

Kinetics of Miniemulsion Polymerization of Vinyl Acetate with Nonionic and Anionic Surfactants

X. Q. WU, F. J. SCHORK

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Received 16 May 2000; accepted 16 October 2000

ABSTRACT: The kinetics of miniemulsion polymerization of vinyl acetate, in which nonionic surfactant, Brij-35 [polyoxyethylene(23) lauryl ether], and hexadecane were used, was investigated. For comparison, experiments were also carried out using an anionic surfactant (sodium lauryl sulfate). The results show that, for all experiments, both distributions for the particle size of the latices and the molecular weight of polymers were unimodal. The effects of surfactant and initiator levels on the particle number and the polymerization rate were studied. For the system using Brij-35, the power orders for the dependence of particle number on surfactant and initiator concentrations were 1.33 and 0.68, respectively. The polymerization rate was proportional to the 0.38 power of surfactant level and the 0.84 power of initiator concentration. The hydration layer outside the monomer-swollen particles in the system of nonionic surfactant may exert a retardation effect on the entry of oligomeric radicals into the particles. The result of GPC analysis indicates that the surfactant concentration inversely affects the molecular weight. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1691–1699, 2001

Key words: miniemulsion; polymerization; vinyl acetate; batch; nonionic surfactant; anionic surfactant

INTRODUCTION

A nonionic surfactant provides colloidal stabilization via a steric effect rather than an electrostatic repulsion effect as an ionic surfactant does. This feature decreases the sensitivity of latices to the pH or ionic strength in the aqueous solution, and provides additional freeze–thaw stability. An appropriately proportioned mixture of nonionic and ionic surfactants is often used to synergistically stabilize a colloidal system.

Surfactant plays a significant role in conventional emulsion (macroemulsion) and miniemul-

sion polymerization systems, in which the surfactant is considered preferentially absorbed onto the oil–water interfacial area. In the emulsion system, as a result of Ostwald ripening (the tendency of a monomer to diffuse from smaller monomer droplets to larger ones, to minimize the total interfacial energy of the system), the droplets are relatively large and the total interfacial area is unable to accommodate all of the surfactant. The unabsorbed surfactant molecules remain in aqueous phase and form micelles if the concentration of the surfactant is above the critical micelle concentration (CMC). In accordance with the Smith–Ewart (S-E) theory,¹ the nucleation of particles primarily occurs in micelles, and the droplets serve as monomer reservoirs, providing the monomer to the propagation loci. On the other hand, in a miniemulsion process, a coemulsification sys-

Correspondence to: F. Schork.

Contract grant sponsor: Air Products and Chemicals, Inc.

Journal of Applied Polymer Science, Vol. 81, 1691–1699 (2001)
© 2001 John Wiley & Sons, Inc.

tem of surfactant/hydrophobe can retard Ostwald ripening. Thus, very small monomer droplets produced by high shear rates can be stabilized. The submicron droplets with large interfacial area are capable of capturing most of the oligomeric free radicals and the droplets become the loci of nucleation. In addition, if a large fraction of the droplets are nucleated, then transport of monomer across the aqueous phase becomes less significant, because the preponderance of the monomer participating in the polymerization resides within the polymerizing droplet/particle. The preceding description holds for ionic surfactants, whereas this study focuses on the effects of a nonionic surfactant on the miniemulsion process.

Reported work demonstrated interesting features of the emulsion polymerization process stabilized by nonionic surfactant.^{2,3} In their work on emulsion polymerization with the nonionic surfactant Emulphogene BC-840 [octyl phenoxy poly(ethyleneoxy) ethanol], Piirma and Chang² found that the conversion–time profiles showed two constant rate regions. The transition point was at about 40% conversion. Bimodal particle size distributions (PSDs) and molecular weight distributions (MWDs) were reported. They noted that the surfactant solubility in the monomer was the primary reason for this phenomenon. A two-stage nucleation mechanism for particles (micellar nucleation below 40% conversion and a mixture of homogeneous and micellar nucleation above 40% conversion) was proposed to account for the features of the conversion–time curves. Ozdeger et al.³ investigated the role of the nonionic surfactant Triton X-405 in the emulsion polymerization of styrene. They also found two constant rate regions and bimodal PSD. By determining the partition coefficient of the surfactant, they found that, because of a high solubility of nonionic surfactant in the oil phase, the concentration of surfactant in the aqueous phase was lower than the CMC when the total amount of surfactant was below a certain value. In this case, they showed an initially slow, constant-rate region. Homogeneous nucleation was thought to occur in this region. At higher rates of conversion, the surfactant is released to the aqueous phase from the shrinking droplet phase, causing secondary micellar nucleation. If the total amount of surfactant was over the critical value, the concentration of surfactant in the aqueous phase exceeded the CMC, and the slow, constant-rate region disappeared.

According to the S-E theory, the polymerization rate during Interval II (R_p) and the particle number (N_p) exhibit the following relationships:

$$R_p = \bar{n}N_p k_p [M]_p / N_A \quad (1)$$

$$N_p \propto [S]^{n_s} [I]^{n_i} \quad (2)$$

where \bar{n} is the average number of free radicals in particles, k_p is propagation rate constant, $[M]_p$ refers to the monomer concentration inside the swollen-polymer particles, N_A is Avogadro's number, and $[S]$ and $[I]$ are the concentrations of surfactant and initiator, respectively. For the cases following the S-E theory, n_s and n_i are 0.6 and 0.4, respectively. However, investigations in the literature^{2,4–6} indicate that the involvement of nonionic surfactants in emulsion polymerization systems could lead to a significant deviation from the S-E theory. Chern et al.^{4,5} studied the emulsion polymerization of styrene using mixed SLS/NP-40 surfactants, and reported that the values of n_s and n_i varied at different ratios of SLS/NP-40. Piirma and Chang² reported n_s of 2.66 for the emulsion polymerization of styrene with Emulphogene BC-840. They interpreted this dramatic deviation from the S-E theory by introducing a concept of effective concentration of surfactant. Because of the high oil solubility of nonionic surfactant, the amount of surfactant playing an effective role in emulsification is much less than the total amount surfactant used. However, this effective concentration is not easy to determine, as they noted. Ozdeger et al.⁶ obtained the value of n_s of 2.67 at low surfactant level and 3.98 at high level in the emulsion copolymerization of styrene and butyl acrylate with Triton X-405.

Because of a different nucleation mechanism exhibited in miniemulsion polymerization, compared with that in macroemulsion polymerization, the possible effect of a nonionic surfactant must be much different. There are few reports of miniemulsion polymerization with nonionic surfactants. Wang and Schork⁷ used polymeric surfactant and hydrophobe as emulsifier and cosurfactant for miniemulsion polymerization. This treatment may avoid the adverse effect of the small-molecule surfactant and cosurfactant on the end-use properties of latices. Chern and Liou⁸ observed the influence of the mixed SLS/NP-40 surfactants on the miniemulsion polymerization of styrene in the presence of dodecyl methacrylate or stearyl methacrylate. Landfester et al.⁹ re-

ported work on styrene miniemulsion polymerization using polyoxyethylene(50) hexadecyl ether in the presence of hexadecane. Chern and Chen¹⁰ used NP-40 coupled with different hydrophobes as cosurfactants to observe the Ostwald ripening in the styrene miniemulsion systems. It was noted that the more hydrophobic the cosurfactant, the more effective it was in retarding the Ostwald ripening. Chern and Liou¹¹ studied the miniemulsion polymerization of styrene stabilized by NP-40/dodecyl methacrylate. The effects of surfactant, cosurfactant, and initiator on the polymerization rate, particle size, and nucleation features were discussed. Under the conditions of their experiments, they noted that the nucleation mechanism could be mixed micellar/droplet nucleation. The temperature of polymerization in their experiment was 80°C. At such a high temperature, the emulsifying effect of NP-40 may have been reduced significantly.

The main focus of the present work is to investigate the effect of nonionic surfactant on the kinetics of miniemulsion polymerization of vinyl acetate (VAc) using the nonionic surfactant, polyoxyethylene(23) lauryl ether (Brij-35). This study looks at miniemulsion polymerization with nonionic surfactant of VAc rather than styrene. We believe it is the first to do so, with the exception of Wang et al.,⁷ who used polyvinyl alcohol. Vinyl acetate differs substantially from styrene in its (quite high) water solubility. In addition, nonionic surfactants are generally not as soluble in VAc as in styrene. Finally, the range of nonionic surfactant used ranges down to approximately 2 wt % on monomer, a very low level for typical nonionic surfactants.

Some comparisons are made between the results obtained with nonionic and anionic surfactants. Furthermore, the effect of nonionic surfactant concentration on the molecular weight of polymer is observed.

EXPERIMENTAL

Materials

Reagent-grade VAc was provided by Aldrich Chemicals (Milwaukee, WI) and was treated with an inhibitor remover column (Inhibitor remover, disposable column, for removing hydroquinone and hydroquinone monomethyl ether; Aldrich) to remove the inhibitor. The purified VAc was stored at -2°C until used. Potassium persulfate (KPS,

Table I Recipes and Conditions of Experiment

Experiment Code	Surfactant/Content (mol/L water)	KPS (mol/L water)
B1	Brij-35/0.008	0.02
B2	Brij-35/0.02	0.02
B3	Brij-35/0.03	0.02
B4	Brij-35/0.05	0.02
B5	Brij-35/0.07	0.02
B6	Brij-35/0.02	0.01
B7	Brij-35/0.02	0.03
S1	SLS/0.008	0.02
S2	SLS/0.02	0.02
S3	SLS/0.05	0.02

Oil/(Oil + water): 0.3 wt; HD: 1.5 wt % in oil; oil + water: 300 g; temperature: 55°C; impeller speed: 300 rpm.

99%; Aldrich), polyoxyethylene(23) lauryl ether [Brij-35, C₁₂H₂₅(OCH₂CH₂)_{2n}OH, *n* ~ 23, \bar{M}_n ~ 1198, hydrophobic/lipophobic balance ~ 16.9; Aldrich], sodium lauryl sulfate (SLS, 98%; Aldrich), hexadecane (HD, 99%; Aldrich), and hydroquinone (98%; Fisher Scientific, Springfield, NJ) were used as supplied. The water was deionized before use.

Recipes and Conditions

The recipes and conditions of the experiments were as shown in Table I.

Polymerization

The cosurfactant (HD) was dissolved in VAc. A part of the recipe's total water (20%) was taken for the preparation of the initiator solution. Brij-35 was dissolved in the rest of the water. The monomer and surfactant solutions were mixed and stirred, to form a preemulsion. The miniemulsion was formed by sonicating the preemulsion with a Fisher 300-W Sonic Dismembrator working at a relative output of 60%. The miniemulsion was charged into a 500-mL reactor, equipped with nitrogen purging tube, cooling coil, condenser, thermometer, and stirrer. With nitrogen purging, the miniemulsion was heated to 55°C for 20 min. The initiator solution was then injected into the reactor to start the polymerization. Samples of 5–6 g were removed from the reactor with a syringe at intervals for gravimetric conversion analysis. The capped vials for collecting samples contained a little amount of 0.5 wt % hydroquinone solution to quench the polymerization in the samples.

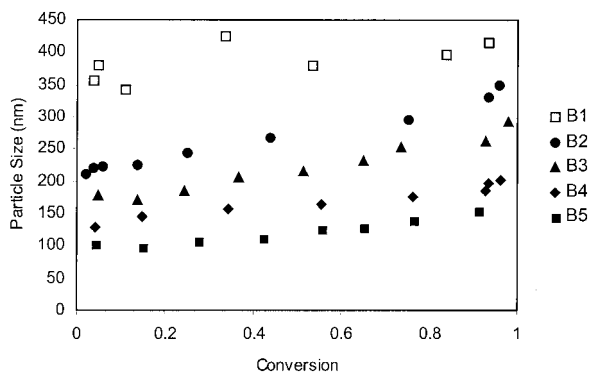


Figure 1 Particle size versus conversion with Brij-35.

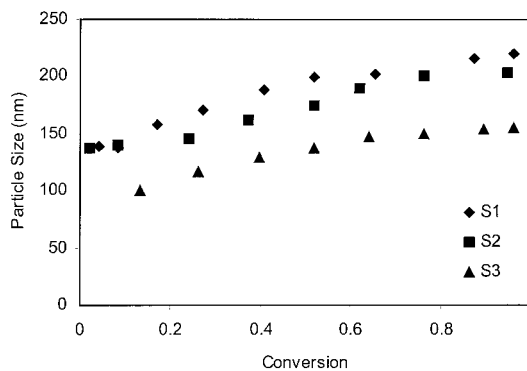


Figure 2 Particle size versus conversion for the system using SLS.

Particle Size

Polymer particle sizes were measured by light scattering with a ProteinSolution LSR-TC dynamic light scattering instrument. To measure polymer particle size, a drop of latex was diluted by a factor of several hundred with DI water. The diluted particle suspension was placed in a plastic cuvette for analysis.

Molecular Weight

A Waters gel permeation chromatography (GPC) system (Waters Instruments, Rochester, MN) was used to measure the molecular weight of the synthesized polymers. The GPC system included a Waters 2690 separation module, Waters 410 refractive index detector, and three columns (300×7.8 mm, in series, gel pore sizes of 10^3 , 10^4 , and 10^6 Å). The Waters Millennium³² software was used to calculate the molecular weight via conventional calibration relative to polystyrene standards. The samples were prepared by dissolving the dried latex in tetrahydrofuran (THF) at a concentration of 5 mg/ml THF. The GPC was operated at room temperature and a flow rate of mobile phase (inhibitor-free HPLC-grade THF) of 1.0 mL/min.

RESULTS AND DISCUSSION

Effect of Surfactant and Initiator on the Colloidal Property of Polymerized Latices

Several experiments with different Brij-35 or SLS levels were carried out to observe the effect of surfactant level on the particle size and number. Figures 1 and 2 show the relationships of particle size versus conversion at different surfactant lev-

els for both nonionic and anionic surfactants. An evident dependence of particle size on the surfactant level can be seen: the higher the surfactant level, the smaller the particle size. The particle size formed in the system with nonionic surfactant was significantly larger than the size in the system with anionic surfactant. This is also seen in macroemulsion polymerization.¹²

The latices produced in these systems were monodisperse, unlike the bimodal distributions reported in the literature for macroemulsion polymerization with nonionic surfactant.^{2,3} The polydispersity indices characterizing the distributions of particle size are shown in Figures 3 and 4. Using more nonionic surfactant appears to result in a more narrow distribution of particle size. However, when the Brij-35 level was more than 0.03 mol/L water, the differences in polydispersity index were negligible. At low surfactant level, the particle size and polydispersity fluctuated drastically with monomer conversion, which implies

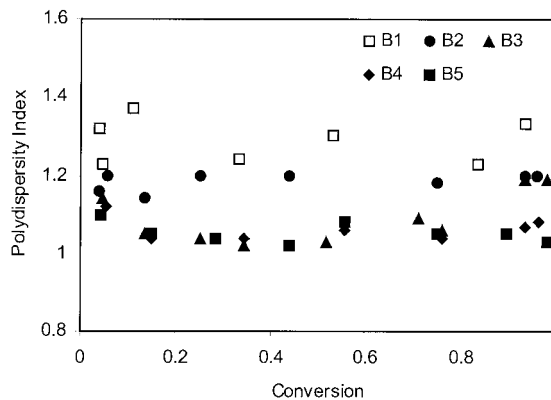


Figure 3 Polydispersity index of particle size distribution versus conversion for B1–B5.

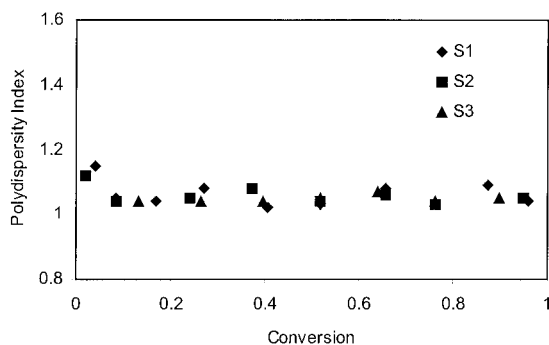


Figure 4 Polydispersity index of particle size distribution versus conversion for S1–S3.

that the colloidal system produced with too low an amount of nonionic surfactant is not very stable. However, in the system with SLS, this instability does not exist in the experimental range. As expected, the anionic surfactant was more effective than the nonionic for emulsification and stabilization in the miniemulsion process.

The particle number–conversion relationships at various surfactant levels are shown in Figures 5 and 6. The data indicate that the nucleation of particles occurs until 20 to 40% monomer conversion. However, for the cases of high surfactant level, the nucleation continued into the high conversion region. Comparisons between B1 and S1, B2 and S2, or B4 and S3 indicate that the anionic surfactant produces more particles than does the nonionic surfactant at the same concentration. To correlate the dependence of the particle number of the final latex N_p on the surfactant concentration $[S]$, log–log plots of N_p versus $[S]$ are shown in Figure 7. The order of the dependence of N_p on $[S]$ (n_s) estimated from the slopes of lines through

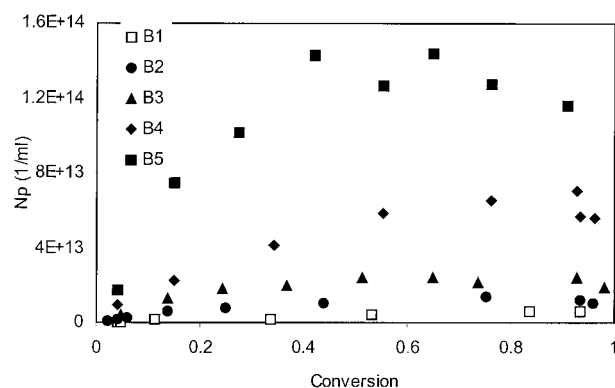


Figure 5 Particle number versus conversion with Brij-35.

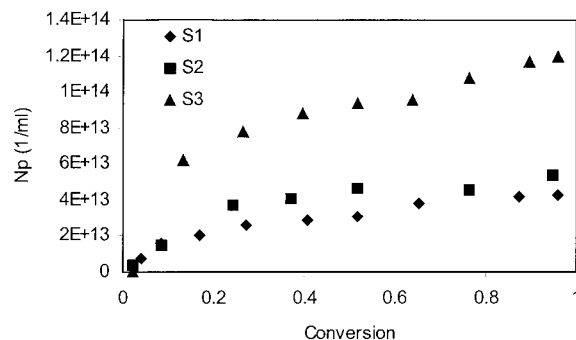


Figure 6 Particle number versus conversion with SLS.

the data were 1.33 for Brij-35 and 0.56 for SLS. The effect of surfactant level on the particle number is more pronounced in the Brij-35 system than in the SLS system. Delgado et al.¹³ found a 0.25 power dependence for the miniemulsion copolymerization of VAc–BA (50 : 50) with surfactant level less than 0.01 mol/L water. Fontenot and Schork¹⁴ reported a value of 0.77 in the miniemulsion polymerization of MMA. As mentioned in the previous section, in macroemulsion polymerization using nonionic surfactant, the order of dependence ($n_s = \sim 2.66$ – 3.98) is much higher than the order for the system using anionic surfactant ($n_s \sim 0.6$) because of the relatively high solubility of nonionic surfactant in the oil phase. This difference between nonionic and anionic surfactants for the miniemulsion system is not as drastic as that for the emulsion system, the reason for which can be attributed to the different particle nucleation mechanisms in the two systems.

The effect of initiator concentration on particle number in final latex was investigated under a condition of fixed Brij-35 level. A double-logarithmic relationship between N_p and $[I]$ is shown in Figure 8. The particle number is proportional to

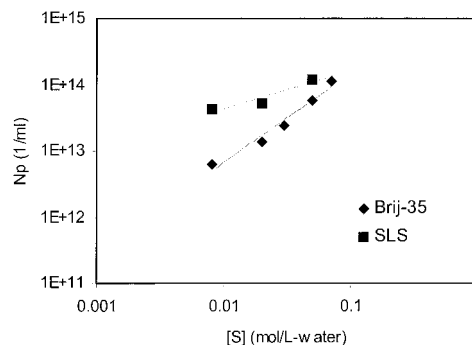


Figure 7 Particle number versus surfactant level.

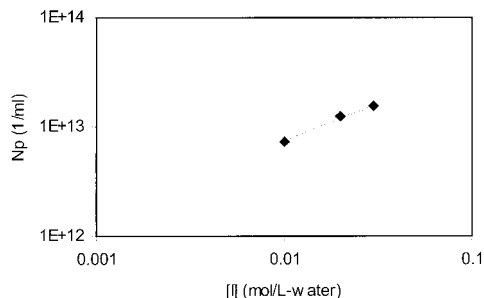


Figure 8 Particle number versus initiator level.

the 0.68 power of the initiator concentration. In the systems with anionic surfactant, the value of n_i was reported in a wide range from 0.11 to 0.8.¹³⁻¹⁵

Effect of Surfactant and Initiator on the Rate of Polymerization

The conversion-time curves for different surfactant levels are shown in Figures 9 and 10. There are no two constant-rate regions in the conversion-time curves, as noted in the case of macroemulsion polymerization with nonionic surfactant. The rate of polymerization, which can be calculated from the conversion-time curve, is approximately constant over the conversion region of about 15 to 45%. This range was used to calculate rates of polymerization. The double-logarithmic relationship between polymerization rate R_p and $[S]$ is shown in Figure 11 for the systems with Brij-35 and SLS, respectively. The slopes of lines give the order of dependence of R_p on $[S]$ as 0.38 for Brij-35 and 0.27 for SLS. The difference between the two systems is not significant. The result for SLS is in agreement with the data re-

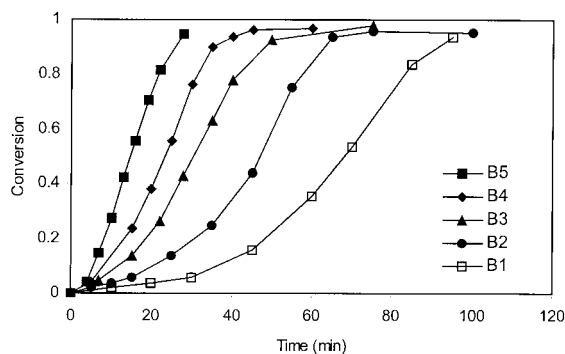


Figure 9 Conversion-time curves for various Brij-35 levels.

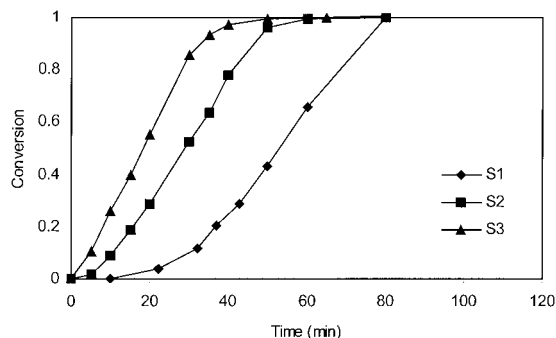


Figure 10 Conversion-time curves for various SLS levels.

ported in the literature for the system using anionic surfactant.^{13,14}

Based on the polymerization rate, particle number, and monomer concentration, the average number of radicals per particle \bar{n} can be estimated. The values of k_p and $[M]_p$ used for estimation are $6000 \text{ L mol}^{-1} \text{ s}^{-1}$ ¹⁶ and 7.075 mol/L particle (assumed at 35% conversion). There might conceivably be an effect of surfactant level on $[M_p]$ as a result of either a dilution of the monomer droplet with dissolved surfactant or a lowering of the interfacial tension, resulting in reequilibration of the monomer in the particles. These effects are thought to be negligible, although to eliminate this source of error, $[M_p]$ was calculated from the measured monomer conversion (i.e., $[M_p]$ was calculated at 35% monomer conversion, assuming 100% droplet nucleation, and R_p was estimated at the same point). Thus, the value of \bar{n} around 35% conversion was estimated and correlated with the concentration of surfactant, and is shown in Figure 12. For the system with nonionic surfactant, the value of \bar{n} depends significantly on the concentration of sur-

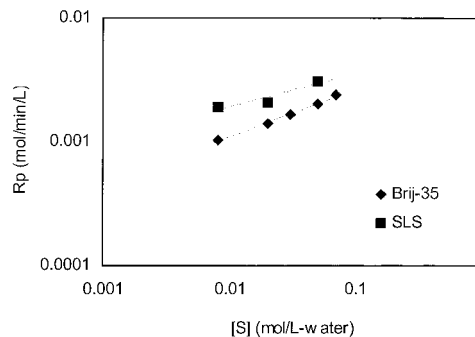


Figure 11 Polymerization rate versus surfactant concentration.

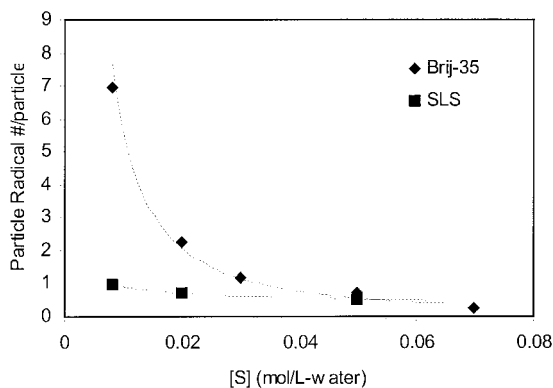


Figure 12 Average free radical number (per particle) versus surfactant concentration.

factant. Because the particle number varies from experiment to experiment, the free radical number per mole of monomer in particles \bar{N} [= \bar{n} /(mole monomer in particles at 35% conversion)] was estimated and plotted versus surfactant concentration (Fig. 13). It is clear that, at low surfactant concentration, \bar{N} is lower, although the larger monomer-swollen particle can accommodate more free radicals. With the increase of surfactant level, \bar{N} becomes higher and higher, and leads to the observed increase in the rate of polymerization. At the same surfactant concentration, the number of particles nucleated in the SLS system is much larger than that in the Brij-35 system. Thus, the effectiveness of free radical capture is much higher in the SLS system than that in the Brij-35 system, and \bar{N} is consequently higher.

Similarly, change in the average number of free radicals per particle with monomer conversion can be estimated based on $[M]_p$ at the corresponding conversion. This relationship is shown in Figure 14, from which one can see a marked

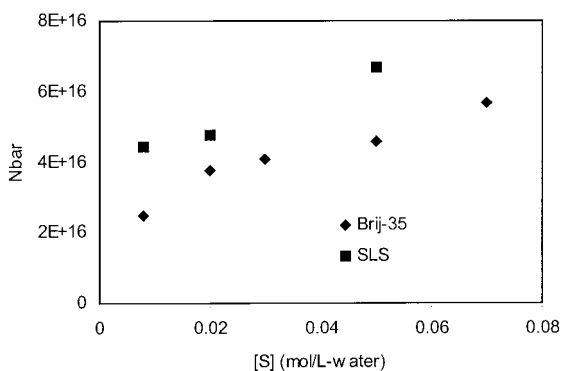


Figure 13 Free radical number (per liter particle) versus surfactant concentration.

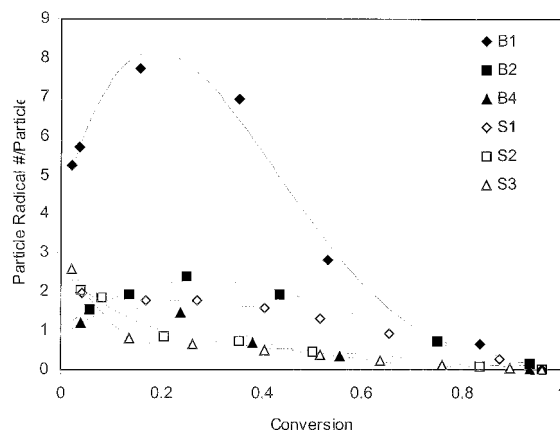


Figure 14 Average free radical number (per particle) versus conversion at various surfactant levels.

difference between nonionic and anionic surfactants. After initiation, \bar{n} for the nonionic surfactant goes up to a maximum then declines gradually. For the anionic surfactant, \bar{n} continuously decreases with increasing conversion. This behavior for the nonionic surfactant is probably caused by the barrier of the hydration layer at the surface of the particles. When Brij-35 is absorbed on the oil–water interface, hydrophobic lauryl groups will extend into the oil phase, whereas the hydrophilic polyoxyethylene will extend into the aqueous phase. Because of the hydration effect of the polyoxyethylene chain, a relatively stable and viscous hydration layer will be formed outside the monomer-swollen particles. This layer may hinder the oil-soluble oligomeric free radicals' entry into the particles, so that \bar{n} will go through a period from low to high. On the other hand, for the system using anionic surfactant, no such hydration layer exists and \bar{n} quickly reaches a maximum value after the system is initiated, then decreases as the monomer-swollen particle shrinks as a result of polymerization. Ozdeger et al.¹⁷ reported a similar tendency of retardation in the macroemulsion polymerization of butyl acrylate with the nonionic surfactant Triton X-405.

The effect of initiator on the rate of polymerization for the system using Brij-35 was investigated. The double-logarithmic relationship of polymerization rate versus the concentration of initiator is plotted in Figure 15. The polymerization rate is proportional to an exponential concentration of initiator. The order of dependence was estimated as 0.84, compared with about 0.39–0.6 for the miniemulsion process with anionic surfactant.^{13,14}

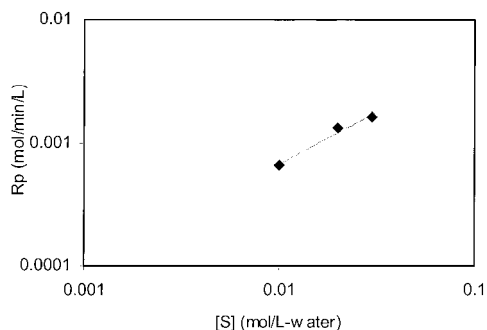


Figure 15 Polymerization rate versus initiator level at constant Brij-35 concentration.

Molecular Weight and Distribution

For experiment B2, the polymers collected at different conversions were analyzed by GPC. The elution spectra are shown in Figure 16. In each spectrum, the left peak is the polyvinyl acetate, and the right peak is primarily the Brij-35 ($\bar{M}_n \sim 1198$). The distributions of molecular weight at four conversions are nearly unimodal, unlike the reported results for macroemulsion polymerization with nonionic surfactant.² The molecular weights and distributions for these spectra are shown in Figure 17. With increasing conversion, the weight-average molecular weight \bar{M}_w increases quickly then begins to level off before the end of the polymerization. The rapid rise in molecular weight can be attributed to the strong tendency of vinyl acetate toward chain transfer to polymer and subsequent long-chain branching.

Figure 18 shows the GPC spectra for the final polymers produced at three Brij-35 levels. The average molecular weights and distributions are

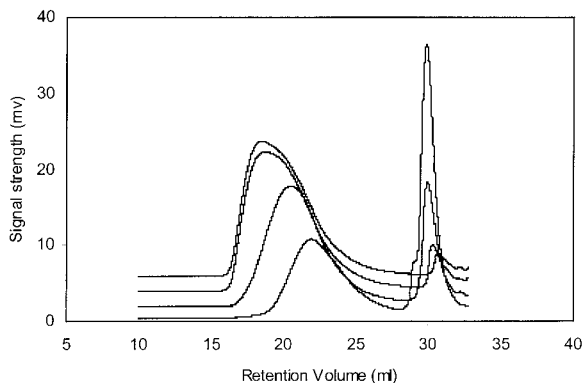


Figure 16 GPC elution spectra for the samples in experiment B2. (From bottom to top, the conversions are 0.06, 0.25, 0.75, and 0.96.)

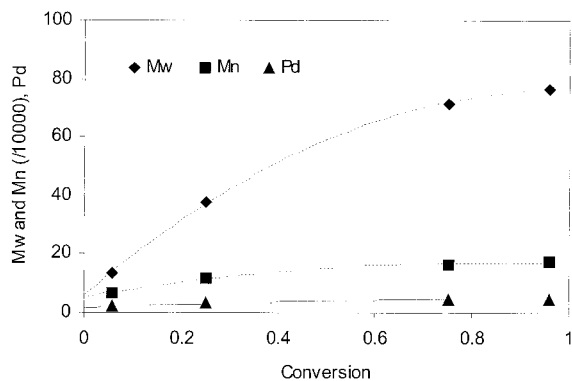


Figure 17 Molecular weight and polydispersity change versus conversion for experiment B2.

listed in Table II. There is an obvious influence of surfactant level on the molecular weight. At high surfactant levels, the molecular weight is decreased. This tendency may be interpreted by considering the number of radicals per mole of monomer in particles \bar{N} , which for B1 through B3 are 2.47 , 3.77 , and 4.56×10^{16} , respectively. As can be expected, a lower value of \bar{N} results in a higher average molecular weight. Also, there is likely a component of chain transfer to surfactant, causing a reduction in molecular weight with surfactant level.

CONCLUSIONS

This investigation of the miniemulsion polymerization of vinyl acetate using nonionic surfactant demonstrated that the shape of the conversion-time curve is similar to the one obtained in the system with anionic surfactant, and both distri-

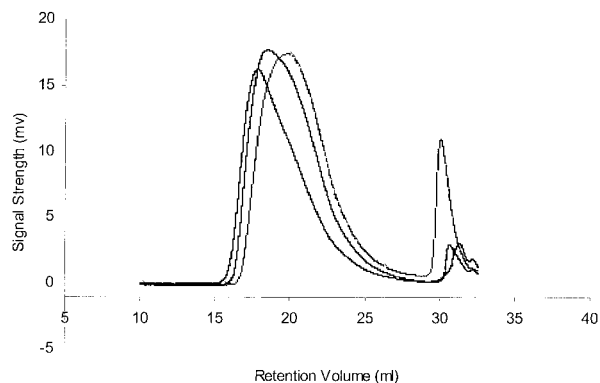


Figure 18 GPC elution spectra for final polymers at various Brij-35 levels. (From left to right, the spectrum codes are B1, B2, and B4.)

Table II Molecular Weight and Distribution for the Final Resultant Polymers

Experimental Code	M_w ($\times 10^4$)	M_n ($\times 10^4$)	Polydispersity
B1	98.25	21.51	4.568
B2	76.22	17.15	4.444
B4	57.78	14.42	4.008

butions for the particle size of the latices and the molecular weight of polymers are unimodal.

The number of particles produced in the miniemulsion polymerization is less with nonionic surfactant than with anionic surfactant. The order of dependence of particle number on surfactant level is 1.33 and 0.56, respectively. This difference between the two values is not as dramatic as is the case for the macroemulsion process because of the nature of the nucleation process. At the constant Brij-35 level, the particle number is proportional to the 0.68 order of the concentration of initiator.

The dependence order of the surfactant level on the polymerization rate for nonionic and anionic surfactants is similar, although the polymerization rate for the anionic surfactant is higher. The polymerization rate is dependent on the 0.84 power of the concentration of initiator. The hydration layer outside the monomer-swollen particles in the nonionic system surfactant may exert a retardation effect on the entry of oligomeric radicals into the particles.

The molecular weight of the resultant polymers is influenced by the concentration of surfactant, decreasing with the increase of concentration. This tendency can be correlated to the difference in the number of free radicals in per mole monomer in particles.

The authors gratefully acknowledge the financial support of Air Products and Chemicals, Inc.

REFERENCES

1. Smith, W. V.; Ewart, R. H. *J Chem Phys* 1948, 16, 592.
2. Piirma, I.; Chang, M. *J Polym Sci Part A Polym Chem* 1982, 20, 489.
3. Ozdeger, E.; Sudol, E. D.; El-Aasser, M. S.; Klein, A. *J Polym Sci Part A Polym Chem* 1997, 35, 3813.
4. Chern, C. S.; Lin, S. Y.; Chen, L. J.; Wu, S. C. *Polymer* 1997, 38, 1977.
5. Chern, C. S.; Lin, S. Y.; Chang, S. C.; Lin, J. Y.; Lin, Y. F. *Polymer* 1998, 39, 228.
6. Ozdeger, E.; Sudol, E. D.; El-Aasser, M. S.; Klein, A. *J Polym Sci Part A Polym Chem* 1997, 35, 3837.
7. Wang, S.; Schork, F. J. *J Appl Polym Sci* 1994, 54, 2157.
8. Chern, C. S.; Liou, Y. C. *Macromol Chem Phys* 1998, 199, 2051.
9. Landfester, K.; Bechthold, N.; Tiarke, F.; Antonietti, M. *Macromolecules* 1999, 32, 2679.
10. Chern, C. S.; Chen, T. J. *J Colloid Polym Sci* 1997, 275, 1060.
11. Chern, C. S.; Liou, Y. C. *Polymer* 1999, 40, 3763.
12. Gritskova, I. A.; Medvedev, S. S.; Margaritova, M. F. *Colloid J USSR* 1964, 26, 140.
13. Delgado, J.; El-Aasser, M. S.; Silebi, C. A.; Vanderhoff, J. W. *J Polym Sci Part A Polym Chem* 1990, 28, 777.
14. Fontenot, K.; Schork, F. J. *J Appl Polym Sci* 1993, 49, 633.
15. Choi, Y. T.; El-Aasser, M. S.; Silebi, C. A.; Vanderhoff, J. W. *J Appl Polym Sci* 1985, 23, 2973.
16. Brandrup, J.; Immergut, E. H. Eds. *Polymer Handbook*; Wiley: New York, 1975.
17. Ozdeger, E.; Sudol, E. D.; El-Aasser, M. S.; Klein, A. *J Polym Sci Part A Polym Chem* 1997, 35, 3827.