Compartmentalization in TEMPO-Mediated Styrene Miniemulsion Polymerization

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ABSTRACT: TEMPO-mediated styrene miniemulsion polymerizations were conducted at varying particle sizes (∼50, 90, and 180 nm) to study possible effects of compartmentalization. Polymerizations were initiated using a TEMPO-terminated polystyrene macroinitiator that also acted as costabilizer for the miniemulsion. A bulk polymerization was conducted as a control. Conversion, molecular weight distribution, and the chain livingness were measured to assess the effects of particle size. Decreasing particle size resulted in lower rates of polymerization; after 6 h of polymerization, conversions were 59% for ∼180 nm particles and 43% for ∼50 nm particles. More importantly, large differences in the polymer chain livingness were observed, with smaller particles exhibiting superior livingness at equivalent conversions. Minor effects were also observed on molecular weight; decreasing particle size resulted in higher M_n at a specified conversion, signifying lower chain concentrations in smaller particles.

Introduction

Advances in living/controlled radical polymerization (L/CRP) have created a myriad of opportunities for new materials development, offering the promise of facile control of polymer microstructure and morphology. A significant fraction of all commercial polymers made by free radical processes are made using aqueous dispersions such as emulsion polymerizations. There has consequently been extensive interest in adapting L/CRP techniques to aqueous dispersions.[1−3] While the fundamental kinetics of conventional emulsion (macroemulsion) and miniemulsion polymerization have been elucidated, basic questions remain about the nature of emulsion-based L/CRP. Perhaps the most significant question for L/CRP systems based on reversible termination mechanisms (atom transfer radical polymerization (ATRP) and nitroxide-mediated polymerization (NMP)) is whether compartmentalization is relevant.

Compartmentalization is responsible for high reaction rates and high molecular weights in conventional emulsion polymerization. Segregating propagating radicals in small reaction volumes leads to reduced occurrence of mutual termination. While it is accepted that compartmentalization does occur in reversible transfer L/CRP systems (e.g., RAFT (reversible addition fragmentation transfer), MADIX (macromolecular design via interchange of xanthate)),[4−7] it has been generally believed, on the basis of theoretical considerations[8] and limited experimental studies,[9−12] that in reversible termination systems (ATRP, NMP) compartmentalization effects do not exist. (Particle size effects were recently observed in TEMPO-mediated SDBS-stabilized miniemulsions, and it was suggested that TEMPO preferentially locating at/near the particle interface may play a role.[13]) A few theoretical mathematical modeling studies have suggested they may occur at sufficiently small particle size,[14−16] but as yet there has been no experimental data published that provides evidence of the existence of compartmentalization in nitroxide-mediated emulsion-based polymerizations.

Charleux[14] presented a theoretical framework by adapting the Smith−Ewart approach for propagating radical segregation in considering the SG1-mediated (*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide) polymerization of styrene in a dispersed medium and concluded compartmentalization effects would occur. Butte et al. accounted for segregation of the nitroxide (TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl) in addition to the propagating radicals (Charleux considered segregation of only propagating radicals). Zetterlund and Okubo[16] have recently extended Butte's model and provided extensive discussion on the nature of compartmentalization in NMP.

Charleux, Butte, and Okubo all predicted that compartmentalization effects should be evident for NMP, although the nature of their predictions sometimes conflicted. All agreed smaller particles should have higher livingness than larger particles, but while Charleux predicted smaller particle sizes would yield faster polymerizations, Butte and Okubo predicted the opposite. Despite the importance of such a fundamental question, the issue of whether compartmentalization effects exist in emulsion-based NMP remains unresolved. What is currently lacking is a careful experimental study suitable for comparison with conflicting theoretical predictions and that is able to shed light on the questions posed by previous studies.

To probe the issue of potential compartmentalization in NMP emulsion-based systems, we have conducted TEMPO-mediated styrene miniemulsion polymerizations in which the particle diameter was varied from approximately 50 to 180 nm (weight-average diameter). We avoided using hexadecane as a costabilizer to avoid its possible effects on the polymerization and to better mimic a true emulsion polymerization environment. Conversion, molecular weight distribution, and polymer livingness were quantified. In addition, a bulk polymerization was run as control experiment representing a nonheterogeneous

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Table 1. Summary of Experiments[a]

expt ID	[DOWFAX 8390] mM	conv (%)	M_n (g/mol)	PDI	D_w (nm)	D_w/D_n
E1 (bulk)	N/A	86.5	20 700	1.14	N/A	N/A
E2 (180 nm)	4.6	58.6	17 800	1.16	184.7	1.13
E3 (90 nm)	23.0	49.9	16 500	1.17	92.3	1.11
E4 (50 nm)	46.0	43.3	18 100	1.15	54.5	1.17

[a] Conversion (conv), number-average molecular weight (M_n), polydispersity (PDI), and weight- and number-average diameters (D_w, D_n) are based on final values. Temperature = 135 °C for all experiments.

environment in which compartmentalization and radical exit/entry effects are not factors. We present clear evidence that particle size effects in TEMPO-mediated polymerizations do exist, influencing both the rate of polymerization and the polymer chain livingness and to a lesser extent the polymer chain concentration.

Experimental Section

Materials. Styrene (Aldrich, 99%) was washed three times with an equal volume of 2 wt % NaOH (Aldrich, 99+%) solution to remove inhibitor. This step was repeated using distilled water, followed by drying over $CaCl_2$ (Aldrich, 96+%) and vacuum distillation. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl, Aldrich, 98%), Vazo 88 (1,1-azobis(cyclohexanecarbonitrile), DuPont), and DOWFAX 8390 (Dow Chemical, 35% actives in water) were used as received. N-TEMPO [4-(1-naphthoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl] was prepared following Jones et al.[17] N-TEMPO-PhEt [naphthoyloxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine] was synthesized using the procedure reported by Scott et al.[18]

Polymerizations. *(a) Preparation of TEMPO-Terminated Oligomers of Polystyrene (TTOPS).* Vazo 88 (2.44 g, 0.0100 mol) and TEMPO (2.96 g, 0.0189 mol) were dissolved in 600 mL (5.19 mol) of distilled styrene. The mixture was polymerized under nitrogen (Praxair, Ultra High Purity) in a 1 L round-bottom flask at 135 °C for 2 h, yielding TTOPS with conversion of 15.7%; number-average molecular weight $M_n = 3930$ g/mol; polydispersity PDI = 1.15 ([TTOPS] = 0.0191 M).

(b) Miniemulsion Polymerizations. TTOPS (prepared as described above) was used as both macroinitiator and costabilizer. One batch of TTOPS was used for all experiments to minimize variability. No hexadecane was used in these polymerizations. The aqueous phase was prepared by dissolving Dowfax 8390 (5−46 mM) in deionized water (DIW) (150 g). The organic phase (40 g), which consists of the TTOPS−styrene mixture, was mixed into the aqueous phase. The mixture was homogenized using a Microfluidizer 110S (Microfluidics International Corp.) (three cycles at 300 kPa inlet pressure). The miniemulsion was charged into a 300 mL Parr stainless steel reactor, purged with nitrogen, and then polymerized at 135 °C for 6 h under nitrogen pressure of 300 kPa. Samples were collected over the course of reaction. Initial droplet size was controlled by varying the surfactant concentration, as reported by El-Aasser et al.[10,19] The conditions for each formulation are summarized in Table 1.

(c) Bulk Polymerization. A TTOPS−styrene mixture (60 mL) prepared in part (a) was purged with nitrogen and then heated at 135 °C for 6 h in a round-bottom flask.

Characterization. All samples were analyzed for monomer conversion (gravimetry), molecular weight distribution, and particle size. The “livingness” of selected samples was analyzed using method of Scott et al.,[18] employing joint RI and fluorescence GPC detectors as described below.

Particle Size Measurements. The particle sizes of the latexes reported in this paper were measured using a Matec Applied Sciences capillary hydrodynamic fractionation (CHDF) 2000 unit. The UV detector was set to 220 nm. The eluant was a 20:1 mixture of deionized water and GR500-1X (Matec Applied Sciences). Samples were diluted with the eluant to ~3.5 wt % solids and sonicated for 5 min. Samples were passed through a 0.5 μm pore size filter prior to injection. The marker was a 2 wt % solution of sodium benzoate.

Gel Permeation Chromatography (GPC). Molecular weight distributions were measured using a Waters 2960 separation module with a Waters 410 differential refractometer (DRI) (480 nm). Four Waters Styragel columns (100, 500, 10^3, and 10^4 Å) were maintained at 40 °C. The flow rate of the eluent (distilled tetrahydrofuran, THF) was 1.0 mL/min. Polystyrene (PS) standards were used for calibration. Data were collected and processed using Waters Empower software (version 5.00).

Livingness Measurements. The degree of livingness (DOL) is defined as the mole fraction of chains terminated with TEMPO. Polymer samples were precipitated from solution using methanol and filtered to isolate the precipitate. The polymer was dissolved in chlorobenzene (0.012 M) (Aldrich, 99+%), mixed with N-TEMPO (50 equiv), degassed with three freeze−thaw cycles, and heated at 123 °C for 154 min under nitrogen. The reaction mixture was added dropwise into methanol to precipitate the polymer, which was again dissolved in THF. Following reprecipitation from methanol (Aldrich, 99.9%), the polymer was dried. To measure the alkoxyamine concentration, a Waters 474 scanning fluorescence detector (690 nm) was added to the GPC in series after the DRI. The alkoxyamine 4-naphthoyloxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (N-TEMPO-PhEt), used as an internal standard, was dissolved in THF to give a concentration of 1.2×10^{-4} M. 10 mL of this solution was added to about 5 mg of each polymer sample, which was analyzed with GPC. Chromatograms of polystyrene standards and N-TEMPO-PhEt at different concentrations were collected from both detectors. From the fluorescence detector, the PS chromatograms allowed the area under a sample chromatogram to be corrected for the fluorescence of the PS backbone. The N-TEMPO-PhEt chromatograms allow calculation of the amount of alkoxyamine (NTEMPO-terminated chains) in the polymer sample from the corrected area. Chromatograms from both detectors were aligned and processed with the same calibration curve using the N-TEMPO-PhEt peak. The quantity of NTEMPO-terminated chains in a sample was then calculated. DOL is determined using the living chain distribution obtained from the fluorescence detector and the total chain distribution obtained from the DRI detector.

Results

Polymerizations were run at varying surfactant concentrations to yield final mean particle diameters (weight-average) of approximately 50, 90, and 180 nm. A bulk polymerization was also run as a control experiment. A macroinitiator was used as it allows us to eliminate two concerns that may influence the kinetics. First, there will be negligible desorption of the macroinitiator from the particles into the aqueous phase. Low molecular weight alkoxyamines can desorb, thereby decreasing the chain concentration in the particles. Second, the use of a macroinitiator allows us to eliminate hexadecane from our formulation since the macroinitiator functions as both initiator and costabilizer. Experimental conditions used for each experiment are shown in Table 1. The measured degree of livingness of the TTOPS macroinitiator was 98%. DOWFAX 8390 was selected as surfactant as prior experience in our laboratory has shown that its effect on rate in TEMPO-mediated miniemulsion polymerizations is minimal, unlike SDBS (sodium dodecyl

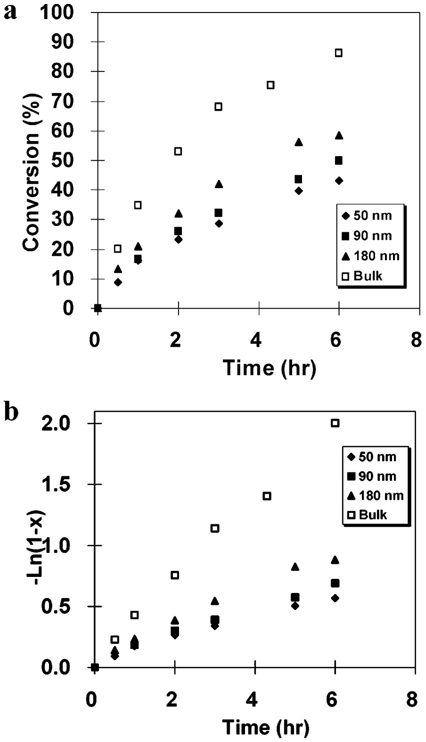

Figure 1. Conversion (x) (a) and $-\ln(1 - x)$ (b) vs time for TEMPO-mediated styrene miniemulsion and bulk polymerizations. Temperature = 135 °C. Particle size was varied by changing [DOWFAX 8390] (Table 1).

benzenesulfonate) which is capable of significantly enhancing the rate.[20,21] The particle size distributions were all monomodal, and all had similar breadths as measured by D_w/D_n values. Ideally, a monodisperse particle size distribution could be used for kinetic studies, but monodispersity cannot be achieved in these systems.

Effect of Particle Size on Kinetics. Figure 1 shows conversion vs time profiles for the three different particle diameter experiments and the bulk polymerization. There is a pronounced trend of decreasing conversion with decreasing particle diameter, with the bulk polymerization exhibiting the highest conversions throughout the experiment. The 6 h conversions for the 50 and 180 nm particles were 43% and 59%, respectively, representing a 37% difference. At 3 h, the relative difference in conversion for these two particle sizes was 45% (29% vs 42% conversion). Experimental error (estimated at <5% of the conversion value) is significantly less than the observed differences between experiments at different particle sizes. Figure 2 shows the evolution of the particle size for the three miniemulsion experiments during the polymerization. All experience some increase in diameter. The particle size increase is similar to that seen by El-Aasser.[10]

Effect of Particle Size on Evolution of Molecular Weight and Polydispersity. Evolution of M_n with conversion is shown in Figure 3 for the three miniemulsions and the bulk polymerization. Polydispersities are shown in Figure 4. There are not large differences between the different conditions, although there is a consistent trend of smaller particle size polymerizations displaying higher M_n than the larger particle size experiments. This result implies the chain concentration was slightly lower for the smaller particles. Polydispersities exhibit a similar trend for all conditions, decreasing slightly at the outset of polymerization and then gradually increasing as the polymerization progressed to a final value of ~1.15.

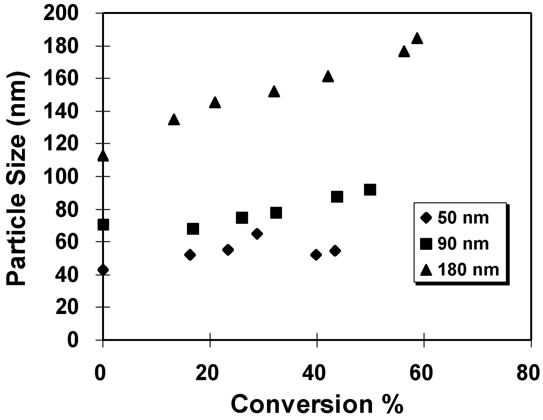

Figure 2. Weight-average particle diameter (D_w) vs conversion for TEMPO-mediated styrene miniemulsion polymerizations. Temperature = 135 °C. Particle size was varied by changing [DOWFAX 8390] (Table 1).

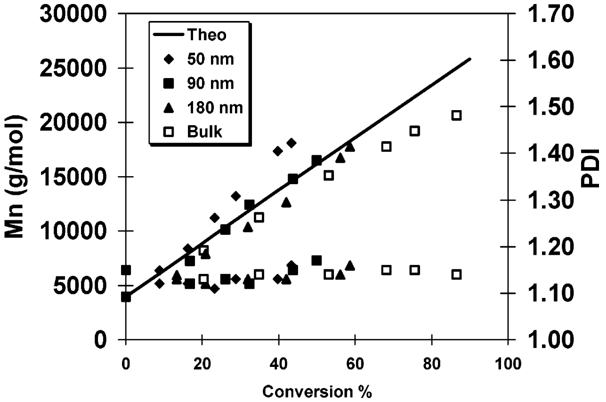

Figure 3. Number-average molecular weight (M_n) (a) and polydispersity (PDI) (b) vs conversion for TEMPO-mediated styrene miniemulsion and bulk polymerizations. Temperature = 135 °C. Particle size was varied by changing [DOWFAX 8390] (Table 1).

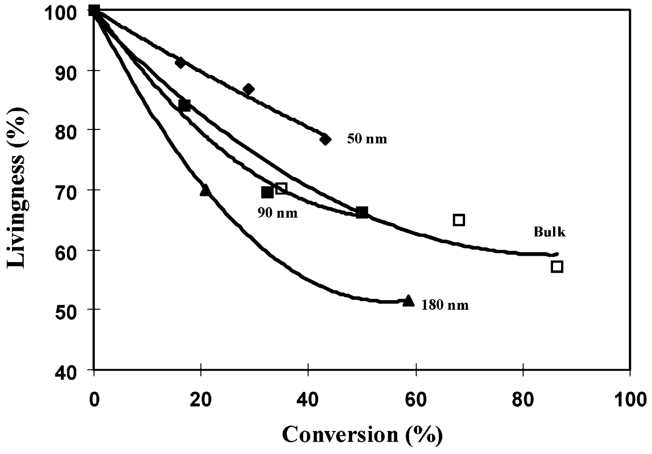

Figure 4. Degree of livingness (DOL) for TEMPO-mediated styrene miniemulsion and bulk polymerizations. Temperature = 135 °C. Particle size was varied by changing [DOWFAX 8390] (Table 1).

Effect of Particle Size on Livingness. The DOL is shown in Figure 4 for all polymerizations. Livingness decreased in the order 50 nm > 90 nm ~ bulk > 180 nm. The smallest particles (50 nm) displayed noticeably higher livingness at equivalent conversions compared to the other runs. As particle diameter increased, the livingness decreased. Curiously, the bulk polymerization exhibited a livingness profile intermediate to the three miniemulsion results, most closely resembling the 90 nm miniemulsion experiment. GPC traces for the 50 nm experiment

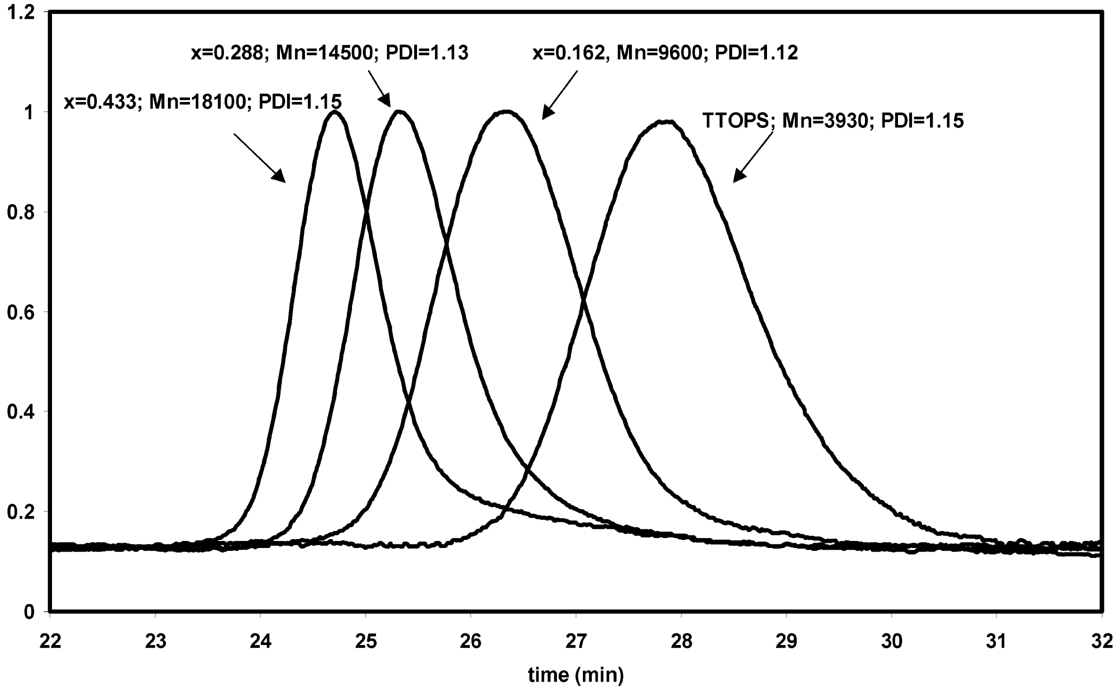

Figure 5. GPC chromatograms for TEMPO-mediated styrene miniemulsion polymerization experiment E4 (50 nm particles).

(E4) (Figure 5) reveal a clean evolution of the molecular weight distribution, with only slight evidence of tailing at lower molecular weights.

Discussion

The data presented above provide, for the first time, experimental evidence that compartmentalization effects do exist in TEMPO-mediated emulsion-based systems. As particle size is decreased, rate decreases and the livingness of the polymer chains increases. In addition, there is an increase in molecular weight (lower chain concentration) in smaller particles at a given conversion. The bulk polymerization behaves distinctly from the miniemulsion runs, with pronounced differences in rate and livingness even, thus dispelling the view that NMP miniemulsions exhibit kinetics that are similar to bulk.

Mathematical modeling studies have predicted the existence of compartmentalization effects but there has not yet been data published to establish their existence. Predictions from the modeling studies of Butte et al.[15] and Zetterlund and Okubo[16] are in qualitative agreement with the experimental data presented in this paper with regards to the effects of particle size on polymerization rate and polymer livingness. The livingness trends are consistent with Charleux's predictions while the particle size predictions are not.[14] Zetterlund and Okubo calculated livingness up to 10% conversion. Their livingness values, however, seem very high (>99.85% on a number basis for all particle sizes). While there is agreement with our data in the livingness trend with respect to particle size, there are pronounced differences in the absolute values.

Butte concluded that the reduced rate predicted in smaller particles would be caused by geminate recombination of thermally generated radicals, leading to reduced thermal initiation rates and thus a lower overall polymerization rate. Zetterlund and Okubo expanded this discussion, emphasizing the role of enhanced deactivation of radicals within a small volume that would result in decreasing rates as particle size decreases. The enhanced deactivation is also predicted to result in reduced rates of termination and therefore increased livingness in smaller particles. If geminate recombination of thermal radicals is important and dependent on particle size, there should be an impact on the number of chains. The M_n data (Figure 3) are consistent with the postulated fate of thermal radicals, as the number of chains decreases with particle size.

Reduction of rate by geminate termination of thermally generated radicals was also postulated by Pan et al.,[12] who provided experimental data showing reduced rates in TEMPO-mediated styrene miniemulsions compared to a bulk polymerization. In TEMPO-mediated styrene miniemulsion polymerization conducted without initiator (i.e., thermal polymerization), the chain number in bulk polymerizations was consistently greater than in miniemulsion. This was attributed to higher thermal initiation efficiencies in bulk compared to miniemulsion. Furthermore, they noted the initial polymerization rate was higher in bulk than in miniemulsion, consistent with our observations.

From Figure 1, it is possible to calculate the average radical and TEMPO concentrations inside the particles during polymerization as well as the average number of propagating radicals per particle and the average number of TEMPO molecules per particle. (As these are approximate calculations only, we assumed the dormant chain concentration was the same as the initial TTOPS concentration. Other required parameters were taken from Ma.[22]) As shown in Table 2, the average propagating radical concentration decreases in the order bulk > 180 nm > 90 nm > 50 nm. For the miniemulsion polymerizations, the average number of radicals per particle decreases with decreasing particle size, from ~0.045 at 180 nm to ~0.000 67 at 50 nm. Of considerable interest is the average number of TEMPO

Table 2. Results of Kinetic Analyses of Figure 1[a]

expt ID	$[\mathrm{R}^\bullet]$ (M)	$[\mathrm{TEMPO}^\bullet]$ (M)	n	n_T
E1 (bulk)	4.63×10^{-8}	2.09×10^{-5}	N/A	N/A
E2 (180 nm)	2.28×10^{-8}	4.24×10^{-5}	4.53×10^{-2}	84.2
E3 (90 nm)	1.60×10^{-8}	6.01×10^{-5}	3.97×10^{-3}	14.9
E4 (50 nm)	1.32×10^{-8}	7.32×10^{-5}	6.74×10^{-4}	3.74

[a] $[\mathrm{R}^\bullet]$ = average radical concentration in particles; $[\mathrm{TEMPO}^\bullet]$ = average TEMPO concentration in particles; n = average number of propagating radicals per particle; n_T = average number of TEMPO molecules per particle.

molecules per particle, which also decreases with decreasing particle size, from ∼84 at 180 nm to ∼3.7 at 50 nm.

It is anticipated that compartmentalization effects should become evident in NMP (or ATRP) when the number of deactivating molecules (nitroxide) approaches a value sufficiently low to impact the deactivation kinetics. The low average number of TEMPO molecules per particle for the 90 and 50 nm experiments is consistent with this expectation. These values are within ∼1 order of magnitude of those predicted by both Zetterlund and Butte, with propagating radical concentrations $\sim 10^{-8}$ M and TEMPO concentrations $\sim 10^{-5}$ M. The experimental conditions simulated by Charleux are quite different with regards to both temperature and nitroxide type, and therefore direct comparisons are difficult.

While the predictions of the Butte and Zetterlund models generally agree qualitatively with our data, there is one notable inconsistency. The inconsistency lies in the relative livingness of the bulk and miniemulsion data. Butte and Zetterlund predicted bulk polymerization should have lower livingness than any particle size; however, we observe the bulk livingness is comparable to that of the 90 nm particle experiment, and bulk livingness is higher than for large (180 nm) particles. The reason(s) for this discrepancy are unknown, but one possibility is that the much higher polymerization rate in bulk would lessen the impact of disproportionation, which has been shown to significantly lower livingness.[22,23] (Disproportionation was not accounted for in the models.)

The observed bulk polymerization rate was also significantly faster than the miniemulsion system, even for particle sizes of 180 nm. (In conventional emulsion polymerization, compartmentalization leads to an increase in rate.[24]) The Butte and Zetterlund models predict there is an upper limit (∼100 nm) to the particle size for which compartmentalization effects will be apparent and that large particles should have a similar rate to bulk polymerization. Our data are qualitatively consistent with the model predictions in that the bulk polymerization is fastest; however, the limiting particle size may be significantly larger than 100 nm.

The higher rate observed in bulk polymerization compared to miniemulsion indicates lower overall [TEMPO] during polymerization. In addition to the previously mentioned predictions of geminate recombination of thermal radicals and enhanced deactivation, the exit of small radicals generated by thermal polymerization (or to a lesser extent by chain transfer to monomer), which is not accounted for in the models, could also play a role. Exit of monomeric radicals would decrease the rate in an emulsion-based system relative to the bulk polymerization. In conventional styrene emulsion polymerization, radical exit as a result of transfer to monomer can play a role in reducing rate for significant decreases in particle size. There are important differences in a TEMPO-mediated system however. First is that the rate of transfer events is much lower due to the much lower average number of radicals per particle, which is ∼0.4−0.5 for conventional styrene emulsion polymerization but only ∼0.001−0.01 for a TEMPO-mediated system. Second, the presence of a large excess of TEMPO ensures deactivation of a monomeric radical is rapid, so that its probability of desorbing is reduced. While the fate of exited radicals in a conventional emulsion polymerization may often be to reenter particles (depending on the experimental conditions),[24] the fate of exited radicals could be much different in NMP.

The presence of finite amounts of TEMPO in the aqueous phase will likely result in rapid deactivation of the exited radical. Using Ma's[25] measured TEMPO partition coefficients for the styrene−water system, it is calculated that ∼2−3% of the free TEMPO in the system will reside in the aqueous phase. Based on an estimate of [TEMPO] $\sim 10^{-5}$ M in the particle phase once a pseudo-stationary state is established, and a 4:1 ratio of aqueous phase:organic phase, [TEMPO] in the aqueous phase will be $\sim 10^{-7}$ M. Moreover, because of rapid diffusion between the aqueous and organic phases,[26] this value will remain approximately constant during polymerization. Once an exited radical is deactivated, its probability of adding monomer units and reentering another particle will be reduced compared to conventional (mini)emulsion polymerization because of the lower polymerization rate in the aqueous phase. (Low aqueous phase styrene concentration, coupled with an equilibrium favoring dormant chains, results in low aqueous phase polymerization rates.[22]) However, the chains are also less likely to terminate in the aqueous phase. The overall outcome is a reduction in the average propagating radical concentration within the particles and consequently a lower rate. To obtain a sense of how potentially important this effect may be, consider the characteristic times for dormant chain activation (λ_a), deactivation of active radicals (λ_d), and propagation (λ_p) in the aqueous phase (values for the rate parameters are from ref 22; values for TEMPO partition coefficient and aqueous styrene concentration are from ref 25):

$$\lambda_a = 1/k_a \approx 1/3.99 \times 10^{-3}\ \mathrm{s}^{-1} \approx 251\ \mathrm{s}$$

$$\lambda_d = 1/(k_d[\mathrm{TEMPO}]_{aq}) \approx 1/(8 \times 10^7\ \mathrm{M}^{-1}\,\mathrm{s}^{-1} \times 10^{-7}\ \mathrm{M}) \approx 1.25 \times 10^{-1}\ \mathrm{s}$$

$$\lambda_p = 1/(k_p[\mathrm{styrene}]_{aq}) \approx 1/(2936\ \mathrm{M}^{-1}\,\mathrm{s}^{-1} \times 0.0167\ \mathrm{M}) \approx 2.04 \times 10^{-2}\ \mathrm{s}$$

A chain is activated approximately every 4 min. The ratio of characteristic times for deactivation to propagation is 6.1. In contrast, for the particle phase, assuming a mean styrene concentration of 5 M

$$\lambda_d = 1/(k_d[\mathrm{TEMPO}]_{org}) \approx 1/(8 \times 10^7\ \mathrm{M}^{-1}\,\mathrm{s}^{-1} \times 10^{-5}\ \mathrm{M}) \approx 1.25 \times 10^{-3}\ \mathrm{s}$$

$$\lambda_p = 1/(k_p[\mathrm{styrene}]_{org}) \approx 1/(2936\ \mathrm{M}^{-1}\,\mathrm{s}^{-1} \times 5\ \mathrm{M}) \approx 6.81 \times 10^{-5}\ \mathrm{s}$$

The ratio of characteristic times for deactivation to propagation in the particle phase is 18.4. Therefore, the ratio λ_d/λ_p is ∼3 times lower in the aqueous phase, meaning that dormant chains in the aqueous phase will grow more slowly than in the particles. The critical chain length for reentry of an aqueous polystyrene oligomer to a particle is only ∼2−3 units,[24] which would mitigate the magnitude of the effect. In conclusion, the net effects on the polymerization rate of TEMPO in the aqueous phase deactivating desorbed radicals are unclear. However, the reduced rate of transfer to monomer in NMP will reduce the potential impact of radical desorption on the overall polymerization rate.

The lower polymerization rate in miniemulsion compared to bulk (or presumably very large droplets) is a critical issue for any emulsion-based NMP process (macroemulsion, miniemulsion, microemulsion) in which there may be droplet polymerization because it implies there may be little or no thermodynamic driving force for monomer transfer from droplets to particles, since the polymer concentration may be higher in large droplets/particles. Therefore, monomer droplets will not be consumed in the polymerization as they do in conventional emulsion polymerizations (even when some droplet polymerization does occur). This may explain why repeated attempts to develop an NMP emulsion process have failed, with the exception of Charleux,[27] who wisely used a semibatch starved feed approach to eliminate droplets from the system.

The bulk system also showed unexpectedly higher livingness than the large particle size miniemulsions, despite the higher rate of polymerization in bulk which would be expected to yield higher rates of termination. Previously, however, we have shown in both modeling[22,28] and experimental[23,29,30] studies that alkoxyamine disproportionation may account for a significant loss of livingness at 135 °C in TEMPO-mediated styrene miniemulsions. The practical implication of this is that longer reaction times results in greater loss of livingness due to increased disproportionation and inversely that shorter reaction times tend to yield higher livingness provided the rates are not so high that termination becomes significant.

Our data may appear to be contradictory to the data published by El-Aasser,[10] who observed no significant difference in rates for final volume average particle sizes ranging from ~60 to ~150 nm. They employed a similar approach, using DOWFAX 8390 and TTOPS; however, they also used hexadecane (HD) as a costabilizer, and their experiments were run at 125 °C while ours were run at 135 °C. While HD is widely used in miniemulsion polymerizations, it is not present in emulsion polymerizations. HD is not required in miniemulsions if a low molecular weight, highly water-insoluble component is present, such as TTOPS. We have run limited experiments using HD and also found that particle size effects were not as significant in the presence of HD. We observed that HD had little effect on large particle experiments or on bulk polymerization, but it did yield a faster polymerization for smaller particles (compared to a formulation without HD). The reason(s) for the differences in behavior with HD is not currently known but is being investigated. It is possible that the exit rate of small radicals is reduced in the presence of HD.

Conclusion

Particle size in TEMPO-mediated miniemulsion polymerization influences important features of the polymerization, including rate, polymer livingness, and to a lesser degree the chain concentration (molecular weight). Smaller particles showed slower rates of polymerization than larger particles. Furthermore, the rate and livingness of bulk polymerizations have been shown to differ from miniemulsion polymerizations, with the bulk polymerization being faster than the miniemulsions. Quantitative analysis of the livingness revealed that higher livingness was preserved in the smaller particles. Bulk polymerization, despite having a relatively fast polymerization rate, had livingness almost identical to the 90 nm particles and higher than the 180 nm particles.

The model predictions and explanations of Butte et al. and Zetterlund and Okubo on compartmentalization effects and influence of particle size are consistent with our experimental data. Geminate recombination of thermally generated radicals in confined volumes will reduce rate by effectively reducing the thermal initiation rate as well as leading to lower chain concentrations (higher M_n) in smaller particles. Enhanced deactivation of propagating radicals by TEMPO in the confined volume of a small particle will result in reduced termination (increased livingness) and lower rate.

These results represent the first experimental evidence of compartmentalization effects in emulsion-based NMP and are relevant for future development of macro-, mini-, and microemulsion processes. The influence of particle size on the polymerization rate suggests it may not be possible to achieve nitroxide-mediated emulsion polymerization with any droplets present, since it implies loss of thermodynamic driving force for monomer transfer from droplets to particles. Because of mechanistic similarities between NMP and ATRP (both are based on reversible termination of propagating radicals), the effects reported here may also be relevant to ATRP in emulsion-based systems. We are currently investigating this phenomenon.

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