Stability in Styrene/HD Miniemulsions Containing a RAFT Agent

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ABSTRACT: Styrene miniemulsions stabilized by sodium lauryl sulfate surfactant and hexadecane costabilizer were prepared and polymerized with the RAFT (reversible addition fragmentation chain transfer) agent cumyl dithiobenzoate. The instability noted by others in controlled radical miniemulsion polymerizations via RAFT was seen in these reactions as well and was investigated to determine the nature of this instability. Clues were found in the phase-separated emulsions and latexes as they evolved during polymerizations. Methods of improving the stability provided additional information along with some control studies excluding the RAFT agent. Instability was attributed to an initial Ostwald ripening leading to large micron-size droplets with a relatively low concentration of the RAFT agent and hexadecane, which separated as an oil layer upon centrifugation. At the other end, the Ostwald ripening created small droplets containing high concentrations of the RAFT agent, and these coagulated to form droplets significantly larger than the droplets remaining in the miniemulsion (50−250 nm). These were separated as an emulsion layer at the top of the centrifuge tube. Polymerization in these differing loci produced polymer with a bimodal molecular weight distribution and particles with broad or multimodal size distributions. Systems with no RAFT agent also showed some characteristics of this instability.

Introduction

Miniemulsions have become popular as the means of producing polymer colloids via controlled radical polymerization because of the convenience and reliability of locating the controlled radical agent in the loci of polymerization, namely the submicron monomer droplets. This is true in SFRP (stable free radical polymerization), RAFT, and ATRP (atom transfer radical polymerization) processes. This was first demonstrated in nitroxide-mediated miniemulsion polymerizations using TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy).[1]

Those reporting on RAFT polymerizations have commonly noted some instability during the reactions as sometimes described by a colored organic layer (RAFT agents can be highly colored) forming on the latex early in the polymerization.[2,3] The other controlled radical methods have also indicated some signs of instability. Conventional miniemulsion polymerizations are typically not reported to suffer from these instabilities, although this has generally not been the subject of study. In most cases, the stability was improved by altering the surfactant concentration or changing the type of surfactant. The mechanism of the instability has been examined in several publications, primarily attributing it to the generation of low molecular weight oligomers in the early stages of the polymerizations.[4,5] This has been addressed both experimentally and theoretically. This would seem a natural choice in that this is the primary difference between controlled and normal free radical polymerizations; the latter produces high molecular weight polymer with broad distribution from the beginning of the reaction as a consequence of radical segregation. However, both the experimental and theoretical studies stop short of describing mechanistically just how the appearance of oligomers leads to the instability. The latter study attributed the instability to “super-swelling” of the droplets containing the oligomers, but it is not clear how this causes the instability.

In our studies, we have noted similar instability in RAFT miniemulsion polymerizations of styrene using SLS and HD as stabilizer and costabilizer, respectively. Our further examination of this has led us to a differing conclusion as to the nature of the instability as described in the following.

Experimental Section

Materials. Styrene (Sigma-Aldrich, 99+%) was distilled under reduced pressure (30 mmHg, 50 °C) before each polymerization. 2,2′-Azobis(isobutyronitrile) (AIBN, Sigma-Aldrich, 98%), sodium lauryl sulfate (SLS, Fisher), hexadecane (HD, Sigma-Aldrich, 99%), and sodium bicarbonate (BDH, 99%) were used as received. 1,4-Dioxane (Sigma-Aldrich, 99.9% HPLC grade) was used as an internal standard for the monomer content measurement by gas chromatography. Deionized (DI) water was used in all waterborne polymerizations.

The dithioester type of RAFT agent 2-phenylprop-2-yl dithiobenzoate (or cumyl dithiobenzoate, CDB) was prepared in the lab and employed in the RAFT styrene miniemulsion polymerizations.[6−8]

Procedures. a. Miniemulsion Preparation and Polymerization. The recipe used in preparing the miniemulsions is given in Table 1. The aqueous (SLS, DI water) and oil (AIBN, HD, CDB, styrene) phases were first prepared separately and then mixed via magnetic stirring for 10 min in a 150 mL beaker. This was followed by sonification using a Branson sonifier (model 450) at a power output setting of 8 and a duty cycle of 50% with the beaker placed in an ice bath to absorb the excess heat produced. 10 min was the standard time of sonification although this was varied in some control experiments. The miniemulsion was charged into a three-neck 250 mL round-bottom flask, equipped with a condenser, mechanical stirrer (Teflon, half-moon), and N_2 inlet. The miniemulsion was degassed by purging with high-purity N_2 (Zero grade, Airgas) for 10 min. All polymerizations were carried out at 70 °C under a N_2 blanket. Samples (∼2 g) were taken periodically and quenched by cooling in an ice bath and by adding 1 drop of a 3 wt % hydroquinone aqueous solution.

Characterization. The conversion was determined gravimetrically. The molecular weight distributions were determined by gel permeation chromatography (GPC; Waters Styragel columns HR3,

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Table 1. Recipe for the RAFT Miniemulsion Polymerization of Styrene

ingredient	weight (g)	concentration
DI water	96.00	
SLS	0.2768	10 mM[a]
styrene	24.24	20 wt % on total
hexadecane	0.8696	40 mM,[a] 3.6 wt %[b]
CDB	0.1915	0.79 wt %,[b] 26 mM[b]
AIBN	0.1202	0.49 wt %,[b] 27 mM[b]

[a] Based on water. [b] Based on monomer.

Table 2. Styrene Miniemulsion Recipe

ingredient	weight (g)	concentration
DI water	96.00	
SLS	0.2768	10 mM[a]
styrene[c]	24.24	20 wt % on total
hexadecane	0.8696	40 mM,[a] 3.6 wt %[b]

[a] Based on water. [b] Based on monomer. [c] The styrene monomer was replaced with hexadecane to prepare the hexadecane miniemulsions.

HR4, and HR6 at 35 °C) using a Waters 410 differential refractometer as the detector and THF as the eluant (1.0 mL/min). The particle size distributions of the latexes were characterized by capillary hydrodynamic fractionation (CHDF, model 1100; Matec Applied Sciences).

a. Stability. The relative stability of miniemulsions was inferred from the amount of oil phase separated by centrifugation (20 min at 10 000 rpm; IEC HT; Damon/IEC Division). This choice of method and conditions must be recognized as being somewhat arbitrary as no guidelines have been developed and adopted for such a stability analysis although ultracentrifugation has been previously applied to miniemulsions to determine optimal surfactant and costabilizer ratios and concentrations.[9] Styrene miniemulsions were prepared (Table 2) by sonification for various times (from 1 to 10 min) and by varying the number of passes through the microfluidizer (model 110T; Microfluidics, Inc.). For comparison, miniemulsions were prepared with hexadecane used as the sole oil phase component. Any oil layer at the top of the tube was collected by syringe and weighed.

Similarly, the stability of the RAFT-containing styrene miniemulsion was studied, and centrifugation was also applied to samples taken with increasing conversion during polymerization. These latexes separated into different layers that were collected and analyzed in terms of molecular weight and particle size distributions and the concentrations of CDB and monomer. The content of the RAFT agent was determined by UV/vis spectroscopy (Spectronic Genesys2 spectrophotometer; Milton Roy). The monomer content was measured by gas chromatography (HP 5890; calibrated using 1,4-dioxane as internal standard).

b. Droplet Size. The volume-surface average droplet diameters (D_{vs}) of the styrene miniemulsions with and without RAFT agent CDB were determined by surfactant titration.[10] The surface tension of the miniemulsion was continuously measured at room temperature using a bubble tensiometer (Sensadyne, model 6000), while a concentrated surfactant solution (2 g of SLS in 20 g of H_2O; i.e., 347 mM) was added at a precise flow rate (0.11 mL/min) to the miniemulsion using a syringe pump (Harvard Apparatus model 975). The miniemulsion was stirred at 150 rpm to promote uniform mixing of the added surfactant. The cmc, noted as an inflection point, was used to determine the total surface area occupied by the surfactant with a saturation value of 71.2 Å^2 per molecule.[10]

c. Interfacial Tension. To examine the effect of the presence of the RAFT agent on the surface properties of the miniemulsion droplets, the interfacial tension between oil (containing styrene, 3.6 wt % hexadecane, and 0.8 wt % RAFT agent) and aqueous (containing 10 mM SLS) phases was determined by the drop-volume method. The interfacial tension (γ) is calculated from the volume of a drop (V) that detaches under the influence of gravity from the horizontal tip of a sharply cut and polished capillary (glass in this case) of accurately known radius, r:

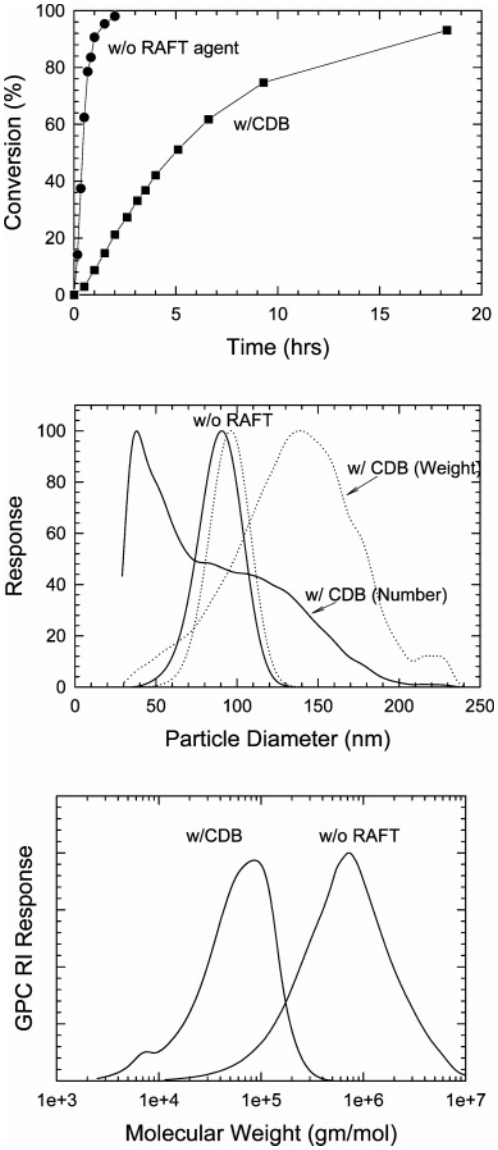

Figure 1. Comparison of miniemulsion polymerizations with and without CDB: (a) conversion vs time, (b) number and weight particle size distributions, and (c) molecular weight distributions.

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

where $\Delta\rho$ is the density difference between the dropping liquid and surrounding fluid, g is the gravitational constant, and F is a correction factor which is obtained from a table of F vs $r/V^{1/3}$ values.[11]

Results and Discussion

Miniemulsions with and without the RAFT agent cumyl dithiobenzoate (CDB) were prepared according to Table 1 and polymerized at 70 °C. The results are presented in Figure 1 as the conversion−time histories and the final particle size and molecular weight distributions. Large differences exist between all the results for the two systems. First, the polymerization was slowed greatly by the presence of the RAFT agent only reaching 93% conversion after 18 h while without the RAFT agent the reaction was essentially complete in 2 h. This has been reported in a number of publications and is attributed to retardation by the dithioester. The resulting particle size distributions show

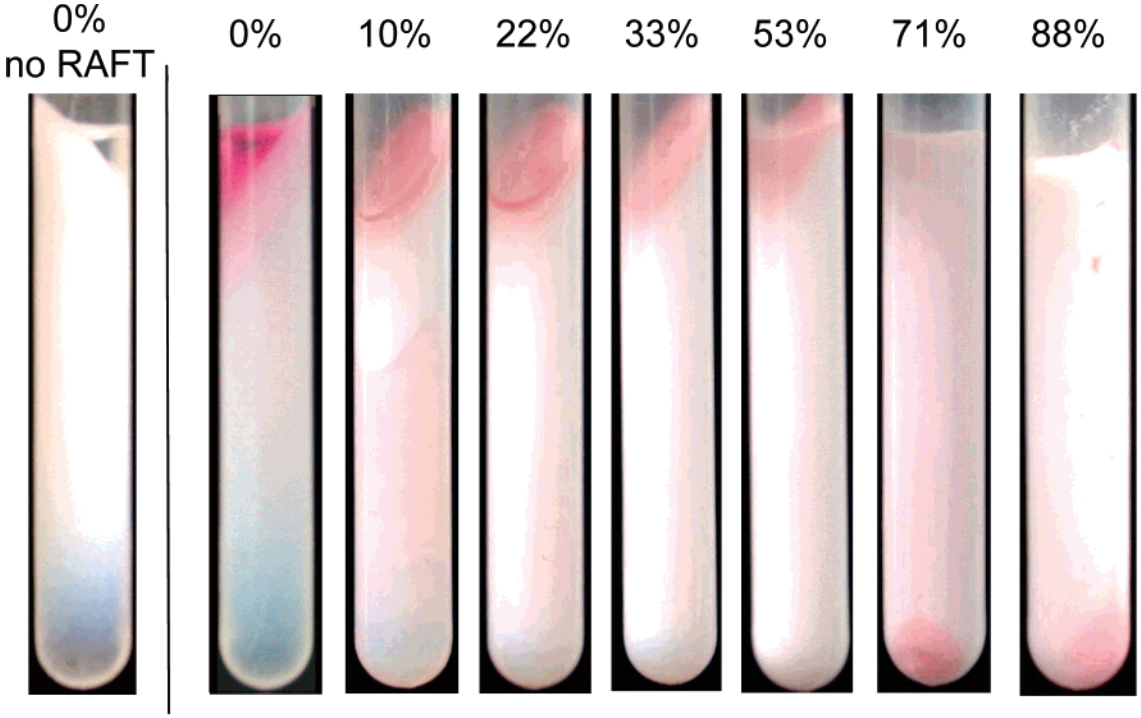

Figure 2. Centrifuged (10 000 rpm, 20 min) samples taken during miniemulsion polymerization of styrene with CDB. Miniemulsion prepared in the absence of RAFT agent shown at left. Percent conversion reported above each tube.

that the miniemulsion polymerization without the RAFT agent produced a unimodal distribution with number-average diameter (D_n) of 82 nm and a polydispersity index (PDI) of 1.065. This is similar to what is reported for most miniemulsion polymerizations. The distribution was considerably broadened when CDB was present ($D_n = 85$ nm, PDI $= 1.561$), showing a significant population of smaller particles in the number distribution. In addition, some coagulum was detected in the RAFT system comprising about 3% of the polymer, and the appearance was that of a pink solid, reflecting some content of the CDB, which has a deep purple color in its original form. No coagulum was found in the miniemulsion latex polymerized in the absence of the RAFT agent. Obviously some difference in these systems was brought about by the presence of the RAFT agent.

The molecular weight distributions (MWD) differed considerably as expected where the distribution without RAFT agent was broad and of higher average molecular weight ($M_n = 2.88 \times 10^5$ g/mol, PDI $= 3.34$) than the RAFT system ($M_n = 3.06 \times 10^4$ g/mol, PDI $= 2.07$) where the goal was to produce polymer of significantly lower polydispersity. However, it was also noted that the MWD for the CDB-mediated polymerization was bimodal with a small peak at low molecular weights. The molecular weight of the coagulum was measured and found to closely resemble the lower molecular weight peak.

On the basis of these results, a fuller exploration of the cause of these significant differences was warranted. A more detailed study of the miniemulsion polymerization with CDB was carried out. The miniemulsion itself and subsequent samples taken during the reaction were analyzed by centrifuging the samples at 10 000 rpm for 20 min, observing any separation, and then removing various portions of the samples for analysis.

Figure 2 shows a series of pictures taken of the test tubes after centrifugation of samples of increasing conversion. A centrifuged miniemulsion prepared without CDB is also shown for comparison. First, note that indeed there is some stratification in the test tubes. Both the emulsion prepared with CDB and without it exhibited some monomer separated as an oil layer. The RAFT system shows a colored oil phase separated at the top, indicating the presence of CDB with a colored emulsion layer just below followed by a white layer which becomes diffuse nearing the bottom of the tube. The oil phase was removed, weighed, and analyzed for the concentration of the RAFT agent; it comprised about 18% of the oil phase with a 0.60 wt % concentration of CDB, significantly lower than that of the recipe (0.79 wt %). This layer is considered to be formed by the breaking (coalescence) of primarily large (micron size) droplets upon centrifugation where they readily rise to the top because of their large size. These droplets can be seen in an optical microscope, and some are several microns in size.[12] These droplets are considered to exist immediately after the miniemulsification process. They were never broken down to the miniemulsion size, or they formed by combination of droplets in the shear field. Ostwald ripening allowed them to grow even larger and resulted in the dilution of the slow diffusing species, namely the RAFT agent and the hexadecane.

The pink layer immediately below the oil phase was removed and analyzed for the presence of the RAFT agent and was found to comprise 2.8 wt % CDB based on the styrene, a significantly *larger* concentration (3.5×) than in the original recipe. These are important clues as to the stability behavior of the miniemulsion.

The stratification in the samples taken during the polymerization do not contain any measurable separated oil phase but do show a pink latex layer at the top of samples up to 53% conversion and at the bottom of the last tubes at 70.7 and 87.7% conversions. Samples of the pink and white latexes were removed and analyzed for molecular weight and compared to the molecular weight distributions of the whole latexes (i.e., prior to separation). The results are reported in Figure 3. Several observations can be made immediately: (1) the whole latex has a bimodal MWD and is comprised of particles from the pink and white layers, which themselves are primarily unimodal in

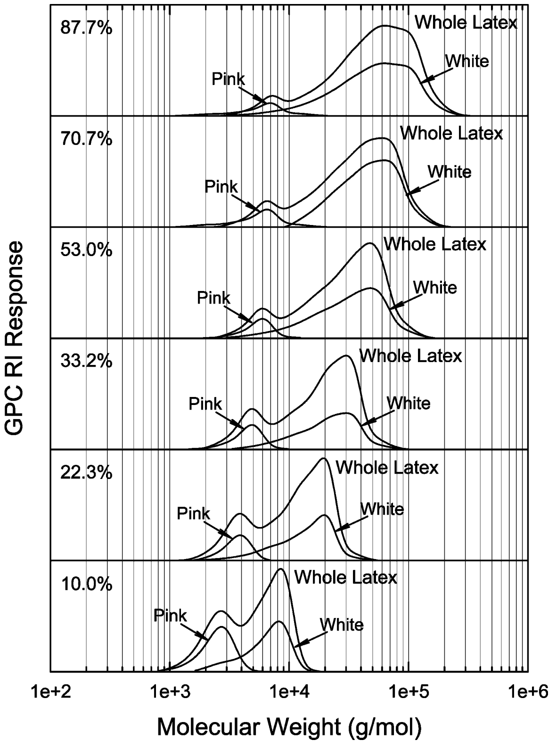

Figure 3. Molecular weight distributions as a function of conversion of polymers from samples separated by centrifugation, taken during the miniemulsion polymerization of styrene with the RAFT agent CDB.

distribution; (2) both species grow in molecular weight as the polymerization proceeds, evidence for a controlled radical growth; (3) the white species has a higher molecular weight and grows faster, producing more polymer than the pink species, and its distribution broadens (PDI is 1.2 at 10% conversion and 1.8 at 88% conversion). For the pink layer to be at the top of the centrifuge tube, the particles comprising it obviously must have some combination of size and density that allow them to cream to the top. How they might come to be this way is discussed in the following.

It is clear that there is some instability in the RAFT system based on the coagulum found. In addition, the presence of the monomer phase upon centrifugation can also be taken as evidence for some instability prior to polymerization that produces droplets sufficiently large to coalesce into a macroscopic monomer phase upon centrifugation. The question then is what the nature of the apparent instability in these miniemulsions is. The fact that some monomer separated whether CDB was added might be taken to mean that it does not contribute to this phenomenon. On the other hand, the particle size distributions of the final latexes are drastically different as illustrated in Figure 1b, which could imply differences in stability between the two systems.

Because of the differences in the two systems, the first thought was that the RAFT agent somehow influenced the stability of the miniemulsion prior to polymerization. Two experiments were performed as a check. The average droplet size in each miniemulsion was determined by soap titration, and the interfacial tension between the oil and aqueous phases was measured by the drop volume method at various SLS concentrations. The soap titrations gave similar results; the volume-surface average diameter of the miniemulsion droplets was 76 nm without CDB and 80 nm with CDB. In these measurements it was assumed that the area of adsorption per SLS molecule was the same (71.2 Å^2). As a check, the interfacial tensions were measured versus SLS concentration (0.1−15 mM) and were found to vary in identical fashion with and without the RAFT agent. Thus, no influence of the RAFT agent on droplet stability or more precisely the ability to affect the oil/water interface was seen.

The question remains as to the mechanism that produces the larger droplets that do not break upon centrifugation (to become part of the oil layer) but are at the top of the centrifuged miniemulsion and contain relatively high concentrations of the RAFT agent. Miniemulsions are normally thought to evolve on the following manner. Prior to formation, the separate phases are mixed to form homogeneous solutions. In this case, the RAFT agent and HD are dissolved in the styrene monomer, while the SLS is dissolved in the water. The oil phase is added to the water phase with relatively gentle mixing with a magnetic bar for several minutes forming a crude emulsion, which would separate quickly to form the two phases if the stirring was stopped. This is then sonified with mixing by magnetic bar to promote exposure of all elements of the mixture to the shear created under the sonifier horn. This initially breaks the oil phase into droplets over a wide range of sizes, each comprising the same composition. What happens next is not all that clear, however. As soon as small, submicron droplets are created, the surfactant adsorbs on their surface to provide some stability against aggregation. At the same time, thermodynamics dictates that some of the monomer should diffuse from these small droplets to larger ones to achieve equilibrium, provided that the monomer has some water solubility. This should begin to occur from their first formation. The rate of monomer diffusion will determine how quickly equilibrium will be established and is dependent upon its water solubility. As sonification proceeds, more small droplets are formed, and some may combine with others as they collide in the shear field. So the process of diffusion, breakup, and recombination are expected to occur simultaneously during sonification. This should produce a miniemulsion with a relatively broad range of droplet sizes and varying composition, where the small droplets are expected to have higher concentrations of RAFT agent and HD, which diffuse little if any on the time scale of experiment because of their extremely low water solubilities. It is generally not expected that equilibrium is attained until sometime after the sonification is stopped. The process of diffusion continues from small to large droplets and slows as equilibrium is approached. This should broaden the distribution of droplet size with the small droplets containing the highest concentrations of the HD and the RAFT agent. If the process stopped here, then it would be just the opposite of that observed in the experiments described above. And usually the picture of how miniemulsions evolve stops here. Since this apparently cannot be correct in this case, another mechanistic step must be involved, and the obvious choice is the aggregation and coalescence of the smallest droplets to form large size droplets, which can be separated by creaming and further coalescence into the macrophase noted in the centrifugation experiments. Why would this occur? First, the vast surface area of the droplets created by the shear action of the sonifier results in a low concentration of the surfactant on the surface of the droplets, reducing their colloidal stability. Surface coverages have been estimated to be as low as 15% when a miniemulsion is prepared.[13] Second, small colloidal species are expected to be less stable than larger ones particularly toward themselves as described by Derjaguin[14] as part of the DLVO theory of stability:

$$V_S = \frac{2\pi a_1 a_2}{a_1 + a_2}\int_d^\infty V(x)\,dx \tag{2}$$

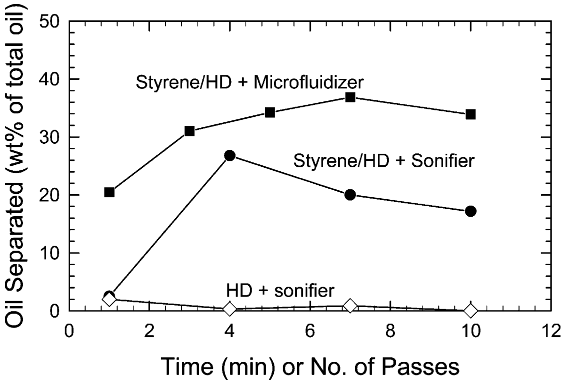

Figure 4. Percentage of the oil phase separated by centrifugation (20 min at 10K rpm) of miniemulsions prepared under varying homogenization conditions.

where V_S is the energy of interaction of spherical particles of radii a_1 and a_2 separated at a distance x. $V(x)$ is the energy of interaction for flat plates. From this it can be seen that particles of small size will have the lowest energies of repulsion and thus would be least stable toward themselves. Although qualitative, this can explain the appearance of large droplets containing relatively high concentrations of the RAFT agent. The aggregation of the small droplets, although not exclusive of all other droplets, would have to dominate to result in the large increase in concentration of the RAFT agent. And this would necessarily involve the aggregation and coalescence of large numbers of the smallest droplets. If this is indeed the mechanism of instability in this system, the question remains as to whether this is a general mechanism in miniemulsions that has gone unnoticed or unreported. If so, it would be important to determine this.

The centrifugation methodology (20 min at 10K rpm) was applied to a series of miniemulsions prepared under varying shear conditions (time/passes and apparatus (sonifier/microfluidizer)) and using different oil phases (styrene/HD and HD alone). The results for the amounts of oil phase separated are presented in Figure 4. Note that all miniemulsions processed through the microfluidizer were first sonified for 1 min. The results are intriguing. If indeed these are an indication of the stability in these miniemulsions, the longer sonification times (beyond 1 min) or processing through the microfluidizer leads to the formation of significant amounts (by volume) of large droplets that can be separated by the centrifugation.

This is not what was expected. Only the hexadecane itself shows little separation indicating good stability. However, the fact that some oil phase could be separated by centrifugation implies some larger droplets did exist in these miniemulsions. Since Ostwald ripening is not considered to be a possible mechanism for this, then some colloidal instability might exist owing to a low surface coverage by the surfactant or the process of sonification with the breakup and combination of droplets in the shear field may still result in some larger droplets. The fact that a significant amount of styrene can be separated by centrifugation would indicate that a significant population of larger droplets is produced. One mechanism is that described above (Ostwald ripening followed by coalescence) while several others are also possible. Ostwald ripening itself could lead to the larger droplets, and in this case the HD would effectively be diluted in these droplets. Or larger droplets might exist as a result of some inefficiency in the homogenization process (as noted by the small amounts of HD separated). In this case the HD concentration would not differ much from the original amount provided that Ostwald ripening is limited in the time scale of the experiment. Obviously, the HD concentration in the separated styrene layer should be measured. This will be reported in a separate ongoing investigation.

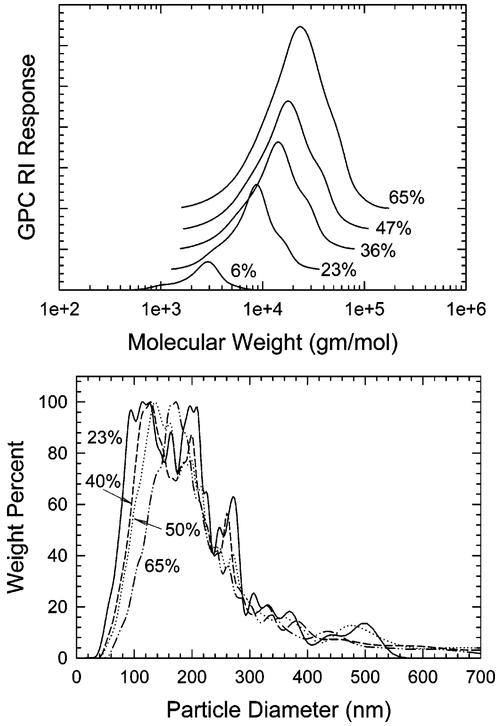

Figure 5. Molecular weight (top) and particle size distributions as a function of conversion in the miniemulsion polymerization of styrene with RAFT agent CDB. The miniemulsion was prepared by 1 min sonification.

Increasing Stability in Miniemulsions. A number of approaches are available to reduce the apparent instability in these miniemulsion systems, which can be either by increasing the stability against diffusional degradation or reducing the colloidal instability, or both. The former relies on both the costabilizer (or oil phase composition) and stabilizer (interfacial tension) while the latter is effected by the stabilizer. We have tried a number of approaches in the RAFT miniemulsions, and several of these will be highlighted here.

On the basis of the results in Figure 4, the 1 min sonification time would seem to be an interesting and counterintuitive choice. This miniemulsion was characterized for average droplet size by soap titration and found to be 158 nm (D_{vs}), about twice the average size of those prepared by sonification for 10 min. One consequence of this is that the surfaces of the droplets possess a greater coverage by the surfactant. The fractional surface coverage was estimated to be 30% in this case while only 15% coverage was achieved with 10 min sonification. The miniemulsion was polymerized using AIBN initiator, and samples were taken throughout for molecular weight and particle size characterization. The results are shown in Figure 5. The molecular weight distributions no longer show the low molecular weight peak attributed to the instability while the particle size distributions remain rather broad. The latter would normally be expected qualitatively for such a short sonification time where all droplets would not be exposed equally to the shear field under the sonifier horn. Nonetheless, the apparently increased stability based on the centrifugation results seems to be borne out by the molecular weight data.

The surface coverage by surfactant was next increased to determine its effect in increasing stability. This was not done by increasing the surfactant concentration in the original

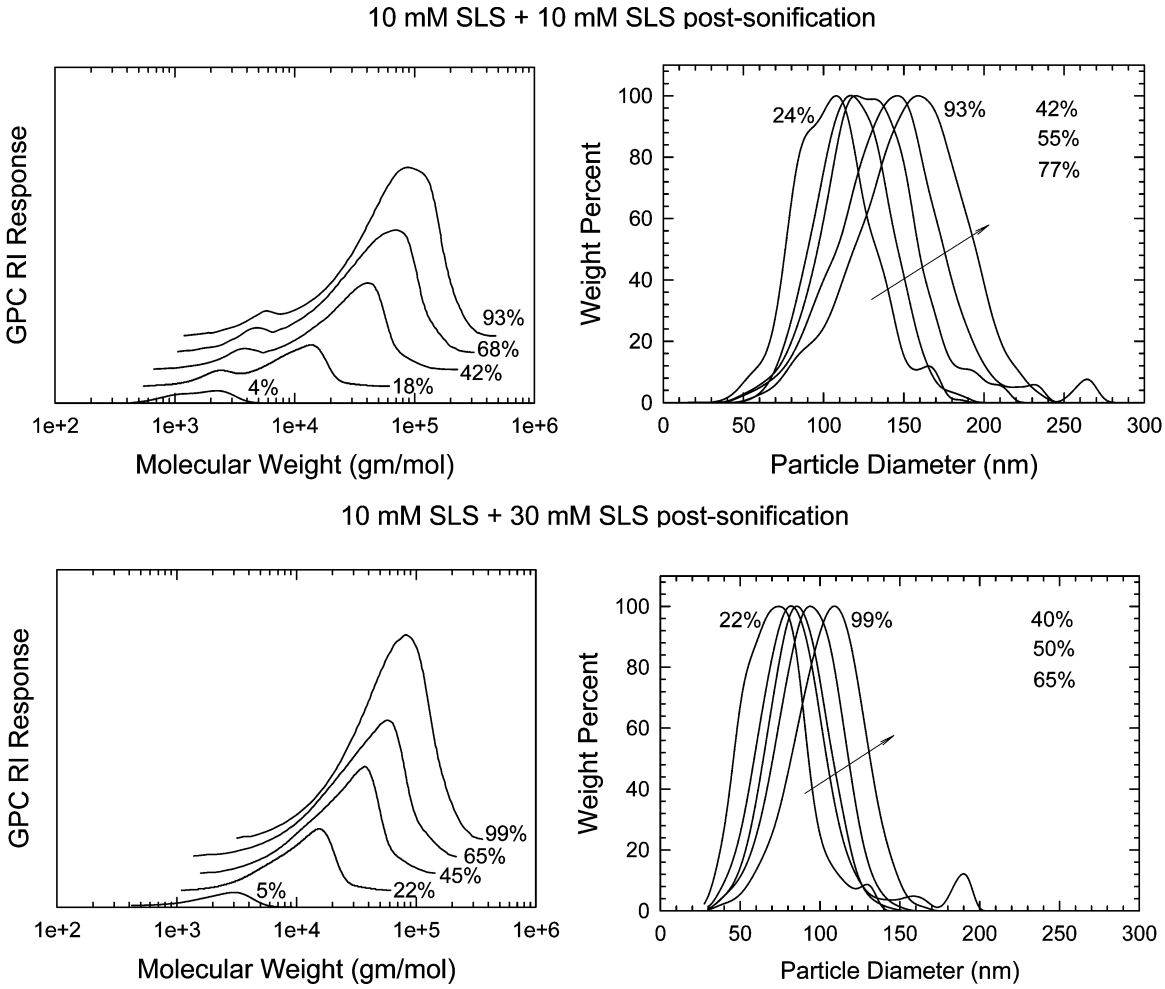

Figure 6. Effect of additional SLS on the evolution of the molecular weight and particle size distributions in miniemulsion polymerizations of styrene with RAFT agent CDB: top) 10 mM SLS + 10 mM SLS postsonification; bottom) 10 mM SLS + 30 mM SLS postsonification.

miniemulsion as others have done but instead was achieved by first preparing the miniemulsion with 10 mM SLS and adding additional SLS *after* creating the miniemulsion. This was accomplished by addition of a concentrated aqueous SLS solution within seconds of completing the 10 min sonification. Two levels of SLS were studied: 20 mM (10 mM added) and 40 mM (30 mM added). The results are reported again as the evolution of the molecular weight and particle size distributions, as shown in Figure 6. The 10 mM added amount, which was estimated to increase the surface coverage to 34%, does not appear to be adequate to prevent the formation of the lower molecular weight polymer attributed to instability, while the extra 30 mM SLS has eliminated this peak in the molecular weight distributions. The surface coverage in this case was estimated to be increased to 75% with the additional surfactant. The particle size distributions also become more uniform and well-behaved with increasing added surfactant, which might be expected with improved colloidal stability. Here it might be useful to report for comparison the evolution of the PSD found for the control system containing no added RAFT agent. As shown in Figure 7, the PSDs were narrower. The polydispersity indexes (PDI) for the final particles presented in Figures 5−7 are 1.454 (1 min sonification; $D_v = 146$ nm), 1.225 (10 mM + 10 mM SLS; $D_v = 115$ nm), 1.138 (10 mM + 30 mM SLS; $D_v = 90$ nm), and 1.065 (no RAFT; $D_v = 81$ nm). The PDI for the latex produced with added CDB and 10 min sonification (Figure 1) was 1.561 ($D_v = 102$ nm), the broadest of all presented here. These indicate that the presence of a higher surface coverage by the SLS promotes the stability with higher coverages, resulting in narrower distributions for the reactions where the RAFT agent is present. Without CDB, the distributions are narrower and the average size smaller. One possible reason for this is the large difference in reaction times for the systems with and without CDB; the conventional miniemulsion polymerization is essentially complete in 2 h while the RAFT agent containing reactions take about an order of magnitude longer. These longer reaction times are considered to allow for some limited aggregation of the particles, which can broaden the PSDs. This was observed in a control experiment where a miniemulsion polymerized via thermal initiation (no added

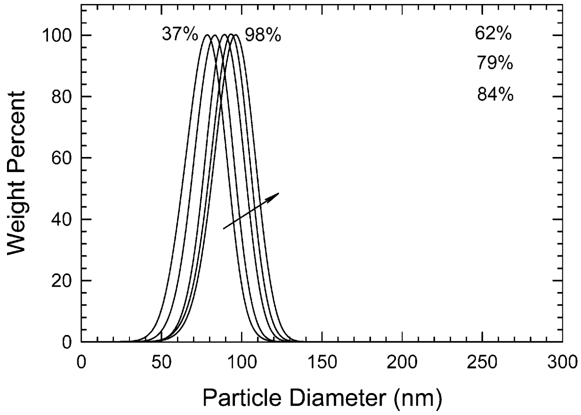

Figure 7. Evolution of particle size weight distributions (CHDF) with conversion for the miniemulsion polymerization of styrene with AIBN and no RAFT agent.

initiator) produced a larger particle size and broader distribution ($D_v = 135$ nm; PDI = 1.178) than produced with AIBN initiator. The polymerization time was also similar to the RAFT system (14 h to reach 90% conversion).

The concentration of the costabilizer, hexadecane, was next varied to determine its effect on system stability. Two additional concentrations were studied: 5 and 10 wt % on monomer. At 5 wt % HD, the modest increase over 3.6 wt % did not result in any measurable improvements in the observed stability of the system; similar results were obtained. However, when the level of HD was increased to 10 wt %, significant differences were observed. The additional HD was expected to increase the stability against Ostwald ripening and thus result in a more stable latex. When the latex was centrifuged at various conversions, some pink material could still be collected as before. When the molecular weights were measured, the two populations were much closer in molecular weight and overlapped to such an extent that a second peak was not observable in the whole latex samples. This indicates that Ostwald ripening was reduced considerably as the CDB concentration in the two species had to be much closer than in results reported for 3.6 wt % HD. However, the system showed decreased colloidal stability in that 25% of the polymer formed ended up as coagulum. This is a large increase over the 3% noted in the latter reaction, and it is not clear why this occurred. The final particle size data ($D_v = 104$ nm; PDI = 1.568) are similar to the results reported for the 3.6 wt % HD system and offer no additional insight into this phenomenon. One possibility is that indeed increased stability against Ostwald ripening was achieved, but this had the consequence of maintaining a greater surface area and thus a lower surface coverage, resulting in increased instability during the long polymerization (compared to the short reaction time in the parallel system without RAFT).

Conclusions

The stabilization of RAFT-containing styrene miniemulsions prepared with hexadecane costabilizer and sodium lauryl sulfate surfactant is more complex than originally conceived. Ostwald ripening leads to large droplets (micron size) containing substantially lower concentrations of the RAFT agent. The other consequence of the Ostwald ripening is the formation of a complementary small droplet species containing substantially higher concentrations of the RAFT agent. These apparently coagulate to form droplets significantly larger than the main miniemulsion population as determined by their position in the centrifuged samples and with higher RAFT concentrations. In the subsequent polymerization, they become particles (and form some coagulum) containing significantly lower molecular weight polymer compared to the main population. These mechanisms were uncovered in an effort to prepare narrow molecular weight polymers using the RAFT agent cumyl dithiobenzoate. Increased stability can be brought about primarily by increasing the surface coverage by the SLS surfactant. Increasing the HD concentration reduced the Ostwald ripening but did not improve the overall stability. The implication of these findings is being explored in systems not containing the RAFT agent.

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