

Successful Use of RAFT Techniques in Seeded Emulsion Polymerization of Styrene: Living Character, RAFT Agent Transport, and Rate of Polymerization

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ABSTRACT: Reversible addition–fragmentation chain transfer (RAFT) polymerization techniques are successfully used to control molecular weight and polydispersity in the seeded emulsion polymerization of styrene. A novel technique was used to assist the transport into the seed particles of a RAFT agent that is of very low water solubility, ensuring the RAFT agent was localized in the particle phase. The polymer produced in these experiments was seen to have low molecular weight polydispersity ($1.1 < M_w/M_n < 1.4$), and the molecular weight could be controlled by the amount of RAFT agent used. The procedure permitted living polymerization to be performed in an emulsion polymerization system. Importantly, the RAFT agent had no adverse effect on latex stability, and unusual amounts of coagulum were not observed. Reductions in the rate of polymerization (measured by dilatometry) were observed along with significant inhibition periods, for which possible explanations and remedies are discussed. This appears to be the first instance where good living character has been demonstrated in a true emulsion polymerization of styrene while maintaining good colloidal stability.

Introduction

Reversible addition–fragmentation chain transfer (RAFT) polymerization techniques are well developed for solution and bulk polymerization systems,^{1–4} and various results have been reported for its application in emulsion^{3,5–7} and miniemulsion^{8–10} systems. The use of RAFT in emulsion polymerization systems has, until recently, been quite unsuccessful; previous studies have reported high levels of coagulum, thick red layers (phase separation) forming during the course of the polymerization, and very slow polymerization rates.^{7,11} Indeed, these results have led to speculation that RAFT cannot be made to work in dispersed systems, although recent results in miniemulsions^{8,10} and the results reported here for emulsion polymerizations would tend to suggest otherwise.

Here, the successful use of RAFT in a true emulsion polymerization is reported. (The word “true” is used to distinguish this work as being on (seeded) emulsion polymerizations, where the latex particles do not arise from droplets, as distinct from miniemulsion polymerizations.) The use of seeded emulsion polymerization in this study opens the way to measuring important kinetic parameters for these systems such as the rate coefficients for the entry of radicals into particles.

In addition, it is hoped that these systems will achieve faster rates of polymerization while maintaining good temperature control and, most importantly, would have the well-known significant environmental advantages of emulsion polymerization compared to solution systems.

Review of Previous Studies. As previous studies have shown,^{5,12} the additional physical events involved in an emulsion polymerization experiment (such as the entry of an oligomeric radical into a particle and the complexities of particle formation) make the already intricate process of RAFT polymerization significantly more complex.

A survey of the current work in this field shows that, other than a single report of an *ab initio* polymerization of butyl methacrylate,¹ all published experiments have exhibited one or more of the following problems: (i) poor colloidal stability,^{7,11} (ii) poor control of the number-average molecular weight,^{5,7,11} or (iii) poor control of the polydispersity.^{3,5,6,11,13} The work presented here does not suffer from any of these problems.

It should be noted that the poor control of the polydispersity in some studies is due to the use of xanthates as the RAFT agent.^{5,6,13} While xanthates are easily included in emulsion polymerizations (with no significant colloidal stability problems), they are unable to produce polymers of low polydispersity even in the most ideal conditions. Indeed, the use of slightly surface-active RAFT agents (such as the MADIX agents of Smulders et al.¹⁴ or the amide-functionalized RAFT agent of Uzulina et al.⁷) appears to be important to the success of the experiment; the use of highly water-insoluble RAFT agents without facilitating RAFT agent transport has so far been unsuccessful.¹¹ The water-soluble RAFT agent used by Uzulina et al.⁷ was also quite unsuccessful, presumably due to significant and detrimental effects on the aqueous phase chemistry that is so important in an emulsion polymerization.^{15,16} The mechanistic implications of this observation will be investigated further in the Discussion.

RAFT Agent Transport. One of the most significant difficulties in the application of RAFT to emulsion polymerizations is the transport of the RAFT agent into

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the latex particles. RAFT agents are often quite water-insoluble, making this process very slow; while the synthesis of water-soluble RAFT agents is possible, previous studies have shown significant inhibition from such RAFT agents.⁷ Once the RAFT agent has been dissolved in the monomer and then added to the water phase, the kinetic and thermodynamic barriers to the transport of the RAFT agent into the particles could be quite large.

With analogy to styrene dimer, Monteiro et al.¹¹ estimated that, for RAFT agents similar to the one used here, the rate of transport should be quite fast ($\sim 10^6$ s⁻¹). However, as the water solubility of the RAFT agent is often less than the purity of the prepared compound, accurate estimates for the rate of transport cannot be prepared.

It is important to note that even if the kinetic rate of transport is much faster than the rate of propagation (e.g., in this case), it is still possible for thermodynamic barriers to prevent sufficient RAFT agent transport. As the RAFT agent will initially partition with approximately equal concentration between the monomer droplet and particle phases, a significant amount of RAFT agent would be present in the monomer droplets. This could allow RAFT polymerization within the droplets, making oligomeric RAFT adducts (dormant chains), that would be unable to transport across the aqueous phase and result in a viscous, highly colored layer as the monomer droplets evaporate.¹¹

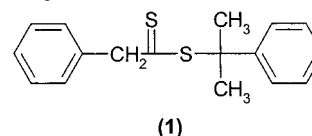
An alternative approach to transporting the RAFT agent from monomer droplets to the locus of polymerization (i.e., the particles) is therefore desirable. Addition of an organic cosolvent (such as acetone) is known to facilitate transport of hydrophobic species in the aqueous phase in emulsion polymerization reactions. This allows the RAFT agent to be transported to the preformed particles of a seed latex before the onset of polymerization, allowing the kinetics of the actual RAFT mechanism to be studied with reference to the kinetics of particle growth, uncomplicated by particle formation events.

Seeded Emulsion Polymerization. The use of a preformed latex, or seed, on which subsequent polymer may be grown is a common technique in both academic studies and industrial processes.¹⁵ In this work, a seed latex is used to eliminate the complexities of particle formation, allowing the effect of the RAFT agent on polymerization to be more easily studied.¹⁵ Coupling seeded experiments with the acetone transport technique reported here also obviate the need to address issues surrounding RAFT agent transport to the particles during the reaction.

In this study, a small polystyrene seed was used, and the new, living polymer formed was also polystyrene. The use of the same polymer for the seed and new polymer obviates the need to make assumptions about polymer miscibility that "heteroseeded emulsion polymerization" entails.¹⁷ As the molecular weights of the new and old polymer used in this study are quite distinct, it is sufficient to use GPC signal subtraction as detailed below to measure the molecular weight distribution (MWD) of the new polymer.

The overall objective of the present paper is to test the expectation that use of an acetone transport system, together with seeded emulsion polymerization, would lead to the same sort of living character as is seen for a corresponding solution RAFT polymerization. This ex-

Scheme 1. RAFT Agent 2-Phenylprop-2-yl phenyldithioacetate (PPPDTA)



(1)

pectation is be no means a certainty as other authors have noted in other RAFT/emulsion studies.^{7,11} Emulsion polymerization kinetics can be quite different from those in bulk due to compartmentalization effects (isolation of the radicals in particles), and moreover, it has already been observed that xanthate RAFT agents display some surface activity that can result in very different kinetics from what is seen in a corresponding emulsion polymerization system.¹⁴

A seeded emulsion polymerization experiment may start in either interval II (monomer droplets present) or interval III (no monomer droplets), depending on the ratio between the amount of monomer added and the amount of seed polymer present (strictly also the volume of water in the system, although for styrene this effect is negligible). Most of the emulsion polymerization experiments reported here were carried out in interval III, although successful RAFT/emulsion experiments were also carried out in interval II.

RAFT Techniques. The RAFT process has been well described elsewhere.²⁻⁴ The RAFT agent 2-phenylprop-2-ylphenyldithioacetate (**1**, PPPDTA) was used in this study, shown in Scheme 1. This RAFT agent was chosen as it has previously been seen to produce good results in bulk and solution polymerization experiments with styrene, it is quite water insoluble (thus it should not affect the aqueous-phase chemistry which is so important for emulsion polymerization¹⁵), and preliminary work for this study was quite promising.

Experimental Section

Materials. All materials were used as received from Aldrich with the following exceptions. Inhibitors were removed from the styrene using a commercial inhibitor removal column (Aldrich), carbon disulfide was purified with several freeze-thaw cycles, and α -methylstyrene was purified with a basic alumina column. Demineralized water was used throughout the experiments.

Synthesis of RAFT Agent. The RAFT agent PPPDTA was synthesized using a method analogous to the synthesis of 2-phenylprop-2-yl dithiobenzoate described elsewhere.³ The synthetic route used here was developed by Thang¹⁸ and has been separately described by Quinn et al.^{19,20}

Benzyl chloride (40 g) was added dropwise over 20 min to magnesium turnings (7.7 g) and dry diethyl ether (150 cm³, redistilled over sodium wire) under a nitrogen atmosphere at 4 °C. The mixture was stirred for 1 h and then heated to reflux for 30 min. Carbon disulfide (24 g) was added dropwise with stirring over 15 min to the chilled mixture. The reaction mixture was maintained at 0 °C for a further 3 h. The mixture was poured into ice water (150 cm³), and the aqueous layer was extracted with diethyl ether (2 \times 50 cm³). The aqueous layer was acidified with cold hydrochloric acid solution (10% w/w) to pH \sim 2 and extracted with several portions of ether. The combined ether portions were dried over anhydrous magnesium sulfate. After removal of the drying agent and evaporation of the ether, the crude phenyldithioacetic acid (32.2 g, 64.0% yield) was isolated as a yellow oil that later solidified to a yellow/orange solid. ¹H NMR (CDCl₃): δ (ppm) 4.29 (s, 2H), 5.90 (br s, 1H) and 7.30–7.43 (m, 5H).

Phenyldithioacetic acid (30.4 g), α -methylstyrene (21.4 g), and carbon tetrachloride (36 cm³) were combined under nitrogen and heated at 70 °C for 18 h. After removal of the

carbon tetrachloride solvent, the crude product was dissolved in the minimum amount of boiling hexane/ether (80:20) and then recrystallized at 2 °C. The purified product was isolated by filtration and a second crop of crystals obtained by the same recrystallization method. (No attempt was made to obtain further crops of crystals.) RAFT agent 2-phenylprop-2-yl phenyldithioacetate (PPPDTA) was isolated as orange needles (21.4 g, mp 56 °C, 23.7% yield on benzyl chloride, estimated purity 99%). ¹H NMR (CDCl₃): δ (ppm) 1.92 (s, 6H), 4.20 (s, 2H), 7.20–7.40 (m, 8H) and 7.47 (d, 2H). ¹³C NMR (CDCl₃): δ (ppm) 27.9, 56.3, 59.2, 126.6, 126.8, 127.0, 128.4, 128.9, 137.1, 143.9, and 223.3 (C=S).

An attempt was made to estimate the water solubility of PPPDTA as follows. The absorption maximum at 311 nm (characteristic of C=S) was monitored using a Cary 5 UV–vis spectrometer (Varian) in both phases of an equilibrated solution of PPPDTA in an octanol–water mixture for a range of added amounts of PPPDTA. The concentration of chromophores in the water-phase component was always less than 0.5% of that in the organic phase. This is less than the level of minor impurities in the PPPDTA sample (e.g., other species containing C=S arising from the preparation); the only quantitative statement that can be made about the amount of PPPDTA in the water phase is that it is less than 0.5% of that in the particles, i.e., less than 1×10^{-4} M.

Preparation of Polystyrene Seed. Sodium dodecyl sulfate (10 g) and sodium hydrogencarbonate (0.5 g) were dissolved in water (0.73 dm³) in a 1 dm³ jacketed glass reactor at 85 °C. The reaction mixture was stirred throughout using a three-blade turbine stirrer at 300 rpm with a constant flow of nitrogen through the reactor. After thermal equilibrium had been reached, styrene (250 g) was added, and the mixture was allowed to equilibrate for a further 15 min. Sodium persulfate solution (12 cm³, 0.882 mol dm⁻³) was then added. The mixture was allowed to react for 3½ h, yielding a 25% solids latex with particle radius $\bar{r}_w = 39$ nm, $\bar{r}_w/\bar{r}_n = 1.18$, particle number concentration $N_c = 2.2 \times 10^{18}$ (calculated from \bar{r}_n), molecular weight $\bar{M}_n = 7.4 \times 10^4$, and $\bar{M}_w/\bar{M}_n = 3.4$.

Acetone Transport Technique. In a typical preparation, seed latex (10 g), water (55 g), and acetone (20 g) were combined with stirring. RAFT agent (30 mg) was added to this mixture as fine crystals. The mixture was allowed to stir for 24–72 h. After this time, the crystals of RAFT agent were no longer visible. Liquid (acetone/water mixture, 30 g) was stripped from the mixture using a rotary evaporator at 30 °C over 45 min, and the mixture was made back up to volume with more water (10 g).

Determination of Acetone Residue. At the conclusion of the seed preparation by the acetone transport technique detailed above, some residual acetone may be left in the latex despite the fact that acetone/water mixtures are zeotropic.²¹ To estimate the level of residual acetone, an acetone/water mixture (same proportions as above) was subjected to rotary evaporation at 30 °C over 45 min. Additionally, a series of seven acetone/water standards ranging from 65 to 130 ppm were prepared gravimetrically. Using a Cary 5 UV–vis spectrometer (Varian), the carbonyl absorbance of acetone (265 nm) was measured for the standards and unknown. The standards gave a linear calibration to high precision ($R^2 > 0.999$), indicating that the acetone level in the seed latex was 92 ppm. When this seed was further diluted as described below, the actual polymerization reactions were carried out in the presence of 60 ppm acetone.

Hydrolysis of RAFT Agent. The dithiocarbonyl functional group of the RAFT agents may be expected to hydrolyze given suitable reaction conditions. A solution of RAFT agent (9×10^{-5} mol dm⁻³) in ethanol/water mixture (50% w/w) was prepared and separated into nine aliquots. The samples were heated to 50 °C (the reaction temperature for the polymerization experiments described below) for periods between 30 min and 5 h. The hydrolysis of the dithiocarbonyl group was observed spectroscopically by comparing the peak absorbance (312 nm) of the C=S group of an unheated sample to each of the heated samples using a Cary 5 UV–vis spectrometer (Varian). Over 5 h, the absorbance was reduced by 5%. The

same experiment performed at 85 °C showed a reduction in absorbance of 30% after 1 h. Since in these seeded emulsion polymerization experiments reported here the RAFT agent is not solubilized into the water phase with ethanol (instead of partitioning strongly into the particle phase), the hydrolysis of PPPDTA would not be expected to be problematic in this study.

Seeded Emulsion Polymerizations. The seeded emulsion polymerization experiments used the diluted seed prepared by the acetone transport technique described above. Note that for the control experiments the seeds were still subjected to the acetone transport technique, but without the RAFT agent.

In a typical experiment, the latex from the acetone transport technique (65 g, 3.1% solids) was combined with sodium hydrogencarbonate (33 mg), sodium dodecyl sulfate (0.20 g), water (35 g), and styrene (4.0 g). Sodium persulfate solution (1 cm³, 0.042 mol dm⁻³) was added once thermal equilibrium had been reached. The buffer, initiator, and surfactant were all added as aqueous solutions, and the mixture was stirred throughout the process. The reactions were carried out at 50 °C, and the particle number (calculated using the particle size) in each reaction was about 1×10^{17} dm⁻³ (range 9.6×10^{16} – 1.2×10^{17} dm⁻³).

Dilatometry. The dilatometry experiments were carried out in a jacketed glass vessel approximately 100 cm³ in volume. The temperature was controlled using a water bath. The cold reaction mixture (without monomer and initiator) was thoroughly degassed under vacuum, backfilling with nitrogen. Once the reaction mixture had reached thermal equilibrium at the reaction temperature, the degassed initiator solution was added and the capillary topped up with decane. The height of the meniscus in the capillary was followed using a computer-controlled tracking device.

Rate data were extracted from the meniscus height data using the densities for styrene and polystyrene from Hawkett et al.^{22,23} Conversion of the final latex from each dilatometry experiment was determined by gravimetry and MWDs by gel permeation chromatography (GPC).

Sampled Reactions. These reactions were performed at the 250 cm³ scale as a direct scale-up of the dilatometry recipe presented above. As degassing under vacuum was not practical, nitrogen was bubbled through the reaction mixture for at least 1 h before polymerization commenced, and the reaction was carried out with a slight positive pressure of nitrogen. The reaction mixture was stirred using a three-blade turbine stirrer at 300 rpm. Samples of around 5 cm³ were taken periodically from the reactor using a syringe. The samples were quenched using hydroquinone and placed in an ice bath. Conversion and MWD data were collected for each of the samples.

Latex Characterization. Particle Sizing. For each of the latexes prepared, the particle size distribution was measured by a combination of Fraunhofer light scattering and polarization intensity differential scattering techniques using a Coulter LS230 instrument (lower size limit 40 nm diameter).²⁴ For each of the seeded experiments, the number-average diameter (between 84 and 100 nm) agreed with the predicted size to within 4%. Additionally, the shape and broadness of the distribution were unchanged, and neither new nucleation nor coagulum was observable. There were no systematic differences between RAFT and non-RAFT particle sizes.

The accuracy of the Coulter LS230 sizer for particles of this type was compared to that of a Matec CHDF (capillary hydrodynamic fractionator) using two other latexes ($\bar{r}_w = 55$ and 180 nm by CHDF).²⁵ The values of \bar{r}_w and \bar{r}_n obtained by CHDF were within 5% of those obtained by the Coulter LS230.

Molecular Weights. Molecular weight distributions were measured by GPC. Samples of dried latex were dissolved in THF (1 mg cm⁻³) and filtered using a 0.2 μ m PTFE filter. Analyses were carried out using four PLgel columns (three Mixed-C columns and one Mixed-E column, Polymer Labs). Injection volumes of 100 μ L were used with a Waters 410 differential refractive index detector and a flow rate of 1 cm³ min⁻¹. Cubic calibration curves were generated using 13 polystyrene standards (Polymer Labs) with molecular weights

ranging from 264 to 2.56×10^6 . GPC signal analyses were performed using the software GPC for Windows (Chemware).

GPC Signal Subtraction. For the seeded emulsion polymerization experiments, the molecular weight distribution that pertained to the new polymer formed was isolated from the raw GPC data using a method similar to that of Clay et al.²⁶ In this treatment, we use the raw GPC data and look only at the differences between new and old polymer, rather than using the calculated number distribution and pseudo-instantaneous distributions.

Consider two polymer samples, *seed* and *new*, that would give GPC DRI signals, g_{seed} and g_{new} , normalized to unit area. When samples of the polymer are mixed using masses m_{seed} and m_{new} , the resulting (normalized) GPC signal, g , will be

$$(m_{\text{seed}} + m_{\text{new}})g = m_{\text{seed}}g_{\text{seed}} + m_{\text{new}}g_{\text{new}} \quad (1)$$

given that the DRI response is linear in the mass of polymer in the detector.²⁷ Note that this also assumes that the calibration of the GPC is unchanged (e.g., when the samples are run sequentially).

Given that the experimentally measured signal will be $(m_{\text{seed}} + m_{\text{new}})g$, which may be normalized to unit area to yield g , the signal from just one of the components may be calculated to be

$$\frac{m_{\text{new}}}{m_{\text{seed}} + m_{\text{new}}} g_{\text{new}} = g - \frac{m_{\text{seed}}}{(m_{\text{seed}} + m_{\text{new}})} g_{\text{seed}} \quad (2)$$

Further taking into account the formation of the new polymer as a function of the mass of monomer added to the system, m_{mon} , and the fractional conversion for the sample, x

$$g'_{\text{new}} = g - \frac{m_{\text{seed}}}{m_{\text{seed}} + xm_{\text{mon}}} g_{\text{seed}} \quad (3)$$

where g'_{new} is an unnormalized GPC trace from the new polymer.

Signal subtraction may thus be performed using eq 3 to yield a GPC trace reflecting solely the contribution of the new polymer. It is important to note that even when the values of the coefficients in eq 3 were varied by $\pm 10\%$, the values of \bar{M}_n , \bar{M}_w , and the polydispersity index (\bar{M}_w/\bar{M}_n) were not significantly changed for the experiments reported here.

GPC Signal Debroading. In some low-conversion samples it was evident from the GPC trace that the GPC columns had separated the discrete populations of oligomers. In this case, it is reasonable to undertake a deconvolution of the signal to attempt to remove the effect of column broadening to clarify the oligomer distribution. Between 75 and 100 debroading cycles were applied, using a sharp solvent peak as the basis for the deconvolution, following of Tung et al.^{28–30}

Results and Discussion

Based on work by other authors, the first criterion for success of RAFT in an emulsion system is the colloidal stability of the latex during the course of the polymerization.^{7,11} In the polymerization experiments performed in this work, coagulum was rarely observed, and in the cases when some polymer was left as a vortex plug in the dilatometer, the amount of coagulum was insignificant (less than 0.5% of the total polymer). Moreover, highly colored creamed oils observed on the top of the reaction mixtures, as reported by other authors,^{7,11} were not seen at any stage during the polymerization experiments.

While some reduction in the rate of polymerization was observed (see below), the reaction was not retarded to the same degree as has been observed in previous studies.⁷

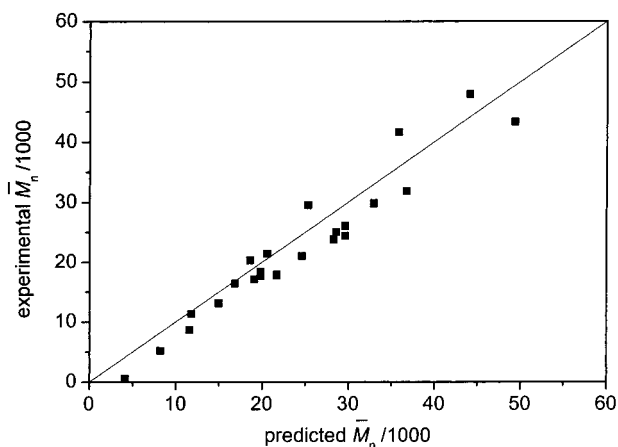


Figure 1. \bar{M}_n determined experimentally plotted against \bar{M}_n predicted by eq 4. While there is some scatter around the line of slope 1, good molecular weight control has been achieved. Each of the points on this plot has molecular weight polydispersity \bar{M}_w/\bar{M}_n less than 1.4 and in most cases 1.25 or better.

Molecular Weight Control. One of the features that characterizes a living system is the ability to control the molecular weight of the polymer produced. In the case of RAFT polymerization, this control is on the basis of the ratio $[\text{monomer}]/[\text{RAFT}]$, providing that the transfer constant, C_{tr} is greater than two.^{3,31} For a given mass of monomer, m_{mon} , and a given amount of RAFT agent, n_{RAFT} , in the system, this relationship may be formalized as

$$\bar{M}_n^{\text{pred}} = \frac{xm_{\text{mon}}}{n_{\text{RAFT}}} \quad (4)$$

where x is the conversion at which the sample was taken and \bar{M}_n^{pred} is the target \bar{M}_n . This relation holds for bulk, solution, and emulsion polymerizations in both intervals 2 and 3 (presence and absence of monomer droplets), with the proviso in the case of interval 2 polymerizations that the RAFT agent is at the locus of polymerization (i.e., in the particles) and that significant uncontrolled droplet polymerization is absent. For good control of the molecular weight, the value of \bar{M}_n should also be lower in a RAFT system than in a control reaction.

A number of \bar{M}_n values determined in this study are shown in Figure 1. It may be seen that the control of \bar{M}_n in these systems is quite good, although there is some scatter around the 45° line. Importantly, each of these samples shown in this plot has molecular weight polydispersity, \bar{M}_w/\bar{M}_n , less than 1.4 and in most samples 1.25 or better. The data shown include experiments carried out in both intervals II and III, along with a wide range of $[\text{RAFT}]/[\text{I}]$ and $[\text{monomer}]/[\text{RAFT}]$ conditions.

The \bar{M}_n and polydispersity values for the control reactions could not be determined as the polymer formed had significant amounts of material in excess of the exclusion limit of the columns (molecular weight around 6×10^6). This implies a significant molecular weight reduction compared to polymer prepared in the same conditions in the absence of RAFT agents.

The molecular weights reported here are similar to those generated in other seeded RAFT/emulsion systems that showed poor molecular weight polydispersity,^{7,11} indicating that previously reported failures were not due to an insurmountable limitation of RAFT/emulsion systems.

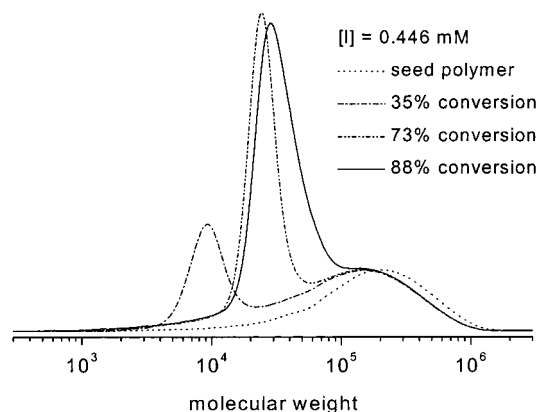


Figure 2. Molecular weight distributions for a seeded polymerization at $[I] = 0.446$ mM, $[RAFT]/[I] = 2.75$, and $[monomer]/[RAFT] = 324$. MWD traces were rescaled so that the seed polymer peak was the same height in each plot.

Evolution of the Molecular Weight Distribution.

For a RAFT agent with a transfer constant $C_{tr} \gg 1$, such as the one used here, evidence of living character in a homopolymerization is seen in the linear increase of \bar{M}_n with conversion. From the sampled reactions, the evolution of the molecular weight distribution may be observed. In each of the molecular weight distributions presented here, the contribution to the signal of seed polymer is still present, although this was subtracted for the calculation of \bar{M}_n and \bar{M}_w as described above.

The evolution of the MWD follows the expected behavior for a living polymerization system, rather than following the typical progress of a normal emulsion polymerization experiment. In each experiment, the molecular weight distribution shows a comparatively sharp peak of new polymer superposed onto the seed polymer peak. Two representative MWD evolutions are shown in Figure 2 and Figure 3. The value of \bar{M}_n from each of these experiments is plotted against conversion in Figure 4, showing a linear increase of \bar{M}_n as a function of conversion.

It is interesting to note the low molecular weight region of the lowest conversion sample in Figure 3. Enlarged in Figure 3b, this sample shows the presence of polymer with molecular weight around 1000. Apply-

ing column-debroadening algorithms to this trace, the debroadened MWD in Figure 3b is obtained. Since the presence of the oligomeric species is already evident from the original MWD, the debroadening algorithm provides a guide to the eye to assist in the estimation of the spacing between the peaks. Indeed, the spacing observed is around 100 in molecular weight, consistent with the assignment of these peaks to oligomeric species. As this peak is not evident in subsequent traces (even at higher magnifications than presented here), and it lies on the \bar{M}_n vs conversion curve shown in Figure 4, it can be concluded that these molecules are oligomeric species with living character (presumably the dormant form of the growing chain in the RAFT mechanism) that have subsequently grown in molecular weight.

While Figure 4 shows a linear increase of \bar{M}_n as a function of conversion as expected for a living system, the linear fit for the higher initiator experiment does not pass through the origin (i.e., predicted \bar{M}_n values are consistently higher than the experimental value at all conversions). This effect is consistent with increased termination in the system, although the effect does not appear to be large.

Rate of Polymerization. One common characteristic of living polymerization systems is a reduction in the rate of polymerization, although the extent of this effect appears to be RAFT-agent dependent.³ In the case of RAFT/emulsion systems, previous studies have shown significant reduction in the rate of polymerization.^{11,14} The systems presented here are no different; the addition of RAFT agent to the system leads to both an increase in the inhibition period and a retardation in the polymerization rate.

In this system, inhibition periods of 45 min to 3 h were seen, accompanied by a reduction in the rate of polymerization to between 30 and 50% of its previous value, as shown in Figure 5.

It is interesting to note from this plot that increasing the initiator concentration by a factor of about 9 appears to remove these detrimental effects. Moreover, at this higher initiator concentration, good molecular weight control and narrow polydispersity are still seen, as seen in Figures 3 and 4, although it should lead to the

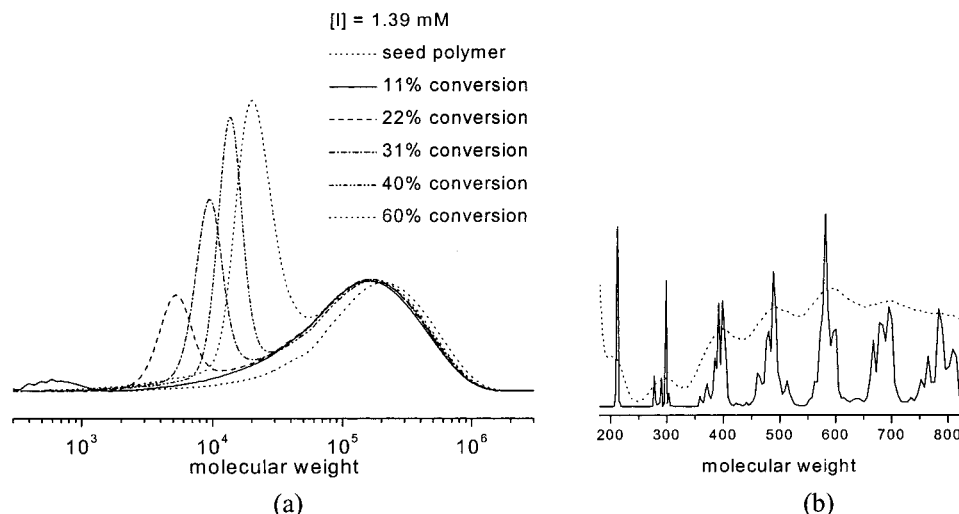


Figure 3. (a) Molecular weight distributions for a seeded polymerization at $[I] = 1.39$ mM, $[RAFT]/[I] = 0.93$, and $[monomer]/[RAFT] = 360$. (b) Low molecular weight region of the 17% conversion sample showing the original data (dotted line) and the debroadened data (solid line). The debroadened data indicated the peaks are around 100 separation in molecular weight. MWD traces were rescaled so that the seed polymer peak was the same height in each plot.

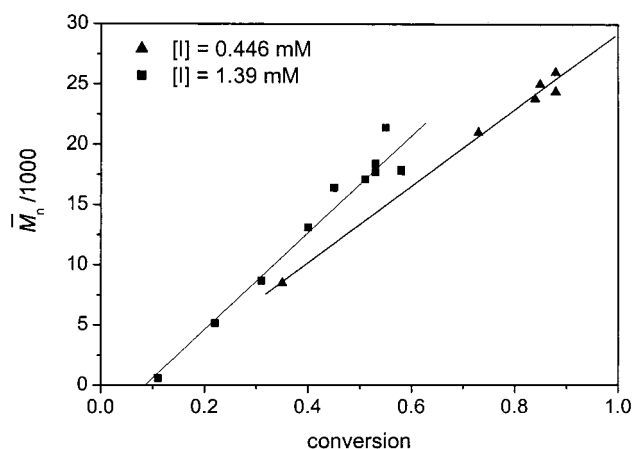


Figure 4. \bar{M}_n as a function of conversion for the seeded polymerizations shown in Figures 2 and 3. Each of the points on this plot has molecular weight polydispersity $1.2 < \bar{M}_w/\bar{M}_n < 1.4$. While both sets of points lie on straight lines as expected, the plot for the higher initiator concentration system does not pass through the origin.

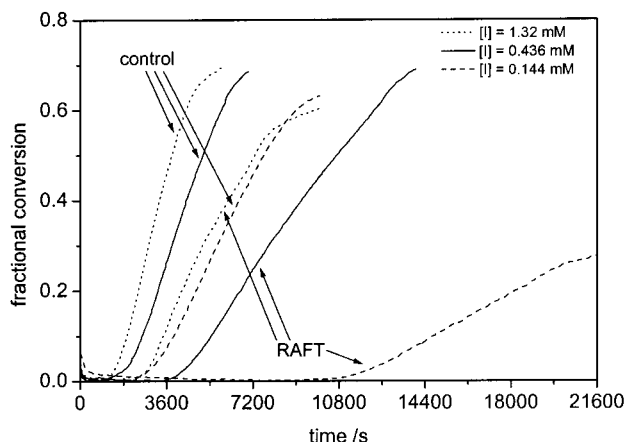


Figure 5. Conversion vs time plots showing the effect of adding the RAFT agent to the emulsion polymerization system at varying initiator concentrations: 1.32 mM (dotted line), 0.436 mM (solid line), and 0.144 mM (dashed line). In each case, the addition of the RAFT agent leads to a longer inhibition period and slower rate of polymerization compared to the control reaction.

production of more dead chains.¹ Using higher initiator concentrations may provide a suitable way of overcoming the twin problems of the inhibition period and reduction in polymerization rate.

Mechanistic Discussion. While this study has shown that RAFT/emulsion systems may be successfully used to make controlled molecular weights, there are still some difficulties to be addressed. In particular, the mechanisms involved in the inhibition, retardation, and RAFT agent transport are unknown.

While it is desirable to compare the rates of polymerization in these RAFT/emulsion experiments to previous studies (such as those of Monteiro et al.^{5,11}), it should be recognized that the rate of polymerization is a poor measure of the performance for an emulsion polymerization. Instead, the quantity that should be compared is the average number of *propagating* (not bipolymeric intermediates) radicals per particle, \bar{n} , which removes variations due to minor changes in particle size and particle number concentration.¹⁵ As discussed below, even measuring \bar{n} is a somewhat fruitless task until new models to describe RAFT/emulsion behavior are developed.

Inhibition and Retardation. The causes of the increased induction period and retardation are unclear at this stage. While RAFT techniques in solution polymerization are known to sometimes produce a small induction period and a reduction in the polymerization rate (depending on the RAFT agent used),^{2,3} the induction periods and retardation seen in emulsion systems are more significant. It appears likely that these effects have both a chemical and physical cause.

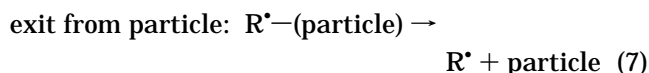
Evidence from solution polymerization experiments indicates that there is a portion of the inhibition period that may be linked to the chemical nature of the cumyl radical.³ It has been postulated that the cumyl radical may be quite poor at reinitiating by analogy with the behavior of poly(α -methylstyrene),³ although previous radical addition studies do not support this conclusion.^{32,33} However, the reaction of cumyl radicals with the original RAFT agent in preference to the reaction with monomer may go some way to explaining the retardation seen in solution polymerization.³ Indeed, the observed retardation with cumyl-based RAFT agents is significantly greater than with cyanoisopropyl-based RAFT agents.³

Other authors have postulated that the exit of the RAFT leaving group (the cumyl radical in this study) from the latex particle is the primary cause of the inhibition period.^{11,14} This is certainly a distinct possibility, as the high diffusion coefficient of the cumyl radical allows it to exit quite rapidly,¹¹ and for that reason we now examine this in detail from a theoretical viewpoint. Following the method described by Monteiro et al.,¹¹ it is possible to express the probability that the cumyl radical will exit the latex particle in terms of the first-order rate coefficient for the desorption of the radical, k_{dR} , and the rate coefficient for the addition of the radical to monomer, k_{add}^R :

$$P(\text{exit}) = \frac{k_{dR}}{k_{dR} + k_{add}^R C_p} \quad (5)$$

where C_p is the concentration of monomer in the particle.

It is important to note that there are three possible processes that the cumyl radical may undergo (with the monomer, M, and the particle):



However, the reaction shown in eq 8 does not actually change the concentration of R^* in the particle. This reaction may thus be ignored in the model, allowing the event scheme to be reduced to the processes in eqs 6 and 7, yielding eq 5 from the (pseudo)-first-order rate coefficients. A full mathematical exposition of this argument is set out in the Appendix.

The desorption of a radical may be expressed as a diffusive process:³⁴

$$k_{dR} = \frac{3D_w^R C_w^R}{r_s^2 C_p^R} \quad (9)$$

Table 1. Parameters (from a Typical Experiment) for Calculating the Probability of Exit of a Cumyl Radical from a Latex Particle, $P(\text{exit})$

parameter	value
r_s/nm	45
C_w^R/C_p^R	6.2×10^{-4}
$D_w/\text{cm}^2 \text{ s}^{-1}$	1.6×10^{-5}
$C_p/\text{mol dm}^{-3}$	5.5

Table 2. Rate Coefficient for the Addition of a Cumyl Radical onto Styrene and the Probability of Exit of a Cumyl Radical from a Latex Particle, $P(\text{exit})$

$k_{\text{add}}^R/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$P(\text{exit})$
1.3×10^3 ^a	0.19
2.86×10^3 ^b	0.098

^a Based on the method described by Monteiro et al.;¹¹ see text.^b Using the experimental data from Fischer et al.^{32,33}

where D_w is the diffusion coefficient of the small radical in water, r_s is the swollen radius of the particle, and C_w^R and C_p^R are the equilibrium concentrations of the cumyl radical in the water and particle phases, respectively. It will be seen that these C_w^R and C_p^R terms can prove rather difficult to estimate, depending on the monomer and radical involved.

Monteiro et al.¹¹ implicitly assumed that the cumyl radical is similar enough to styrene so that the equilibrium concentration of cumyl radicals may be expressed as a mole fraction of the equilibrium concentration of styrene molecules. This is in line with the method of Ugelstad et al.^{15,34} for the determination of the rate coefficient for the desorption of the monomeric radical. Writing the mole fraction of cumyl radicals on styrene radicals as χ_R , C_w^R and C_p^R may be written as

$$C_w^R = \chi_R C_w \quad (10)$$

$$C_p^R = \chi_R C_p \quad (11)$$

The ratio C_w^R/C_p^R for the cumyl radical in the presence of styrene may thus be approximated as

$$\frac{C_w^R}{C_p^R} = \frac{\chi_R C_w}{\chi_R C_p} = \frac{C_w}{C_p} \quad (12)$$

where C_w and C_p are the concentrations of styrene in the water and particle phases, respectively. While this approach would appear to be valid for a cumyl radical in a styrene/polystyrene matrix, its applicability to other non-styrene-like radicals (such as the ethyl methacrylate radical¹¹) in a styrene/polystyrene matrix is unclear.

Additionally, D_w will be similar to that of styrene. Monteiro et al.¹¹ further suggested that a reasonable approximation for k_{add}^R was $5k_p^{\text{sty}}$, where k_p^{sty} is the rate coefficient for the propagation for styrene radicals from pulsed laser polymerization data.³⁵ Alternative values for k_{add}^R may be obtained from the experimentally determined Arrhenius parameters of Fischer et al.^{32,33}

The values for the parameters used in the calculation of $P(\text{exit})$ are summarized in Tables 1 and 2, along with the calculated values of $P(\text{exit})$. It is interesting to note that the value of $P(\text{exit})$ is quite sensitive to the parameter k_{add}^R . Even so, in both of the estimates of $P(\text{exit})$ prepared here, the actual probability of a cumyl

radical exiting is quite low. This tends to suggest that the influence of radical exit may be less than first supposed.

Nevertheless, a small amount of exit will lead to a reduction in polymerization rate,³⁶ as there are the possibilities of aqueous phase termination between the cumyl radical and other radicals and reentry of the cumyl radical into a growing particle leading to rapid termination. It is important to note that the exit of radicals only has the potential to explain retardation or inhibition in the first few percent of conversion, as after that time all the initial RAFT agent has been converted to the dormant species on a chain end. Obviously, to understand these effects, more experimental work accompanied by suitable modeling of these systems is required.

Another possibility for the retardation is some surface activity of the RAFT agent; this effect has been used to explain retardation in RAFT/emulsion systems using xanthates as the RAFT agent.¹⁴ This surface excess of transfer agent is thought to cause an increase in the exit rate coefficient and a decrease in the entry rate coefficient. However, it is felt that the present case with **1**, PPPDTA, is unlikely to show significant surface activity.

Two additional mechanisms for retardation in RAFT systems have been recently proposed. Both mechanisms involve the intermediate bipolymeric radical ($P_n\text{--S--CZ--S--P}_m$) in the RAFT equilibration reaction. Barner-Kowollik et al.^{20,37} reported that kinetic simulations of bulk RAFT reactions indicated that this radical may be long-lived enough so as to cause significant amounts of retardation. Monteiro et al.¹² suggested that this radical may become involved in a termination reaction with other polymeric radicals in the reaction, thus retarding polymerization.

While both of these mechanisms offer insights into the retardation seen in bulk and solution polymerization, they do not explain why these effects are worse in emulsion polymerization. Now, for styrene, the particle size of the system studied here is such that it should follow "zero-one" kinetics;¹⁵ entry of a radical from the aqueous phase into a particle already containing a growing radical results in virtually instantaneous termination. It is worth noting that the intermediate radical termination mechanism¹² would not lead to retardation in an emulsion polymerization following zero-one kinetics; the compartmentalization of radicals means that an oligomeric radical has to enter the particle before the intermediate radical termination reaction could take place, but the "zero-one" assumption¹⁵ indicates that termination should take place pseudo-instantaneously even in the absence of RAFT and this mechanism.

RAFT Agent Transport. As discussed in the Introduction, it is postulated here that the one of the principal problems experienced in other studies is the transport of RAFT agent to the locus of polymerization. These problems may be either kinetic or thermodynamic in origin. The experimental results presented here and those of other recent studies of RAFT/emulsion systems are consistent with this postulate.

Thanks to the work of many authors, a general pattern may now be observed in the literature. It has been suggested that RAFT agents with some surface activity^{7,14} may be used in emulsion polymerization without considerable difficulty. This may be mechanistic

cally justified by considering the effects of the RAFT agent on the aqueous-phase chemistry and the transport of the RAFT agent from monomer droplets to the locus of polymerization (the particles):

(i) If a RAFT agent is quite hydrophobic, its water solubility is small enough (especially after one or more addition–fragmentation steps have occurred within a monomer droplet) so as to prevent it from reaching the particles¹¹ early enough in the reaction to commence controlled polymerization (as all RAFT agents should undergo their first fragmentation quite early in the reaction, or else molecular weight control will be poor³).

(ii) If a RAFT agent is quite water-soluble, considerable chain transfer will occur in the water phase. Hence, it will take quite some time for z -meric species (oligo-radicals that are capable of entering a particle^{15,38}) to be formed. In such a situation, the RAFT agent becomes an effective inhibitor.⁷

(iii) If a RAFT agent is surface active,^{5,6,13,14} it may have enough water solubility to transport across the aqueous phase from the droplets to the particles, but the relatively low water solubility associated with its surface activity will keep it out of the aqueous phase chemistry. Even still, partitioning of the RAFT agent between droplets and particles may lead to poor control of \bar{M}_n .⁵

While experimental proof of these suggestions is still quite limited, all available data on RAFT/emulsion polymerizations are consistent with these postulates.

It may be expected that the RAFT agent could diffuse back out of the particles once polymerization has started; however, the relatively fast rate of addition of styrenic radicals to PPPDTA^{20,37} should mean that all the PPPDTA is consumed to form polystyryl-PPPDTA adducts (the dormant species) within the first few percent conversion.³¹ Moreover, as the water solubility of PPPDTA is immeasurably low (below the impurity level of the sample prepared here), the RAFT agent would not be expected to have a significant impact on the entry of radicals into latex particles.^{15,38}

Conclusions

The key result of this work is that RAFT techniques can be successfully applied to seeded emulsion polymerization systems, producing controlled molecular architectures and retaining living character. Evidence of the living character of these systems was seen in the control of the final molecular weight based on the amount of RAFT agent used, the evolution of the molecular weight distribution as a function of conversion, and the low polydispersities of the polymers obtained.

Some detrimental effects of the use of RAFT agents in emulsion polymerization systems are also noted, namely significant inhibition periods and a reduction in the rate of polymerization. These difficulties were overcome by using higher levels of initiator; this did not appear to compromise living character.

The extension of the acetone transport technique outlined here to other RAFT agents and other monomers is a natural next step in the implementation of RAFT/emulsion techniques. Further experimental and concomitant modeling work is required to fully understand the inhibition and retardation effects seen in RAFT/emulsion systems. Using the experimental techniques described here decouples RAFT agent transport from other RAFT/emulsion behaviors, allowing the

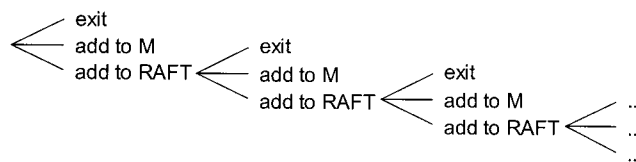


Figure 6. First three steps of the event scheme for the cumyl radical in a styrene/polystyrene particle, described by in eqs 6–8.

chemical and physical aspects of inhibition and retardation to be more easily elucidated.

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Appendix: Simplification of $P(\text{exit})$ Model

In calculating the probability of a process occurring, complications arise within event models when one or more reactions are reversible or have some products that are also reactants. It will be shown that while these make diagrams of the event model much more complex, they may be readily simplified and that the additional reactions may often be neglected.

Let us consider the specific example of cumyl radicals and styrene monomer in a polystyrene particle. The three processes that may occur are shown in eqs 6–8 in the text. The event model for this system is quite complicated; in the first instance it should be drawn as shown in Figure 6 where the series continues ad infinitum.

Mathematical Abstraction and Simplification. First, it is necessary to define some notation for this exercise. For simplicity of notation, let us commence by using events “A”, “B”, and “C” rather than the more complicated chemical descriptors “exit”, “add to M”, and “add to RAFT”.

Next, define the number of A events at step i to be $n_i(A)$, the total number of A events be $n(A)$, and the probability of an A event occurring $P(A)$, with similar definitions for B and C events. The final value for $P(A)$ is thus

$$P(A) = \frac{n(A)}{n(A) + n(B) + n(C)} \quad (\text{A1})$$

which may be reexpressed in terms of infinite series:

$$P(A) = \frac{\sum_{i=1}^{\infty} n_i(A)}{\sum_{i=1}^{\infty} n_i(A) + \sum_{i=1}^{\infty} n_i(B) + n_{\infty}(C)} \quad (\text{A2})$$



Figure 7. Mathematically simplified event scheme for the abstracted system.

The numerator of eq A2 may be rewritten in terms of the $n_i(C)$:

$$\sum_{i=1}^{\infty} n_i(A) = P(A)n + P(A)n_1(C) + P(A)n_2(C) + \dots \quad (\text{A3})$$

which in turn may be expressed as the sum of a geometric progression, since $n_i(C) = n[P(C)]^i$:

$$\sum_{i=1}^{\infty} n_i(A) = P(A)n \sum_{i=0}^{\infty} P(C)^i \quad (\text{A4})$$

A similar expression for $n(B)$ in terms of $P(B)$, n , and $P(C)$ may be readily obtained.

Since the allowable range for $P(C)$ is $0 \leq P(C) < 1$ (the case $P(C) = 1$ is a trivial case in which pathways A and B do not actually exist), the two limit expressions may be readily evaluated:

$$\sum_{i=0}^{\infty} P(C)^i = \frac{1}{1 - P(C)} \quad (\text{A5})$$

$$n_{\infty}(C) = 0 \quad (\text{A6})$$

This allows eq A2 to be simplified to be

$$P(A) = \frac{\frac{P(A)n}{1 - P(C)}}{\frac{P(A)n}{1 - P(C)} + \frac{P(B)n}{1 - P(C)} + 0} \quad (\text{A7})$$

Recognizing that by definition $P(A)n = n_1(A)$ and $P(B)n = n_1(B)$, this may be rewritten as

$$P(A) = \frac{n_1(A)}{n_1(A) + n_1(B)} \quad (\text{A8})$$

which is equivalent redrawing the original event model as shown in Figure 7. This may be readily applied to the specific case of the RAFT polymerization outlined above.

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