

The Influence of RAFT on the Rates and Molecular Weight Distributions of Styrene in Seeded Emulsion Polymerizations

MICHAEL J. MONTEIRO, MARCELLE HODGSON, HANS DE BROUWER

Department of Polymer Chemistry & Coatings Technology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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ABSTRACT: Seeded emulsion polymerizations of styrene in the presence of two reversible addition–fragmentation chain-transfer (RAFT) agents were studied. We designed the seed to be small to observe the effects of exit and, we made the seed of poly(methyl methacrylate) so that the molecular weight distributions of poly(styrene) by gel permeation chromatography could be obtained independently by UV detection. The rates were significantly retarded by the presence of a RAFT agent, with the retardation being greater with an EMA RAFT agent [2-(ethoxycarbonyl)propyl-2-yl dithiobenzoate] than with a cumyl RAFT agent (2-phenylprop-2-yl dithiobenzoate). We propose that exit from the particles after fragmentation was the main cause of retardation. In addition, the number-average molecular weight and polydispersities (broad) did not resemble the characteristic living behavior found in bulk or solution. This was a result of the continuous transportation of RAFT agent into the particles during interval II and the transportation of a small amount during interval III. A conspicuous red layer was also observed at the beginning of the polymerization. The red layer consisted of low molecular weight dormant species swollen with monomer. Once the switch from interval II to interval III occurred, the low molecular weight species coalesced to form a red coagulant. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 3864–3874, 2000

Keywords: RAFT; emulsion polymerization; free radical; living; seeded

INTRODUCTION

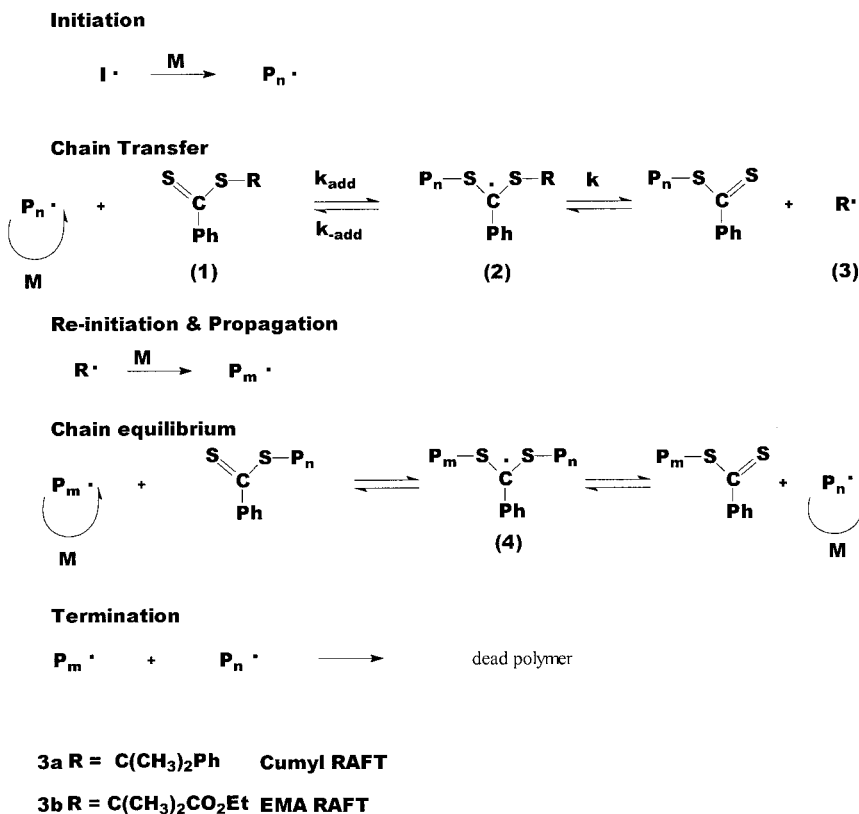
Recently, a new living free-radical technique has been developed using the reversible addition–fragmentation chain-transfer (RAFT) process.^{1–4} The process, as shown in Scheme 1, relies first on the chain transfer of active species ($P_n \cdot$) to the RAFT agent (1), which then undergoes fragmentation to reinitiate polymerization. The active moiety from the RAFT agent is now attached to the polymeric chain end, making it a dormant species. Once the RAFT agent is consumed, equi-

librium is established between active and dormant species. The living character is very much dependent on the chain-transfer constant of the active species to the dormant chain end ($C_{tr,RAFT}$). If $C_{tr,RAFT}$ is much greater than 1, living behavior, as exhibited by a linear increase in number-average molecular weight (\bar{M}_n) and low polydispersities (PDs), can be found.⁵ However, as with all free-radical processes, this process is influenced by the amount of bimolecular radical termination, and the radical concentration in these systems must, therefore, be much lower than the RAFT agent concentration. Therefore, the application of this technique in bulk and solution is limited by the low rates of polymerization.

Emulsion polymerization provides an ideal alternative for overcoming this problem. High rates

Correspondence to: M. J. Monteiro (E-mail: m.j.monteiro@tue.nl)

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Scheme 1. General mechanism of the RAFT process.

with low termination are found in emulsions because of the compartmentalization of the radicals in individual particles; radicals in one particle have no access or contact with radicals in another. High rates are achieved by the number of particles being controlled by the choice of surfactant and initiator concentrations. In conventional emulsion polymerization, very high molecular weights are found,⁶ showing that bimolecular termination is not prevalent; therefore, the main-chain stopping events are primarily through transfer to monomer.

An important aspect of the RAFT process in emulsion that needs to be considered is the effect of the exit of the transfer species (3) on the rate and control of the molecular weight. Lichti et al.⁷ found that the addition of the transfer agent CBr₄ in seeded emulsion significantly retarded the rate of polymerization. In a more complete study of the kinetics⁸ (via γ relaxation) of the transfer for CBr₄ and CCl₄, they found that the exit of the incipient transferred radical from the particles was the main source of retardation. The fate of these radicals⁹⁻¹¹ depended on the radical concentration in the aqueous phase. Cross-termina-

tion of the exited radical occurred primarily with (1) radicals in the aqueous phase when the radical concentration was high and (2) radicals in the particles via reentry when the radical concentration was low. The results also supported that during interval II, exit is under diffusion control, where the size of the particles, the diffusion coefficient, and the partition coefficient of the exited free radical in the water phase determine the exit rate coefficient.¹²

The heterogeneity of emulsion polymerizations results in a mechanism of a complex nature.¹³ The work described so far^{1,2} with RAFT in emulsions was carried out under semibatch conditions with unusual feed conditions. It was done this way presumably so that all the RAFT agent reacted inside the particles at the beginning of the reaction. However, the two-film theory¹³ suggests that the rate of diffusion of RAFT agent from the droplets to the particles should be at the rate of transfer. This is only satisfied if the RAFT agent used has a high diffusion coefficient. Therefore, living behavior should be exhibited in the presence of droplets. Uzulina et al.¹⁵ found that living characteristics were observed with up to a 40%

flocculation. They attributed this to slow diffusion of RAFT to the particles.

The aim of this work was to gain insight into the mechanisms operating for the RAFT process in the presence of droplets. Seeded systems are extremely useful for this purpose because they eliminate many variables and can be used to explore the effects of exit and droplets on the rate and control of molecular weight in RAFT systems. Two RAFT agents with similar $C_{tr,RAFT}$ values were used in this study (see Scheme 1), each having a different leaving group (**3**).

BACKGROUND THEORY AND EXPERIMENTAL DESIGN

Probability of Exit for **3**

Exit can reduce the rate significantly.⁸ The more water-soluble the leaving group (**3**) is, the greater the extent of exit is.¹⁶ The leaving radicals from cumyl RAFT (2-phenylprop-2-yl dithiobenzoate) and EMA RAFT [2-(ethoxycarbonyl)propyl-2-yl dithiobenzoate] are cumyl radical (**3a**) and 2-(ethoxycarbonyl)prop-2-yl radical (**3b**), respectively. The coefficient for desorption of a monomeric free radical (exit) from a particle with swollen radius r_s is given by the following:¹²

$$k_{dm} = \frac{3D_w C_w}{r_s^2 C_p} \quad (1)$$

The probability of exit can then be determined with eq 2:

$$P(\text{exit}) = \frac{k_{dm}}{k_{dm} + k_p^1 C_p} \quad (2)$$

where D_w is the diffusion coefficient of **3** in water, C_w and C_p are the concentrations of **3** in the aqueous phase and particle, respectively, and k_p^1 is the propagation rate coefficient for **3** to monomer. With the approximation that D_w was 1.6×10^{-5} for the two radicals and C_w was similar to the monomer equivalent, $P(\text{exit})$ was determined (see Table I). **3b** had a far greater probability of escape than **3a**. This suggests that retardation should only be effective when RAFT agents are present in the system. With a high value for $C_{tr,RAFT}$ assumed (found experimentally¹⁷ to be approximately 6000 for polymeric RAFT agents), all the RAFT agent should be consumed in the

Table I. Probability of Escape, $P(\text{exit})$, Determined for RAFT Agents with Leaving Groups **3a** and **3b**

	3a	3b
k_p^1	1705	9390
k_{dm}	3.98×10^3	6.89×10^4
$P(\text{exit})$	0.29	0.56

^a k_p^1 was determined for **3a** by $\langle kp \rangle$ (STY)³² by being multiplied by 5 (comparable for small radical reactions); for **3b**, $\langle kp \rangle$ (EMA)³³ was multiplied by 5 and also by 2 to compensate for the reactivity ratio of EMA to STY.

^b The unswollen radius was 20 nm, which gave a swollen radius of 29.5 nm.

first few percentage points of monomer conversion (see eq 5). After this conversion, exit should no longer be the dominant retardation mechanism.

Molecular Weights and PDs in the RAFT Systems

The equations used to predict the molecular weight and PD of a polymer produced by the RAFT method in bulk or solution were those derived by Müller et al.⁵ for living processes involving active and dormant species. The equations were obtained via the method of moments. For $C_{tr,RAFT}$ much greater than 1, the \bar{M}_n and PD can be closely approximated by the following expressions:

$$\bar{M}_n(\text{theory}) = \gamma x M_o \quad (3)$$

$$PD = \frac{1}{\gamma x} + \frac{1}{x} \left[2 + \frac{\beta - 1}{\alpha - \beta} (2 - x) \right] - \frac{2\alpha(1 - \alpha)}{(\beta^2 - \alpha^2)x^2} [1 - (1 - x)^{1+\beta/\alpha}] \quad (4)$$

where γ is $[M]_o/[RAFT]_o$, M_o is the molar mass of the monomer, x is the fractional conversion, α is $[P_n \cdot]/[RAFT]$, and β is $C_{tr,RAFT}$. The concentration of RAFT as a function of conversion is given by the following expression:

$$[RAFT]_x = (1 - \alpha)[RAFT]_0(1 - x)^\beta \quad (5)$$

The assumptions made in these expressions are that the steady-state radical concentration ($[P_n \cdot]$) is very low, the efficiency of the RAFT agent is 100%, and bimolecular termination events are negligible. Equations 3 to 5 can be used as a good approximation for seeded emulsion po-

lymerizations if the RAFT agent transports from the droplets to the particles at the rate of transfer during Interval II (see ref. 13 for definitions of the various Intervals).

Experimental Design

Design of the Seed

The design of the seed is crucial for understanding the events that control the molecular weight distribution (MWD). The size of the seed must be as small as possible to explore the effects of exit because exit is proportional to the inverse of the particle radius squared (see eq 1).^{16,18} However, the seed must have a minimum size; otherwise, the concentration of monomer will change drastically during particle growth. This, to a good approximation, is determined by the Morton equation^{19,20} and shows that for particles with unswollen radii greater than 20 nm, the monomer concentrations inside the particles remain relatively constant during interval II. Therefore, the unswollen seed radius for these styrene polymerizations was chosen to be approximately 20 nm.

In addition, a heteroseed, consisting of poly(methyl methacrylate) (PMMA), was used so that we could only observe the MWD of polystyrene by UV detection ($\lambda = 254$ nm) because PMMA is invisible at this wavelength. For these experiments, polymer immiscibility was neglected. This assumption seemed valid because of the presence of monomer (which acts as a plasticizer), the very small size of the seed, and the low molecular weight polymer being produced. Another important design parameter was that the number of particles had to be high to avoid secondary nucleation.²¹ Therefore, the N_c value, the number of particles per unit volume of water, chosen for this work was approximately 4×10^{17} .

Polymerizations in Seeded Systems

The experimental conditions were chosen so that the changeover from interval II to III occurred close to a 10% conversion. This still gave us information on the influence of droplets and its effect on the MWD. In addition, the effects of exit and transportation of RAFT on the rate up to the changeover were studied.

Deviations from Zero–One Conditions

Zero–one conditions are obeyed when the size of the seed is sufficiently small such that the entry

of a z -mer²² radical [e.g., $^{-}\text{SO}_4(\text{STY})_z$] into a particle already containing a growing chain results in instantaneous termination. The criteria for zero–one conditions were described by Maeder and Gilbert.²³ In simple terms, it depends on the probability of termination upon the entry of a small radical to the probability of propagation to form a polymer.

Based on the mechanism of the RAFT process, the system may not obey the zero–one condition. For example, if the entry of a z -mer should react first with a dormant species, a long polymeric radical (active species) is formed. This can either react with the monomer or terminate with the already growing chain. The chances of long–long chain termination are highly unlikely, so the probability of bimolecular termination is reduced significantly. This means that two or more radicals can reside in the same particle. In the presence of RAFT, the probability of termination was calculated with eq 6, where the same formalism and values as those of Maeder and Gilbert²³ were used. The results that follow are based on the seeded system starting in interval II:

$P(\text{termination})_z$

$$= \frac{\frac{k_t^{zL}}{N_A V_s}}{\frac{k_t^{zL}}{N_A V_s} + k_p C_p + k_{tr, \text{RAFT}} [\text{RAFT}]_p} \quad (6)$$

The dormant species concentrations inside the particles, $[\text{RAFT}]_p$, were 1.5×10^{-3} and 10.5×10^{-3} mol dm⁻³, which were the lowest and highest RAFT agent concentrations used in this study. The value $z = 3$ was used for styrene;^{13,18,22} in addition, an unswollen radius of 20 nm was used.

The probability of termination without RAFT was 0.82, but this probability increased rapidly to 1 as the chain grew. The addition of RAFT decreased the probability to 0.65 and 0.28 for $[\text{RAFT}]_p$ of 1.5×10^{-3} and 10.5×10^{-3} mol dm⁻³, respectively. The results clearly show that zero–one conditions may not hold when high concentrations of RAFT are used. However, the chain length of the dormant and active species was a function of both the RAFT agent concentration and conversion according to eq 3. Consequently, the long–long termination assumption used may not hold up to conversions of approximately 10%. Nevertheless, this shows that the RAFT system

Table II. Recipe for the Preparation of PMMA Seed (with an Unswollen Radius of ~ 20 nm) at 90 °C

	Amount (g)
Deionized water	821.0
Aerosol MA 80 (surfactant)	14.11
NaHCO ₃ (buffer)	1.074
Methyl methacrylate	130.0
KPS (initiator)	3.631

can deviate from zero–one conditions simply through an increase in the amount of dormant species (or initial RAFT agent).

EXPERIMENTAL

Materials

Styrene and methyl methacrylate (Aldrich) were purified of inhibitor by being passed through an inhibitor-removal column (Aldrich). Sodium dodecylsulfate (SDS; Fluka) and sodium peroxodisulfate (Merck) were used as received.

RAFT Agents

The two RAFT agents, cumyl RAFT and EMA RAFT (see Scheme 1), were synthesized according to the method used by Rizzardo et al.¹

Preparation of the PMMA Seed Latex

The recipe for the preparation of the PMMA seed latex is given in Table II. The surfactant, buffer, and most of the water were charged to a 1.3-L stainless steel reactor with baffles, and the reactor contents were allowed to reach 90 °C. The reactor contents were then degassed by argon being bubbled through the mixture for 1 h with stirring. Methyl methacrylate monomer (from which the inhibitor had been removed by being passed through an inhibitor-removal column) was then added to the reactor and allowed to stir for 5 min. Initiator that had been dissolved in the remaining water was then added to the reactor, after which the polymerization was allowed to proceed for 3 h. The resulting latex was dialyzed for 2 weeks, with twice daily changes of the deionized water to remove residual contaminants. The solids content after the dialysis of 5.8% was much lower than expected because of coagulation.

The number-average diameter of the PMMA seed was determined to be 43.8 nm by capillary hydrodynamic fractionation (CHDF) techniques (Matec Applied Sciences CHDF 2000 2.73) and 39.4 nm by dynamic light scattering (Malvern 4700 multiangle light scatterer with PCS for Windows). This strongly supports the production of a narrow particle size distribution. The PMMA seed was diluted in the seeded studies to give an N_c value of 4.37×10^{17} , which was above the critical particle number needed to avoid secondary nucleation.

Procedure for the Seeded Polymerizations

The PMMA seed latex (50 mL) was measured into the dilatometer reactor, and 78 mL of deionized water was added to the reactor to achieve a solids content of approximately 2.8% and an N_c value of 4.37×10^{17} . Argon was then bubbled through the stirred latex at 60 °C for 30 min. A small portion of SDS (0.032 g, well below its critical micelle concentration) was then added to prevent coagulation during the reaction. Styrene (purified by being passed through an inhibitor-removal column) and RAFT agent were then added to the dilatometer reactor, and swelling was allowed to proceed overnight at 60 °C.

KPS was dissolved in deionized water, heated to the reaction temperature, and then added to the reactor through the septum. The volume of water used was added carefully so that the reaction mixture would be forced up slightly into the dilatometer bore. We observed the start of the reaction by monitoring the decrease in the height of the reaction mixture in the capillary tube.

Samples were drawn at regular intervals for the gravimetric determination of conversion. The dried samples were then dissolved in tetrahydrofuran (1 mg mL⁻¹) and filtered for size exclusion chromatography (SEC) analysis. CHDF was used for particle size analysis of the emulsion samples to make sure that secondary nucleation was avoided.

SEC Analysis

SEC analysis was carried out with a Waters 510 pump, a Waters WISP 712 autoinjector, a 410 refractive index detector, and a 486 UV detector (at 254 nm). The columns used were a PL gel guard 5- μ m 50 \times 7.5 mm precolumn and two PL gel mixed-C 10- μ m 300 \times 7.5 mm columns (40 °C) in series. Tetrahydrofuran was used as an eluent

Table III. Saturation Concentrations of Monomer in PMMA Seed at 60 °C in the Presence of RAFT Agent and the Concentration of the RAFT Agent in the Monomer Layer and the Particles

	Control (mol dm ⁻³)	Cumyl RAFT (1a) (mol dm ⁻³)	EMA RAFT (1b) (mol dm ⁻³)
C_p^{sat}	5.61	5.54	5.97
[RAFT] in styrene before swelling		2.33×10^{-2}	2.33×10^{-2}
[RAFT] in styrene after swelling		2.74×10^{-2}	3.01×10^{-3}
[RAFT] in the particle		9.08×10^{-4}	1.63×10^{-3}

(flow rate = 1.0 mL/min), and calibration was done with polystyrene standards ($M = 580\text{--}7.1 \times 10^6$). Data acquisition was performed with Waters Millennium 32 (version 3.05) software.

Determination of C_p^{sat}

The saturation monomer concentration within the seed latex particles (C_p^{sat}) was determined by the creaming of experiments according to the method used by Ballard et al.²⁴

The monomer saturation concentrations were also determined in the presence of cumyl RAFT and EMA RAFT agents. These were dissolved in the styrene monomer before the swelling of the seed. The concentration of the RAFT agent in the creamed monomer layer was then determined by UV absorption (in methanol) at a wavelength of 325 nm, which was above the styrene absorption range.

RESULTS AND DISCUSSION

The concentration of monomer and RAFT agent in the separate monomer phase after creaming was determined by UV absorption spectroscopy. Table III shows the saturation concentration of monomer in the presence of the RAFT agents. The C_p^{sat} of styrene in the PMMA seed was 5.61 mol dm⁻³, which remained roughly constant when cumyl RAFT was added to the monomer but increased to 5.97 mol dm⁻³ for EMA RAFT. Moreover, the concentration of cumyl RAFT in the particles was much less than the concentration of EMA RAFT. Water solubilities (C_w) of both RAFT agents were in the region of 10^{-4} to 10^{-5} mol dm⁻³, which was much lower than C_w for styrene (5×10^{-3} mol dm⁻³ at 50 °C).²⁵

Seeded emulsion polymerizations of styrene were carried out at 60 °C under an argon atmosphere. The KPS and RAFT concentrations are

given in Tables IV and V. In all the polymerizations, the emulsion at the beginning of the reaction was light pink because of the red color of the RAFT agents. During the course of polymerization, a conspicuous red layer on top of the emulsion (when agitation was briefly ceased) was then observed. The appearance of the red layer occurred shortly after the commencement of polymerization. At conversions of approximately 10%, which for our systems was the changeover from interval II to interval III, a red coagulant was formed. NMR and gel permeation chromatography (GPC) analysis of the red coagulant showed low molecular weight polystyrene ($M_p = 2100$) without the presence of a RAFT agent (1).

The formation of this red layer was still unclear. One could be led to believe that the transportation of the RAFT agents into the particle was slow on the polymerization timescale. The rate of transportation was calculated from eq 7, which was derived from Smoluchowski's equation. With a diffusion coefficient (D_w) similar to that of two styrene chain units,^{13,26} the rate of transportation was approximately 10^6 s⁻¹. This value was much greater than the rate of propagation and on the timescale of the reaction diffusion should not be a factor. Therefore, the red layer seemed to be more likely due to low molecular weight dormant species swollen with monomer. The diffusion²⁷⁻²⁹ of these species was extremely slow on the reaction timescale, so the transportation into the particles was slow. Once the changeover from interval II to interval III had occurred, these dormant species coalesced together to form the red coagulant, which was not in the samples analyzed for GPC:

$$\text{Rate of transportation} = 4\pi D_w r N_A C_w \quad (7)$$

The conversion profiles of these seeded experiments at different KPS and cumyl RAFT concen-

Table IV. \bar{M}_n and Polydispersity of Styrene in PMMA Seed at 60 °C at Different Cumyl RAFT (**1a**) and KPS Concentrations

Experiment	[Cumyl RAFT] (mol dm ⁻³) ^a	[KPS] (mol dm ⁻³) ^a	x^b	\bar{M}_n	PD	M_p	\bar{M}_n (Theory) ^d
1	High 1.46×10^{-2}	High 1.0×10^{-3}	0.22	73,394	2.10		15,137
			0.29	74,432	2.40		19,621
			0.35	81,200	2.33		24,137
			0.50	86,472	2.28		34,017
			0.63	92,045	2.59		42,736
2	Low 2.65×10^{-3}	High 1.0×10^{-3}	0.41	396,139	2.33	1,063,508	154,006
			0.57 ^c			1,092,418	215,674
			0.82 ^c			1,061,563	311,033
			0.86 ^c			1,039,443	326,505
3	High 2.0×10^{-2}	Low 1.0×10^{-4}	0.10	13,277	1.23		5,036
			0.14	8,805	1.61		6,863
4	Low 5.58×10^{-3}	Low 1.0×10^{-4}	0.04	33,654	1.03		—
			0.14	45,896	3.10		24,905
			0.17	43,297	3.67		31,183
			0.20	62,204	3.13		35,273
			0.33	58,436	3.28		59,825

^a The concentrations for RAFT and KPS were determined for the monomer volume and water plus the seed latex volume, respectively.

^b Conversion data are placed in the order of the polymerization time.

^c The molecular weight distribution was beyond the exclusion limits of SEC, so the peak molecular weights are given.

^d The \bar{M}_n was calculated according to eq 1.

trations are given in Figures 1 and 2. The starting time was taken when KPS was added to the reaction mixture. At a high KPS concentration (Fig. 1), the rate decreased as the RAFT concentration increased. Similarly, at a low KPS concentration (Fig. 2), the trend was repeated but the retardation of the rate was less drastic. For EMA RAFT, at a high KPS concentration (Fig. 3) the rate also decreased as a function of the EMA RAFT concentration. Therefore, a very high KPS concentration (5 times higher) was required to gain rates similar to that of the control (i.e., without a RAFT agent). At a low KPS concentration, a fractional conversion of about 20% was reached, similar to the conversion for the control. A comparison of the conversion profiles between the cumyl RAFT and EMA RAFT agents at high KPS concentrations are given in Figure 4. The retardation effect was more predominant for the EMA RAFT polymerization than for the cumyl RAFT polymerization.

Retardation with RAFT agents has been observed in bulk and solution experiments.³⁰ The possible explanations that have been given are (1) the slow fragmentation of adducts **2** and **4**, (2) the slow reinitiation by the expelled radical **3**, and (3) the specificity of **3** and the propagating radical to add to the RAFT agent rather than to monomer.

These mechanisms, however, do not explain the difference in rates between the cumyl and EMA RAFT agents because the free-radical chemistry, once the RAFT agent has been consumed, will be identical. Therefore, it is believed that the main retardation effect for the two RAFT agents used in these emulsion systems was due to the higher exit rate of **3b** in comparison with **3a** from the particles (see the Background Theory section), in agreement with what Lichti et al.⁸ found for normal transfer agents. This also suggests that the destabilization of the emulsion by the RAFT caused a slow rate of transportation of RAFT into the particles possibly by a substantial decrease in the surface area of the droplets (producing an organic layer on top of the reaction mixture). At a high KPS concentration, the most probable cause of the termination of **3** was radicals in the aqueous phase, whereas at low KPS concentrations, termination between the reentry of **3** into a particle with a growing chain was the most likely process.

However, retardation was effective during intervals II and III. A possible reason for this, even though droplets were no longer present in interval III, was the further transportation of RAFT agent into the particles from the water phase.

Table V. \bar{M}_n and Polydispersity of Styrene in PMMA Seed at 60 °C at Different EMA RAFT (**1b**) and KPS Concentrations

Experiment	[EMA RAFT] ^a	[KPS] ^a	x^b	\bar{M}_n	PD	\bar{M}_n (Theory) ^c
5	High 1.50×10^{-2}	Very high 5.0×10^{-3}	0.38	57,755	2.18	24,766
			0.46	59,336	2.25	30,306
			0.84	98,364	2.53	54,819
			0.95	69,893	3.36	62,240
6	High 1.40×10^{-2}	High 1.0×10^{-3}	0.11	98,938	8.68	7,847
			0.16	105,927	6.40	10,949
			0.22	156,717	6.42	15,552
7	Low 2.5×10^{-3}	High 1.0×10^{-3}	0.25	79,373	1.60	99,227
			0.28	80,890	2.51	111,892
			0.34	96,276	1.97	133,297
			0.39	95,476	2.56	155,089
			0.53	111,088	2.61	212,569
			0.87	83,988	4.68	342,322
			0.85	77,489	3.53	336,631
8	Low 2.5×10^{-3}	Low 1.0×10^{-4}	0.18	69,727	1.55	68,454
			0.21	62,371	2.32	79,974
			0.22	67,700	1.58	84,776
			0.20	56,434	1.60	78,418

^a The concentrations for RAFT and KPS were determined for the monomer volume and water plus the seed latex volume, respectively.

^b Conversion data are placed in the order of the polymerization time.

^c The \bar{M}_n was calculated according to eq 1.

The influence of both cumyl RAFT and KPS on \bar{M}_n and PD with fractional conversion is given in Table IV. At high RAFT and KPS concentrations (experiment 1), \bar{M}_n increased with conversion, but PD remained in the range 2.1–2.6. In addition, the \bar{M}_n (theory) values calculated via eq 1 were far

lower than the experimental values. When the RAFT concentration was lowered (experiment 2), only one \bar{M}_n value could be obtained; above that value, part of the MWD was beyond the exclusion limit of the SEC columns, so only peak molecular weights (M_p) are given. \bar{M}_n at a 0.41 conversion

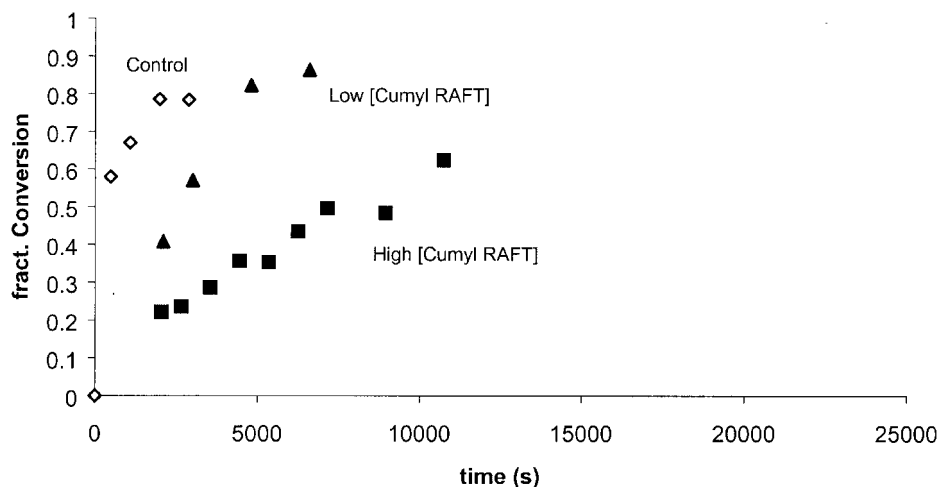


Figure 1. Conversion profiles of styrene in the presence of cumyl RAFT (**1a**) at a high KPS concentration ($1 \times 10^{-3} \text{ mol dm}^{-3}$) at 60 °C.

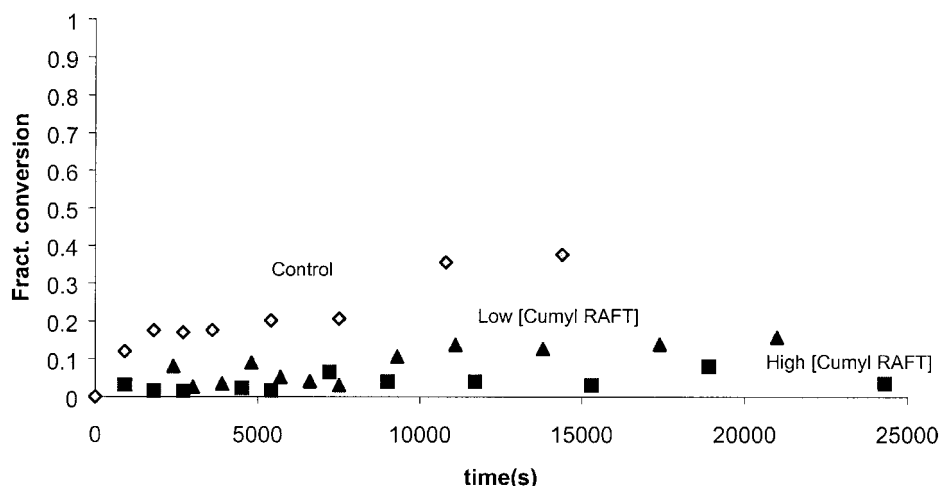


Figure 2. Conversion profiles of styrene in the presence of cumyl RAFT (**1a**) at a low KPS concentration (1×10^{-4} mol dm $^{-3}$) at 60 °C.

was greater than \bar{M}_n (theory), with a PD of 2.33. In experiment 3, conversions reached 0.14 in 25 h, so only two \bar{M}_n data points were taken in which these values were greater than \bar{M}_n (theory). Experiment 4, at the lowest RAFT and KPS concentrations, showed the closest correlation between \bar{M}_n (experimental) and \bar{M}_n (theory); however, the PDs were high and ranged from 3.1 to 3.7. These results showed for all experiments that \bar{M}_n increased with conversion and the PDs remained relatively constant. Furthermore, \bar{M}_n (theory) was always lower than \bar{M}_n obtained experimentally.

The influence of EMA RAFT on the MWDs is given in Table V. For a high EMA RAFT concen-

tration, the \bar{M}_n values in experiment 5 (very high KPS concentration) increased with conversion and were slightly greater than \bar{M}_n (theory), with PDs ranging from 2.1 to 3.4. Conversely, at a lower KPS concentration (experiment 6), the \bar{M}_n values were far greater than the theoretical values, with PDs as high as 6.4. When the RAFT concentration was low, the \bar{M}_n values were in fact below the theoretical values, in which the PDs increased for experiment 7 but remained relatively constant for experiment 8. The results suggested that the ratio of RAFT agent and KPS concentrations had a greater influence on the MWD for the EMA RAFT experiments than for the cumyl RAFT experiments. This was presu-

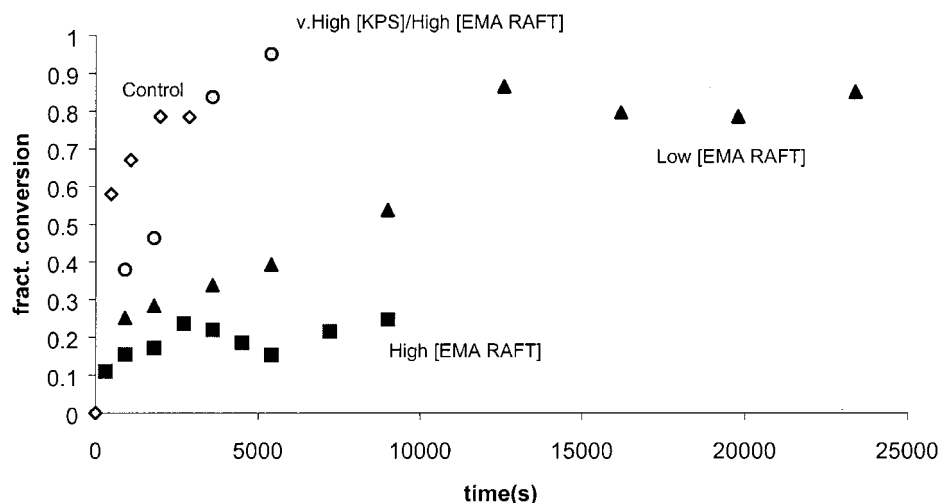


Figure 3. Conversion profiles of styrene in the presence of EMA RAFT (**1b**) at a high KPS concentration (1×10^{-3} mol dm $^{-3}$) at 60 °C.

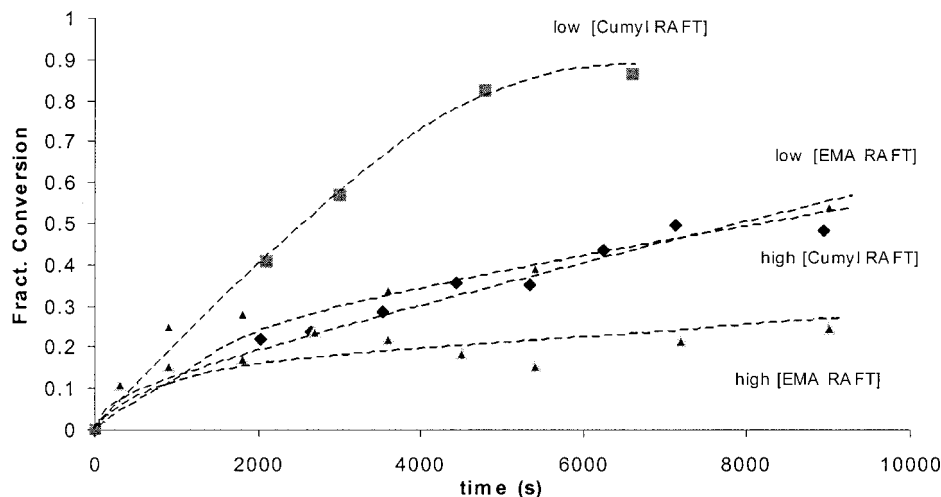


Figure 4. Comparison of the conversion profiles of cumyl RAFT (**1a**) and EMA RAFT (**1b**) agents at a high KPS concentration ($1 \times 10^{-3} \text{ mol dm}^{-3}$) at 60°C . The dashed lines are a guide for the eye.

ably due to the different rates and fates of the exited radicals.

The very broad PDs even at low KPS concentrations were a result of the continuous transportation of RAFT into the particles during interval II and the transportation of a small amount during interval III, when small chains were continually being formed. Therefore, it was not unexpected to find PDs much greater than 1. The higher values of \bar{M}_n observed experimentally suggested that there was a much lower than expected amount of dormant species available for reaction inside the particles. This was also supported by the argument put forth for retardation (i.e., the slow transportation of RAFT into the particles).

The deviation of \bar{M}_n from theory was also caused by the concentration of KPS. The higher the KPS concentration was, the greater the deviation from theory was. These results suggested that bimolecular termination due to entry was not negligible at high KPS concentrations (experiments 1 and 7). Thus, over the time of the reactions, the number of chains formed from initiator was similar to the number formed by the RAFT agents, consequently reducing \bar{M}_n . At low KPS concentrations (experiments 4 and 8), \bar{M}_n 's were closer to the theoretical values, suggesting only a small proportion of the chains was formed from initiator. Therefore, the deviation from theory is proposed to be a combination of the lower than expected RAFT agent available for reaction and the amount of initiator decomposed, concomitantly acting to increase and decrease \bar{M}_n , respectively.

CONCLUSION

The use of seeded experiments allowed the mechanisms affecting the RAFT process in emulsion to be studied. One of the important aspects of this study was rate retardation, which was greater for the EMA RAFT than for the cumyl RAFT. This is proposed to be due to greater exit of the radicals from the particles, formed after the fragmentation of the EMA RAFT agent. In addition, the presence of monomer droplets resulted in polymers with broad PDs. This is proposed to result from the continuous transportation of RAFT agent into the particles, primarily during interval II, and the transportation of a small proportion during interval III. The red layer was also a result of the presence of droplets. Once the switch from interval II to interval III occurred, the low molecular weight species coalesced to form the red coagulant. The deviation from theoretical values of \bar{M}_n were due to a high amount of chains being formed through radical-radical termination and the lower than expected RAFT agent in the particles caused by trapped dormant species in the red coagulant. Therefore, the ideal system should contain large particles to reduce exit, and a stable system³¹ should be sought to determine the effects of RAFT transportation into the particles.

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