Enhanced Droplet Nucleation in Styrene Miniemulsion Polymerization. 1. Effect of Polymer Type in Sodium Lauryl Sulfate/Cetyl Alcohol Miniemulsions

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Received December 22, 1998; Revised Manuscript Received June 29, 1999

ABSTRACT: Predissolving polystyrene into the styrene monomer prior to homogenization in miniemulsions created using cetyl alcohol as the cosurfactant has been shown to result in a large increase in the polymerization rate and reduction in the particle size compared to similar systems with no predissolved polymer. This phenomenon has been termed “enhanced droplet nucleation”. The effects of varying the molecular weight and end group of the predissolved polystyrene in sodium lauryl sulfate/cetyl alcohol stabilized styrene miniemulsions are investigated here to gain a clearer understanding of this phenomenon. Predissolving polystyrene with either H or SO_3^- end groups and molecular weights over a range from $M_n = 39\,000$ to 206 000 g/mol results in the same level of enhancement in the kinetics independent of the polymer characteristics. This is taken as evidence against either a droplet surface modification or a change in droplet viscosity being the determining factor in “enhanced droplet nucleation”. However, measurement of the droplet size when no polymer is included indicates that these droplets undergo degradation by which the average size increases over time. Therefore, it is suggested the predominant cause of “enhanced droplet nucleation” from the addition of polymer is that the polymer adds extra stability to the miniemulsion droplets both prior to and during the polymerization. This is supported by calorimetric and particle size data.

Introduction

Miniemulsions are comprised of relatively stable oil droplets, ranging in size from 50 to 500 nm, suspended in an aqueous phase. Ugelstad et al.[1] were the first to show that the predominant mechanism of nucleation in miniemulsions shifts from either micellar or homogeneous nucleation to droplet nucleation. The stability of the small droplets in miniemulsions arises from the use of an ionic surfactant and a low molecular weight, highly water-insoluble cosurfactant in the miniemulsification process. Typical materials that have been used are long-chain alkanes and fatty alcohols.[1−3] These materials slow molecular diffusion of the monomer from the small droplets to the larger droplets. This diffusion is inherent in all emulsion systems because the small droplets have higher vapor pressures than the larger droplets due to the variation of Gibbs free energy with droplet size. Thus, to minimize the free energy in the system, small droplets tend to disappear with time by diffusion into the larger droplets. However, the rate of degradation of an emulsion has been shown to be governed by the diffusion rate of the least soluble component in the droplets. Ugelstad et al.[4] were able to show that as the chain length of the cosurfactant increased, the stability of the miniemulsion increased. Furthermore, a long-chain alkane was more effective in stabilizing the droplets than the fatty alcohol with the same chain length. This was taken as indication that the effectiveness of the cosurfactant increases as the water solubility decreases. For fatty alcohols, an additional mechanism may provide stability to the initial miniemulsion droplet distribution.[5−8] An ordered interfacial complex of ionic surfactant and fatty alcohol has been postulated to reduce the rate of coalescence. This complex has been proposed to be liquidlike and electrically charged.

Choi[9] was the first to suggest that during polymerization only a fraction of the initial miniemulsion droplets formed in the miniemulsification process capture radicals and become polymer particles. Some of this phenomenon may be due to simple repartitioning of the monomer during the reaction. As the polymer particles grow during the reaction, the monomer will redistribute in the system to satisfy thermodynamic requirements. Thus, monomer will diffuse from the unentered monomer droplets to the growing polymer particles, reducing the effective surface area of the droplets for radical capture. However, Delgado et al.[10] used thermodynamics to show that monomer droplets will not disappear by diffusion alone due to the presence of a cosurfactant. Instead, they suggested that monomer droplets must instead disappear by collision with polymer particles. Consequently, the longer a droplet goes without capturing a radical in miniemulsion polymerization, the less likely that event will occur.

Several researchers have also suggested that monomer droplets are less efficient than polymer particles in capturing aqueous phase radicals. Chamberlain et al.[11] and Choi,[9] using mathematical modeling, reported that radical entry into droplets must be an order of magnitude lower than particles for the model to accurately predict experimental data. Both researchers suggested that the interfacial complex formed by the fatty alcohol cosurfactant may be preventing radical entry into the droplets. Tang[12] conducted seeded experiments to determine the effect of changing the monomer-to-polymer ratio on radical entry in systems containing

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10.1021/ma981975v CCC: $18.00

cetyl alcohol. A cetyl alcohol gel phase was adsorbed onto latex particles followed by the addition of a quantity of monomer that varied from a 1.36:1 to a 50:1 monomer-to-polymer ratio. It was observed only at high swelling ratios that there is a noticeable reduction in the radical entry rate caused by the cetyl alcohol. It was suggested that at the high swelling ratios the highly swollen polymer particles resemble droplets, and thus droplets are less efficient than particles in capturing radicals. Miller et al.[13−15] studied the kinetics of miniemulsion systems formed with cetyl alcohol in which the droplets contained a low weight fraction polymer. The polymer was predissolved into the monomer prior to miniemulsification with a high shear homogenizer, the Microfluidizer. They reported a significant enhancement in both the number of droplets nucleated and the rate of polymerization. Furthermore, they were able to show that the final number of particles in the system was equivalent to the initial number of droplets. The authors stated that the droplets containing a low weight fraction polymer resemble polymer particles, and the cause for the significant enhancement in nucleation is due to particles being more efficient than droplets in capturing aqueous phase radicals.[16] Possible reasons given by the authors for the difference in radical capture abilities of particles and droplets were (1) polymer chains disrupt the order of the condensed phase residing at the oil−water interface that results in “openings” which facilitates radical entry; (2) as polymer chains are introduced, the viscosity of the droplets increases which, in turn, could provide a longer residence time for radicals to propagate rather than desorb from the modified droplet; and (3) the polymer may provide extra stability to the small, uninitiated monomer droplets, allowing them to compete for radicals.

This paper studies the effect of varying the properties of the polymer that is predissolved into the monomer prior to miniemulsification. By varying the end group and molecular weight of the predissolved polymer chains, the importance of both disruption of the condensed phase and viscosity of the droplets on radical entry will be examined. Using this new information, competition between droplets and particles for aqueous phase radicals will be examined.

Experimental Section

Experimental work contained in this paper was conducted in facilities at both Lehigh University and BASF AG. Thus, the materials and reactors varied slightly between the laboratories. However, it has been shown that the differences in the kinetic results obtained between the two facilities are negligible.[17]

Materials. Styrene (BASF or Aldrich) was distilled under a reduced pressure of 15 mmHg and stored at −5 °C for later use. Sodium lauryl sulfate, SLS (Fluka, 99% pure or BDH Biochemical, Ultrapure Bioreagent, 99% pure), was used as received. Potassium persulfate, KPS (Fluka or FMC Corp.), was recrystallized from deionized water and dried under vacuum. The following chemicals were used as received: cetyl alcohol, CA (Fluka or Aldrich), and sodium bicarbonate (Fluka or 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 miniemulsions. The polystyrene samples prepared at BASF were synthesized by anionic polymerization to provide polymers with narrow molecular weight distributions and the desired end group.

Recipe and Procedures. The ingredients used in the formulation of the miniemulsions are given in Table 2. First an aqueous gel phase was created by mixing the SLS, CA, distilled water (less 1% of the water which was saved to dissolve the initiator), and $NaHCO_3$ for 2 h at 70 °C. The gel phase was then cooled under agitation and sonified (Branson Sonic Power Co.) at 50% duty, power 7, and pulsed for 60 s. When polystyrene was used, it was predissolved in the monomer until all visible traces of the polymer disappeared. The oil phase was then added to the gel phase and mixed in a beaker for 20 min using a stir bar. The resulting emulsion was then sonified for 60 s at 50% duty, power 7, and pulsed. Finally, emulsion was passed through the Microfluidizer (Microfluidics Corp.) for 10 passes at 80 psi inlet pump pressure. The resulting miniemulsion was then added to the reactor where the KPS/water solution was added after heating the miniemulsion to 70 °C. Table 3 lists the experiments and the variables.

Table 1. Properties of the Polymers Used in the Miniemulsion 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 ZK751/34b	103 000	110 000	1.07	SO_3^-
BASF ZK751/34c	149 000	161 000	1.08	SO_3^-
BASF R2/910	39 000	45 100	1.16	H
BASF R2/939	94 200	105 000	1.11	H
BASF R2/913	206 000	263 000	1.28	H
DOW LS-1101	62 600	193 000	3.08	SO_4^-

Table 2. Basic Recipe for the Miniemulsion Polymerizations

ingredient	amount	grams
styrene	19.8−20.0 parts	300.5−303.5
polystyrene[a]	0.0−0.2 parts	0.0−3.04
deionized water	80 parts	1207.7
sodium lauryl sulfate[b]	10 mM	3.440
cetyl alcohol[a,b]	30 mM	8.675
sodium bicarbonate[b]	0.67 mM	0.067
potassium persulfate[b]	0.67 mM	0.213

[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	laboratory
LE25	none	none	BASF
LE20	39 000	H	BASF
LE24	94 200	H	BASF
LE22	206 000	H	BASF
LE46	40 400	SO_3^-	BASF
LE23	103 000	SO_3^-	BASF
LE27	149 000	SO_3^-	BASF
KPS2	62 600[a]	SO_4^-	Lehigh

[a] Polydisperse $M_n = 62\ 600$ g/mol $M_w = 193\ 000$.

Interfacial Tension Measurements. Interfacial tension was measured by the drop volume method in which the volume of a drop of liquid that breaks away from the tip of a capillary of a known diameter is measured. Equation 1 relates the volume of the drop that breaks away from the capillary to the interfacial tension:

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

where V is the drop volume (cm^3), $\Delta\rho$ is the density difference between the drop and the surrounding fluid into which it falls (g/cm^3), g is the gravitational constant (cm/s^2), r is the capillary radius (cm), and F is a correction factor. F has been tabulated in tables presented by Lando and Oakly[18] and is a function of ($r/V^{1/3}$). A 2 mM SLS (BDH Biochemical, Ultrapure Bioreagent 99% pure) solution was pumped using a constant flow rate syringe pump through a capillary into toluene (Aldrich) kept at 25 °C by a constant temperature water bath. The toluene contained 30 mM (based on the oil phase) cetyl alcohol and various amounts of the polystyrene (0, 0.5, 1, 2, or 4%). The effect on interfacial tension of three different end groups on the polystyrene chains was studied: hydrogen, SO_3^-, and SO_4^-. The average of 5 drops was taken, and the resulting standard deviation of the interfacial tension was typically less than 0.2 dyn/cm.

Cryoreplication-TEM. Samples were prepared by shock freezing a specimen in liquid nitrogen (~−210 °C). The sample was then freeze fractured. The fractured sample was then replicated by shadowing with a platinum/carbon film. The resulting film was then used to study the droplet size in a transmission electron microscope.

Apparatus. Polymerizations conducted at Lehigh University were carried out in a Mettler RC1 calorimeter while those carried out at BASF used a custom-made calorimeter designed by BASF researchers. The heat of reaction (Q_r), measured by calorimetry, can be related to the rate of polymerization by the following expression:

$$R_p = \frac{Q_r}{\Delta H_p V_{H_2O}} \tag{2}$$

where ΔH_p is the heat of polymerization (J/mol), R_p is the rate of polymerization (mol/(dm^3 s)), and V_{H_2O} is the volume of water in the reactor (dm^3). The following expression can be used to compute the apparent fractional conversion determined by calorimetry at any time during the reaction:

$$x(t) = \frac{\int_0^t Q_r \, dt}{\Delta H_p M_0} \tag{3}$$

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

Samples withdrawn during the reaction for particle size analysis were short stopped with a 1% hydroquinone solution and placed in an ice bath. These were stripped of monomer under reduced pressure in a Buchler Instruments Flash-Evaporator. Capillary hydrodynamic fractionation (CHDF) and transmission electron microscopy (TEM) were used to determine the particle size distributions. The Matec CHDF-1100 was used for CHDF analysis. The Phillips 400 TEM was used for electron microscopy, and a minimum of 1500 particles was counted using the Zeiss MOP3 digital analyzer. The number of particles per dm^3 of water (N_p) was computed from the following relation:

$$N_p = \frac{6 M_{mw} x}{\pi \rho_p D_v^3} \tag{4}$$

where M_{mw} is the initial monomer-to-water ratio, x is the conversion, ρ_p is the polymer density, and D_v is volume average diameter.

Results and Discussion

Effect of the Molecular Weight of the Predissolved Polymer. Figure 1 shows the effect on the miniemulsion polymerization kinetics of varying the molecular weight of the hydrogen-terminated polymer which is predissolved in the miniemulsion droplets. A similar miniemulsion system that does not contain any polymer is included for reference. For all three molecular weight polymers, there is a significant enhancement in the rate of polymerization that is consistent with the results seen by Miller et al.[13,14] However, the most interesting result shown in Figure 1 is that the level of enhancement in the rate of polymerization is not obviously affected by the molecular weight of the polymer that is predissolved. Since it is expected that the interior viscosity of the droplet should increase as the molecular weight of the predissolved polymer increases, this is an indication that the effective radical capture by droplets is unaffected by the modified droplet's interior viscosity. Dilute solution viscosity measurements were performed to quantify the relative change in the bulk viscosity for the different molecular weight polymers that were predissolved into the miniemulsions. Measurements were made at 25 °C for the various polymers dissolved in toluene. Table 4 lists the experimental values for the intrinsic viscosity coupled with the computed viscosity average molecular weight from the Mark−Houwink equation (using parameters $K = 8.48 \times 10^{-3}$ and $a = 0.748$[19]). The data show that there is more than a 250% increase in intrinsic viscosity from the polymer with $M_n = 39\,000$ g/mol to the polymer with $M_n = 206\,000$ g/mol. This result, coupled with the calorimetric data showing no dependence of enhanced droplet nucleation on the molecular weight of the predissolved polymer, is a strong indication that the internal viscosity of the modified droplets does not have an effect on the radical entry efficiency.

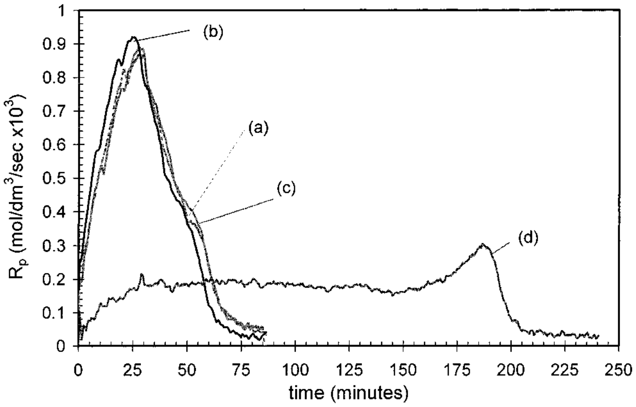

Figure 1. Effect of predissolving various molecular weight hydrogen-terminated polystyrene polymers on the rate of polymerization versus time in styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase: (a) $M_n = 39\,000$ g/mol, (b) $M_n = 94\,000$ g/mol, (c) $M_n = 206\,000$ g/mol, and (d) no polymer. [KPS] = 0.67 mM, $T_r = 70$ °C.

Table 4. Dilute Solution Viscometry Measurements of Intrinsic Viscosity

M_n (GPC), g/mol	M_v (GPC), g/mol	intrinsic viscosity, dL/g	M_v (viscosity), g/mol
39 000	43 000	0.2412	41 000
94 200	104 000	0.4563	97 000
206 000	255 000	0.8929	238 000

The effect on the miniemulsion polymerization kinetics of varying the molecular weight of the predissolved polymer possessing a hydrophilic SO_3^- end group is shown in Figure 2. Again, the miniemulsion containing no added polymer is included for reference. As before, for all three polymers ($M_n = 40\,400$, 103 000, and 149 000 g/mol), there is a significant enhancement in the rate of polymerization. However, as seen with the hydrogen-terminated polymers, the level of enhancement in the miniemulsions containing the different predissolved polymers is the same within experimental error. Since the hydrophilic end group will anchor the polymer chains at the surface of the droplets, it can be expected that the viscosity of the interface should be affected by the addition of the sulfonate-terminated polymer. Thus, it appears that an increase in interfacial viscosity will not have an effect on the effective radical entry rate into the polymer modified miniemulsion droplets.

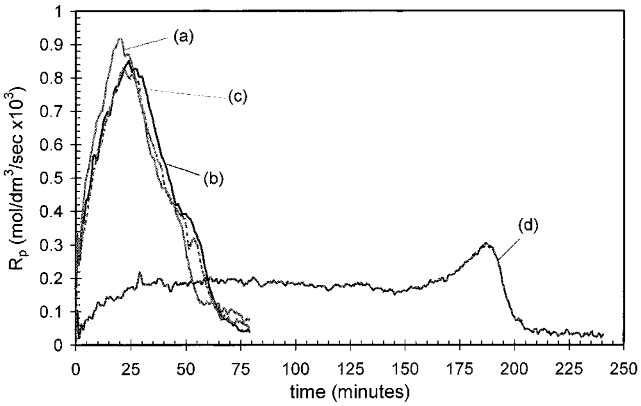

Figure 2. Effect of predissolving various molecular weight sulfonate-terminated polystyrene polymers on the rate of polymerization versus time in styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase: (a) $M_n = 40\,400$ g/mol, (b) $M_n = 103\,000$ g/mol, (c) $M_n = 149\,000$ g/mol, and (d) no polymer. [KPS] = 0.67 mM, $T_r = 70$ °C.

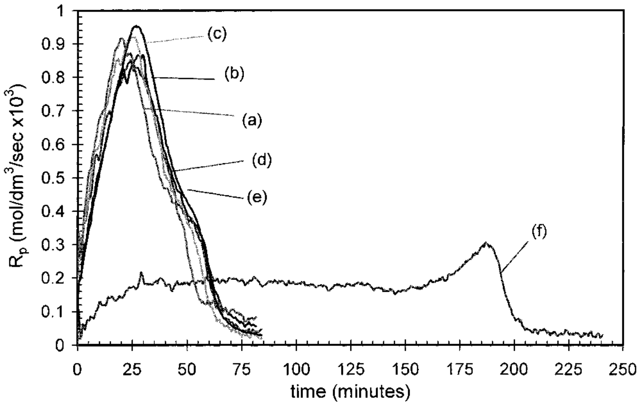

Figure 3. Effect of predissolving polystyrene terminated with different end groups on the rate of polymerization versus time in styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase: (a) SO_3^- end group, $M_n = 40\,400$ g/mol; (b) H end group, $M_n = 39\,000$ g/mol; (c) SO_3^- end group, $M_n = 94\,200$ g/mol; (d) H end group, 103 000 g/mol; (e) SO_4^- end group, $M_n = 62\,600$ g/mol; and (f) no polymer. [KPS] = 0.67 mM, $T_r = 70$ °C.

Effect of the End Group of the Predissolved Polymer. The effect of varying the end group of the predissolved polymer chains on the miniemulsion polymerization kinetics is shown in Figure 3. Again, all of the polymers with various chain end groups show the phenomenon of enhanced droplet nucleation, but the level of enhancement is always the same. Both the sulfate and sulfonate groups are hydrophilic and will anchor the polymer chains at the surface of the droplets. The polymer chains terminated with hydrogen have no affinity for the aqueous phase and will entropically avoid the surface of the droplets. It has been suggested that the polymer chains at the surface of the polymer modified droplets disrupt the condensed structure formed by the cetyl alcohol and sodium lauryl sulfate, creating “openings” through which the radicals can more readily enter the droplets. Thus, since the hydrogen-terminated and the sulfonate (and sulfate)-terminated polymer chains should have significantly different levels of surface disruption, there should be a significant effect on the rate of polymerization of the end group of the predissolved polymer chains if surface disruption of the condensed phase is important. Figure 3 shows that there is no measurable effect of the end group of the polymer chain on enhanced droplet nucleation, and therefore, it seems unlikely that polymer chains creating a surface disruption of the condensed phase is the correct reason for the enhanced droplet nucleation.

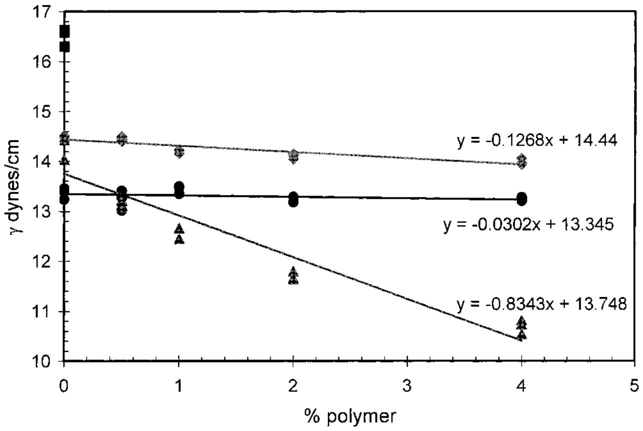

Figure 4. Effect of the end group of the predissolved polystyrene polymer on the interfacial tension between a 2 mM SLS solution and various styrene/cetyl alcohol/polystyrene solutions: (a) no CA (■), (b) 30 mM CA with $M_n = 40\,400$ g/mol and SO_3^- end group (◆), (c) 30 mM CA with $M_n = 39\,000$ g/mol and H end group (●), and (d) 30 mM CA with $M_n = 62\,600$ g/mol and SO_4^- end group (▲); $T = 25$ °C.

Interfacial Tension Measurements. To check whether the type of end group of the predissolved polymer chains could have an effect on the level of surface disruption, the interfacial tension of several polymer solutions (in toluene containing 30 mM cetyl alcohol) was measured against a 2 mM sodium lauryl sulfate solution. If the different end groups on the polymer chains disrupt the water–oil interface to varying degrees, the change in the interfacial tension as the polymer concentration is increased should be different for each end group.

Figure 4 shows the effect of the type of end group on the polystyrene chains on the interfacial tension measured by the drop volume method at 25 °C. It is apparent that the addition of cetyl alcohol to this system reduces the interfacial tension. The scatter in the data for the systems with no polymer is due to the measurements being conducted on separate days. It is apparent that the measurement is strongly dependent on minor fluctuations in the stock solution, syringe dimensions, room temperature, etc. However, the absolute value of each data point is not of extreme importance, but rather the trend in the data with increasing polymer concentration. Increasing the hydrogen-terminated polystyrene concentration has little effect on the interfacial tension. This is not surprising since it was expected that these polymer chains would entropically avoid the surface of the miniemulsion droplets and thus would have little effect on interfacial tension. Increasing the polymer content with an SO_3^- end group slightly reduced the interfacial tension. Although this result is not as dramatic as expected, interfacial tension measurements suggest there is a difference in the level of surface disruption created by the hydrogen- and SO_3^--terminated polymers. The results for polystyrene chains with SO_4^- end groups indicate the largest change in interfacial tension as a function of polymer concentration. This is most likely due to the broad molecular weight distribution of the SO_4^- polystyrene ($M_n = 62\,600$ g/mol, $M_w = 193\,000$ g/mol). The smallest chains in the molecular weight distribution can diffuse to the interface much more readily than the higher molecular weight chains

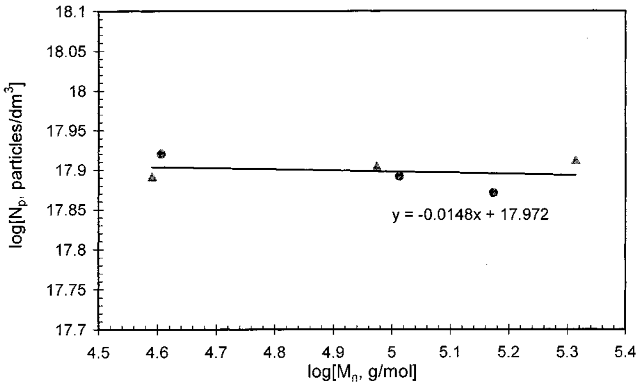

Figure 5. Effect of the molecular weight and end group of the predissolved polystyrene on the final number of particles produced from styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase: (a) hydrogen-terminated polymer (▲) or (b) SO_3^--terminated polymer (●); [KPS] = 0.67 mM; T_r = 70 °C.

of the SO_3^-- and hydrogen-terminated polymers. Therefore, the fraction of low molecular weight chains with SO_4^- end groups will more significantly affect the interfacial tension compared to the chains terminated with SO_3^- or hydrogen. Thus, it is apparent that the end group of the predissolved polymer does have an effect on interfacial tension. Specifically, the polymer chains with hydrophilic end groups appear to be anchored at the oil−water interface by the end group. Miller et al.[16] postulated that the polymer with the hydrophilic end group displaces a certain amount of cetyl alcohol at the interface, which in turn could destroy any molecular packing of the cetyl alcohol and sodium lauryl sulfate at the interface. However, it is apparent from Figure 3 that the proposed change in the molecular packing does not significantly affect radical entry into the polymer modified droplets.

Number of Particles. Figure 5 shows the effect on the final number of particles produced in the various miniemulsion systems of varying the molecular weight and end group of the predissolved polymer. As expected from the calorimetric data, there is no dependence of the final number of polymer particles on the properties of the predissolved polymer. This is additional evidence that the level of surface disruption provided by the polymer chains is not an important factor in determining enhanced droplet nucleation. Also, changing the viscosity of the miniemulsion droplets does not appear to change the level of radical capture by miniemulsion droplets during the polymerization.

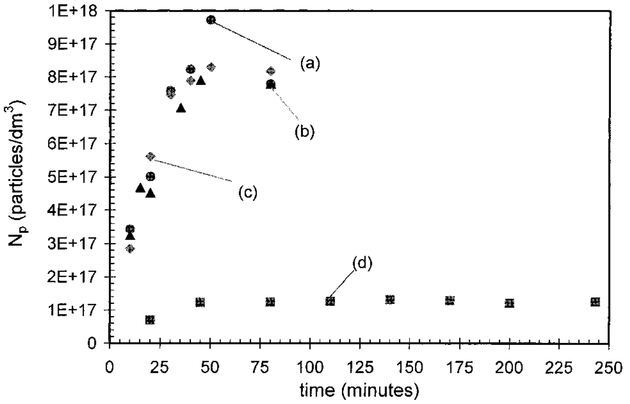

Figure 6. Effect of predissolving various polystyrene polymers terminated with different end groups and having different molecular weights on the number of particles nucleated versus time in styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase: (a) H end group, M_n = 39 000 g/mol (●); (b) SO_3^- end group, M_n = 103 000 g/mol (▲); (c) H end group, 206 000 g/mol (◆); and (d) no polymer (■). [KPS] = 0.67 mM, T_r = 70 °C.

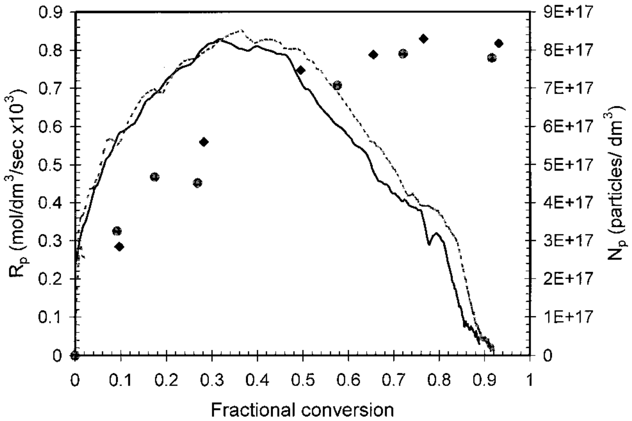

Figure 7. Rate of polymerization (lines) and number of particles (points) versus conversion in styrene miniemulsions containing 1% predissolved polystyrene polymer and formed from a 10 mM SLS/30 mM CA gel phase: (a) SO_3^- end group, M_n = 103 000 g/mol (dashed line and ●); or (b) SO_3^- end group, 149 000 g/mol (solid line and ◆). [KPS] = 0.67 mM, T_r = 70 °C.

Figure 6 shows the effect of predissolving polymers of different molecular weights and end groups on the evolution of the number of particles during the miniemulsion polymerizations of styrene. For comparison, the data for the miniemulsion not containing predissolved polymer is included. As expected from the calorimetric data, there is a large enhancement in the number of particles nucleated when there is 1% predissolved polymer present in the miniemulsion system. This enhancement is the same, within experimental error, regardless of the property of the predissolved polymer. Another interesting effect of the polymer is that nucleation of droplets continues well past the maximum in the rate of polymerization curve. This is shown in Figure 7 where the rate of polymerization and the number of particles are both plotted as a function of conversion for miniemulsions containing 1% sulfonate-terminated 103 000 and 149 000 g/mol polystyrene. Miller et al. have shown with an extensive series of TEM measurements that, in miniemulsion systems stabilized with cetyl alcohol that do not contain predissolved polymer, nucleation ceases between 40% and 60% conversion.[15] It is apparent from Figure 7 that nucleation can be extended up to almost 80% when the miniemulsion contains predissolved polymer. This is most likely due to the stabilizing effect of the polymer on the droplets during the reaction. The thermodynamic equilibrium between monomer and polymer reduces the monomer diffusion from the unentered monomer droplets to the growing polymer particles which enables the droplets to be available for nucleation at much later times in the reaction.

Figure 8 shows the evolution of the particle size distribution measured by TEM as a function of conversion in miniemulsions stabilized with cetyl alcohol and containing 1% predissolved polymer (M_n = 64 000 g/mol and SO_4^- end group). At higher conversions, there is a distinct bimodality in the particle size distribution. Miller et al.[15] have shown this bimodality is due to the final particle size distribution being comprised of par-

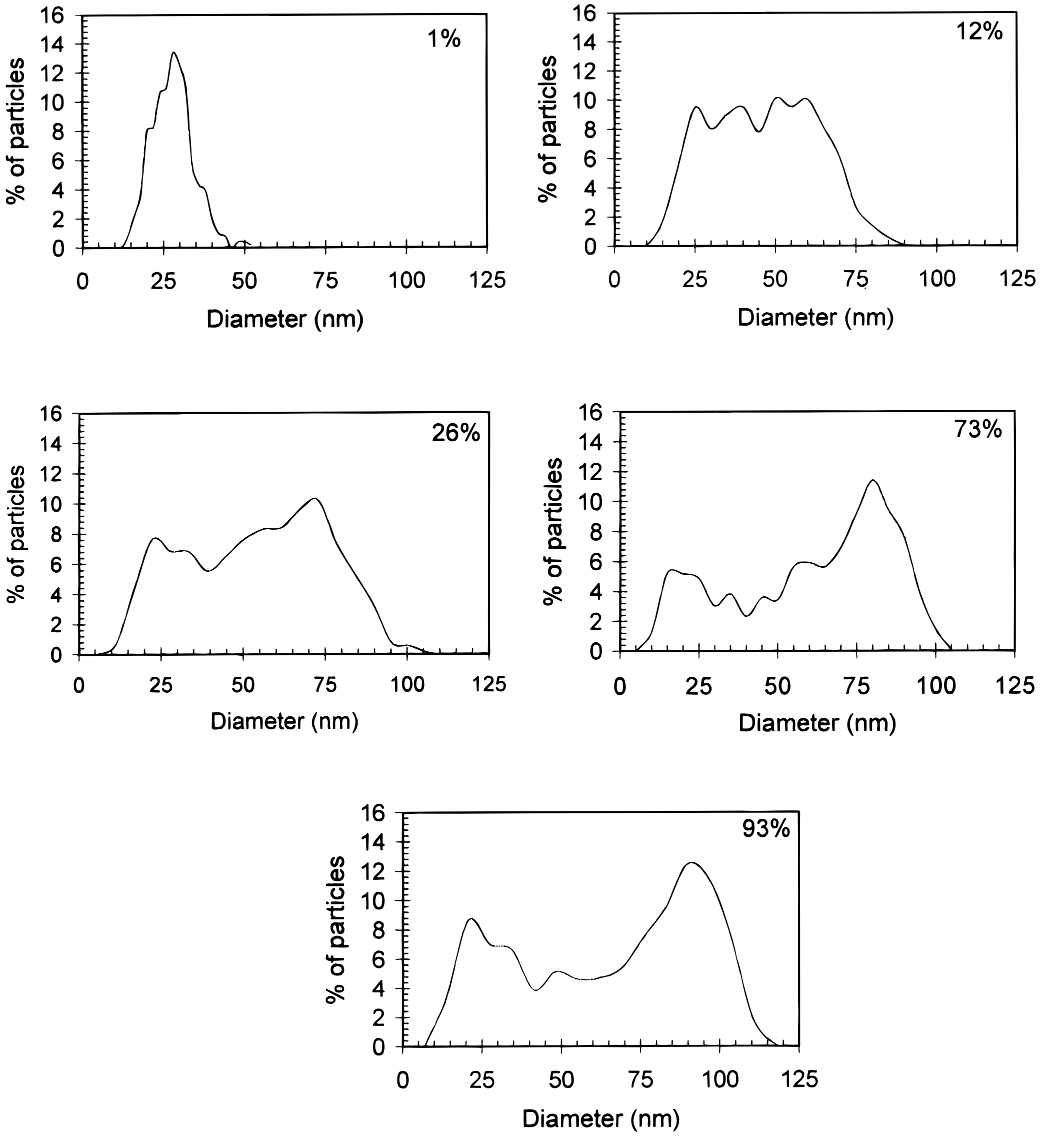

Figure 8. Particle size distributions measured by TEM at various conversions of a styrene miniemulsion formed from a 10 mM SLS/30 mM CA gel phase that contains 1% predissolved polystyrene polymer (M_n = 64 200 g/mol and SO_4^- end group); [KPS] = 0.67 mM; T_r = 70 °C.

ticles created by two different phenomena. The larger sized particles were created by the nucleation of miniemulsion monomer droplets. However, the smaller particles were created by the diffusion of monomer out of the initial droplets containing 1% predissolved polymer and 30 mM cetyl alcohol. These particles are the polymer modified droplets that are not yet nucleated. Thus, it is expected that these small droplets contain a high quantity of cetyl alcohol. During the reaction, the relative magnitude of these two distributions shifts. The fraction of droplets that are entered as a function of conversion is estimated in Figure 9. Here it was assumed that if a particle's diameter was greater than 40 nm, it had been created by radical entry into a droplet. Therefore, the fraction of the droplets that were entered by a radical is estimated by dividing the number of particles beyond 40 nm by the total number of particles represented by the distribution. As expected from the previous results for particle number versus time, nucleation of droplets may possibly occur up to nearly 80% conversion. This is again attributed to the preservation of monomer droplets at higher conversions by the presence of the 1% polymer.

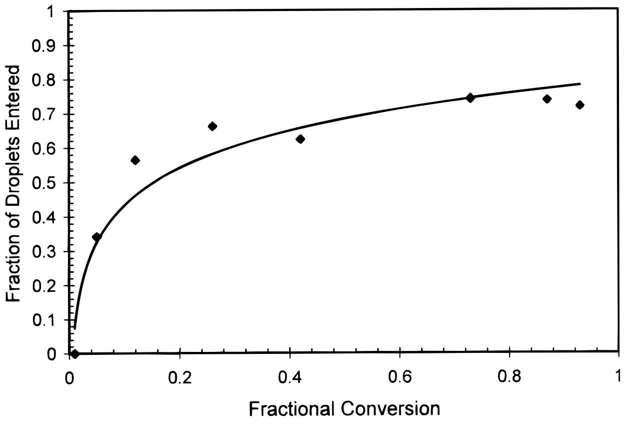

Figure 9. Estimated fraction of droplets nucleated as a function of conversion in a styrene miniemulsion formed from a 10 mM SLS/30 mM CA gel phase that contains 1% predissolved polystyrene polymer (M_n = 64 200 g/mol and SO_4^- end group); [KPS] = 0.67 mM; T_r = 70 °C.

Possible Explanations for "Enhanced Droplet Nucleation". There is no dependence of the degree of enhancement in miniemulsion polymerization rates on the property of the polymer that is predissolved into the styrene prior to homogenization. It was shown that changing the molecular weight of the polymer will change the bulk viscosity of the dilute polymer solutions. Also, modifying the end group of the polymer chain will change the level of surface disruption provided by the polymer chains of a proposed cetyl alcohol/sodium lauryl sulfate condensed phase at the oil/water interface. Since there is no effect on the polymerization kinetics of changing the viscosity of the droplets or the level of surface disruption, it is unlikely that these factors are what dominate the phenomenon termed "enhanced droplet nucleation". However, it is possible in a dilute solution that the polymer segment density at the interface will not depend on either the molecular weight or end group of the polymer chain. Since no direct measurement of the polymer segment density at the oil−water interface was made, a viscosity or surface disruption mechanism at the interface cannot be completely ruled out.

The extension of nucleation up to nearly 80% in the miniemulsion polymerizations containing 1% predissolved polymer is a strong indication that polymer acts to preserve the droplets for longer periods during the polymerization compared to conventional miniemulsions. Close examination of Figures 1−3 reveals that the enhancement in the rate of polymerization occurs from the very start of the polymerization. Thus, there must be an additional effect beyond stabilizing the unentered monomer droplets against monomer diffusion (and thus disappearance) to the growing polymer particles. On these grounds, it is suggested that the dominant mechanism that is creating the phenomenon of "enhanced droplet nucleation" is the preservation of the number of droplets by the predissolved polymer even before the polymerization has begun. In the experimental procedure, a period of 2 h elapses between when the miniemulsion is formed and the initiator is added. Thus, it is suggested in this time period that the miniemulsion droplets can degrade and disappear by Ostwald ripening. Several research groups have measured the droplet size as a function of time when cetyl alcohol has been used as a cosurfactant.[4,20,21] All the groups observed a similar behavior where the initial droplet size degraded into a relatively stable larger droplet size. Polymer does not exhibit "typical" cosurfactant behavior because of its high molecular weight. Thus, it is unable to preserve the size of the initial monomer droplet distribution, but the droplets will not disappear since there is a thermodynamic balance between monomer and polymer that will be maintained. Therefore, even though the size of the droplets may be reduced since polymer is not an effective swelling promoter, the number of droplets formed during homogenization will stay constant (in the absence of any colloidal instability). Thus, it is proposed that the dominating cause of "enhanced droplet nucleation" is the preservation of the number of monomer droplets by the presence of polymer. However, it is important to emphasize that the droplet distribution will be comprised of two main populations. There will be a large number of relatively small size droplets that are the polymer preserved monomer droplets. However, a significant amount of the monomer will be contained in large off-size droplets that are a result of the diffusion of monomer out of the polymer preserved droplets. Although these droplets are most likely not a large percentage of the total number of droplets by a number, by mass percentage these droplets most likely contain a significant amount of the monomer in the system. Since the predissolved polymer will not transport through the aqueous phase from droplet to droplet, the polymer preserved droplets will be thermodynamically stable and therefore should remain stable for an indefinite time period.

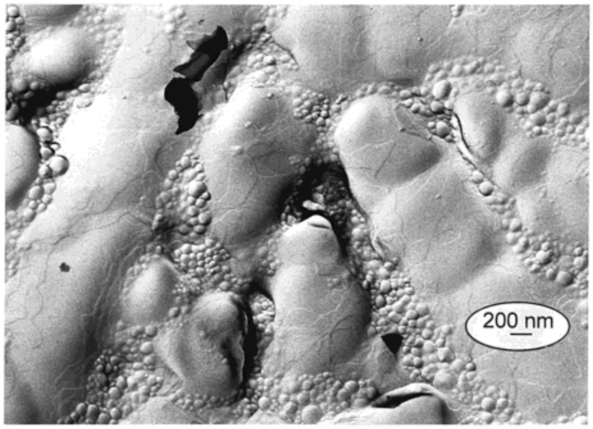

Figure 10. Cryoreplication TEM micrograph of a styrene miniemulsion formed from a 10 mM SLS/30 mM CA gel phase and containing 1% predissolved polystyrene in the styrene prior to homogenization: $M_n = 206\,000$ g/mol, hydrogen terminated.

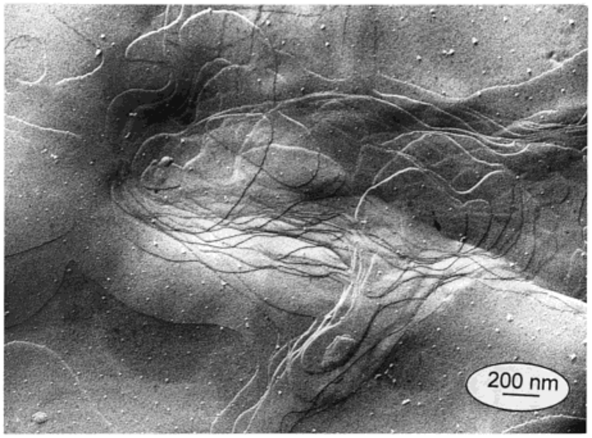

Figure 11. Cryoreplication TEM micrograph of a styrene miniemulsion formed from a 10 mM SLS/30 mM CA gel phase and containing no predissolved polystyrene in the styrene prior to homogenization.

Cryoreplication TEM. An attempt was made to determine the initial droplet size of miniemulsions either containing 1% predissolved polymer or no predissolved polymer by cryoreplication TEM. Figures 10 and 11 show the results from cryoreplication TEM for miniemulsions that either contain predissolved polymer or do not contain predissolved polymer, respectively. Only when polymer was predissolved into the initial miniemulsion was the technique able to detect droplets smaller than 100 nm. Unfortunately, the technique was unable to detect any droplet size for the miniemulsion containing no predissolved polymer. Thus, this experiment was unable to settle the issue of whether the droplet distributions are drastically different when polymer is predissolved into the miniemulsion compared to a system with no predissolved polymer. However, this technique strongly suggests that predissolving polymer into the initial miniemulsion droplets significantly increases the stability of the droplets.

Conclusions

In this paper, the effect on the polymerization kinetics of changing the properties of the polymer that is predissolved prior to homogenization in miniemulsions formed with cetyl alcohol as the cosurfactant was studied. It was determined that varying the molecular weight between 39 000 and 206 000 g/mol in systems containing 1% polymer did not change the kinetics. Also, changing the end group of the polymer chain from a hydrophobic end group to a hydrophilic end group had no effect on the kinetics in 1% polymer systems. However, predissolving 1% polymer in a miniemulsion always results in a significant enhancement in the kinetics compared to similar systems not containing predissolved polymer. The experimental results suggest that this enhancement in the kinetics from predissolving polymer is not due to either a change in the interior viscosity of the droplets or a disruption of the condensed phase formed by cetyl alcohol and sodium lauryl sulfate. Instead, it was suggested that the enhancement can be primarily attributed to a preservation of the droplet number by the presence of polymer in each of the miniemulsion droplets formed during homogenization. It is important to note that polymer does not act as a swelling promoter due to its high molecular weight, but it does act to preserve the droplet due to the thermodynamic balance between monomer and polymer. Thus, polymer is unable to preserve the size of the droplets produced during homogenization, but instead only the number produced during homogenization.

Acknowledgment. Financial Support from BASF AG and the National Science Foundation under Grant CTS-9628783 is greatly appreciated. Anionic polymerizations conducted by Dr. Konrad Knoll and cryoreplication TEM work by Dr. Frechen are highly appreciated. The laboratory assistance of Mr. Ruediger Janotte and Mr. Stephan Wahl is also acknowledged.

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MA981975V