polymerization, higher surfactant concentration gives rise to smaller micelle diameters and a larger number of micelles, leading to more polymerization loci and higher polymerization rates. Also, a higher surfactant concentration results in higher system stability, favoring the capture of radicals. Finally, the number of radicals produced from decomposition of SDS increases, which leads to a dramatic rise in polymerization rate.

### Copolymer structure and properties

A typical spectrum of copolymer is shown in Figure 4. It can be seen that the FTIR of copolymer has both the bands of AREO7 and the bands of St. The ratio  $\beta$  is the band intensities of C=O stretching mode of the surfmer AREO7 at  $1733\text{ cm}^{-1}$  and C—H out-of-plane bending mode of the aromatic ring in St at  $754\text{ cm}^{-1}$ , which is well suited for the determination of the surfmer composition in copolymer. The ratio  $\beta$  reflects the relative composition of AREO7 in the copolymer.

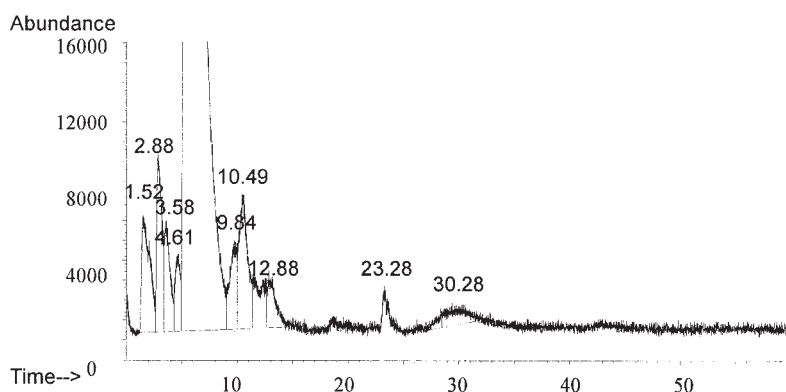


Figure 7 GC spectrum of P(S-AREO7) polymerized by ultrasonically irradiated emulsion polymerization.

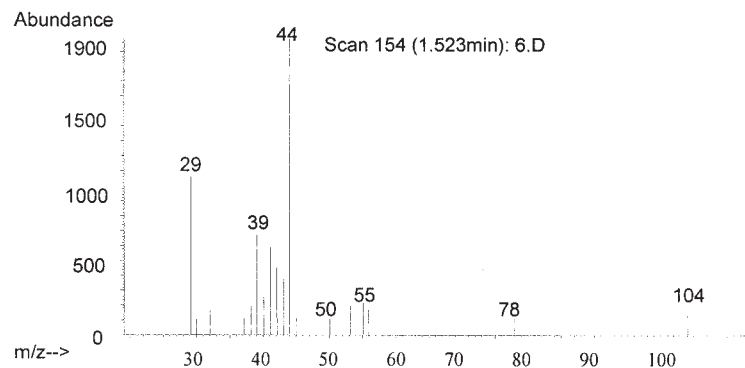


Figure 8 Mass spectrum of peak at 1.52 min in the GC spectrum of P(S-AERO7).

The relative AERO7 composition in copolymer was plotted versus the corresponding AERO7 added concentration in Figure 5. It is found that the relative AERO7 composition increased with concentration of AERO7 added.

The composition of copolymer was also analyzed by using GC-MS. GC spectra of polystyrene (PS) and polystyrene-*co*-AERO7 (P(St-AERO7)) produced with same reaction conditions are given in Figures 6 and 7, respectively. The band at 1.52 min in GC spectra of P(St-AERO7) was checked by MS (see Fig. 8), which is not found in GC spectra of PS. It turned out that the band at 1.52 min in GC spectra was the proton band of etheroxy chain originated from AERO7. The relative intensity of band at 1.52 min in GC spectrum was calculated in Table II. The result is similar to the results from FTIR. The FTIR and GC-MS data confirmed that the polymer, which was produced by ultrasonic emulsion polymerization of St with AERO7, was the copolymer of St and AERO7.

Intrinsic viscosity  $[\eta]$  of the polymer with lower AERO7 concentration was measured with a viscometer (Table II).  $[\eta]$  may partly reflect the molar mass of polymer. The ps made without AERO7 gives a value of  $[\eta]$  563.75, and the value of  $[\eta]$  of copolymer prepared with  $6.6 \times 10^6$  g/mL AERO7 is 479.70, which was lower than that of homopolymer of St. So, adding surfmer AERO7 may lead to the decrease of molecular weight of copolymer. This observation can be inter-

preted by the low activity of AERO7. Moreover, the  $[\eta]$  analysis of copolymers with higher AERO7 composition was impossible, because these copolymers were partially insoluble in the solvent THF. It may be explained by the incorporation of AERO7 by copolymerization.

The particle morphology was investigated by electron microscopy (Fig. 9). It is clear that small particle size with diameters ranging from 30 to 60 nm can be obtained by using a smaller amount of surfmer in ultrasonically irradiated emulsion polymerization compared to conventional emulsion polymerization. In ultrasonically irradiated emulsion polymerization, the high radical produced rates that correspond to a large number of particles, and the nucleation is very rapid, resulting in small particles. From Figure 9, we can also see that with AERO7 concentration increased, and the adhesion between particle was much more obvious. Because of low activity of double bond in

| [AERO7], $\times 10^3$ g/mL | AERO7 composition in copolymer, <sup>a</sup> % | $[\eta]$       |
|-----------------------------|--|----------------|
| 0                           | 0  | 563.8          |
| 6.6                         | 0.67   | 479.7          |
| 13.2                        | 1.38   | — <sup>b</sup> |
| 19.7                        | 2.97   | —              |

<sup>a</sup> Obtained by GC-MS.

<sup>b</sup> Partially insoluble.

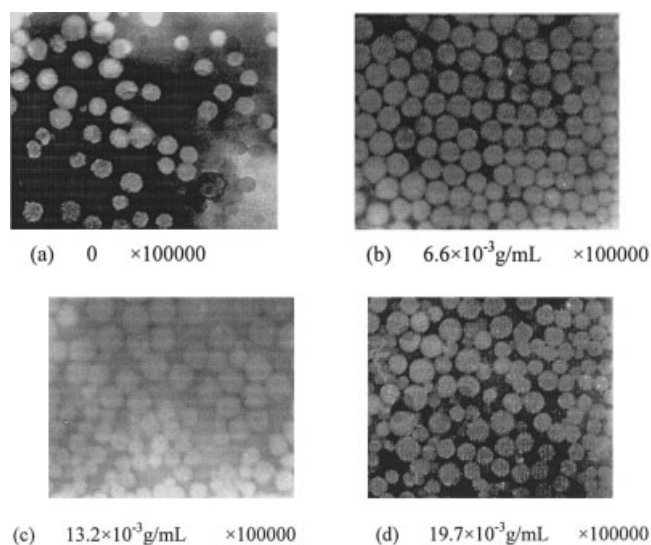


Figure 9 TEM of latices polymerized by ultrasonically irradiated emulsion polymerization at various AERO7 concentrations.



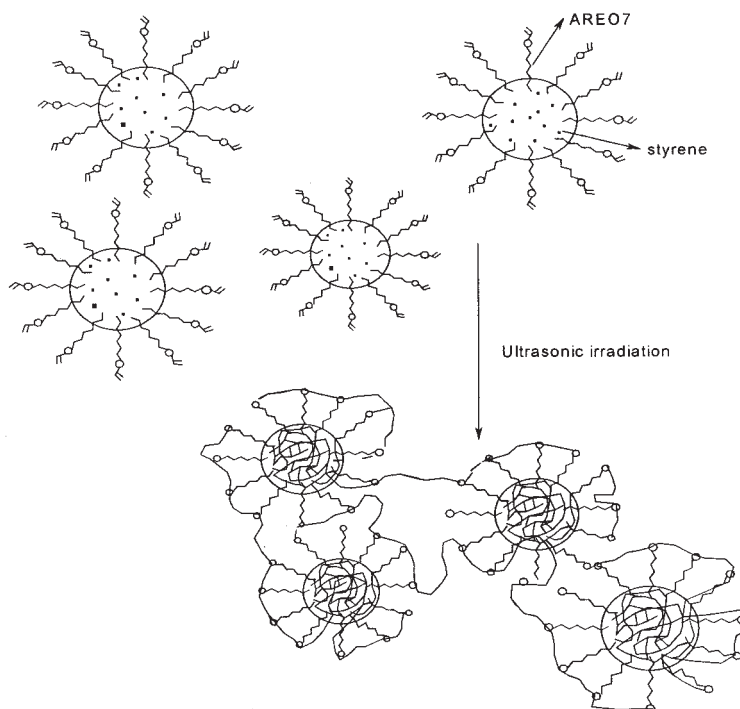


Figure 10 Structure model of ultrasonically emulsion polymerization of styrene with AREO7 (h-type surfmer).

AREO7, homopolymerization of AREO7 is unfavorable; thus, hydrosoluble or surface-active homopolymer should be little. Moreover, owing to the low concentration of St in the water phase, it is very unlikely that copolymerization occurs in the aqueous phase. Copolymerization most probably occurs at particle and water interface where the concentration of AREO7 is higher. It is likely that polar domains of polymerized surfmer molecules are formed in aqueous medium and its hydrophobic tails are adjacent to the PS domains. Finally, the small PS domains and surfactant polymer chains formed the network structure, as shown in Figure 10. This also resulted in insolubility of copolymers in THF.

DSC analysis of the PS homopolymer prepared by ultrasonic emulsion polymerization showed the glass transition temperature ( $T_g$ ) of 102.40°C in Table III. Copolymers made by employing polymerizable emulsifier AREO7 exhibited dramatically lower  $T_g$ 's. It

should have been expected that  $T_g$  decreases with incorporation of AREO7 with etheroxy group. However, the decrease of  $T_g$  is too great for the little AREO7 composition in copolymer. There must be other reasons for the observation. Possibly, the lower molar masses of the copolymer may result in the decrease of  $T_g$ . As listed in Table II, the value of  $[\eta]$  of copolymer was much lower than that of homopolymer of St.

All ultrasonically irradiated emulsion polymerization systems were stable. There was no precipitate even after 6 months under ambient conditions. Exposure to stress by freezing and thawing resulted in complete precipitation of the latices prepared without AREO7 after one freeze–thaw cycle. However, latices made with AREO7 concentration higher than  $6.6 \times 10^{-3}$  g/mL could be redispersed after thawing many times, thus demonstrating greatly improved stability (Table III). This can be explained by the chemical incorporation of AREO7 into the latex particles during the course of the polymerization and formation of the latex networks, which prevented the migration and accumulation of the emulsifier.

TABLE III  
 $T_g$  and Freeze–Thaw Stability of P(S-AREO7) Copolymer at Various AREO7 Compositions in Copolymers

| AREO7 relative composition (%) | $T_g$ (°C) | Times of freeze–thaw cycle |
|--------------------------------|------------|----------------------------|
| 0                              | 102.40     | 1                          |
| 0.67                           | 86.02      | 1                          |
| 1.38                           | 67.18      | 3                          |
| 2.97                           | 38.24      | 5                          |
| —                              | 20.52      | 5                          |

## CONCLUSION

The ultrasonically irradiated emulsion polymerization of St in the presence of polymerizable surfactant AREO7 was studied. Stable nanoparticles having a surface-active group could be prepared. It turned out that the added AREO7 improved the emulsion solid

content because of the excellent surface activity. The h-type molecular structure of AREO7 resulted in a special network structure consisting of PS domains and interpenetration surfactant polymer chains. With AREO7 concentration increased, the adhesion between particles was much more obvious.  $T_g$  of copolymers decreased greatly with incorporation of AREO7 with etheroxy group and the decrease of molecular weight of copolymers. The stability of copolymer emulsion hesitating freezing and thawing was improved dramatically due to the chemical incorporation of AREO7 into the latex particles.

The authors are grateful to the National Natural Science Foundation of China (50303013) for financial support of this work.

## References

1. Smith, P. F.; Price, G. J. *J Polym Int.* 1991, 24, 159.
2. Kruss, P.; Patroboy, T. J. *J Phys Chem* 1985, 89, 3379.
3. Makino, K.; Mossoba M. M.; Rlesz P. *J Phys Chem* 1983, 87, 1369.
4. Chen, K.; Shen, Y.; Li, H.; Xu, X. *J Macromol Sci, Chem A* 1986, 23, 1415.
5. Chou, H. C.; Stoffer, J. O. *J Appl Polym Sci* 1999, 72, 797.
6. Stoffer, J. O.; Sittton, O.; Morales, C.; Kao, H. L. *Polym Mater Sci Eng* 1992, 66, 120.
7. Stoffer, J. O.; Sittton, O. C.; Kim, Y. *Polym Mater Sci Eng* 1992, 67, 242.
8. Chou, H. C.; Stoffer, J. O. *Polym J Appl Polym Sci* 1999, 72, 797.
9. Biggs, S.; Grieser, F. *Macromolecules.* 1995, 28, 4877–4882.
10. Ooi, S. K.; Biggs, S. *Ultrason Sonochem* 2000, 7, 125.
11. Melanic, Bradley; Franz, Grieser. *J Colloid Interface Sci.* 2002, 251, 78.
12. Unezúe, M. J.; Schoonbrood, H. A. S.; Asua, J. M.; Montoya Goñi A.; Sherrington, D. C.; Stähler, K.; Goebel, K. H.; Tauer, K.; Siöber, M.; Holmberg, K. *J Appl Polym Sci.* 1997, 66, 1803.
13. Schoonbrood, H. A. S.; Unezúe, M. J.; Beck, O. J.; Asua, J. M.; Montoya, Goñi A.; Sherrington, O. C., *Macromolecules.* 1997, 30, 6024.
14. Michael, Dreja; Wim, Pyckhout-Hintzen; Bernd, Tieke. *Macromolecules.* 1998, 31, 272.
15. Urquiola, M. B.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S., *J Polym Sci Part A; Polym Chem.* 1992, 30, 2631.
16. Schoonbrood, H. A. S.; Unezúe, M. J.; Amalvy, J. I.; Asua, J. M. *J Polym Sci, Part A; Polym Chem* 1997, 35, 2561.
17. Cochin, D.; *Macromolecules* 1994, 27, 77.
18. Ya, Cao; Huilin Li. *Polym J* 1999, 31(11), 920.