

# Styrene Miniemulsion Polymerization Stabilized by Carboxylated Polyurethane. I. Stability and Polymerization

Zhang-Qing Yu,<sup>1,2</sup> Doug-Youn Lee,<sup>1</sup> In-Woo Cheong,<sup>1</sup> Jin-Sup Shin,<sup>1</sup> Young-Jun Park,<sup>1</sup>  
Jung Hyun Kim<sup>1</sup>

<sup>1</sup> Nanosphere Process & Technology Lab, Department of Chemical Engineering, Yonsei University, Seoul 120-749, South Korea

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

Received 30 August 2001; accepted 14 May 2002

**ABSTRACT:** Stability of the styrene miniemulsion costabilized by carboxylated polyurethane resins was investigated. The shelf life and the droplet size were measured. The results show that styrene miniemulsion costabilized by carboxylated polyurethane can be prepared although it is not as efficient as is hexadecane. The shelf life of the miniemulsion is influenced by the amount of the polyurethane and sodium dodecyl sulfate. The alkaline condition and the smaller molecular weight of the polyurethane are in favor of the stability of the miniemulsion. The polymerization results show that the hydrophilicity of the particle or droplet surface plays

an important role in the process of the nucleation and polymerization. Homogeneous nucleation and droplet nucleation coexist in these systems. Nucleation lasts to 40–60% conversion of the monomer in the acid medium, but it continues until the end of the polymerization in the alkaline medium. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1933–1940, 2003

**Key words:** nucleation; miniemulsion polymerization; carboxylated polyurethane; stability

## INTRODUCTION

Miniemulsion is finely divided oil-in-water dispersions with a typical droplet size of 50–500 nm prepared by shearing a system containing oil, water, a surfactant, and a cosurfactant or costabilizer.<sup>1</sup> The stability of a miniemulsion is endowed by the synergic effect of a suitable surfactant and a hydrophobic and monomer-soluble costabilizer. The costabilizer suppresses or even prevents the diffusional degradation of the monomer droplets from a small droplet to a big one (Ostwald ripening) and the surfactant precludes the coalescence of the droplets. Because of its small droplet size, droplet nucleation, which is negligible in conventional emulsion polymerization, becomes predominant in typical miniemulsion polymerization although other particle nucleation mechanisms can also occur.<sup>2–8</sup>

Long-chain alkane (hexadecane) and fatty alcohol (cetyl alcohol) are the typical costabilizers used in miniemulsion polymerization.<sup>2,3,9–15</sup> However, these low molecular weight compounds remain in the particles after polymerization and reduce the mechanical

properties of the polymer. Furthermore, the slow evaporation of these costabilizers pollutes the atmosphere. To avoid these negative effects, some new kinds of costabilizers have been investigated such as monomer-soluble polymers<sup>5–7,16–21</sup> and a highly hydrophobic monomer.<sup>22,23</sup> Chain-transfer and hydrophobic initiators also have been used as costabilizers in miniemulsion polymerization but the polymer produced has a relative low molecular weight.<sup>24–26</sup>

Although a polymeric costabilizer is not as efficient as hexadecane or cetyl alcohol in costabilizing the miniemulsion droplets, it is adequate to stabilize the droplets against diffusional degradation long enough to nucleate them into polymer particles. Reimers and Schork<sup>5</sup> found that the addition of a monomer-soluble polymer into a miniemulsion could slow the effects of Ostwald ripening and impart the miniemulsion with partial stability, which is sufficient to allow initiation of the droplets before extensive degradation occurs. Furthermore, these systems were more robust in nucleation and were less sensitive to variations in the recipes or contaminants. The best molecular weight of poly(methyl methacrylate) (PMMA) to costabilize the styrene miniemulsion droplets depends on the amount of surfactant and the hydrophobe, which is in the range of 350,000 to 750,000.<sup>6</sup> Aizpurua et al.<sup>7</sup> investigated the influence of poly(vinyl acetate) and polystyrene on the kinetics of vinyl acetate miniemulsion polymerization above the CMC. They found that the vinyl acetate miniemulsions costabilized by poly-

Correspondence to: J. H. Kim.

Contract grant sponsor: Korea Institute of Science and Technology Evaluation and Planning; contract grant number: M1-9911-00-0044.

TABLE I  
Molecular Weight and Acid Number of Polyurethanes

Polymer ID	PPG2000	DMPA	IPDI	$M_w$ ( $10^4$ )	$M_n$ ( $10^4$ )	Polydispersity	Acid no.
PU1	0.10	0.20	0.30	3.1	1.5	2.13	31.7
PU2	0.10	0.25	0.35	3.9	1.7	2.27	41.5
PU3	0.10	0.20	0.30	1.5	0.7	2.14	29.8

Unit of acid no. is mg KOH/g resin, DMPA is the abbreviation for 2,2-bis(hydroxymethyl)propionic acid; IPDI, for isophorone diisocyanate; and NMP, for 1-methyl 2-pyrrolidone.

(vinyl acetate) or polystyrene was not stable, and 60% of phase separation was observed in 20 min. However, this miniemulsion still retained some characteristics of miniemulsion polymerization (nucleation of a droplet polymer). Wang and Schork<sup>21</sup> also tried different kinds of polymers as the costabilizer in the miniemulsion polymerization of vinyl acetate. The miniemulsion costabilized with poly(vinyl acetate) was found to be quite unstable, with shelf lives less than 1 h. However, the miniemulsion costabilized with PMMA or polystyrene had enough stability to allow the occurrence of predominant droplet nucleation.

Recently, miniemulsion polymerization in the presence of a polymer has been used to synthesize hybrid latex such as unsaturated polyester/polyacrylate latex<sup>16</sup> and alkyd/polyacrylate latex.<sup>17-19</sup> In these systems, the hydrophobic resins were employed as both costabilizers and the reactants; therefore, the amounts of them used were much higher than those in the systems aforementioned. Gooch et al.<sup>20</sup> obtained a crosslinkable hybrid latex composed of oil-modified polyurethane and acrylates (methyl methacrylate, butyl acrylate, and acrylic acid) using oil-modified polyurethane as a costabilizer. The miniemulsion showed excellent shelf-life stability (>5 months) when the amount of the oil-modified polyurethane ranged from 30 to 100 wt % based on the monomer. However, the rate of polymerization was found to be much slower than that in the equivalent recipe without oil-modified polyurethane and decreases with an increase in its amount.

The availability of an oil-resolvable initiator and redox initiator system in miniemulsion polymerization was also investigated in addition to the typical aqueous initiator.<sup>11,27-30</sup> It was found that 2,2'-azobisisobutyronitrile (AIBN) promotes nucleation in the monomer droplets during styrene miniemulsion polymerization costabilized by dodecyl or stearyl methacrylate.<sup>30</sup> The high decomposition rate of the redox initiator system was reported to be in favor of the droplet nucleation and can produce latex with a very narrow polydispersity.<sup>11,27</sup>

Polyurethane is easy to change in composition and hydrophilicity. The carbonyl, carboxyl, and urethane group in its structure makes it easy to adsorb onto the organic or inorganic particle surface, which endows it with the potential to disperse organic or inorganic particles in water or organic medium when miniemul-

sion polymerization is used to encapsulate particles. It has not been reported that carboxylated resin was used as a costabilizer in miniemulsion polymerization. In this article, the availability of carboxylic polyurethane resin used as costabilizer in the miniemulsion polymerization of styrene was investigated. The effects of the initiator type, the acid number, and the molecular weight of the carboxylic polyurethane, the amount of polyurethane, and the pH of the aqueous phase on the shelf life and some polymerization behavior were investigated. More details about the kinetics will be reported in another article.

## 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, Samchun Pure Chemical, Korea), 2,2'-azobisisobutyronitrile (AIBN, Jusei Chemical Co., Japan), sodium dodecyl sulfate (SDS, Ducksan Chemical Ind., Korea), hexadecane (HD), and hydroquinone were analytical grade and used as received. Distilled and deionized water was used throughout.

### Synthesis of carboxylated polyurethane

The carboxylated polyurethane resins were synthesized in a 1-L round-bottom glass reactor by solution condensation. Before the reactants were added, the reactor was dried and purged with N<sub>2</sub> for 10 min. PPG 2000, 2,2-bis(hydroxymethyl)propionic acid, and 1-methyl-2-pyrrolidone were added into the reactor and agitated for 1 h to ensure the homogeneity of the mixture. When the temperature was increased to 80°C, the reaction was initiated by adding isophorone diisocyanate. The temperature was kept for 5.5 h. After the polymerization, the resins were washed several times with DDI water and dried in a vacuum oven for 24 h. The composition, molecular weight, and the acid number of the polyurethane resins are listed in Table I. The carboxylated polyurethane resins all could dissolve in water at pH of 13.

**TABLE II**  
**Monomer Droplet Size and Shelf Life of the Miniemulsion**

Sample code	HD (g)	PU1 (g)	SDS (g)	Droplet size (nm)	PDI	Shelf life (h)
1	1.0	0	0.4	152.2	0.169	>60 days
2		1.0 <sup>a</sup>	0.4	267.8	0.013	6.0
3		1.0 <sup>b</sup>	0.4	244.3	0.005	12.0
4		1.0	0.4	275.2	0.005	6.5
5		2.0	0.4	280.3	0.166	6.0
6		4.0	0.4	264.3	0.158	2.5
7		6.0	0.4	269.3	0.200	2.0
8	1.0	1.0	0.4	173.0	0.232	>60 days
9	1.0	2.0	0.4	178.2	0.218	>60 days
10	1.0	4.0	0.4	166.4	0.186	26 days
11	1.0	6.0	0.4	120.8	0.258	25 days
12		1.0	0.8	340.7	0.053	3.5
13		1.0	1.2	378.3	0.181	2.0
14		1.0	1.6	406.6	0.014	1.5

The amount of styrene and water is 50 and 200 g, respectively

<sup>a</sup> the polyurethane used to prepare the miniemulsion was PU2.

<sup>b</sup> The polyurethane used to prepare the miniemulsion was PU3.

**Preparation and polymerization of miniemulsion**

A typical recipe of miniemulsion is as follows: 200 g DDI water, 50.0 g St, 1.0 g polyurethane resin, 0.40 g SDS, and 0.1 g AIBN or KPS (it was not included in the miniemulsions for the shelf life study). Specific compositions of the runs for shelf life and polymerization are tabulated in Tables II and III. The miniemulsion was prepared by dissolving the surfactant in water and polyurethane and AIBN in St, respectively. The oily phase and aqueous phase were mixed with a magnetic stirrer at high speed for 15 min. The resultant emulsion was then homogenized (Omni Macro Homogenizer, 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 miniemulsion was purged with

nitrogen for 10 min while the reactor temperature was heated to the reaction temperature. The polymerization temperature and the agitation speed were kept constant at 70°C and 300 rpm, respectively. For polymerizations initiated by KPS, the reaction was commenced by the addition of an aqueous solution of KPS. Samples were withdrawn at regular intervals and the polymerization was shortstopped with a hydroquinone ethanol solution. The conversion was determined gravimetrically.

**Shelf life of miniemulsion**

The shelf life of the miniemulsion was monitored by placing about 20 cm<sup>3</sup> of the sample in a capped test tube at room temperature and observing the time necessary for a visible creaming line to appear. Two

**TABLE III**  
**Compositions and Some Properties of the Latex and Sty Miniemulsion Polymerizations Costabilized by Carboxylated Polyurethane**

Experiment ID	HD (%)	PU1 (%)	PU2 (%)	PU3 (%)	AIBN (mM)	pH	X (%)	D <sub>d</sub> (nm)	D <sub>p</sub> (nm)	Zeta (mv)
MHDA	2				2.43 <sup>a</sup>	4.5	77.9	254.7	103.2	-62.26
MHP1A	2	2			2.43	4.5	99.8	194.4	99.6	-60.27
MP1A		2			2.43	4.5	94.8	351.3	104.1	-57.95
MP1K		2			1.47 <sup>b</sup>	4.5	99.4	353.3	77.3	-73.85
MP1R		2			1.47 <sup>c</sup>	4.5	93.2	294.2	78.4	-66.78
MP2A			2		2.43	4.5	92.1	374.9	106.3	-52.98
MP3A				2	2.43 <sup>d</sup>	4.5	92.7	374.8	113.5	-53.17
MpH7		2			2.43	7.0	95.8	395.5	106.8	-45.48
MpH8		2			2.43	8.0	97.8	380.8	89.5	-46.82

<sup>a</sup> Reaction time, 240 min.

<sup>b</sup> Reaction time, 120 min.

<sup>c</sup> The value is the concentration of KPS. The weight ratio of NaHSO<sub>3</sub> to KPS was 1:1. The reaction temperature and time was 50°C and 150 min, respectively.

<sup>d</sup> Reaction time, 210 min.

drops of a water-soluble red-pigment solution were added into each sample to increase the contrast between the phases.

### Droplet and latex particle size

The z-average sizes of monomer droplet and latex particle were measured by dynamic light scattering (Zetaplus Analyzer, Brokehaven Co.), with a scattering angle of 90° and a temperature of 23°C. Polydispersity (PDI), which is given by the instrument manufacturer, was used to characterize the distribution of the particle size. 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 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.

### Zeta potential of the particles

The zeta potential of the latex particles was measured by the Zetaplus analyzer at an angle of 90° at 24°C. The latex sample was diluted with DDI water to ensure that the average count rate was below 900 kcps. The reported value is the mean value of measurements taken five times.

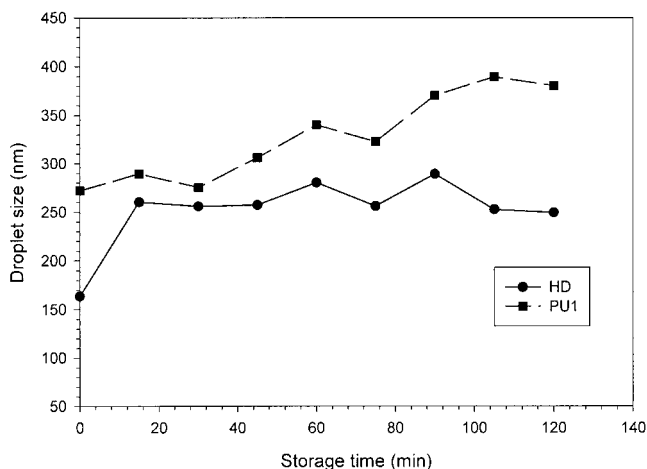
## RESULTS AND DISCUSSION

### Droplet size and shelf life

A stable monomer miniemulsion must be obtained to carry out a miniemulsion polymerization successfully. The stability of the miniemulsion is directly dependent on the droplet size, which was, in turn, significantly influenced by the shear condition, surfactant concentration, costabilizer concentration, rate of the organic phase, and water solubility of the monomer.<sup>31</sup>

Three kinds of carboxylated polyurethane resins (PU1, PU2, and PU3) were used as costabilizers to prepare the miniemulsions. They were composed of poly(propyl glycol), isophorone diisocyanate, and dimethylol propionic acid and could be dissolved in an alkaline solution. However, they were different in molecular weight and acid number (Table I). For the sake of comparison, miniemulsion costabilized by HD was also prepared. Preliminary tests showed that shear strength over level 7 and homogenizing time over 6 min have little effect on the decrease in droplet size of the resultant miniemulsion. Therefore, miniemulsion was prepared by homogenizing the preemulsion at level 7 for 6 min in further work.

The composition, droplet sizes, polydispersities, and shelf lives of the miniemulsions are listed in Table II. The results indicate that the droplet size of the

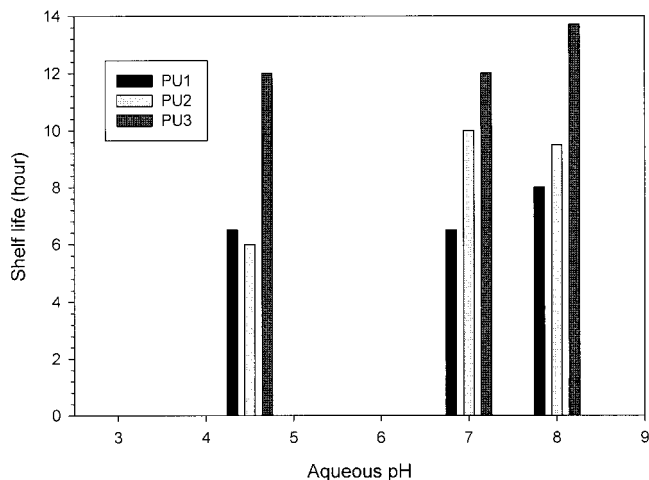


**Figure 1** Evolution of the droplet size of the miniemulsions prepared with HD and carboxylated polyurethane PU1.

monomer is between 120.8 and 406.8 nm, within the range of the miniemulsion (50–500 nm). The shelf lives of the miniemulsion are between 1.5 and 12.0 h, which is longer than those of the methyl methacrylate (MMA) miniemulsion using PMMA as the costabilizer (2 min to 6 h)<sup>6</sup> but shorter than the acrylate monomer miniemulsion costabilized with a higher amount of alkyd or polyester.<sup>16–18,20</sup> It was also noticed that the aqueous phase separated from the miniemulsion prepared with polyurethane was very turbid. Aizpurua et al.<sup>7</sup> observed a similar phenomenon in the vinyl acetate miniemulsion costabilized with poly(vinyl acetate) or polystyrene. They analyzed the droplet size of the bottom part separated from the miniemulsion at different times and found that the turbidity of the aqueous phase was caused by the existence of small monomer-swollen particles in the water phase.

The evolution of the droplet size of the miniemulsion prepared with PU1 and HD is shown in Figure 1. It indicates that the carboxylated polyurethane is not as effective as HD in costabilizing the St miniemulsion and there is some diffusional degradation occurring in the miniemulsion droplets. The results in Table II show that the shelf life of the miniemulsion prepared by HD together with different amounts of PU1 is not changed obviously when the amount of PU1 is below 8 wt % based on the monomer. However, the shelf life decreases when the amount of PU1 exceeds 8 wt %. The droplet size of the miniemulsion decreases as the amount of PU1 increases in the range of the experiment.

The effect of the amount of PU1 on the shelf life and the droplet size of the miniemulsion is shown in Table II (runs 4–7) when only PU1 is used as the costabilizer. At the same level of SDS, the shelf life of the miniemulsion decreases as the amount of PU1 increases. The droplet size did not change obviously with an increasing amount of PU1; however, some monomer



**Figure 2** Effect of the aqueous pH on the shelf lives of the miniemulsion prepared by different carboxylated polyurethanes.

beads were found on the surface of the miniemulsion prepared with 8 and 12 wt % PU1 after homogenization and more monomer beads were found at a higher level of PU1. This may result from less efficiency of homogenization with the higher viscosity of the oil phase and the higher ratio of the oil phase to the water phase.<sup>31</sup> The broader distribution of the droplet size also contributed to the decrease in the shelf life. The inconsistency between the shelf life and the droplet size may lie in that visible monomer beads were excluded in the sample for the latter.

In comparing the results of run 2 with run 4, no obvious change was found in the shelf lives of the miniemulsions when replacing PU1 with PU2, with a similar molecular weight but higher acid number (31.7–41.5 mg KOH/g PU). However, when PU1 is substituted by PU3, which has a similar acid number but lower molecular weight ( $3.1\text{--}1.5 \times 10^4$ ), the shelf life of the miniemulsion was obviously prolonged.

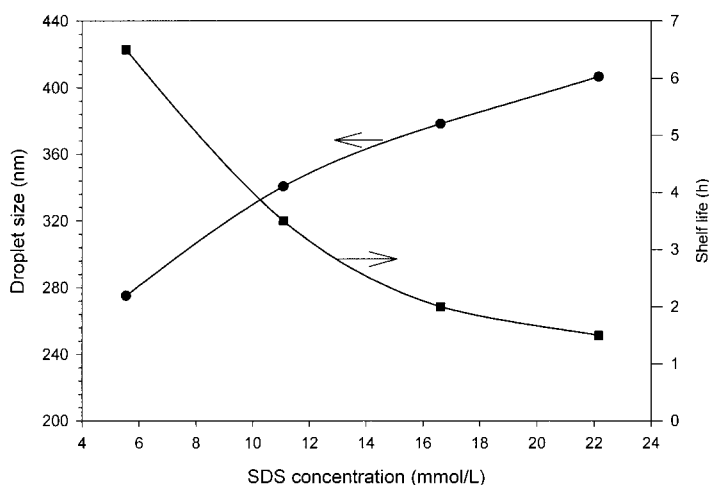
This means that the lower molecular weight of the carboxylated polyurethane favors the stability of the miniemulsion. This may be attributed to that smaller molecules of the carboxylated polyurethane can diffuse to the interface of the droplet more easily than can the bigger molecules and, therefore, give rise to a reduction in the interface tension of the droplet. Low molecular weight also contributes to its more effectiveness as a costabilizer.<sup>32</sup>

The effect of the aqueous pH on the shelf life is shown in Figure 2. It is seen that the miniemulsions have a higher stability in a higher pH of the aqueous phase. When the aqueous phase is changed to an alkaline condition, some of carboxylated PU1 that diffused to the interface of the droplet could be neutralized by the alkaline in the aqueous phase. This could increase the hydrophilicity of the PU1 molecules and reduce the interface energy of the system. As a result, the stability of the miniemulsion increases.

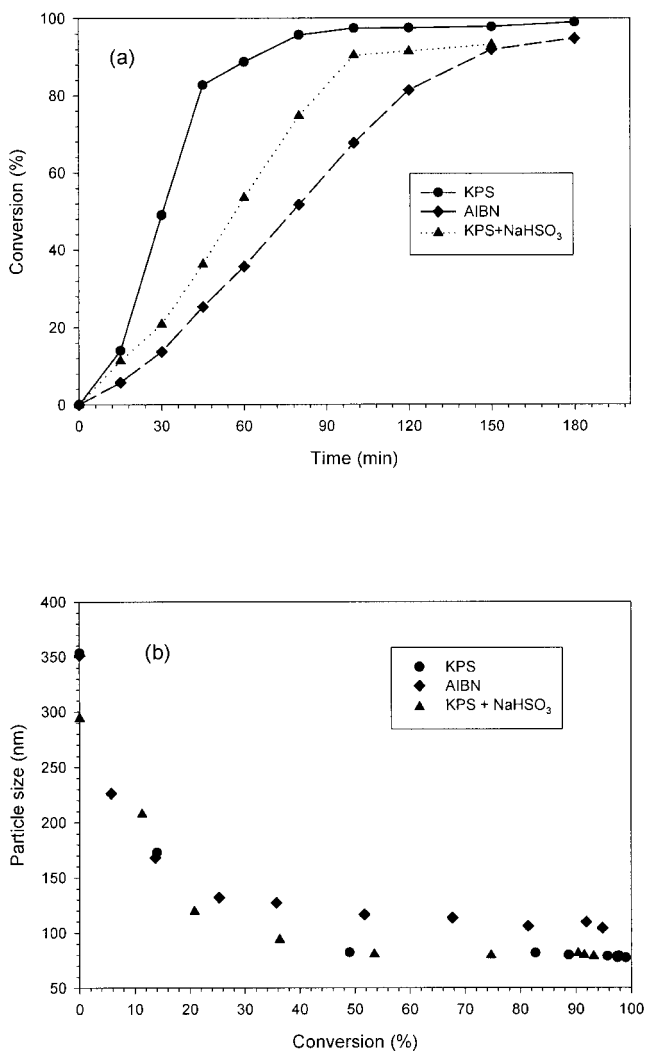
Figure 3 shows the effect of the amount of SDS on the shelf lives and droplet sizes of the miniemulsions. The droplet size becomes bigger and the shelf life shortens as the concentration of SDS increases. It was noticed that a great deal of foam existed on the surface of the miniemulsion after homogenization and many more foams were found with an increase in the amount of SDS. This is in accord with results of the MMA miniemulsion costabilized by HD or PMMA using SDS as the surfactant.<sup>6,31</sup> When the concentration of SDS was increased, more of the costabilizer and the monomer dissolved in the aqueous phase, which is unfavorable to the stability of the miniemulsion.

**Polymerization of miniemulsion**

Table III lists the compositions and some properties of the resultant latexes of the miniemulsion polymerization runs. When the surfactant concentration is below



**Figure 3** Effect of the amount of SDS on the shelf lives and droplet sizes of the miniemulsions costabilized by PU1.



**Figure 4** Conversion curves and evolution of the particle size during miniemulsion polymerization initiated by different initiators.

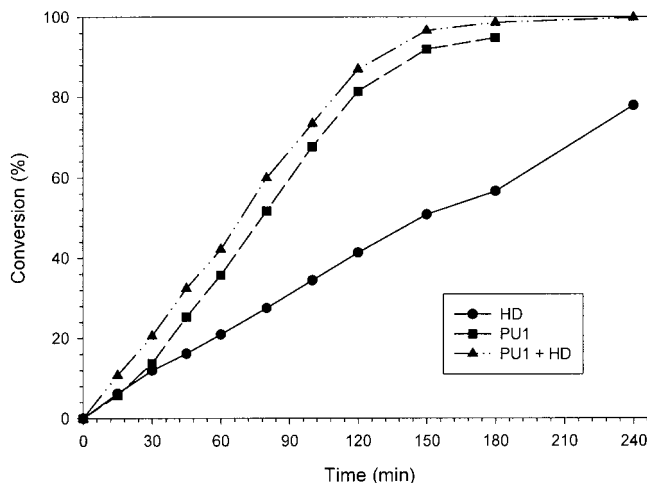
its CMC, the possible nucleation mechanisms for miniemulsion polymerization are the droplet nucleation and homogeneous nucleation.

If no homogeneous nucleation is involved and the miniemulsion is stable enough, the particle size will keep its size throughout the polymerization. The kinetics and the evolution of the particle size during the polymerization with different initiators are shown in Figure 4. It can be seen from Figure 4(a) that the rates of polymerization with water-soluble initiators (KPS) are higher than those with the oil-soluble initiator (AIBN) and that the particle size of the latex of the former is smaller than that of the latter. Furthermore, the particle size is much smaller than is the initial droplet size. This means that homogeneous nucleation and droplet nucleation coexist in the process of polymerization (Table III). The results also show that an oil-soluble initiator is less efficient than is the water-soluble initiator in homogeneous nucleation because

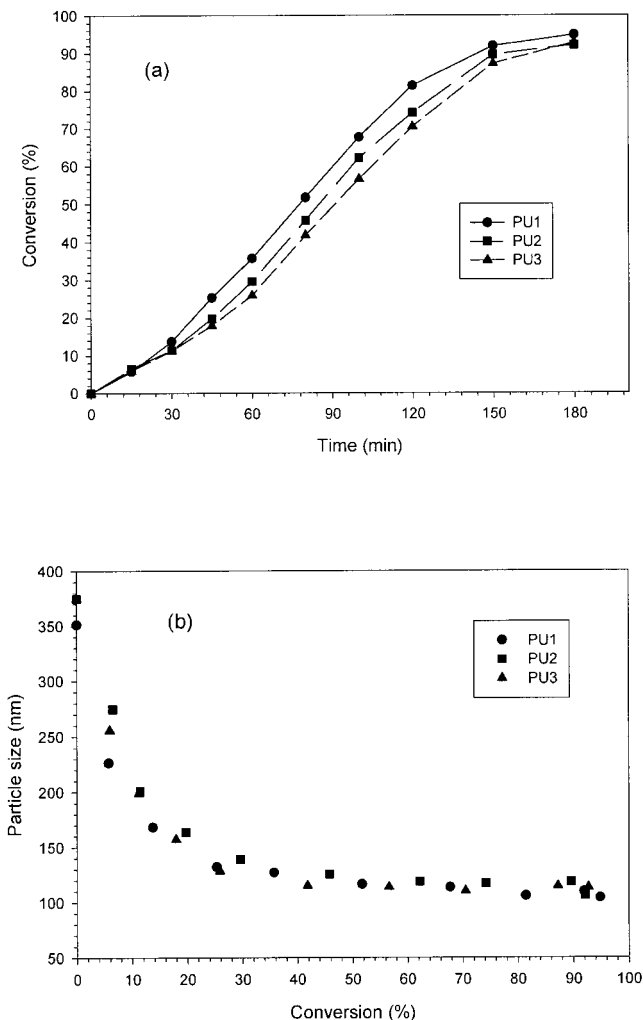
of its lower solubility. The redox initiator system (KPS + NaHSO<sub>3</sub>) was designed to investigate the effect of temperature on the stability of the droplets and, therefore, on the polymerization process. In comparing the evolution of the particle size initiated with KPS and that with KPS + NaHSO<sub>3</sub> in Figure 4(b), we can deduce that decreasing the reaction temperature has no visual influence on the evolution of the particle size and, therefore, cannot increase the proportion of the droplet nucleation.

It has been reported that the dominant nucleation mechanism of the miniemulsion prepared with HD as a costabilizer is droplet nucleation and some pre-dissolved polystyrene in the St monomer can increase the rate of the polymerization because of the "enhanced droplet nucleation."<sup>6,15,33</sup> The presence of the polystyrene, however, has no effect on the evolution of the particle size during the polymerization when AIBN is used as an initiator.<sup>34</sup> In comparing the droplet sizes with the particle sizes in Table III, we can see that some homogeneous nucleation was occurring in these systems ([SDS] was less than the CMC). The conversion-time curves of the miniemulsions prepared with different costabilizers (Fig. 5) indicate that the miniemulsion prepared with HD has a slower rate of polymerization than that of the miniemulsions pre-dissolved with 2 wt % PU1 in the St monomer when using AIBN as the initiator. However, the miniemulsions prepared with PU1 and HD + PU1 have a similar rate of polymerization although the latter has a much longer shelf life (see Table II). This shows that "enhanced droplet nucleation" is still effective in these systems, although homogeneous nucleation existed. It is also hints that homogeneous nucleation plays an important role during polymerization.

Using AIBN as an initiator, the effect of the different polyurethane resins on the kinetics and evolution of the particle size is shown in Figure 6. The kinetic



**Figure 5** Curves of conversion with time with different costabilizers.

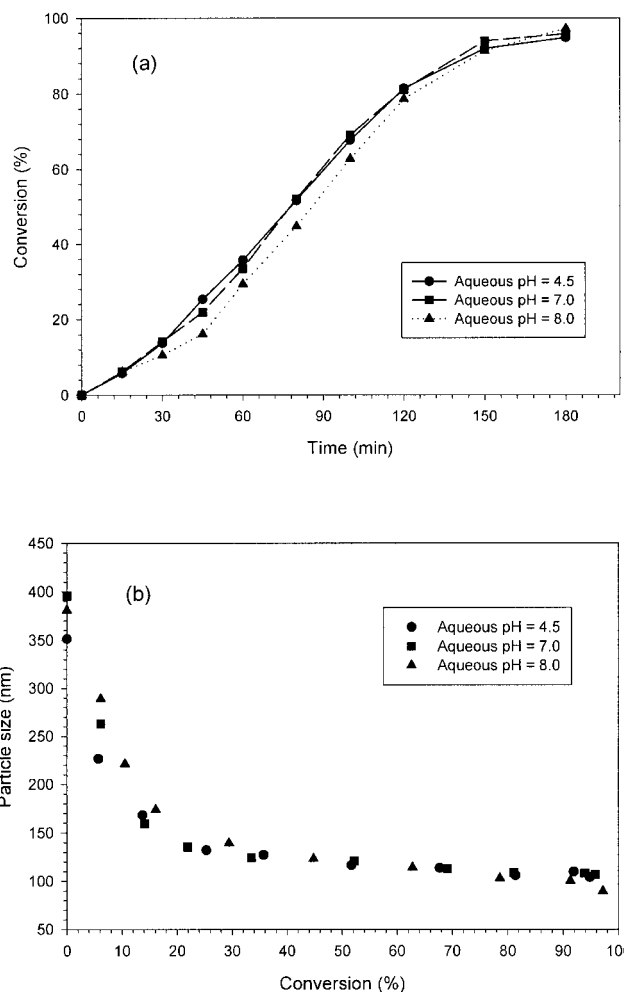


**Figure 6** Kinetic curves and evolution of the particle size during miniemulsion polymerization costabilized by different polyurethane resins.

curves show that the miniemulsion prepared with PU1 has the highest rate of the polymerization and the miniemulsion prepared with PU3 (lower molecular weight compared to PU1) has the lowest rate of polymerization. For an oil-soluble initiator, single radicals are formed by desorption of radicals from the particles into the aqueous phase and the entry of the hydrophobic reactive oligomer produced in the aqueous phase.<sup>35,36</sup> The hydrophilicity of the particle surface disfavors the hydrophobic radical desorption from the particles and the entry of the lipophilic reactive oligomers. As mentioned above, the miniemulsion prepared with PU3 has a higher hydrophilicity of the droplet interface because the molecules can diffuse to the interface of the droplet and aqueous phases more easily. However, the miniemulsion prepared with PU1, which is lower in acid number than is PU2 and has a higher molecular weight than that of PU3, has the lowest hydrophilicity. This deduction is supported by the zeta potential of the latex particles listed in Table III.

From the evolutions of particle size during the polymerization, we can see that the particle size decreases until the conversion reaches about 40–60%. This means that homogeneous nucleation existed during the polymerization besides the droplet nucleation. Also, we can deduce that the nucleation period lasts to a monomer conversion of 40–60%. It is coincident with the results observed by Miller et al.<sup>37</sup> but discordant with the results observed by Fontenot and Schork<sup>12</sup> and Chamberlain et al.<sup>38</sup> in the St miniemulsion polymerization initiated by KPS. They found that the nucleation period lasts to 10–30% of the conversion.

The results in Figure 7(a) show that the initial rate of the polymerization decreased obviously when the aqueous pH increased from 4.5 to 8.0. However, there is no perceptible difference between the kinetic curves of the miniemulsion of the aqueous pH 4.5 and 7.0. This is agreement with the result observed in the shelf life. When the aqueous pH is adjusted above 7, the carboxylic group that diffused to the surface of the



**Figure 7** Kinetic curves and evolution of the particle size during miniemulsion polymerization with different aqueous pH's.

droplet will be neutralized and exist in the ionized form. This results in an increase in the hydrophilicity of the surface of the droplet or particle and, consequently, a decrease in the entry rate of the reactive oligomer and the desorption rate of the radicals from the particles. Also, this is demonstrated by the zeta potential of the latexes in Table III.

Figure 7(b) indicates that the particle size decreases; therefore, the particle number increases, until the end of the polymerization when the aqueous pH is at 8.0. In other words, nucleation never stops until the end of the polymerization. When the aqueous pH is below 7.0, the particle size decreases first and then levels off, that is, the nucleation ends at the conversion of 50%.

### CONCLUSIONS

Miniemulsion of St costabilized by carboxylated polyurethane can be prepared with monomer droplet sizes in the range of miniemulsion. However, it is not as efficient as is the conventional costabilizer HD. Addition of carboxylated polyurethane to the miniemulsion prepared by HD has no perceptible effect on the shelf life when the amount is low. However, it will decrease the stability of the miniemulsion when the amount is above 4.0 wt % based on the monomer. The shelf life of the miniemulsion is decreased with increase in the amounts of the polyurethane and the surfactant SDS. The alkaline condition and the smaller molecular weight are in favor of the stability of the miniemulsion costabilized by carboxylated polyurethane.

Homogeneous nucleation and droplet nucleation coexist in the polymerization of the miniemulsion costabilized by carboxylated polyurethane. Nucleation lasts to the conversion of 40–60% of the monomer in the acid medium but it continues until the end of the polymerization in an alkaline medium. The molecular weight and acid number of the polyurethane used have some effect on the nucleation process and the rate of the polymerization. An increase in the hydrophilicity of the droplet or particle surface decreases the rate of the miniemulsion polymerization initiated by AIBN.

The financial support by the Korea Institute of Science and Technology Evaluation and Planning (National Research Laboratory Program, Number M1-9911-00-0044) is gratefully acknowledged by the authors.

### References

- Schork, F. J.; Poehlein, G. W.; Wang, S.; Reimers, J.; Rodrigues, J.; Samer, C. *Colloids Surf A Physicochem Eng Asp* 1999, 153, 39.
- Dewald, R. C.; Hart, L. H.; Carroll, W. F., Jr. *J Polym Sci Polym Chem Ed* 1984, 22, 2931.
- Delgado, J.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Part A Polym Chem* 1986, 24, 861.
- 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.
- Reimers, J.; Schork, F. J. *J Appl Polym Sci* 1996, 59, 1833.
- Reimers, J. L.; Schork, F. J. *J Appl Polym Sci* 1996, 60, 251.
- Aizpurua, I.; Amalvy, J. I.; Barriaran, M. J. *Colloids Surf A Physicochem Eng Asp* 2000, 166, 59.
- Chern, C. S.; Chen, T. J.; Liou, Y. C. *Polymer* 1998, 39, 3767.
- Delgado, J.; El-Aasser, M. S.; Silebi, C. A.; Verhoff, J. W.; Guillot, J. *J Polym Sci Part B Polym Phys* 1988, 26, 1495.
- Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *Macromolecules* 1995, 28, 2754.
- Huang, H.; Zhang, H.; Li, J.; Cheng, S.; Hu, F.; Tan, B. *J Appl Polym Sci* 1998, 68, 2029.
- Fontenot, K.; Schork, F. J. *J Appl Polym Sci* 1993, 49, 633.
- Rodriguez, V. S.; El-Aasser, M. S.; Asua, J. M.; Silebi, C. A. *J Polym Sci Part A Polym Chem* 1989, 27, 3659.
- Samer, C. J.; Schork, F. J. *Ind Eng Chem Res* 1999, 38, 1801.
- Blythe, P. J.; Morrison, B. R.; Mathauer, K. A.; Sudol, E. D.; El-Aasser, M. S. *Langmuir* 2000, 16, 898.
- Tsavalas, J. G.; Gooch, J. W.; Schork, F. J. *J Appl Polym Sci* 2000, 75, 916.
- Wu, X. Q.; Schork, F. J.; Gooch, J. W. *J Polym Sci Part A Polym Chem* 1999, 37, 4159.
- Wang, S. T.; Schork, F. J.; Poehlein, G. W.; Gooch, J. W. *J Appl Polym Sci* 1996, 60, 2069.
- Van Hamersveld, E. M. S.; Van Es, J. J. G. S.; Cuperus, F. P. *Colloids Surf A Physicochem Eng Asp* 1999, 153, 285.
- Gooch, J. W.; Dong, H.; Schork, F. J. *J Appl Polym Sci* 2000, 76, 105.
- Wang, S.; Schork, F. J. *J Appl Polym Sci* 1994, 54, 2157.
- Reimers, J.; Schork, F. J. *Polym React Eng* 1996, 4, 135.
- Chern, C. S.; Liou, Y. C.; Chen, T. J. *Macromol Chem Phys* 1998, 199, 1315.
- Wang, S.; Poehlein, G. W.; Schork, F. J. *J Polym Sci Part A Polym Chem* 1997, 35, 595.
- Mouran, D.; Reimers, J.; Schork, F. J. *J Polym Sci Part A Polym Chem* 1996, 34, 1073.
- Reimers, J. L.; Schork, F. J. *Ind Eng Chem Res* 1997, 36, 1085.
- Wang, C. C.; Yu, N. S.; Chen, C. Y.; Kuo, J. F. *J Appl Polym Sci* 1996, 60, 493.
- Blythe, P. J.; Klein, A.; Phillips, J. A.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci Part A Polym Chem* 1999, 37, 4449.
- Alduncin, J. A.; Forcada, J.; Barriaran, M. J.; Asua, J. M. *J Polym Sci Part A Polym Chem* 1991, 29, 1265.
- Chern, C. S.; Liou, Y. C. *J Polym Sci Part A Polym Chem* 1999, 37, 2537.
- Fontenot, K.; Schork, F. J. *Ind Eng Chem Res* 1993, 32, 373.
- Ugelstad, J.; Mork, P. C.; Kaggerud, K. H.; Ellingsen, T.; Berge, A. *Adv Colloid Interf Sci* 1980, 13, 101.
- Blythe, P. J.; Klein, A.; Sudol, E. D.; El-Aasser, M. S. *Macromolecules* 1999, 32, 6952.
- Lfester, K.; Bechthold, N.; Forster, S.; Antonietti, M. *Macromol Rapid Commun* 1999, 20, 81.
- Capek, I.; Potisk, P. *Eur Polym J* 1995, 31, 1296.
- Asua, J. M.; Rodriguez, V. S.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci Part A Polym Chem* 1989, 27, 3596.
- Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *J Polym Sci Part A Polym Chem* 1995, 33, 1391.
- Chamberlain B. J.; Napper D. H.; Gilbert, R. G. *J Chem Soc Faraday Trans I* 1982, 78, 591.