

Polymerization of Miniemulsions Prepared from Polystyrene in Styrene Solutions. 3. Potential Differences between Miniemulsion Droplets and Polymer Particles

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ABSTRACT: In two previous papers, it was demonstrated that the addition of a small amount of polystyrene to the styrene used in preparing miniemulsions results in a substantial increase in the overall polymerization rate and the number of polymer particles formed. In this paper, this behavior is attributed to a basic difference in the abilities of miniemulsion droplets and polymer particles to capture aqueous phase free radicals. It is hypothesized that miniemulsions prepared from polystyrene in styrene solutions resemble the polymer particles formed in normal (i.e., no polymer) miniemulsion polymerizations at early conversions. This being the case, these polymer-containing droplets are able to effectively compete with growing polymer particles for free radicals, whereas their counterparts which contain no polymer are not, and as a result a greater fraction of the initial droplets become polymer particles. Based on this mechanism, it is speculated that the presence of the polymer increases the capture efficiency of the droplets by modifying either their interior (i.e., by increasing the interior viscosity, thereby increasing the probability of a radical to propagate rather than exit) or the droplet/water interface (i.e., by disrupting a SLS/CA interfacial barrier to radical entry). Experimental results are reported which support the latter.

Background

The previous two papers in this series^{1,2} demonstrated that when styrene miniemulsions were prepared by adding a small amount of polystyrene to the monomer, the polymerization rate and number of particles produced were substantially increased. The polymerization was considered to proceed by aqueous phase free radical entry into the highly monomer-swollen, preformed polymer particles, and this entry was suggested to be substantially easier for miniemulsion droplets containing 1 wt % polymer than those prepared without polymer. As a result, a much greater fraction of miniemulsion droplets succeeded in capturing radicals, resulting in the greater polymerization rates and particle numbers noted above.

In this paper, some potential reasons for this difference between miniemulsion droplets and polymer particles (or, alternatively, droplets containing small amounts of polymer) with respect to their abilities to capture radicals are discussed. In addition, indirect experimental evidence is provided which suggests that this behavior is indeed attributable to basic differences between droplets and particles with respect to their abilities to capture aqueous phase free radicals.

Experimental Section

Polymerizations. The recipe, procedures, and apparatus used in this work are essentially the same as described in the previous papers. Table 1 gives the basic recipe for the miniemulsion polymerizations. Table 2 gives the experimental conditions used for all of the experiments. The key variables of note are the amount of polymer introduced into the oil phase of the miniemulsion (0, 1, or 2%) and the initial location of the cetyl alcohol (i.e., the aqueous (gel) or oil phase). 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. When the cetyl alcohol was initially located in the aqueous phase, a gel was prepared by mixing the distilled-

Table 1. Recipe for Polymerizations

ingredient	amount	grams
DDI H ₂ O	80 parts	560
SLS	10 mM ^a	1.61
CA or KPS	30 mM ^a or 1.33 mM ^a	4.07 or 0.201
NaHCO ₃	1.33 mM ^a	0.03
styrene	20.2, 20, or 19.8 parts	141.4, 140, or 138.6
polystyrene	0, 0.2, or 0.4 parts	0, 1.41, or 2.83

^a Based on the water.

Table 2. Identification of Polymerizations Performed

experiment identifier	% polymer ^a	location of cetyl alcohol
JBRC-2	0	aqueous (gel) phase
RC1-29	0	oil phase
JBRC-1	1	aqueous (gel) phase
JBRC-4	1	oil phase
JBRC-12	2	aqueous (gel) phase

^a Based on the monomer phase.

deionized water, SLS, and CA 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. When the cetyl alcohol was initially located in the oil phase, the cetyl alcohol was first dissolved in the styrene along with the polystyrene (if used). If either case, the aqueous phase and the oil phase were then mixed together 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. This reactor was baffled and equipped with a turbine stirrer (45° pitch) which was run at 300 rpm during the experiments. Further details on the Mettler RC1 were provided in the previous paper.¹

Interfacial Tensions. The drop volume method was used to measure interfacial tensions between aqueous surfactant solutions and polymer/monomer solutions. This technique measures the interfacial tension by determining the volume of a drop of a liquid which breaks away from the tip of a capillary of known diameter. The volume of the drop is related to the interfacial tension by

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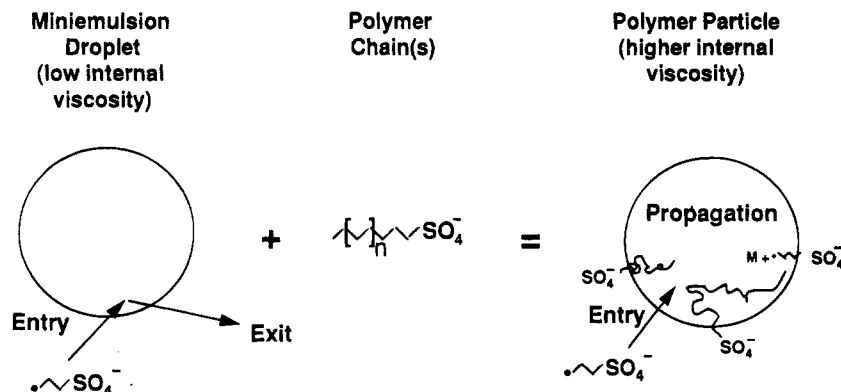


Figure 1. Schematic depiction of how the addition of polymer to miniemulsion "droplets" may increase the probability for radical capture by increasing the interior viscosity of the polymer particles.

$$\gamma = \frac{V(\Delta\rho)g}{r}F \quad (1)$$

where V is the drop volume, $\Delta\rho$ is the density difference between the drop and the surrounding fluid through which it falls, g is the gravitational constant, r is the capillary radius, and F is a correction factor that has the physical significance of being the ratio of the weight of the part of the liquid that breaks away to the total weight of the drop at the instant it breaks away. F is a function of $r/V^{1/3}$ and was obtained from the tables of Lando and Oakly.³ Drops were formed by pumping aqueous surfactant solutions through the capillary into styrene/polystyrene/cetyl alcohol solutions using a constant flow rate pump. Two different types of polystyrene were used in these experiments: polystyrene from a monodisperse latex and polystyrene from a commercial product (Dajac Laboratories; $M_w = 60\,300$, $M_n = 24\,400$). The flow rate was selected such that the drops did not break off before 4 min had elapsed. The average volume of ten drops was taken for each measurement. The interfacial tensions measured using this technique had standard deviations less than 0.5 dyn/cm.

Results and Discussion

As mentioned above, the addition of a small amount of polystyrene (as little as 0.05%) to the oil phase of an otherwise normal styrene miniemulsion was shown to result in a substantial increase in the overall polymerization rate and the number of polymer particles formed. Since these polymer-containing droplets should, in many respects, resemble polymer particles at early conversions, this result suggests that miniemulsion droplets and the polymer particles formed by radical entry into these droplets behave differently with respect to their abilities to capture aqueous phase free radicals. Specifically, it is suggested that miniemulsion droplets are less efficient at capturing radicals than polymer particles. This is an unusual result since these species should physically resemble one another, particularly at low conversions when each particle contains only a small amount of polymer.

Since the chemical compositions of the two different species, droplets and particles, are so similar, it seems logical to conclude that this is not the principal cause of the observed behavior. An attractive alternative for explaining this behavior is a change in the physical nature of the droplets upon addition (or formation) of a few polymer chains. This being the case, some hypotheses can be generated, and, based on these, appropriate experiments may be designed to test these.

Possible Differences between Miniemulsions Prepared with and without Polymer. Several researchers have suggested that the rate of radical entry into miniemulsion droplets is slower than into normal

latex particles.⁴⁻⁶ This interpretation is consistent with the experimental results noted above; i.e., the addition of a small amount of polymer to miniemulsion droplets results in a substantial increase in the number of particles formed. It seems reasonable to conjecture that if this is true, the addition of polymer to miniemulsion droplets can change their ability to capture radicals by modifying either the interior or the oil/water interface of the droplets. For the former to be true, it would be expected that the addition of polymer primarily affects the rate of desorption of radicals from the droplets by increasing the interior viscosity. For the latter to be true, a portion of the polymer should reside at the droplet/water interface, thereby modifying the surface characteristics. These two possibilities are considered below.

The first idea described above concerns the possibility that the polymer modifies the interior of the droplets by increasing the viscosity of the oil phase, thereby increasing the likelihood that a radical which enters a droplet will propagate rather than exit. It is well known that the viscosity of polymer solutions increases with increasing polymer concentration. It has also been suggested that the entry of radicals into latex particles may involve hundreds of entry and exit events before propagation occurs (i.e., true entry), particularly for "oligomers" of smaller sizes (e.g., 0, 1, or 2 monomeric units).⁷ The rate of diffusion of small molecules, such as oligomers, is known to be inversely proportional to the viscosity of the solution. Therefore, the question to be asked is how much polymer is necessary to reduce the rate of diffusion of radicals inside a droplet so as to increase the probability that a radical will propagate rather than exit. This idea is illustrated schematically in Figure 1.

The second idea described above concerns the possibility that the polymer modifies the droplet/water interface, thereby allowing radicals to more easily enter and propagate. It has been demonstrated by a number of researchers⁸⁻¹¹ that aqueous long-chain alcohol-surfactant (i.e., cetyl alcohol-sodium lauryl sulfate) systems form ordered lamellar structures. These structures have also been shown to exist at the surface of monomer droplets stabilized using these materials.¹¹ This has led to the speculation that these structures contribute to the overall stability of the emulsion by forming interfacial barriers preventing coalescence of droplets. These barriers have been postulated to be liquid-like, electrically charged, and of high strength.^{8,12,13} The presence of these barriers may also hinder the entry of radicals into the monomer droplets, and if their order is disrupted by the addition (or formation) of polymer

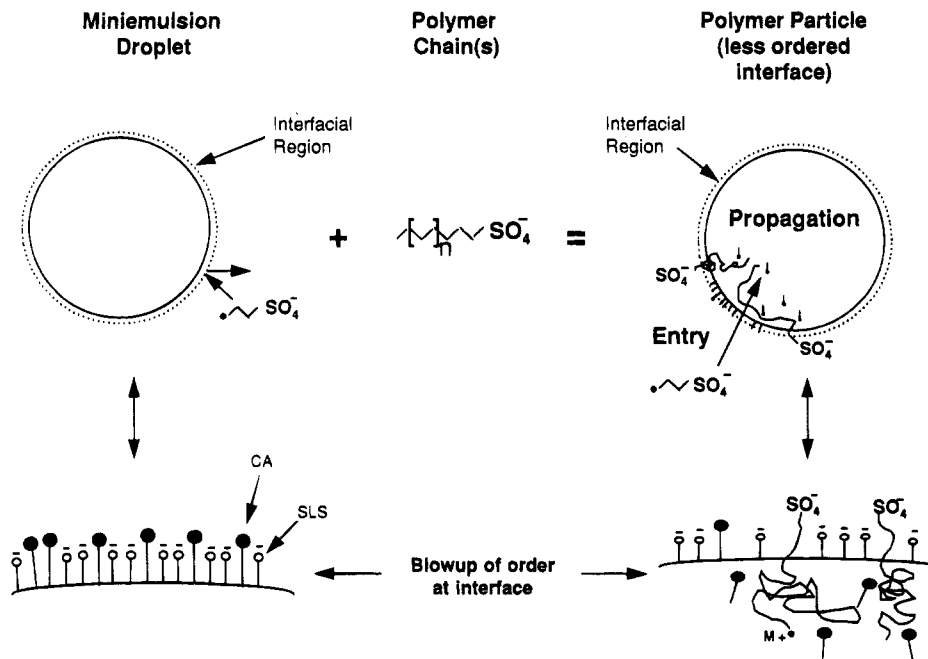


Figure 2. Schematic depiction of how the addition of polymer to miniemulsion "droplets" may increase the probability for radical capture by disrupting the interfacial packing of cetyl alcohol and sodium lauryl sulfate.

to the interior of the droplets, may explain the experimental results. That is, the order of the interface hinders the entry of radicals into monomer droplets relative to those which contain some polymer (i.e., polymer particles). This idea is illustrated schematically in Figure 2.

It is apparent from these two ideas that the location of the polymer in the particles may play a critical role in determining which of these mechanisms is operative. In addition, it might be expected that the location of the absorbed radicals also plays an important role. That is, radicals which can penetrate the interfacial layer are more likely to propagate than those which cannot. Based on these considerations, it might be expected that the type and molecular weight of polymer and its end groups could play an important role in determining the behavior of the particle. Polymer prepared with sulfate end groups, such as those produced in emulsion polymerization, will be likely to have at least a portion residing at the particle/water interface, while a hydrophobic polymer (e.g., polystyrene) without hydrophilic end groups will more likely reside in the interior of the particle. This effect may be more pronounced for higher molecular weight polymer chains. In addition, the radius of gyration of the polymer in monomer should also be an important parameter. Since styrene is a good solvent for polystyrene, it would be expected that the polymer should be expanded in the particle, possibly forcing some toward the interface. On the other hand, for a different type of polymer, the monomer may not be a good solvent, forcing the polymer to curl up on itself. In this case, if the polymer has a hydrophilic end group a large portion may be forced to the interface. If, however, no hydrophilic end groups are present, the polymer may coil up in the center of the particle, relatively far from the interface.

In the first paper of this series,¹ it was shown that changing from a polymer made by emulsion polymerization to a polymer produced by bulk polymerization resulted in the formation of slightly fewer particles, indicating that the emulsion polymerization produced polymer had a greater effect on the radical capture

efficiency than the bulk polymer. This result may be attributed to the different end groups of the two polymers, or to the different molecular weights (emulsion polymer $M_w = 193\,300$; bulk polymer $M_w = 60\,300$) for some of the reasons discussed above. The molecular weight and end group of the polymer are clearly areas that deserve further study.

Another effect that is worth considering is the role of the polymer in the thermodynamic stability of the miniemulsion droplets. It has been shown that miniemulsion droplets stabilized with cetyl alcohol undergo a ripening attributed to the slow transport of cetyl alcohol from smaller to larger droplets via diffusion through the aqueous phase.¹⁴ As a result, the average size of these miniemulsions increases with time. It might also be expected that smaller droplets can disappear by this mechanism when all of the cetyl alcohol has been transported from smaller to larger droplets. This being the case, the polymer may serve to increase the stability of these small droplets by preventing their complete disappearance due to the inability of the polymer to be transported through the aqueous phase. It should be noted that even with this mechanism operative, the cetyl alcohol is still a necessary component for preparing stable miniemulsions since it acts as a swelling promoter (as well as a diffusion retarder), while polymer has a high molecular weight and, therefore, cannot be swollen by monomer to the degree necessary to be a true miniemulsion.

Experimental Evidence for Differences between Droplets and Particles. The two basic ideas discussed above provide a framework for designing experiments to determine the differences between droplets and particles with respect to their abilities to capture radicals. This difference has been referred to as a difference in the radical capture *efficiencies* of the two species. Since this term has not been previously defined, the following section is intended to loosely define this term and explain its relationship to a more familiar term, the initiator efficiency.

Radical Capture Efficiencies. Aqueous phase free radicals are formed by either initiator decomposition or

desorption from polymer particles. The former is determined by the rate of initiator decomposition, given as

$$R_d = 2fk_i[I] \quad (2)$$

$$[I] = [I]_0 e^{-k_i t} \quad (3)$$

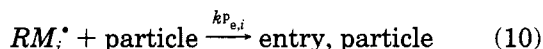
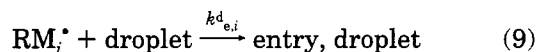
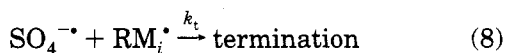
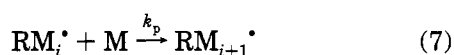
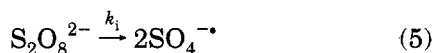
where R_d is the rate of production of radicals by thermal homolysis of initiator, k_i is the initiator decomposition rate coefficient, and f is the initiator efficiency. The latter is defined as the fraction of the radicals produced by homolysis that initiate polymer chains. In emulsion polymerization, the value of f is difficult to ascertain due to the many aqueous phase reactions contributing to the initiator efficiency. In any case, this value is usually less than 1.

The rate of production of desorbed free radicals is given by

$$R_{\text{desorp}} = \frac{k\bar{n}N_p}{N_a}\phi_w \quad (4)$$

where k is the desorption rate coefficient, \bar{n} is the average number of radicals in the polymer particles, N_p is the total number of polymer particles, N_a is the Avogadro's number, and ϕ_w is the volume fraction of water in the aqueous phase. In styrene emulsion polymerizations, the value for k is usually relatively small; thus the rate of desorption of radicals from polymer particles is fairly slow. Morrison et al.¹⁵ and Casey et al.¹⁶ have suggested that the radicals produced by initiator decomposition and desorption have different probabilities for entry into polymer particles. For the purpose of this discussion, desorbed monomeric free radicals will not be considered.

With these assumptions in mind, the following reaction mechanism can be proposed for entry into droplets and particles.



where k_{p1} is the initial propagation rate coefficient, k_p is the propagation rate coefficient for oligomers, k_t is the termination rate coefficient in the aqueous phase, and $k_{e,i}^d$ and $k_{e,i}^p$ are the second-order entry rate coefficients into droplets and particles, respectively.

It is clear from the above reaction mechanism that there will be a competition between droplets and particles for the available free radicals. In addition, those free radicals which do not enter a droplet or particle may terminate or propagate in the aqueous phase. Therefore, entry into droplets and particles is also in competition with these aqueous phase events.

The probability for entry into droplets or particles has been proposed to increase with increasing length of the oligomeric radical, to the point where at a critical length, z , all oligomeric radicals enter into either a droplet or particle (z has been proposed to be between 2 and 3 monomer units for entry into polystyrene/styrene latex particles).⁷ This length may vary for droplets and particles, and if so, entry would be greatly favored for the species with a smaller z value. In any event, the total rates of entry into droplets, R_{drop} , and particles, R_{part} , may be expressed as

$$R_{\text{drop}} = \frac{dN_p}{dt} = -\left(\frac{dN_d}{dt}\right) = \sum_{i=0}^n k_{e,i}^d [\text{RM}_i^{\cdot}] N_d \quad (11)$$

$$R_{\text{part}} = \sum_{i=0}^n k_{e,i}^p [\text{RM}_i^{\cdot}] N_p \quad (12)$$

During the polymerization, the numbers of droplets and particles differ, as do the diameters of the droplets and particles. This may contribute to different entry probabilities based on either diffusional,¹⁷ collisional,¹⁷ or propagational⁷ mechanisms. However, in order to explain the experimental results as being due to a difference in the radical capture efficiencies of droplets and particles, the different rates of radical capture for droplets and particles should be independent of the diameter or number of particles and should be reflected as an inherent difference in the entry rate coefficients, $k_{e,i}^d$ and $k_{e,i}^p$. These then, should show functional dependencies as expressed below:

$$k_{e,i}^p = \phi(r_p, \text{RM}_i^{\cdot}, P_{p,i}) \quad (13)$$

$$k_{e,i}^d = \phi'(r_d, \text{RM}_i^{\cdot}, P_{d,i}) \quad (14)$$

where ϕ and ϕ' represent functions, r_p and r_d are the diameters of the particles and droplets, respectively, RM_i^{\cdot} is the length of the entering species, and $P_{p,i}$ and $P_{d,i}$ are related to the fraction of oligomers which intercept the reaction radius of the particles or droplets, respectively, and succeed in starting polymerization. The latter term should only vary for different species, i.e., droplets and particles, while the other terms may vary for any two species (e.g., two polystyrene latex particles having different sizes). For example, if the entry rate coefficient is given by the Smoluchowski expression (i.e., diffusion determines the rate of collision of oligomers with droplets/particles)

$$k_{e,i} = 4\pi D_i r N_a P_i \quad (15)$$

where D_i is the diffusion coefficient of an i -mer. It is apparent that the entry rate coefficient will vary with the radius and the length of the entering species (through the diffusion coefficient). The term P_i , therefore, accounts for the fact that not all collisions of oligomers with particles result in entry. Note that P_i is a function of the length of the entering species. It is proposed that for the same size droplet and particle and the same length oligomer, this term is smaller for droplets than for particles. This will have the direct effect of changing the number of droplets which capture radicals to become growing polymer particles, since once particles are present, there will be a competition for radicals favoring the particles.

Having explained the basic concept of radical capture efficiency, it is now necessary to test whether this explanation is consistent with the experimental data. Clearly, many different explanations for an increase in the polymerization rate upon addition of polymer could be formulated, and perhaps each of these might have some attractive features. As a start, the early polymerization rate data may be examined for consistency with the postulate that the efficiency of radical capture is increased by the addition of polymer to the miniemulsion droplets.

In the first paper of this series, it was demonstrated that the overall polymerization rate and number of particles formed increase with increasing polymer concentration in the droplets. In the context of the above discussion, this result suggests that the radical entry rate coefficient into miniemulsion "droplets" (i.e., k_d^e) increases with increasing amount of polymer initially present. This effect may be quantified by considering the change in the radical capture efficiency, f_{cap} , with increasing initial polymer concentration. At the beginning of the reaction, the radical capture efficiency is simply the probability of a free radical entering into a droplet compared to participating in an aqueous phase reaction (i.e., termination, propagation). Therefore, at the beginning of the reaction, the theoretical maximum polymerization rate can be compared to the experimental rates as a measure of this efficiency.

The rate equation for emulsion polymerization is given as

$$R_p = \frac{k_p[M]_p N_p \bar{n}}{N_a} \quad (16)$$

where $[M]_p$ is the concentration of monomer in the polymer particles. At the beginning of the polymerization, \bar{n} in the "active" particles should be close to one, since these particles will only have had time to capture one radical. In addition, early in the polymerization, k_p will be constant and $[M]_p$ will be approximately equal to $[M]_d^0$, the initial concentration of monomer in the droplets. Therefore, at the beginning of the reaction the polymerization rate should be proportional to the number of droplets (i.e., with or without polymer, depending upon the recipe) present alone. For miniemulsion polymerization, the latter may be given as

$$N_p = \varrho_d N_d \Delta t \quad (17)$$

where Δt represents a small time interval and ϱ_d is the first-order entry rate coefficient for radical entry into the miniemulsion droplets, which is related to the previously defined second-order droplet entry rate coefficient by

$$\varrho_d = k_d^e [R]_w \quad (18)$$

where $[R]_w$ is the concentration of radicals in the aqueous phase.

If the addition of polymer has no effect on the entry rate coefficient for miniemulsion droplets (i.e., droplets with and without polymer have the same radical capture efficiencies), then the first-order entry rate coefficients for radicals into the miniemulsion droplets should be independent of the amount of initial polymer. As demonstrated above, if the polymer does affect the entry into miniemulsion droplets, then this behavior should be reflected in the values of ϱ_d .

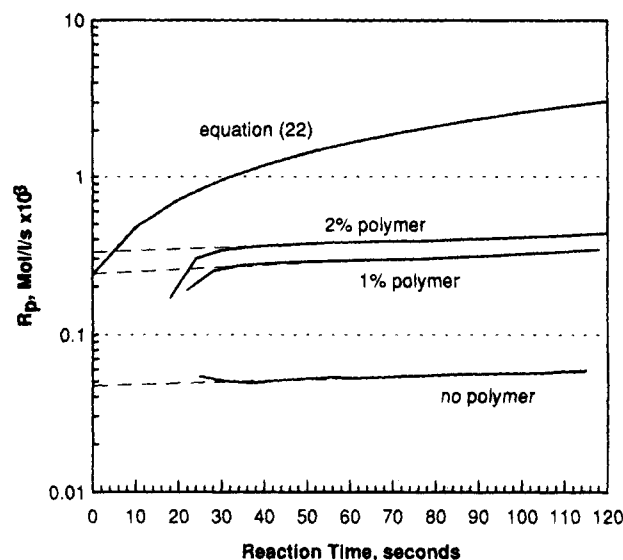


Figure 3. Polymerization rates at early times ($t < 2$ min) for styrene miniemulsions prepared with 0, 1, and 2% polymer ($[KPS] = 1.33$ mM, $T_r = 70$ °C) compared with the theoretical prediction for the maximum rate obtainable given by eq 21. Note: the bottom three curves are experimental data obtained from the Mettler RC1 calorimeter where data are obtained every 6 s.

If all of the free radicals arising from initiator decomposition enter into miniemulsion droplets, then the entry rate coefficient (ϱ_{max}) at the beginning of the reaction is given by

$$\varrho_{max} = 2k_i[S_2O_8^{2-}]N_d/N_d \quad (19)$$

The radical capture efficiency at the beginning of the reaction is then defined as

$$f_{cap} = \varrho_d/\varrho_{max} \quad (20)$$

where ϱ_d is the actual entry rate coefficient into droplets with varying amounts of polymer. The concentration of the initiator at time, t , is determined from its rate of thermal decomposition:

$$[S_2O_8^{2-}] = [S_2O_8^{2-}]_0 e^{-k_i t} \quad (21)$$

If the same assumptions are employed as outlined above, eqs 16, 17, 19, and 21 may be combined to give the maximum polymerization rate obtainable at early conversions:

$$R_{p(max)} = 2k_p[M]_d^0 k_i [S_2O_8^{2-}] \quad (22)$$

This calculated polymerization rate can be compared to the experimentally measured polymerization rates extrapolated to time zero to determine the value of the radical capture efficiency at the beginning of the reaction, and any differences in these values should be related to the difference in the rate of entry of radicals into miniemulsion droplets with different amounts of initial polymer (i.e., differences in k_d^e). Figure 3 shows the results for the polymerization rate calculated using eq 22 and the experimental polymerization rates for miniemulsions prepared with 0, 1, and 2% polymer. Values of $k_p = 425.6$ dm³ mol⁻¹ s⁻¹ and $k_i = 2.4 \times 10^{-4}$ s⁻¹ were used in this calculation,¹⁸ and the initiator efficiency, f , was assumed to be 1. The first 20 s of the reaction is experimentally unavailable due to the addition of the initiator which perturbs the system, and

similarly the first several data points may be erroneous since the reactor is still compensating for this effect. However, if the first several data points are neglected, the intercepts of the data with the ordinate may be calculated and compared with the theoretical calculation as a measure of the radical capture efficiency. Based on these approximations, Figure 3 shows that about 100% of the initiator radicals succeed in entering into the monomer droplets for polystyrene concentrations of 1 and 2%, indicating the radical capture efficiency, f_{cap} , is close to 1, and at the beginning of the reaction the probability for entry into droplets is very high. On the other hand, for the miniemulsion prepared without polymer only about 20% of the radicals succeed in entering monomer droplets, indicating that the probability for entry into the droplets was considerably reduced. Radical capture efficiencies for entry into polystyrene latex particles have been measured experimentally and determined to be in the range of 0.01–0.5.^{7,17,19} These values are clearly lower than 1, indicating that the estimate used in the current study may be in error. Any error in the calculation could arise from the assumptions used and the fact that the polymerization rates are not available as $t \rightarrow 0$. In addition, the initiator is heated to 70 °C prior to injection into the reactor. This preheating takes about 1 or 2 min and will obviously cause some initiator decomposition. In other words, the time used in the calculation of the maximum rate of polymerization should have been started at this value rather than zero. Regardless, it is clear from this figure that at the beginning of the reaction the "droplet" radical capture efficiency decreases with decreasing polymer concentration.

It is important to make a clarification concerning the above calculation of the droplet radical capture efficiencies. Since, at the beginning of the reaction, all of the droplets contain the same amount of polymer (the initial amount), the efficiency estimated above was for radicals to enter into droplets versus participating in other aqueous phase reactions. Based on this, it was shown that the probability for entry increases with increasing polymer concentration initially present in the droplets. However, this efficiency will change once the concentration of polymer differs between the active particles and the droplets. For example, if aqueous phase reactions are favored 5 to 1 over entry into a miniemulsion droplets (without polymer) but entry into a polymer particle (e.g., >2% polymer) is favored 5 to 1 over an aqueous phase reaction, then entry into these polymer particles will be favored 25 to 1 over entry into the miniemulsion droplets.

Internal and Interfacial Viscosity. The above discussion establishes that the increase in the polymerization rate and number of particles produced upon the addition of polystyrene to styrene miniemulsions may be attributable to a basic difference in the abilities of droplets and particles to capture aqueous phase free radicals. The following sections are intended to discuss in detail the two possible mechanisms for these differences outlined previously.

The first idea proposed to explain the difference between droplets and particles with respect to their abilities to capture radicals is that the presence of polymer increases the viscosity of the oil phase, thereby increasing the likelihood that a radical which enters a droplet will propagate rather than exit. This feature has several attractive qualities to it. First, it implies that there will be a gradual increase in the capture

efficiency of the droplets as the amount of polymer is increased, which is consistent with what was observed experimentally. Second, it may provide a means for determining the cutoff between the "droplet" behavior and the "particle" behavior if it can be shown that this changeover occurs when the system changes either from the dilute to the semidilute regime (c^* , the point at which the polymer chains are "indistinguishable" from one another and begin to interact) or shortly thereafter when the polymer solution enters the concentrated regime (c^{**}). At this point, radicals which enter a particle would be trapped in a polymer, "cage", and their rate of diffusion may be reduced substantially, thus favoring propagation rather than exit. However, this idea is very difficult to prove since it requires an understanding of the rate of diffusion of oligomers in solution to determine their rate of exit from droplets and particles. Only recently has this complicated situation been subjected to experimental investigation.

Piton et al.²⁰ measured the self-diffusion coefficients for a series of styrene oligomers in solutions of polystyrene ($M_w = 125\,000$ – $250\,000$) in benzene with varying weight percents of polystyrene. The critical chain overlap concentration (c^*) for this system was found to be 0.03 g/mL solution. This work clearly illustrates that the rate of diffusion of oligomers (less than 5 carbons in length) decreases with increasing polymer concentration in solution. In addition although not many data points were obtained in the dilute regime (i.e., $c < c^*$), the results also showed that the self-diffusion coefficients may decrease the most rapidly during this regime. The essential point is that this data supports the notion that the interior viscosity should have an influence on the rate of diffusion of radicals inside the miniemulsion droplets or polymer particles. The work also showed that this effect may be more important for smaller oligomers, which have the highest self-diffusion coefficients in polymer solutions. This suggests that the addition of polymer may allow smaller oligomers (i.e., 1 or 2 monomer units) which are still quite hydrophilic (i.e., due to the sulfate end group) to be absorbed into/onto polymer particles and thereby propagate.

In the above discussion, the aqueous phase oligomers were assumed to enter into the monomer droplets and subsequently either propagate or desorb. Based on this analysis, it was shown that an increase in the interior viscosity would tend to gradually decrease the rate of diffusion, thereby favoring propagation. This effect was suggested to be more important for smaller oligomers, since these will not yet have added enough monomer units to render them water insoluble. In using this treatment, an important experimental fact was neglected: sulfate end groups have been shown to be anchored at the surface of the polymer particles.²¹ This being the case, it might be expected that a radical is more likely to enter the interfacial region of a droplet or particle (as opposed to the interior) and then either propagate or desorb. Consequently, it might be argued that the true variable which should be measured is the interfacial viscosity of the miniemulsion droplets (at the droplet/water interface). This explanation requires the polymer to modify the interface by increasing the interfacial viscosity and is therefore a cross between the two pictures presented in Figures 1 and 2.

The viscosity of the droplet/water interface is a difficult property to measure. Durbin²² measured the interfacial viscosity between aqueous gel phases of SLS and CA and air using an angular displacement mea-

surement system.²³ This work showed that the interfacial viscosity increased with increasing cetyl alcohol concentration until a maximum was reached between 1:1 and 2:1 CA:SLS molar ratio. This molar ratio was considered to correspond to the closest molecular packing of cetyl alcohol and SLS at the interface. A similar situation may occur for the droplet/aqueous phase interface if a portion of the cetyl alcohol resides at the interface, thus packing with the SLS. This could have the effect of changing the relative rates of propagation and desorption of aqueous phase radicals by changing their rate of diffusion in the interfacial layer. No work has been reported on what the effect of polymer would be on this packing; however, it may change the viscosity if a portion resides at the interface. In such a case, the polymer may increase the interfacial viscosity in much the same way as it increases the viscosity of a bulk solution. Such a change may be responsible for the differences observed between droplets and particles.

Interfacial Barriers Preventing Radical Entry.

The second possible explanation for the difference between droplets and particles with respect to their abilities to capture radicals concerns the possibility that the polymer modifies the droplet/water interface, thereby allowing radicals to more easily enter and propagate. This idea is similar to that presented in the last paragraph above, except that the polymer is presumed to modify the interface to allow easier entry of radicals, as opposed to changing the interfacial viscosity, thereby changing the relative rates of desorption and propagation. Perhaps the most compelling reason for using this explanation is the wealth of experimental data suggesting the existence of interfacial complexes at the oil/water interface of droplets stabilized using cetyl alcohol and sodium lauryl sulfate.

It has been demonstrated by a number of researchers^{8-13,24,25} that aqueous long-chain alcohol-surfactant (i.e., cetyl alcohol-sodium lauryl sulfate) systems form ordered lamellar structures. These structures have also been shown to exist at the surface of monomer droplets stabilized using these materials.¹¹ This has led to the speculation that these structures contribute to the overall stability of the emulsions by forming an interfacial barrier preventing coalescence of droplets.^{8,12,13} The presence of these barriers may also hinder the entry of radicals into the monomer droplets and, if the order is disrupted by the addition of polymer to (or formation in) the droplets, may explain the experimental results; i.e., the order at the interface hinders the entry of radicals into monomer droplets relative to those which contain some polymer (i.e., polymer particles).

Chen^{26,27} observed that when polystyrene (obtained from a monodisperse latex) was added to styrene, it lowered the interfacial tension between this solution and aqueous phases comprising different types of surfactants (Igepal CO-990 (nonylphenol poly(ethylene oxide)), 100 mol of ethylene oxide, GAF Co.) and Pluronic F-108 (poly(ethylene oxide-propylene oxide), 80% poly(oxyethylene), BASF/Wyandotte)). This indicates a preference for this polymer to be located at the oil/water interface, thereby lowering the interfacial tension. In this case, the presence of polystyrene at the droplet/water interface could serve to disrupt the cetyl alcohol/sodium lauryl sulfate packing. Recently, Lee and Rudin²⁸ visually observed that when polystyrene in styrene solutions were added to aqueous solutions of surfactant, the polystyrene tended to precipitate at the

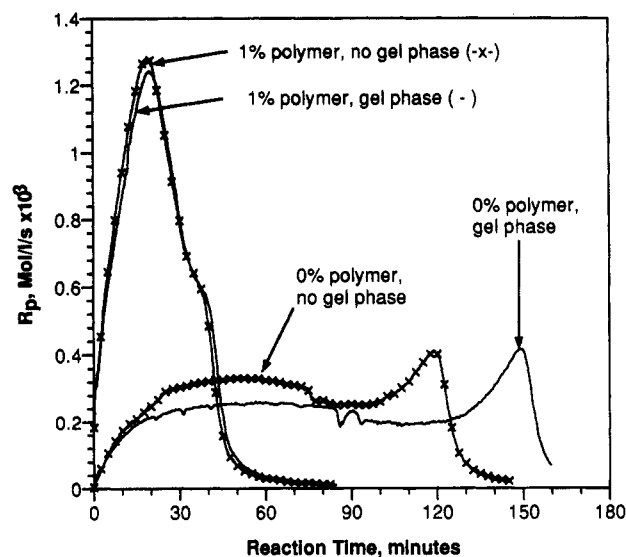


Figure 4. Polymerization rate versus time curves for styrene miniemulsions prepared with and without 1% polystyrene and with 30 mM cetyl alcohol initially located in the aqueous or oil phase, as indicated. ([SLS] = 10 mM, [KPS] = 1.33 mM, $T_r = 70^\circ\text{C}$).

interface. This precipitation was observed to be more pronounced when the polystyrene was prepared with hydrophilic end groups (i.e., sulfate end groups from emulsion polymerization) than when functional end groups were not present. However, even when the polymer was prepared with hydrogen end groups, some precipitation was observed. If a similar situation is occurring in this system, the precipitated polymer could serve to disrupt the interfacial layer, thereby allowing radicals to preferentially enter into "droplets" in which some polymer has been added (i.e., polymer particles) over normal miniemulsion droplets.

It is well known that miniemulsions stabilized using cetyl alcohol and sodium lauryl sulfate can be prepared by introducing the cetyl alcohol into either the aqueous phase or the oil phase. If aqueous phase free radical entry is assumed to be hindered by the presence of an interfacial barrier caused by the formation of an ordered SLS/CA structure, it might be expected that this ordering is greater when the cetyl alcohol is initially present in the aqueous phase with the SLS than when the cetyl alcohol is initially present in the oil phase. This would result from the preformed structures present when the cetyl alcohol is in the aqueous phase, which may form to a lesser extent when the cetyl alcohol must migrate from the bulk (interior) of the droplet to the interface. In such a case, in the absence of polymer, the miniemulsion prepared with the cetyl alcohol in the aqueous phase would be expected to react more slowly and form fewer polymer particles than that with the cetyl alcohol initially introduced in the oil phase. On the other hand, in the presence of 1% polymer, the ordering of the cetyl alcohol and sodium lauryl sulfate may be disrupted, and the initial location of the cetyl alcohol may be less important.

Experiments were performed to determine the effect of the initial location of cetyl alcohol on the polymerization kinetics of styrene miniemulsions prepared with 0 and 1% polystyrene. The results are shown in Figure 4. It is clear from this figure that when 1% polymer is added to the miniemulsions, the initial location of the cetyl alcohol has almost no effect on the polymerization rate. On the other hand, in the absence of polymer,

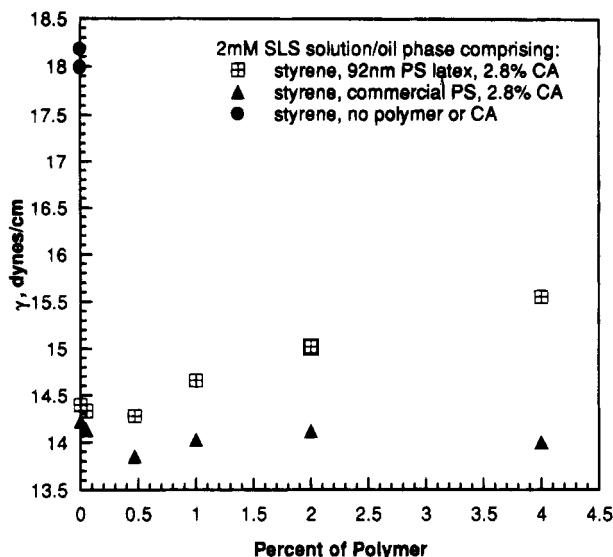


Figure 5. Interfacial tensions between a 2 mM SLS solution and styrene/cetyl alcohol/polystyrene solutions as a function of the amount of polymer (from a 92 nm latex or a commercial product).

the overall polymerization rate is greater for the miniemulsion prepared with the cetyl alcohol initially located in the oil phase than in the aqueous phase. It is important to note that these results do not prove that the initial location of cetyl alcohol changes the number of droplets which capture free radicals, since an equally valid interpretation would be that the initial droplets sizes and their distributions vary in the absence of polymer depending on the initial location of the cetyl alcohol. However, these results are consistent with the idea that the entry of radicals is hindered by the formation of a SLS/CA interfacial barrier.

If the addition of polymer has an effect on the droplet/water interface, it seems likely that this behavior should affect the interfacial tension between these phases, and this effect should be measurable using standard techniques. The drop volume method for measuring interfacial tensions was employed to test this hypothesis.

The interfacial tensions between a 2 mM SLS solution and solutions of cetyl alcohol (2.8%, 30 mM) and varying amounts of polystyrene in styrene were measured. This surfactant concentration was selected based on previous work which suggested that it is representative of the actual free surfactant concentration in a miniemulsion. The results are plotted in Figure 5. The solid circles in this figure show the value for the interfacial tension between a 2 mM SLS solution and pure styrene monomer. Two separate measurements were made at different flow rates to demonstrate the reproducibility of the technique. The values obtained were 18.1 and 18.0 dyn/cm, which are in good agreement.

Solutions of cetyl alcohol and polystyrene in styrene monomer were then prepared at compositions which matched those used in the polymerizations presented in the previous papers (i.e., 30 mM CA based on the aqueous phase). Specifically, the amount of cetyl alcohol was adjusted to be 2.77% based on the total, and the amount of polymer was varied from 0 to 4% (i.e., 0, 0.05, 0.5, 1, 2, and 4% based on the oil phase). Two different types of polymer were used in the measurements (i.e., polymer obtained from the 92 nm latex and a commercially available polymer (Dajac Laboratories)), and these again were the same as used in the experimental work presented in the previous publications.^{1,2} These

results also appear in Figure 5. It is apparent from this figure that the cetyl alcohol behaves as a surfactant, lowering the oil/water interfacial tension. Specifically, the interfacial tension was lowered from about 18 dyn/cm to about 14.3 dyn/cm. The latter value is in good agreement with that obtained by Goetz²⁹ using the same method. Physically, this suggests that a portion of the cetyl alcohol is residing at the oil/water interface. When the amount of the commercial polystyrene added to the styrene/cetyl alcohol solution was increased (from 0 to up to 4%), the interfacial tension was observed to remain approximately unchanged. However, when the polystyrene obtained from the 92 nm latex was added to the styrene/cetyl alcohol solution, the interfacial tension was observed to increase with increasing amount of polystyrene up to 15.6 dyn/cm for 4% polymer. These results suggest that for polystyrene prepared by emulsion polymerization, a portion of this polymer resides at the oil/water interface, causing an increase in the interfacial tension. Such an increase may occur due to the polymer displacing cetyl alcohol from the interface, thereby forcing it into the oil phase. This phenomenon was not observed for the commercially available polymer, which suggests that the sulfate end groups of the emulsion-polymerized polymer aid in allowing it to reside at the interface. Based on these results, it would appear that the polymer may be effective in modifying the droplet/water interface, thereby changing the ease with which radicals are able to penetrate this interface to begin polymerization.

After the interfacial tensions for the 92 nm latex polymer solutions were measured, the solutions were placed on a shelf in the dark (room temperature = 22 °C) and allowed to age for 1 day, after which these solutions were examined. All of the polymer solutions showed two phases, a clear lower aqueous phase and a slightly yellow upper (oil) phase. However, for the solution prepared with the highest polymer concentration (4%), a precipitate was clearly observed at the oil/water interface. This precipitate was isolated and was determined by addition of methanol to be comprised of the initial polymer. This result is similar to that observed by Lee and Rudin²⁸ and provides strong evidence that the polymer tends to go to the oil/water interface. This behavior may be responsible for the increased interfacial tension observed upon addition of increasing amounts of polymer to a cetyl alcohol in styrene solution. In other words, in order to reach the oil/water interface, the polymer must displace a considerable amount of cetyl alcohol. This could destroy any molecular packing at the surface, thereby allowing radicals to more easily enter the particle and propagate.

Summary and Conclusions

The experimental results reported in the previous papers demonstrated that the addition of polystyrene to styrene miniemulsions results in a substantial increase in the overall polymerization rate obtained and the number of polymer particles formed. The mechanism for this polymerization was reported to proceed by radical entry into preformed, highly monomer-swollen polymer particles. It was also suggested that a much greater fraction (approaching one) of these species capture radicals, in contrast to normal (i.e., no polymer) miniemulsion polymerizations in which only about 10–20% of the initial droplets capture radicals at an equivalent initiator concentration. In this paper, this behavior was explained by considering that the

mini-emulsion "droplets" prepared from polystyrene in styrene solutions resemble polymer particles at early conversions in normal mini-emulsion polymerizations. These species were considered to be more efficient at capturing aqueous phase free radicals, thus favoring their entry as compared with normal mini-emulsion droplets. As a result, unentered droplets in these systems were hypothesized to be more likely to be entered than normal mini-emulsion droplets, resulting in a greater number becoming polymer particles. Based on this explanation, it was speculated that the presence of the small amount of polystyrene increases the capture efficiency of mini-emulsion droplets by modifying either the interior of the droplets (i.e., by increasing the interior viscosity, thereby increasing the probability for a radical to propagate rather than exit) or the droplet/water interface (i.e., by disrupting a SLS/CA interfacial barrier to radical entry). Some experiments were performed which suggest that the latter is at least partially responsible for the observed behavior. Specifically, it was demonstrated through interfacial tension measurements that the polystyrene does show some ability to modify the droplet/water interface, perhaps by displacing cetyl alcohol from this interface.

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