Miniemulsion Copolymerization of Styrene and Butyl Acrylate Initiated by Redox System at Lower Temperature: Reaction Kinetics and Evolution of Particle-Size Distribution

HE HUANG, HONGTAO ZHANG, FANG HU, ZHAOQUAN AI, BIEN TAN, SHIYUAN CHENG, JIANZONG LI

Faculty of Chemistry and Materials Science, Hubei University, Wuhan 430062, People's Republic of China

ABSTRACT: The kinetics of the miniemulsion copolymerization of styrene (St) and butyl acrylate (BA) initiated by redox initiators, $(NH_4)_2S_2O_8/NaHSO_3$, at lower temperature (45°C) was studied. The polymerization rate in miniemulsion copolymerization is lower than that of the corresponding conventional emulsion copolymerization. In regard to the rate of polymerization, the initiator concentration plays a more important role in miniemulsion copolymerization than in conventional emulsion polymerization, while the surfactant concentration has a more important role in conventional emulsion polymerization than in miniemulsion polymerization. These are attributed to their different nucleation mechanisms, which are the same as those found in the miniemulsion polymerization carried out at higher temperatures. While by eliminating nucleation via micelle and ensuring against homogeneous nucleation, miniemulsion polymerization can be carried out by the sole nucleation mechanism—monomer droplet nucleation—at lower temperature. Because of this, the particles become narrower during the polymerization and, finally, monodisperse polymer particles are obtained. The result of the particle numbers indicated that a continuous nucleation will cease at about 60% conversion. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 315–322, 1999

Key words: miniemulsion polymerization; redox system; kinetics; particle-size distribution; nucleation mechanism

INTRODUCTION

Since Ugelstad et al. first reported miniemulsion polymerization in the 1970s,[1] much work has been done on this subject.[2–32] Most elucidated the mechanisms involved in the miniemulsion polymerization process. Also, some applied studies on high solid latexes via miniemulsion polymerization[2,3] were done. In the basic studies, much attention was paid to the functions of the cosurfactant, the means of carrying out the homogenization, and the kinds of initiator.[30]

In the past, however, the effect of temperature, especially lower temperature, on miniemulsion polymerization has been paid little attention. Temperature might also be important to the nucleation mechanism of miniemulsion polymerizations, because higher temperature might cause some unfavorable effects on the stabilities of miniemulsions and their polymerization and increase the solubilities of monomers and surfactants in the aqueous phase, etc., which might lead to the complicated mechanism of miniemulsion polymerization.

Thus, although the main locus of particle nucleation was on monomer droplets, 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 multimodel 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. In a previous article,[30] both the preparation and copolymerization of styrene (St) and butyl acrylate (BA) miniemulsions were carried out successfully using a redox initiator, $(NH_4)_2S_2O_8/NaHSO_3$, at a lower temperature (45°C).

In this work, the kinetics of the miniemulsion copolymerization of St and BA was compared to that of the conventional emulsion copolymerization. Also, the change of the particle-size distribution during polymerization was also investigated. The experimental results at lower temperature provided strong support to monomer droplet nucleation and the monodisperse polymer particles are obtained due to the sole mechanism of monomer droplet nucleation.

EXPERIMENTAL

Materials

St and 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 (HDE), cetyl alcohol, and sodium hydrosulfite were used as received. The water was deionized.

Miniemulsion Copolymerization Process and Particle Sizes

All polymerizations were carried out in a batch process using a glass reactor equipped with a stirrer, a reflux condenser, a sampling device, and inlet systems for nitrogen and the reactants. The copolymerization recipes and the preparation of the miniemulsions were described in a previous article.[30] When the miniemulsions were ready, an aqueous solution of the initiator, ammonium persulfate, and sodium hydrosulfite was injected and 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 and their distributions were measured by a Malvern Auto Sizer Loc-Fc963 apparatus.

Figure 1 Effect of initiator concentration on the miniemulsion coolymerization of St and BA: (1) 0.2%; (2) 0.4%; (3) 0.6%; (4) 0.8%.

RESULTS AND DISCUSSION

Kinetics

Kinetic studies of miniemulsion polymerization have been performed by a number of researchers. These studies have not only demonstrated many differences between miniemulsion and conventional emulsion polymerizations, but they have also demonstrated differences in the polymerization mechanisms for miniemulsions prepared using different types and concentrations of surfactants, cosurfactants, and initiators. In the reported works, the temperatures used were usually 60 or 70°C or even 80°C. Kinetic studies of miniemulsion polymerization at lower temperature have been paid little attention.

Figure 1 shows the conversion–time curves for a set of polymerizations where the initiator content was varied from 0.2 to 0.8% and the temperature was 25°C. The overall polymerization rate increased with an increasing amount of the initiator. While 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%). But the polymerization at 45°C with a medial amount of the initiator is quite good (Fig. 2). The induction period decreased, and the polymerization was quicker. The monomer conversion reached nearly 90% after 4 h. So, 45°C, which is much lower than the temperatures used in the literature, was chosen as the polymerization temperature.

Figures 3 and 4 demonstrate the effects of the surfactant concentration on the miniemulsion

Figure 2 Conversion–time curve for the miniemulsion copolymerization at 45°C. $[I]$ = 0.5%.

and the conventional emulsion copolymerization of St and BA at this temperature (45°C). It can be seen that the polymerization rate is higher in the case of conventional emulsion than for the miniemulsion process, which is one of the main differences about their kinetics found in the literature. The difference in the polymerization rate between the miniemulsion process and the conventional emulsion polymerization is mainly due to the different numbers of polymer particles generated in these systems (Fig. 5). In conventional emulsion polymerization, the number of particles is much more than that in miniemulsion polymerization and it increases faster. In addition, the presence of a cosurfactant (HDE) may further reduce the rate of the miniemulsion polymerization because the cosurfactant affects the concentration of the monomers in the polymer particles in such a way that an increase of the HDE concentration in the

Figure 4 Effect of surfactant concentration on conventional emulsion copolymerization: (1) 5 mM; (2) 10 mM; (3) 15 mM. St/BA = 1/1; $[I]$ = 0.5%; 45°C.

monomer droplets reduces the concentration of the monomers in the polymer particles.

From the experimental results, the log Rp − log[S] and log Rp − log[I] plots, the plot of the log of Rp, and the concentration of the monomers were obtained. Also, the following equations were also obtained[15]:

$$Rp(\text{mini}) = k_1[I]^{0.56}[S]^{0.70}[\text{St}]^{-0.10}[\text{BA}]^{0.10}$$

$$Rp(\text{conv}) = k_2[I]^{0.40}[S]^{1.1}[\text{St}]^{-0.43}[\text{BA}]^{0.43}$$

where Rp is the rate of polymerization; $[I]$, the concentration of the initiator; and $[S]$, the concentration of the surfactant.

It can be seen that the effect of the initiator concentration on the rate of the miniemulsion

Figure 3 Effect of surfactant concentration on miniemulsion copolymerization: (1) 5 mM; (2) 10 mM; (3) 15mM. St/BA = 1/1; $[I]$ = 0.5%, 45°C.

Figure 5 Number of particles formed during miniemulsion and conventional emulsion copolymerization of St and BA: (1) miniemulsion; (2) conventional emulsion.

Figure 6 Effect of monomer ratio on copolymerization: (1) St-10%; (2) St-30%; (3) St-70%; (4) St-90%.

polymerization is more than that of the conventional emulsion polymerization, and the effect of the surfactant concentration on the rate of the conventional emulsion polymerization is more obvious than that of the miniemulsion polymerization. This can be explained by their different mechanisms of nucleation. For conventional emulsion polymerization, the polymer particles are formed via micelles. The amount of micelles plays a great role in affecting the rate of polymerization. Also, the amount of micelles depends on the surfactant concentration. However, miniemulsion polymerization has a mechanism of monomer droplet nucleation. The polymerization rate will depend on the free-radical concentration and the rate of radical absorption by the monomer droplets. So, the initiator amount will be important to the polymerization rate.

It also can be seen from the above equations that the rate of the miniemulsion polymerization will increase with increase of the BA concentration, but will decrease with increase of the St amount (see also Fig. 6). The above results indicate that the effect of the water solubility of the monomers on the polymerization rate is obvious. One of the reasons is probably that the lower water solubility of St increases the desorption rate of the radicals or reduces the radical absorption of the monomer droplets.

Only the monomer droplet nucleation mechanism was used to explain the above differences between the miniemulsion and the conventional emulsion polymerizations. Actually, in miniemulsion polymerization, nucleation could take place not only in the monomer droplets, but also in the

micelles (if present) and in the aqueous phase (homogeneous nucleation). This leads to the complicated mechanism of miniemulsion polymerization. Although it is important for making high solids emulsion, because it produces latexes with larger particles, broader distributions, and lower viscosities than their conventional counterparts, however, miniemulsion polymerization is often prepared with the intent of eliminating nucleation via micellar and aqueous phase routes (i.e., nucleation only in miniemulsion droplets). So, many efforts, such as the choice of cosurfactants, the means of carrying out the homogenization, and the kinds of initiators, have been made to achieve predominate nucleation in monomer droplets.[30]

Eliminating nucleation via micelle is accomplished by keeping the aqueous phase concentration of the surfactant below its critical micelle concentration (cmc). As shown in the previous article,[30] all the experiments were carried out with the residual concentration of the surfactant (SDS) in the aqueous phase less than the cmc of SDS. This indicates that there are no micelles in the water phase. So, there is no micellar nucleation.

Ensuring against homogeneous nucleation in miniemulsion polymerization is not as straightforward. This is one of the reasons why a broader or multimodel particle-size distribution appeared in many studies. In this work, for comparison, a bulk copolymerization of St and BA was carried out with the same concentration of the initiator (BPO) as was used in the miniemulsion (Fig. 7), where a water-soluble inhibitor (hydroquinone)

Figure 7 Comparison of miniemulsion and its corresponding bulk polymerization of St and BA: (1) miniemulsion; (2) bulk.

Table I   Particle Size and Distribution During Miniemulsion Copolymerization of St and BA

	Time (min)										
	0	30	60	90	120	150	180	210	240	300	360
Conversion (%)	0	4	16	20.3	38.7	47.9	62.6	73.3	87.9	88.6	90.6
Diameter (nm)	178.5	155.6	124.0	116.7	123.6	130.4	133.6	136.5	147	152.1	158.1
Poly	0.806	0.225	0.146	0.096	0.093	0.049	0.186	0.056	0.012	0.013	0.006

was added to prevent homogeneous nucleation. As expected, curve 2 is nearly identical to curve 1.The slightly lower rate observed in the miniemulsion polymerization was properly due to the partitioning of the inhibitor into the monomer droplets which retarded the rate or the partitioning of BPO into the aqueous phase which lowered the BPO concentration in the monomer droplets. This indicates that there is little opportunity of homogeneous nucleation. Actually, at this lower temperature, the solubilities of the monomers, initiators, surfactant, etc., cannot be increased so much that the monomers are not easy to polymerize in the aqueous phase.

From the above, we can determine that only monomer droplet nucleation exists in the miniemulsion copolymerization of St and BA at this lower temperature. So, monodisperse polymer particles are obtained at the end of the polymerization (Table I).

Particle Size and Its Distribution During Polymerization

The past studies have provided a considerable amount of evidence that particle formation in miniemulsion polymerizations occurs by radical entry into the small monomer droplets. However, only a limited amount of research has been conducted on particle growth during miniemulsion polymerization. Fontenot and Schork[28] reported some results for particle growth during miniemulsion and conventional emulsion polymerization of methyl methacrylate. Their results suggested that nucleation in miniemulsion systems using HDE as the cosurfactant occurs until conversions of 10–30%, which agreed with the results of Chamberlain et al.[10] about the miniemulsion polymerization of St. However, the data obtained in this work were highly scattered.

Miller et al.[29] studied in detail the evolution of the number of particles as a function of the fractional conversion for the different initiator con-

centrations studied. Their results suggested that the conversion at which nucleation ceases is determined to be between 40 and 60% conversion. They also stated that there was still a considerable amount of error in the data resulting in scatter within the curves.

It seems that it is difficult to obtain reliable data (particle number) over the entire range of conversions in miniemulsion polymerization. It also seems that different systems might have different nucleation periods, because they have different rates of radical absorption, which might be the key factor affecting the formation of particles when other factors are fixed. However, further confirmation is required.

Nevertheless, the evolution of the particle-size distribution may be of critical importance in miniemulsion polymerizations, since a variety of particle-size distributions of the final latexes have been reported in the literature (i.e., "narrow," "broad," "multimodel," "skewed," "monodisperse," etc.). Also, if we can determine the causes of these different particle-size distributions, we can know well the process and nucleation mechanism of miniemulsion polymerization. So, the change of particle sizes and distributions during the miniemulsion copolymerization of St and BA were measured (Fig. 8 and Table I)

Figure 8 shows the growth and sizes of the particles for the miniemulsion and conventional emulsion copolymerization of St and BA. There are larger particle sizes and a lower growth rate of particles in the miniemulsion copolymerization. This was explained by their different nucleation mechanisms.[14] Wang et al.[14] obtained a similar diagram of the diameter of the particles versus the conversion for miniemulsion and emulsion polymerization using an Otsuka DLS700 laser scattering spectrophotometer. But no details about the particle-size distribution during the process were given.

Figure 8 Evolution of particle size during copolymerization; (1) miniemulsion; (2) conventional emulsion.

Table I shows the particle size and distribution during the miniemulsion copolymerization of St and BA, where "Poly" is a variable indicating the particle-size distribution. The value of Poly varies between 0 and 1. The closer to 0 the Poly value, the narrower the particle-size distribution. It can be seen that the particle-size distribution is broader at the beginning of the polymerization and becomes narrower as the polymerization proceeds. At the end of the polymerization, monodisperse polymer particles were obtained, while Miller et al.[29] reported from the miniemulsion polymerization of St that the particle-size distribution is narrower at the beginning of the polymerizations and generally becomes broader as the polymerization proceeds.

The difference between the particle-size distribution at the beginning of the polymerization was attributed to the method used in our experiment to determine the particle size and its distribution (Malven Auto Sizer Loc-Fc963). It cannot only measure the size of the monomer-swollen polymer particles, but it can also measure the sizes of the monomer droplets. So, the "particle" size measured here is not only for the monomer-swollen polymer particles, but also for the monomer droplets.

From the apparatus used, it also can be found that the particles measured in the literature[14] also were both monomer droplets and monomer-swollen polymer particles. But the particles measured in Miller et al.'s work[29] were neither mono-

mer droplets nor monomer-swollen polymer particles: They were pure polymer particles.

Nevertheless, some important information still can be obtained. Before the polymerization, the "particle" size and distribution is actually the size and distribution of the monomer droplets. It has a larger size and broader distribution. At the initial stage of polymerization (less than 20% conversion), the "particle" (namely, monomer droplets and monomer-swollen polymer particles) size decreases and its distribution becomes narrower.

There might be two aspects of this: One is the shrinkage of the polymer formed after the large monomer droplets were entered by radicals, meaning that some large monomer droplets may polymerize by radical entry at the beginning of the polymerization. This has been proved to be possible in the miniemulsion polymerization of St. This being the case, it would be expected that these particles would grow faster than those formed by radical entry into smaller droplets, thereby further distancing them (in volume) from the mean of the distribution. Also, then, a broader particle-size distribution would be gained, while this is in contradiction to the experimental results in Table I. Therefore, large monomer droplets should not polymerize at the beginning of the polymerization in this system.

If not entered so early by the radicals in the polymerization, the large droplets will lose monomers by molecular diffusion to growing polymer particles, thereby becoming smaller and approaching the main population. For the smaller droplets, they may polymerize or collide with each other or with existing polymer particles to become larger and approach the main population.

After 20% conversion, the "particle" size began to increase and its distribution continued to become narrower until the end of the polymerization. This is because the monomer-swollen polymer particles obtain monomers from the monomer droplets and the droplets collide with the polymer particles to approach the main population, provided there is no radical entry into the monomer droplets. If this is the case, the end of the nucleation should be about 20% conversion. This would be consistent with the results found by Chamberlain et al.[10] and Fontenot et al.,[28] while according to the number of particles obtained during the polymerization (Fig. 5), it seems that the end of nucleation in this system should be around 60% conversion. Because the maximum or plateau in the number of particles may be considered to correspond to the end of

nucleation of new polymer particles, then the result will be consistent with that obtained by Miller et al.,[29] meaning that a continued nucleation is still going on after 20% conversion. Also, then, the diffusion and collision of droplets need to continue until the end of the polymerization.

During the whole process of the miniemulsion copolymerization of St and BA, the "particle"-size distribution becomes narrower, and, finally, monodisperse polymer particles are obtained. We cannot separately obtain the sizes of the monomer droplets and the monomer-swollen polymer particles. But from the narrowing "particle"-size distribution, it can be suggested that they are becoming close to each other until the disappearance of the monomer droplets. This is attributed to the sole nucleation mechanism—monomer droplet nucleation—at this lower temperature.

SUMMARY AND CONCLUSIONS

The miniemulsion copolymerization of St and BA was carried out successfully at lower temperature (45°C) using a redox initiator, $(NH_4)_2S_2O_8/$NaHSO$_3$. It was found that the polymerization rate in the miniemulsion copolymerization of St and BA is lower than that in the conventional emulsion copolymerization. The effect of the initiator concentration on the rate of the miniemulsion copolymerization is more than that of the conventional emulsion polymerization, while the function of the surfactant in the miniemulsion copolymerization is less than that in the conventional emulsion copolymerization of St and BA. These are attributed to their different mechanisms of nucleation.

Eliminating micelle nucleation is accomplished by keeping the aqueous-phase concentration of the surfactant (SDS) below its cmc. Ensuring against homogeneous nucleation in the miniemulsion copolymerization is demonstrated by a comparison study of a bulk copolymerizaton and a miniemulsion copolymerization of St and BA. So, the miniemulsion copolymerization of St and BA was carried out with a sole nucleation mechanism—monomer droplet nucleation—at the lower temperature.

The particle size and distribution during the miniemulsion copolymerization of St and BA were measured. The particle-size distribution becomes narrower as the reaction proceeds. Finally, monodisperse polymer particles are obtained, which is attributed to the sole mechanism—monomer

droplet nucleation—in this system. There was an obvious transition about the particle size around 20% conversion. But the result of the number of particles during the polymerization demonstrated that the end of nucleation is about 60% conversion.

REFERENCES

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

19. Durbin, D. P.; El-Aasser, M. S.; Poehlein, G. W.; Vanderhoff, J. W. J Appl Polym Sci 1979, 24, 703.

20. Dewald, R. C.; Hart, L. H.; Carroll, W. F., Jr. J Polym Sci Polym Chem Ed 1984, 22, 2923.

21. Dewald, R. C.; Hart, L. H.; Carroll, W. F., Jr. J Polym Sci Polym Chem Ed 1984, 22, 2931.

22. Rodriguez, V. S.; El-Aasser, M. S.; Asua, J. M.; Silebi, C. A. J Polym Sci Polym Chem Ed 1989, 27, 3659.

23. Delgado, J.; El-Aasser, M. S.; Silebi, C. A.; Vanderhoff, J. W. J Polym Sci Polym Chem Ed 1989, 27, 193.

24. Delgado, J.; El-Aasser, M.; Silebi, C. A.; Vanderhoff, J. W. J Polym Sci Polym Chem Ed 1990, 28, 777.

25. Alduncin, J. A.; Forcada, J.; Bariaran, M. J.; Asua, J. M. J Polym Sci Polym Chem Ed 1991, 29, 1265.

26. Tang, P. L .; Sudol, E. D.; Aams, M. E .; El-Aasser, M. S.; Asua, J. M. J Appl Polym Sci 1991, 42, 2019.

27. Tang, P. L.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. J Appl Polym Sci 1991, 43, 1059.

28. Fontenot, K.; Schork, F. J. J Appl Polym Sci 1993, 49, 633.

29. Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. J Polym Sci Polym Chem Ed 1995, 33, 1391.

30. Huang, H.; Zhang, H. T.; Li, J. Z.; Cheng, S. Y.; Hu, F.; Tan, B. E. J Appl Polym Sci 1998, 68, 2029– 2039.

31. Wang, S.T.; Poehlein, G. W.; Schork, F. J. J Polym Sci Part A Polym Chem 1997, 354, 595–603.

32. Reimers, J. L.; Schork, F. J. Polym Prepr Am Chem Soc Div Polym Chem 1997, 381, 461–462.