

Miniemulsion Polymerization—A Comparative Study of Preparative Variables

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SYNOPSIS

Variations in the conditions used to prepare miniemulsions of monomers in water have resulted in substantial differences in polymerization kinetics and final particle sizes and distributions. These variations have included (1) surfactant amount and type; (2) cosurfactant amount and type; (3) monomer(s) type; (4) temperature of preparation and polymerization; (5) means and conditions of homogenization; and (6) degree of aging of the emulsion. In an effort to unify some of the disparate information of previous work, a systematic study of some of the above variables was undertaken using styrene as the oil phase with sodium lauryl sulfate as surfactant. Based on the polymerization kinetics and particle sizes obtained, the following conclusions are drawn: The finest droplet size miniemulsions are obtained by (1) using a cosurfactant; (2) homogenizing at elevated temperature; (3) homogenizing using a uniform high shear device (Microfluidizer); and (4) limiting the aging time prior to polymerization.

INTRODUCTION

Miniemulsions are relatively stable submicron (50–500 nm) dispersions of oil (such as monomer) in water prepared by shearing a system containing oil, water, surfactant, and, additionally, a “cosurfactant.” The principle behind the making of stable miniemulsions is the introduction of a low molecular weight and relatively water-insoluble compound (the “cosurfactant”) inside the monomer droplets to retard substantially the diffusion of monomer out of the monomer droplets. It is well known that the chemical potential of a phase is a function of the molal surface area of that phase,¹ so a small crystal dissolves much faster than does a larger one and small droplets would have a higher vapor pressure than do the larger ones. In conventional emulsions, the smaller monomer droplets that have a higher chemical potential dissolve while the larger droplets grow at their expense; thus, conventional emulsions

are not stable and usually phase separate upon standing for a short time. However, in miniemulsions, the presence of a low molecular weight and relatively water-insoluble compound such as hexadecane or cetyl alcohol in the monomer droplets retards the diffusion of monomer out of the droplets. Higuchi and Misra² used diffusion theory to show that the diffusion of the more water-soluble compound in the droplets is governed by the diffusion of the water-insoluble one. Initially, when the monomer is broken up into droplets, some monomer would diffuse out of the smaller droplets, thus the concentration of the water-insoluble compound would be increased in the smaller droplets, until the concentration of the water-insoluble compound is high enough to offset the chemical potential of the smaller droplets and significantly retard the diffusion process. Some miniemulsions can be prepared that are stable upon standing for months.

For the cetyl alcohol system, the enhanced stability is also attributed to the formation of “intermolecular complexes” at the oil/water interface. These complexes would be liquid condensed and electrically charged, creating a low interfacial ten-

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sion and high resistance to droplet coalescence.³⁻⁶

In conventional emulsion polymerization, the principal locus of particle nucleation is the aqueous phase or the monomer swollen micelles depending on the degree of water solubility of the monomers and the amount of surfactant used; lower water solubility monomer and higher amounts of surfactant would favor particle nucleation in monomer swollen micelles.⁷ Monomer droplets are considered only to act as monomer reservoirs supplying monomer to the growing polymer particles. However, in the miniemulsion polymerization, the small size of the monomer droplets enables them to become the principal locus of particle nucleation. Thus, different conditions used in their preparation produce miniemulsions with different average droplet sizes and size distributions, which, in turn, exhibit different polymerization kinetics and final particle size distributions.

Since the introduction of miniemulsion polymerization in the early 1970s,⁸ many investigators have studied the subject and have used many different methods to prepare miniemulsions.⁹⁻¹⁷ The important parameters in preparing miniemulsions are the type and amount of cosurfactant (usually hexadecane or cetyl alcohol) and the means of carrying out the homogenization. Hansen and Ugelstad¹¹ used styrene as monomer, hexadecane as cosurfactant, and a two-stage homogenizer (Manton Gaulin S. A.) as the means of homogenization. Chamberlain et al.¹⁴ used styrene, cetyl alcohol, and a sonifier. Choi et al.¹⁵ used styrene, cetyl alcohol, and the Microfluidizer (Microfluidics Corp.). Delgado et al.¹⁶ used vinyl acetate and butyl acrylate as monomers, hexadecane as cosurfactant, and both the Omni mixer (Ivan Sorvall, Inc.) and a sonifier (Branson Sonic Power Co.), and Rodriguez¹⁷ used styrene and methyl methacrylate as monomers, both cetyl alcohol and hexadecane as cosurfactants, and a sonifier. This lack of consistency in the preparation of miniemulsions necessitates the evaluation of the effect of the different methods of preparing miniemulsions, particularly the effect on the polymerization kinetics and the final particle size distribution.

EXPERIMENTAL

Materials

Styrene (Polysciences) was distilled under reduced pressure (20 mmHg) of nitrogen. The purified monomer was stored at -2°C for no more than 4

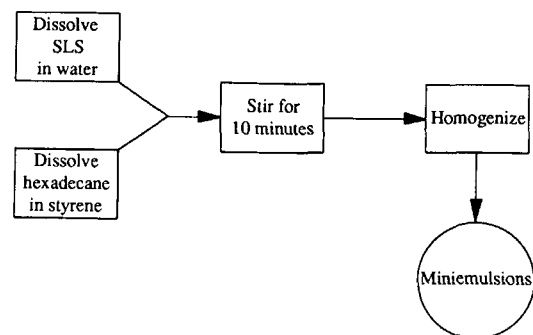
weeks before use. Potassium persulfate (FMC) was recrystallized from distilled deionized water and then dried at room temperature under vacuum. Sodium lauryl sulfate (BDH Chemicals), hexadecane (Aldrich), cetyl alcohol (Aldrich), and sodium bicarbonate (Fisher) were used as received. The water was distilled and deionized (DDI).

The Polymerization Process

The recipe used in this study consists of 80 wt % DDI water, 20 wt % styrene, with 2.66 mM sodium bicarbonate, 2.66 mM potassium persulfate, 5 or 10 mM sodium lauryl sulfate, and 15–40 mM (all based on water) cosurfactant (cetyl alcohol or hexadecane). The reaction temperature was 70°C .

There are some differences in the procedures for preparing styrene miniemulsions with hexadecane versus cetyl alcohol (Fig. 1). In the preparation of miniemulsions with hexadecane, sodium lauryl sul-

PREPARATION OF MINIEMULSIONS WITH HEXADECANE



PREPARATION OF MINIEMULSIONS WITH CETYL ALCOHOL

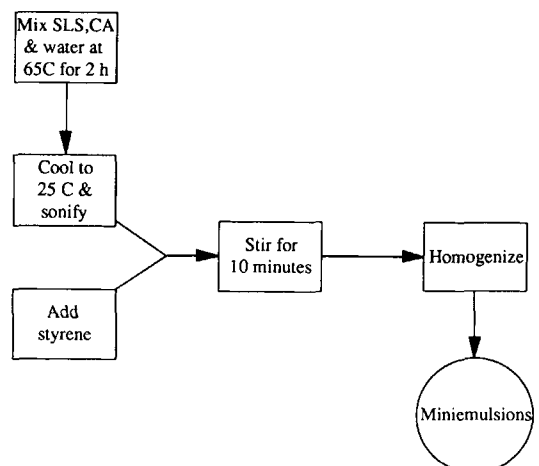


Figure 1 Method of preparation of stable miniemulsions with hexadecane (top) and with cetyl alcohol.

fate is first dissolved in the water and the hexadecane in the styrene monomer. The two solutions are mixed with a magnetic stirrer for 10 min followed by homogenization to break the monomer into the small droplets forming a miniemulsion. A few extra steps are involved in the preparation of miniemulsions with cetyl alcohol. Sodium lauryl sulfate, cetyl alcohol, and water are mixed at 65°C for 2 h, cooled to room temperature, and sonified to break up the gel phase.¹⁷ Styrene is then mixed with the gel phase for 10 min with a magnetic stirrer followed by homogenization to form the miniemulsion.

The Microfluidizer-110 (Microfluidics Corp.) and Sonifier Disruptor W-350 (Branson Sonic Power Co.) were used to provide the high shear required to produce submicron monomer droplets. In the Microfluidizer, the inlet stream is pressurized and forced into an interaction chamber. There it is directed into precisely defined microchannels, causing the streams to instantly accelerate to high velocities and, when recombined in the interaction region, to produce an emulsion with fine droplets and a narrow size distribution as a result of shear, turbulence, and cavitation forces.¹⁸ The sonifier produces rapid local pressure variations below the probe tip, bringing about cavitation and shear. The Microfluidizer is expected to produce more uniform monomer droplets than does the sonifier, because of its more uniform exposure of the entire fluid to the shear forces

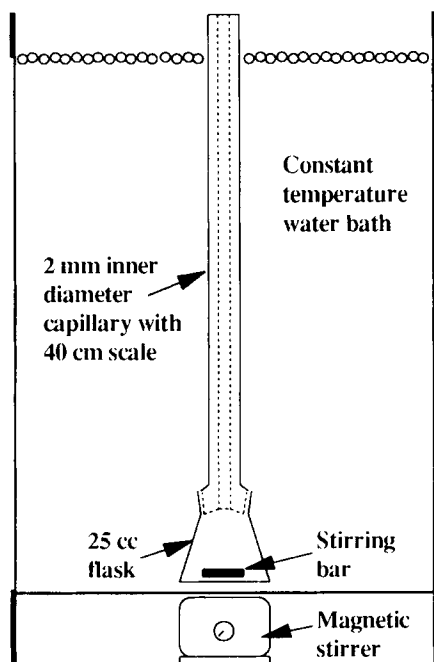


Figure 2 Schematic representation of the dilatometer used for monitoring polymerization kinetics.

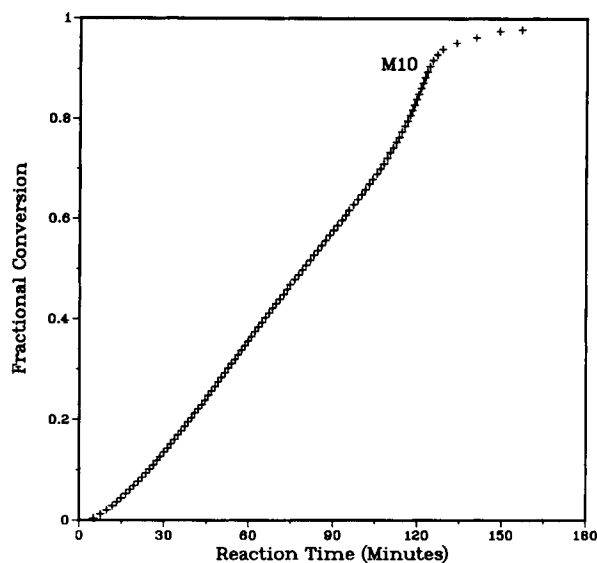


Figure 3 Conversion versus time curve of run M10 obtained by dilatometry.

breaking up the oil droplets. In this work, the Microfluidizer was operated at 80 psi inlet pressure and about 7000 psi outlet pressure with the smallest orifice size available (A10) and 10 passes of the emulsion. The sonifier was operated at 50% duty cycle and power 7 for 60 s of sonification time.

Dilatometry is applied to monitor the conversion-time behavior of the polymerizations. Its principle is based on the difference in density between monomer and polymer. Polystyrene has a density of 1.037 g/cc at 70°C, which is higher than the 0.860 g/cc of styrene at the same temperature.¹⁹ As the polymerization proceeds, styrene is converted to polystyrene, and this, in turn, causes the contraction of the volume of the mixture inside the dilatometer. Therefore, the conversion at time t can be calculated from the initial amount of monomer and the volume contraction at time t . Because the conversion depends on the volume change of the reaction mixture, the emulsion is degassed to avoid any gas bubbles from forming inside the dilatometer during the polymerization. The bath was controlled at a temperature of $70 \pm 0.02^\circ\text{C}$.

The apparatus used in this study is shown in Figure 2. The dilatometer is immersed in a constant temperature water bath that is controlled by a heating and circulating device. The mixture inside the dilatometer is kept uniform by a stirring bar and a magnetic stirrer. After the emulsion is degassed at a pressure of about 20 mmHg for 20 min using an aspirator, it is loaded into the 25 cc flask, and the capillary is quickly inserted to avoid entrapment of air between the flask and the capillary. It takes about

5 min for the mixture to reach 70°C. To start the polymerization, an initiator solution, also at 70°C, is injected into the dilatometer with a microsyringe connected to a small polyethylene tube. Much data can be obtained with frequent readings. Typical conversion-time behavior is shown in Figure 3, which contains about 100 data points.

Calibrated transmission electron microscopy (TEM) is used to determine the final latex particle size distribution. A monodisperse polystyrene standard with diameter of 824 nm is added to a latex sample before the sample is placed on a TEM grid. For samples with a wide particle size distribution, at least 1,000 particles are counted, and for narrow particle size distributions, at least 500 particles are counted.

RESULTS AND DISCUSSION

The conditions for all experiments are described in Table I. The variables in these experiments are the concentration of sodium lauryl sulfate, the type and

Table I Conditions of Polymerization of Emulsions Prepared by Different Methods

Run	Description
C2	"Conventional," Microfluidizer, 10 mM sodium lauryl sulfate (SLS)
C6	"Conventional," Microfluidizer, 5 mM SLS, 2 h unstirred at 25°C before initiation
C7	"Conventional," Microfluidizer 5 mM SLS, 1 h with stirring at 70°C before initiation
C8	"Conventional," Microfluidizer, 5 mM SLS
M6	Microfluidizer, 10 mM SLS, 30 mM cetyl alcohol (CA), monomer added to SLS-CA solution at 65°C
M10	Microfluidizer, 5 mM SLS, 15 mM CA, monomer added to SLS-CA solution at 65°C
M11	Microfluidizer, 5 mM SLS, 15 mM CA, monomer added to SLS-CA solution at 25°C
M12	Microfluidizer, 5 mM SLS, 20 mM hexadecane
M13	Sonifier, 5 mM SLS, 20 mM hexadecane

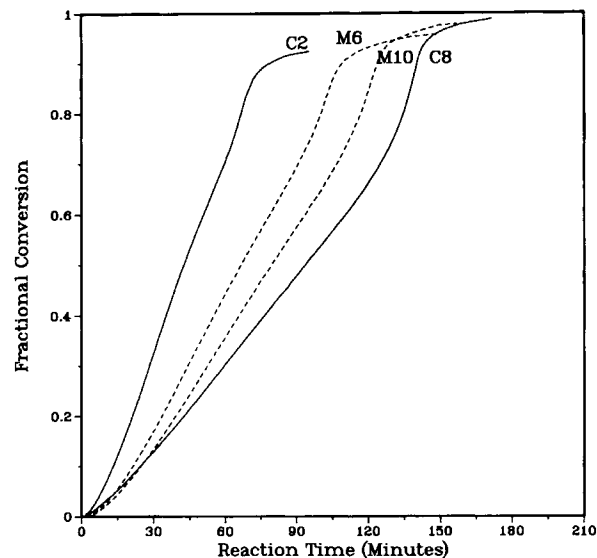


Figure 4 Conversion versus time curves for runs C2 (Microfluidizer, 10 mM SLS), C8 (Microfluidizer, 5 mM SLS), M6 (Microfluidizer, 10 mM SLS/30 mM CA), and M10 (Microfluidizer, 5 mM SLS/15 mM CA).

amount of cosurfactant, and the device used for homogenization.

Delgado et al.¹⁶ found that for the same surfactant concentration the overall rate of polymerization of a conventional emulsion system is usually faster than that of a miniemulsion system. Most of these comparisons were carried out with a total concentration of surfactant above its critical micelle concentration (cmc). The monomer swollen micelles are an order of magnitude smaller than the miniemulsion droplets, which means that the number of monomer swollen micelles is much larger than is the number of monomer droplets. Thus, more particles are nucleated in the conventional system than in the miniemulsion system. However, when the concentration of surfactant is below the cmc, the rate of polymerization is greater for the miniemulsion system because there are no monomer swollen micelles present in the conventional emulsion system. This phenomenon can be seen from the results given in Figure 4 in which the variables studied were the concentrations of sodium lauryl sulfate and cetyl alcohol. Curves C2 and M6 were obtained using recipes containing 10 mM sodium lauryl sulfate, whereas curves C8 and M10 contained 5 mM (the cmc of this surfactant was determined to be 7.4 mM). The recipe used to obtain the solid curves (C2 and C8) did not contain any cosurfactant, whereas those represented by the dashed curves contained cetyl alcohol. All these emulsions were

subjected to high shear with the Microfluidizer prior to polymerization. The results in Figure 4 show that for emulsions prepared with 10 mM sodium lauryl sulfate the polymerization kinetics of the "conventional" case (C2) is faster than that of the miniemulsion case (M6). However, for those prepared with 5 mM sodium lauryl sulfate, the polymerization kinetics of the "conventional" case (C8) is slower than that of the miniemulsion case (M10). These results also show that the polymerization rates of miniemulsions (M6 and M10) prepared with varying surfactant and cosurfactant levels do not differ as much as those (C2 and C8) prepared without cosurfactant. The final particle numbers (sizes) are consistent with the kinetic results (Table II); the faster polymerizations produced greater numbers of particles.

From the conversion-time data of Figure 4, the polymerization rate versus conversion is obtained as shown in Figure 5. These results indicate that the polymerization rates of all the runs exhibit similar behavior with respect to conversion; the polymerization rates increase to a maximum at about 30% conversion followed by a decrease. No significant constant rate period is observed. This phenomenon has been reported previously¹⁵ and would indicate that when the nucleation is predominantly in the monomer droplets it continues until all droplets disappear (by either nucleation or consumption by growing particles); thus, no constant rate period is seen. This postulate is supported by results found in a study of semicontinuous miniemulsion polymerizations by Tang et al.,²⁰ which showed that particle nucleation takes place whenever miniemulsion droplets are present in the reaction system. The polymerization rate continues to decrease until about 60% conversion when the gel effect, which

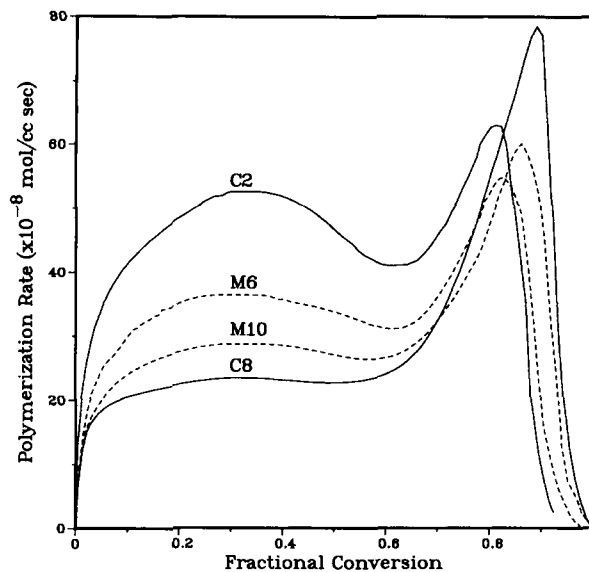


Figure 5 Polymerization rate versus conversion curves for runs C2 (Microfluidizer, 10 mM SLS), C8 (Microfluidizer, 5 mM SLS), M6 (Microfluidizer, 10 mM SLS/30 mM CA), and M10 (Microfluidizer, 5 mM SLS/15 mM CA).

brings about a decrease in the rate of termination inside the particle, causes the rate to increase. The polymerization rate continues to increase to about 85% when the particles reach their glass transition point,²¹ bringing about a reduction in the propagation rate and thus reducing the polymerization rate.

Another set of experiments was carried out to evaluate the effect of emulsion stability on the polymerization kinetics. The results are shown in Figure 6. The emulsions used in these experiments were prepared using the Microfluidizer but without cetyl alcohol, and they were polymerized after aging under varying conditions. These emulsions were relatively unstable without the cosurfactant, the droplets becoming larger with time due to their instability against diffusion degradation. The emulsion in run C8 was initiated just after degassing, whereas C7 was stirred at 70°C for 1 h and C6 was left unstirred for 2 h at room temperature before initiation. The results from Figure 6 show that the polymerization rate decreased with increased aging of the emulsion. These results are also consistent with the final particle numbers (Table II).

Different methods of preparing miniemulsions with the same recipe can also result in different kinetics and final particle concentrations. This can be seen from the results in Figure 7 in which miniemulsions were prepared with cetyl alcohol (see Fig. 1) and the only difference is that M10 was prepared

Table II Volume Average Diameter, Coefficient of Variation, and Final Particle Concentration Obtained by Polymerization of Emulsions Prepared by Different Methods

Run	D_v (nm)	S_n/D_n	$N_p \cdot 10^{13}/cc$
C2	115	0.13	26.8
C6	169	0.06	8.75
C7	168	0.05	9.34
C8	160	0.08	10.8
M6	134	0.12	18.4
M10	147	0.11	13.4
M11	168	0.14	9.36
M12	145	0.06	15.7
M13	271	0.18	2.5

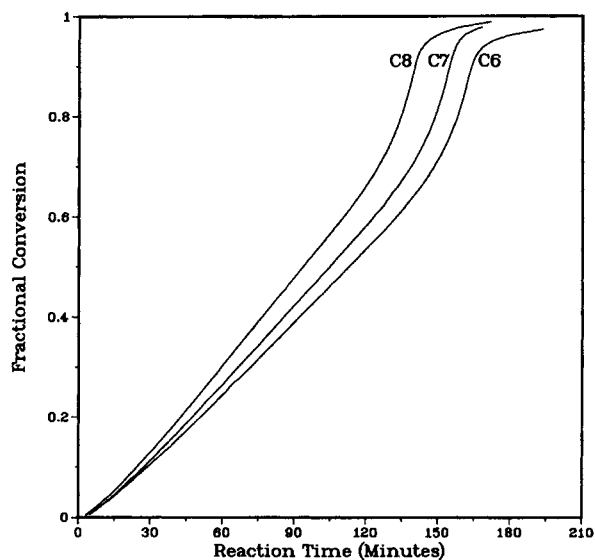


Figure 6 Conversion versus time curves for runs C8 (Microfluidizer, 5 mM SLS and no aging time), C7 (Microfluidizer, 5 mM SLS and one hour at 70°C) and C6 (Microfluidizer, 5 mM SLS and two hours at 25°C prior to polymerization).

without cooling the gel phase. The styrene was added to the gel solution (sodium lauryl sulfate, cetyl alcohol, and water) at 65°C before being homogenized with the Microfluidizer, whereas in run M11, the gel solution was cooled to room temperature and sonified to break up the gel phase before adding the sty-

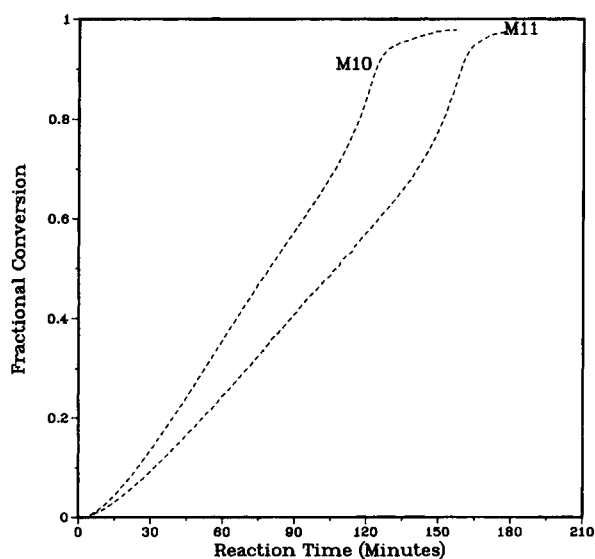


Figure 7 Conversion versus time curves for runs M10 (Microfluidizer, 5 mM SLS/15 mM CA, styrene added to the gel phase at 65°C) and M11 (Microfluidizer, 5 mM SLS/15 mM CA, styrene added to the gel phase at 25°C).

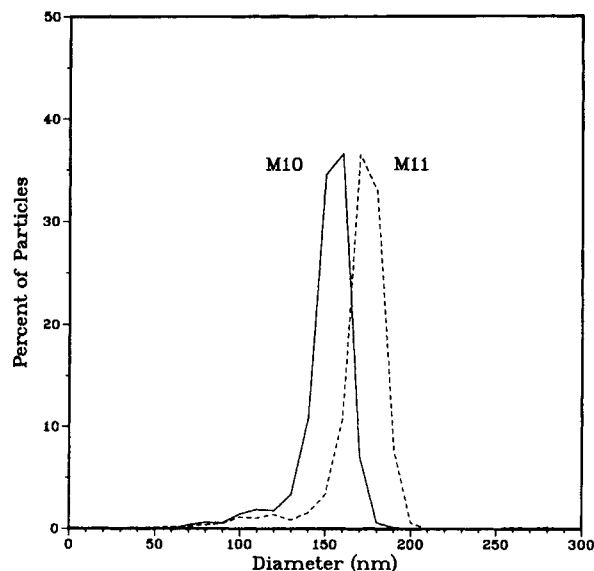


Figure 8 Particle size distributions for runs M10 (Microfluidizer, 5 mM SLS/15 mM CA, styrene added to the gel phase at 65°C) and M11 (Microfluidizer, 5 mM SLS/15 mM CA, styrene added to the gel phase at 25°C).

rene followed by homogenization. The kinetics of run M10 is significantly faster than that of run M11. This indicates that the emulsion droplets of run M10 are smaller than those of run M11. This is probably because the viscosity of the emulsion prepared at higher temperature (M10) is lower than that at room temperature (M11), allowing more effective homogenization. The final particle numbers are consistent with the kinetic results (Table II). The corresponding particle size distributions (Fig. 8) exhibit similar shapes and show a significant number of small particles. This indicates that some particle nucleation occurs continuously throughout the polymerizations.

Another study was carried out to evaluate the effect of the type of homogenization on the polymerization kinetics and final particle size distribution. The results are shown in Figure 9 in which the only difference is that the emulsion in run M12 was homogenized using the Microfluidizer, and in run M13, by the sonifier; both contained 20 mM hexadecane. The polymerization rate in run M12 was much faster than that of run M13, which agrees with the final particle numbers (Table II). Figure 10 shows that the particle size distribution of run M12 is much narrower than that of run M13 (which has a considerable number of large particles), which is consistent with the claim that the Microfluidizer provides a greater and more uniform shear than does the sonifier.

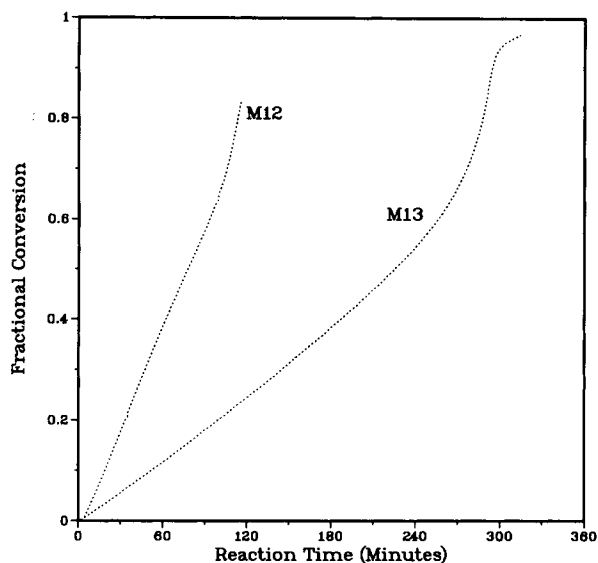


Figure 9 Conversion versus time curve for runs M12, homogenized with the Microfluidizer and M13, homogenized with the sonifier.

A comparison of the various methods of preparing miniemulsions can be made from the combined results illustrated in Figure 11. At conversions higher than about 30%, all runs exhibit similar kinetics, but at lower conversions, some differences can be noted. This region is magnified in Figure 12. The initial polymerization rates of the miniemulsions prepared with cetyl alcohol (M10 and M11) are

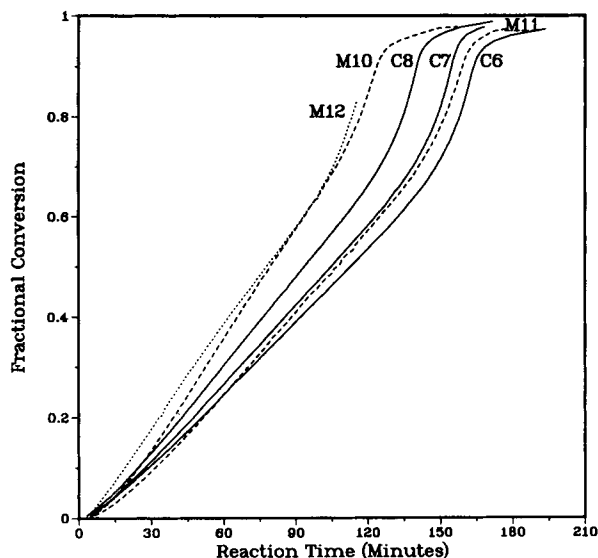


Figure 11 Conversion versus time curves for runs C6, C7, and C8, "conventional" cases; M10 and M11, miniemulsions with cetyl alcohol; and M12, miniemulsion with hexadecane.

slower than those prepared with hexadecane (M12) and those without cosurfactant (C6, C7, and C8). However, the rate in run M10 increases faster and surpasses those of the "conventional" cases. This may indicate that particle nucleation is slowed by the presence of cetyl alcohol on the surface of the monomer droplets. This is the subject of further investigations.

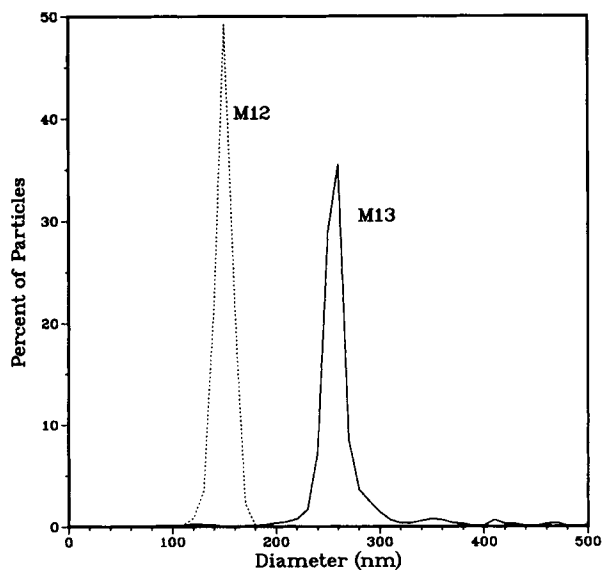


Figure 10 Particle size distributions for runs M12, homogenized with the Microfluidizer and M13, homogenized with the sonifier.

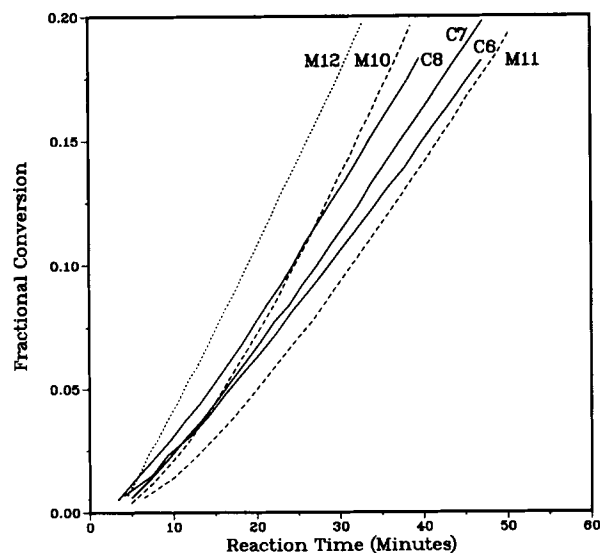


Figure 12 Conversion versus time curves magnified for runs C6, C7, and C8, "conventional" cases; M10 and M11, miniemulsions with cetyl alcohol; and M12, miniemulsion with hexadecane.

SUMMARY

A comparative study was carried out to evaluate the effect of the variation in parameters important to the preparation of styrene emulsions on the polymerization kinetics and the resulting particle size distributions. The variables studied were the type of cosurfactant and the means of homogenization. The results show that when the concentration of sodium lauryl sulfate is above its cmc, the overall rate of the "conventional" polymerization is faster than that of the miniemulsion system. However, it is the opposite when the concentration of sodium lauryl sulfate is below its cmc. When the emulsion is allowed to age, thereby increasing the monomer droplet size, the polymerization was found to decrease with aging time (or with increasing droplet size). Different temperatures used in preparing cetyl alcohol miniemulsions with the same recipe can also result in different kinetics; the miniemulsion prepared with styrene added to the gel solution at 65°C had a faster reaction rate than did the one prepared with styrene added to the gel solution at 25°C. The polymerization rates agree with the final particle size; the faster rates correspond to the smaller final particle size. The results indicate that, under the reported conditions, the Microfluidizer provides a greater and more uniform shear than does the sonifier, thus resulting in smaller and more uniform final particle size distributions. The results also indicate that particle nucleation is slowed by the presence of cetyl alcohol on the surface of the monomer droplets.

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