

Styrene Miniemulsion Polymerization Stabilized by Carboxylated Polyurethane. II. Kinetics

Zhang-Qing Yu,^{1,2} Doug-Youn Lee,¹ In-Woo Cheong,¹ Jin-Sup Shin,¹ Young-Jun Park,¹ Jung-Hyun Kim¹

¹ Nanosphere Process & Technology Lab, Department of Chemical Engineering, Yonsei University, Seoul 120-749, Korea

² Department of Chemistry and Chemical Engineering, Soochow University, Suzhou 215006, People's Republic of China

Received 30 August 2001; accepted 14 May 2002

ABSTRACT: A styrene miniemulsion was prepared using carboxylated polyurethane as the sole costabilizer and sodium dodecyl sulfate as the surfactant. The effects of the amount of carboxylated polyurethane, the amount of the initiator and surfactant, the presence of a water-phase inhibitor (sodium nitrite), and the reaction temperature on the kinetics of the miniemulsion polymerization were investigated. The evolution of the particle size during the polymerization was measured. The results show that the

polymerization rate was proportional to the 0.21 power of the surfactant concentration and the 0.30 power of azobisisobutyronitrile. The droplet nucleation and homogeneous nucleation were found to be coexistent in the polymerization. The hydrophilicity of the particle surface plays a key role in the nucleation of the particle and, therefore, has an important effect on the kinetics of the polymerization. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1941–1947, 2003

INTRODUCTION

A miniemulsion is a stable submicrometer oil-in-water dispersion stabilized by a surfactant and a costabilizer. The kinetics and nucleation mechanism of miniemulsion polymerization have been investigated by many researchers.^{1–17} In an ideal miniemulsion polymerization, particles are formed by droplet nucleation and the same sizes and size distributions between the primary droplet and the final particle can be kept.¹ However, homogeneous nucleation coexists with droplet nucleation in styrene miniemulsion polymerization when the costabilizer is not effective enough.^{5,15}

In a typical miniemulsion polymerization, there is no interval II of the constant reaction rate as in conventional emulsion polymerization because of the droplet nucleation mechanism.^{13,14} The reaction has been divided into three different intervals according to the average number of radicals in the particle, that is, interval I ($0 < \bar{n} < 0.5$), interval III ($\bar{n} = 0.5$), and interval IV ($\bar{n} > 0.5$) in a styrene miniemulsion stabilized by sodium dodecyl sulfate and hexadecane.¹³ The reaction process has been divided into four intervals according to the characteristics of the polymer-

ization rate by Miller et al.¹⁴ The first two intervals are similar to those above-mentioned. However, interval IV is divided into two intervals (gel effect and rate-decreasing interval).

Predissolving 0.05–1 wt % of polystyrene in the styrene miniemulsion was reported to result in a substantial increase in the rate of polymerization when cetyl alcohol or hexadecane was used as the costabilizer.^{17–21} Miller et al.²¹ attributed it to the increase in the droplet viscosity and the reduction of the possibility of the exit of free radicals. Blythe et al.^{17–20} found that the increase in the overall rate of polymerization is due to the increase in the stability of the small droplets and more particles formed during polymerization. This phenomenon, which is defined as “enhanced droplet nucleation” by the authors, is influenced by the molecular weight predissolved, the costabilizer used, and the shear strength during the miniemulsion preparation.

The kinetics of miniemulsion costabilized by a monomer-resoluble polymer only was also investigated.^{4,7–10,22–26} Reimers et al.^{7,8} found that adding 4 wt % of polystyrene based on the monomer could impart a styrene miniemulsion with a partial stability that is sufficient to allow initiation of the droplets before extensive degradation occurs. By increasing the amount of polystyrene from 3 to 4%, the rate of polymerization was decreased slightly. Several investigators also found that the rate of polymerization decreased evidently when increasing the polymer amount in their research on hybrid miniemulsion polymerization.^{22–26} The impedance effect of the pres-

Correspondence to: J.-H. Kim.

Contract grant sponsor: Korea Institute of Science and Technology Evaluation and Planning (National Research Laboratory Program); contract grant number: M1-9911-00-0044.

ence of resin on the monomer transport, the impurity in the resin, or the inactive radical produced by chain transfer may contribute to the decrease in the polymerization rate.

In a previous article of the work,²⁷ the stability of the styrene miniemulsion using carboxylated polyurethane as the sole costabilizer and the effect of the polyurethane type as well as aqueous pH on the polymerization were investigated. It was found that droplet nucleation and aqueous phase nucleation coexist in the polymerization process and 2,2'-azobisisobutyronitrile (AIBN) is more propitious to droplet nucleation than is potassium persulfate. The present work aimed to study the kinetics of miniemulsion polymerization at different polyurethane amounts, different sodium dodecyl sulfate (SDS) amounts, different temperatures, and different AIBN amounts and in the presence of a water-phase retarder (sodium nitrite). The nucleation mechanism of the polymerization is also discussed.

EXPERIMENTAL

Materials

Styrene (St; Junsei Chemical Co., Japan) was purified of the inhibitor by passing it through an inhibitor removal column for removing hydroquinone and hydroquinone monoethyl ether (Aldrich) and stored in a refrigerator before use. Potassium persulfate (KPS; Samchen Pure Chemical, Korea), 2,2'-azobisisobutyronitrile (AIBN; Junsei Chemical Co.), sodium dodecyl sulfate (SDS; Ducksan Chemical Ind., Korea), hexadecane (HD; Ducksan Chemical Ind.), and hydroquinone (Junsei Chemical Co.) were analytical grade and used as received. The carboxylated polyurethane (PU1) was synthesized in the lab. The molecular weight and the acid number of the PU1 resin are $M_n 1.5 \times 10^4$ ($M_w 3.1 \times 10^4$) and 31.7 mg KOH/g PU. Purified water, which was passed through a Millipore purification system (Millipore, France) with a resistivity of 18.2 M Ω cm, was used throughout this work.

Preparation and polymerization of miniemulsion

A typical recipe of miniemulsion is as follows: 200 g DDI water, 50.0 g St, 1.0 g PU resin, 0.40 g SDS, and 0.1 g AIBN. The miniemulsion was prepared by dissolving the surfactant in water and PU1 and AIBN in St, respectively. The oily phase and the aqueous phase were mixed with a magnetic stirrer at high speed for 15 min. The resultant emulsion was then homogenized (Omni Macro Homoginizer, USA) at level 7 for 6 min. Immediately after homogenization, the resultant miniemulsion was transferred into the a 500-mL jacketed glass reactor equipped with a mechanical stirrer, nitrogen inlet, and reflux condenser. The reac-

tor was purged with nitrogen for 10 min while the miniemulsion was heated to the reaction temperature. The polymerization temperature and the agitation speed were kept constant at 70°C and 300 rpm, respectively, except for the experiments at different temperatures. Samples were withdrawn at regular intervals and the polymerization was shortstopped with three drops of 1% of a hydroquinone ethanol solution. The conversion was determined gravimetrically. The rate of the miniemulsion polymerization was obtained from the conversion–time curve over conversion lower than 70% unless otherwise stated.

Droplet and latex particle size

The sizes of the monomer droplet and the latex particle were measured by dynamic light scattering (Zeta-plus Analyzer, Brokehaven Co., U.K.). The monomer droplet size was measured by diluting the miniemulsion with a 0.6 wt % SDS solution saturated with the St monomer to ensure that the average count rate of the measurement is below 900 kcps. The particle size of the resultant latex was measured by diluting the sample with 0.6 wt % of the SDS solution without the monomer.

RESULTS AND DISCUSSION

Effect of the carboxylated polyurethane amount

The conversion–time curves of the miniemulsion polymerizations and the evolution of the particle size at different amounts of PU1 are shown in Figure 1. It is seen that the rate of polymerization decreases evidently when the amount of PU1 is increased from 2 to 4 wt % based on the monomer amount, which is consistent with the results reported in the literature for St miniemulsion with polystyrene as the sole costabilizer.⁶ In the polymerization rate of the miniemulsion prepared with 8 wt %, however, an interesting phenomenon was found in that its polymerization rate was lower at first and became higher after some time than that of the two miniemulsions above. The evolution of the particle sizes in Figure 1(b) show that the particle size of the miniemulsion with 8 wt % PU1 became smaller than with 2 and 4 wt % PU1 after conversion around 10 and 35%, respectively, and decreased continuously until 92% conversion. It was just coincident with the results observed in the rate of polymerization. This hinted that the phenomenon was caused by the continuous nucleation in the aqueous phase because of the low stability of the miniemulsion prepared with a higher amount of PU1.^{27,28}

Effect of the SDS amount

The conversion–time curves and the evolution of the particle sizes at different SDS amounts are shown in Figure 2. The relationship between the polymerization

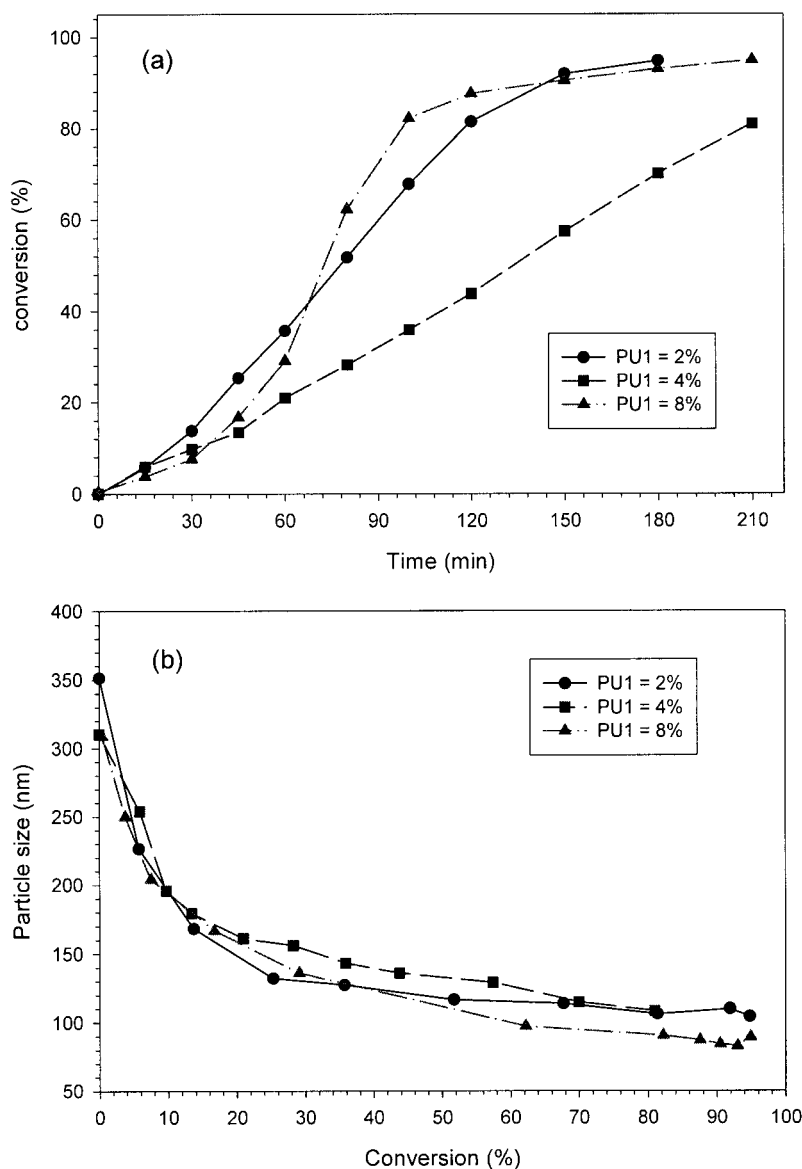


Figure 1 (a) Conversion versus time curves and (b) particle size versus conversion of the miniemulsion polymerization of St at different amounts of carboxylated polyurethane PU1.

rate and the concentration of SDS appears complicated. The rate of the polymerization increased with an increase in the concentration of SDS in first hour and showed no obvious dependence on the SDS concentration thereafter. The evolution of the particle size at different concentrations of SDS showed a similar trend. The particle size became smaller in the first hour of polymerization when the SDS concentration was increased, that is, the particle number was larger in higher SDS concentrations. This means that the difference of the reaction rate is ascribed mainly to the difference of the particle number in the polymerization systems at different surfactant concentrations; in other words, droplet and homogeneous nucleation coexisted in this system.

The conversion data for the first hour were used to calculate the rate of polymerization; the dependence

of $\ln R_p$ on $\ln[\text{SDS}]$ is 0.21 as shown in Figure 3. The result was agreement with the data in the miniemulsion copolymerization of vinyl acetate and butyl acrylate using sodium hexadecyl sulfate as the surfactant and hexadecane as the costabilizer,²⁹ although carboxylated polyurethane was used as the sole costabilizer in the present system. However, it was lower than the values reported in the miniemulsion polymerization of vinyl acetate²⁸ and in the miniemulsion copolymerization of St and butyl acrylate³⁰ when hexadecane was used as the costabilizer.

Effect of the temperature and aqueous pH

Because of the hydrophilicity of the carboxylated polyurethane, the polymerization temperature and the

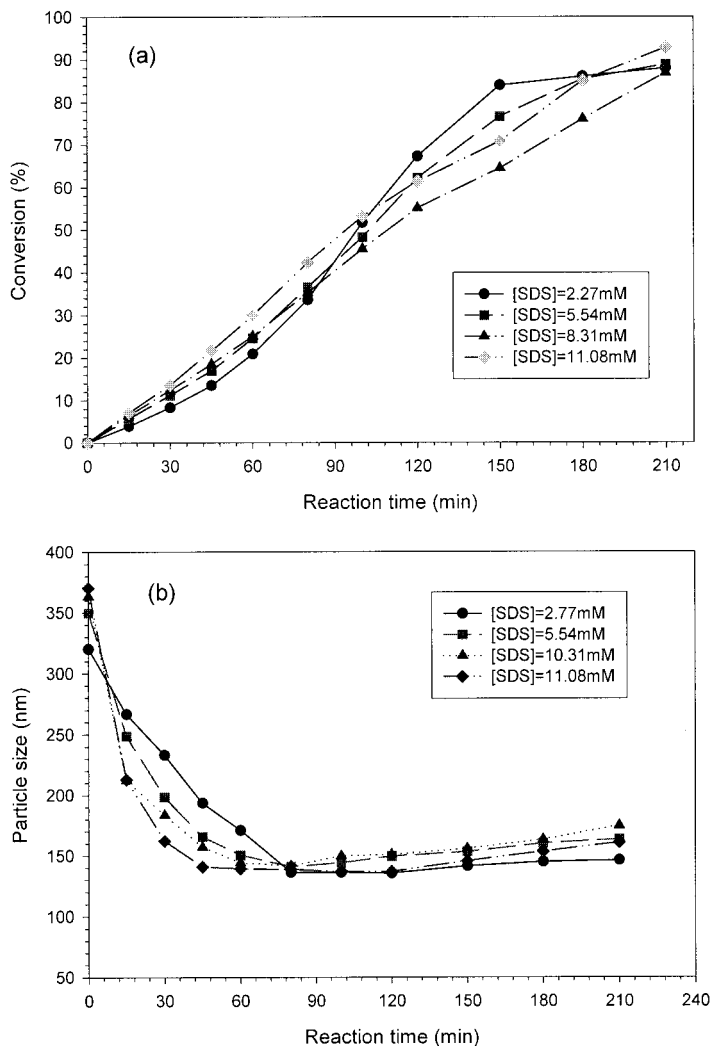


Figure 2 Effect of SDS amount on the miniemulsion polymerization of St using PU1 as the sole costabilizer: (a) conversion versus time curves; (b) evolution of particle size.

aqueous pH value may have some influence on the diffusion of polyurethane molecules from the inner droplet or particle to the surface and, therefore, may influence the kinetics of polymerization. The conversion–time curves at different temperatures at aqueous pH 4.5 and 8.0 are shown in Figure 4. The rates of polymerization increased as expected when the temperature was increased at aqueous pH 4.5 and 8.0 because of the higher decomposition rate of AIBN at higher temperature. The relationship between the rates of polymerization and temperature calculated from Figure 4 is shown in Figure 5. No visible difference was observed between the two lines at different aqueous pH’s although the rate of polymerization at pH 8.0 is lower than that at pH 4.5 at the same temperatures. This means that an increase in the aqueous pH has no or little influence on the active energy of the polymerization of St although it may increase the hy-

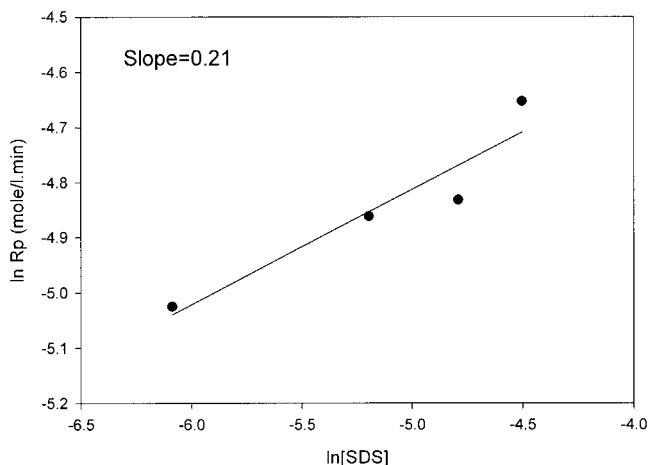


Figure 3 Relationship between the rate of polymerization (R_p) and the concentration of SDS in logarithm.

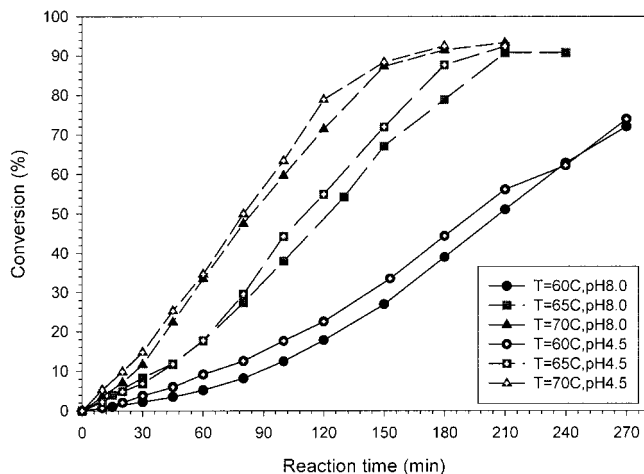


Figure 4 Effect of reaction temperature and aqueous pH on the miniemulsion polymerization of St costabilized by PU1.

drophility of the particle surface and, consequently, decrease the rate of polymerization.^{27,28}

Effect of the initiator

In this series experiment, the amount of AIBN was varied from 1.46 to 9.72 mM while [SDS], the PU1 amount, and the polymerization temperature were kept constant at 5.54 mM, 2 wt % based on the monomer, and 70°C, respectively. The profiles of conversion and particle size versus time are shown in Figure 6(a,b). It is seen that the rate of polymerization becomes higher as the AIBN concentration is increased. An unexpected lower rate of polymerization was also noticed at the lowest concentration of AIBN. Figure 6(b) shows that the particle size of the latex at the lowest initiator concentration is reduced more slowly

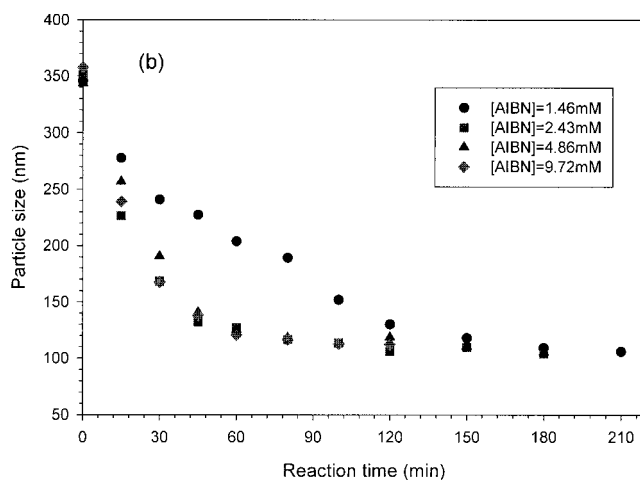
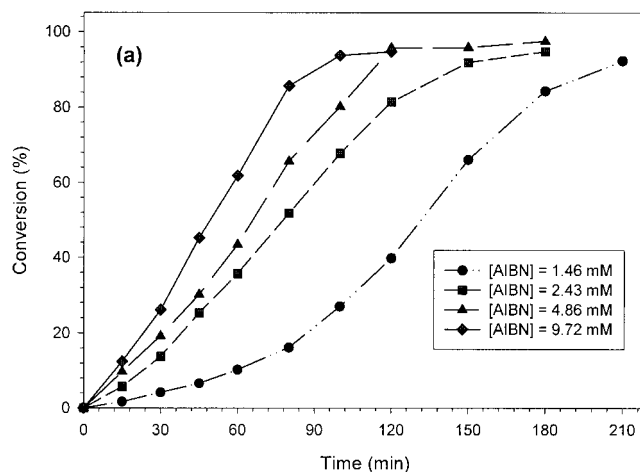


Figure 6 (a) Conversion versus time curves and (b) evolution of particle size of the miniemulsion polymerization of St at different amounts of AIBN.

than that at higher initiation concentrations; however, the other three concentrations show similar profiles of particle size versus time, which hints that some differ-

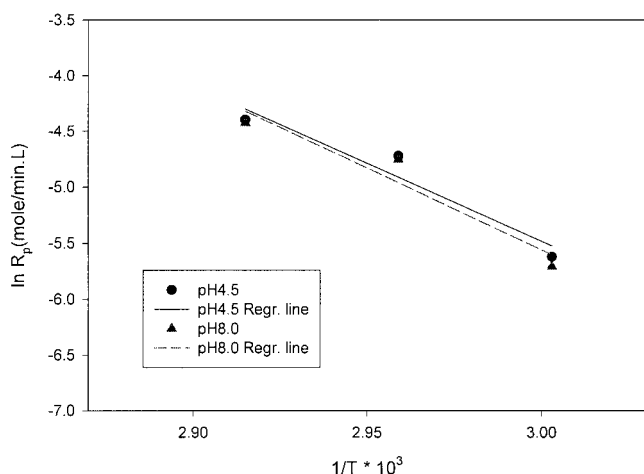


Figure 5 Relationship between the rate of polymerization (R_p) and reciprocal of the reaction temperature at aqueous pH of 4.5 and 8.0.

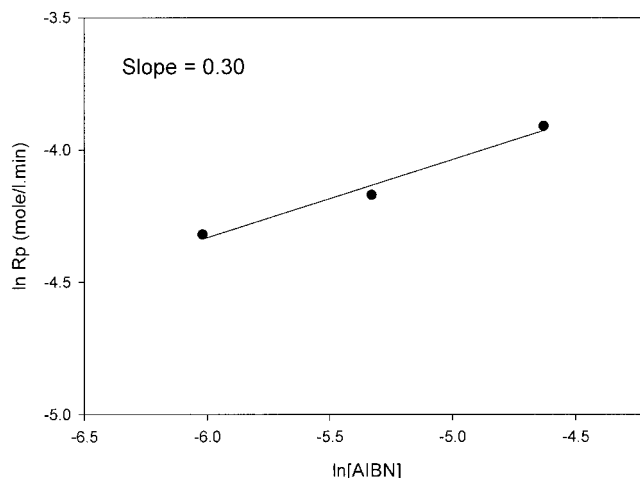


Figure 7 Relationship between the rate of polymerization (R_p) and concentration of AIBN in logarithm.

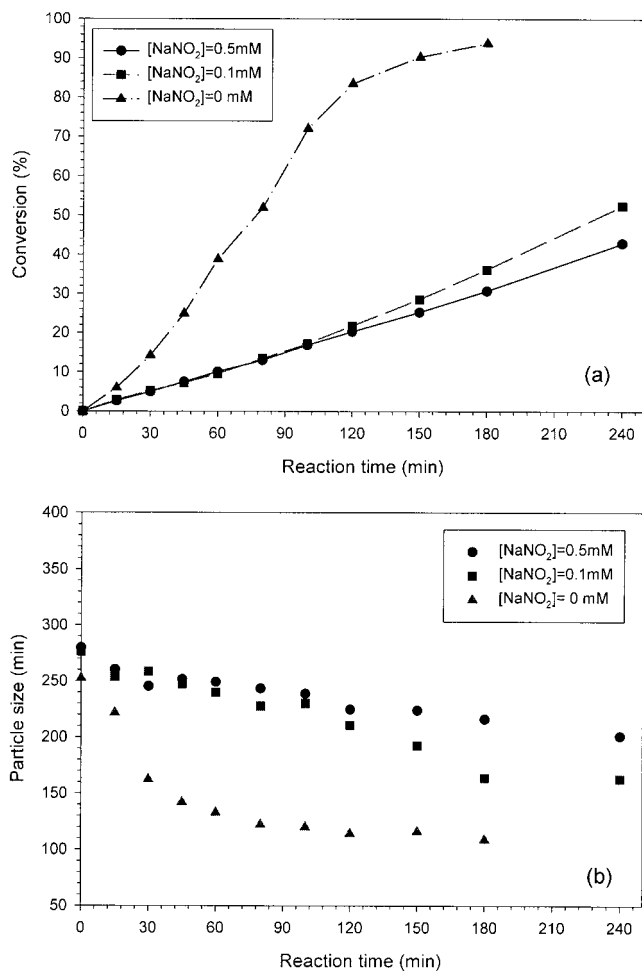


Figure 8 Effect of sodium nitrite amount on the miniemulsion polymerization of St using PU1 as the sole costabilizer: (a) conversion versus time curves; (b) evolution of particle size.

ence in the nucleation mechanism may have occurred among them.

The relationship between $\ln R_p$ and $\ln[AIBN]$ of this series holds the slope of 0.30 as shown in Figure 7. In this figure, the rate of polymerization at a concentration of 1.46 mM was not included, considering the possible different nucleation mechanism. This slope is consistent with the slope of methyl methacrylate miniemulsion polymerization using hexadecane and SDS as a costabilizer and surfactant.³¹ However, it is lower than are the slopes in the miniemulsion polymerizations of St using a reactive costabilizer²⁹ and the copolymerization of St and butyl acrylate using a redox initiator.³⁰ In view of the similar profiles of particle size, the difference of the polymerization rate must be caused by the higher average radical number in the particles at higher AIBN concentration.

Effect of aqueous retarder amount

Figure 8(a,b) shows the rate of polymerization and the evolution of the particle size in the presence of differ-

ent concentrations of sodium nitrite. For the sake of comparison, the data of the rate of polymerization and the evolution of particle size with similar initial droplet sizes but without sodium nitrite are also included in the figure. It is seen from Figure 8(a) that the rate of polymerization decreased remarkably in the presence of sodium nitrite and it does not depend on the concentration of sodium nitrite for a long time after initiation.

It was reported that the rate of the miniemulsion polymerization of methyl methacrylate remained at a similar value when the concentration of sodium nitrite was below 1 mM and fell off at the concentration of 5 mM when potassium peroxide and poly(methyl methacrylate) were used as the initiator and the costabilizer, respectively.⁷ As a water-soluble initiator is more sensitive to the water-phase retarder than is an oil-soluble initiator, the difference may be attributed to the hydrophilicity of the particle caused by diffusion of the carboxylated polyurethane from inside to the surface and, consequently, the hindrance of the oligomeric radical's entry into the particle. Therefore, the rate of polymerization becomes more sensitive to the presence of an aqueous retarder.

In comparing the conversion-time curves and the evolutions of particle size in Figure 8(a,b), it was found that the particle size decreased obviously when the rate of polymerization increased and the divergence point of the polymerization rate was consistent with that of the particle size. This suggests that the higher rate of polymerization is accompanied by higher nucleation in the aqueous phase; therefore, aqueous nucleation plays an important role in this system.

Various mechanisms for the generation of single radicals have been reported in miniemulsion polymerization using an oil-soluble initiator.³² The data above show that the polymerization rate was dramatically influenced by the existence of an aqueous retarder and increased simultaneously with the particle number. This is clearly evidence that AIBN free radicals undergo desorbance from monomer droplets or particles, then reabsorbance as oligomers to start the polymerization.

CONCLUSIONS

This investigation of a St miniemulsion using carboxylated polyurethane as the sole costabilizer and SDS as the surfactant demonstrates that droplet nucleation and aqueous nucleation coexist during the polymerization. A higher amount of carboxylated polyurethane or a higher aqueous pH has an impedance effect on the polymerization rate and is favorable to homogeneous nucleation. The kinetic results also showed that the polymerization rate was increased when the reaction temperature was increased and was propor-

tional to the 0.30 power of the concentration of AIBN. The polymerization rate was found to depend on the 0.21 power of the surfactant concentration during the initial process of polymerization; however, it has no obvious relation to the surfactant amount in the mass.

Financial support by the Korea Institute of Science and Technology Evaluation and Planning (National Research Laboratory Program, no. M1-9911-00-0044) is gratefully acknowledged by the authors.

References

1. Landfester, K.; Bechthold, N.; Forster, S.; Antonietti, M. *Macromol Rapid Commun* 1999, 20, 81.
2. Chambelain, B. J.; Napper, D. H.; Gilbert, R. G. *J Chem Soc Faraday Trans I* 1982, 78, 591.
3. Delgado, J.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Part A Polym Chem* 1986, 24, 861.
4. Miller, C. M.; Blythe, P. J.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *J Polym Sci Part A Polym Chem* 1994, 32, 2365.
5. Chern, C. S.; Chen, T. J.; Liou, Y. C. *Polymer* 1998, 39, 3767.
6. Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *Macromolecules* 1995, 28, 2754.
7. Reimers, J.; Schork, F. J. *J Appl Polym Sci* 1996, 59, 1833.
8. Reimers, J. L.; Schork, F. J. *J Appl Polym Sci* 1996, 60, 251.
9. Aizpurua, I.; Amalvy, J. I.; Barandiaran, M. J. *Colloids Surf A Physiochem Eng Asp* 2000, 166, 59.
10. Wang, S.; Schork, F. J. *J Appl Polym Sci* 1994, 54, 2157.
11. Chern, C. S.; Sheu, J. C. *Polymer* 2001, 42, 2349.
12. Chern, C. S.; Sheu, J. C. *J Polym Sci Part A Polym Chem* 2000, 38, 3188.
13. Bechthold, N.; Landfester, K. *Macromolecules* 2000, 33, 4682.
14. Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *J Polym Sci Part A Polym Chem* 1995, 33, 1391.
15. Chern, C. S.; Liou, Y. C. *Polymer* 1999, 40, 3763.
16. Choi, Y. T.; El-Aasser, M. S.; Sudol, E. D.; Vanderhoff, J. W. *J Polym Sci Polym Chem Ed* 1985, 23, 2973.
17. Blythe, P. J.; Morrison, B. R.; Mathauer, K. A.; Sudol, E. D.; El-Aasser, M. S. *Langmuir* 2000, 16, 898.
18. Blythe, P. J.; Klein, A.; Sudol, E. D.; El-Aasser, M. S. *Macromolecules* 1999, 32, 6952.
19. Blythe, P. J.; Morrison, B. R.; Mathauer, K. A.; Sudol, E. D.; El-Aasser, M. S. *Macromolecules* 1999, 32, 6944.
20. Blythe, P. J.; Klein, A.; Sudol, E. D.; El-Aasser, M. S. *Macromolecules* 1999, 32, 4225.
21. Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *Macromolecules* 1995, 28, 2765.
22. Tsavalas, J. G.; Gooch, J. W.; Schork, F. J. *J Appl Polym Sci* 2000, 75, 916.
23. Wu, X. Q.; Schork, F. J.; Gooch, J. W. *J Polym Sci Part A Polym Chem* 1999, 37, 4159.
24. Wang, S. T.; Schork, F. J.; Poehlein, G. W.; Gooch, J. W. *J Appl Polym Sci* 1996, 60, 2069.
25. Van Hamersveld, E. M. S.; Van Es, J. J. G. S.; Cuperus, F. P. *Colloids Surf A Physiochem Eng Asp* 1999, 153, 285.
26. Gooch, J. W.; Dong, H.; Schork, F. J. *J Appl Polym Sci* 2000, 76, 105.
27. Yu, Z. Q.; Kim, J. H., submitted for publication in *J Appl Polym Sci*.
28. Wu, X. Q.; Schork, F. J. *J Appl Polym Sci* 2001, 81, 1691.
29. Delgado, J.; El-Aasser, M. S.; Silebi, C. A.; Vanderhoff, J. W. *J Polym Sci Part A Polym Chem* 1990, 28, 777.
30. Huang, H.; Zhang, H.; Hu, F.; Ai, Z.; Tan, B.; Cheng, S.; Li, J. *J Appl Polym Sci* 1999, 73, 315.
31. Fontenot, K.; Schork, F. J. *J Appl Polym Sci* 1993, 49, 633.
32. Capek, I. *Adv Colloid Interf* 2001, 91, 295.