Living Radical Polymerization by Reversible Addition−Fragmentation Chain Transfer in Ionically Stabilized Miniemulsions

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ABSTRACT: In theory, a miniemulsion should be an ideal environment for "living" radical polymerization via the reversible addition−fragmentation chain transfer process (RAFT). Compartmentalization minimizes radical−radical termination events, and droplet nucleation eliminates the mass transfer limitation found in conventional "living" emulsion polymerizations. In practice, however, several phenomena were observed when using the RAFT technique, indicating a deviation from this idealized theory when the miniemulsion was stabilized by an ionic surfactant. Inefficient droplet nucleation, a steadily rising polydispersity over the reaction, and the appearance of a separate organic phase after initiation were all indications of particle instability. A distinct difference between standard polymerizations and those that involve highly active RAFT agents is the fact that in RAFT polymerization there is a time interval early in the reaction where oligomers dominate the molecular weight distribution. The presence of large quantities of oligomers is postulated to be the culprit behind the destabilization observed through a detrimental interaction with the ionic surfactant of the miniemulsion. Conductivity measurements verified the increase of free surfactant in the aqueous phase over the course of reaction. Despite this, results showed clear indication of "living" character with a linear evolution of molecular weight until roughly 40% monomer conversion, after which the molecular weight showed contributions from initiator-derived chains.

Introduction

Miniemulsion polymerizations are rapidly becoming a useful tool in the synthesis of complex polymer architectures (e.g., "living" radical polymerizations[1−5]). The advantages over conventional emulsion polymerizations (denoted here as macroemulsions) are that the number of polymer colloid particles is predetermined by the amount of monomer droplets initially present,[6] exit of the "living" agents is negligible due to the size of droplets, and all reaction species are contained within the droplets (typically 50−300 nm in diameter).[7] This, along with the fact that the droplets themselves are being nucleated,[6] should eliminate mass transport through the aqueous phase.

Recent literature[3,5,8,9] illustrates the use of reversible addition−fragmentation chain transfer (RAFT; see Scheme 1) in free radical macro- and miniemulsion polymerizations. Recent work in this laboratory has found that RAFT macroemulsions stabilized by sodium dodecyl sulfate (SDS) resulted in destabilization with a conspicuous red layer at the beginning of polymerization, leading to nonliving behavior.[10,11] This was postulated to be due to a combination of transport limitation and/or destabilization of the colloid particles through unknown interactions of SDS with the RAFT agent. Minemulsions stabilized with SDS or for that matter any ionic surfactant also led to destabilization,[5] even though transportation is no longer a dominant factor. Only when nonionic surfactants were used could destabilization be alleviated, and successful "living" polymers were produced with polydispersities below 1.1. Destabilization of RAFT miniemulsion systems in the presence ionic surfactants is unexpected, and the highlight of this investigation attempts to understand the mechanism by which destabilization takes place for an SDS system.

Experimental Section

Reagents. Demineralized Super Q water, with conductivity below 5 μS/cm, was used for the continuous phase of the miniemulsion. All monomers were obtained from Aldrich Chemicals with inhibitor removed by distillation and passing through an inhibitor removal column (Aldrich; specific to the inhibitor type). Potassium persulfate (KPS), 2,2′-azobis(isobutyronitrile) (AIBN), hexadecane (HD), potassium nitrodisulfonate (Fremy's salt), and sodium hydrogen carbonate (buffer) were obtained from Aldrich and were used as received. Sodium metabisulfite (redox) and sodium dodecyl sulfate (SDS) were obtained from Fluka, and hydroquinone, used to quench gravimetric samples, was obtained from Merck; all were used as received. 2-Phenylprop-2-yl dithiobenzoate ("Cumyl-RAFT", Scheme 1, compound **I**)[4] and 2-cyanoprop-2-yl dithiobenzoate (compound **II**)[12] were synthesized in-house according to literature procedures.

Kinetic Analysis. Conversion of monomer to polymer was followed through dry solids (gravimetric analysis). Samples were taken regularly through the polymerization, quenched with a few crystals of hydroquinone, and dried in a vacuum oven.

GPC Analysis. GPC analyses were performed on a Waters system with both UV and RI detection through two PLgel Mixed-C columns. Reported molecular weights are from the number-average peak and are apparent values expressed in polystyrene equivalents. Although Mark−Houwink parameters were available for the polymers studied, a correction procedure was not applied as this technique is valid only for molar masses exceeding approximately 2.0 × 10^4 Da.

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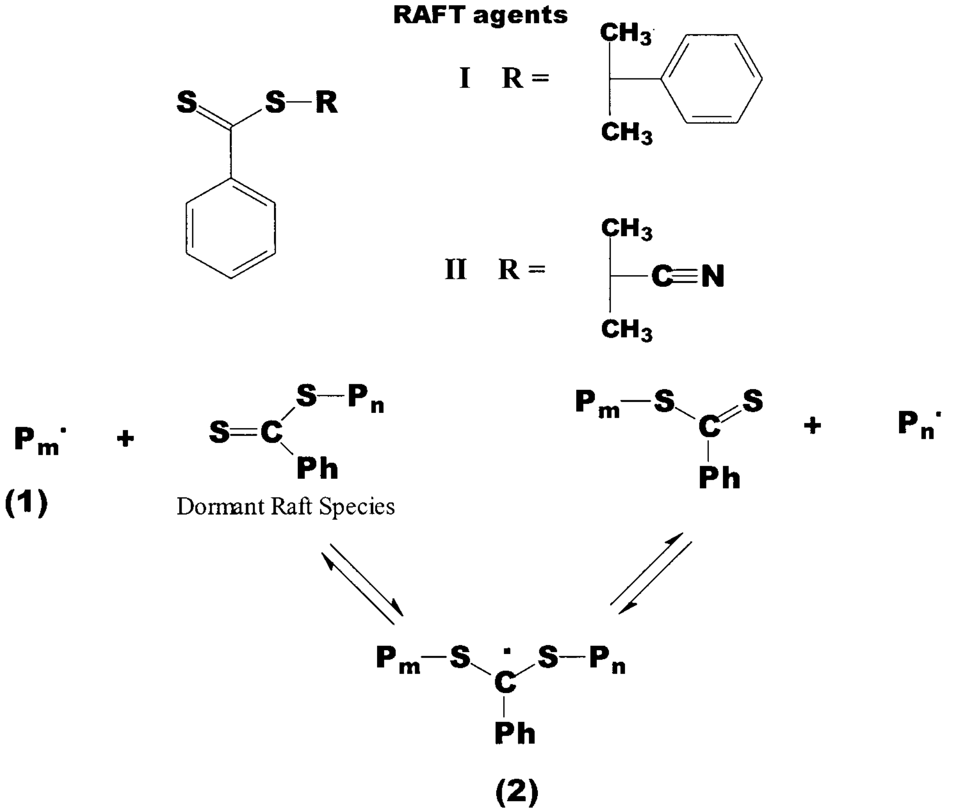
Scheme 1. Raft Agents Used in This Study; Mechanism of the RAFT Process of the Dormant RAFT Species



Conductivity Analysis. Conductivity of the continuous phase was measured by sampling as on-line probe tips were suspect to accumulate polymer that would give anomalous readings. Samples were taken from the reactor and immediately measured using a radiometer Copenhagen CDM 80 conductivity meter (20 μS/cm to 2000 mS/cm).

Preparation of Miniemulsion. Monomer (purified from inhibitor) was first mixed with hydrophobe and RAFT agent (and oil-soluble initiator, if used) comprising the preliminary organic phase. This phase was thoroughly mixed by magnetic stirring until homogeneous. Under constant agitation, this mixture was added dropwise to the continuous phase, a solution of surfactant in water. A small portion of the pure water was held aside to dissolve aqueous phase initiator, when appropriate. The emulsion was then left under rapid agitation for a period of 60 min to homogenize. To achieve characteristic miniemulsion monomer droplet size, this "presheared" emulsion was subjected to sonication using a probe (Dr. Hielscher UP400S, 400W) inserted into the flask contents. The emulsion was sonicated (amplitude 30%, cycle 1.0) for a period of 10–12 min in a cooled water bath to keep the temperature generated to a minimum. (Ten to twelve minutes was found to be the optimum duration of sonication for these recipes, leading to almost immediate polymerization after injection of initiator. When contents were sonicated for roughly 30 min, retardation in the early stages of polymerization was observed.) The miniemulsion was then transferred to a three-necked 250 mL round-bottom flask equipped with reflux cooler and under argon so as to create an oxygen-free reaction environment. Reactor contents were further purged and allowed to come to reaction temperature (75 °C), at which point the initiator solution was injected to start the polymerization. Samples were taken at regular time intervals through the reaction for analysis.

Results and Discussion

To establish a basis for comparison of the RAFT experimental data accumulated, a conventional styrene miniemulsion was performed. The recipe consisted of a typical miniemulsion concentration of SDS surfactant (0.01 mol/L in H_2O) and a somewhat low concentration of KPS initiator (0.005 mol/L in H_2O). This initiator concentration was chosen such that transfer to RAFT agents or dormant RAFT polymer chains would dominate over bimolecular (radical–radical) termination.[3] Table 1 provides the ingredients, and Table 2 provides concentrations of the various components for each experiment. A sample taken from the miniemulsion prior to initiation was monitored on shelf for several weeks with no visible monomer cream, indicating a stable miniemulsion recipe. The miniemulsion recipe was then expanded to include the RAFT agent **I**, with all other concentrations held constant. In this manner, the effect of this RAFT agent on an otherwise stable system could be studied.

Table 1. General Recipe and Components

general recipe	concentrations
deionized water	(*continuous phase*)
styrene	25% of total solids
sodiium dodecyl sulfate (SDS)	0.01 mol/L H_2O
potassium persulfate (KPS)	(0.005–0.01) mol/L H_2O
hexadecane (HD)	2 wt % monomer
where appropriate	
RAFT agent (cumyl or cyano)	(0.03–0.123) mol/L monomer
sodium metabisulfite (redox)	1.26 equiv [KPS]
sodium hydrogen carbonate (buffer)	0.012 mol/L H_2O
2,2′-azobis(isobutyronitrile) (AIBN)	(0.03–0.123) mol/L monomer
potassium nitrodisulfonate (Fremy's salt)	0.025 mol/L H_2O
(2-ethyl)hexyl methacrylate (EHMA)	25% of total solids
butyl methacrylate (BMA)	25% of total solids

Kinetics. The conversion–time plots for the styrene polymerizations with and without **I** are given in Figure

Table 2. Recipe Details for Specific Experiments

expt	monomer (g)	RAFT agent (g)	water (g)	initiator (g)	surfactant (g)	hexadecane (g)	Fremy's salt (g)	redox couple (g)	buffer (g)
1	39.30		160.00	0.24	0.46	0.79			
2	20.40	0.19	83.00	0.11	0.24	0.41			
3	19.60	0.18	90.00	0.14	0.23	0.40		0.13	
4	19.60	0.19	90.00	0.25	0.23	0.40		0.22	
5	19.50	0.18	80.00	0.14	0.23	0.78	0.054	0.19	
6	20.00[c,e]	0.50	80.00	0.20	0.25	0.40			
7	20.00[d,e]	0.50	80.00	0.20	0.25	0.40			
8	14.83		60.00		0.17	0.30			
9	14.83[c]		60.00		0.17	0.30			
10	14.83	0.14	60.00		0.17	0.30			
11	14.83[c]	0.14	60.00		0.17	0.30			
12	22.26	0.21	90.00	0.26	0.27	0.53			
13	14.66	0.14	60.00	0.16	0.17	0.30			
14	14.66[c]	1.37	60.00	0.16	0.17	0.30			
15	21.91		90.00	0.24	0.26	0.44			0.09
16	14.12	0.13	60.00	0.16	0.17	0.30			0.06
17	17.11	0.16	70.00	0.562[f]	0.20	0.34			0.07
18	20.00		80.00		0.25	0.40			
19	19.80	0.20	80.00		0.25	0.40			
20	19.65	0.35	80.00		0.25	0.40			
21	19.35	0.20	80.00		0.25	0.40			

[a] Monomer used is styrene unless otherwise stated. [b] RAFT agent **I** was used unless otherwise stated. [c] EHMA. [d] BMA. [e] Raft agent used is **II**. [f] AIBN was used as initiator. [g] Moles of RAFT agent is constant for expts 19–21.

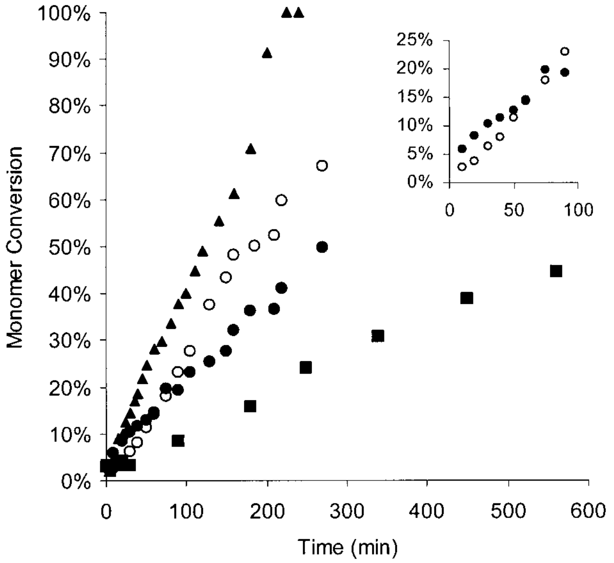


Figure 1. Conversion–time plots for miniemulsion polymerizations of styrene carried out at 75 °C in the presence of RAFT agent **I** (MEP). Styrene "blank" MEP (expt 1, ▲), styrene + RAFT MEP (expt 2, ■), styrene + RAFT + redox (expt 3, ●), styrene + RAFT + (2×)redox (expt 4, ○). Note: all shown experiments emulsified by SDS and initiated by KPS.

1. A large drop in the reaction rate is evident when comparing the basis experiment (expt 1, ▲) to the same recipe including **I** (expt 2; 0.03 mol/L monomer, ■). In principle, the nucleation of the particles should be the same with and without RAFT agent. The decrease in rate can be attributed to two factors: exit of the transferred radical R$^\bullet$ (see Scheme 1) to terminate with radicals in the aqueous phase or termination through reentry into a particle already containing a growing chain[13,14] or termination of the entering radical **1** or R$^\bullet$ with the intermediate radical **2**.[15] On the basis of the partition coefficient of the R group between the monomer and water phase, the large size of the droplets, and the rate coefficient for reinitiation of R$^\bullet$ to monomer, the probability of exit is very low.[14,16] To further support this, the RAFT agent should be consumed within the first few percent of conversion (since $C_{\mathrm{tr,RAFT}} \cong 6000$).[17] Once the RAFT is consumed (at low conversion), exit becomes unlikely due to the length of the oligomeric chain and should no longer be a significant contribution to reaction rate. This suggests that retardation when **I** is added to the miniemulsion is due to termination of the intermediate radical **2**, which has been shown to be the most likely mechanism at play in retarding the rate in bulk and solution experiments.[15]

The water-soluble initiator used in the above experiments was potassium persulfate (KPS). Given that the propagation rate constant (k_p) for styrene[18] at 75 °C is 563 L mol^{-1} s^{-1}, the low entry rate coefficient (ρ) of persulfate initiators in styrene macroemulsions,[19] and the low initiator concentration, a long polymerization time is not surprising. However, when this low rate is exacerbated by the retardation mechanisms described above, the KPS decomposition becomes an issue late in the reaction time frame. This is seen more clearly in Figure 2 where the experimental molecular weight of the styrene/RAFT miniemulsion system is compared to theoretical calculations. The solid points are the experimental values for the number-average molecular weight ($\bar{M}_n$) corresponding to the appropriate monomer conversion. The solid line represents the theoretical molecular weight as calculated using eq 1, which only accounts for RAFT-derived chain growth and neglects any radical–radical termination and also assumes that all the RAFT agent is consumed within the first few percent of polymerization. FW$_{\mathrm{mon}}$ is the formula weight of monomer, x is conversion, and Mol is the moles of reagent.

$$\bar{M}_{\mathrm{n,theory}} = \mathrm{FW}_{\mathrm{RAFT}} + \frac{\mathrm{Mol}_{\mathrm{mon}}\mathrm{FW}_{\mathrm{mon}}x}{\mathrm{Mol}_{\mathrm{RAFT}}} \qquad (1)$$

The dashed curve, calculated with eq 2, also represents the theoretical molecular weight but additionally accounts for initiator-derived chains that terminate and is equal to the initiator decomposed over the reaction time assuming termination by combination. f_I is the initiator efficiency for addition of initiator radicals to monomer, f_{entry} is the efficiency for entry before termi-

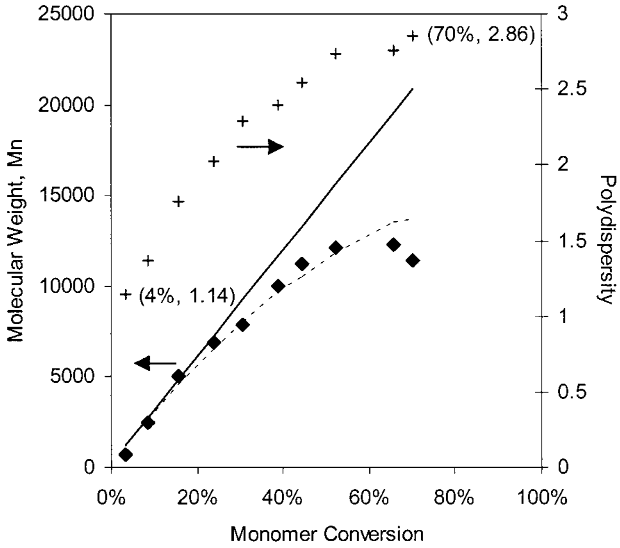


Figure 2. Number-average molecular weight for miniemulsion polymerizations of styrene carried out at 75 °C in the presence of SDS, RAFT agent **I** initiated by KPS (expt 2). Experimental $\bar{M}_n$ (◆), theoretical $\bar{M}_n$ accounting for RAFT derived chains only (—), theoretical M_n accounting for RAFT derived chains and initiator derived chains (- - -), polydispersity (+, right axis).

nation in the aqueous phase, k_d is the decomposition rate coefficient for initiator in the aqueous phase, C_w is the monomer concentration in the aqueous phase, $k_{t,aq}$ is the termination rate coefficient in the aqueous phase, z is the number of monomer units required such that the oligomer is surface active, t is time in seconds, and [I] is the initial concentration of initiator in the aqueous phase.

$$\bar{M}_{n,theory} = FW_{RAFT} + \frac{Mol_{mon}FW_{mon}x}{Mol_{RAFT} + A} \quad (2)$$

where

$$A = 2f_1 f_{entry}(1 - e^{-k_d t}) \quad (3)$$

and

$$f_{entry} = \left(\frac{\sqrt{k_d[I]k_{t,aq}}}{k_{p,aq}C_{w,mon}}\right)^{1-z} \quad (4)$$

There are several points to note in Figure 2. Until roughly 30% monomer conversion, the theoretically derived molecular weight relationship described by eq 1 was in good agreement with the experimental molecular weight. The linear relationship with conversion, matching theory, indicates "living" polymerization behavior. From roughly 30% conversion onward the experimental points fall below the solid theoretically derived curve from eq 1; however, the points can now be fitted by taking into account the presence of initiator-derived chains as described in eq 2. Because of the drastic retardation, there is little conversion of monomer to polymer after approximately 70%, but there is still an increase in the number of chains from initiator decomposition and thus the M_n decreases.

More significant to note is the trend in polydispersity (+, right axis) which increased with conversion and reaction time. Figure 2 shows the polydispersity increased from a value of 1.14 (4% monomer conversion) to a final recorded value of 2.86 at 70% conversion. Theoretically[20] in RAFT living systems, polydispersity should decrease with conversion ending close to unity upon full conversion if termination is negligible (i.e., if the number of initiator derived chains is small compared to the number of dormant chains). The method of moments derived by Müller et al.[20] for group transfer can be used to accurately describe the profile of polydispersity as a function of conversion, assuming that miniemulsions have the same kinetics as in bulk. Using Müller's equations, the theoretical profile of polydispersity is calculated in Figure 3 for the conditions of this run. The simulated polydispersity results show that the system should in fact exhibit a decrease in polydispersity after the consumption of the RAFT agent. Also depicted in Figure 3 is the effect of the rate of consumption of the RAFT agent on the polydispersity. When $C_{tr,RAFT}$ is increased (k_{tr}/k_p), the RAFT agent is consumed faster, and the polydispersity is maintained at a lower value. The significance of this figure is that, in theory, the polydispersity of this system *should* be decreasing, in contrast to what was observed experimentally. This shows that initiation is a factor that cannot be ignored and has a significant effect on the polydispersity.

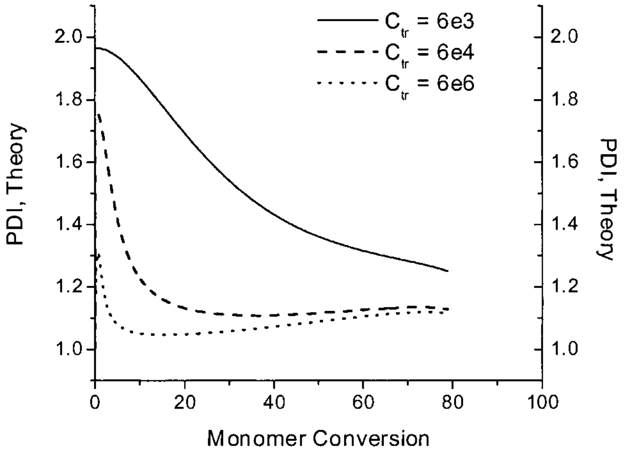


Figure 3. Simulations of polydispersity using Müller's equation.[20]

A further observation from this data set that is not seen numerically but that surely plays a role in the trends seen in Figure 2 is a distinct visual indication of an unstable miniemulsion, which has also been observed in macroemulsions.[10,11] Immediately following initiation of the reaction, a red monomer phase appeared in the vortex of the reactor, indicating some degree of phase separation. The red hue is due to the dithiobenzoate group of the RAFT agent, and GPC analysis divulged that this phase consisted of monomer-swollen oligomers/polymers with a broad molecular weight distribution (i.e., polydispersities between 3 and 5). Over the course of reaction, the percentage of volume occupied by this organic phase slowly increased. This stability issue will be discussed in more detail later in this paper and is stated at this point for the reader to better understand the phenomena that lead to the results presented in Figure 2.

The styrene/RAFT results (expt 2) suggest inefficient nucleation of the initial monomer droplet distribution due to the drastic retardation and red layer. To determine whether the red layer is caused due to the slow rate of polymerization, a REDOX couple was added.

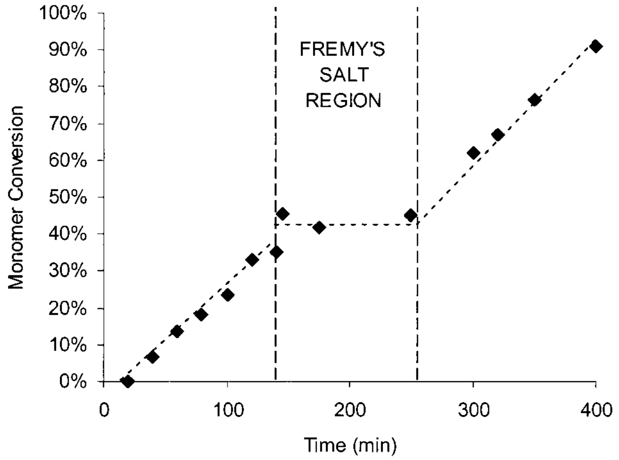


Figure 4. Miniemulsion of styrene using a redox system in the presence of **I** and Fremy's salt (expt 5). The Fremy's salt was added at 45% conversion. (Note: dotted line is "for the eye" and is not a fitted curve).

Since a catalytic REDOX agent was not desired, but instead one that would merely aid in faster decomposition of KPS, sodium metabisulfite was chosen as the couple (expt 5). This is confirmed by the addition of Fremy's salt (potassium nitrosodisulfonate) at roughly 35% monomer conversion. Potassium nitrodisulfonate is a stable nitroxide radical that partitions strongly in the aqueous phase and will scavenge any carbon-centered radicals. It has some degree of solubility in the droplets, so it may also terminate active chains in the particles. In Figure 4, monomer conversion is shown with the region of Fremy's salt addition through to its consumption indicated. The Fremy's salt did in fact stop the polymerization for roughly 100 min (the point at which it was fully consumed); afterward, polymerization continued at a similar rate to that prior to addition of Fremy's salt. This allowed confirmation that the redox system is indeed an accelerator for initiator decomposition and also allowed an approximate k_d value for the decomposition of initiator to be calculated, which is required for $\bar{M}_{n,\text{theory}}$ (eq 2).

For the first 10% of monomer conversion (referring again to Figure 1), the RAFT styrene miniemulsion polymerization with redox (expt 3, ●; same [KPS] as "blank") showed no decrease in rate compared to the "blank" (expt 1, ▲) styrene system (i.e., no RAFT, no redox) of the same recipe and conditions. From 10% conversion onward, the rate was found to be less than that of the "blank" yet still markedly faster than that of the RAFT system without redox. Assuming the same number of droplets initially present for both reactions, this indicated that a larger percentage of droplets were nucleated, effectively increasing the reaction rate. Figure 5 illustrates several beneficial effects of the redox agent on the molecular weight and polydispersity evolution. Similar to the case without redox, the experimental molecular weight agrees with the theoretically derived relations, yet with an increased reaction rate the disparity between the curve derived from eq 2 and the line described by eq 1 is less pronounced. Molecular weight again showed contributions from initiator-derived chains and the polydispersity still has an increasing trend. However, the polydispersity with redox initiation increased at a slower rate than that seen in Figure 2 (no redox, expt 1), and when Figure 2 and Figure 5 are compared at roughly 50% monomer conversion, 2.18 and 2.73, respectively, the benefit of a greater number of droplets being nucleated is evident.

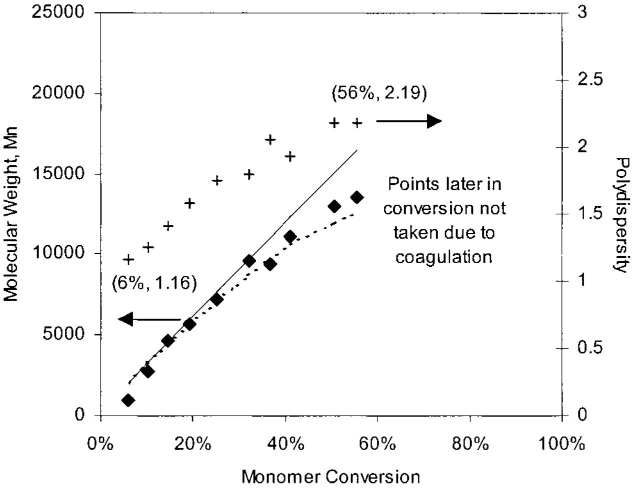


Figure 5. Number-average molecular weight for miniemulsion polymerizations of styrene carried out at 75 °C in the presence of SDS, RAFT agent **I** initiated by a redox couple (expt 3). Experimental $\bar{M}_n$ (◆), theoretical $\bar{M}_n$ accounting for RAFT derived chains only (—), theoretical $\bar{M}_n$ accounting for RAFT derived chains and initiator derived chains (- - -), polydispersity (+, right axis).

When the radical flux of the redox system was increased (by doubling both the concentrations of KPS and sodium metabisulfite), a further increase in polymerization rate was observed (expt 4, ○, Figure 1). In fact, after the first 10% of conversion, the polymerization rate was comparable to that of the "blank". When the two redox systems are compared (inset, Figure 1), this is even clearer. The low radical flux recipe (expt 3, ●) is considerably faster that that of the higher radical flux (expt 4, ○) until a conversion of roughly 14%, when the two profiles cross. The most probable explanation for the slower start of the higher radical flux run is a larger probability of termination in the aqueous phase, after which the rate is higher presumably due to a greater number of droplets nucleated. Conversion profiles from late in the redox reactions are not shown in Figure 1 due to coagulation. At a reaction temperature of 75 °C and long reaction times, some degree of coagulation is not unexpected.

A decrease in the ratio of [**I**]/[KPS] will increase the amount of chains terminated by radical−radical reactions and consequently produce a broader molecular weight distribution. This does not seem to be the case when the trends shown in Figure 6 are compared to those of Figure 5. The increase in radical flux of the system does not seem to have markedly affected the $\bar{M}_n$ or polydispersity. This is not unexpected since by increasing the number of particles, due to a greater nucleation process, the entry rate (ρ) decreases and so too does the amount of radical−radical termination.[19]

To determine whether polymerization rate plays a role in the stability or control of these RAFT miniemulsions, two experiments (expts 6 and 7) were performed, keeping all other recipe concentrations constant while substituting methacrylic monomers for styrene and substituting RAFT agent **II** for **I**. Methacrylates have higher propagation rate constants than styrene at 70 °C ($k_{p,\text{styrene}} = 440$, $k_{p,\text{BMA}} = 1220$, $k_{p,\text{EHMA}} = 1470$).[21] The results indicated that macromolecular control with the methacrylates was much easier to achieve. Figures 7

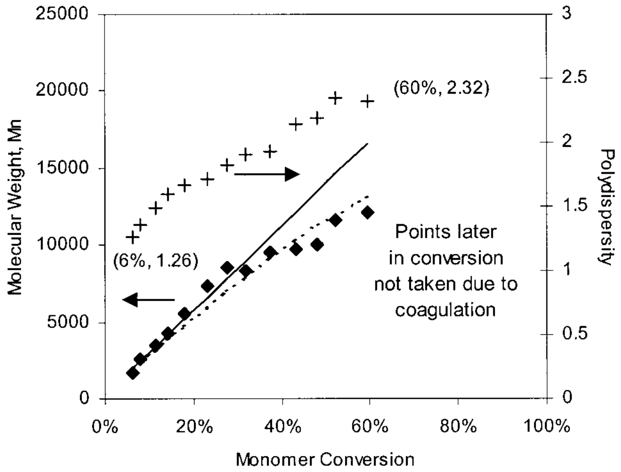


Figure 6. Number-average molecular weight for miniemulsion polymerizations of styrene carried out at 75 °C in the presence of SDS, RAFT agent **I** initiated by a redox couple (expt 4, [KPS] doubled from Figure 5). Experimental $\bar{M}_n$ (◆), theoretical $\bar{M}_n$ accounting for RAFT derived chains only (—), theoretical $\bar{M}_n$ accounting for RAFT derived chains and initiator derived chains (- - -), polydispersity (+, right axis).

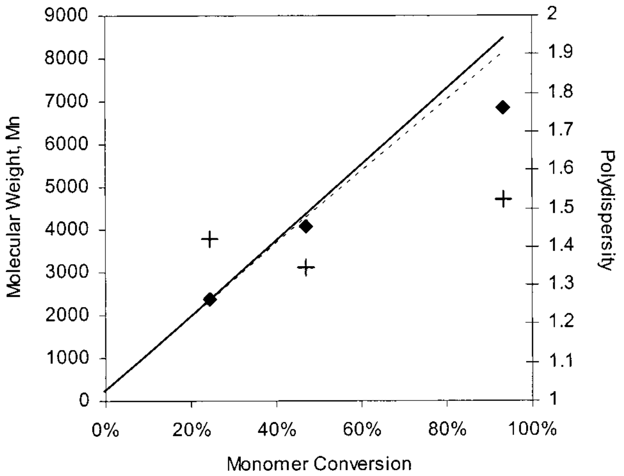


Figure 8. Number-average molecular weight for miniemulsion polymerizations of BMA carried out at 75 °C in the presence of SDS, cyano RAFT agent **II** initiated by KPS (expt 7). Experimental $\bar{M}_n$ (◆), theoretical $\bar{M}_n$ accounting for RAFT derived chains only (—), theoretical $\bar{M}_n$ accounting for RAFT derived chains and initiator derived chains (- - -), polydispersity (+, right axis).

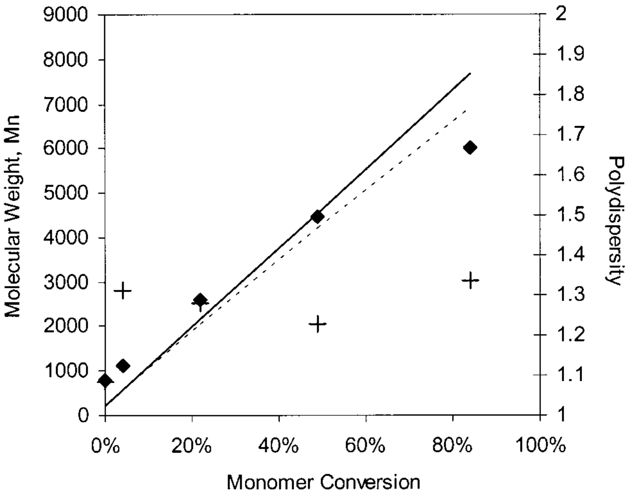


Figure 7. Number-average molecular weight for miniemulsion polymerizations of EHMA carried out at 75 °C in the presence of SDS, cyano RAFT agent **II** initiated by KPS (expt 6). Experimental $\bar{M}_n$ (◆), theoretical $\bar{M}_n$ accounting for RAFT derived chains only (—), theoretical $\bar{M}_n$ accounting for RAFT derived chains and initiator derived chains (- - -), polydispersity (+, right axis).

and 8 both show the polydispersity to remain below 1.5, a dramatically lower value than that found in any of the styrenic systems, but regardless of better control the same miniemulsion destabilization phenomena were apparent. With the faster reaction rate, the appearance of the red organic layer was much more immediate, and up to 35% of the organic material was lost to coagulation. This illustrates that the destabilization of the droplets is not related to the monomer type or rate and that a deleterious interaction with SDS surfactant (similar to macroemulsions) is present in all these systems.

In another paper,[5] the authors describe a means of lowering the polydispersity of these RAFT miniemulsion systems by using nonionic surfactants in place of SDS. Those polymerizations were also not thermodynamically stable but were considered kinetically stable (i.e., the miniemulsion was stable over the time frame of the reaction). Molecular weight closely followed theory throughout the reaction, living character was also confirmed by the production of block copolymers in a second step, and the polydispersity was found to remain as low as 1.09 at full conversion. Samples were taken from unreacted RAFT miniemulsions (stabilized by nonionic surfactant) and were found shelf stable for at least 4−5 days after which visible monomer cream started to become apparent. In most cases, no red organic layer was present during polymerization, and the latex product was shelf stable for several months. In light of this, it is likely that similar events were occurring in these nonionic surfactant stabilized miniemulsions, but the detrimental effects seen here were suppressed by a larger degree of miniemulsion stability and integrity over the polymerization time frame in those reactions. Hints of instability were present in certain cases where minor phase separation was observed in the first 15 min of polymerization, but these signs would quickly disappear with no noticeable effect on the product. This leads one to suspect that the presence of the RAFT agent was in some manner causing SDS to be displaced from the particle surface (in the ionically stabilized miniemulsions), breaking down an integral part of the miniemulsion stability mechanism. It should be noted that it would be markedly more difficult to displace a nonionic polymeric surfactant from the particle surface since its diffusion coefficient in the aqueous phase is substantially lower.

Conductivity and pH Considerations. In an ideal stable miniemulsion, there should be no change in aqueous phase conductivity since there is negligible change in interfacial area and consequently little rearrangement of surfactant.[22,23] Conversely, in a conventional macroemulsion the larger monomer droplets serve as reservoirs continually diffusing monomer across the continuous phase to the locus of polymerization in nucleated micelles. As these reservoirs are depleted, the total interfacial area of the system decreases and surfactant desorbs from the particle interface resulting in an increase in conductivity.[23] This is the theoretical foundation behind the conductivity experiments. Since a stable miniemulsion should exhibit a flat conductivity

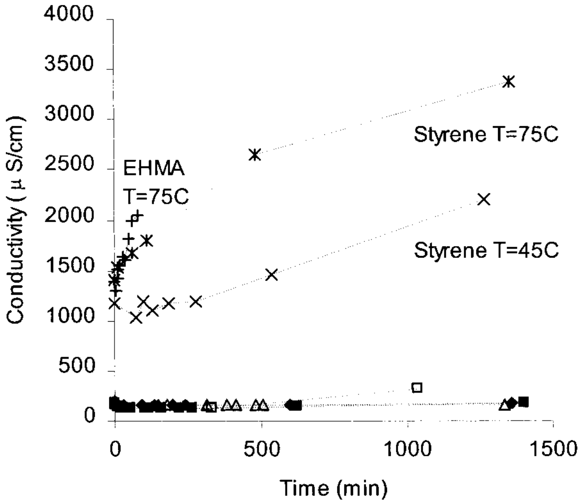


Figure 9. Conductivity of miniemulsions of styrene and EHMA on shelf and during polymerization. Shelf experiments: expt, 8, △; expt 9, ◆; expt 10, □; expt 11, ■. Polymerizations: expt 12, ×; expt 13, *; expt 14, +.

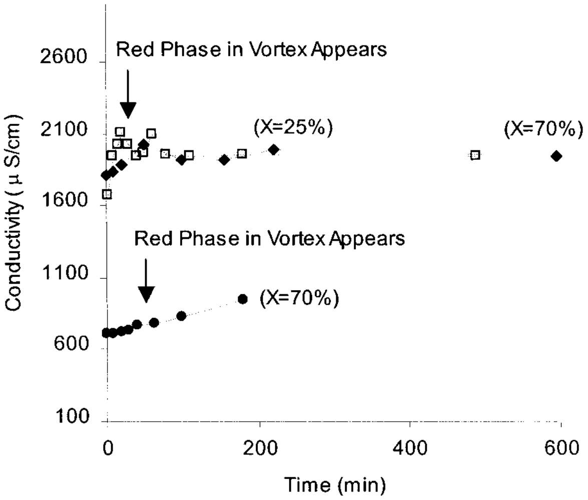


Figure 10. Conductivity of miniemulsion polymerizations of styrene under buffered conditions: styrene blank (expt 15, □), styrene/KPS/**I** (expt 16, ◆), styrene/AIBN/**I** (expt 17, ●).

profile over conversion (all other factors constant, such as pH), an increase would indicate SDS being dispelled into the aqueous phase. This, it was postulated, was the cause of the destabilization phenomena observed in the ionically stabilized systems.

Without ample surface coverage of SDS, hexadecane alone will not suffice to keep the Gibbs free energy of monomer droplets low enough to maintain their small diameter. As the Gibbs free energy for the droplet rises, the driving force for monomer diffusion out of the droplets (Ostwald ripening) increases, and the droplets swell until their diameter reaches a new kinetically stable size. Miniemulsions are inherently thermodynamically unstable (the droplets will eventually grow due to a positive Gibbs free energy) but are considered kinetically stable over the time frame of polymerization. Of course, there would also have to be a reason for the SDS to be expelled into the aqueous phase. Destabilization of the miniemulsion is a secondary effect and caused by SDS leaving the particle surface. Conductivity is an easy and accurate method to measure the amount of SDS residing in the aqueous phase during the polymerization.

The first series of conductivity experiments compared the stability of miniemulsions on shelf (unpolymerized) to those same recipes when polymerized. Samples were taken over typical reaction times with further samples taken up to a time of 3 days. The shelf samples are all seen as a cluster of flat lines in the lower portion of Figure 9. These shelf experiments included “blank” runs and those in the presence of RAFT for both styrene (expt 8) and (2-ethyl)hexyl methacrylate (EHMA, expt 9). Styrene was chosen due to the most pronounced level of instability observed in its miniemulsion RAFT systems, and EHMA was chosen for comparison purposes to see if instability was in any part a function of monomer characteristics. The flat profiles of all these shelf experiments suggest that the interaction of RAFT with other reagents is not a significant issue until polymerization is started. However, even in shelf samples, a small degree of instability was observed in the slow formation of a monomer cream. The styrene shelf sample that included RAFT, depicted with open squares (expt 10, □) in Figure 9, showed a slight increase in conductivity but only after a shelf time of over 500 min. It should be noted that these shelf experiments were not under agitation.

Reacted samples, however, showed clear signs of an increase in surfactant concentration in the aqueous phase during polymerization, as evident in their increasing conductivity profiles in Figure 9. The styrene/RAFT miniemulsion polymerization (expt 13, *) at a reaction temperature of 75 °C showed a more dramatic increase in conductivity than that of the same reaction (expt 12, ×) conducted at a reaction temperature of 45 °C. The reaction involving EHMA/RAFT (expt 14, +) exhibited the fastest increasing rate of conductivity. This higher rate corresponds to EHMA’s considerably larger propagation rate constant than styrene’s. It seems the conductivity increases in these reactions in a proportional manner to the rate of polymerization.

The fact that the shelf experiments including RAFT did not show significant signs of increasing conductivity, while all reaction experiments did, leads to the conclusion that the destabilization is not only a matter of an incompatibility of the RAFT with typical emulsion components. Moreover, it tentatively suggests the culprit behind destabilization is partially to do with oligomer formation. This is the only distinction between the shelf and reaction experiments.

An interesting point to note, however, is that when a styrene “blank” (expt 8) polymerization was monitored for conductivity, the profile showed a decreasing trend over conversion, eventually flattening out late in the reaction. This “blank” was initiated by KPS, known to hydrolyze into sulfuric acid in an aqueous environment over time.[24] This effectively lowers the pH of the reaction medium with a profound effect on conductivity. In addition, the hydrolyzed form of KPS is no longer ionic—also affecting the conductivity toward lower values. For these reasons, sodium bicarbonate was added as a buffer, and new reactions were again measured for conductivity, as shown in Figure 10.

In a buffered environment, after an initial increase in the first 25 min, the conductivity profile for the styrene “blank” reaction (expt 15, □) in miniemulsion remained flat, as expected. The initial, albeit short-lived, rise in conductivity might be due to reactor contents coming to temperature. In a buffered environment, the styrene RAFT miniemulsion polymerization, stabilized by SDS and initiated by KPS, showed no notable change in conductivity over the reaction (expt 16, ◆, Figure 10). Actually, the conductivity profile looked strikingly similar to the "blank" without RAFT. This was a significant result as the same recipe without buffer was found to be the most unstable. Even more significant is the appearance of the red organic phase in the vortex of the buffered styrene/RAFT miniemulsion polymerization although the conductivity was observed constant.

In attempt to rule out the persulfate group of the KPS initiator as a contributor to the RAFT destabilization phenomenon, a further buffered RAFT conductivity experiment was performed (expt 17, ●, Figure 10) initiated by oil-soluble 2,2′-azobis(isobutyronitrile) (AIBN). KPS was in fact proven not to be a large contributor (if at all) to the destabilization in these ionically stabilized systems. Even when initiated by AIBN, the same signs of destabilization and formation of the red organic layer were apparent.

All the evidence presented point to the notion that phenomena occurring during the first few percentage points of conversion are the most pertinent to the miniemulsion destabilization. In this conversion period, small oligomers are created and exit into the aqueous phase is possible, thus forming the red organic layer. A distinct difference between these RAFT miniemulsion systems and traditional miniemulsion systems in the first few percent of monomer conversion is the chain length of polymer. In a traditional miniemulsion, much higher molar mass polymer would be formed when compared to that of a RAFT system at the same reaction time. If the particle interface were undergoing a great deal of traffic, as is the case with exit and reentry of species at very low conversion, the presence of higher molar mass would aid in the particle stability through hydrophobic contributions to the Gibbs free energy. These hydrophobic contributions are absent in RAFT miniemulsion systems due to the presence of only oligomers at this stage of conversion and reaction time.

To test the conjecture that dormant oligomers (i.e., oligomers with dithiosulfate end groups) are the culprit behind most of the discussed phenomena, the conductivity of miniemulsions in the presence of specially designed oligomeric species was monitored. Conditions of these runs were similar to the previously discussed shelf conductivity experiments, yet the contents were stirred under argon and reflux coolers (without heating) and were monitored for over 3 weeks. The synthesized oligomers were prepared by solution polymerization from a reaction of 0.2 g of RAFT with monomer and initiator. The conductivity experiments were then performed using the same recipe as previous shelf experiments. This data set consisted of a "blank" (expt 18), a normal RAFT experiment (expt 19), a synthesized short dormant oligomer (expt 20, oligo1, average of 2 monomer units), and a synthesized long dormant oligomer (expt 21, oligo2, average of 5–6 monomer units).

Just from the conductivity data in Figure 11, it can be concluded that the RAFT agent does in fact play a role in destabilization, and the longer it grows, the smaller the effect. Apparently, the length of oligo2 (the longer synthesized oligomer) is already such that the added stability through its hydrophobic contribution is at least as large as the destabilization effect. That is, the oligo2 curve is remarkably similar to the "blank" curve in Figure 11. However, conductivity does not divulge everything as the reactor contents showed clear signs of the red organic phase within a few hours while the conductivity of oligo1 (the short synthesized oligomer) does not show signs of instability until around 3 weeks after the inception of the experiment.

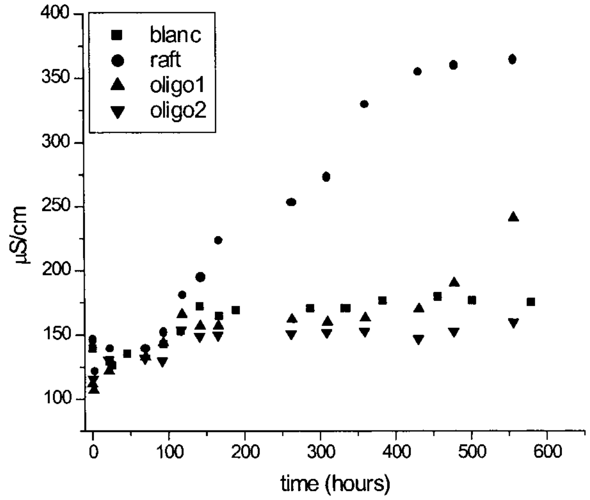


Figure 11. Conductivity of miniemulsion polymerizations of styrene carried out in the presence of different RAFT agents: no RAFT, expt 18; **I**, expt 19; oligo1, expt 20; and oligo2, expt 21.

Possibly a more significant observation is that destabilization is observed at a maximum when RAFT miniemulsions are initiated. This destabilization effect is also observed much faster than seen in any of the "static" experiments. This suggests that the destabilization is due to more than just the *presence* of oligomeric species because in the reaction experiments polymers grow to the "stable" oligo2 chain length (roughly 5 monomer units) quite rapidly.

When nonionic surfactants[5] are substituted for the SDS of these recipes, destabilization is markedly reduced. In some cases, a red droplet becomes visible after about 5–10 min of reaction time—exactly the same red organic phase seen in the SDS reactions. However, the distinction is that after another 10 min or so in the nonionic system the red organic phase disappears. With the SDS system, this is just the beginning of the destabilization, and it rapidly becomes worse.

The destabilization phenomena observed in RAFT miniemulsion polymerization are not believed to be specific to miniemulsions or the RAFT agent itself. Matyjaszewski et al.[2] report strikingly similar observations of instability in studies of ATRP polymerizations in dispersed media, and El-Aasser et al.[1] report data that imply similar instability phenomena are occurring in nitroxide-mediated living miniemulsion polymerization. The only literature that does not indicate instability phenomena is that of RAFT agents (of the xanthates type)[9] or degenerative transfer agents (e.g., perfluorohexyl iodide);[25] however, polydispersity stays relatively high (1.5–3.2).[9,26] The distinction between this system and other forms of living polymerization is the activity of the chain transfer agent ($C_{\mathrm{tr,\ styrene}} = 0.8-1.4$),[27,28] which dictates that the molecular weight at low conversions is close to the final M_n when using a RAFT agent with a very high C_{tr}.[20] This further emphasizes the role of oligomers in the destabilization phenomena seen in (mini)emulsion polymerization with highly active chain transfer agents.

Conclusion

From a theoretical standpoint, a miniemulsion offers many advantages over conventional emulsion, bulk, or solution environments for living RAFT polymerization. This work, however, has shown that in practice it is difficult to realize these desired conditions with our current limited understanding of the interaction of RAFT with other emulsion components. The data obtained leads one to postulate that the formation of large amounts of oligomers early in the polymerization is one cause for destabilization, although this alone cannot account for all the observed phenomena. It is also postulated that a concomitant cause is due to an unknown complexation between the RAFT and ionic surfactant, possibly allowing the RAFT agent to become surface active. Whatever the case, the presence of RAFT has influenced the stability of the miniemulsion (or macroemulsion),[10,11] resulting in the appearance of a separate organic phase and a high polydispersity.

The application of RAFT living polymerization in a miniemulsion is still a relatively unexplored field. Although the results presented include phenomena such as particle instability and some phase separation, the RAFT system did in fact work in a miniemulsion.[3-5] An understanding of the interaction of RAFT with other emulsion components has not fully developed yet, but with the increasing attention living polymerization systems are acquiring (particularly in dispersed media) major developments can be expected in the near future.

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