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Enhanced Droplet Nucleation in Styrene Miniemulsion Polymerization. 2. Polymerization Kinetics of Homogenized Emulsions Containing Predissolved Polystyrene

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ABSTRACT: The effect on the subsequent polymerization of predissolving polystyrene into the styrene monomer prior to its homogenization via a Microfluidizer was studied. It was noted that particle nucleation shifted from either the micelles or the aqueous phase to the monomer droplets when polymer is predissolved. This shift to the droplets was a result of the droplets being preserved by the presence of the polymer in the initial droplet distribution. When homogenized emulsions do not contain predissolved polymer, the majority of the droplets disappear by Ostwald ripening. Homogenized emulsions that contain predissolved polymer exhibit higher rates of polymerization and numbers of particles nucleated compared to similar systems not containing predissolved polymer. This enhancement in the kinetics was similar (although to a slightly lesser extent) to what was noted for miniemulsions containing cetyl alcohol as cosurfactant. Since both homogenized emulsion and miniemulsion systems (using cetyl alcohol as the cosurfactant) initially possess unstable droplet size distributions, the enhancement in both of these systems was taken as evidence that "enhanced droplet nucleation" caused by predissolving polymer is primarily a result of preserving the droplet number due to the presence of the polymer.

Introduction

Homogenized emulsions are comprised of surfactant, monomer, and water and are created by applying a high level of shear. Unlike miniemulsions, these systems do not contain a cosurfactant. Therefore, the monomer droplets are unstable to Ostwald ripening causing the droplet size distribution to degrade quickly. Miller[1,2] has suggested that the droplet size in these systems degrades to the point where virtually no nucleation in droplets occurs.

Reimers and Schork[3] have suggested that the addition of approximately 4% monomer soluble polymer (weight of polymer/weight of monomer) can significantly reduce Ostwald ripening in homogenized emulsions to a degree where the droplet size is preserved for time periods long enough for droplet nucleation to occur. It is important to recognize that the polymer does not behave like a true cosurfactant. Ugelstad et al.[4] derived a thermodynamic equation that predicts the efficiency of cosurfactants:

$$\Delta\bar{G}_1 = 0 = RT\left(\ln \phi_1 + \left(1 - \frac{1}{j_2}\right)\phi_2 + {\phi_2}^2\chi + \frac{2V_{1M}\gamma}{rRT}\right) \tag{1}$$

where $\Delta\bar{G}_1$ is the partial molar free energy of mixing of monomer in the droplets, R is the universal gas constant, T is the temperature, ϕ_1 and ϕ_2 are the volume fractions of monomer and cosurfactant respectively, r is the radius of the droplets, χ is the interaction parameter, γ is the interfacial tension, V_{1M} is the molar volume of the monomer, and j_2 is the ratio of the molar volume of the monomer to the molar volume of the cosurfactant. The swelling capacity of the droplets in the presence of a cosurfactant can be computed by setting $\Delta\bar{G}_1$ equal to zero in eq 1. Equation 1 indicates that for a cosurfactant to super-swell with monomer, it must have a low j_2 value (which corresponds to a low molecular weight). Thus, polymer is not a cosurfactant in that it does not super-swell with monomer. However, Reimers and Schork[3] used light scattering to show in 4% poly(methyl methacrylate)/96% methyl methacrylate homogenized emulsions that the droplet size was effectively stabilized by the polymer. It was also shown that the dominant nucleation mechanism in these systems in the absence of a cosurfactant is the monomer droplets.

In the preceding paper in this series,[5] it was suggested that the phenomenon responsible for "enhanced droplet nucleation" in miniemulsions utilizing cetyl alcohol as the cosurfactant is the preservation of the droplet number by the presence of polymer coupled with the cetyl alcohol. This paper will investigate the effect of predissolving polymer into the monomer prior to homogenization in emulsions that do not use a cosurfactant. It is expected that a significant enhancement in the rate of polymerization and the number of particles formed during the reaction in these homogenized emulsions will be seen if the preservation of the droplets by the predissolved polymer is the dominant mechanism controlling "enhanced droplet nucleation".

Experimental Section

Materials. Styrene (Aldrich) was distilled under a reduced pressure of 15 mmHg and stored at −5 °C for later use. Sodium lauryl sulfate, SLS (BDH Biochemical, Ultrapure Bioreagent, 99% pure), was used as received. Potassium persulfate, KPS (FMC Corp.), was recrystallized from deionized water and dried under vacuum. The following chemicals were used as received: cetyl alcohol, CA (Aldrich), and sodium bicarbonate (Fisher). Deionized water was used in the experiments.

Table 1 lists the different polymers that were dissolved into the monomer prior to homogenization to form the miniemulsion. The polystyrene samples from BASF were prepared by anionic polymerization to provide polymers with narrow molecular weight distributions and the desired end group.

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Table 1. Properties of the Predissolved Polymers Used in the Homogenized Emulsion Polymerizations

sample	M_n, g/mol	M_w, g/mol	PDI (M_w/M_n)	end group
BASF ZK751/34a	40 400	42 300	1.05	SO_3^-
BASF ZK751/34c	149 000	161 000	1.08	SO_3^-
BASF R2/910	39 000	45 100	1.16	H
DOW LS-1101	62 600	193 000	3.08	SO_4^-

Table 2. Basic Recipe for the Polymerizations

ingredient	amount	grams
styrene	19.8−20.0 parts	138.6−140.0
polystyrene[a]	0.0−0.2 parts	0.0−1.4
deionized water	80 parts	560.0
sodium lauryl sulfate[b]	10 mM	1.595
cetyl alcohol[a,b]	30 mM	4.023
sodium bicarbonate[b]	1.33 mM	0.0621
potassium persulfate[b]	1.33 mM	0.1975

[a] Not present in all recipes. [b] Based on the aqueous phase.

Table 3. Experimental Variables Studied

expt identifier	polymer M_n (g/mol)	polymer end group	surfactant level	reaction type
CM5	none	none	10 mM SLS	conventional
LE71	40 400	SO_3^-	10/30 mM SLS/CA	miniemulsion
KPS6	149 000	SO_3^-	10 mM SLS	homogenized
KPS7	149 000	SO_3^-	10 mM SLS	homogenized
KPS8	none	none	10 mM SLS	homogenized
KPS4	none	none	10/30 mM SLS/CA	miniemulsion
JBRC9a	62 600	SO_4^-	10 mM SLS	homogenized
CM1	none	none	5 mM SLS	conventional
LE90	39 000	H	5 mM SLS	homogenized
LE91	39 000	H	5 mM SLS	homogenized
LE92	none	none	5 mM SLS	homogenized
LE93	none	none	5 mM SLS	homogenized
CM2	62 600	SO_3^-	5/15 mM SLS/CA	miniemulsion
CM6	none	none	5/15 mM SLS/CA	miniemulsion

Recipe and Procedures. The ingredients used in the formulation of the homogenized emulsions are given in Table 2. First, the aqueous phase was created by mixing the SLS, deionized water (less 1% of the water that was saved to dissolve the initiator), and $NaHCO_3$ for 2 h at 70 °C. When polystyrene was used, it was predissolved in the monomer until all visible traces of the polymer had disappeared. The oil and aqueous phases were then mixed in a beaker for 20 min using a stir bar. The resulting emulsion was then sonified (Branson Sonic Power Co.) for 60 s at 50% duty, power 7, and pulsed. Finally, the resulting emulsion was passed through the Microfluidizer (Microfluidics Corp.) for 10 passes at 80 psi inlet pressure. The resulting homogenized emulsion was then added to the Mettler RC1 calorimeter where the KPS/water solution was added after heating the homogenized emulsion to 70 °C. The Mettler RC1 calorimeter provides a virtually continuous measurement of the heat evolved from the reaction that can be directly related to the rate of polymerization. Miniemulsions stabilized with cetyl alcohol were made with the procedure presented in the previous paper.[5] Conventional emulsions were made by adding the ingredients directly into the reactor and using the shear provided by the stainless steel turbine impeller. Table 3 lists the variables studied in these experiments. All particle size measurements were made by capillary hydrodynamic fractionation (CHDF) with the Matec CHDF-1100 unit.

Results and Discussion

Polymerizations above the cmc. Figure 1 shows the rate of polymerization versus time behavior for parallel conventional emulsion, homogenized emulsion, and miniemulsion systems without any added polymer. Here, these serve as reference experiments. The fastest rate of polymerization was found in the conventional emulsion, while the homogenized emulsion had slightly lower rates of polymerization, and the miniemulsion, stabilized with cetyl alcohol, exhibited significantly slower kinetics. This trend can be attributed to the number of reaction sites available for polymerization. In the conventional emulsion, nucleation takes place in micelles (the cmc of SLS is 6.2 mM[6]). In the homogenized emulsion system, there is slightly over an hour delay from homogenization to the addition of initiator. In this time period, there is most likely a substantial degradation in droplet size by Ostwald ripening occurring in the system. Therefore, the droplets will have become relatively large and will not serve as the dominant site for nucleation. However, the number of micelles will be reduced in the homogenized emulsion compared to the conventional emulsion since more surfactant will be adsorbed on the surface of the droplets. This phenomenon would explain the difference in the rate of polymerization versus time data for the conventional and homogenized emulsions. In the miniemulsion polymerization, nucleation has shifted from the micelles to the monomer droplets. Since the number of droplets in the miniemulsion system is less than the number of micelles in either the homogenized or conventional emulsion systems, it is expected the rate of polymerization would be lower in the miniemulsion system (assuming equal entry into droplets and micelles).

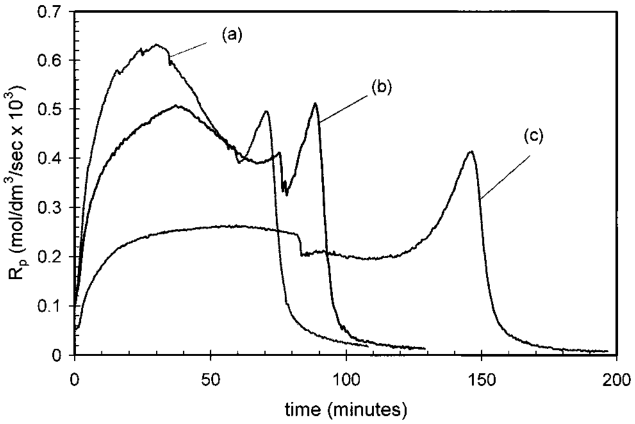

Figure 1. Rate of polymerization versus time for (a) conventional styrene emulsion, 10 mM SLS; (b) homogenized styrene emulsion, 10 mM SLS; and (c) styrene miniemulsion, 10 mM SLS/30 mM CA. [KPS] = 1.33 mM, T_r = 70 °C.

It is apparent from Figure 1 that there is an instability (the sharp vertical drop) in the heat curve before the onset of the gel effect in both the homogenized emulsion and miniemulsion systems. Miller[1] reported similar results before the onset of the gel effect for miniemulsion polymerizations using cetyl alcohol as the cosurfactant. His sampling performed at this point in the reaction did not reveal a definite cause for this instability in the heat curve. However, Miller did postulate that it was due to limited aggregation occurring at this point in the polymerization. It is interesting to note that the conventional emulsion polymerization exhibited this unstable period to a much lesser extent than is seen in both the homogenized and miniemulsion polymerizations.

Figure 2 shows the effect of predissolving polymer into the monomer prior to homogenization for emulsions

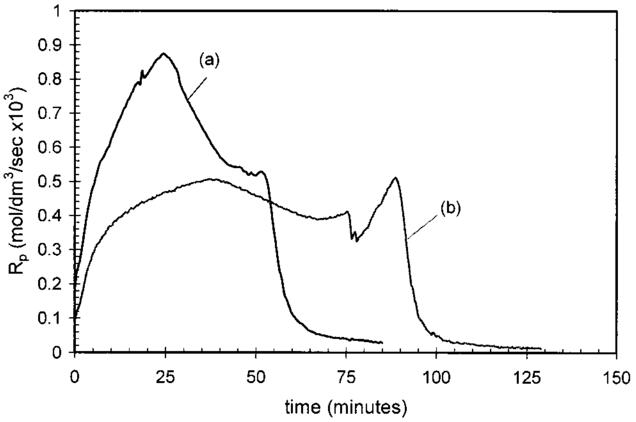

Figure 2. Effect on the rate of polymerization versus time of predissolving polystyrene in a homogenized styrene emulsion: (a) 1% predissolved polymer, M_n = 149 000 g/mol and SO_3^- end group and (b) no polymer. [SLS] = 10 mM, [KPS] = 1.33 mM, T_r = 70 °C.

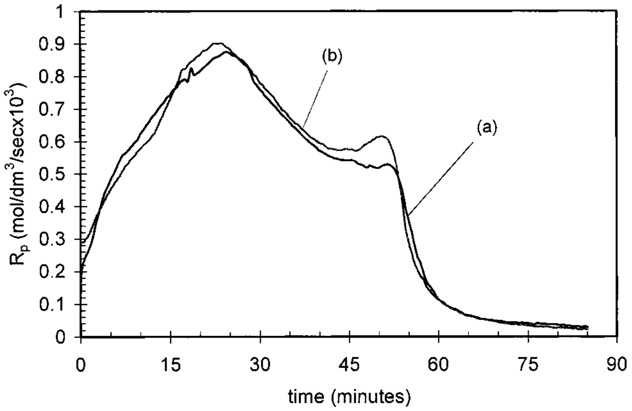

Figure 3. Effect of the length of emulsion aging time on the rate of polymerization versus time in homogenized styrene emulsions that contain predissolved polystyrene: (a) approximately 1 h aging and (b) approximately 25 h aging. Predissolved polystyrene, M_n = 149 000 g/mol and SO_3^- end group, [SLS] = 10 mM, [KPS] = 1.33 mM, T_r = 70 °C.

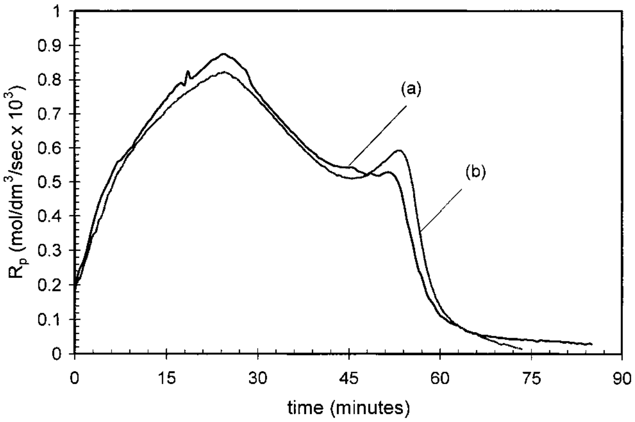

Figure 4. Effect of predissolving different polystyrene into homogenized styrene emulsions on the rate of polymerization versus time: (a) M_n = 149 000 g/mol and SO_3^- end group and (b) M_n = 62 600 g/mol and SO_4^- end group. [SLS] = 10 mM, [KPS] = 1.33 mM, T_r = 70 °C.

prepared without cosurfactant (homogenized emulsions). There is a significant enhancement in the rate of polymerization in the system containing 1% predissolved polymer. For homogenized emulsions, it is proposed that this enhancement is due to a shift of the dominant nucleation site. As previously mentioned, in the homogenized emulsion that does not contain polymer, the dominant site for nucleation is considered to be the micelles. However, in the homogenized emulsion containing 1% polymer, the dominant site for nucleation is proposed to shift to polymer preserved monomer droplets. The droplet number is preserved thermodynamically by the presence of the polymer. For polystyrene, the value of $1/j_2$ in eq 1 is negligible. Thus, the polymer will not super-swell with monomer. Therefore, much of the monomer in the droplets formed during homogenization will diffuse by Ostwald ripening into off-size droplets. (The off-size droplets will be the largest droplets formed during homogenization.) Measurement of the creaming rate versus time indicates that the homogenized emulsion with 1% polymer will cream at a rate of ~2.8 mm/h in the first 16 h after homogenization. The rate of creaming, u, can be computed from eq 2:

$$u = \frac{2gr^2(\rho_m - \rho_p)}{9\eta} \qquad (2)$$

where g is the gravitational constant, r is the droplet radius, 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. Using the appropriate constants at 25 °C, eq 2 predicts a droplet radius of approximately 1.9 μm. Creaming behavior is dominated by the large droplets in the droplet size distribution. Thus, the homogenized emulsions containing 1% predissolved polymer are comprised of two distinct populations of monomer droplet sizes: (1) small droplets thermodynamically preserved by the predissolved polymer (as predicted in eq 1 with a j_2 value of ∞) and (2) large droplets created by monomer diffusion out of the smaller droplets into the larger ones. Monomer diffuses from the small droplets because polymer does not behave as a true cosurfactant and is unable to super-swell with monomer beyond its thermodynamic equilibrium. It is important to note that polymer is not able to diffuse through the aqueous phase from droplet to droplet. Therefore, the small polymer preserved droplets are preserved for an indefinite time period and are thermodynamically stable (although the swelling of polystyrene with styrene may be as low as 1:1).

The effect on the polymerization kinetics of allowing the homogenized emulsion that contains 1% predissolved polymer to age for a period of 24 h is shown in Figure 3. There is almost no effect on the kinetics. This is an indication that the droplet number in both systems is virtually identical. This is not surprising since the site for nucleation has been proposed to be the thermodynamically preserved monomer droplets. Theoretically, these droplets should remain stable for an indefinite period of time. This is unlike what is theoretically predicted for miniemulsions where the droplets are predicted to be only kinetically stable (albeit for long time periods of up to several months).

Figure 4 shows the effect of predissolving polymers of different molecular weights and end groups on the rate of polymerization in homogenized emulsions. Similar to the results in the previous paper for miniemulsions stabilized with cetyl alcohol, there is virtually no effect of varying the properties of the predissolved polymer on the reaction kinetics. This can be taken as further evidence that the viscosity of the monomer

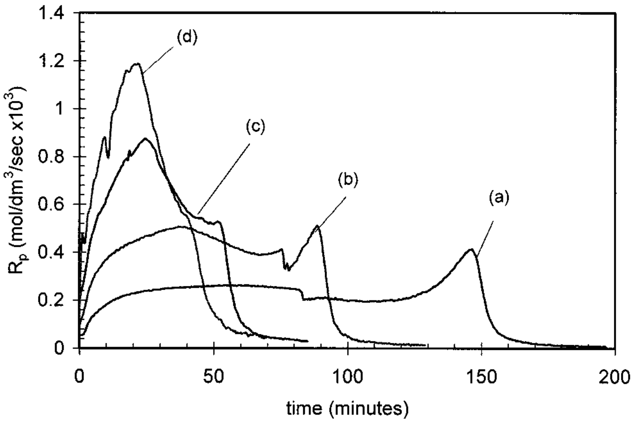

Figure 5. Effect on the rate of polymerization versus time of predissolving polystyrene into either a homogenized styrene emulsion or a styrene miniemulsion: (a) miniemulsion with no polymer; (b) homogenized emulsion with no polymer; (c) homogenized emulsion with 1% polystyrene, $M_n = 149\,000$ g/mol and SO_3^- end group; and (d) miniemulsion with 1% polystyrene, $M_n = 62\,600$ g/mol and SO_4^- end group. [SLS] = 10 mM, [KPS] = 1.33 mM, $T_r = 70$ °C.

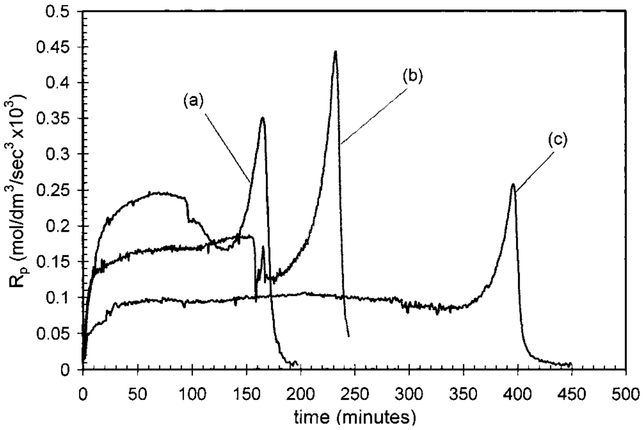

Figure 6. Rate of polymerization versus time for (a) styrene miniemulsion, 5 mM SLS/15 mM CA; (b) homogenized styrene emulsion, 5 mM SLS; and (c) conventional styrene emulsion, 5 mM SLS. [KPS] = 1.33 mM, $T_r = 70$ °C.

droplets does not affect the overall efficiency of radical entry from the aqueous phase. The enhanced kinetics are not a function of the properties of the polymer, but instead it is the miscibility of the polymer and monomer that appears to be of importance in ensuring the preservation of the droplet number.

Figure 5 compares the levels of enhancement in the kinetics created by predissolving 1% polymer into the monomer prior to homogenization in miniemulsions stabilized with cetyl alcohol and homogenized emulsions. Both of these systems exhibit significant enhancement in the rate of polymerization from the addition of the 1% polymer. However, the miniemulsion stabilized with cetyl alcohol has a higher maximum in the rate of polymerization than does the homogenized emulsion containing 1% polymer. It is proposed that the difference in the kinetics is due to a difference in the initial droplet number formed during the homogenization step. This difference could be caused by several phenomena, including (1) reduction in the interfacial tension between the droplets and aqueous phase by the presence of the cetyl alcohol, (2) increased stability of the droplets against coalescence during collisions by the presence of the SLS/CA interfacial barrier, and (3) increased surface area being created and stabilized by the presence of the cetyl alcohol in addition to the SLS. These are discussed in more detail in the following.

Cetyl alcohol may act to reduce the interfacial tension of the miniemulsion droplets. Work in this area has been contradictory. Under conditions where the droplet surface was saturated with SLS ([SLS] = 16.7 mM), the addition of cetyl alcohol increased the apparent surface tension of the monomer droplets as measured by the spinning drop method.[7] The cetyl alcohol in these experiments was added to the system as part of a gel phase. However, under conditions where the droplet surface was not saturated with SLS ([SLS] = 2 mM), the addition of cetyl alcohol reduced the interfacial tension at the monomer–water interface as measured by the drop volume method.[1] In these experiments, the cetyl alcohol was dissolved directly into the oil phase. Under the experimental conditions used in these experiments, it is not known what the level of surface coverage of the monomer droplets with SLS is. It is also possible that the method of cetyl alcohol addition to the system may have an effect on the interfacial tension. However, if the monomer–water interfacial tension of the monomer droplets is reduced, this would enable smaller droplets to be formed during the homogenization step.

The physical nature of the condensed layer of SLS and cetyl alcohol has been theorized to reduce the loss of droplets by mutual collision.[8] Since this layer is not present in homogenized emulsions, collision between droplets may be an important event in these systems, resulting in a reduction of polymerization sites. However, this seems unlikely since, as seen in Figure 3, there was no change in the kinetics (and thus the droplet number) over a 24 h time period.

The final factor that may be creating the difference in the number of droplets created during the homogenization step is the surface-active nature of the cetyl alcohol. In the miniemulsion system, a large portion of the cetyl alcohol will reside at the surface of the droplet and will occupy a significant surface area of the droplets. As a result, the combined sodium lauryl sulfate and cetyl alcohol is able to stabilize emulsion droplets with a greater surface area than sodium lauryl sulfate alone. Thus, the droplet size in miniemulsions containing cetyl alcohol will be smaller (resulting in a higher droplet number) than the homogenized emulsions that do not contain cetyl alcohol.

Polymerizations below the cmc. The assumption has been made up to this point that nucleation in homogenized emulsions containing 1% predissolved polymer takes place entirely in the polymer preserved monomer droplets. However, at 10 mM SLS, there is the possibility that micelles could be present and serve as sites for nucleation. To eliminate any possibility of micellar nucleation, a similar series of polymerizations were conducted at 5 mM SLS (below the cmc of SLS).

Figure 6 shows the rate of polymerization versus time data obtained for a miniemulsion prepared with cetyl alcohol, a homogenized emulsion, and a conventional emulsion at conditions below the cmc. The miniemulsion exhibits the fastest kinetics, the homogenized emulsion exhibits slightly slower kinetics, and the conventional emulsion has significantly slower kinetics. The slow kinetics in the conventional emulsion has been typically ascribed to homogeneous nucleation. Since there is not enough surfactant to form micelles, particles are formed by precipitation of oligomeric species formed in the

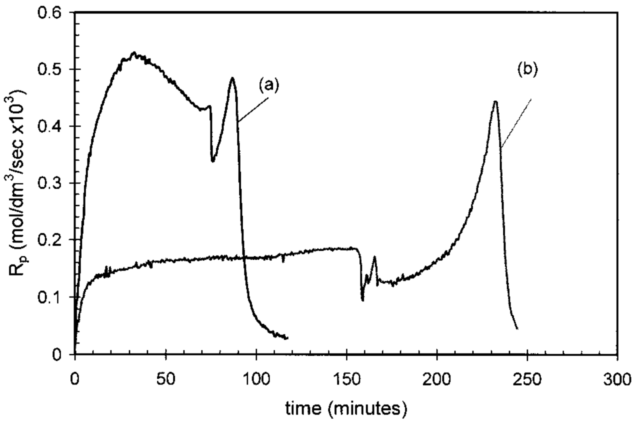

Figure 7. Effect on the rate of polymerization versus time of predissolving polystyrene into a homogenized styrene emulsion: (a) 1% predissolved polymer, $M_n = 39\ 000$ g/mol and H end group; (b) no polymer. [SLS] = 5 mM, [KPS] = 1.33 mM, $T_r = 70$ °C.

aqueous phase. Since the water solubility of styrene is extremely low, homogeneous nucleation is a relatively inefficient process in the conventional emulsion polymerization of styrene below the cmc, which leads to the slow kinetics. Homogenized emulsions exhibit significantly faster kinetics compared to the conventional emulsion system. This is most likely due to a dual nucleation mechanism in this system, namely droplet and homogeneous. Once again, micelles will not be present in the homogenized emulsion and thus cannot be a site for nucleation. Furthermore, if homogeneous nucleation was the sole means of nucleation, it would be expected that the rate of polymerization would be slower in the homogenized emulsion compared to the conventional emulsion. This is because homogenization should decrease the level of free surfactant available in the aqueous phase that is able to stabilize the precursors formed by homogeneous nucleation. Thus, the reason for the faster rate in the homogenized emulsion versus the conventional emulsion below the cmc is the presence of droplet nucleation. The miniemulsion stabilized with cetyl alcohol exhibits the fastest rate of polymerization. Nucleation in this system occurs in the monomer droplets. The most likely explanation for this system exhibiting the fastest rates of polymerization of the three systems is the high droplet number available for nucleation.

Figure 7 shows the effect of predissolving polymer into the monomer prior to homogenization in systems employing 5 mM SLS and no cosurfactant. Predissolving polymer causes a significant enhancement in the rate of polymerization. The most likely explanation for this enhancement is the preservation of droplet number by the presence a small quantity of polymer in each droplet formed by the homogenizer. The polymer acts to thermodynamically preserve the droplet number by swelling with monomer. As stated previously, the polymer is unable to super-swell with monomer, so a large portion of the monomer will diffuse out of the droplets into larger off-size monomer droplets. Thus, polymer is able to preserve the droplet number but not the droplet size. Thus, the mechanism proposed to bring about the enhancement in the rate of polymerization in the homogenized emulsions is the same mechanism that has been proposed to be the dominant mechanism causing “enhanced droplet nucleation” in miniemulsions stabilized with cetyl alcohol.

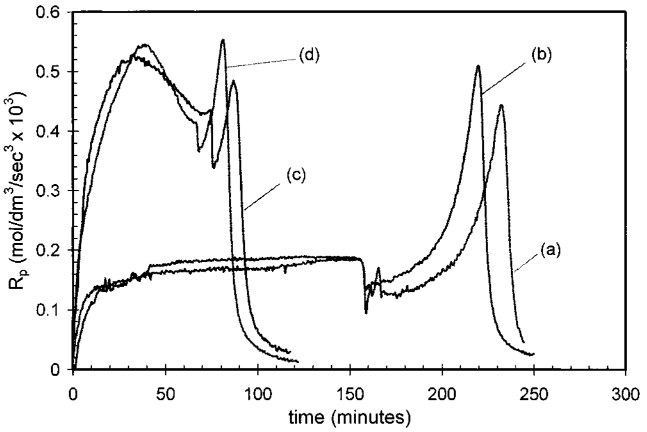

Figure 8. Effect of aging time on the rate of polymerization versus time in homogenized styrene emulsions with (a) no polymer and approximately 1 h aging; (b) no polymer and approximately 25 h aging; (c) 1% predissolved polystyrene and approximately 1 h aging; and (d) 1% predissolved polystyrene and approximately 25 h aging. Predissolved polystyrene, $M_n = 39\ 000$ g/mol and H end group. [SLS] = 5 mM, [KPS] = 1.33 mM, $T_r = 70$ °C.

Figure 8 shows the effect of aging time on the rates of polymerization for homogenized emulsions with and without predissolved polymer. The kinetics for both the homogenized emulsion with polymer and without polymer do not change significantly as the emulsions are aged. This is not surprising for the homogenized emulsion containing 1% polymer. The droplets preserved by the presence of polymer are the result of the thermodynamic equilibrium between monomer and polymer, and thus the droplet number is not expected to change as a function of time. However, the result that the kinetics in the homogenized emulsion containing no predissolved polymer do not change with aging time is surprising. It seems intuitive that the kinetics exhibited by the homogenized emulsion after a significant period of aging would eventually resemble the kinetics seen in a conventional emulsion. This is not seen experimentally after 25 h of aging. In fact, there is no indication that the droplets in the homogenized emulsion have significantly degraded to any extent. The most likely explanation for this is the monomer droplets created by a high shear homogenizer in the absence of polymer and cosurfactant will not degrade into the droplet size formed by simple low shear mixing. This result is still not completely understood.

A comparison of the results obtained by predissolving polymer into the monomer prior to homogenization in miniemulsions stabilized with cetyl alcohol versus homogenized emulsions below the cmc is shown in Figure 9. Both systems undergo significant enhancement in the rate of polymerization from the addition of a small amount of polymer. However, the maximum in the rate of polymerization for the miniemulsion containing predissolved polymer is greater than the homogenized emulsion containing predissolved polymer. This is in accord with the experiments above the cmc. Again, it is suggested the rate of polymerization is higher in the miniemulsion because more droplets are formed in the miniemulsions stabilized with cetyl alcohol that contain predissolved polymer than the homogenized emulsions that contain predissolved polymer.

Final particle size data for the various latexes prepared below the cmc are listed in Table 4. It can be seen the smallest particle sizes resulted from the polymeri-

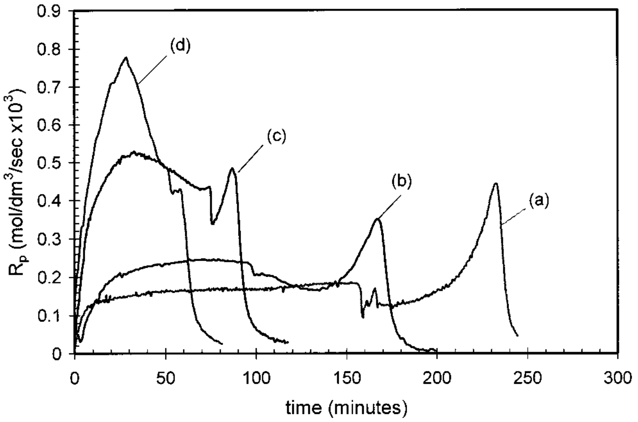

Figure 9. Effect on the rate of polymerization versus time of predissolving polystyrene into either a homogenized styrene emulsion or a styrene miniemulsion: (a) miniemulsion with no polymer; (b) homogenized emulsion with no polymer; (c) homogenized emulsion with 1% polystyrene, $M_n = 39\,000$ g/mol and H end group; and (d) miniemulsion with 1% polystyrene, $M_n = 62\,600$ g/mol and SO_4^- end group. [SLS] = 10 mM, [KPS] = 1.33 mM, $T_r = 70$ °C.

Table 4. Particle Size Measurements by the CHDF for Emulsion Polymerizations of Styrene below the cmc of SLS

sample	polymer	aging time (h)	D_n (nm)	D_w (nm)	PDI
miniemulsion	yes	2	86.4	101.0	1.17
homogenized emulsion	yes	1	110.0	118.8	1.08
homogenized emulsion	yes	25	109.8	118.7	1.08
miniemulsion	no	2	161.7	169.8	1.05
homogenized emulsion	no	1	195.1	199.3	1.02
homogenized emulsion	no	25	195.8	196.9	1.01
conventional emulsion	no		265.9	268.2	1.01

zation of the miniemulsion containing predissolved polymer. The homogenized emulsion containing predissolved polymer has a larger final particle size than the miniemulsion containing predissolved polymer. This supports the idea that the difference in the rates of polymerization is due to a change in the initial droplet number between the two systems. As expected from the kinetic data, there is no effect of aging time on the final particle size produced. It is also interesting to note that the final particle sizes obtained for the homogenized emulsions containing predissolved polymer are significantly less than the homogenized emulsions that do not contain polymer. This corresponds to the behavior seen in cetyl alcohol miniemulsions with and without predissolved polymer.

Ramifications for "Enhanced Droplet Nucleation". Significant enhancement in the rate of polymerization occurred by predissolving 1% polymer in the monomer prior to homogenization in emulsions created without cosurfactant. This same behavior was noted in miniemulsions formed from a cetyl alcohol gel phase (although the maximum R_p in these systems is greater than the 1% polymer homogenized emulsion systems). Homogenized emulsions are unstable emulsions in which the droplet size degrades rapidly with time. In the previous paper, it was suggested that the cause of "enhanced droplet nucleation" in miniemulsions that use cetyl alcohol as the cosurfactant is the preservation of the droplet number by the predissolved polymer.[5] Also, literature has shown that the droplet size distribution in cetyl alcohol miniemulsions degrades with time.[9] Thus, the experimental results for homogenized emulsions support the idea that an enhanced rate of polymerization and number of particles nucleated can be created by predissolving polymer into an emulsion subjected to high shear but using no cosurfactant. Thus, the results from this paper further support the proposal that the dominant cause of enhanced droplet nucleation in miniemulsion polymerizations utilizing cetyl alcohol as the cosurfactant is the preservation of the droplet number by the presence of polymer in the miniemulsion droplets.

Conclusions

This paper describes the results obtained by predissolving 1% polymer into the monomer prior to homogenization in homogenized emulsions (no cosurfactant) at conditions above and below the cmc. It was noted that there is a significant increase in the rate of polymerization and number of particles formed during the reaction when polymer is predissolved. Above the cmc in homogenized emulsions not containing predissolved polymer, it was proposed that nucleation predominantly takes place in micelles, although a limited amount of droplet nucleation will occur. Below the cmc in these systems, both droplet and homogeneous nucleation take place. However, at conditions above and below the cmc, it was proposed that the dominant site for nucleation shifts to polymer preserved droplets when polymer is predissolved in the monomer for the homogenized emulsions. The similarity (and dissimilarity) between the miniemulsions stabilized with cetyl alcohol and homogenized emulsions was presented. Both miniemulsions stabilized with cetyl alcohol and homogenized emulsions have been shown to undergo droplet degradation. However, the extent of degradation is different between the two systems. Both of these systems exhibit "enhanced nucleation" from predissolving polymer, although to a different degree.

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References and Notes

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