Polymerization of Miniemulsions Prepared from Polystyrene in Styrene Solutions. 1. Benchmarks and Limits

C. M. Miller, E. D. Sudol, C. A. Silebi, and M. S. El-Aasser*

Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015-4732

Received August 18, 1994; Revised Manuscript Received January 20, 1995[®]

ABSTRACT: Recently, experimental results indicating differences between the polymerization kinetics of styrene miniemulsions prepared with and without small amounts of polystyrene added to the oil phase have been reported. The work is expanded here to better define the range of conditions under which this behavior is observed. Styrene miniemulsions and conventional emulsions prepared with and without the addition of a small amount of polystyrene to the oil phase were polymerized at 70 °C in an automated reaction calorimeter. The results show that miniemulsions prepared with as little as 0.05 wt % polymer based on the oil phase exhibit a substantial increase in the polymerization rate and number of polymer particles produced over miniemulsions prepared in the absence of polymer. An increase in the polymerization rate was observed when either cetyl alcohol or hexadecane was used as the cosurfactant; however, the increase was greater for cetyl alcohol. In addition, the homogenization of a polymer solution without a cosurfactant was demonstrated to yield an unstable miniemulsion (i.e., a cosurfactant is required for the formation of a stable miniemulsion). Samples withdrawn before and after the polymerization of a 1% polystyrene in styrene miniemulsion (using cetyl alcohol as the cosurfactant) revealed that the initial number of miniemulsion droplets was nearly the same as the final number of polymer particles. The latter is taken as partial proof that a large fraction (approaching 1) of the initial number of droplets captured aqueous phase free radicals and became polymer particles during this polymerization.

Background

The formation of latex particles by polymerization in monomer droplets has been the subject of a considerable amount of research. In the first publication in this area, Ugelstad et al.[1] demonstrated that when monomer droplets were prepared via a miniemulsification process to produce submicron droplets, these droplets could effectively complete with other nucleation mechanisms in the formation of polymer particles. This was attributed to the larger surface area and enhanced surfactant adsorption of the monomer droplets, allowing them to become principal locus of polymerization. The droplets produced by miniemulsification processes are typically in the range of 50–500 nm and are stabilized by using an ionic surfactant and a cosurfactant which is typically a low molecular weight, low water solubility compound such as a long-chain alkane or fatty alcohol.[1–3] The purpose of the cosurfactant is twofold: (1) its low water solubility reduces the rate of diffusion of monomer from smaller to larger droplets,[4] enabling these droplets to remain stable for unusually long periods of time (e.g., weeks to months); and (2) its low molecular weight acts as a swelling promoter, enabling the polymer particles to absorb many times their normal swelling capacity in monomer.[5] In addition to stabilization against diffusion, it has been postulated that for the fatty alcohols, additional stabilization may be provided by the formation of interfacial barriers to coalescence. Such barriers have been postulated to be liquid-like and electrically charged.[6,7] In this case, the action of the cosurfactant may be truly one of a surface-active agent; however, this type of stabilization is not considered to be operative for the long-chain alkanes, which are almost certainly located in the interior of the droplets. Therefore, the use of the term "cosurfactant" to describe the action of the long-chain alkanes is not strictly correct, since these compounds serve no other purpose than to prevent degradation caused by molecular diffusion.

Although much research has been conducted to determine the mechanisms operative in miniemulsion polymerization, only a limited amount of commercial interest has been generated for this process. This is in part due to the relative newness of the technology but may also be attributed to the relatively slow polymerization rates reported as compared to parallel conventional emulsion polymerizations. This has been attributed to the fact that, regardless of the recipe selected or the polymerization conditions employed, radical capture by miniemulsion droplets has been shown to be an inefficient process whereby only a fraction of the initial number of droplets present capture radicals and become growing polymer particles.[2,8,9] This has the drawback that the remaining droplets must supply monomer to the growing polymer particles by diffusion or collision, so that many benefits of polymerization in monomer droplets are negated. Recently, Miller et al.[10] reported that the fraction of miniemulsion droplets which capture radicals could be greatly increased by the addition of a small amount of polymer to the monomer phase of the miniemulsion (i.e., as little as 0.05 wt % based on the oil phase). This result is significant since nucleating a greater fraction of droplets would result in higher polymerization rates, greater particle numbers, and perhaps nucleation of 100% of the initial monomer droplets. Under certain circumstances, these would represent significant practical advantages for utilizing miniemulsions instead of conventional emulsions for production of latex particles. The purpose of this paper is to present several benchmark experiments and to establish the limits under which this behavior is observed. In a second paper,[11] the mechanism for polymerization of miniemulsions prepared from polystyrene in styrene solutions is investigated, and in a third[12] some potential reasons for this behavior are discussed.

---

* To whom correspondence should be addressed.

[®] Abstract published in *Advance ACS Abstracts*, March 15, 1995.

0024-9297/95/2228-2754$09.00/0

Table 1. Standard Recipe for Polymerization Experiments

ingredient	amount	grams
DDI H_2O	80 parts	560
SLS	10 mM[a]	1.61
CA or HD	30 mM[a] or 40 mM[a]	4.07 or 5.07
KPS	1.33 mM[a]	0.201
$NaHCO_3$	1.33 mM[a]	0.03
styrene	20.2, 20.19, 19.19, 19.998, or 19.796 parts	141.4, 141.3, 140.7, 140, or 138.6
polystyrene	0, 0.01, 1.01, 0.202, or 0.404 parts	0, 0.07, 0.71, 1.41, or 2.83

[a] Based on the water.

Experimental Section

Materials. The following materials were used in all of the experiments.

Styrene (Aldrich) was washed three times with an aqueous solution of 10% sodium hydroxide followed by three washes with distilled-deionized water. The styrene was then dried over anhydrous sodium sulfate (Aldrich) overnight and distilled under a reduced pressure of 15 mmHg. The styrene was stored in a freezer at −5 °C prior to usage.

Potassium persulfate, KPS (FMC Corp.), was recrystallized from distilled-deionized water and dried under vacuum.

The polystyrene used was obtained either from a commercial product (Dajac Laboratories, lot no. 212-28; M_w(GPC) = 60 300, M_n(GPC) = 24 400) or, in most cases, from a 92 nm latex (LS-1039E, Dow Chemical Co.) which was first cleaned of surfactant by serum replacement and then subjected to successive washes with methanol and distilled-deionized water. The molecular weight of this polymer was characterized by GPC to have M_w = 193 300 and M_n = 52 600. The type of polymer used is given where appropriate.

The following additional chemicals were used as received: sodium lauryl sulfate, SLS (J.T. Baker, Ultrapure Bioreagent 99% pure), cetyl alcohol, CA (Aldrich), hexadecane, HD (Aldrich), sodium bicarbonate (Fisher), and phosphotungstic acid (Fisher). The critical micelle concentration of the SLS was determined by conductivity measurements to be 7.7 mM at room temperature. The water used in these studies was distilled and deionized (DDI).

Recipe and Procedures. Table 1 indicates the recipe used for all reactions. For those reactions in which polymer was used, the total amount of monomer and polymer always added up to 20.2 parts. For reactions in which no cosurfactant was used (i.e., cetyl alcohol or hexadecane), the recipe was identical in all other aspects. The initiator was kept constant for all of the experiments at 1.33 mM (KPS) based on the aqueous phase.

The following procedure was used in preparing the miniemulsions. The basic recipe is given in Table 1, where 1% of the water and the KPS were not used in the homogenization step. These were mixed together just prior to polymerization and added to the reactor. In those experiments in which cetyl alcohol was used, an aqueous gel phase was prepared by mixing the distilled-deionized water, SLS, and CA at 70 °C for 2 h followed by cooling and sonifying (Branson Sonic Power Co.) the resulting gel for 1 min at 50% duty, power 7, pulsed. When polymer was used, the polystyrene and the styrene monomer were mixed until the polymer had fully dissolved in the monomer. The polymer/monomer solution (or monomer if no polymer was used) was then added to the aqueous gel phase and mixed in a beaker for 20 min using a magnetic stir bar. The resulting emulsion was then sonified for 10 pulses and passed through the Microfluidizer (Model 110-T, Microfluidics Corp.) for ten recycle passes. The Microfluidizer was operated with an inlet pressure of 80 psig, which provided an outlet pressure of about 6000 psig. An alternative method for preparing miniemulsions was also used for comparison. In this method, hexadecane was dissolved in the oil phase (i.e., styrene or 1% polystyrene in styrene). This solution was then added to an aqueous solution of sodium lauryl sulfate, mixed 20 min, and homogenized as described above.

Table 2. Experimental Variables Studied

experiment identifier	wt % polymer	KPS, mM	cosurfactant employed (location)	homogenization (Microfluidizer)
JBRC-1[a]	1	1.33	30 mM CA (gel)	yes
JBRC-2[a]	0	1.33	30 mM CA (gel)	yes
JBRC-3[a]	0.5	1.33	30 mM CA (gel)	yes
JBRC-5[a]	0.05	1.33	30 mM CA (gel)	yes
JBRC-9	1	1.33	none	yes
JBRC-10[a]	1	1.33	30 mM CA (gel)	yes
JBRC-12[a]	2	1.33	30 mM CA (gel)	yes
RC1-47[a]	0	1.33	40 mM HD (monomer)	yes
JBRC-14[a]	1	1.33	40 mM HD (monomer)	yes
JBRC-15	1	1.33	none	no
RC1-33	0	1.33	none	yes
RC1-44	0	1.33	none	no

[a] Designates those runs considered to be miniemulsions.

When a cosurfactant was used and homogenization was applied, the system was considered to be a miniemulsion. All of the miniemulsions appeared homogeneous and opaque. A portion of each miniemulsion was placed on a shelf in a vial and allowed to cream for a period of 1 week. For some of the experiments where polymer was used, another portion of the initial miniemulsion was analyzed for its particle size distribution and molecular weight. For particle size analysis, the monomer was first distilled off under vacuum, and the "unswollen" polymer particle size distribution was determined by transmission electron microscopy (TEM). For molecular weight analysis, the polymer was isolated by drying the miniemulsion followed by washes with methanol and distilled-deionized water and again drying the resulting polymer. The molecular weight was determined using gel permeation chromatography (GPC (Waters); Ultrastyragel columns: linear 10^6 Å, linear 10^2 Å, 10^4 Å, and 10^3 Å (Waters); calibrated using polystyrene standards (Polymer Laboratories, Inc.)).

The experiments performed in this study are identified in Table 2. The key variables of note are the amount and type of polymer initially present, the amount and type of cosurfactant used (i.e., cetyl alcohol or hexadecane), and the method of preparation (i.e., whether homogenization was applied). The amount of polystyrene dissolved in the styrene is indicated as weight percent and was varied from 0 to 2%. In all of the experiments except JBRC-10, the polystyrene was obtained from a monodisperse latex seed as described above. For JBRC-10, the commercial polymer was used. The method of preparation prior to polymerization is indicated in Table 2 by whether or not a cosurfactant was used and whether or not homogenization was applied. As mentioned above, when a cosurfactant was used and homogenization was applied, the resulting system was considered to be a miniemulsion (JBRC-1 to -5, -10, -12, -14; RC1-47). A conventional emulsion polymerization is denoted RC1-44, where no cosurfactant was used and no homogenization was applied. Several control experiments were conducted for comparison: JBRC-15, where a conventional emulsion was prepared from an oil phase consisting of a 1% polystyrene in styrene solution (no cetyl alcohol, no homogenization); JBRC-9, where 1% polymer dissolved in the monomer was homogenized in an aqueous solution of sodium lauryl sulfate (in the absence of cetyl alcohol); and RC1-33, where the monomer (without polymer) was homogenized in an aqueous solution of sodium lauryl sulfate (in the absence of cetyl alcohol).

Apparatus. Polymerizations were conducted in the Mettler RC1 reaction calorimeter at 70 °C. The reactor was equipped with a stainless steel impeller (45° pitch, run at 300 rpm) and baffle. The Mettler RC1 offers the advantage of providing an almost continuous heat of polymerization curve throughout the reaction (data were obtained every 6 s). The expression relating the heat of reaction to the polymerization rate in a calorimeter is given by

$$R_p = \frac{Q_r}{\Delta H_p V_r} \qquad (1)$$

where Q_r is the rate of heat evolution (J/s), ΔH_p is the heat of polymerization (J/mol), and V_r is the volume of the material in the reactor (L), usually expressed for emulsion polymerization as the volume of water present in the reactor. From this expression, the fractional conversion can be determined by

$$x(t) = \frac{\int_0^t Q_r \, dt}{\Delta H_p M_0} \qquad (2)$$

where $x(t)$ is the fractional conversion at time t and M_0 is the initial moles of monomer present.

Prior to loading any materials, the reactor was purged with nitrogen for at least 0.5 h. For experiments in which the emulsion was prehomogenized using the Microfluidizer, about 600 g of the emulsion was added to the reactor and nitrogen (zero grade, JWS Technologies, Inc.) was bubbled through the mixture for 20 min, after which the nitrogen was turned off for the rest of the experiment. For reactions in which homogenization was not applied, the aqueous phase was first added to the reactor, and then the oil phase was slowly added with continuous agitation (100 rpm). In either case, the emulsions were heated to 70 °C and held for about 40 min while the calorimeter was calibrated to determine its operating parameters. The initiator was then mixed with 1% of the water (reserved for this purpose), heated to 70 °C, and injected to begin the reaction.

The final particle size distributions for most of the latexes were determined by transmission electron microscopy (TEM). To accomplish this, the latexes were diluted with a 2% phosphotungstic acid solution and placed in the cold stage of a Phillips 400 TEM. Representative sections of the samples were photographed, and more than 1500 particles were measured using a Zeiss MOP 3 analyzer to determine the particle size distributions. For JBRC-15, the particle size distribution was determined by capillary hydrodynamic fractionation (CHDF, MATEC Applied Sciences).

Results and Discussion

Establishing the Technique: Benchmark Experiments. In order to establish a basis for comparison, a normal miniemulsion polymerization (JBRC-2), a conventional emulsion polymerization prepared under parallel conditions (RC1-44), and a "conventional" emulsion polymerization in which homogenization was applied (RC1-33) were run. The latter will be referred to as a "pseudoconventional" emulsion polymerization for the purpose of this discussion. From an experimental point of view these reactions should be similar, the only difference being the addition of 30 mM of cetyl alcohol and a preemulsification step to the miniemulsion, compared with no cetyl alcohol for the pseudoconventional emulsion, and no cetyl alchol or preemulsification for the conventional emulsion. However, it has been demonstrated by a number of researchers[1-3,8,9] that the nucleation mechanisms differ in these systems depending upon the size of the initial monomer droplets. The use of the homogenization step in the preparation of miniemulsions produces submicron (~100 nm) monomer droplets, which are stabilized against diffusion degradation by the cetyl alcohol. As a result, it has been demonstrated both experimentally[1-3,8-10] and theoretically through surface area considerations[1,10] that the monomer droplets serve as the principal locus of particle formation in miniemulsion polymerization. In contrast, in conventional emulsion polymerization the droplets are relatively large (~5 μm) and therefore, the principal locus of particle formation is the monomer-swollen micelles ([S] > cmc). Following this line of reasoning, in the pseudoconventional emulsion polymerization the droplets are initially small, but following homogenization are unstable to diffusion degradation. Therefore, for this type of emulsion, diffusion degradation should begin immediately after homogenization, causing a net decrease in the droplet surface area (increase in the average droplet size), and as a result the droplets should be larger than in the miniemulsion but smaller than in the conventional emulsion. In this case, the principal locus of nucleation will most likely be monomer-swollen micelles, but perhaps also the monomer droplets, depending upon their size at the time of initiator addition.

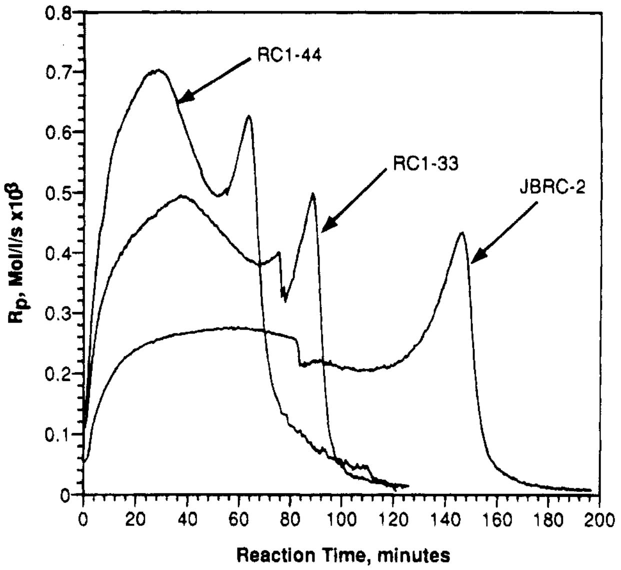

Figure 1. Polymerization rate versus time curves for a styrene miniemulsion prepared from an aqueous gel phase consisting of 10 mM SLS/30 mM CA (JBRC-2), a styrene conventional emulsion polymerization prepared with 10 mM SLS (RC1-44), and a styrene emulsion prepared with 10 mM SLS and homogenized using the Microfluidizer (RC1-33). [KPS] = 1.33 mM, T_r = 70 °C.

Figure 1 shows the polymerization rate versus time for a miniemulsion (JBRC-2), a conventional emulsion (RC1-44), and a pseudoconventional emulsion (RC1-33). The surfactant concentration employed for all of these experiments is above its "cmc" (10 mM SLS, compared with 7.7 mM at the cmc). All these polymerization rate curves show the same general behavior; they rise to a maximum, fall off, and then experience a second maximum prior to their final falloff when the polymerizations near completion. Experiment JBRC-2 was repeated several times and was found to be reproducible. The first rise in the rate reflects the increase in the number of particles formed; a greater maximum value results from a greater number of particles. The subsequent decrease in the rate is caused by a decreasing monomer concentration in the particles as polymer is produced. The miniemulsion and pseudoconventional emulsion polymerizations both show an "instability" during this rate decrease. This behavior has not been observed previously and is most likely associated with the calorimetric technique which is sensitive to small changes in the characteristics of the reactor such as the heat transfer coefficient and the heat capacities of the reactor contents. The former may change suddenly if some coagulum is formed on either the reactor wall or the tempeature sensor. The second rise is attributed to the well-known gel effect which brings about an increase in the average number of radicals per particle through decreased diffusivity of the propagating radicals within the latex particles, effectively decreasing the termination rate. At high conversion, the monomer/polymer particles become glassy (T_g(polystyrene) = 100 °C), which reduces the monomer diffusivity, thereby effectively reducing the propagation rate coefficient and bringing about the final decrease in the polymerization rate.

As expected, the fastest polymerization rate was obtained for the conventional emulsion polymerization. When homogenization was applied (pseudoconventional emulsion polymerization), the polymerization rate decreased due to the decrease in the number of micelles available for particle formation. It was mentioned above that for this type of polymerization, the locus of nucleation may shift to the monomer droplets if they are small enough when the polymerization is initiated. For this experiment, the emulsion was aged at 25 °C for about 1 h and 70 °C for about 40 min prior to initiator injection. Therefore, it is expected that the monomer droplets should be quite large and not serve as a significant locus of nucleation. The miniemulsion reacted the slowest of the three shown in Figure 1. This is probably a consequence of the different nucleation mechanism involved in this polymerization. The initial number of droplets in the miniemulsion is less than the number of micelles for either of the other two; as a consequence, the miniemulsion polymerization was expected to be the slowest (i.e., fewer number of particles nucleated).

At this point, it would appear that the greatest polymerization rates obtainable are for conventional emulsion polymerizations where homogenization is not applied. This is attributed to the large number of micelles available for particle formation in these polymerizations. If the initial number of micelles or droplets was the only factor affecting the polymerization rates, this would indeed be true. However, it is well known that not all micelles or miniemulsion droplets succeed in becoming polymer particles. Therefore, the fraction of droplets or micelles which capture radicals is also a concern. If the *efficiency* of radical capture were to change for either of the systems, a change in the number of species nucleated would result, and changes in the resulting polymerization rates would be expected.

It was postulated above that the rate at which miniemulsion droplets capture radicals may be changed by the addition of a small amount of polymer to the monomer droplet phase. Therefore, some initial experiments were conducted to determine the effect of the addition of a small amount of polymer to miniemulsion droplets on the kinetics of polymerization. In the work of Tang et al.,[13] it was demonstrated that the differences between droplets and particles begin to become important at monomer to polymer ratios of 50/1. This work was conducted using monodisperse seed latex particles swollen with cetyl alcohol and monomer. These results suggested that more dramatic differences should be observable at swelling ratios of 100 parts monomer to 1 part polymer. Therefore, benchmark experiments were conducted at this "swelling ratio" using this new technique, i.e., dissolving polymer in the monomer prior to preparing the miniemulsion.

Figure 2 shows the polymerization rate curves obtained for miniemulsions prepared with no polymer (normal miniemulsion, JBRC-2) and 1% polymer (JBRC-1) as well as the same curve for a parallel conventional emulsion polymerization (RC1-44). For the miniemulsion prepared with 1% polymer (JBRC-1), the molecular weight of the initial polymer after homogenization was determined to be somewhat lower than the original molecular weight before homogenization (M_w = 193 000 (M_w/M_n = 3.7) before homogenization versus M_w = 153 000 (M_w/M_n = 2.4) after homogenization), indicating that a limited degradation of the polymer had occurred during the homogenization.

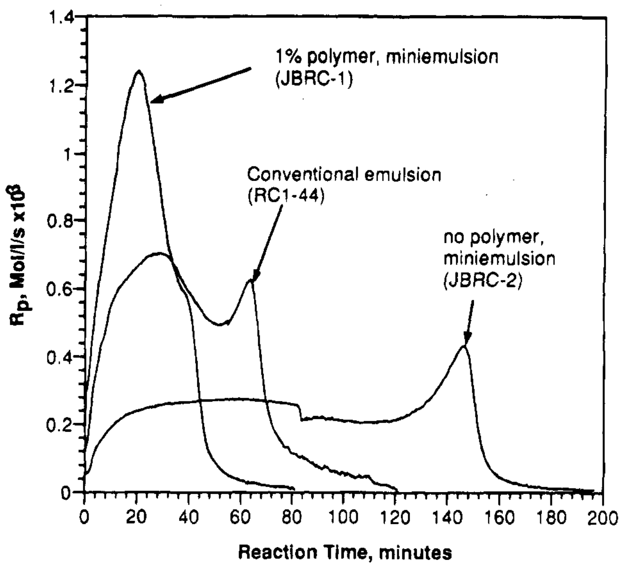

Figure 2. Polymerization rate versus time curves for a styrene conventional emulsion prepared with 10 mM SLS (RC1-44), a styrene miniemulsion prepared from an aqueous gel phase consisting of 10 mM SLS/30 mM CA (JBRC-2), and a miniemulsion prepared from a 1% polystyrene in styrene solution homogenized into an aqueous gel phase consisting of 10 mM SLS/30 mM CA (JBRC-1). [KPS] = 1.33 mM, T_r = 70 °C.

All of the curves in Figure 2 show similar behaviors, i.e., an initial rise in the polymerization rate to a maximum followed by a decrease, and finally an increase or shoulder due to the gel effect prior to the final gradual dropoff to zero. It is apparent from this figure that the addition of only a small amount of polymer has a profound effect on the polymerization rate of the miniemulsion. The miniemulsion prepared from a 1% polystyrene in styrene solution has a maximum rate (first maximum) of polymerization nearly 5 times that of the miniemulsion prepared without polymer and nearly 2 times that of the parallel conventional emulsion polymerization. These results are most likely due to a greatly increased fraction of the droplets in the miniemulsion prepared from the polystyrene in styrene solution succeeding in capturing radicals. Simply put, although there was a larger number of micelles initially present in the conventional emulsion, only a relatively small fraction of these formed polymer particles. In contrast, although there was a relatively smaller number of monomer droplets present for the miniemulsion prepared from the 1% polystyrene in styrene solution, a large fraction of these succeeded in forming polymer particles. This fraction was large enough that the number of particles formed exceeded even the number formed in the conventional emulsion polymerization.

Table 3 shows the final particle sizes and number concentrations of these latexes as well as all of the other latexes prepared under the conditions described in Table 2. It is seen from this table that the miniemulsion prepared from a 1% polystyrene in styrene solution

Table 3. Particle Size Analysis and Calculated Numbers of Particles[a]

experiment identifier	D_v, nm	D_n, nm	σ, nm	$N_p/L \times 10^{-17}$
JBRC-1	82.4	78.7	17.2	8.08
JBRC-2	153.4	150.5	21.4	1.25
JBRC-3	81.2	77.2	20.2	8.10
JBRC-5	111.3	107.4	20.2	3.27
JBRC-9	98.5	96.2	15.9	4.55
JBRC-10	82.0	76.1	22.6	8.22
JBRC-12	73.9	68.2	21.0	11.2
RC1-47	119.9	118.6	12.8	2.26
JBRC-14	100.86	97.0	20.6	4.29
JBRC-15[b]	111.7	109.5	15.5	3.20
RC1-33	121.6	119.8	15.4	2.20
RC1-44	106.6	105.2	12.4	3.60

[a] All particle sizes were determined by TEM, except where indicated. [b] By CHDF.

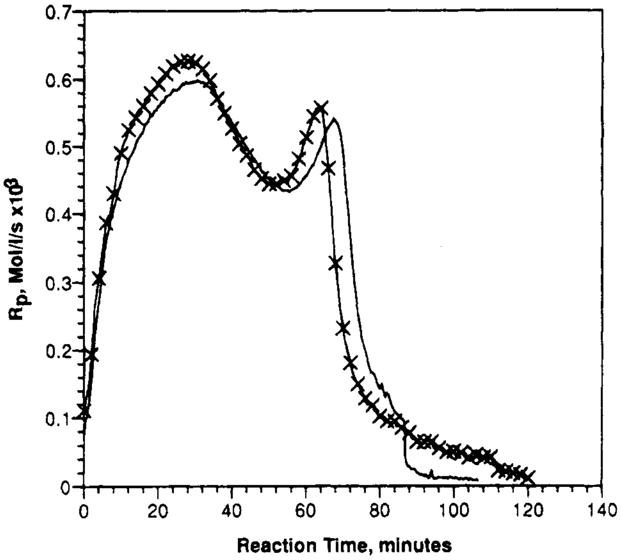

Figure 3. Polymerization rate versus time curves for styrene conventional emulsion polymerizations (no cetyl alcohol, no homogenization) prepared without polymer (RC1-44, ×) or with 1% polymer preadded to the monomer phase (JBRC-15, —). [KPS] = 1.33 mM, T_r = 70 °C.

(JBRC-1) produced a greater number of particles than either the conventional emulsion (RC1-44) or the normal (i.e., no polymer) miniemulsion (JBRC-2). Again, the most likely cause of this behavior is that the original monomer droplets for the former were more efficient in capturing radicals, resulting in a larger fraction of them becoming polymer particles.

In order to establish the role of the polymer in the polymerization of miniemulsions, several other benchmark experiments were conducted. An experiment was performed to determine the effect of the addition of polymer on an otherwise conventional emulsion polymerization. The polymerization rate versus time curve for this experiment (JBRC-15) is shown in Figure 3, along with the results for the conventional emulsion polymerization prepared without polymer (RC1-44). It is apparent from this figure that the addition of polymer to an otherwise conventional emulsion polymerization has very little effect on the polymerization kinetics. There are two small differences between the two experiments: the conventional run with polymer reacted a little more slowly than its counterpart without polymer, and the shape of the final falling rate period differs between the two (i.e., at about 88 min there is a dropoff in the rate of polymerization for JBRC-15 which is not observed in RC1-44). The former may simply be due to experimental variation associated with the reproducibility in the runs or perhaps due to the role of the polymer in retarding the transport of monomer from the droplets to the growing particles. In addition, a small amount of monomer was observed on top of the latex during the conventional emulsion polymerization prepared without polymer. This layer formed upon the addition of the initiator and did not disappear until close to the end (around 90 min) of the reaction. No monomer separation was observed in the conventional emulsion polymerization in which 1% polymer was added. Since, like latex particles, monomer droplets require surfactant for stabilization, it is possible that the reduced number of droplets (after formation of the monomer layer) resulted in more free surfactant available to form micelles. These would increase the number of potential nucleation sites for the conventional emulsion polymerization relative to the conventional emulsion polymerization in which polymer was added, which could explain the greater overall polymerization rate obtained for the former.

After removing the latexes from the reactor, some sticky "stucco-like" coagulum was observed on the reactor inserts (i.e., impeller, baffle, thermocouple, and calibration probe) for the polymerization in which 1% polymer was preadded. This coagulum may have been formed from the initial polymer which was originally present in the large monomer droplets, eventually precipitating onto the reactor inserts. This coagulum may have changed the reactor operating parameters, thus changing the baseline, giving rise to the final dropoff observed at 88 min for the conventional emulsion polymerization in which 1% polymer was added. No coagulum was observed for the conventional emulsion prepared without polymer.

Another benchmark experiment was performed to determine the effect of polymer on a homogenized conventional emulsion polymerization (pseudoconventional). For this experiment, an emulsion was prepared by dissolving 1% polystyrene in styrene and homogenizing this solution into an aqueous solution of sodium lauryl sulfate (JBRC-9). The results are compared with those for a conventional emulsion polymerization (RC1-44), a homogenized conventional emulsion polymerization (RC1-33), and a miniemulsion prepared from a 1% polystyrene in styrene solution (JBRC-1). The latter three polymerizations were discussed above. Figure 4 shows the rate curves for these four polymerizations. It is seen that the addition of polymer to the homogenized conventional emulsion (JBRC-9) resulted in a slightly greater rate of polymerization than the conventional emulsion polymerization (RC1-44) and a substantially greater rate of polymerization than the pseudoconventional emulsion polymerization without polymer (RC1-33). However, the rate of polymerization for the homogenized conventional emulsion polymerization prepared from a 1% polystyrene in styrene solution (JBRC-9) was still substantially slower than that for the miniemulsion prepared from a 1% polystyrene in styrene solution. Interpretation of these results is uncertain due to the different possible nucleation mechanisms in the different polymerizations. One possible explanation is that the conventional emulsion polymerization proceeds by a micellar nucleation mechanism. Therefore, as discussed above (Figure 1), when the conventional emulsion polymerization is homogenized the number of nucleation sites (micelles) is reduced, and consequently the rate of polymerization is reduced. When polymer is added to the monomer and subse-

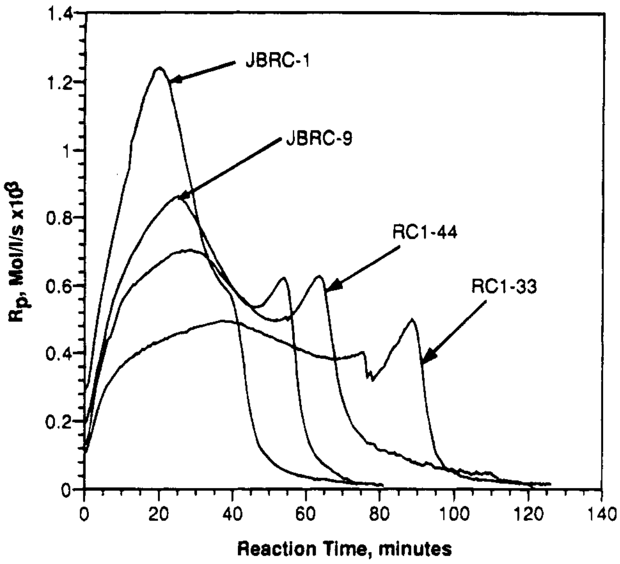

Figure 4. Polymerization rate versus time curves for a styrene conventional emulsion polymerization prepared with 10 mM SLS (RC1-44), a styrene emulsion polymerization prepared with 10 mM SLS and homogenized using the Microfluidizer (RC1-33), a styrene emulsion polymerization prepared by homogenizing a 1% polystyrene in styrene solution into an aqueous solution of 10 mM SLS (JBRC-9), and a styrene miniemulsion polymerization prepared from an aqueous gel phase consisting of 10 mM SLS/30 mM CA (JBRC-1). [KPS] = 1.33 mM, T_r = 70 °C.

quently homogenized into the surfactant solution (as in JBRC-9), there may be two different "nucleation" mechanisms. In this case, some polymer particles may be formed during homogenization. These particles would be expected to be swollen with monomer up to their swelling capacity (2–4 parts monomer to 1 part polymer) and, therefore, would be relatively small compared to miniemulsion droplets containing 1% polymer. The remaining monomer would be present in the form of large monomer droplets. Micelles would still be present in this system and would serve as sites for nucleation, and the monomer-swollen polymer particles (initially present) would also be able to capture radicals and grow (as in a seeded emulsion polymerization). These particles may even be more efficient at capturing radicals than the micelles. Therefore, despite the fact that the number of micelles would be decreased by homogenization, the number of particles produced may be increased due to the contribution of the small, preformed particles. This mechanism should not be confused with the mechanism proposed for the miniemulsion polymerization prepared from a 1% polystyrene in solution (JBRC-1), which produced a much faster rate than any of the others. In this case, the presence of the cosurfactant (cetyl alcohol) allows the "preformed particles" to be swollen to many times their volume in monomer (i.e., 100 to 1). Therefore, these "particles" will resemble miniemulsion droplets and contain all of the monomer. Since the size of the droplets is still small, the number of micelles will either be very low or nonexistent, and the polymerization will proceed by radical entry into the miniemulsion droplets (which contain the preadded polymer).

The difference between the miniemulsion droplets prepared from a 1% polystyrene in styrene solution (JBRC-1) and homogenized conventional emulsion droplets prepared from a 1% polystyrene in styrene solution (JBRC-9) was further demonstrated by their relative creaming rates. While the miniemulsion (JBRC-1) was stable for a relatively long time, the homogenized conventional emulsion prepared from a 1% polystyrene in styrene solution (JBRC-9) fully creamed within a matter of hours. After creaming, it was also observed that the emulsion prepared without cetyl alcohol (JBRC-9) left a turbid water phase, which may indicate the presence of small particles. When cetyl alcohol was used (JBRC-1), the aqueous phase was observed to be clear after creaming. Further details on this measurement will be given in a later section.

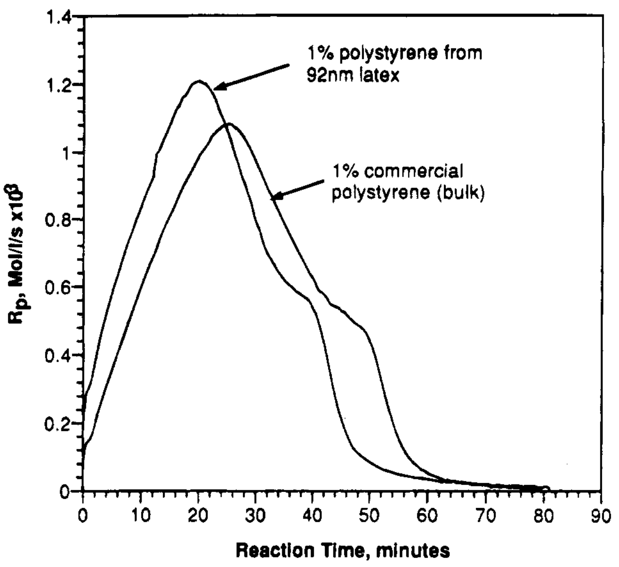

Figure 5. Polymerization rate versus time curves for styrene miniemulsions prepared from 1% polystyrene (obtained from a 92 nm latex or bulk polymerization, as indicated) in styrene solutions homogenized into aqueous gel phases consisting of 10 mM SLS/30 mM CA. [KPS] = 1.33 mM, T_r = 70 °C.

Effect of Polymer Type. The above findings suggest that polymerization of miniemulsions prepared from 1% polystyrene in styrene solutions results in the nucleation of a greater number of miniemulsion droplets as reflected by faster polymerization rates and greater numbers of final polymer particles. These experiments were conducted using polymer which was isolated from a 92 nm monodisperse latex. Considering the source of the polymer, it might be expected that the nature of the end groups on this polymer (e.g., sulfate) may contribute to this behavior. Therefore, an experiment was performed in which a miniemulsion was prepared from a 1% polystyrene in styrene solution where the polystyrene was prepared by bulk polymerization rather than emulsion polymerization. The goal of this experiment was to determine whether a polymer with less hydrophilic end groups (typical initiators in bulk polymerization produce nitrile (AIBN) and phenyl (BPO) end groups) would exhibit the same behavior. A carefully designed experiment would use polymers with the same molecular weights and polydispersities to isolate the effect of the end groups. For example, polymers obtained from anionic polymerization (narrow molecular weight, low polydispersity index, hydrogen terminated) could be sulfonated to eliminate the effects of molecular weight. However, this type of polymer was not available at this time, although it is expected to be the subject of future work. As stated earlier, the polymer obtained from the 92 nm latex was determined to have M_w = 193 300 and M_w/M_n = 3.7. The commercial polymer was determined to have M_w = 60 300 and M_w/M_n = 2.5.

The results of the experiments using the two different polystyrene sources are shown in Figure 5. It is

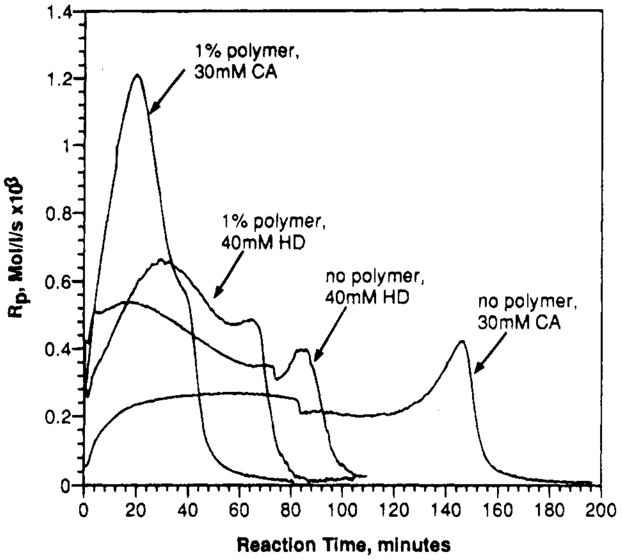

Figure 6. Polymerization rate versus time curves for styrene miniemulsions prepared using 10 mM SLS and either 30 mM CA or 40 mM HD. The miniemulsions were prepared with or without 1% polystyrene dissolved in the styrene phase. [KPS] = 1.33 mM, T_r = 70 °C.

apparent that miniemulsions prepared from both types of polymer produced substantially greater polymerization rates than miniemulsions prepared in the absence of polymer. However, it is also apparent that the miniemulsion prepared from the commercial polymer reacted more slowly than the miniemulsion prpeared from the polymer obtained from the 92 nm latex. Although not shown here, the creaming rates of these two miniemulsions were measured prior to polymerization as a measure of their relative droplet sizes, and these were shown to be identical within experimental error. These results suggest that the miniemulsion prepared from the commercial polymer did not nucleate as many of the initial droplets as the miniemulsion prepared from the polymer obtained from the 92 nm latex. This result may be attributed to either the different end groups, the different molecular weights, or perhaps some other variable (such as the solution viscosity). A more systematic study in this area is expected in the future to provide further insight into the role of the type of polymer on the polymerization kinetics.

Effect of Cosurfactant Type. Another variable which was considered to be important to these studies was the type of cosurfactant used in the preparation of the miniemulsions. In order to investigate this variable, miniemulsions were prepared with and without 1% polystyrene in the styrene using hexadecane as the cosurfactant, and the results are compared with those obtained using cetyl alcohol as the cosurfactant. While both cetyl alcohol and hexadecane are used for preparing stable miniemulsions, it is well known that the miniemulsions prepared using these two cosurfactants give different polymerization kinetics.[9,13,14] The differences have been attributed to differences in the initial droplet size distributions,[14,15] differences in the fraction of the droplets which capture radicals,[9,13,14] differences in the stability of the droplets during the polymerization,[13] or differences in the type of stabilization provided by the cosurfactant (which may affect the rate at which the different types of droplets absorb and desorb free radicals).[14]

Figure 6 shows the polymerization rate versus time curves for styrene and polystyrene/styrene solution miniemulsions prepared using either hexadecane or cetyl alcohol as the cosurfactant. As expected, the polymerization rate curves are different when the different cosurfactants are used. Specifically, in the absence of polymer, the initial time to reach the maximum polymerization rate is shorter (i.e., 20 compared to 60 min) and reaches a greater maximum rate (i.e., 5.8×10^{-4} compared to 2.8×10^{-4} mol L^{-1} s^{-1}) when hexadecane is used than when cetyl alcohol is used as the cosurfactant. This first rise is usually attributed to the formation of new polymer particles. Therefore, it may be stated that the nucleation period is shorter when hexadecane is used as the cosurfactant, while also producing a greater number of polymer particles. This is verified by the number of particles reported in Table 3, where the miniemulsion prepared using cetyl alcohol as the cosurfactant produced 1.3×10^{17} particles/L while the miniemulsion prepared using hexadecane produced 2.26×10^{17} particles/L. When 1% polymer was added to miniemulsions prepared using the two cosurfactants, the overall polymerization rates were observed to increase over the respective miniemulsions prepared without added polymer. However, again the behavior is different depending upon the cosurfactant used. When cetyl alcohol was used as the cosurfactant, the overall polymerization rate increased by nearly a factor of 5 when 1% polystyrene was added to the oil phase, while when hexadecane was used, the overall polymerization rate increased by a factor of 1.5 when 1% polystyrene was added to the oil phase. This behavior is again reflected in the number of polymer particles produced, as shown in Table 3. The addition of 1% polymer to the miniemulsion prepared using cetyl alcohol produced 8.08×10^{17} particles/L, which is about a 550% increase over the miniemulsion prepared without polymer. The addition of polymer to the miniemulsion prepared using hexadecane also showed an increase in the number of particles produced; however, for this system the increase was only about 90% (4.29×10^{17}/L for the miniemulsion prepared with 1% polystyrene compared to 2.26×10^{17}/L for the miniemulsion prepared in the absence of polymer). It is obvious that the addition of polymer also affects the shapes of the polymerization rate curves. Whereas the "nucleation period" (reflected in the length of time to the first maximum in the rate of polymerization) is shortened by the addition of polystyrene when cetyl alcohol is used as the cosurfactant, the opposite effect is observed when hexadecane is used as the cosurfactant. These results are reflected in the standard deviations of the resulting latexes; that is, shorter relative nucleation periods resulted in narrower particle size distributions. Finally, for both miniemulsions prepared without polymer, a rather sudden dropoff or instability is observed in the rate curves relatively late in the polymerizations. This phenomenon is not observed when 1% polystyrene is added to the oil phase. The potential reasons for this behavior were discussed before.

Effect of Polymer Concentration. Having established the effect of polymer on the polymerization kinetics, it was desired to determine quantitatively how much polymer was required to influence this behavior and whether there was an upper limit to the amount of polymer which would continue to show this behavior. To this end, the amount of polystyrene dissolved in the styrene prior to homogenization was varied from 0 to 2%. It was expected that increasing the amount of polymer would increase the efficiency of nucleation,

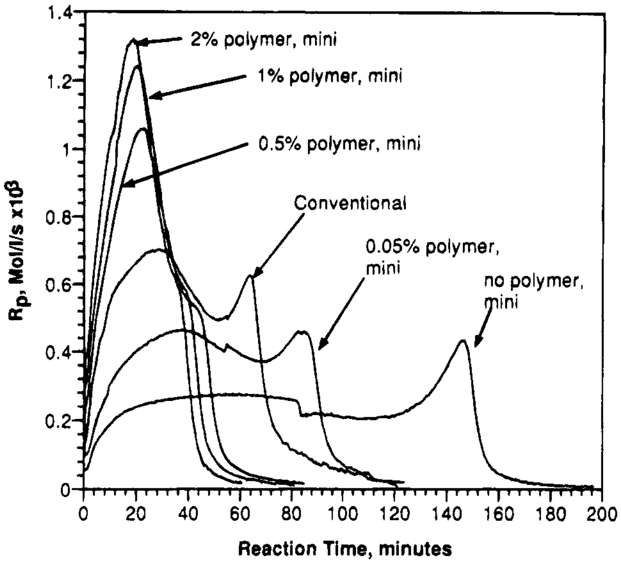

Figure 7. Polymerization rate versus time curves for a styrene conventional emulsion polymerization (RC1-44) and styrene miniemulsion polymerizations prepared from 0, 0.05, 0.5, 1, and 2% polystyrene in styrene solutions, as indicated (JBRC-2, -5, -3, -1, and -12, respectively). [KPS] = 1.33 mM, T_r = 70 °C.

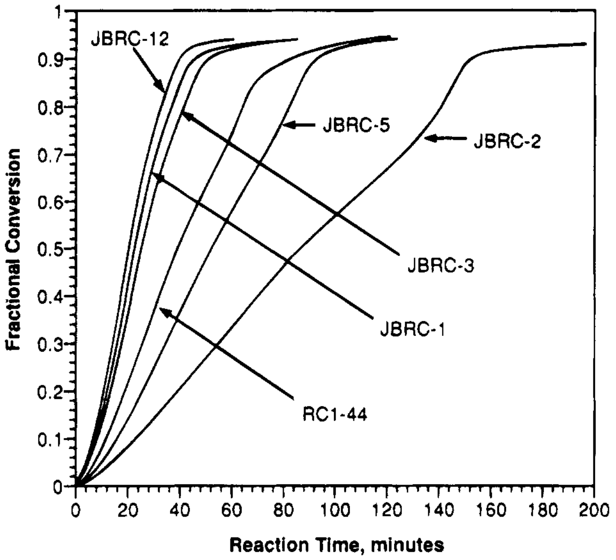

Figure 8. Conversion versus time curves for a styrene conventional emulsion polymerization (RC1-44) and styrene miniemulsion polymerizations prepared from 0, 0.05, 0.5, 1, and 2% polystyrene in styrene solutions, as indicated (JBRC-2, -5, -3, -1, and -12, respectively). [KPS] = 1.33 mM, T_r = 70 °C.

thereby increasing the polymerization rates until some point where the droplets no longer behave as such, but instead behave completely like particles (i.e., the system should resemble a seeded system at sufficiently high volume fractions of polymer).

Figure 7 shows the polymerization rate versus time curves for miniemulsions prepared from 0, 0.05, 0.5, 1, and 2% polystyrene in styrene solutions (JBRC-2, -5, -3, -1, and -12, respectively), and Figure 8 shows the corresponding conversion versus time curves. Included in both of these plots are the results obtained for the conventional emulsion polymerization prepared under parallel conditions (RC1-44). These figures show that, as expected, increasing the amount of polymer added to the miniemulsion increased the polymerization rate. In addition, it is observed that the addition of 0.5% or more polystyrene to the miniemulsions resulted in polymerization rates greater than the conventional emulsion polymerization. Table 3 shows the particle numbers for all of these polymerizations. These results show that, as expected, greater polymerization rates result from a greater number of particles formed during the polymerizations.

It is interesting to note that even for the smallest polymer concentration employed (0.05%), the miniemulsion polymerization rate was doubled over that without added polymer. This indicates that very little polymer is needed to increase the efficiency of radical entry. A calculation can be performed to estimate the number of polymer chains per droplet for this polymerization. Based on a reasonable droplet size of 85 nm (demonstrated below) and an average molecular weight of polymer of 64 000 (M_n after homogenization), the number of chains per droplet can be determined by

$$\text{chains/droplet} = \frac{x_p \pi \varrho_m D^3 N_a}{6 M_{n,p}} \tag{3}$$

where x_p is the weight fraction of polymer in the particles, D is the average diameter of the droplets, N_a is Avogadro's number, and $M_{n,p}$ is the number-average molecular weight of the polymer. Equation 3 gives a value of 1.3 chains per droplet for the miniemulsions prepared from 0.05% polystyrene in styrene solutions. This indicates that the presence of only a small number of polymer chains (maybe even a single chain) changes a droplet's ability to capture radicals. For the case of the lowest polymer concentration, this amount is sufficiently low that some droplets may contain no polymer chains. Similarly, it can be shown that for the miniemulsions prepared from 0.5, 1, and 2% polystyrene in styrene solutions, the number of chains per droplet are much greater than 1, indicating that most, if not all, of the droplets should contain polymer. The increasing number of chains per droplet with increasing initial polymer concentration may explain the increasing polymerization rates observed in Figures 7 and 8.

Thus far, the results for miniemulsions prepared with varying amounts of added polymer have been compared in terms of their rates of polymerization and final particle numbers without consideration of their initial droplet numbers. This can possibly lead to erroneous conclusions since it might be expected that the addition of polymer to the miniemulsion droplets may cause a change in this initial size and consequently a change in the initial number of droplets. In such a case, the results presented above must account for these differences to determine if the resulting rates of polymerization merely reflect the difference in the initial droplet numbers. In order to quantify these differences, two different methods were used to characterize the initial droplet size: (1) measuring the shelf life stability, and (2) measuring the unswollen particle size directly using TEM.

Creaming studies can be used to estimate the relative droplet sizes of emulsions prepared under varying conditions. Usually in these studies, two different measurements of the emulsion's stability are followed: the rate of creaming, which is found by measuring the amount of separation of the emulsion from the aqueous phase over a period of time, and the rate of coalescence of the droplets, which is determined by measuring the amount of oil separated from the emulsion over a period of time. While the latter measurements may be useful

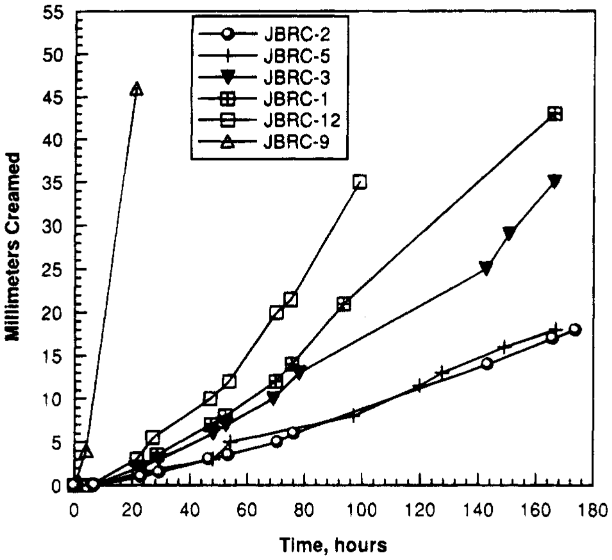

Figure 9. Creaming rates for an emulsion prepared by homogenizing a 1% polystyrene in styrene solution into an aqueous 10 mM SLS solution (JBRC-9) and miniemulsions prepared from an aqueous gel phase consisting of 10 mM SLS/30 mM CA/1.33 mM $NaHCO_3$ and oil phase consisting of styrene and varying amounts of polystyrene: JBRC-2, no polystyrene; JBRC-5, 0.05% polystyrene; JBRC-3, 0.5% polystyrene; JBRC-1, 1% polystyrene; JBRC-12, 2% polystyrene.

in understanding the stability of the emulsion droplets against coalescence, the former measurements are directly related to the size of the emulsion droplets produced (provided the droplets remain stable). This is a consequence of the well-known Stokes–Einstein expression, given by

$$u = \frac{2gr^2(\varrho_m - \varrho_p)}{9\eta} \tag{4}$$

where u is the rate of creaming of the emulsion, g is the gravitational constant, r is the radius of the emulsion droplets, ϱ_m is the density of the continuous phase, ϱ_p is the density of the dispersed phase, and η is the viscosity of the continuous phase. For a stable system in which the droplet diameter is unchanging with time, the droplet creaming rate will be directly proportional to the square of the diameter of the droplets. Quantitative application of this expression is complicated for the system under study because the system is not dilute, the droplet size distributions are polydisperse, and it is known that the average droplet diameter can change with time,[15] particularly for systems using cetyl alcohol as the cosurfactant. Despite these complications, measuring the creaming rates can still provide a useful reference for determining the relative droplet sizes of miniemulsions.

Figure 9 shows the creaming rates for all of the miniemulsions whose polymerization kinetics were shown in Figures 7 and 8 (i.e., JBRC-1, -2, -3, -5, and -12). Included in this figure is the creaming rate of the emulsion prepared by homogenizing a 1% polystyrene in styrene solution into an aqueous solution of SLS in the absence of cetyl alcohol (JBRC-9). The kinetics for this polymerization were presented in Figure 4. The creaming rates for all of these emulsions were measured by visually observing the phase boundary between a clear water phase and the creaming emulsion phase. The general trend in order of decreasing droplet size for these emulsions is given below, based on examining their relative creaming rates and assuming the creaming rate is proportional to the droplet diameter: (1% polymer, no CA:JBRC-9) $\gg$ (2% polymer, CA:JBRC-12) > (1% polymer, CA:JBRC-1) > (0.5% polymer, CA:JBRC-3) > (0.05% polymer, CA:JBRC-5) $\approx$ (no polymer, CA:JBRC-2).

This study shows that the smallest droplets (slowest creaming rates) are produced for miniemulsions prepared without polymer or with 0.05% polymer, and the size increases with increasing polymer content. This trend in the droplet size probably results from the increase in the viscosity of the dispersed (styrene/polystyrene) phase with the addition of increasing amounts of polymer. For a constant shear input, higher viscosities will lead to larger droplet sizes. In addition, the emulsion prepared without cetyl alcohol (with 1% polymer) separated quickly, indicating that it was probably not stable against diffusion degradation. This indicates that this emulsion would probably consist of large monomer droplets, micelles, and small polymer particles, as was suggested previously in the interpretation of its polymerization kinetics. As noted earlier, the aqueous phase for this emulsion was still quite turbid after creaming. This probably results from the presence of small polymer particles swollen only 2–4 times their weight with monomer. These particles would be small enough (i.e., <50 nm) that they would remain suspended in the aqueous phase through their Brownian movement.

In comparing the relative droplet sizes (Figure 9 and eq 4) with the relative polymerization rates (Figures 7 and 8), it is seen that the smallest droplet sizes produced the slowest polymerization rates. Therefore, the increase in the rate with increasing polymer content cannot be attributed to differences in the initial droplet size. If this was the case, the opposite behavior would be expected, since the miniemulsions containing the smallest droplet sizes would have the highest droplet numbers and accordingly would be expected to polymerize the fastest by producing the greatest particle numbers. This point is further demonstrated by examining the relative droplet sizes and polymerization kinetics for the normal miniemulsion (JBRC-2, no polymer) and the miniemulsion prepared from a 0.05% polystyrene in styrene solution (JBRC-5). Figure 9 showed that these two miniemulsions creamed at the same rate, indicating that their droplet sizes should be nearly the same. However, Figure 7 showed that the maximum polymerization rate (first maximum) for the miniemulsion prepared from a 0.05% polystyrene in styrene solution was about two times that of the normal miniemulsion. Therefore, the difference in the polymerization rates cannot be attributed to the initial numbers of droplets present, since these would be expected to be the same.

A more quantitative measure of the initial droplet size distributions can be gained by examining the droplets directly using TEM. In order to avoid complications associated with the volatility of the monomer component of the droplets in the electron beam, this monomer was first removed under vacuum using a Flash-Evaporator (Buchler Instruments). The resulting "particles" were thus in their "unswollen" state, being comprised of the initially added polymer and the cetyl alcohol. The sizes of these polymer particles should be representative of those of the original miniemulsion droplets prepared from polystyrene in styrene solutions and their size distribution should be directly related to their original droplet size distribution.

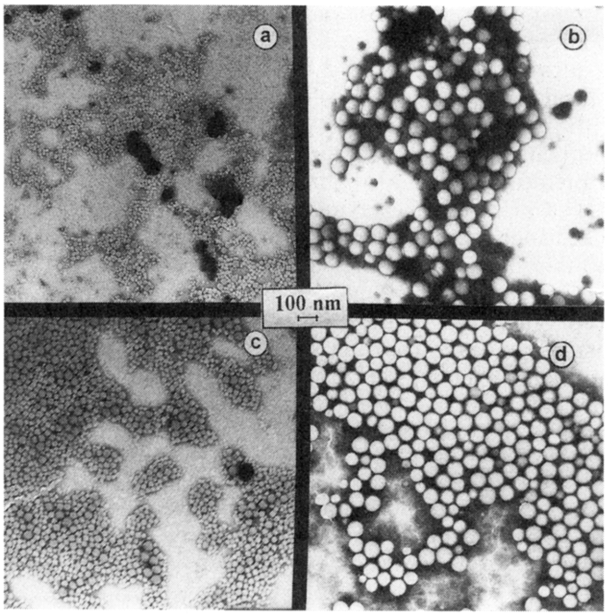

Figure 10. Representative TEM micrographs of polymer particles from miniemulsions: (a) prepared from 0.5% polystyrene in styrene solutions before polymerization; (b) prepared from 0.5% polystyrene in styrene solutions after polymerization; (c) prepared from 1% polystyrene in styrene solutions before polymerization; (d) prepared from 1% polystyrene in styrene solutions after polymerization.

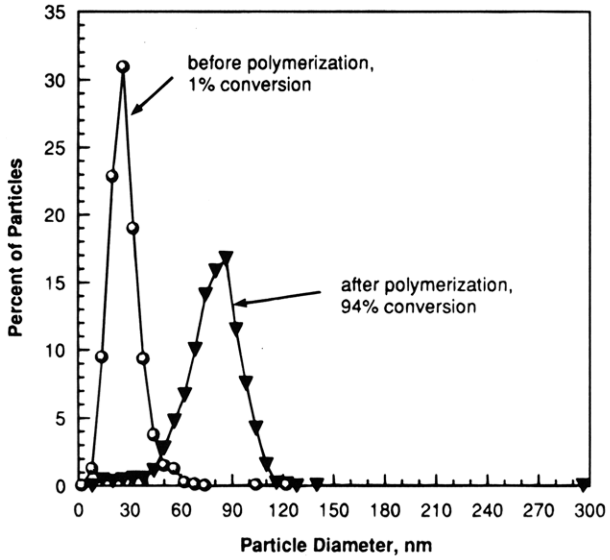

Figure 11. Unswollen particle size distributions before and after polymerization for a miniemulsion prepared from a 1% polystyrene in styrene solution and initiated using 1.33 mM KPS (JBRC-1).

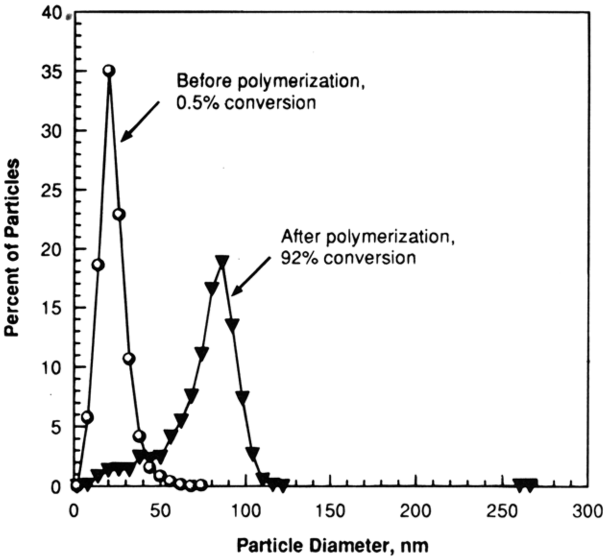

Figure 12. Unswollen particle size distributions before and after polymerization for a miniemulsion prepared from a 0.5% polystyrene in styrene solution and initiated using 1.33 mM KPS (JBRC-3).

Table 4. Particle Sizes and Numbers before and after the Polymerization of Miniemulsions Prepared from 0.5% (JBRC-3) and 1.0% (JBRC-1) Polystyrene in Styrene Solutions

	D_n (before)	$N_p/L \times 10^{-17}$ (before)	D_n (after)	$N_p/L \times 10^{-17}$ (after)
JBRC-3	22.4	11.69	77.18	8.10
JBRC-1	27.1	7.91	78.66	8.08

Figure 10 shows representative TEM micrographs of the resulting particles for miniemulsions prepared with 0.5 and 1% polymer (JBRC-3 and -1, respectively) before and after polymerization, and Figures 11 and 12 show the measured particle size distributions for these two samples, respectively. Several features are apparent in Figure 10. First, polymer particles are clearly observed before and after both polymerizations. This visual confirmation of the existence of small particles serves as partial proof that they were involved as nucleation sites in the polymerization. In addition, the initial droplet size in the miniemulsion prepared from a 0.5% polystyrene in styrene solution is clearly smaller than the initial droplet size in the miniemulsion prepared from the 1% polystyrene in styrene solution. This is consistent with the creaming rate measurements discussed above, which showed that the former creamed more slowly than the latter. Table 4 shows the average particle sizes and numbers of these two samples. The number of particles was calculated by considering the particles to be comprised of both the cetyl alcohol and initially added polymer, as given by:

$$N_p = \frac{6}{\pi \sum_{i=1}^{n} \alpha_i D_i^{\,3}} \left(\frac{M^\circ x}{\varrho_p} + \frac{m_c \mathrm{MW}_c}{\varrho_c} \right) \qquad (5)$$

where M° is the initial mass of monomer and polymer, x is the fractional conversion (including the initial polymer), ϱ_p is the density of the polymer, ϱ_c is the density of the cetyl alcohol, m_c is the moles of cetyl alcohol, MW_c is the molecular weight of cetyl alcohol, and α_i is the fraction of particles with diameter D_i. For the miniemulsions prepared from polystyrene in styrene solutions, the amount of cetyl alcohol in the particles is a known quantity since the total initial amount in the particles should remain constant throughout the polymerization. In contrast, however, the total amount of cetyl alcohol in the particles changes with the fraction of droplets nucleated for normal miniemulsions (those without added polymer). As a result, for miniemulsions prepared in the absence of polymer, the second term in the brackets was assumed to be zero. While the latter simplification might lead to some error at low conversions for normal miniemulsions, the error introduced at higher conversions (such as those calculated in Table 3) should be insignificant.

The data in Table 4 quantify the difference indicated by the creaming rate measurements presented previously; that is, the miniemulsion prepared with 1% polymer contained "droplets" whose dry size was about 5 nm larger than those prepared with 0.5% polymer. Another important result in Table 4 is that the number of particles before and after the polymerization was nearly the same for the miniemulsion prepared from a 1% polystyrene in styrene solution. This is strong evidence that the miniemulsion droplets are serving as the locus of polymerization; i.e., they are capturing radicals and growing in size (polymer content) during the polymerization, as in seeded emulsion polymerizations. It is also observed in Table 4 that the number of particles decreases during the polymerization for the miniemulsion prepared from a 0.5% polystyrene in styrene solution. The most likely cause of this behavior is that, at some point in the reaction, some of the initial miniemulsion droplets are swept up by the growing polymer particles due to collision between the two species. This heterocoagulation of droplets and particles has been suggested to occur for normal miniemulsion droplets (i.e., no polymer initially present) by several researchers.[3,14,16]

Another point may be made regarding Table 4. Knowing the initial number of droplets present, it is possible to estimate more accurately the number of chains/droplet as was done previously using eq 3. In this case, the value for the molecular weight is known (M_n = 64 000), as is the value for the number of particles. Therefore, the number of chains per droplet can easily be determined without further assumptions (i.e., assuming the droplet size previously used in eq 3). Using this approach, it can be shown that the initial average numbers of chains per droplet are 10 and 30 for the miniemulsions prepared with 0.5 and 1% polystyrene solutions, respectively.

Summary and Conclusions

In this paper, the polymerization kinetics of miniemulsions prepared from polystyrene in styrene solutions was investigated. The results showed that the addition of a small amount of polymer (as little as 0.05 wt % based on the oil phase) resulted in a substantial increase in the overall polymerization rate and number of polymer particles formed. This behavior was observed whether cetyl alcohol or hexadecane was used as the cosurfactant but was more pronounced when cetyl alcohol was used. The mechanism for this polymerization was considered to be radical entry into highly monomer-swollen preformed polymer particles (also referred to as miniemulsion droplets containing a small amount of polymer). It was suggested that the addition of increasing amounts of polymer to these droplets results in an increase in the fraction which capture free radicals and become "active" (growing) particles. Samples withdrawn before and after polymerization of a miniemulsion prepared from a 1% polystyrene in styrene miniemulsion revealed that particles were clearly observed prior to the polymerization, validating the proposed mechanism. It was also demonstrated that the number of polymer particles before and after polymerization was nearly unchanged for the miniemulsion prepared from a 1% polystyrene in styrene solution. This result suggests that a large fraction of the initial number of droplets captured radicals, becoming polymer particles.

Acknowledgment. Financial support from the National Science Foundation under Grant CTS-8907600 and the United States Department of Education is greatly appreciated. The laboratory assistance of Mr. P. John Blythe is also acknowledged.

References and Notes

(1) Ugelstad, J.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *111*, 503.

(2) Choi, Y. T.; El-Aasser, M. S.; Sudol, E. D.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2973.

(3) Delgado, J.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 861.

(4) Higuchi, W. I.; Misra, J. *J. Pharm. Sci.* **1962**, *51*, 459.

(5) Ugelstad, J. *Makromol. Chem.* **1978**, *179*, 815.

(6) Hallworth, G. W.; Carless, J. E. *J. Pharm. Pharmacol.* **1972**, *24*, 71.

(7) Lack, C. D.; El-Aasser, M. S.; Silebi, C. A.; Vanderhoff, J. W.; Fowkes, F. M. *Langmuir* **1987**, *3*, 1155.

(8) Chamberlain, B. J.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1*, **1982**, *78*, 591.

(9) Tang, P. L.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *J. Appl. Polym. Sci.* **1991**, *43*, 1059.

(10) Miller, C. M.; Blythe, P. J.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 2365.

(11) Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S., submitted to *Macromolecules*.

(12) Miller, C. M.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S., submitted to *Macromolecules*.

(13) Tang, P. L.; Sudol, E. D.; Adams, M. E.; Silebi, C. A.; El-Aasser, M. S. *Polymer Latexes: Preparation, Characterization, and Applications*; Daniels, E. S., Sudol, E. D., El-Aasser, M. S., Eds.; ACS Symposium Series No. 492; American Chemical Society: Washington, DC, 1992; p 72.

(14) Miller, C. M. Ph.D. Dissertation, Lehigh University, 1994.

(15) Miller, C. M.; Venkatesan, J.; Silebi, C. A.; Sudol, E. D.; El-Aasser, M. S. *J. Colloid Interface Sci.* **1994**, *162*, 11.

(16) Rodriguez, V. S. Ph.D. Dissertation, Lehigh University, 1988.

MA945086T