

Miniemulsion Copolymerization of Styrene and Butyl Acrylate Initiated by Redox System at Lower Temperature-Preparation and Polymerization of Miniemulsion

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ABSTRACT: Miniemulsions of styrene and butyl acrylate with sodium dodecyl sulfate (SDS) as the surfactant and hexadecane (HDE) and cetyl alcohol (HDL) as cosurfactants were prepared under high-speed stirring or ultrasonification. Results indicate that the stability of miniemulsions produced with HDE is more stable than that with HDL, when the feeding method, in which the cosurfactant is mixed with monomers, is used. There is an optimal ratio ($\frac{1}{4}$) of the surfactant to the cosurfactant for maximum stabilization of the miniemulsions. The miniemulsions prepared by ultrasonification are much more stable than those by high-speed stirring. Also, a stable miniemulsion can be prepared at lower temperature (45°C) when homogenizing way of ultrasonification is used. The emulsions were of a droplet-size range common to miniemulsions and some of them exhibited long-term stabilities (3 months). When these emulsions were initiated, particle formation occurred predominantly by monomer droplet nucleation. The effects of temperature, ultrasonification time, ratio of monomers, and concentrations of surfactant, cosurfactant, and initiator on the polymerization rate, conversion, and particle size were determined. It was found that the miniemulsion copolymerization of styrene and butyl acrylate with a midial amount of a redox initiator ((NH₄)₂S₂O₈/NaH SO₃) at lower temperature (45°C) can be carried out successfully by using a suitable amount of the surfactant SDS (10 mM) and the cosurfactant HDE (40 mM), when a homogenizing way of ultrasonification is applied. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2029–2039, 1998

INTRODUCTION

Miniemulsions are relatively stable submicron (50–500 nm) dispersions of oil in water prepared by homogenizing a system containing oil, water, surfactant, and, additionally, a “cosurfactant.” Miniemulsions are stable for long periods of time and exhibit unique polymerization kinetic behavior when a monomer is used as the dispersing oil

phase. Since Ugelstad et al. first reported miniemulsion polymerization in the 1970s,¹ many investigators have studied this subject, and a number of studies about it have appeared in the literature.^{2–29} Most of the reported works are basic studies that elucidate the mechanisms involved in the miniemulsion polymerization process. Only several applied studies on high solid content latexes^{2,3} have been done. In the basic studies, much attention has been paid to the functions of the cosurfactant, the means of carrying out the homogenization, and the kinds of initiator.

The cosurfactants used in miniemulsions are usually of a low molecular weight, of low water solubility, and monomer-soluble materials (such as hexa-

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decane and cetyl alcohol) which are added in small amounts (1–5%) to the droplets. Because these cosurfactants cannot diffuse readily through the aqueous phase (due to their high water-insolubility), they retard Ostwald ripening, because removing the monomer from a small monomer droplet will cause an increase in the concentration of the cosurfactant. In addition, for the fatty alcohols such as cetyl alcohol, the enhanced stability of the miniemulsions may also be due to the formation of an interfacial complex of cosurfactant and surfactant. Such complexes would be liquid-like and electrically charged, creating a barrier to droplet coalescence. This mechanism for enhanced stability is considered only to be operative in the case where a long-chain alcohol is used as the cosurfactant, since a long-chain alkane is almost certainly located within the droplets, as opposed to at the droplet/water interface. Therefore, application of the term “cosurfactant” is not accurate in the strictest sense when referring to the long-chain alkenes.⁴ However, the above cosurfactants are volatile organic chemicals. They must be removed from the latex after polymerization. Several years ago, Schork et al.⁵ used a polymer as a cosurfactant in miniemulsion polymerization, because a polymer made from the monomer of which the miniemulsion is to be made will be highly water-insoluble, and most polymers are quite soluble in their own monomers. It has been demonstrated that it is possible to create miniemulsion latexes with a polymer.^{4–7} The polymeric cosurfactant is thought to delay Ostwald ripening sufficiently to allow nucleation of the monomer droplets by water-phase radicals (primary or oligomeric). Once the droplets are nucleated, the polymer produced adds additional diffusional stability. Nevertheless, Reimers and Schork⁷ noted that the monomeric miniemulsions formed are not true miniemulsions in the sense that they are not stable over a period of months. However, Ostwald ripening can be reduced to permit the polymerization to be carried out. The latexes produced from polymer-stabilized emulsions have all the characteristics of miniemulsion latexes and derive from droplet nucleation. Therefore, they feel justified in referring to the products of such polymerizations as miniemulsion latexes, although they will refrain from referring to polymer-stabilized monomeric emulsions as miniemulsions. So, they refer the polymer used to stabilize the droplet against diffusion as the hydrophobe rather than the cosurfactant, just like hexadecane, since it is not a good

surfactant in the currently used sense. A polymer has been shown to perform as well as hexadecane in stabilizing the droplets for the short periods necessary to ensure nucleation. It has the added advantages of being totally innocuous in the final product, very soluble in the monomer, and very water-insoluble. This kind of work herein indicates that miniemulsion polymerization may be an alternative to seeded polymerization as a way of maintaining robust control of the particle number.

Very recently, Schork et al.⁸ also reported the preparation and polymerization of methyl methacrylate miniemulsions with dodecyl mercaptan (DDM) as the cosurfactant (or hydrophobe). Results showed that the emulsions were of a droplet size range common to miniemulsions and exhibited long-term stability (greater than 3 months). The DDM retarded Ostwald ripening and allowed the production of a stable miniemulsion. When these emulsions were initiated, particle formation occurred predominantly by monomer droplet nucleation. The above results may provide the chemist and engineer with the flexibility to exploit the advantages of miniemulsion polymerization without the practical problems of removing the cosurfactant after polymerization.

Another important parameter in the preparation and polymerization of miniemulsions is the means of carrying out the homogenization. Hansen and Ugelstad⁹ used a two-stage homogenizer (Manton Gaulin S.A.), Chamberlain et al.¹⁰ used a sonifier, Choi et al.¹¹ used the Microfluidizer (Microfluidics Corp.), Delgado et al.¹² used both the Omni mixer (Ivan Sorvall, Inc.) and a sonifier (Branson Sonic Power Co.), and Rodringez¹³ used a sonifier. 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 processes. The miniemulsion process first used a high-shearing mixer, then transferred to a reactor to polymerize with magnetic stirring or another low-shearing agitator. To simplify the two-stage miniemulsion polymerization to one stage, Wang et al.¹⁴ designed a new agitation mixer for the miniemulsion polymerization of styrene. The mixer used should have enough mechanical mixing to obtain submicron monomer droplets but not to destroy the stability of the latex particles in the polymerization. In their study, a saw-toothed blade mixer was successfully used for mini-

emulsion polymerization with a rotating rate over 500 rpm.

The effects of the kinds of initiators on miniemulsion polymerization are also very important. Water-soluble and oil-soluble initiators have been extensively used. But they led to the results that the particle-formation stage is unusually long. In addition, numerous micelles could be formed when the concentration of the surfactant was too high in the miniemulsion polymerization. Consequently, some of the primary particles could be derived from the micelle nucleation. Thus, although the main locus of particle nucleation was in monomer droplets rather than in micelles, micelles and homogeneous nucleation could still occur in the miniemulsion polymerization. This is just one of the reasons why the latexes obtained contain a broad or multimodal size distribution in some polymerizations. Therefore, if the content of homogeneous and micelle nucleation is decreased, the particle-size distribution might become narrower in miniemulsion polymerization. Wang et al.¹⁴ used a fast dissociated redox initiator system (cumene hydroperoxide/ Fe^{2+} /ethylenediminetetraacetic acid–disodium salt/sodium formaldehyde sulfoxylate) to prepare a miniemulsion polymer and monodisperse polystyrene was obtained. This is because the redox initiator produced hydrophobic radicals that not only initiate polymerization in the monomer droplets but also shortened the induction period of time and prevent homogeneous nucleation. Therefore, the conversion curves do not contain a zero-order period in miniemulsion polymerization and the particle-size distribution is very narrow.

In the past, however, the effect of temperature on the preparation and polymerization of miniemulsions have been paid little attention. In the reported works, the temperatures used were usually 60 or 70°C, and some even reached 80°C.² But the higher temperature might bring some unfavorable effects on the stabilities of miniemulsions and their polymerization, which might lead to the complicated mechanism of miniemulsion polymerization.

This article focuses on the use of a redox initiator [$(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{NaHSO}_3$] in the miniemulsion copolymerization of butyl acrylate and styrene at lower temperature (45°C). The effects of operation variables, such as reaction temperature, concentrations of initiator, emulsifier, and cosurfactant, monomer ratios, and the time of ultrasonification, were studied. Details of the reaction

kinetics and mechanism of nucleation will be the topic of our next article.¹⁵

EXPERIMENTAL

Materials

Styrene (St) and butyl acrylate (BA) monomers were distilled under reduced pressure. Ammonium persulfate was recrystallized and then dried at room temperature under a vacuum. Sodium dodecyl sulfate (SDS), hexadecane, cetyl alcohol, and sodium hydrosulfite were used as received. The water was deionized.

Preparation and Characterization of Miniemulsions

Preparation

Two methods were used in the preparation of the styrene–butyl acrylate miniemulsions: In method A, the SDS and cosurfactant were dispersed in water at 50°C, stirred for 15 min at high speed, and ultrasonified for a certain time at a frequency of 26 ± 3 kHz. The monomer mixture was then added to the preemulsion under agitation. Finally, the above emulsion was stirred for 1 h at high speed or ultrasonified for a certain time.

In method B, only SDS was dissolved first in water at 50°C. The cosurfactant (hexadecane or cetyl alcohol), when used, was dissolved in the monomer mixture (50 : 50 molar ratio) at room temperature. Other processes were the same as in method A.

Centrifugational Stability

Once the miniemulsions were prepared, a certain amount of each emulsion was centrifuged at 20,000 rpm. The amount of the monomer mixture separated from each emulsion after centrifugation was measured and related to the centrifugational stability.

Droplet Size

Analysis of the droplet size was carried out on a Malvern Auto Sizer Loc-Fc963 apparatus.

The Residual Concentration of Surfactant in the Water Phase

The amount of emulsifier remaining in the water phase was determined by titrating the aqueous

Table I Miniemulsion Copolymerization Recipes of St/BA Mixture

| No. | SDS (mM) | HDE (mM) | [I] (%) | [St] (%) | Ultrasonification Time (min) | Temperature (°C) |
|-----|----------|----------|---------|----------|------------------------------|------------------|
| 1 | 10 | 40 | 0.2 | 50 | 0 | 25 |
| 2 | 10 | 40 | 0.4 | 50 | 0 | 25 |
| 3 | 10 | 40 | 0.6 | 50 | 0 | 25 |
| 4 | 10 | 40 | 0.8 | 50 | 0 | 25 |
| 5 | 10 | 40 | 0.5 | 50 | 0 | 45 |
| 6 | 5 | 40 | 0.5 | 50 | 0 | 45 |
| 7 | 15 | 40 | 0.5 | 50 | 0 | 45 |
| 8 | 20 | 40 | 0.5 | 50 | 0 | 45 |
| 9 | 10 | 20 | 0.5 | 50 | 0 | 45 |
| 10 | 10 | 60 | 0.5 | 50 | 0 | 45 |
| 11 | 10 | 40 | 0.5 | 10 | 0 | 45 |
| 12 | 10 | 40 | 0.5 | 30 | 0 | 45 |
| 13 | 10 | 40 | 0.5 | 70 | 0 | 45 |
| 14 | 10 | 40 | 0.5 | 90 | 0 | 45 |
| 15 | 10 | 40 | 0.5 | 50 | 2 | 45 |
| 16 | 10 | 40 | 0.5 | 50 | 4 | 45 |
| 17 | 10 | 40 | 0.5 | 50 | 6 | 45 |

phases, separated by centrifugation of the miniemulsions at 20,000 rpm for 40 min, with hexadecylammonium bromide, using the titration method with chloroform and a mixed indicator (disulfine blue/sulfuric acid).

The Miniemulsion Copolymerization Process and Particle Sizes

All polymerizations were carried out in a batch process using a glass reactor equipped with a stirrer, reflux condenser, sampling device, and inlet systems for nitrogen and the reactants. The copolymerization recipes are given in Table I. The preparation of miniemulsions was described in method B mentioned above. The only difference is that the preparation temperature is 45°C. After this, the aqueous solution of initiator, ammonium persulfate, and sodium hydrosulfite was injected. Also, the polymerization began.

Samples were withdrawn during the reaction, the polymerization was short-stopped with hydroquinone, and the conversion was determined gravimetrically. The particle sizes were measured by a Malvern Auto Sizer Loc-Fc963 apparatus.

RESULTS AND DISCUSSION

Droplet Sizes and the Stabilities of Miniemulsions

As seen in Table II the miniemulsion droplets ranged from 139 to 360 nm, within the typical

range for miniemulsions (50–500 nm). Droplet size decreases with increasing cosurfactant concentration (at constant surfactant concentration) (Fig. 1). A further increase in the amount of the cosurfactant (HDL) results in a slight decrease in the size of the droplet which almost levels off at an HDL/SDS molar ratio of 4, i.e., there is an optimal ratio of surfactant to cosurfactant for maximum stabilization (smallest droplets). This result is consistent with those obtained by Azad and co-workers.¹⁶

Table III shows the residual concentration of the surfactant (SDS) in the water phase. It can be seen that, in all the cases, the residual concentration of the surfactant (SDS) in the water phase are less than the critical micelle concentration (CMC) of SDS (CMC = 8.1 mM). This indicates that there are no micelles in the water phase. Combined with the effect of the SDS concentration on the stability (Table II), the optima of SDS and HDL in preparing the miniemulsions are 10 and 40 mM, respectively.

The feeding method A was compared with method B. For the SDS/HDL system, there is little difference in the droplet size and the stability of the miniemulsions between them, while for the SDS/HDE system, the emulsion prepared by method B is much more stable and its droplet size is smaller. The above results imply that HDL can be used as a cosurfactant to prepare miniemulsions with the above two methods, while for rela-

Table II Droplet Sizes and Stabilities of the Miniemulsions

| | Dd (mM) | Stabilities (days) | HDL (mM) |
|-------------------------|--------------|-----------------------|---------------|
| SDS (mM) | | | |
| 20 | 290 | 30 | 40 |
| 10 | 232 | 60 | |
| 5 | 360 | 12 | |
| Feeding method | | | |
| A | 230 | 60 | [SDS] = 10 mM |
| B | 242 | 60 | [HDL] = 40 mM |
| A | 341 | 30 | [SDS] = 10 mM |
| B | 182 | 90 | [HDE] = 40 mM |
| Means of homogenization | | | |
| High-speed stirring | 342 | 20 | [HDE] = 40 mM |
| Ultrasonification | 230 | 90 | [SDS] = 10 mM |
| Ultrasonification time | | | |
| 0 | 394 | 12 | [SDS] = 10 mM |
| 1 | 194 | 30 | [HDL] = 40 mM |
| 2 | 187 | 60 | |
| 3 | 149 | 90 | |
| 4 | 139 | 54 | |

tively water-insoluble HDE it is more suitable to be mixed with the monomer first, then mixed with a water solution of the surfactant when used to create stable miniemulsions. This is the result of the little difference between HDL and HDE in the mechanism of enhanced stability. It is well known that, in miniemulsions, the presence of a low molecular weight and water-insoluble compound such as cetyl alcohol (HDL) in monomer droplets

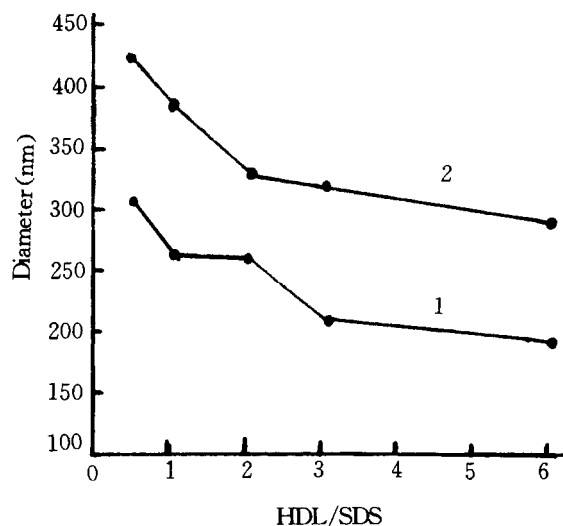


Figure 1 The effect of HDL/SDS ratio on droplet size: (1) [SDS] = 10 mM; (2) [SDS] = 20 mM.

retards the diffusion of the monomer out of the droplets. For the cetyl alcohol (HDL) system, the enhanced stability is also attributed to the formation of “intermolecular complexes” at the oil/water interface. These complexes would be liquid condensed and electrically charged, creating a low interfacial tension and high resistance to droplet coalescence. But for HDE, the mechanism of enhanced stability is just reducing the Ostwald ripening (diffusional degradation). So, the homogeneous distribution of HDE in the monomers will lower the Gibbs free energy of the droplet, thereby decreasing the driving force for diffusion. This kind of function of HDE is larger than that of HDL due to its being more hydrophobic. Therefore, it can be found in Table II that the emulsion with the same components produced by the SDS/HDE system is much more stable than that of SDS/

Table III Residual Concentration (mM) of Surfactant (SDS) in Water Phase

| SDS (mM) | HDL/SDS | | | | |
|-------------|---------|-----|-----|-----|-----|
| | 0.5 | 1 | 2 | 3 | 6 |
| 20 | 7 | 5.8 | 4.2 | 3.9 | 3.8 |
| 10 | 3.3 | 1.4 | 1.0 | 0.4 | 0.2 |
| 5 | 1.2 | 1.1 | 0.7 | 0.3 | 0.3 |

Table IV Stabilities of Emulsions Prepared at Various Temperatures

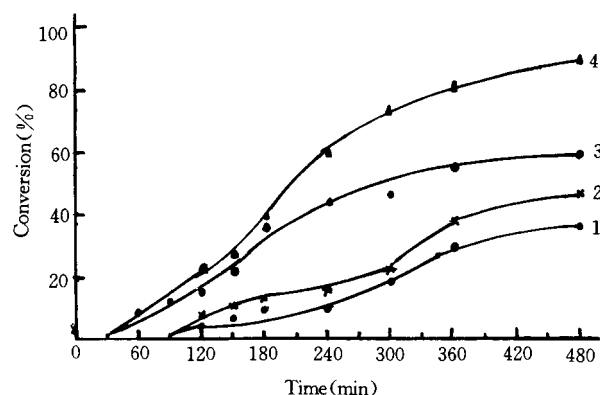
| | Temperature (°C) | | |
|----------------------------------------|------------------|-----|------|
| | 25 | 45 | 65 |
| Height of monomer phase separated (cm) | 10 | 0.7 | 1.20 |

[SDS] = 10 mM; [HDL] = 40 mM.

HDL, and the droplet size of the former is much less than that of the latter, when method B was used.

About the effects of the homogenizing ways on the stability of emulsion, it can be seen that the emulsion produced by ultrasonification was stable upon storage for 3 months, while the emulsion produced by high-speed stirring was stable for only 20 days. The effects of ultrasonification time on the droplet size and the stability of the miniemulsion is also remarkable. It can be seen that the droplet size decreased and stability of the emulsion increased with increasing the time of ultrasonification, but the stability of the miniemulsion decreased after a certain time of ultrasonification (> 3 min). This may be due to the destroying function of overultrasonification on the complex structure of the surfactant and cosurfactant and enhanced the diffusion of the monomers.

In addition, the effects of the emulsifying temperature on the stability of the miniemulsions were also studied (Table IV). It can be seen from Table IV that 45°C is the optical temperature in

**Figure 2** The effect of initiator concentration on copolymerization: (1) 0.2%; (2) 0.4%; (3) 0.6%; (4) 0.8%.**Table V** Effects of Emulsifying and Storage Temperatures on Stabilities of Miniemulsions with SDS/HDE System

| Emulsifying Temperature (°C) | Storage Stabilities (Day) at Various Temperatures (°C) | | | | |
|------------------------------|--------------------------------------------------------|----|----|-----|------|
| | 1 | 20 | 40 | 60 | 80 |
| 0 | 20 | 15 | 2 | 0.5 | 0.2 |
| 20 | 50 | 40 | 6 | 0.8 | 0.2 |
| 40 | > 70 | 60 | 10 | 1 | 0.1 |
| 60 | 60 | 50 | 3 | 0.2 | 0.1 |
| 80 | 15 | 10 | 1 | 0.1 | 0.05 |

preparing miniemulsions of BA and St. At 25°C, HDL (mp 49°C) cannot be dissolved completely, and its role as a cosurfactant decreases remarkably. While at 65°C, the activity of monomers and (co)surfactant increases obviously, which leads to the result that it is easier for monomers to diffuse out of droplets, i.e., the stability is reduced. A similar phenomenon in the SDS/HDE system was also found (Table V). The worse stability will make the miniemulsion polymerization complicated. This is just one of the reasons why we carried out the miniemulsion copolymerization with the redox system under a lower temperature several years ago.¹⁷ Another reason is that only a few studies^{2,3,12,22} have been done on miniemulsion copolymerization. Finally, the copolymer products of St and BA have been extensively used in many fields.

Miniemulsion Copolymerization

Droplet-size measurements (see Table II) show that it is capable of producing stable droplets in the miniemulsion size range under all the experimental conditions, with free surfactant levels in the water phase below the critical micelle concentration (CMC) of the surfactant (SDS). As a result, droplet nucleation may be the dominant mechanism in miniemulsion copolymerization of St and BA. The site of nucleation, which to a large extent is controlled by the presence of the cosurfactant, affects numerous aspects of the system, such as rates of polymerization, particle size and distribution, and the properties of the final product. The conditions for all polymerization experiments are described in Table I. The variables in these experiments are the temperature, concen-

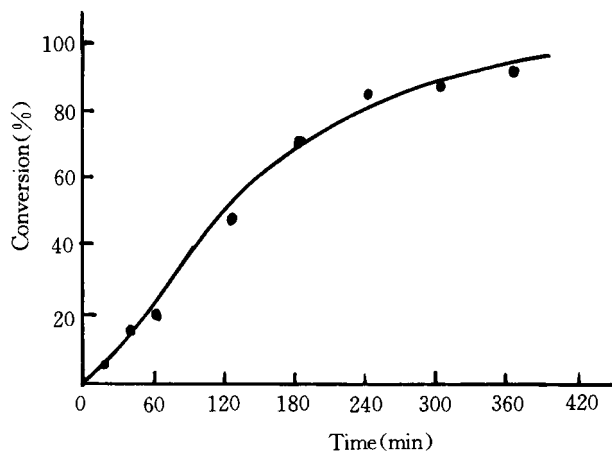


Figure 3 Conversion–time curve for the miniemulsion copolymerization at 45°C: ($[I] = 0.5\%$).

trations of initiator, emulsifier, and cosurfactant, monomer ratios, and the time of ultrasonification.

Initiator Amount and Temperature

The results of polymerization at 25°C with various amounts of the initiator $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{NaHSO}_3$ are shown in Figure 2. It is observed that the induction period is very long, and the polymerization is slow. The final conversion of the monomer after 8 h is not very high, even though the amount of initiator is much higher (0.8%). In fact, the stability results given previously have also indicated that 25°C is not suitable in preparing the miniemulsion. So, we tried to carry out the polymerization at a little higher temperature (45°C) with a midial amount of initiator (0.5%) (Fig. 3). Obviously, the induction period was decreased, and the polymerization was quicker. The monomer conversion reached nearly 90% after 4 h. But the conversion leveled off after 4 h, i.e., the conversion was not high enough. So, a little more initiator was needed to increase the conversion to a much higher position at this condition.

Surfactant Concentration

The effects of surfactant concentration on the polymerization and particle size are shown in Figures 4 and 5, respectively. It can be seen that as the concentration of the surfactant increased both the polymerization rate and conversion increase, while the particle size decreased. This is in agreement with the result of Delgado et al.¹² Also, this type of behavior is actually similar to conventional emulsion polymerization when the concen-

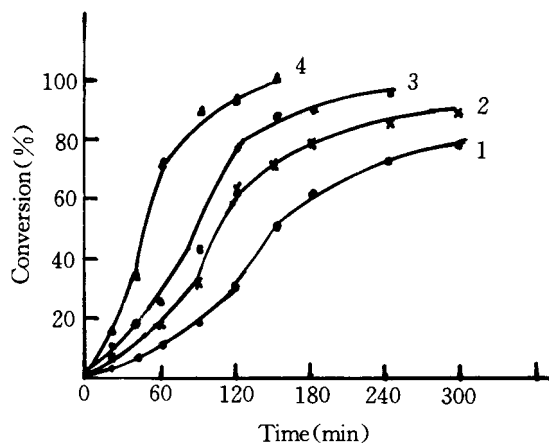


Figure 4 The effect of surfactant concentration on copolymerization: (1) 5 mM; (2) 10 mM; (3) 15 mM; (4) 20 mM.

tration of the surfactant is increased. However, the particle-size distribution increases with increasing surfactant concentration. This is because the residual concentration of the surfactant in the water phase increases at a higher surfactant concentration (Table III) and presumably led to another mechanism of nucleation (homogeneous nucleation).

Cosurfactant Concentration

Figure 6 presents conversion–time curves for the kinetic runs of three miniemulsions with various cosurfactant concentrations. Comparison between

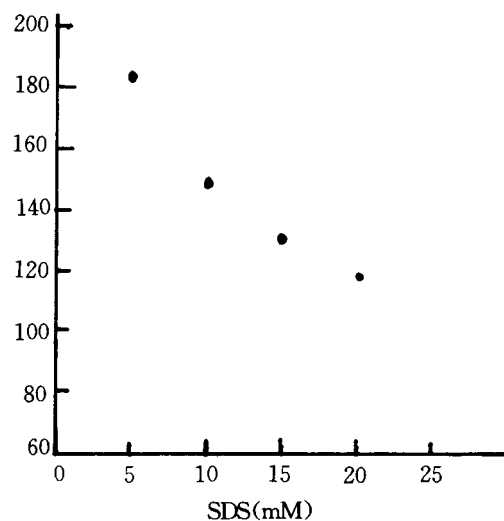


Figure 5 The particle size of miniemulsion latex as a function of surfactant concentration.

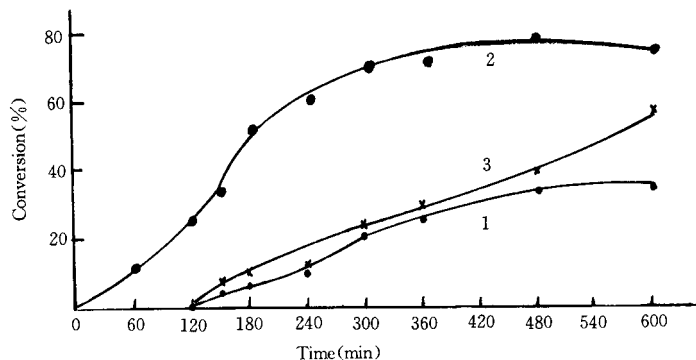


Figure 6 The effect of cosurfactant (HDE) concentration on copolymerization ($[SDS] = 10 \text{ mM}$): (1) 20 mM; (2) 40 mM; (3) 60 mM.

the curves for Nos. 1 and 2 shows that No. 2, prepared with 40 mM HDE, has a faster polymerization rate and a much higher conversion than has No. 1, prepared with 20 mM HDE. This is due to the greater number of particles nucleated in run No. 2 as a result of the smaller-size droplets initially present in No. 2 as compared to No. 1 (Table VI). On the other hand, when curves Nos. 3 and 2 are compared, the polymerization rate and conversion of curve No. 3 is smaller than No. 2. This is not a droplet-size effect again.

The data in Table VI show that, when the concentration of HDE increases from 40 to 60 mM, the droplet size and number of the miniemulsions are very close to each other. But the concentration of HDE in the droplet increases sharply, which increases the surface resistivity to the rate of entry of the free radical which is formed in the aqueous phase, i.e., it reduces the polymerization rate. In addition, the much higher amount of HDE may further reduce the miniemulsion polymerization rate because the cosurfactant affects the concentration of the monomer in the polymer particles

Table VI Droplet Sizes and Number of Miniemulsions with Various Cosurfactant Contents

| | HDE/SDS | | |
|----------------------------------|---------|-------|-------|
| | 2 | 4 | 6 |
| Droplet size (nm) | 176.1 | 145.4 | 141.6 |
| Droplet no. ($\times 10^{19}$) | 6.0 | 9.8 | 10.2 |

$[SDS] = 10 \text{ mM}$.

in such a way that an increase of the HDE concentration in the monomer droplets reduces the concentration of the monomers in the polymer.¹⁸ Finally, the particle size decreases (Fig. 7). It also can be seen from Figure 8 that the polymerization rate of conventional emulsion (without HDE) is much higher than that of the miniemulsion.

Ratio of Styrene/Butyl Acrylate

As shown in Figures 9 and 10, the copolymerization rate of St-BA becomes slower, the conversion lower, and the particle size larger when the ratio of St/BA is increased from 1/9 to 9/1. The above results indicate that the effect of the water solu-

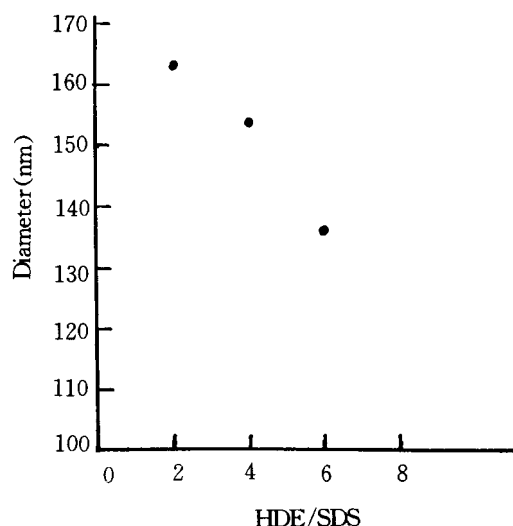


Figure 7 The effect of cosurfactant concentration on particle size of latex ($[SDS] = 10 \text{ mM}$).

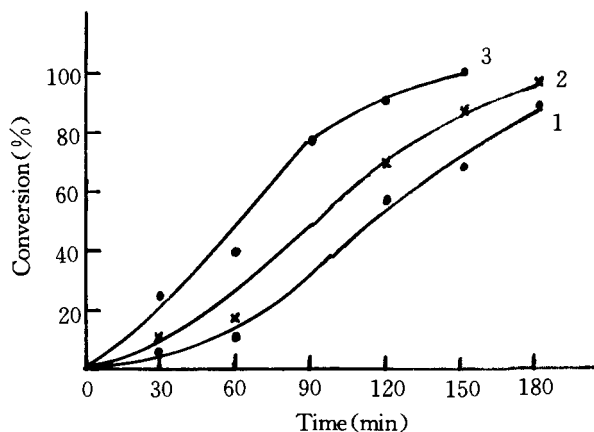


Figure 8 The copolymerization as a function of emulsifier concentration in conventional emulsion polymerization: (1) 5 mM; (2) 10 mM; (3) 15 mM.

bility of monomers on the polymerization rate is obvious. One of the reasons is probably that the lower water solubility of St makes the desorption rate of the radicals larger.

Ultrasonification Time

The copolymerization rate of St/BA miniemulsions become faster, the conversion higher, and the particle size smaller when the time of ultrasonification is increased from 2 to 6 min (Figs. 11 and 12). These phenomena result from the smaller droplet size (Table II) when the time of ultrasonification is increased. In addition, the fi-

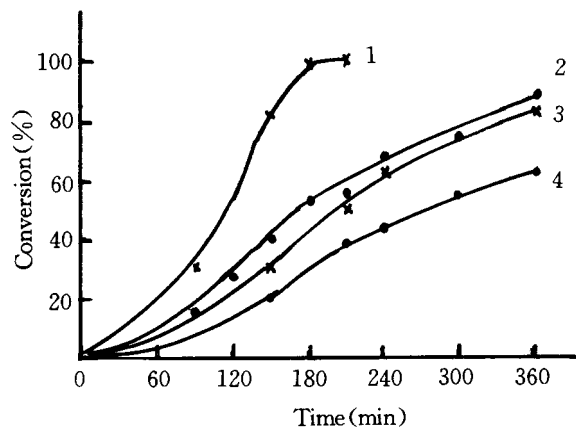


Figure 9 The effect of monomer ratio on copolymerization: (1) St—10%; (2) St—30%; (3) St—70%; (4) St—90%.

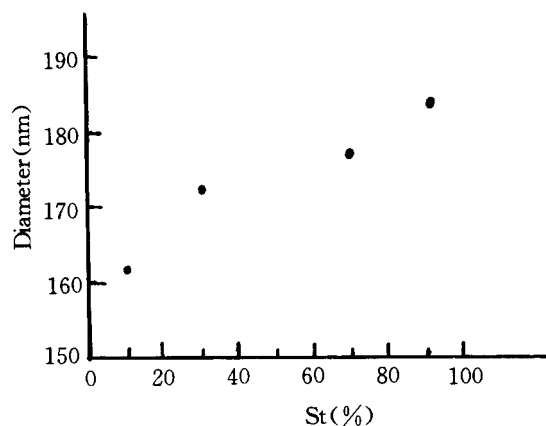


Figure 10 The effect of monomer ratio on particle size of latex.

nal conversions are almost unchanged when the time of ultrasonification is in the range of 4–6 min, and their conversions reached 100% after 6 h. The above results also demonstrate that ultrasonification is much more effective for the polymerization of miniemulsions than is high-speed stirring.

CONCLUSIONS

In the foregoing, both the preparation and polymerization of St and BA miniemulsions were carried out. It was found that droplet size decreased with an increasing cosurfactant amount at a constant surfactant concentration. A further increase

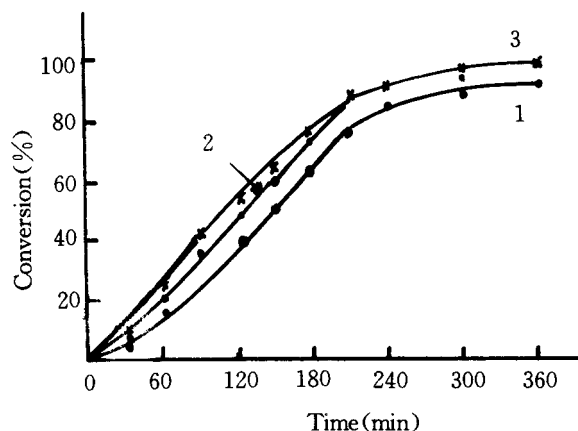


Figure 11 The effect of ultrasonification time on copolymerization: (1) 2 min; (2) 4 min; (3) 6 min.

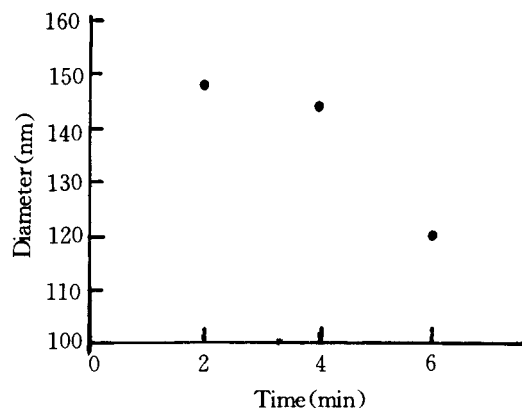


Figure 12 The effect of ultrasonification time on particle size of latex.

in the amount of the cosurfactant resulted in a slight decrease in the size of the droplet which almost leveled off at an HDL/SDS molar ratio of 4, i.e., there was an optimal ratio of surfactant to cosurfactant for maximum stabilization.

The stability of the miniemulsion produced with HDE was more stable than that with HDL, when the feeding method, where cosurfactants were mixed with monomers first, then mixed with solution of surfactant, was used. In the comparison of homogenizing methods, the miniemulsion produced by ultrasonification was much more stable than that by high-speed stirring. The droplet size decreased and the stability of the miniemulsion increased with increasing the time of ultrasonification, while the stability was decreased after a certain time of ultrasonification. In addition, the miniemulsion can be produced under a lower temperature (45°C).

In all the experimental conditions, the stable droplets produced are in the miniemulsion size range with free surfactant levels in the water phase below the critical micelle concentration (CMC). So, droplet nucleation may be the dominant mechanism in the miniemulsion copolymerization of St and BA. In the copolymerization process, the effects of the variables on the copolymerization rate, conversion, and particle size have been considered. To carry out the miniemulsion copolymerization successfully at lower temperature (45°C) with a midial amount of initiator, the suitable amount of surfactant (SDS) and cosurfactant HDE were 10 and 40 mM, respectively.

Also, a homogenizing method of ultrasonification should be applied.

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REFERENCES

1. J. Ugelstad, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Lett.*, **11**, 503 (1973).
2. J. A. Masa, L. L. DE Arbina, and J. M. Asua, *J. Appl. Polym. Sci.*, **48**, 205 (1993).
3. M. J. Unzue and J. M. Asua, *J. Appl. Polym. Sci.*, **49**, 81 (1993).
4. C. M. Miller, P. J. Blythe, E. D. Sudol, C. A. Silebi, and M. S. El-Aasser, *J. Polym. Sci. Polym. Chem. Ed.*, **32**, 2365 (1994).
5. K. Fontenot, J. L. Reimers, and F. J. Schork, in *4th International Workshop on Polymer Reaction Engineering*, DECHEMA. Monographs, Weinheim, Germany, 1992.
6. J. E. Reimers and F. J. Schork, *J. Appl. Polym. Sci.*, **59**, 1833 (1996).
7. J. E. Reimers and F. J. Schork, *J. Appl. Polym. Sci.*, **60**, 251 (1996).
8. D. Mouran, J. Reimers, and F. J. Schork, *J. Polym. Sci. Polym. Chem. Ed.*, **34**, 1073 (1996).
9. F. K. Hansen and J. Ugelstad, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 3069 (1979).
10. B. J. Chamberlain, D. H. Napper, and R. G. Gillbert, *J. Chem. Soc. Faraday Trans. I*, **78**, 591 (1982).
11. Y. T. Choi, M. S. El-Aasser, E. D. Sudol, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 2973 (1985).
12. J. Delgado, M. S. El-Aasser, E. D. Sudol, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 861 (1986).
13. V. S. Rodriguez, PhD Dissertation, Lehigh University, 1988.
14. C. C. Wang, N. S. Yu, C. Y. Chen, and J. F. Kuo, *J. Appl. Polym. Sci.*, **60**, 493 (1996).
15. H. Huang, F. Hu, H. T. Zhang, B. E. Tan, S. Y. Cheng, and J. Z. Li, to appear.
16. A. R. M. Azad, J. Ugelstad, R. M. Fitch, and F. K. Hansen, in *Emulsion Polymerization*, I. Piirma and J. Gardon, Eds., ACS Symposium Series 24, American Chemical Society, Washington, DC, 1976, p. 1.
17. J. Z. Li, H. T. Zhang, S. Y. Cheng, and Z. Q. Ai, *J. Hubei Univ. (Natural Sci. Ed.)*, (4), 315 (1992).
18. J. Delgado, M. S. El-Aasser, C. A. Silebi, J. W. Vanderhoff, and J. Guillot, *J. Polym. Sci., Polym. Phys. Ed.*, **26**, 1495 (1988).
19. D. P. Durbin, M. S. El-Aasser, G. W. Poehlein, and J. W. Vanderhoff, *J. Appl. Polym. Sci.*, **24**, 703 (1979).

20. R. C. Dewald, L. H. Hart, and W. F. Carroll, Jr., *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 2923 (1984).
21. R. C. Dewald, L. H. Hart, and W. F. Carroll, Jr., *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 2931 (1984).
22. V. S. Rodriguez, M. S. El-Aasser, J. M. Asua, and C. A. Silebi, *J. Polym. Sci. Polym. Chem. Ed.*, **27**, 3659 (1989).
23. J. Delgado, M. S. El-Aasser, C. A. Silebi, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.*, **27**, 193 (1989).
24. J. Delgado, M. S. El-Aasser, C. A. Silebi, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.*, **28**, 777 (1990).
25. J. A. Alduncin, J. Forcada, M. J. Barandiaran, and J. M. Asua, *J. Polym. Sci. Polym. Chem. Ed.*, **29**, 1265 (1991).
26. P. L. Tang, E. D. Sudol, M. E. Aams, M. S. El-Aasser, and J. M. Asua, *J. Appl. Polym. Sci.*, **42**, 2019 (1991).
27. P. L. Tang, E. D. Sudol, C. A. Silebi, and M. S. El-Aasser, *J. Appl. Polym. Sci.*, **43**, 1059 (1991).
28. K. Fontenot and F. J. Schork, *J. Appl. Polym. Sci.*, **49**, 633 (1993).
29. C. M. Miller, E. D. Sudol, C. A. Silebi, and M. S. El-Aasser, *J. Polym. Sci. Polym. Chem. Ed.*, **33**, 1391 (1995).