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# Polymerization of Miniemulsions Prepared from Polystyrene in Styrene Solutions. 2. Kinetics and Mechanism

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ABSTRACT: The kinetics and mechanism of polymerization of miniemulsions prepared from 1% polystyrene in styrene solutions were investigated by conducting reactions with a varying potassium persulfate initiator concentration, and the results were compared with those for miniemulsions prepared in the absence of polymer. The addition of the polystyrene to the miniemulsions was shown to greatly increase the number of polymer particles produced and the overall polymerization rate obtained. The final number of polymer particles was determined for both systems and was shown to vary with the 0.31 power of the initiator concentration in the absence of polymer but was independent of the initiator concentration for miniemulsions prepared from 1% polystyrene in styrene solutions. The final particle size distributions also differed when polystyrene was added to the miniemulsions. The miniemulsions prepared in the absence of polymer produced negatively skewed particle size distributions, the particle size decreasing with increasing initiator concentration. The miniemulsions prepared from 1% polystyrene in styrene solutions produced bimodal particle size distributions for all but the highest initiator concentration employed. By treating the system in an analogous fashion to seeded emulsion polymerization, it was demonstrated that the mechanism for polymerization of miniemulsions prepared from 1% polystyrene in styrene solutions proceeds by radical entry into highly monomer-swollen, preformed polymer particles. Calculation of the average number of radicals per particle for this system revealed that Smith–Ewart case 1 and/or case 2 kinetics were obeyed.

## Background

The experimental results presented in a previous paper[1] showed a difference in the polymerization behavior for styrene miniemulsions prepared with and without small amounts of polystyrene added to the monomer phase. Specifically, it was demonstrated that the addition of as little as 0.05 wt. % polystyrene (based on monomer) resulted in a large increase in the number of polymer particles formed, and correspondingly an increase in the overall polymerization rate. This behavior was shown to occur when either cetyl alcohol or hexadecane was used as the cosurfactant but was more pronounced when cetyl alcohol was used. By examining the "particles" (i.e., initial droplets with monomer removed) of a miniemulsion prepared from a 1% polystyrene in styrene solution (using cetyl alcohol as the cosurfactant) prior to polymerization by transmission electron microscopy, it was demonstrated that the initial number of miniemulsion droplets was close to the final number of polymer particles, indicating that either all of the droplets became active particles (i.e., by entry of free radicals) or at least those that did not become active particles maintained their identity throughout the polymerization. It was postulated that this behavior most likely results from a change in the rate at which miniemulsion "droplets" capture aqueous phase free radicals brought on in some way by the presence of the polymer in the droplets. By this reasoning, increasing the amount of polymer preadded to the miniemulsion "droplets" thus increased the fraction of these droplets which captured radicals and grew during the polymerization.

In this paper, the kinetics and mechanism of miniemulsion polymerization of 1% polystyrene in styrene solutions are compared with those for miniemulsions prepared without polymer, i.e., normal miniemulsions. From an experimental point of view, the only difference between these two systems is the addition of the small amount of polymer to the former. However, it is clear that the presence of the polymer plays an important role in these polymerizations. In order to investigate the differences between these systems, miniemulsions prepared with and without polymer are polymerized using a varying potassium persulfate concentration. For the miniemulsions prepared from 1% polystyrene in styrene solutions, interpretation of the polymerization kinetics is accomplished by considering this system to be analogous to a seeded emulsion polymerization with a highly monomer-swollen latex.

## Experimental Section

The recipe, procedures, and apparatus used in this work are essentially the same as described in the previous paper.[1] Table 1 gives the basic recipe for the miniemulsion polymerizations where the key variables are the initiator concentration employed and whether or not 1% polystyrene was added to the oil (styrene) phase. Table 2 gives the experimental conditions used for all of the experiments. Note that in this paper all of the systems were considered to be miniemulsions (i.e., cetyl alcohol was used as the cosurfactant and homogenization was applied). The polystyrene used in these experiments was obtained from a 92 nm latex (LS-1039E, Dow Chemical Co.; $M_w = 193\,300$, $M_n = 52\,600$) which was cleaned of surfactant via serum replacement. To prepare the miniemulsions, an aqueous gel was first prepared by mixing the distilled-deionized water, SLS, CA, and $NaHCO_3$ at 70 °C for 2 h followed by cooling and homogenizing the resulting gel with a sonifier (Branson Sonic Power Co.) for 1 min at 50% duty, power 7, pulsed. This gel was then mixed with the styrene phase for 20 min, sonified for 10 pulses as described above, and passed through the Microfluidizer (Model 110-T, Microfluidics Corp.) for 10 passes to form the miniemulsion.

The polymerizations were conducted in the Mettler RC1 reaction calorimeter at 70 °C. The particle size distributions were determined by transmission electron microscopy. Further details on both of these techniques were provided in the previous paper.[1]

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**Table 1. Standard Recipe for Polymerization Experiments**

| ingredient | amount | grams |
|---|---|---|
| DDI $H_2O$ | 80 parts | 560 |
| SLS | 10 mM[a] | 1.61 |
| CA | 30 mM[a] | 4.07 |
| KPS | 0.33, 0.67, 1.33, 2.66, or 5.32 mM[a] | 0.05, 0.101, 0.201, 0.402, or 0.804 |
| $NaHCO_3$ | same as KPS[a] | 0.016, 0.032, 0.063, 0.125, or 0.25 |
| styrene | 19.998 or 20.2 parts | 140 or 141.4 |
| polystyrene | 0.202 or 0 parts | 1.414 or 0 |

[a] Based on the water.

**Table 2. Experimental Variables Studied[a]**

| experiment identifier | wt % polymer | KPS,[b] mM |
|---|---|---|
| JBRC-8 | 1 | 0.33 |
| JBRC-7 | 1 | 0.67 |
| JBRC-1 | 1 | 1.33 |
| JBRC-6 | 1 | 2.66 |
| JBRC-11 | 1 | 5.32 |
| RC1-21 | 0 | 0.33 |
| RC1-20 | 0 | 0.67 |
| RC1-18 | 0 | 1.33 |
| RC1-19 | 0 | 2.66 |
| RC1-45 | 0 | 5.32 |

[a] All recipes were prepared with 10 mM SLS/30 mM CA and were homogenized using the Microfluidizer. [b] Based on the water.

## Results and Discussion

**Effect of Initiator Concentration.** The previous paper demonstrated that increasing the initial amount of polymer added to a miniemulsion resulted in an increase in the overall polymerization rate and the number of polymer particles produced. It was also demonstrated that for miniemulsions prepared from 1% polystyrene in styrene solutions, the number of polymer particles was the same at the beginning and end of the polymerization. These results suggest that the miniemulsion droplets formed from 1% polystryene in styrene solutions behave similarly to a latex "seed", capturing radicals and growing during the polymerization. It should be noted that the monomer to polymer swelling ratio in this system is 99 parts monomer to 1 part polymer, much higher than could be attainable in a seeded system (without employing a cosurfactant such as cetyl alcohol). Based on these results, it is postulated that this system may be treated like a seeded system, and experiments may be designed accordingly to determine the mechanisms of polymerization. One common method for treating seeded systems is to determine the effect of initiator concentration on the polymerization kinetics.[2-4] In this way, the effects of radical entry and exit can be systematically studied by determining the variation of $\bar{n}$ with the initiator concentration. The rate equation governing emulsion polymerization is given as

$$R_p = \frac{k_p[M]_p N_p \bar{n}}{N_a} \tag{1}$$

where $k_p$ is the propagation rate coefficient, $[M]_p$ is the concentration of monomer in the polymer particles, $N_p$ is the number of polymer particles, $\bar{n}$ is the average number of radicals per polymer particle, and $N_a$ is Avogadro's number. In conventional emulsion and miniemulsion polymerizations, the number of particles will increase during the nucleation stage (0–60% conversion in miniemulsion polymerization). Therefore, the determination of $\bar{n}$ is not straightforward; it requires a knowledge of the evolution of the number of particles, which is not always available. In seeded emulsion polymerizations, however, the experiments are designed to keep $N_p$ constant, and therefore $\bar{n}$ can be calculated if $k_p$ and $[M]_p$ are known. The value of $k_p$ has been shown to be constant up to relatively high conversions, and values for this constant are widely available in the literature. The latter term, $[M]_p$, has been derived for seeded emulsion polymerizations using sparingly water-soluble monomers:

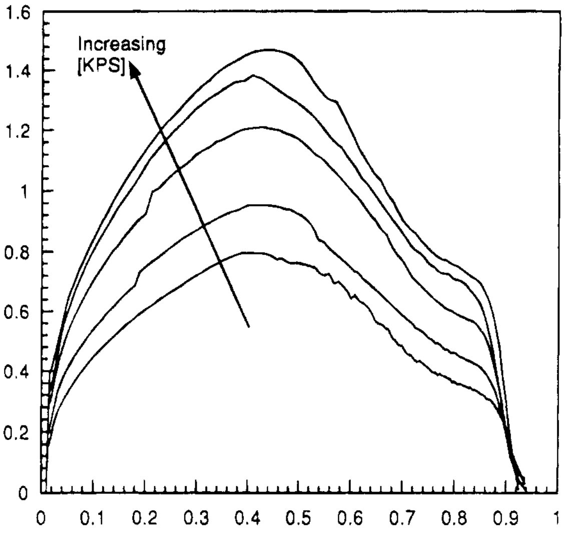

**Figure 1.** Polymerization rate versus fractional conversion curves for miniemulsions prepared from 1% polystyrene in styrene solutions initiated using 0.33, 0.67, 1.33, 2.66, and 5.32 mM KPS as indicated by the arrow. $T_r$ = 70 °C.

$$[M]_p = \frac{(1-x)M^\circ_m/MW_m}{M^\circ_m\bar{V}_{sm} + M^\circ_p\bar{V}_{sp} + xM^\circ_m(\bar{V}_{sp} - \bar{V}_{sm})} \tag{2}$$

where $MW_m$ is the molecular weight of the monomer, $M^\circ_m$ is the initial grams of monomer, $M^\circ_p$ is the initial grams of polymer, and $\bar{V}_{sm}$ and $\bar{V}_{sp}$ are the partial specific volumes of the monomer and polymer, respectively. The latter have units of volume/mass (i.e., 1/density).

It was speculated above that for this new system (i.e., miniemulsions prepared from polystyrene in styrene solutions), the behavior is similar to seeded emulsion polymerizations having polymer concentrations greater than or equal to 1%. This speculation was based on the fact that the number of particles before and after the polymerization remained constant, as is always true in a seeded system without secondary nucleation or coagulation. In this section, further evidence is provided for this polymerization mechanism by systematically investigating the effect of initiator concentration on the polymerization kinetics of miniemulsions prepared from polystyrene in styrene solutions.

**Polymerization Kinetics.** Figure 1 shows the polymerization rate versus conversion curves for miniemulsions prepared from 1% polystyrene in styrene solutions and initiated using a range of initiator concentrations ([KPS] = 0.33, 0.67, 1.33, 2.66, or 5.32 mM). Figure 2 shows the conversion–time curves corresponding to the rate curves given in Figure 1. Figure 3 shows the polymerization rate versus conversion curves for miniemulsions prepared without polymer initiated using

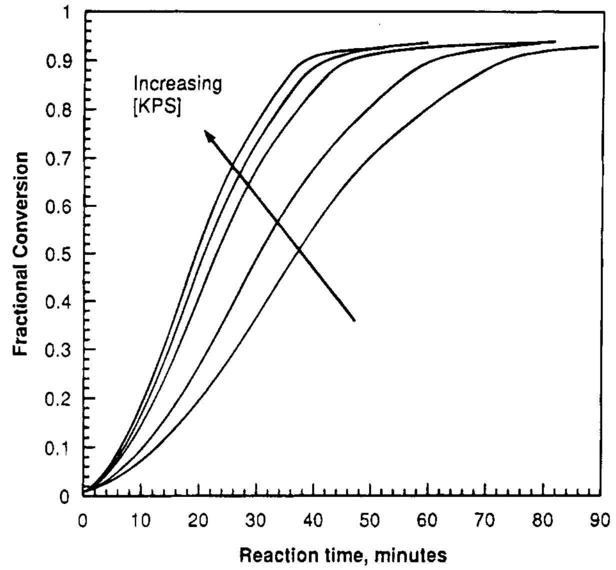

**Figure 2.** Conversion versus time curves for miniemulsions prepared from 1% polystyrene in styrene solutions initiated using 0.33, 0.67, 1.33, 2.66, and 5.32 mM KPS as indicated by the arrow. $T_r$ = 70 °C.

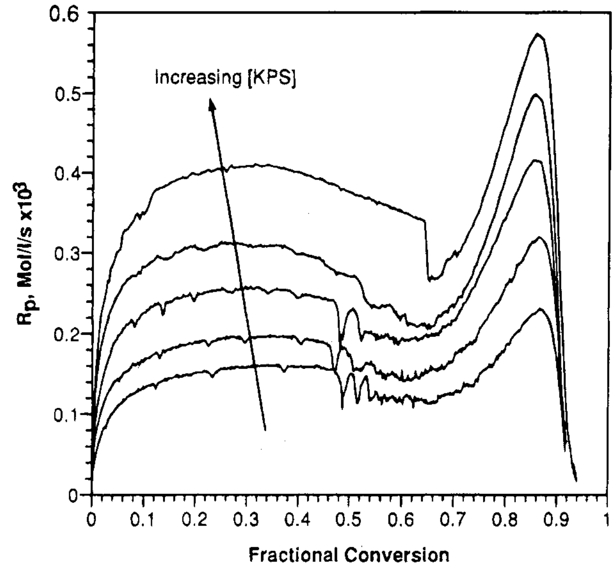

**Figure 3.** Polymerization rate versus fractional conversion curves for normal miniemulsions (prepared in the absence of polymer) initiated using 0.33, 0.67, 1.33, 2.66, and 5.32 mM KPS as indicated by the arrow. $T_r$ = 70 °C.

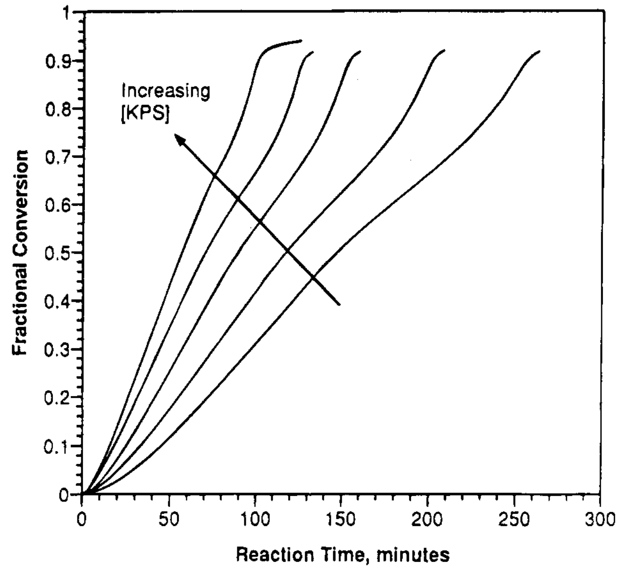

**Figure 4.** Conversion versus time curves for normal miniemulsions (prepared in the absence of polymer) initiated using 0.33, 0.67, 1.33, 2.66, and 5.32 mM KPS as indicated by the arrow. $T_r$ = 70 °C.

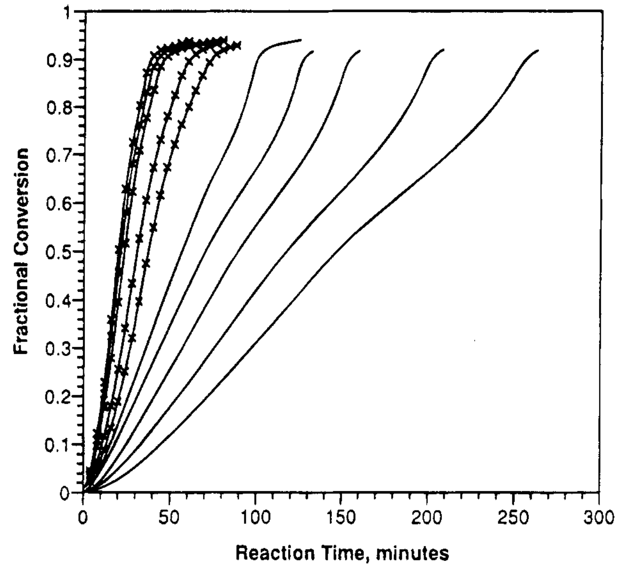

**Figure 5.** Conversion versus time curves for normal (i.e., no polymer) styrene miniemulsions (—) and miniemulsions prepared from 1% polystyrene in styrene solutions (×) initiated using 0.33, 0.67, 1.33, 2.66, and 5.32 mM KPS. $T_r$ = 70 °C.

the same initiator concentrations, and Figure 4 shows the corresponding conversion–time curves.

Figures 1 and 3 show that the polymerization rates increase with increasing initiator concentration for both systems (i.e., miniemulsions prepared with 0 or 1% polymer). The main difference between the miniemulsions prepared from 1% polystyrene in styrene solutions (Figures 1 and 2) and the normal miniemulsions (i.e., no polymer, Figures 3 and 4) is that the overall polymerization rates are much greater in the former. This can be more clearly demonstrated by comparing the conversion–time curves for all of the polymerizations, as shown in Figure 5. This figure clearly shows that the reaction using the lowest initiator concentration (0.33 mM KPS) to polymerize the miniemulsion prepared with 1% polymer was faster than any of the normal miniemulsions, even at the highest initiator concentration used (5.32 mM). In addition, by comparing Figures 1 and 3 it is observed that the normal miniemulsions (Figure 3) have a much more pronounced gel effect (the second peak at high conversion) than the miniemulsions prepared from polystyrene in styrene solutions (Figure 1). This is a consequence of the size of the polymer particles produced in the two polymerizations, as given in Table 3. The normal miniemulsions result in larger size latex particles than those produced from 1% polystyrene in styrene solutions. As a result, the normal miniemulsions will have a lower rate of bimolecular termination in the region of high conversion (>65%) compared to the miniemulsions prepared from polystyrene in styrene solutions, resulting in a more pronounced gel effect in the former. The rate curves also differ in the shape of the initial increase in the rate of polymerization to a maximum. For those prepared without polymer, the slope of the rate curve decreases rapidly over the first 10% conversion and then slowly until the maximum is reached (i.e., $dR_p/dx = 0$). In contrast, for the miniemulsions prepared with 1%

**Table 3. Particle Size Analysis and Calculated Numbers of Particles for Miniemulsions Polymerized according to the Recipe and Conditions Given in Tables 1 and 2**[a]

| experiment identifier | KPS,[b] mM | $D_v$, nm | $D_n$, nm | $\sigma$, nm | $N_p$/L × $10^{-17}$ |
|---|---|---|---|---|---|
| JBRC-8[c] | 0.33 | 78.6 | 67.3 | 30.2 | 9.24 |
| JBRC-7[c] | 0.67 | 80.8 | 73.6 | 24.9 | 8.56 |
| JBRC-1[c] | 1.33 | 82.4 | 78.7 | 17.2 | 8.08 |
| JBRC-6[c] | 2.66 | 76.8 | 71.4 | 20.2 | 9.97 |
| JBRC-11[c] | 5.32 | 78.6 | 75.5 | 15.7 | 9.19 |
| RCl-21[d] | 0.33 | 174.5 | 171.3 | 23.9 | 0.76 |
| RCl-20[d] | 0.67 | 159.3 | 156.0 | 22.7 | 1.01 |
| RCl-18[d] | 1.33 | 153.9 | 151.2 | 20.4 | 1.11 |
| RCl-19[d] | 2.66 | 144.6 | 142.3 | 1.33 | 1.33 |
| RCl-45[d] | 5.32 | 132.2 | 128.5 | 21.1 | 1.88 |

[a] All particle sizes were determined by TEM. [b] Based on the water. [c] 1% polystyrene. [d] 0% polystyrene.

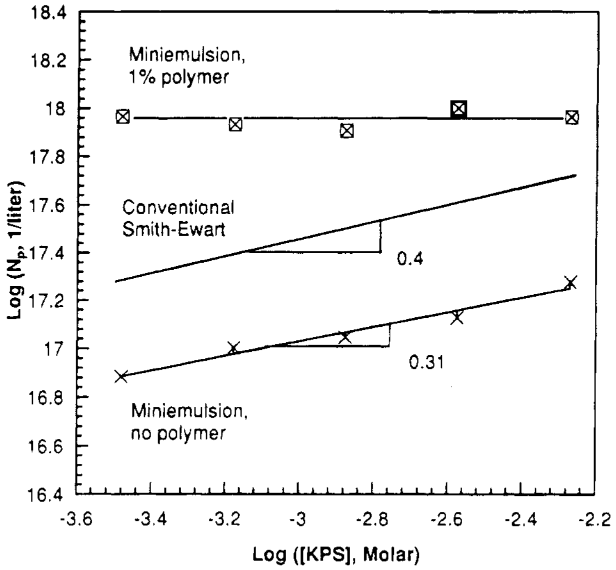

**Figure 6.** log($N_p$) versus log([KPS]) for normal styrene miniemulsion polymerizations (i.e., no polymer), conventional styrene emulsion polymerizations, and miniemulsion polymerizations of 1% polystyrene in styrene solutions. $0.33 \leq$ [KPS] $\leq 5.32$ mM, $T_r = 70$ °C.

polymer, the rate of polymerization is immediately fairly high, and then the increase is more gradual (but steep compared to the normal miniemulsion) until a relatively sharp peak is reached at the maximum. Finally, the fluctuations in the rate curves observed after 45% conversion for the miniemulsions prepared without polymer are not observed for the miniemulsions prepared from 1% polystyrene in styrene solutions.

It is well known that, for miniemulsions prepared without polymer, the number of polymer particles produced is sensitive to the initiator concentration employed. This has been attributed to the nucleation of only a fraction of the initial number of droplets present, this fraction increasing with increasing initiator concentration.[6,7] For the miniemulsions prepared from 1% polystyrene in styrene solutions, the final number of particles is expected to remain constant if the system behaves like a seeded system. Table 3 shows the final particle numbers obtained for these polymerizations. Figure 6 shows the relationship between the log of the final number of particles and the log of the initiator concentration employed for conventional emulsion polymerizations, normal miniemulsion polymerizations, and miniemulsion polymerizations of 1% polystyrene in styrene solutions. This figure shows that, as would be expected for a seeded system, the number of particles is independent of the initiator concentration used for the polymerization of the miniemulsions prepared from 1% polystyrene in styrene solutions. This result is contrasted to the result found for the normal miniemulsion polymerizations (0.31 slope), and the well-known theoretical prediction for conventional emulsion polymerizations (0.4 slope).

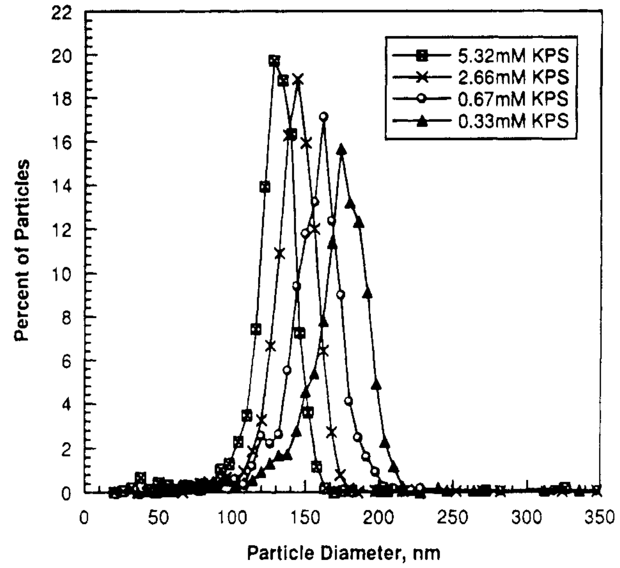

**Figure 7.** Final particle size distributions for normal miniemulsions (i.e., no polymer) initiated using 5.32, 2.66, 0.67, and 0.33 mM KPS, as indicated.

By extrapolation, the intersection of the two lines representing the normal miniemulsions (i.e., no polymer) and the miniemulsions prepared from polystyrene in styrene solutions can be used as a rough estimate of the amount of initiator that would be required to nucleate all of the droplets in miniemulsions prepared in the absence of polymer. This calculation results in a value of about 1.5 M KPS, indicating that, in the absence of polymer, the amount of initiator which must be added to nucleate all of the monomer droplets is prohibitively large. This amount is well above the critical coagulation constant determined in the work of Goetz[7] (~0.5 M for NaCl added to toluene miniemulsions), indicating that the addition of this much electrolyte would destroy the colloidal stability of the emulsion before polymer particles could be formed.

**Particle Size Distributions.** The independence of the particle number on the initiator concentration supports the idea that miniemulsions prepared from 1% polystyrene in styrene solutions behave similarly to seeded systems. If the system is truly behaving like a seeded system, the increase in the polymerization rates shown in Figure 1 with the increasing initiator concentration cannot be explained as resulting from an increase in the number of particles. The only alternative explanation would be that $\bar{n}$ is increasing with increasing initiator concentration. However, at this point further evidence is still needed to prove that this system is behaving like a seeded emulsion polymerization. This evidence may be provided by measuring the final particle size distributions. For a seeded system, these would be expected to be almost independent of the initiator concentration, perhaps broadening slightly with decreasing initiator concentration.

Figure 7 shows the final particle size distributions for the normal miniemulsions initiated using 0.33, 0.67, 2.66, and 5.32 mM KPS, and Figure 8 shows the final particle size distributions for miniemulsions prepared

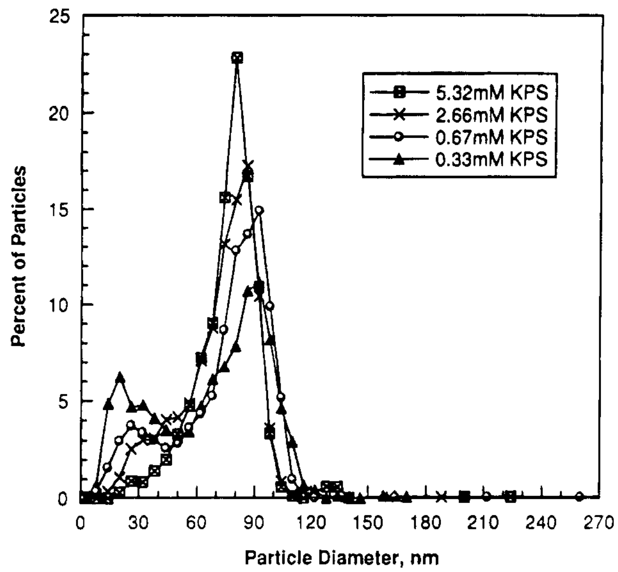

**Figure 8.** Final particle size distributions for miniemulsions prepared from 1% polystyrene in styrene solutions and initiated using 5.32, 2.66, 0.67, and 0.33 mM KPS, as indicated.

from 1% polystyrene in styrene solutions and polymerized using the same initiator concentrations. It is immediately apparent by comparing Figures 7 and 8 that the particle size distributions are different when polymer is added. The normal miniemulsion final particle size distributions are all negatively skewed (i.e., with a tail of small particles) and show the presence of a few relatively large particles. In addition, the average particle size decreases with increasing initiator concentration. The factors contributing to the shapes of these particle size distributions were reported in detail elsewhere.[8] The decrease in the average size with increasing initiator concentration is the result of the increasing fraction of the initial droplets which become polymer particles. The negative skewing of the particle size distributions results from the long nucleation period, longer nucleation periods resulting in more skewed particle size distributions. Finally, the presence of the large particles results from free radical entry into large monomer droplets early (i.e., <5% conversion) in the polymerization. In contrast to these particle size distributions, the particle size distributions produced for the miniemulsions prepared from 1% polystyrene in styrene solutions are bimodal for all but the highest initiator concentration (5.32 mM KPS). In addition, the fraction of the particles under the first peak decreases with increasing initiator concentration, and the mean diameter of the second peak decreases slightly (by about 2–3 nm) with increasing initiator concentration.

The particle size distributions for the miniemulsions prepared by polymerizing 1% polystyrene in styrene solutions (Figure 8) can be explained by considering the polymerization to occur by entry of aqueous phase free radicals into the highly monomer-swollen, preformed polymer particles (formerly referred to as miniemulsion droplets). As the polymerization proceeds, the number of particles which capture a radical (referred to as "active" particles) increases. Therefore, these active particles will grow at the expense of the particles which have yet to capture a radical (referred to as "unentered" particles). If, by the end of the polymerization, some particles have yet to capture a radical, these particles would be expected to resemble their initial unswollen size. The number of these unentered particles would be expected to decrease with increasing initiator concentration, and in the limiting case that all particles were able to capture radicals, this number will be zero. Based on this mechanism, it can be concluded that the bimodal distributions are a consequence of only a fraction of the initial "droplets" being entered by a free radical during the polymerizations. The first peak, therefore, corresponds to unentered particles, while the second to active particles. For the highest initiator concentration, almost all of the particles succeeded in capturing a radical, and therefore the peak is almost unimodal. The slight increase in the mean diameter of the second peak with decreasing initiator concentration can be attributed to the redistribution of monomer from the unentered polymer particles to the active polymer particles. This redistribution would be expected to be the greatest for the lowest initiator concentration, resulting in the shift toward larger mean diameters. It is important to note that the independence of the final number of particles on the initiator concentration employed indicates that the *total* number of particles in the system (which would be obtained by integrating the distributions) remains constant throughout the polymerizations.

Based on the above explanation, it can be stated that, particularly at the lower initiator concentrations, this system is not behaving exactly like a seeded emulsion polymerization. However, the system sufficiently resembles a seeded system that some of the same data treatment may be applied. The interpretation of the results obtained using these techniques will have to be modified appropriately to include the differences between seeded emulsion polymerizations and polymerization of miniemulsions prepared from 1% polystyrene in styrene solutions.

**Average Number of Radicals per Particle.** It was demonstrated above that for miniemulsions prepared from 1% polystyrene in styrene solutions, the number of particles remains constant throughout the polymerization. This being the case, the average number of radicals per particle, $\bar{n}$, can be calculated for these polymerizations by manipulating eq 1 to give

$$\bar{n} = R_p\left(\frac{N_a}{k_p N_p [M]_p}\right) \qquad (3)$$

It is seen from eq 3 that if the total number of particles is constant and known, the only parameters needed for calculating $\bar{n}$ are the propagation rate coefficient, $k_p$, and the concentration of monomer in the polymer particles, $[M]_p$. The former has been reported to be 425.6 dm$^3$ mol$^{-1}$ s$^{-1}$ (70 °C)[9] for conversions less than about 85% (at which point this value decreases in an unknown manner due to the polymer particles becoming glassy). The latter variable, $[M]_p$, can be calculated using eq 2.

Figure 9 shows the polymerization rate and average number of radicals per particle plotted versus conversion for the miniemulsion prepared from a 1% polystyrene in styrene solution and initiated using 5.32 mM KPS (the highest initiator concentration employed). From this figure, it is seen that $\bar{n}$ increases almost linearly up to about 48% conversion, becomes constant at intermediate conversions ($0.48 < x(t) < 0.72$), and finally increases again at conversions greater than 72%. The initial rise results from the fact that the calculation of $\bar{n}$ is based on the total number of polymer particles, as opposed to the number of active particles. Therefore, at the beginning of the reaction the value calculated for

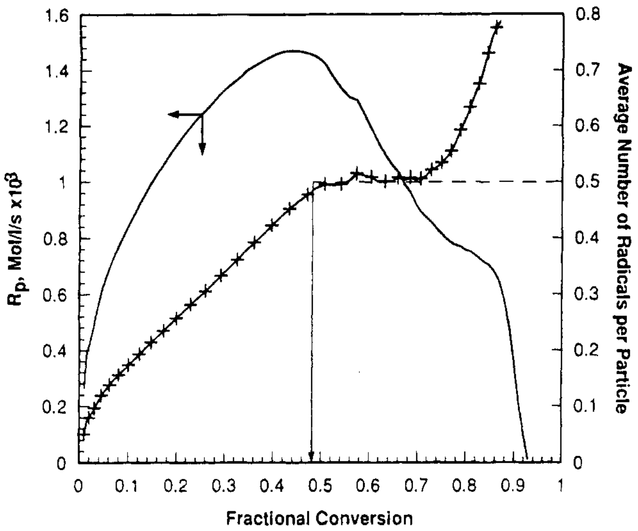

**Figure 9.** Polymerization rate and average number of radicals per particle for a styrene miniemulsion polymerization prepared from a 1% polystyrene in styrene solution and initiated using 5.32 mM KPS. $T_r$ = 70 °C.

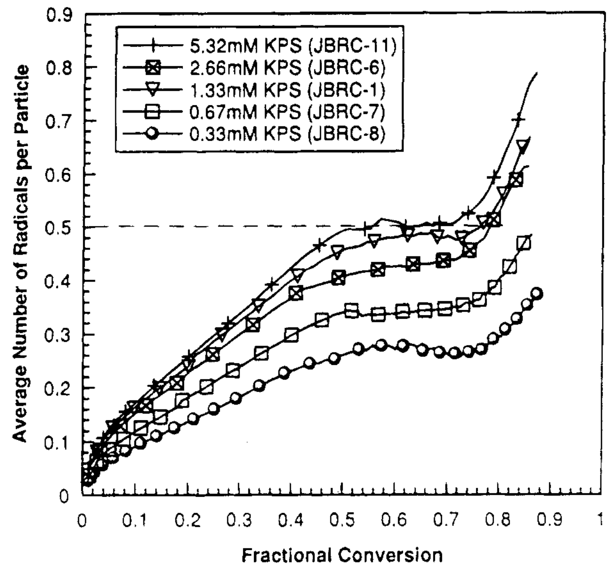

**Figure 10.** Average number of radicals per particle versus fractional conversion for miniemulsions prepared from 1% polystyrene in styrene solutions and initiated using 5.32, 2.66, 1.33, 0.67, or 0.33 mM KPS as indicated (JBRC-11, -6, -1, -7, and -8, respectively). $T_r$ = 70 °C.

$\bar{n}$ will be zero (i.e., due to zero active particles) and this value will increase as the number of active particles increases. Based on this reasoning, it would be expected that during the plateau region in which $\bar{n}$ remains constant the number of active particles remains unchanged. The value for $\bar{n}$ during this period is seen to be about 0.5. This suggests that all of the particles are active during this period, and the system is obeying Smith–Ewart case 2 kinetics. This explanation is consistent with the final particle size distribution observed for this latex (Figure 8), which did not show two distinct peaks, indicating that almost all of the particles were active. The final rise in $\bar{n}$ is attributed to the gel effect, which brings about an increase in the average number of radicals per particle through decreased diffusivity of the radicals, effectively decreasing the termination rate.

Figure 10 shows the calculated values for $\bar{n}$ up to conversions of about 85% for all of the miniemulsions prepared from 1% polystyrene in styrene solutions. All of these curves show the same general behavior, i.e., an increase in $\bar{n}$, followed by a plateau region and another increase. It is seen from this figure that the value for $\bar{n}$ in the plateau region seems to be related to the initiator concentration, a lower initiator concentration resulting in a lower value for $\bar{n}$. There are two potential reasons for this behavior. The first reason concerns the fact that not all of the particles are active. This was apparent from Figure 8, which showed that for lower initiator concentrations, the latex particle size distributions were bimodal, with the smaller particle size becoming more prominent with decreasing KPS concentration. It was concluded, based on this observation, that the fraction of active particles decreased with decreasing initiator concentration. Since the calculation of $\bar{n}$ is based on the total number of particles, if the number of active particles is less than the total number of particles, the value calculated for $\bar{n}$ will be lower than the value in the active particles. The second reason for the decrease in the plateau value for $\bar{n}$ with decreasing initiator concentration is that the actual steady-state value of $\bar{n}$ is less than 0.5 for the lower initiator concentrations. This behavior has been observed previously for seeded emulsion polymerizations.[2] Values of $\bar{n}$ below 0.5 (based on the number of active particles) are usually attributed to radical desorption from the polymer particles. This may become significant at lower initiator concentrations when the value for $\varrho$, the pseudo-first-order entry rate coefficient, becomes less than the value for $k$, the exit rate coefficient. The actual reason for the decreasing value of the plateau in $\bar{n}$ with decreasing initiator concentration can be determined if the number of active particles is known. However, this is not easily obtainable in this system since there is a distribution of birth times of the active particles, making deconvolution of the unentered and active particles difficult.

## Summary and Conclusions

In this paper, the kinetics and mechanism of polymerization of miniemulsions prepared from 1% polystyrene in styrene solutions were investigated by varying the amount of potassium persulfate initiator. In addition, normal (i.e., no polymer) miniemulsions were also polymerized for comparison. The results demonstrated that the addition of 1% polystyrene to the miniemulsion droplets resulted in a significant increase in the number of polymer particles formed and the overall polymerization rate obtained. For miniemulsions prepared from 1% polystyrene in styrene solutions, the number of polymer particles produced was independent of the initiator concentration employed, while for the normal miniemulsions, the particle number showed a 0.31 power dependence on the initiator concentration. The final particle size distributions obtained for the miniemulsions prepared from 1% polystyrene in styrene solutions were bimodal for all but the highest initiator concentration employed. For this system, the polymerization mechanism was postulated to proceed by free radical entry into highly monomer-swollen, preformed polymer particles. The average number of radicals per polymer particle was calculated, and the system was determined to obey Smith–Ewart case 1 and/or case 2 kinetics in the active particles.

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## References and Notes

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

(2) Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1323.

(3) Whang, B. C. Y.; Napper, D. H.; Ballard, M. J.; Gilbert, R. G.; Lichti, G. *J. Chem. Soc., Faraday Trans 1* **1982**, *78*, 1117.

(4) Morrison, B. R.; Casey, B. S.; Lacik, I.; Leslie, G. L.; Sangster, D. F.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 631.

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

(6) Delgado, J.; El-Aasser, M. S.; Silebi, C. A.; Vanderhoff, J. W. *Polym. Mater. Sci. Eng.* **1987**, *57*, 976.

(7) Goetz, R. J.; El-Aasser, M. S. *J. Colloid Interface Sci.* **1991**, *142*, 317.

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

(9) Friis, N.; Hamielec, A. E. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 251.

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