

Robust Nucleation in Polymer-Stabilized Miniemulsion Polymerization

J. REIMERS and F. J. SCHORK*

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

SYNOPSIS

The addition of a monomer soluble polymer to an emulsion was found to slow the effects of Ostwald ripening and impart diffusional stability to the droplets. Droplet nucleation was found to be the dominant nucleation mechanism in the polymerization of these polymer-stabilized miniemulsions (as distinguished from true miniemulsions). As a result these nucleations were more robust, and the polymerizations were less sensitive to variations in the recipe or contaminants levels. This was evident in the rates of polymerization and in the particle numbers. The miniemulsion polymerizations were subjected to changes in initiator concentration, a water-phase retarder, an oil-phase inhibitor, and agitation. Particle number was found to vary with each of these factors to the powers of 0.002, 0.02, 0.0031, and -0.026 , respectively. The corresponding exponents for conventional emulsion were one to two orders of magnitude greater. These results demonstrate the potential of miniemulsion polymerization to greatly reduce the variability in particle number found in conventional emulsion polymerizations. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Emulsions can degrade principally by two means: coalescence and diffusional degradation or Ostwald ripening. Coalescence can be precluded by the addition of a sufficient level of surfactant. Diffusional degradation may be slowed or even prevented by the addition of a monomer-soluble hydrophobe (often referred to as a cosurfactant). Hydrophobes lower the Gibbs free energy of the droplet, thereby decreasing the driving force for diffusion. Typically these hydrophobes have been long-chain alkanes and alcohols,¹⁻³ but recently the use of polymeric hydrophobes has been reported.^{4,5} These polymeric hydrophobes perform reasonably well, and have the added advantage of being innocuous in the recipe.

The inclusion of a small amount, approximately 4% (wt/wt), of a monomer-soluble polymer can significantly reduce the diffusional degradation of an emulsion. These emulsions are not thermodynamically stable, but they can be kinetically stable. This means that the droplets resist diffusional degrada-

tion long enough to allow nucleation to occur. The droplets are typically in the miniemulsion range of 100 to 500 nm in diameter. The small droplet size and consequent large droplet surface area result in most of the surfactant being adsorbed to the droplets with little free surfactant available to form micelles or stabilize aqueous-phase polymerization; hence there may be little or no micellar or homogeneous nucleation. The droplets become the primary locus of particle nucleation. The term "miniemulsion" is commonly used for systems in which particle nucleation is predominantly from small monomer droplets stabilized against Ostwald ripening. In the past, miniemulsions have been stabilized with long-chain alkanes or alcohols (termed "cosurfactants"), forming stable emulsions. As noted above, the use of polymer as the stabilizing agent results in emulsions which are only kinetically stable. To make this distinction clear, the polymer will be referred to as a hydrophobe rather than as a cosurfactant. The resulting emulsions have some of the characteristics of miniemulsion polymerization (droplet nucleation, low number of radicals per particles). We will refer to these materials as polymer-stabilized miniemulsions or, when it is clear to do so, simply as miniemulsions. The term "macroemulsion" will be used

* To whom correspondence should be addressed.

to describe conventional emulsion polymerization, in the absence of a cosurfactant or hydrophobe, in which the primary mechanisms of particle nucleation are micellar and/or homogeneous nucleation.

Droplet nucleation can lead to different polymerization kinetics and different characteristics of the final latex. In the sense of classical Smith-Ewart kinetics, polymerizations resulting exclusively from droplet nucleations would have no Interval II. There would be no dependence on the transport of monomer across the aqueous phase, which may be rate limiting in some macroemulsion polymerizations. In miniemulsion polymerization, radicals enter the droplets and initiate polymerization of the monomer inside them. In the early part of the polymerization, droplets can have higher radical numbers (because of their larger size) than particles nucleated from micelles. Therefore, the rate of polymerization per particle is higher and these systems are converted faster. The characteristics of the final latex may be affected by the nucleation scheme as well. The latexes produced from droplet nucleation tend to be more shear stable and, if other nucleation mechanisms are eliminated, more monodispersed and more reproducible.⁶

This paper deals with the nucleation phenomena in polymer-stabilized miniemulsion polymerizations. The robustness of these nucleations with respect to particle number and particle size distribution is examined. Specifically, the effects of agitation, the presence of inhibitors and retarders, and the concentration of initiator on the rate of polymerization and the number of particles are addressed. These findings are compared with results for equivalent macroemulsion polymerizations.

EXPERIMENTAL

The following is a list of reagents used in the polymer-stabilized miniemulsion polymerization and the macroemulsion polymerization of methyl methacrylate:

- Methyl methacrylate (MMA), inhibited with 10 ppm of hydroquinone, supplied by Aldrich Chemical (Milwaukee, WI). The monomer was washed with a 10% wt/wt solution of NaOH saturated with NaCl, and stored at 5°C.
- Deionized (DI) water.
- Sodium lauryl sulfate (SLS), used as supplied by BDH Limited (Poole, UK).

- Polymethyl methacrylate (PMMA), $M_w = 100,000$ g/gmol, used as supplied by Poly-science (Warrington, PA).
- Diphenylpicrylhydrazol (DPPH), stored at 5°C, used as supplied by Aldrich Chemical (Milwaukee, WI).
- Potassium persulfate, hydroquinone, and sodium nitrite, used as supplied by Fisher Scientific (Pittsburgh, PA).

Polymer-stabilized miniemulsions and macroemulsions were prepared from the following recipes:

Miniemulsion:

250 g DI water
96 g MMA
4 g PMMA
0.72 g SLS
0.034 to 1.352 g $K_2(SO_4)_2$

Macroemulsion:

250 g DI water
100 g MMA
1.44 g SLS
0.676 g $K_2(SO_4)_2$

A low surfactant level was used with the miniemulsions to ensure droplet nucleation. Emulsions were created by dissolving the polymer in the cleaned monomer with agitation from a stirring bar. Then the monomer/polymer solution or the monomer, in the case of macroemulsions, was added to a surfactant solution. This solution contained 200 g of the water and the SLS. Miniemulsions were sonicated with bulk mixing for 10 min at 60% output (180 W) with a Fisher 300 W model sonic dismembrator. The macroemulsions did not undergo sonication. The emulsions were then transferred to a reactor maintained at 60°C and purged with nitrogen for 5 min. Agitation was provided by a paddle-wheel stirrer rotating at 300 ± 7 rpm. An initiator solution, consisting of the persulfate and the remaining water, was charged at the end of 5 min. The course of the reaction was followed by gravimetric analysis. Ten-milliliter samples were drawn up through a syringe every 10 min for a total of 9 samples. These samples were quenched in a 1% solution of hydroquinone and cooled to 5°C. After cooling, the samples were transferred to preweighed aluminum dishes and allowed to dry for 24 h. Conversion was calculated from the dry solids content.

Initiator Dependence

The initiator concentration of the polymer-stabilized miniemulsion polymerizations was varied from

Table I Results of Polymer-stabilized Miniemulsion Polymerizations

[I]	D_d (nm)	D_p (nm)	PDI_p	$N_p \times 10^{-17}$ (L ⁻¹)	N_p/N_d	R_p (mol/min L _{aq})
0.0005	118.1	105.1	1.013	4.452	0.99	0.096
0.001	117.5	104.3	1.015	4.508	1.00	0.102
0.002	116.8	105.1	1.018	4.428	0.98	0.151
0.005	120.2	103.1	1.017	4.328	1.04	0.263
0.01	117.4	105.1	1.016	4.548	1.01	0.199
0.02	—	—	—	—	—	0.176
<hr/>						
[NaNO ₂]						
0.0	117.4	105.1	1.016	4.548	1.01	0.199
0.0001	115.1	103.3	1.027	4.432	0.99	0.253
0.0005	117.3	104.1	1.016	4.780	1.06	0.203
0.001	118.7	102.7	1.011	4.840	1.08	0.201
0.002	117.1	102.9	1.017	4.640	1.03	0.180
0.005	118.2	118.4	1.014	3.304	0.47	0.016
<hr/>						
[DPPH]						
0.0	117.4	105.1	1.016	4.548	1.01	0.199
0.00005	118.2	103.2	1.013	4.704	1.05	0.155
0.0001	118.4	103.3	1.012	4.720	1.05	0.149
0.0005	117.8	102.6	1.014	4.732	1.05	0.146
0.001	117.3	102.1	1.017	4.752	1.06	0.090
<hr/>						
RPM						
100	119.2	107.0	1.012	4.328	0.95	0.086
200	120.2	103.1	1.017	4.096	1.04	0.111
300	120.8	108.1	1.012	4.096	0.97	0.138
400	120.8	107.9	1.015	4.072	0.98	0.144
500	121.0	107.4	1.012	3.996	0.95	0.143

0.0005 to 0.02 M_{aq} , based on the total water content. The initiator solution was added after the nitrogen purge. The effects of this concentration on the number of particles and the rate of polymerization were determined.

Water-Phase Retarder Dependence

A water-phase retarder, sodium nitrite, was added to the aqueous phase of both the miniemulsions and the macroemulsions prior to initiation. The concentrations for both systems ranged from 0 to 0.005 M_{aq} , based on the total water present. The initiator concentration was held constant during these runs at 0.01 M_{aq} . Particle numbers and rates of polymerization for both systems were determined.

Oil-Phase Inhibitor Dependence

The dependence of an oil-phase inhibitor on the number of particles and the rate of polymerization in mini- and macroemulsions was also addressed. DPPH, a stable free radical, was dissolved in the monomer prior to initiation in both systems. The concentration ranged from 0 to 0.001 M , based on the oil phase. The initiator concentration for both systems was again held at 0.01 M_{aq} . Particle numbers and rates of polymerization for both systems were determined.

Agitation Dependence

The effects of agitation were investigated in the polymer-stabilized miniemulsion systems. The paddle-wheel stirrer speed was varied from 100 to 500

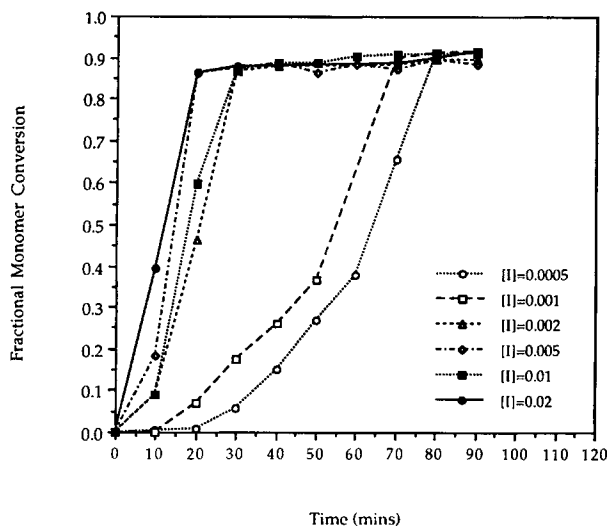


Figure 1 The effects of initiator concentration on the rate of polymerization of polymer-stabilized miniemulsions.

rpm. An initiator concentration of $0.002M_{\text{aq}}$ was chosen for these runs. The dependence of the rate of polymerization and the number of particles on level of agitation on was determined.

Droplet and Particle Sizes

Droplet and particle sizes were measured with a Malvern Autosizer IIc. Droplet sizes were obtained by diluting an emulsion with a $0.005M_{\text{aq}}$ surfactant (SLS) solution saturated with monomer. The dilution was 50 : 1, based on volume. The diluted sample was placed in a quartz cuvette and the sample was analyzed. The reading was accepted if the percent merit was 75% or higher. Similarly, polymer particle sizes were obtained from the final latex. In this case they were diluted with a $0.005M$ surfactant solution.

RESULTS AND DISCUSSION

Results of the polymer-stabilized emulsion polymerizations are shown in Table I. Droplet sizes were found to vary between 115.1 and 121.0 nm. These are in accord with measurements made by Fontenot and Schork⁶ and Rodriguez⁷ for methyl methacrylate miniemulsions stabilized with hexadecane. The particles in the final products were close to the size of the droplets, ranging from 102.6 to 108.1 nm, with polydispersities ranging from 1.011 to 1.027. Therefore the number of droplets and the number of particles are comparable within the accuracy of the

particle sizing technique used. The ratio of the number of particles to the number of droplets (N_p/N_d) was shown to be between 0.95 and 1.08. Thus the majority of the droplets have been nucleated to form polymer particles. Miller and colleagues⁸ have found this to be the case when polymer (less than 1% on monomer) is added to a miniemulsion prepared with an additional cosurfactant, cetyl alcohol. Droplet nucleation leads to polymerization rates comparable to those for the corresponding macroemulsions. For equal concentrations of initiator, $0.01M_{\text{aq}}$, the rates are 0.199 and 0.233 g mol/min L_{aq} for the mini- and the macroemulsion polymerizations, respectively. However, the rates of polymerization for polymer-stabilized miniemulsions were found to be less sensitive to recipe variations. This is also the case with the particle numbers; they are more robust to recipe variations than the corresponding macroemulsions, as shown below.

Initiator Dependence

The effects of the initiator concentration on the polymerization of polymer-stabilized miniemulsions is shown in Table I and in Figure 1. Reference to Table I indicates that an increase in the initiator concentration does not change the number of particles, but does increase the rate of polymerization. Therefore, the rate per particle must be increasing. This is due to an increase in the number of radicals per particle. However, the number of radicals per particle ranged only from 0.5 to 0.8, indicating that

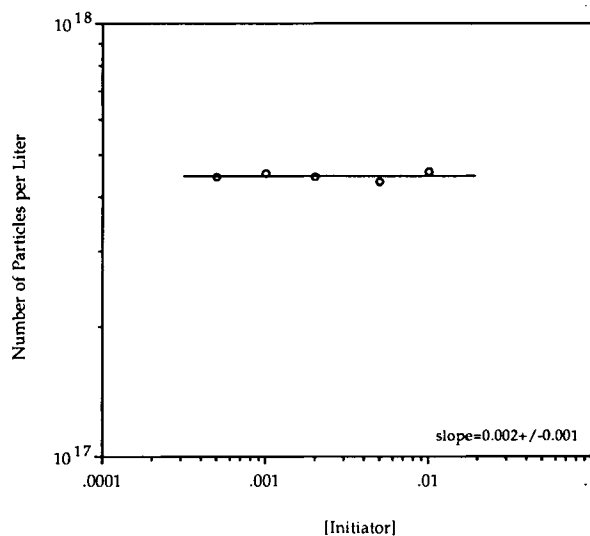


Figure 2 The effects of initiator concentration on the number of particles in a polymer-stabilized miniemulsion polymerization.

Table II Results of Macroemulsion Polymerizations

[NaNO ₂]	D_p (nm)	PDI_p	$N_p \times 10^{-18}$ (L _{aq} ⁻¹)	R_p (mol/min L _{aq})
0.0	80.5	1.011	1.037	0.233
0.0001	82.2	1.013	0.991	0.213
0.0005	79.8	1.010	1.078	0.232
0.001	76.4	1.014	1.193	0.146
0.002	72.7	1.012	1.452	0.106
0.005	59.7	1.016	1.803	0.060

[DPPH]	D_p (nm)	PDI_p	$N_p \times 10^{-18}$ (L _{aq} ⁻¹)	R_p (mol/min L _{aq})
0.0	80.5	1.011	1.037	0.233
0.00005	76.4	1.014	1.244	0.296
0.0001	68.3	1.016	1.661	0.324
0.0005	63.0	1.014	2.136	0.158
0.001	61.6	1.015	2.168	0.106

the kinetics (after nucleation) are still essentially Smith Ewart Case III.

Figure 2 shows that in polymer-stabilized miniemulsion polymerizations, the number of particles is proportional to the initiator concentration raised to a power of 0.002 ± 0.001 . This implies a dependence between the two. The value of this relationship is lower than ones reported by Fontenet and Schork⁶ and Choi and coworkers.⁹ Fontenet and Schork found a value of 0.11 ± 0.05 for the hexadecane-stabilized miniemulsion polymerizations of methyl methacrylate. Choi and colleagues reported a value of 0.37 for the cetyl alcohol-stabilized miniemulsion polymerizations of styrene.

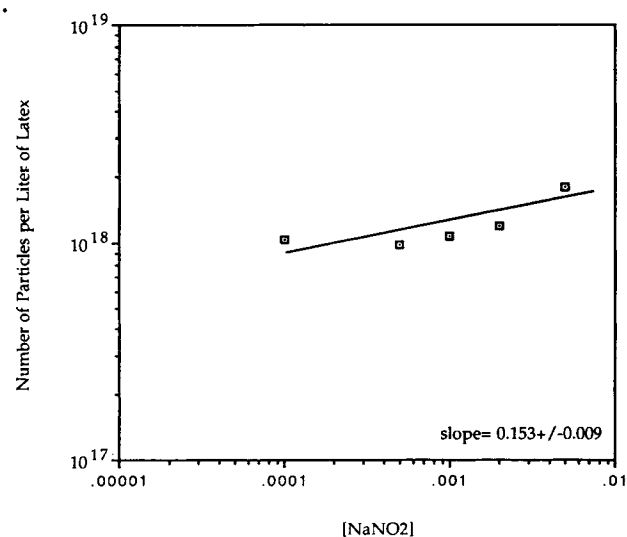


Figure 3 The effect of a water-phase retarder on the number of particles in macroemulsion polymerization.

Macroemulsion polymerizations, in contrast, show a dependence of 0.2 and 0.4 for methyl methacrylate and styrene, respectively.¹⁰ The fact that the exponent approaches zero indicates that all or nearly all the droplets are being nucleated.

Water-Phase Retarder Dependence

A water-phase retarder (sodium nitrite) was added to both the mini- and macroemulsion polymerizations. Table II shows the results for the macroemulsion experiments. The rate of polymerization is reduced with increasing levels of retarder as would be expected. However, the number of particles in-

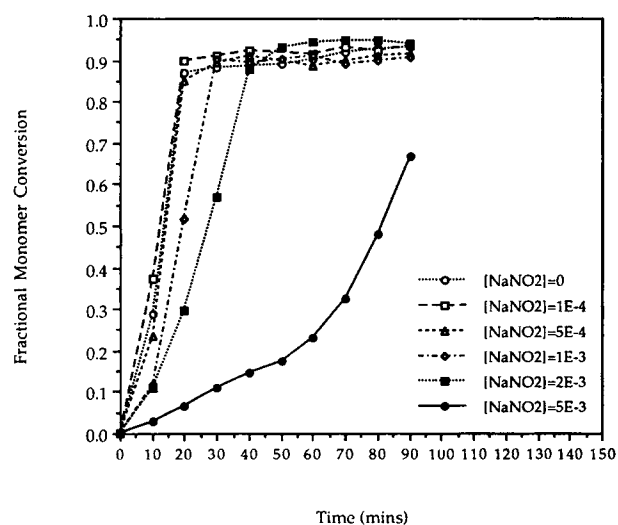


Figure 4 The effects of a water-phase retarder on the rate of polymerization of macroemulsion.

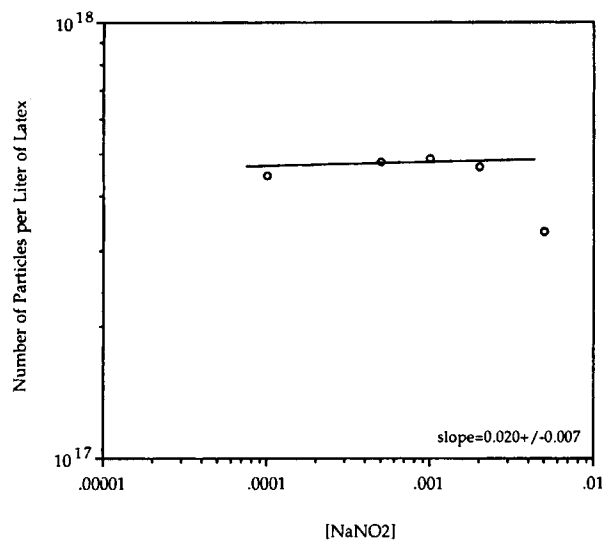


Figure 5 The effects of a water-phase retarder on the number of particles in a polymer-stabilized miniemulsion polymerization.

creased with increasing retarder concentration. This result would be expected only with an oil soluble retarder. The reason for this anomaly is unknown. A linear relationship on a log-log plot exists between the nitrite concentration and the number of particles, as depicted by Figure 3. The slope of this line is 0.153 ± 0.009 . This value is close to the value of 0.2 reported for the initiator dependence, perhaps implying that the function of the water-phase retarder is simply to reduce the effective radical flux to the particles. Rates of polymerization fell off at

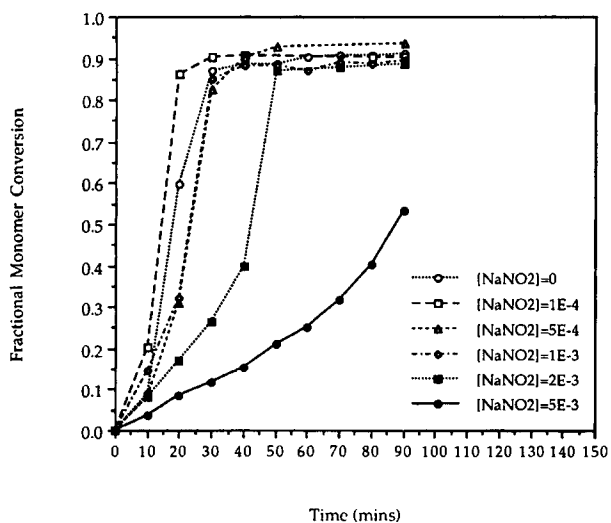


Figure 6 The effects of a water-phase retarder on the rate of polymerization of a polymer-stabilized miniemulsion.

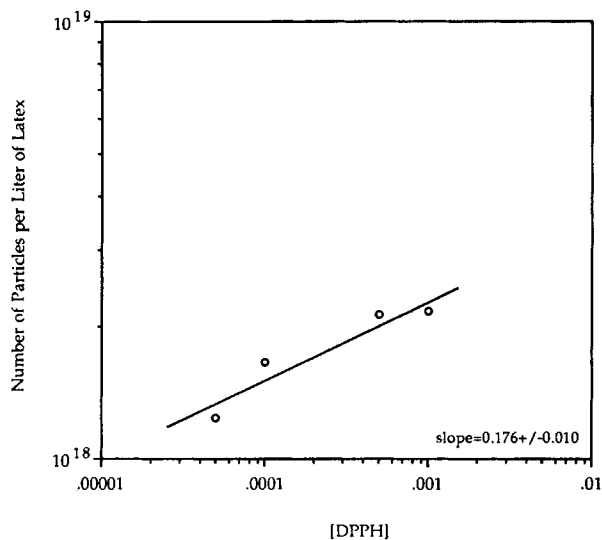


Figure 7 The effect of an oil-phase inhibitor on the number of particles in macroemulsion polymerization.

retarder concentrations greater $0.5 \text{ mM}_{\text{aq}}$. This is seen graphically in Figure 4 and numerically in Table II. Figure 4 also shows that the sodium nitrite is functioning as a retarder rather than an inhibitor, since no induction period was observed.

The polymer-stabilized miniemulsions are far less sensitive to the presence of the retarder than are the macroemulsions, as shown in Table I. The retarder has little effect on the rate of polymerization or the particle number. Particle numbers remained fairly constant up to a concentration of 5 mM_{aq} . Up to this amount, the dependence of the retarder concentration on the number of particles is calculated

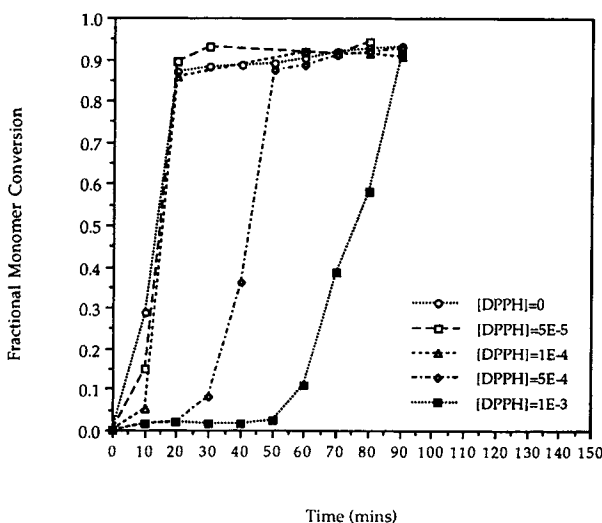


Figure 8 The effects of an oil-phase inhibitor on the rate of polymerization of macroemulsions.

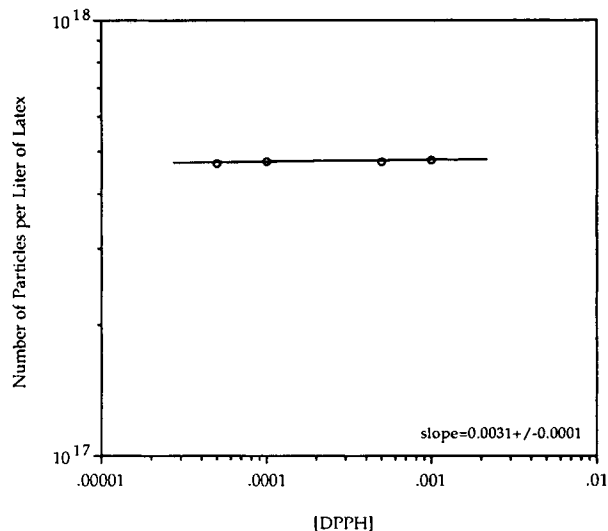


Figure 9 The effects of an oil-phase inhibitor on the number of particles in a polymer-stabilized miniemulsion polymerization.

to be 0.020 ± 0.007 (see Fig. 5). This is significantly less than the value found for macroemulsions. The influences of the nitrite on the rate are also minimal over a wide range of concentrations. Polymerization rates for miniemulsions doped with retarder remained uniform up to a concentration of 5 mM_{aq} , an order of magnitude higher than the corresponding value for the macroemulsions. Reference to Table I will confirm that at 5 mM_{aq} the particle number is substantially less than the droplet number. It is presumed that the high level of retarder prevents a large

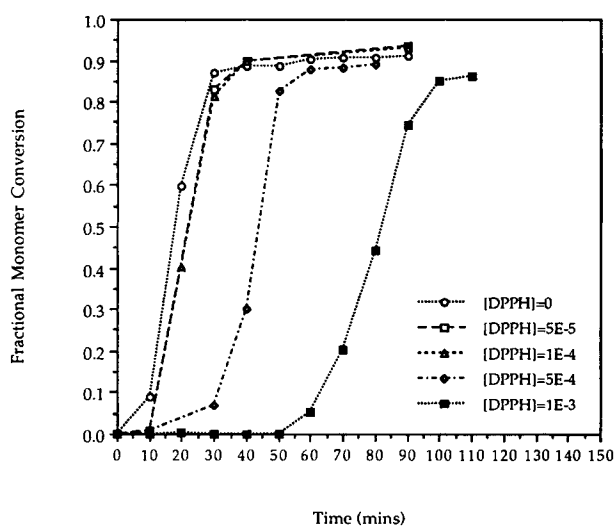


Figure 10 The effects of an oil-phase inhibitor on the rate of polymerization of a polymer-stabilized miniemulsion.

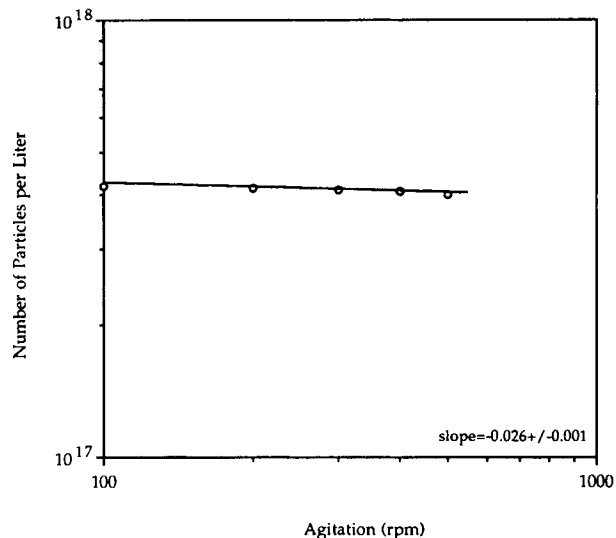


Figure 11 The effect of agitation on the number of particles in a polymer-stabilized miniemulsion polymerization.

fraction of the droplets from ever being nucleated. Figure 6 depicts the conversion-time curves for these polymerizations. The conversions exhibit prolonged nucleation periods, but the rates are not significantly affected. Again the nitrite is acting as a retarder, since no induction period is observed.

Oil-Phase Inhibitor Dependence

Macroemulsion polymerizations carried out in the presence of an oil-phase inhibitor (DPPH) resulted in an increase in the number of particles. Presum-

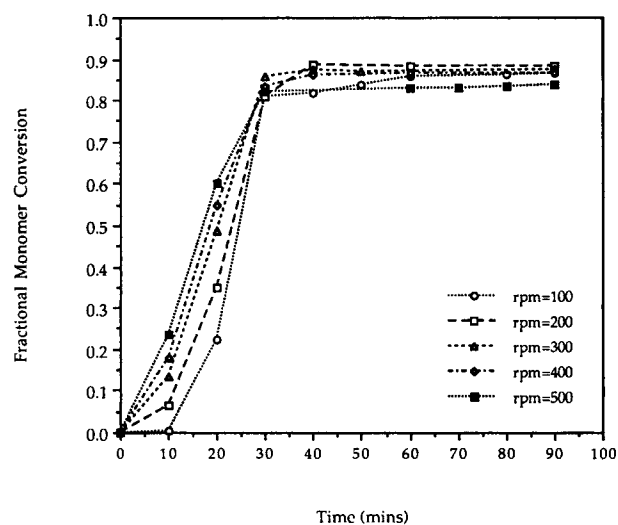


Figure 12 The effects of agitation on the rate of polymerization of polymer-stabilized miniemulsions.

Table III Summary of Dependence of Particle Number on Impurities and Operational Variations: $N_p \propto X^a$

X	a	
	Macroemulsion	Miniemulsion
[I] ¹	0.2 ^a	0.002 ± 0.001
[NaNO ₂]	0.153 ± 0.009	0.020 ± 0.007
[DPPH] ³	0.176 ± 0.010	0.0031 ± 0.0001
RPM	—	-0.026 ± 0.001

¹ [I] and [NaNO₂] in g mol/L_{aq}.

² From Reference 10.

³ [DPPH] in g mol/L_{mon}.

ably, initiator radicals that enter droplets are terminated by the inhibitor, resulting in dead particles. These particles do not grow, and hence do not consume surfactant to stabilize increasing surface area until they absorb another radical. The surfactant not adsorbed by dead particles is available to stabilize new particles, thereby increasing the total number of particles. Since the nucleation period is lengthened, the polydispersity increases, as seen in Table II. Figure 7 shows that the dependence of the inhibitor concentration on the number of particles is 0.176 ± 0.010 . This is close to the initiator and water-soluble retarder dependence—again implying that the nucleation is being affected.

Figure 8 shows the effects of the oil-phase inhibitor on the rates of macroemulsion polymerization. An induction period results from the presence of the inhibitor, but there is still a small amount of monomer conversion. This is presumably due to the creation of dead particles. The rate is seen to rise and then fall off at increasing DPPH concentrations. This is likely due to the offsetting effects of more particles and slower chain initiation.

Since polymer-stabilized miniemulsion polymerization occurs via droplet nucleation, it should be less sensitive to oil-phase inhibition. Initiator radicals will enter the droplet one after the other until all the inhibitor is used up and the monomer polymerizes. This does not affect the number of droplets or particles. As seen in Figure 9, the number of particles is proportional to the DPPH concentration raised to a power of 0.0031 ± 0.0001 . Thus, the number of particles is essentially independent of the inhibitor presence. This is also seen in the dependence on the rate of polymerization. In contrast to the macroemulsion polymerizations, there is no conversion during an induction period for the miniemulsions. Therefore no dead particles are being created. As a result, the rates of polymerization are

fairly constant up to DPPH concentrations of 1 mM (see Fig. 10). In addition, Figure 10 indirectly shows that the droplets are stable (against Ostwald ripening) for at least 50 min. This is the length of the longest induction period, which did not result in a change in the particle number.

Agitation Dependence

One of the advantages of macroemulsion polymerization is its insensitivity to changes in mixing. This makes it ideal for scale-up. To allay concerns with scale-up in polymer-stabilized miniemulsion systems, the effects of agitation on their polymerization was addressed. Rates of polymerization and number of particles were obtained for miniemulsion polymerizations carried out at various stirrer speeds from 100 to 500 rpm. The results appear in Figures 11 and 12.

Figure 11 shows that the number of particles is relatively independent of the agitation. This dependence on a log-log plot is a value of -0.026 ± 0.001 . It is not known why the particle number should decrease slightly upon agitation; perhaps some coalescence is occurring. Rates of polymerization are increased slightly by agitation, and then level off at stirrer speeds above 300 rpm, as seen in Figure 12. The polymerization at the slowest speed, 100 rpm, exhibited an induction period.

CONCLUSION

Polymer-stabilized miniemulsions can be prepared with monomer droplet sizes in the miniemulsion range. These smaller droplet sizes favor droplet nucleation, which dominates over mechanisms of micellar and homogeneous nucleation. As with most miniemulsions, the polymerized product is a latex with particle size in the range to be expected from a conventional emulsion polymerization. The majority of droplets in these miniemulsions are nucleated, as seen in the relative sizes of the droplets and the particles and in the number of each. The ratio of the number of particles to droplets ranges from 0.95 to 1.08.

Shifting the site of nucleation to the droplets greatly enhances the robustness of the nucleation process to recipe variations, inhibition levels, and changes in operating procedure (initiation rate and/or agitation rate). As a result of droplet nucleation, polymer-stabilized miniemulsion polymerizations are far less sensitive to these variations in operation. The particle number dependencies on the concen-

trations of initiator, water-phase retarder, oil-phase inhibitor, and agitation are shown in Table III. The exponents for the variation of particle number with each of these variations were 0.002, 0.02, 0.0031, and -0.026, respectively. The corresponding values for the macroemulsions were one to two orders of magnitude larger. Thus nucleation in polymer-stabilized emulsion polymerizations was found to be more robust than in macroemulsion polymerizations.

An enhanced robustness can benefit a process in a number of ways. Since the polymer-stabilized miniemulsions are less susceptible to disturbances, their polymerization is less likely to be affected by operator error, fluctuations in feed stream concentrations, and residual contaminants in the reaction vessel. Many monomers contain species that can act as inhibitors or retarders as a result of monomer production, storage, or processing. These contaminants also cause batch-to-batch variability in particle number in macroemulsions. In some extreme cases, nucleation of macroemulsions is near chaotic. Evidence that this is a significant problem is to be found in the wide application of seeded emulsion polymerization, which has been adopted in the coatings industry to provide reproducibility of particle number and hence particle size. The work herein indicates that miniemulsion polymerization may be an alternative to seeded polymerization as a way of maintaining robust control of particle number.

The support of the National Science Foundation in the form of Grant 9224813 is gratefully acknowledged.

REFERENCES

1. D. T. Barnette and F. J. Schork, *Chem. Eng. Progress*, **83**, 6, 25 (1987).
2. B. J. Chamberlain, D. H. Napper, and R. G. Gilbert, *J. Chem. Soc. Faraday Trans. 1*, **78**, 591 (1982).
3. D. P. Durbin, M. S. El-Aasser, E. D. Sudol, and J. W. Vanderhoff, *J. Appl. Polym. Sci.*, **24**, 703 (1979).
4. K. J. Fontenot, J. L. Reimers, and F. J. Schork, in *4th International Workshop on Polymer Reaction Engineering, DECHEMA Monographs*, Weinheim, Germany, 1992.
5. J. L. Reimers, A. H. P. Skelland, and F. J. Schork, *Polymer Reaction Engineering*, to appear.
6. K. J. Fontenot and F. J. Schork, *J. Appl. Polym. Sci.*, **49**, 633 (1993).
7. V. S. Rodriguez, Ph.D. Thesis, Lehigh University, Bethlehem, PA, 1988.
8. C. M. Miller, P. J. Blythe, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci., Part A, Polym. Chem. Ed.*, **32**, 2365 (1994).
9. Y. T. Choi, M. S. El-Aasser, E. D. Sudol, and J. W. Vanderhoff, *J. Appl. Polym. Sci.*, **23**, 2973 (1985).
10. G. Odian, *Principles of Polymerization*, 3rd ed., Wiley-Interscience, New York, 1988.

Received March 1, 1995

Accepted July 31, 1995