

Miniemulsion Polymerization of Styrene. I. Preparation by Redox Initiator and New Agitation Mixer

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SYNOPSIS

Miniemulsion polymerization is usually conducted by a two-stage process, miniemulsion and polymerization, where the reactants are first processed using a high shearing machine, then transferred to a reactor to polymerize with magnetic stirring. However, the particles size distributions obtained usually are broad and skewed to small sizes owing to micelle and homogeneous nucleation in the aqueous solution. In this study, a saw-toothed blade mixer was successfully used for miniemulsion polymerization with a rotating rate over 500 rpm. The addition sequence of the components also affected the miniemulsion process in this system. The best result was obtained when the surfactant and cetyl alcohol were first dissolved in water and then the styrene was mixed in. Furthermore, a fast dissociated redox initiator system (cumene hydroperoxide/Fe²⁺/ethylenediaminetetraacetic acid-disodium salt/sodium formaldehyde sulfoxylate) was used to prepare miniemulsion polymer and monodisperse polystyrene. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A miniemulsion, by mixed emulsifiers¹⁻⁵ (ionic surfactant and long chain alkane or alcohol, such as hexadecane and cetyl alcohol) in a shearing system, is defined as a relatively stable submicron dispersion of oil droplets in water. This process can be applied to artificial polymer latices with excellent stability, such as epoxy, polyester, and polyurethane,⁶ which cannot be obtained by traditional emulsion processes. This process also can be applied to synthetic polymer latexes. However, these small size oil droplets in miniemulsion polymerization become the principal locus of particle nucleation in contrast to conventional emulsion polymerization. Since Ugelstad, El-Aasser, and Vanderhoff⁷ first reported miniemulsion polymerization in the early 1970s, many investigators⁸ have studied this subject and have used many different methods to prepare miniemulsions. Ugelstad et al.⁸ studied batch miniemulsion copolymerizations of a styrene, *n*-butyl acrylate, and methacrylic acid monomer mixture. They varied the homogenization pressure to obtain different initial monomer droplet sizes. Rodriguez¹⁰

varied cosurfactant concentrations or the duration of sonification to get different initial monomer droplet sizes. Other investigators used an Omni mixer¹² or Microfluidizer⁹ as the controlling factors to study miniemulsion. In general, the mixer types, cosurfactants, and their concentration in miniemulsion were the main factors controlling the size of oil droplets in those reports. However, the use of high shearing mixers could destroy the stability of polymer particles in the course of polymerization. Thus, all the miniemulsion polymerization processes in those reports were divided into two stage mixing, including the miniemulsion and polymerization process. The miniemulsion process first used a high shearing mixer, then transferred to a reactor to polymerize with magnetic stirring. During the polymerization process, the nucleation period was usually long. Numbers of micelles could be formed when the concentration of surfactant was too high in miniemulsion polymerization. Consequently, some of the primary particles could be derived from the micelles nucleation. Thus, although the main locus of particle nucleation was in monomer droplets rather than micelles, micelles and homogeneous nucleation could still occur in the miniemulsion polymerization. The latexes obtained should contain a broad size distribution in some polymerizations. Therefore, the extent of homogeneous and micelles

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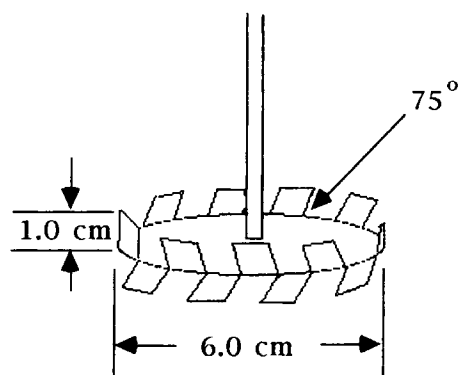


Figure 1 The shape of saw-toothed blades mixer.

nucleation should decrease, and the particle size distribution might become narrower in miniemulsion polymerization.

To simplify the two-stage miniemulsion polymerization to one stage, the mixer used should have enough mechanical mixing to obtain submicron monomer droplets but not to destroy the stability of the latex particles in polymerization. Rapidly dissociating hydrophobic initiators were used to shorten the nucleation period time and enhance the monomer droplets nucleation. Therefore, a new mixer and the redox initiator system [cumene hydroperoxide/ferrous/ethylenediaminetetraacetic acid/sodium formaldehyde sulfoxylate (CHP-Fe²⁺-EDTA-SFS)] were adapted to prepare miniemulsion polymerization of styrene in this study.

EXPERIMENT

Materials

The styrene monomers used for the study were commercially available. Styrene was washed several times first with 5% by weight aqueous solution of sodium hydroxide and afterward with distilled and deionized water until the wash waters were neutral. Sodium formaldehyde sulfoxylate (SFS, Katayama

Table II Calculated Number of Droplets and Distribution of Emulsifiers^a

Average Diameter of Styrene Emulsion Droplets (μm)	Number of Droplets per cm ³ H ₂ O × 10 ⁻¹⁰	Number of Emulsifier Molecules per cm ³ H ₂ O		
		Droplets × 10 ⁻¹⁸	Aqueous Phase × 10 ⁻¹⁸	Micelles × 10 ⁻¹⁷
6.0	0.359	0.813	5.21	2.80
5.0	0.621	0.975	5.05	1.14
4.8	0.702	1.02	5.00	0.68
4.5	0.852	1.08	4.94	0.00
4.0	1.210	1.22	4.80	0.00
1.0	77.60	4.88	1.14	0.00
0.8	152.0	6.097	0.00	0.00

^a Assumptions: (1) All droplets' surface filled with sodium lauryl sulfate (SLS). (2) One SLS molecular could fill areas about 50 Å² on the surface of droplets. (3) The critical micelle concentration of SLS is 8.2 × 10⁻³ M. (4) The monomers, which are solubled in the water phase, were neglected.

Chemical), tetrahydrofuran, cumene hydroperoxide (CHP, Merck Co.), ethylenediaminetetraacetic acid-disodium salt (EDTA, Ishisu Pharm. Co., LTD), ferrous sulfate, and cetyl alcohol (CA, Ishisu Pharm. Co., LTD) were used without further purification. Sodium lauryl sulfate (Ishisu Pharm. Co., LTD) was recrystallized twice in methanol before use. Reagent-grade water was obtained using a Waters Millipore purifying system.

Polymerization

The miniemulsion polymerization of styrene monomers was carried out in a 1-L, five-neck Pyrex kettle equipped with a stirrer, condenser, nitrogen inlet, and thermistor. Three methods were used to prepare styrene miniemulsion with cetyl alcohol.

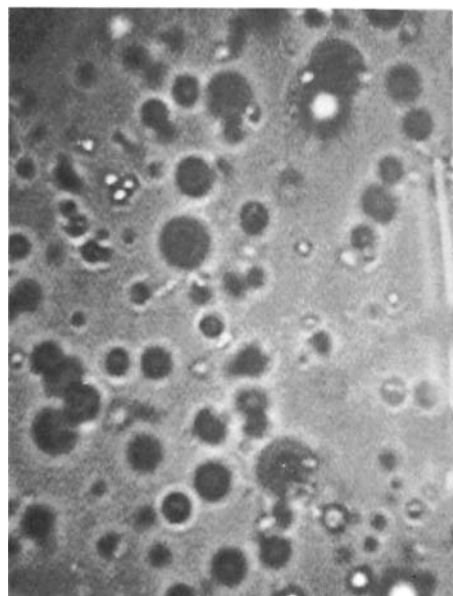
Method A: Sodium lauryl sulfate, cetyl alcohol, and water were mixed by a saw-toothed blade

Table I The General Recipe of Miniemulsion Polymerization

Distilled water	300 g
Styrene monomer	100 g
Sodium lauryl sulfate	0.8652 g (10 mM)
Cetyl alcohol	2.1825 g (30 mM)
FeSO ₄ · 7H ₂ O	0.01924 g (2.3 × 10 ⁻³ M)
Ethylenediaminetetraacetic acid-Disodium salt (EDTA · 2Na)	0.1924 g (1.72 × 10 ⁻³ M)
Cumene hydroperoxide (CHP)	0.2420 g (1.59 × 10 ⁻³ mol)
Sodium formaldehyde sulfoxylate (SFS)	0.4098 g (8.89 × 10 ⁻³ M)

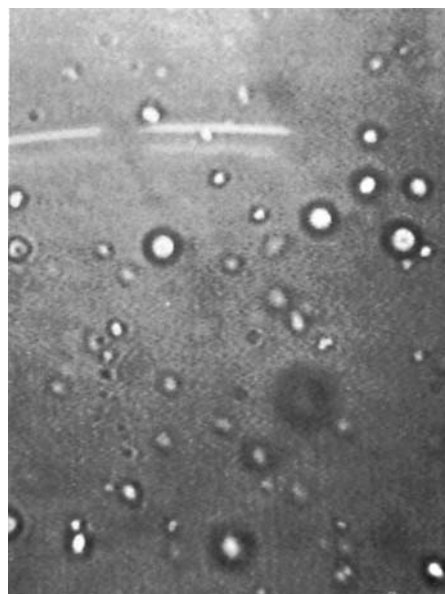
mixer (schematic model in Fig. 1) with a nitrogen purge at 70°C for 1 h. Then the styrene and CHP mixture was mixed with the above aqueous solution for 0.5 h to obtain the miniemulsion.

Method B: Sodium lauryl sulfate was first dissolved in water, with mixing conditions similar to Method A. Cetyl alcohol was added after styrene and the CHP mixture was mixed within the above aqueous solution.



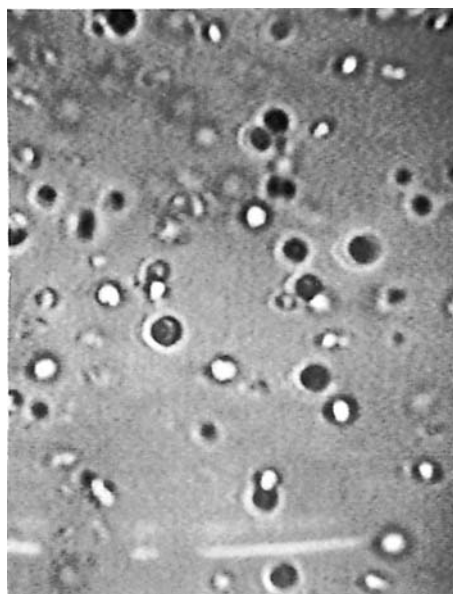
1.0 μ

(A)



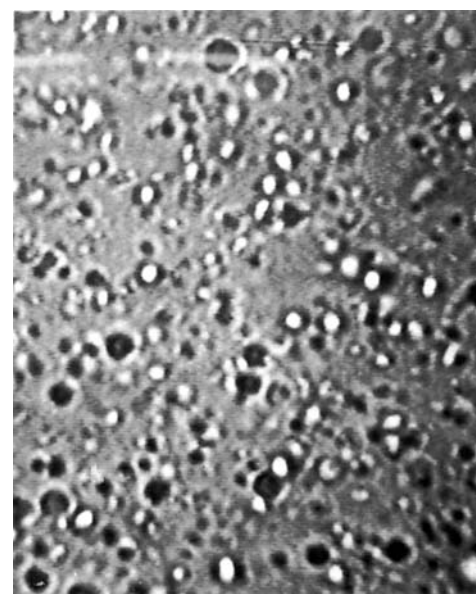
1.0 μ

(B)



1.0 μ

(C)



1.0 μ

(D)

Figure 2 Photograph of monomer droplets produced at various agitation rates: (A) 300 rpm; (B) 500 rpm; (C) 800 rpm; (D) 1000 rpm (styrene/H₂O = 110/300 mL; CHP = 2.38×10^{-3} mol; Fe²⁺ = 2.3×10^{-4} M; EDTA · 2 Na = 1.72×10^{-3} M; SLS/CA = 10/30 mM; temperature = 70°C).

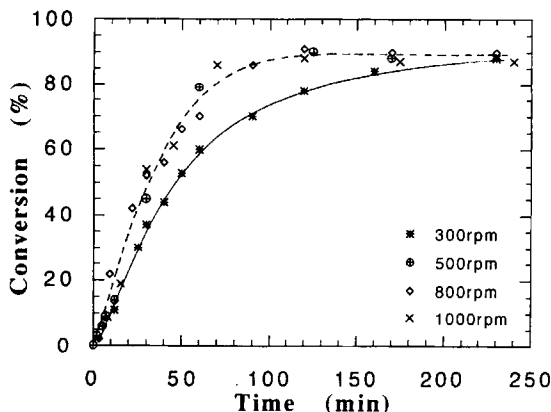


Figure 3 The conversion vs. time curves of various rpm in the course of miniemulsion polymerization.

Method C: Sodium lauryl sulfate was first dissolved in water, and the mixing condition was similar to Method A. Cetyl alcohol, styrene, and CHP were then mixed with the above aqueous solution.

The reaction temperature was controlled at an isothermal set-point using a well thermostatted water bath. The recipes for the polymerization used are shown in Table I. At appropriate intervals, sampling (about 10 mL) was taken for measuring the conversion and diameter of the latex particles. The conversion was determined by the gravimetry method.

Particle Size Measurement

The average diameters of the latex particles were measured by an Otsuka DLS700 laser light scattering spectrophotometer according to the analysis method provided by the instrument supplier. The latex particle morphologies were determined by transmission electron microscopy (TEM) using a Hitachi H-700 TEM.

The zeta-potential value of the latices was measured by using a laser zee meter (Penkem, Inc. Model 510 Laser Meter). Of the latex sample 0.1 mL was diluted to 40 mL by using 0.05M potassium diphosphate.

Molecular Weight Distribution

The molecular weight distribution (MWD) of the polymers was measured using a Waters Associates HPLC/GPC model 510 gel permeation chromatography (GPC). A Waters 410 differential refractometer was used as the detector, and a Waters 745B data module was used for obtaining GPC chromatography number- and weight-average molecular weights, M_n and M_w . Two ultrastyrigel linear packed

columns in series were used. Tetrahydrofuran was used as a carrier solvent. The solvent flow rate was 1.0 mL/min. The calibration curve of the M_n (or peak of molecular weight) vs. elution volume was prepared using standard polystyrenes, and was used for determination of M_n and M_w of the polymers.

RESULTS AND DISCUSSION

One feature of the miniemulsion polymerization is the addition of cosurfactant to stabilize the small monomer droplets. We first estimated the relationship between the monomer droplets sizes and concentration of the surfactant used in our system according to the method reported by J. Ugelstad et al.,⁷ as shown in Table II. The micelles would disappear in the aqueous phase if the size of monomer droplets was less than 4.5 μm , as shown Table II. In other words, it could avoid micelle nucleation in the aqueous solution if the diameter of monomer droplets was much less than 4.5 μm in our miniemulsion polymerization. Various surfactant to cosurfactant ratios were used to prepare miniemulsion, and the most stable small monomer droplets were obtained when it was $\frac{1}{3}$, as indicated by the experiments, which was consistent with Grimm's report. We chose the ratio to be $\frac{1}{3}$ to prepare the miniemulsion polymerization.

The Effect of Mixing Rate

Figure 2 shows photomicroscopic pictures of the sizes of monomer droplets prepared by a saw-toothed blades (STB) mixer. When the agitation rate was higher than 500 rpm, the sizes of the monomer droplets were in the range of miniemulsion (100–400 nm). Obviously, using the STB mixer was ad-

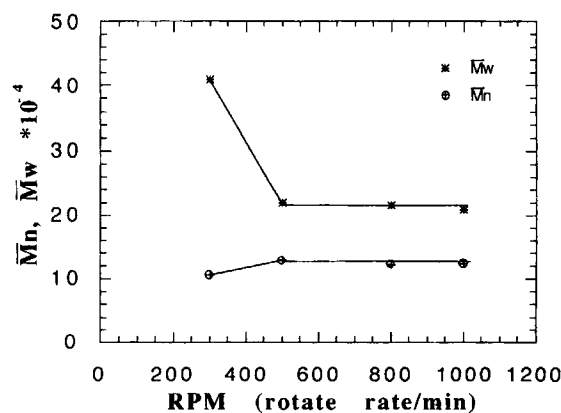
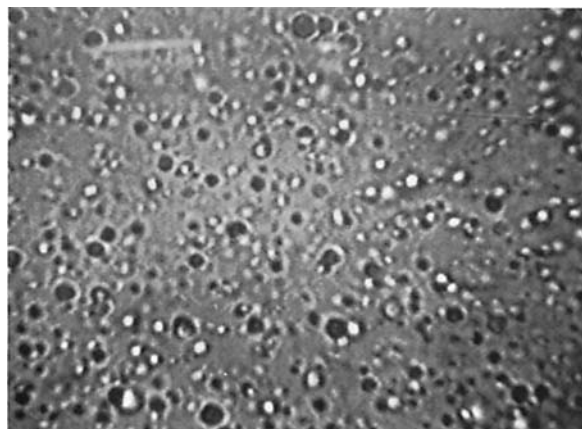
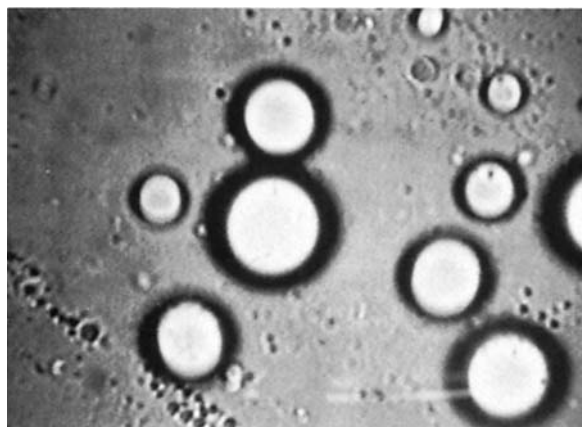


Figure 4 The number (\bar{M}_n) and weight (\bar{M}_w) average molecular weight of polystyrene vs. rpm.

1.0 μ

(A)

5.0 μ

(B)

Figure 5 Photograph of the monomer droplets produced by the (A) miniemulsion process and (B) emulsion (no cetyl alcohol) process, respectively.

equate to disperse the submicron monomer droplets in water. Furthermore, the maximum rotation rate of the STB mixer used in this study was only 1000 rpm, which was much lower than 10000 rpm of a homogenizer, but still maintained stability of the polymer particles in the course of the polymerization process. Thus, the STB mixer was appropriate for miniemulsion polymerization.

Figure 3 shows the conversion vs. time curves for various agitation rates of the STB mixer. Except for the run at 300 rpm, all of the experimental runs showed the reaction behavior to be independent of the agitation rate. The results were different from emulsion polymerization. Increasing agitation rate in a normal emulsion polymerization would decrease the monomer droplets size and thus result in an increase of surface areas. In other words, more sur-

factants would be absorbed on monomer droplets, and the number of micelles in the water phase would decrease relatively. Less micelles meant lower reaction rates. On the contrary, the small sizes of monomer droplets in miniemulsion polymerization should be more conducive to making monomer droplets the main locus of particle nucleation. Thus, the reaction rate at 300 rpm should be lower than the rates at 500, 800, or 1000 rpm.

On the other hand, the redox initiator system used in this study contained the hydrophobic oxidant (CHP) in monomer droplets and hydrophilic reducing agent (Fe^{2+} -EDTA-SFS) in the water phase. They would induce a redox reaction at the interface between the monomer droplets and water phase. The rate for the interfacial redox reaction was determined by the surface areas and the diffusion resistance in both phases. The diffusion step should be the rate-determining step for such a redox reaction if the aqueous phase was not effectively agitated. Vigorous mixing could effectively decrease the thickness of the stagnant layer and thus the diffusion resistance could be neglected. On the other hand, the size of oil droplets depended on the mixing effect. Increasing the mixing rpm could decrease the size of oil droplets and increase the probability of collision of monomer droplets. The aforementioned opposite effects should be equal when the rpm of mixing was increasing. However, when the agitation rate was above 500 rpm in our system, it seemed that the diffusion resistance was negligible according to the results in Figure 2. In contrast to agitation above 500 rpm, the 300 rpm agitation rate does not seem to make the monomer droplets attain the minimum sizes. The large diameters of the monomer droplets not only decreased the reaction rate but also prolonged the radicals life in droplets. Thus, the molecular weight and molecular weight distribution

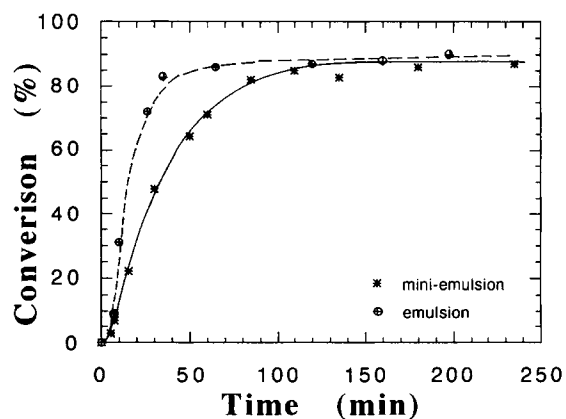
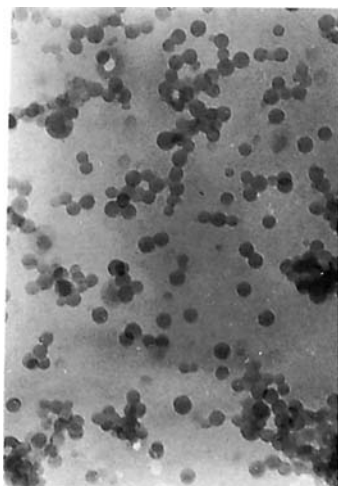
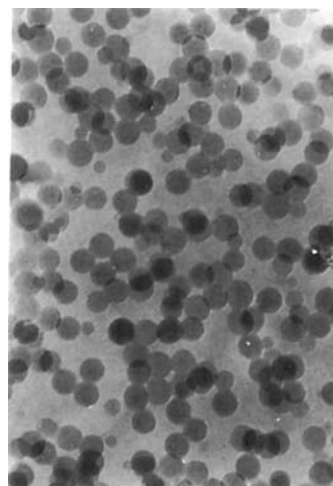


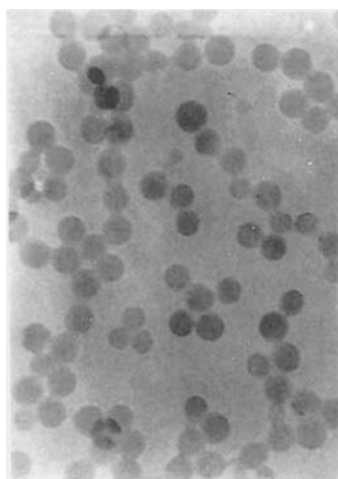
Figure 6 The conversion vs. time curves for mini-emulsion and emulsion (no cetyl alcohol) polymerization.



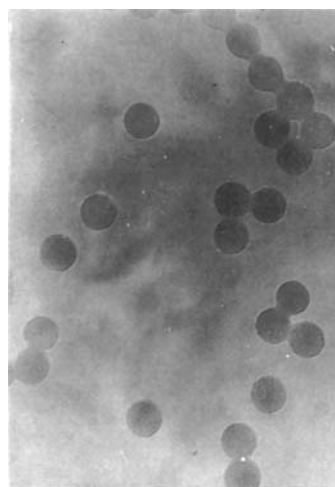
200nm (A)



200nm (B)



200nm (C)



200nm (D)

Figure 7 Transmission electron microscopy picture of polystyrene particles obtained by emulsion (no cetyl alcohol) polymerization at (A) 5% conversion; (B) final particles; and miniemulsion polymerization at (C) 5% conversion; (D) final particles, respectively.

should skew to high molecular weight. As shown in Figure 4, the molecular weight is higher and its polydispersity index (PDI) is broader at 300 rpm than at 500, 800, or 1000 rpm.

The Effect of Cetyl Alcohol Cosurfactant

The cosurfactant was another important factor in the miniemulsion process. One finds that when there was no cetyl alcohol to assist stabilizing the mono-

mer droplets, the monomer droplets could not reach the size range of a miniemulsion even in the presence of vigorous mechanical agitation, as shown in Figure 5. Thus, the behavior of polymerization systems with no cetyl alcohol was similar to emulsion polymerization. Consequently, the addition of the cetyl alcohol cosurfactant effectively reduces the size range of monomer droplets and changes the nucleation mechanism from micelle to monomer droplets. However, the number of monomer droplets in the

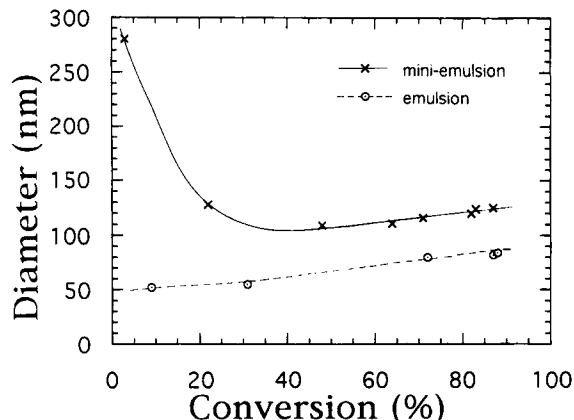


Figure 8 The diameter of particle vs. conversion for miniemulsion and emulsion (no cetyl alcohol) polymerization.

miniemulsion was two orders of magnitude (about $\frac{1}{100}$) smaller than that for monomer swollen micelles of emulsion polymerization. There is no doubt that the reaction rate of miniemulsion polymerization is lower than emulsion polymerization, as shown in Figure 6. Figure 7 shows electron microscopic pictures of the polymer particles from both emulsion and miniemulsion polymerization at 5% conversion and the final latex, respectively. One finds from these pictures that the diameters of miniemulsion polymerization at 5% conversion and final particles were obviously larger than the emulsion polymerization. This was due to the primary particles on miniemulsion polymerization being formed from monomer droplets with diameters larger than the micelles of emulsion polymerization.

Figures 8–10 show the growth, sizes, and size distribution of the polymer particles for miniemulsion polymerization and emulsion polymerization. There

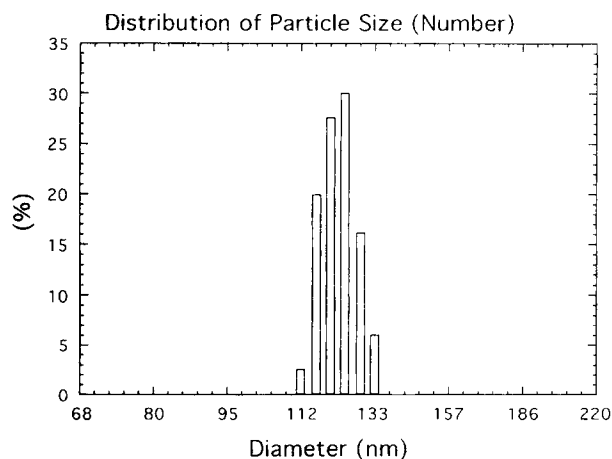


Figure 9 The particle size distribution of miniemulsion polymerization.

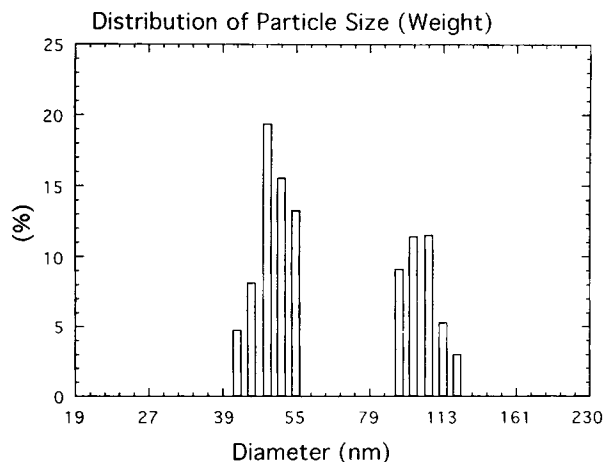


Figure 10 The particle size distribution of emulsion (no cetyl alcohol) polymerization.

are larger particle sizes, narrower particle size distributions, and lower growth rate of polymer particles in the miniemulsion polymerization. This is due to the small monomer droplets in miniemulsion polymerization producing large interfacial areas to absorb mass surfactants. The residual free surfactants were not enough to form micelles in the aqueous phase. In addition, the polymerization was initiated by a high dissociation rate of redox initiator (CHP- Fe^{2+} -EDTA-SFS), which could shorten the induction period time. Finally, the hydrophobic radicals could initiate polymerization directly with the monomer droplets, which would decrease homogeneous nucleation in the aqueous phase. Therefore, no small-size polymer particles were found and

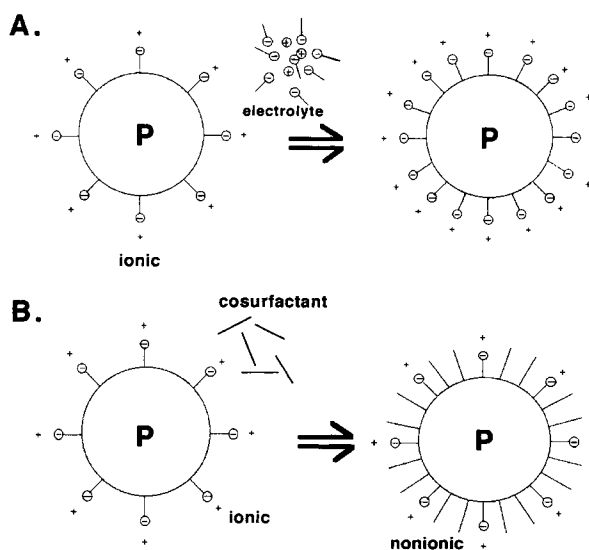


Figure 11 Schematic representation of surface charge on the monomer droplets of (A) emulsion and (B) mini-emulsion.

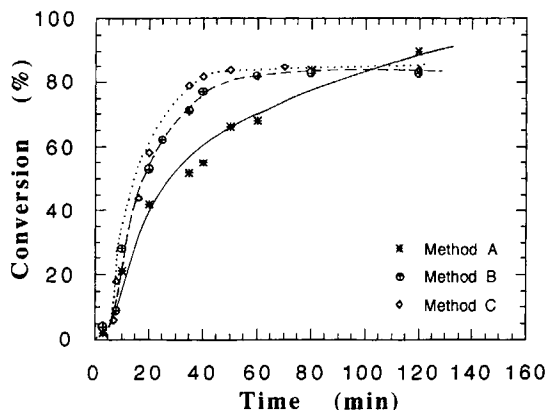


Figure 12 Effect of the addition sequence of surfactant, cosurfactant, and monomer in the course of miniemulsion polymerization.

monodisperse particle sizes were obtained in our study, as shown in Figure 9. Chamberlain et al.¹⁷ and Hansen and Ugelstad¹⁸ also obtained the same results.

Stability of Miniemulsion

The miniemulsion was usually more stable than that emulsion reported from Delgado et al.^{1,2} However, they only mentioned that the excellent stability of latex originated from a complex structure (like liquid crystal), and did not explain how the surfactant-cosurfactant pair formed a complex structure at the interface. In our opinion, because the surfactant generally stabilizes oil droplets by ionic groups attached on the surface of oil droplets, the repulsive forces formed between oil droplets prevents oil droplets coalescing when the distance of neighbor oil droplets is too close. The repulsive force could also form on the neighboring ionic group of surfactants having a negative effect on the stability of the monomer droplets. So, the diameter of the monomer droplets in emulsion polymerization is much larger than that of micelles. However, the nonionic cosurfactant can effectively decrease this repulsive force if these cosurfactants are arranged between the ionic

groups. Excellent stability of small oil droplets was obtained, as shown in Figure 11. Therefore, the miniemulsion could be prepared by using mixed surfactants.

On the other hands, the zeta-potential values of polystyrene latex obtained from miniemulsion polymerization was -45 smaller than -24 from the emulsion polymerization.

The Sequence of Components Added for Preparation of Miniemulsion

Another question in the miniemulsion process is how to make the cosurfactant arrangement in the middle of the ionic groups? Three methods are investigated in this study. The behavior of polymerization for these three methods is shown in Figure 12. According to this figure, the reaction rate of Method C was the fastest and Method A was the lowest. The reaction behavior of Method C was similar to the emulsion polymerization. This resulted from the fact that the majority of hydrophobic CA in Method C had been dissolved into the styrene monomer and hardly diffused to the surface of monomer droplets to form a complex with SLS. For Method B, the SLS had been arranged at the surface before CA was added to the reaction medium. Thus, part of CA was not well diffused to the surface and expelled the neighboring ionic groups. Therefore, its reaction rate and conversion were lower than for Method C. Thus, both methods are not appropriate for miniemulsion. The best way to prepare miniemulsion is Method A, which was the standard method in our miniemulsion process.

Table III shows the particle size, zeta-potential value, growth of particles, and molecular weight for the three methods. The zeta-potential value (-26) in Method C is just slightly higher than that of emulsion polymerization (-24). The other data also show that the reaction behavior of Method C is similar to that of emulsion polymerization. In summary, Method A is the best way to stabilize small monomer droplets in miniemulsion.

Table III Diameters, Zeta Potential Value (ZP) Weight-Average Molecular Weight (\bar{M}_w), and Polydispersion Index (PDI) of the Different Additional Order for Emulsion Components (Methods A, B, and C) in Miniemulsion Polymerization

	Method A	Method B	Method C
Diameter (nm)	123.2	106.5	89.7
ZP (mV)	-45	-31	-26
\bar{M}_w	2.17×10^5	2.41×10^5	2.28×10^5
PDI	1.86	2.01	1.63

CONCLUSIONS

The STB mixer was successfully used for miniemulsion polymerization if the rotation rate was higher than 500 rpm. This one-stage process simplified miniemulsion polymerization. The redox initiator (CHP-Fe²⁺-EDTA-SFS) produced hydrophobic radicals that not only initiated polymerization in the monomer droplets but also shortened the induction period time and prevented homogeneous nucleation. Therefore, the conversion curves do not contain a zero-order period in miniemulsion polymerization and the particle size distribution is very narrow. The sequence for addition of the components could also affect the miniemulsion process in this system. The best result was obtained when the surfactant and cetyl alcohol were first dissolved in water before the styrene was mixed in.

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