Free-Radical Polymerization of Styrene in Emulsion Using a Reversible Addition−Fragmentation Chain Transfer Agent with a Low Transfer Constant: Effect on Rate, Particle Size, and Molecular Weight

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ABSTRACT: The ab initio emulsion polymerizations of styrene in the presence of RAFT agent (1-(*O*-ethylxanthyl)ethylbenzene; **1**) with a low chain transfer constant to styrene ($C_{\mathrm{tr}} \sim 0.8$) were carried out using conventional surfactant (sodium dodecyl sulfate, SDS) and initiator (sodium persulfate, SPS). The influence of varying the concentrations of SDS, SPS, and **1** on the polymerization rate, particle size distribution, and molecular weight distribution were studied. It was found that with an increased concentration of SDS both the average-number particle size decreased and the particle size distribution became narrower, prescribed to be due to a greater number of micelles that are nucleated during interval I. A similar result was also found when the concentrations of **1** increased. It was postulated that R$^{\bullet}$, produced from the fragmentation of **1**, exited particles and reentered micelles, thus creating more particles. At high initiator concentrations, reentry of R$^{\bullet}$ should not play a dominant role due to the high amount of aqueous phase termination. The rate was also influenced by the concentrations of SDS, SPS, and **1**. An increase in the concentration of **1** at a low initiator concentration and at constant SDS concentration resulted in significant retardation in rate, which is prescribed to be due to exit and reentry to terminate radicals already growing in the particles. The rate has been shown to increase by increasing the concentration of SDS. For all polymerizations, the number-average molecular weight ($\bar{M}_{\mathrm{n}}$) is approximately twice as high compared to theoretical calculations. A tentative explanation put forth is that the RAFT agent could be surface active, and therefore the local concentration surrounding the growing radical chains in the particles will be less than the global concentration. Block copolymers of poly(styrene-*co*-butyl acrylate)−acetoacetoxyethyl methacrylate were then synthesized in a second stage polymerization under strarved feed conditions to give a core−shell morphology with a very low gel content (∼3%), in which 76.5% of the polystyrene dormant species were converted to blocks.

Introduction

The main criterion for "living" free-radical polymerization behavior is that experimental conditions must be selected to ensure that radical−radical termination is negligible. To satisfy this criterion, reduction in radical flux must be made, and thus low rates of polymerization are a consequence in solution or bulk reactions. Emulsion polymerization offers a possible solution since the radicals are compartmentalized and the rate is proportional to the number of particles. However, with all "living" free-radical processes (e.g., nitroxide-mediated,[1] ATRP,[2] and RAFT[3,4]) carried out thus far in emulsion under ab initio conditions, the drawbacks have been lack of colloidal stability, retardation of rate, and/or broad molecular weight distributions. In the case of nitroxide-mediated polymerizations,[1] the high temperatures required to obtain living character led to coagulation of the latex particles or unusually large particle. In ATRP, the use of conventional emulsifier such as sodium dodecyl sulfate (SDS) gave high molecular weights with broad distributions, attributed to reaction of the SDS with the copper(II) bromide.[2] Similarly, high molecular weights with high polydispersities were found for highly active chain transfer RAFT agents ($C_{\mathrm{tr}} > 1000$) in a SDS system.[4] Interestingly, the rate was significantly retarded, and a conspicuous red layer of low molecular weight dormant species was also observed at the beginning of polymerization, suggesting that SDS interacts with these RAFT agents in an unknown but deleterious manner. However, these drawbacks were overcome by using semibatch conditions.[5,6]

An alternative and more universal method used to overcome these inherent problems is via the use of miniemulsions[5] and/or the substitution of SDS with nonionic surfactants.[2,7] The amount of nonionic surfactant required is as great as 5% solids by weight (compared to 0.01% for SDS) in latexes containing approximately 20% polymer solids. Impurities in such large amounts will undoubtedly have a significant influence on the properties of the resulting polymer film, especially when considering surfactant migration to the interfaces.

Recent work using degenerative and RAFT type transfer agents with low transfer constants was studied in conventional SDS emulsion systems. Lansalot et al.[8] found no change in rate or particle size distribution for the perfluorinated transfer agent ($C_6F_{13}I$; $C_{\mathrm{tr}} \sim 1.4$). The number-average molecular weight, however, was twice that predicted by theory, which they postulated to be due to the slow rate of diffusion from the droplets to the particles. Work carried out in this laboratory found that the ab initio polymerization of butyl acrylate (BA) in the presence of a low transfer active RAFT agents (**1** in Scheme 1; $C_{\mathrm{tr}} \sim 1.5$) gave retardation in rate, but importantly, the molecular weight and polydispersity could be fitted by theory.[9] The main advantage of "living" radical polymerization is that a variety of

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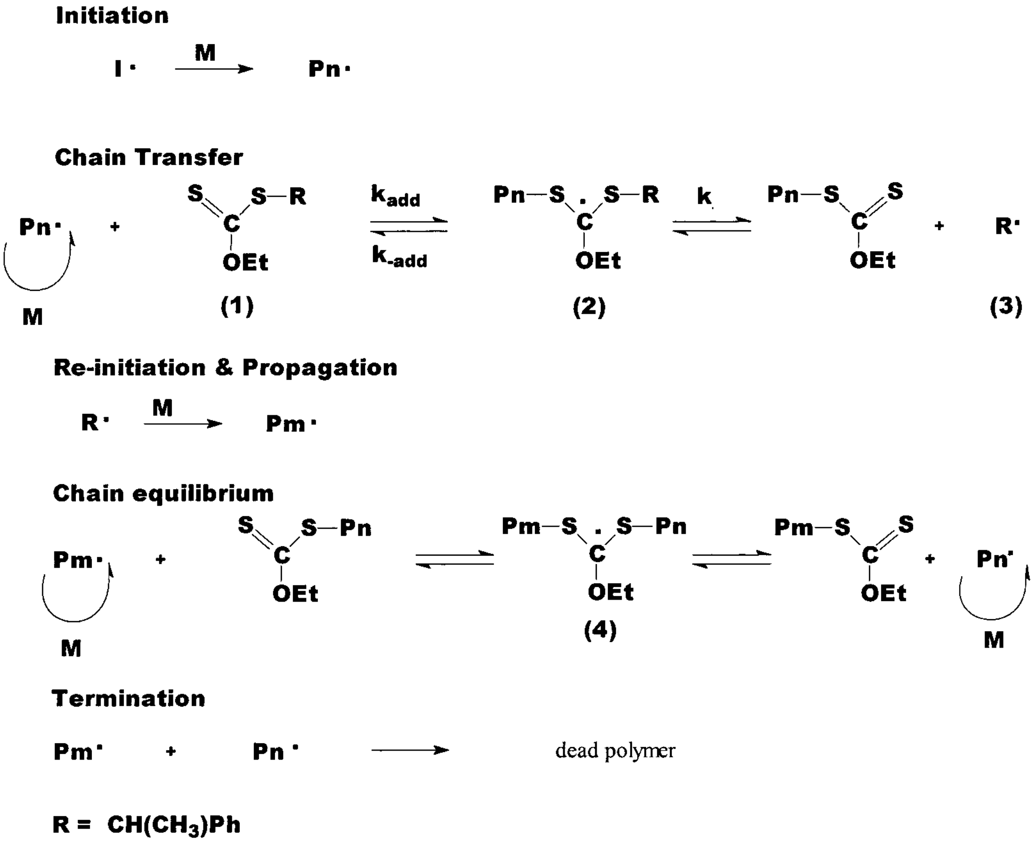
Scheme 1. Proposed RAFT Mechanism



polymer architectures can be synthesized (e.g., block copolymers). In emulsion systems the particle morphology, molecular weight, and the particle size all have a direct influence on the properties of the final film. If all these factors can be controlled, then one could conceivably develop a relationship between the polymer architecture, particle morphology, and film properties. The aim of this work is to study the influence of **1** (a RAFT agent with a low transfer constant of 0.8) on the ab initio emulsion polymerizations of STY on particle size distribution, rate, and molecular weight distribution and further use these styrene seeds to prepare block copolymers with BA and acetoacetoxyethyl methacrylate (AAEMA) with core–shell particle morphologies. The acetoacetoxy moiety in the polymer backbone can then be cross-linked with a diamine to toughen the resulting films. (This will be a future publication concentrating on the mechanical tensile properties of these block copolymers before and after cross-linking and in particular the influence of the location of the AAEMA in the block copolymer.)

Experimental Section

Materials. Styrene, butyl acrylate, and acetoacteoxyethyl methacrylate (Aldrich) were purified of inhibitor by passing through an inhibitor-removal column (Aldrich). Sodium dodecyl sulfate (SDS, Fluka) and sodium peroxydisulfate (SPS, Merck) were used as received. The RAFT agent (1-(*O*-ethylxanthyl)ethylbenzene; **1**) was synthesized according to the literature procedure.[10] Deionized water was used in all polymerizations.

Capillary Hydrodynamic Fractionation (CHDF). The particle size distribution and number-average diameter of the latex particles were determined by capillary hydrodynamic fractionation techniques (CHDF 2000 2.73, Matec Applied Sciences).

SEC Analysis. SEC analysis was carried out using a Waters model 510 pump, a Waters model WISP 712 autoinjector, a model 410 refractive index detector, and a model 486 UV detector (at 254 nm). The columns used were a PLgel guard 5 μm 50 × 7.5 mm precolumn, followed by two PLgel mixed-C 10 μm 300 × 7.5 mm columns (40 °C) in series. THF was used as eluent (flow rate 1.0 mL/min), and calibration was done using polystyrene standards ($M = 580-7.1 \times 10^6$). Data acquisition was performed using Waters Millennium 32 (v3.05) software.

Emulsion Polymerizations. The ab initio emulsion polymerizations were performed in a double-walled 300 mL glass reactor equipped with mechanical stirrer, condenser, and thermometer. The polymerizations were carried out under nitrogen using 180 g of water and 81 g of styrene, with varying amounts of **1**, SDS, and SPS (see Table 1) at 70 °C. Samples were taken periodically to monitor conversion, particle size distribution, and molecular weight distribution. Conversion was determined by gravimetric analysis.

Gel Content. Gel content of the polymer was determined by Soxhlet extraction with THF.

Synthesis of Block Copolymer Core–Shells. The monomers BA and AAEMA were generally introduced as a preemulsion under starved-feed and batch conditions in the reactor containing a polystyrene seed (expt 12, particle diameter 30.9 nm) to produce a random P(BA–AAEMA) copolymer during the second stage. The amount of surfactant used was under the saturating capacity of the latex, which was determined by surface tension measurement. The buffer ($NaHCO_3$, 5 × 10^{-3} M) and the initiator (SPS, 2 × 10^{-3} M) were introduced at the beginning of the reaction at 70 °C. For the starved feed reactions, after 1 h after the commencement of the reaction the monomers were fed in over a 4 h period. The final solid content is 30%, and the ratio STY to BA and AAEMA is 1.

To determine the amount of polystyrene converted to block copolymer, gradient polymer elution chromatography (GPEC) was carried out. GPEC analysis was performed on an Alliance 2690 HPLC (Waters) using a Jordi Gel DVB polyamine column

Table 1. Concentrations of SDS, SPS, and RAFT (1) Used in All Styrene ab Initio Emulsion Experiments at 70 °C[a]

expt	[SDS] × cmc (mol dm^{-3})	[SPS] (mol dm^{-3})	[RAFT] (mol dm^{-3})	D (nm) (no. av)[b]	N_c	ρ (3% entry efficiency)[c]
1	1.5	0.001	0	85.6	1.3×10^{18}	6.14×10^{-4}
2	1.5	0.001	0.005	70.1	2.36×10^{18}	3.37×10^{-4}
3	1.5	0.001	0.01	63.6	3.17×10^{18}	2.52×10^{-4}
4	1.5	0.001	0.04	59.3	3.9×10^{18}	2.04×10^{-4}
5	1.5	0.005	0.005	59.3	3.9×10^{18}	1.02×10^{-3}
6	1.5	0.005	0.01	63.4	3.2×10^{18}	1.25×10^{-3}
7	1.2	0.005	0.01	70.9	2.28×10^{18}	1.74×10^{-3}
8	1.8	0.005	0.01	62.6	3.32×10^{18}	1.20×10^{-3}
9	3	0.005	0.01	51.4	6×10^{18}	6.65×10^{-4}
10	6	0.005	0.01	40.0	1.27×10^{19}	3.13×10^{-4}
11	10	0.005	0.01	36.7	1.65×10^{19}	2.42×10^{-4}
12	15	0.005	0.01	30.9	2.76×10^{19}	1.44×10^{-4}

[a] Data of number-average diameter, which was used to calculate number of particles per unit volume (N_c) and ρ. All concentrations were calculated from the total reaction volume. [b] Measured by CHDF. [c] The entry rate coefficient, ρ, was calculated from a semiempirical equation taking into account N_c and initiator concentration.[13]

(250 mm × 4.6 mm, Alltech) at a flow rate of 0.5 mL/min. The elution gradient starts with 100% heptane; after 15 min the solvent was changed to 100% DCM and then changed to a mixture of 20% THF and 80% DCM after 40 min. Detection was carried out using a multiwavelength and multiangle PL-EMD 960 evaporative light scattering detector (ELSD) (Polymer Laboratories). The calibration of the ELSD detector is carried out by injecting know concentrations of polystyrene to construct a calibration curve. The ELSD response, R, has a power law dependence with polymer concentration and follows $R = 86.315[\text{polymer}]^{1.565}$ The polystyrene peak elutes at 13.5 min. The elution peaks of poly(butyl acrylate) and block copolymers are partially overlapping, so quantitative analysis was difficult, and it was not possible to determine accurately the proportion of homopolybutyl acrylate formed during the reaction.

Cryo-TEM. This technique was used to determined the particle morphology. RuO$_4$ staining is employed to increase the contrast between the polystyrene phase (seen as the black portions in the TEM) and the poly(butyl acrylate) (light) phase. Phosphotungstic acid (PTA) negative staining technique was successfully used to enhance the contrast between the electron-transparent domains of the particles (the PBA phase) and the dense PTA-stained background. Samples were analyzed by cryo-TEM at the CERDATO, ATOFINA, Serquigny, France.

Results and Discussion

The influence of initiator (SPS), surfactant (SDS), and RAFT (**1**) concentrations on the rate, particle size distribution, and molecular weight distributions of styrene was studied. Emulsion polymerizations were carried out according to conventional batch procedures as described in the Experimental Section. All concentrations given in Table 1 are determined from the total volume of the reaction.

Influence of SDS, SPS, and 1 on Particle Size Distribution. The particle size distributions for all experiments were measured by CHDF, which separates the particles on size and provides accurate information on the full distribution. Figure 1 shows the CHDF chromatograms of polystyrene latex particles (close to 100% conversion) prepared with increasing amounts of SDS above its critical micelle concentration (cmc) at constant initiator and **1** concentrations. The particle size distribution of PSTY latex particles became narrower, and the number-average particle size decreased as the SDS concentration was increased, not surprisingly suggesting that the number of particles increased with SDS concentration.

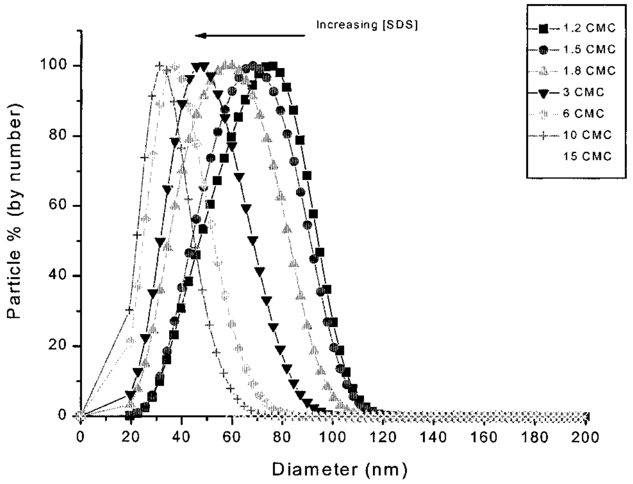


Figure 1. Particle size distributions of styrene latex particles at a constant [SPS] of 0.001 mol dm^{-3} and [RAFT] of 0.005 mol dm^{-3}, while increasing [SDS] above its cmc as measure by CHDF. (All measurements were take close to 100% conversion.)

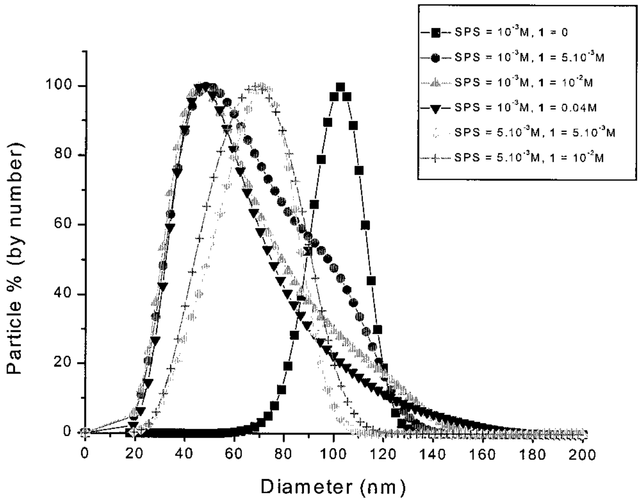


Figure 2. Particle size distributions of styrene latex particles, keeping [SDS] 1.5 times its cmc, while varying [SPS] and [RAFT] as measured by CHDF.

The influence of varying the concentrations of initiator and **1** on the particle size distribution is shown in Figure 2. At constant initiator concentration (10^{-3} M) the distributions became narrower, and the number-average diameter decreased (consequently an increase in the number of particles; see Table 1) as the concentration of **1** was increased. A similar result was found for the ab initio polymerization of butyl acrylate using the same RAFT agent.[9] This suggests R$^{\bullet}$ produced from

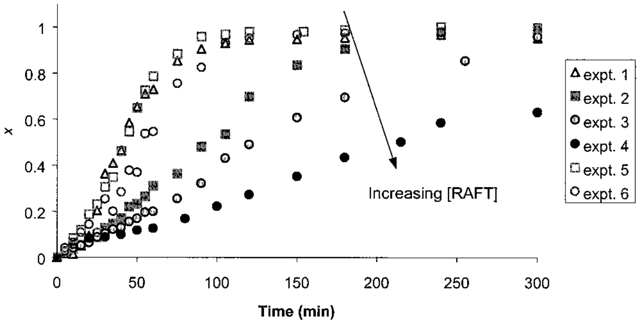


Figure 3. Conversion−time profiles for polymerizations carried out at a constant [SDS] 1.5 times its cmc, while varying both SPS and RAFT concentrations (expts 1−6).

the fragmentation of **1** (see Scheme 1) will exit the particles and reenter micelles to create new particles during the nucleation period (i.e., interval I). Seeded emulsion polymerizations were carried out to determine the effect of entry and exit using this RAFT agent. It was found that indeed the exit rate coefficient increased with an increase in the concentration of **1**.[11] If a comparison is made between experiments with the same concentration of **1** at two different initiator concentrations (i.e., comparing expts 2 with 5 and 3 with 6), it can be seen that the number-average diameter (Table 1) for expt 2 has a greater value than expt 5 and expt 3 has a similar value to expt 6. This alludes to the fact that the nucleation mechanisms are different for both sets of experiments at low and high initiator concentrations. The evidence suggests that exit increases the nucleation rate, but if the aqueous phase radical concentration is high, manifested by a high initiator concentration, then the increased entry rate coefficient,[12] ρ (see Table 1), dominates over reentry with the possibility of the exited radicals being terminated in the aqueous phase.[12−14] This is more clearly shown by the particle size distributions from expts 2 and 3, which have a lower peak diameter compared to expts 5 and 6, respectively, and that although the averages might be the same for expts 3 and 6 the distributions are very different. (A complete description of the events that influence entry and exit in emulsion polymerization is given in refs 13 and 15.)

Influence of SDS, SPS, and 1 on the Rate of Polymerization. The influence of SPS and **1** concentrations on the rate at a constant surfactant concentration (1.5 times greater than its critical micelle concentration, cmc) is given in Figure 3. Increasing the concentration of **1** at low initiator concentration results in a significant retardation in rate. Since retardation is not found when using this RAFT agent in either bulk or solution,[16] retardation is prescribed to exit and then reentry to terminate radicals already growing inside particles. Although exit allows the production of small particles, it has the disadvantage of retarding the rate. To overcome this, the initiator concentration was increased by 5 times (expts 5 and 6), and as can be seen the rate is comparable to expt 1. The rate and particle size data support the postulate that at low initiator concentration termination is primarily due to exit and reentry, whereas at high initiator concentrations, the increased ρ and the possibility of termination of the exited radicals in the aqueous phase negates any termination due to reentry.

The influence of SDS concentration at constant initiator (5×10^{-3} mol dm^{-3}) and **1** (1×10^{-2} mol dm^{-3}) concentrations on the conversion−time profiles is given in Figure 4. Not surprisingly, the rate increased with the increased number of particles per unit volume of water, N_c (Table 1). At 15 times the cmc, high conversions were reached after approximately 40 min with extremely small particle sizes. Although this might seem like a convenient way to increase rate and produce very small particles, the disadvantage is that approximately 4% total solids of SDS is used, which will have a marked effect on the film formation properties. Work already carried out in this laboratory found that migration of surfactant to the film surface was exacerbated by the formation of both low molecular weight polymer and small particles.[9] The main concern therefore is keeping the initiator concentration as high as possible without invoking high amounts of polymeric radical termination. It must be noted that the amount of chains terminated by bimolecular termination should be kept negligible. In bulk this is directly correlated to the amount of initiator that has decomposed. However, in emulsion, since the efficiency for entry is so low for styrene (~3%)[13] this direct relationship is no longer valid. Instead, the entry rate coefficient,[17] ρ, should be used since entry leads to termination inside the particles (see eq 1).

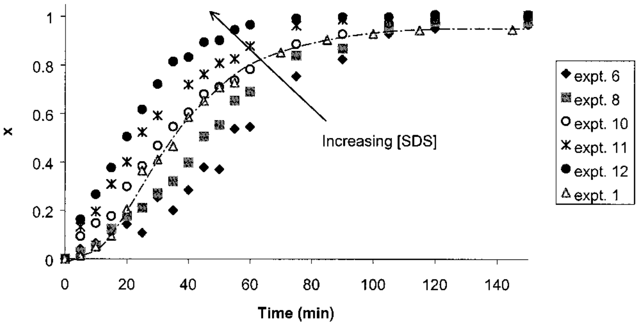


Figure 4. Influence of SDS concentration on the conversion−time profiles, while keeping [SPS] and [RAFT] constant.

Influence of SDS, SPS, and RAFT on the Molecular Weight Distribution. The number-average molecular weight ($\bar{M}_n$) for all experiments at 1.5 times the cmc of SDS is given in Figure 5a. The first observation is that the $\bar{M}_n$ remains relatively constant over the conversion range and decreases with increasing concentration of **1**. The next observation is the decrease in $\bar{M}_n$ when the initiator concentration is increased at a low concentration of **1** (expts 2 and 5), and when **1** is increased, the difference is not observable (expts 3 and 6).

The instantaneous $\bar{M}_n$ can be approximated at low conversions for zero−one emulsion systems by eq 1 and is derived from the rate of propagation over all the rates of termination.[18,19]

$$\bar{M}_n = \left\{ \frac{k_p {C_p}^M}{k_{tr,RAFT} {C_p}^{RAFT} + \rho} \right\} M_0 \tag{1}$$

where k_p is the propagation rate coefficient, $k_{tr,RAFT}$ is the transfer rate coefficient to the RAFT agent, M_0 is the molar mass of styrene, and ${C_p}^M$ and ${C_p}^{RAFT}$ are the concentration of monomer and RAFT agent in the particles, respectively. A zero−one system is one in which particles have either one or zero radicals. Equation 1 is valid for this RAFT agent (**1**) since the C_{tr} is close to one and will by all probability react only once

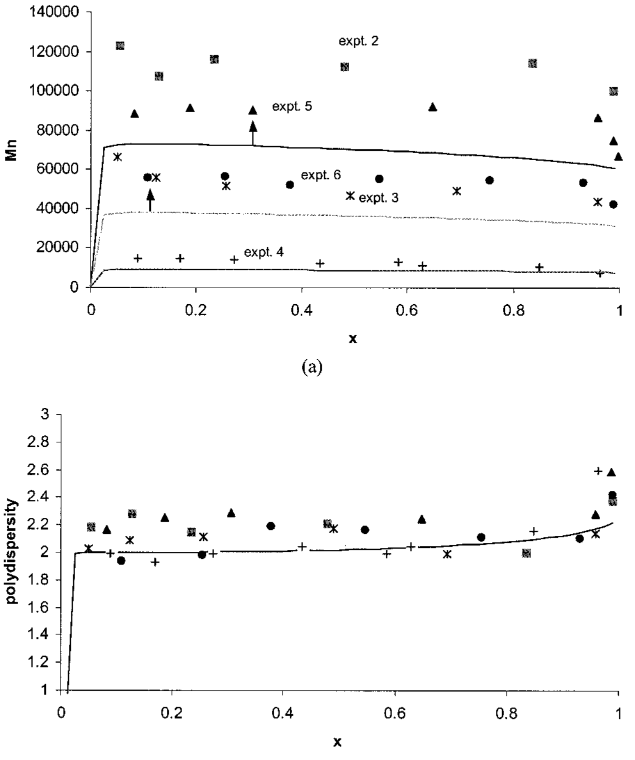


Figure 5. (a) Number-average molecular weight ($\bar{M}_n$) for polystyrene with varied concentrations of SPS and RAFT and at a constant [SDS] (1.5 times its cmc); solid lines are theoretical curves calculated from eq 2. (b) Polydispersities of these polymerizations; solid curve is the theoretical curve calculated from eq 3.

over the polymerization (i.e., acts like a conventional chain transfer agent). All experiments carried out in this work fit the criteria for zero–one conditions,[20] mainly due to the small size of the particles and the low reinitiation constant of the radical[21] (formed through transfer) to styrene. The effect of initiator concentration at a low concentration of **1** (comparing expts 2 and 5) shows that bimolecular termination can decrease the $\bar{M}_n$ (cf. eq 1) due to the fact that ρ for expt 5 is 3 times greater than in expt 2 (see Table 1). When the concentration of RAFT agent is increased (expts 3 and 6), the influence of ρ on $\bar{M}_n$ is negligible, even though ρ is approximately 4 times greater for expt 6 than 3, suggesting that in this case the rate of transfer to RAFT dominates the chain stopping process. The polydispersities of these experiments are all close to 2 (Figure 5b), which is in good agreement with prediction. The only point to note is that when termination plays a role (expts 2 and 5), the polydispersity (PD) increases to a value slightly above 2, whereas at high concentrations of **1** the values fit closely to prediction (see eq 3).

Increasing the SDS concentration has little effect on the $\bar{M}_n$ (Figure 6a). This is not surprising when we consider ρ for these systems (Table 1). It seems that as N_c is increased as a consequence of increased surfactant concentration, ρ decreased, thus further reducing the amount of bimolecular termination in the particles. The polydispersity for this set of experiments (Figure 6b) is close to 2, with a slight increase at conversions greater than 0.9, suggesting the production of smaller chains. This will be further elucidated below with a comparison between experimental data and that of prediction.

The equations used to predict the molecular weight and polydispersity of polymer produced by the RAFT

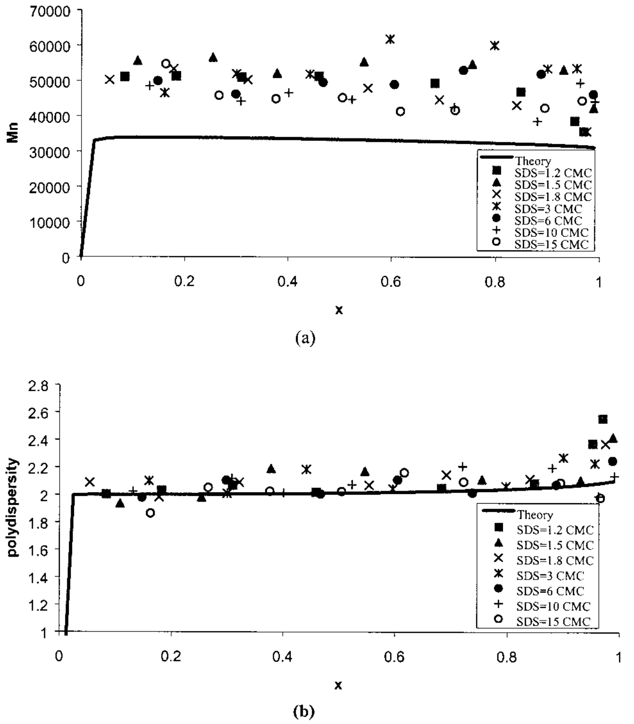


Figure 6. (a) Number-average molecular weight ($\bar{M}_n$) for polystyrene with increasing [SDS], while maintaining SPS and RAFT concentrations constant; solid lines are theoretical curves calculated from eq 2. (b) Polydispersities of these polymerizations; solid line is the theoretical curve calculated from eq 3.

method in bulk or solution are those derived by Müller et al.[22] for living processes involving active and dormant species. The equations are obtained via the method of moments. For $C_{\mathrm{tr,RAFT}}$ close to one, the $\bar{M}_n$ and PD can be approximated by the following expressions, taking into account residual RAFT agent:

$$\bar{M}_n \approx \frac{\gamma_0 x}{1-(1-\alpha)(1-x)^{\beta}} M_0 \qquad (2)$$

$$\mathrm{PD} = \frac{1}{\gamma_0 x} + \frac{1}{x}\left[2 + \frac{\beta-1}{\alpha-\beta}(2-x)\right] - \frac{2\alpha(1-\alpha)}{(\beta^2-\alpha^2)x^2}\left[1-(1-x)^{1+\beta/\alpha}\right] \qquad (3)$$

where $\gamma_0 = [\mathrm{M}]_0/[\mathrm{RAFT}]_0$, x is fractional conversion, $\alpha = [\mathrm{P}_n{}^{\bullet}]/[\mathrm{RAFT}]$, and $\beta = C_{\mathrm{tr,RAFT}}$.

The concentration of RAFT as a function of conversion is given by

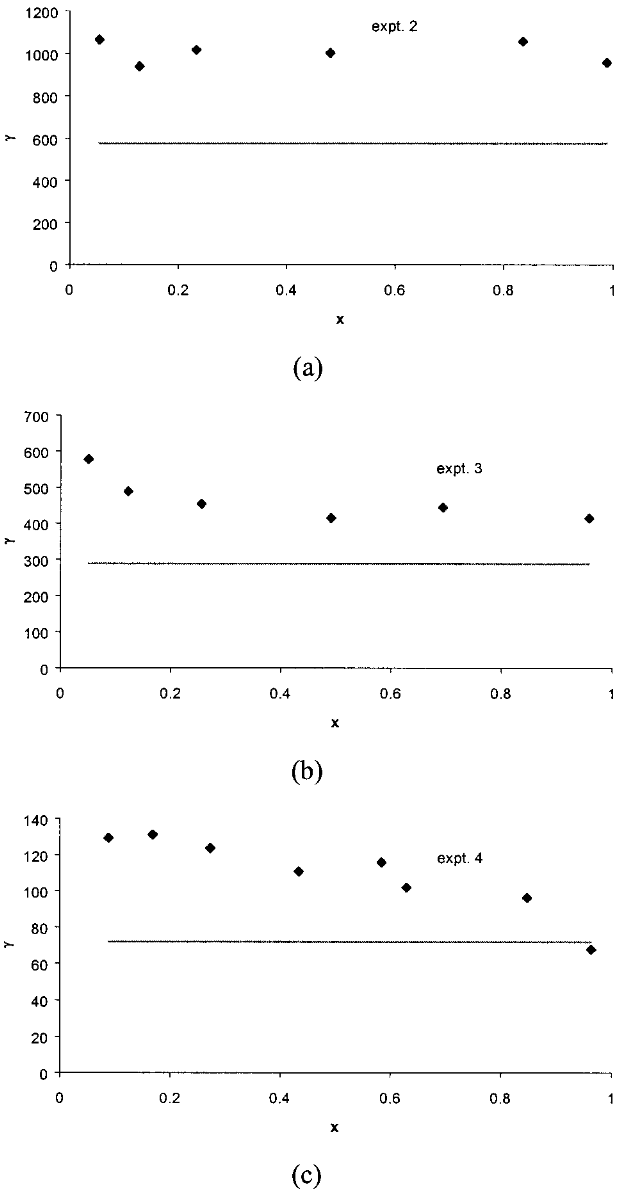
$$[\mathrm{RAFT}]_x = (1-\alpha)[\mathrm{RAFT}]_0(1-x)^{\beta} \qquad (4)$$

The assumptions made in these expressions are that the steady-state radical concentration ($[\mathrm{P}_n{}^{\bullet}]$) is very low, and bimolecular (radical–radical) termination events are negligible. From eq 4 it can be seen that for $C_{\mathrm{tr,RAFT}}$ close to one the RAFT agent would be consumed at a similar rate to monomer. Equations 2 and 3 are valid for the three intervals if the rate of transportation of RAFT from the droplets to the particles equals the rate of transfer and importantly if C_{tr} is close to 1. (Simulations show that this is true for C_{tr} values between 0.8 and 1.5.) If C_{tr} is not close to one, then these equations cannot be used to approximate the values for $\bar{M}_n$ and PD over the conversion range for an ab initio emulsion polymerization. The GEAR algorithm was used to simulate the MWD during the three intervals and supports the validity of Mullers equations for C_{tr} between 0.8 and 1.5. This implies that equilibrium of RAFT between the droplets and the particles is maintained during the polymerization, which is in accord with the "two-films" theory.[23]

The comparison of the theoretically determined $\bar{M}_n$ (eq 2) and the experimental data in Figures 5a and 6a shows that predicted values are always lower than the experimental values using a $C_{tr,RAFT} = 0.8$. In addition, $\bar{M}_n$(expt) gets closer to $\bar{M}_n$(theory) at high conversions. However, the polydispersities are all very similar to theory (eq 3) (Figures 5b and 6b). These results suggest that in order to keep the polydispersity close to theory but have $\bar{M}_n$(expt) greater than $\bar{M}_n$(theory), the ratio of monomer to RAFT agent inside the particles must be higher than γ_0 and that this higher ratio is kept relatively constant throughout most of the polymerization. The increase in polydispersity and the approach of $\bar{M}_n$(expt) to $\bar{M}_n$(theory) at conversions greater than 0.9 are probably a result of transportation of RAFT into the particles during interval III from the water phase.

To further explore this, γ from eq 2 is determined by using the $\bar{M}_n$ from experiment at their corresponding conversion and assuming a very low α (Figure 7). Only three representative experiments are given at three [RAFT]$_0$, since similar trends are found in all experiments. Initially, γ_x calculated is approximately twice as great as γ_0, which remained relatively constant over the conversion range for the lowest RAFT concentration, whereas at increased [RAFT]$_0$, γ_x approaches γ_0 with increasing conversion. It should be noted that the conversion at which the changeover from interval II to III takes place (i.e., when droplets are no longer present) in an ab initio styrene experiment is approximately 0.32. The results from Figure 7 therefore suggest that during Interval I and II the amount of active RAFT inside the particles is half that of [RAFT]$_0$. The postulates to explain such an affect are the following: (1) Chemical deactivation of the RAFT agent by side reactions. SPS, which is know to react with thiols,[24] could react with the RAFT agent or hydrolysis of the RAFT agent. (2) Diffusional resistance[23] through lack of mass transfer in which thermodynamic equilibrium between the particles and droplets is not be reached ("two-films" theory).

In Figure 7 the γ_x at high conversions seems to get closer to γ_0 especially at high RAFT concentrations where the main chain stopping event is transfer to the RAFT agent. This suggests that active RAFT is still being transported into particles and discounts significant amounts of RAFT deactivated by chemical means. However, mechanism 2 should be valid for slower diffusing (high molecular weight) transfer agents and should have little or no effect in our RAFT systems. The rate of transportation into the particles of the RAFT agent is orders of magnitude greater than that of transfer or polymerization, even though the water solubility of this RAFT agent (**1**) is orders of magnitude less than styrene.[13] This is supported by the results from butyl acrylate in the presence of **1**.[9] The $\bar{M}_n$ and PD fit theory, which indicates that equilibrium between the droplets and particles is established during the polymerization even though the rate of polymerization and consequently transfer are at least 2 orders of magnitude greater than for this styrene system.



(a)

(b)

(c)

Figure 7. Calculated γ determined by imputing $\bar{M}_n$(expt) into eq 2 to determine the amount of RAFT agent available for polymerization.

It seems therefore that another explanation needs to be invoked to explain this phenomenon. A tentative explanation could be the result of **1** being surface active, in which **1** is highly concentrated toward the interface of the particles. This would then suggest that the local concentration of **1** around the growing polymeric radicals is less than the global. Evidence for this is not conclusive and is based on the fact that RAFT agents with a phenyl-activating moiety destabilize emulsions[25] and miniemulsions[7] when SDS was used. In addition, from γ relaxation experiments,[11] which allow quantitative values of ρ and exit rate coefficients to be obtained, the exit rate coefficient increased as RAFT agent increased, but surprisingly the values of ρ decreased. This suggests that a radical entering a particle will react preferentially with the RAFT agent rather than monomer. The only means for this to be possible is that the RAFT agent concentration at the particle surface is much greater than inside the particle.

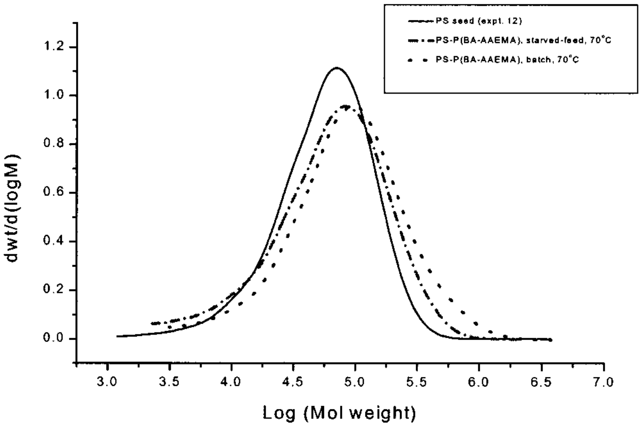


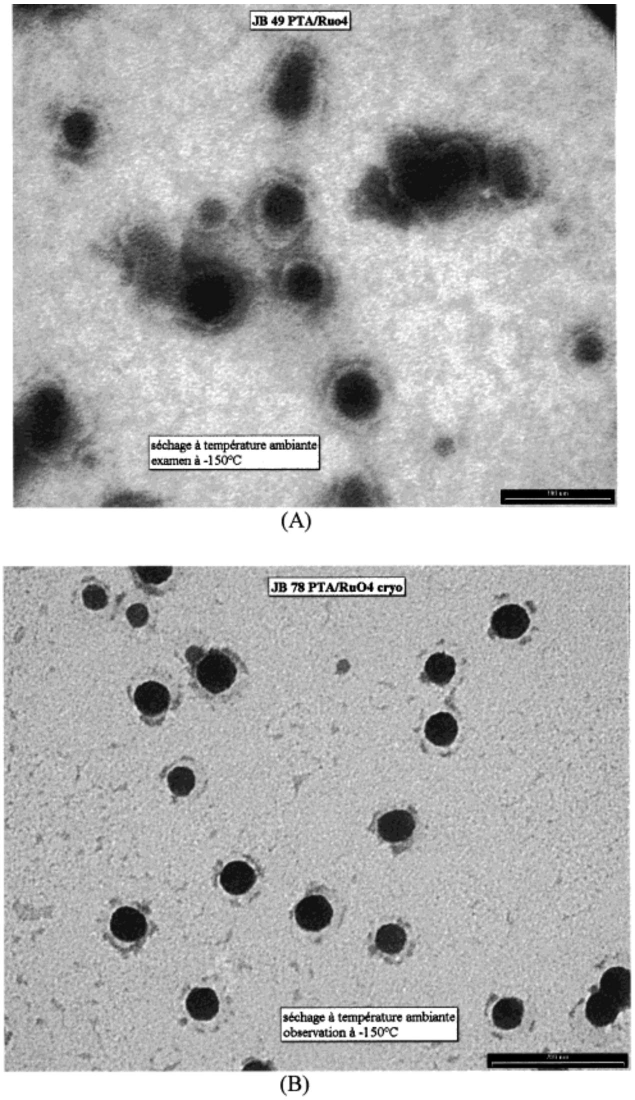
Figure 8. Molecular weight distribution of PSTY-*co*-P(BA−AAEMA) block copolymers synthesized by a second stage polymerization, using a PSTY seed (from expt 12) under starved feed and batch conditions. The detection was DRI.

Synthesis of Block Copolymer Core−Shells. The resulting PSTY seed prepared from expt 12 was used in a second stage polymerization with BA and AAEMA to produce, for the first time, block copolymers with core−shell particle morphologies. The second block of BA and AAEMA was a random copolymer. Figure 8 shows the MWD (using a DRI detector) of the resulting polymer under batch and starved feed. It can be seen that the peak increases slightly to a higher molecular weight, and because the calibration curve is based on polystyrene standards, a quantitative analysis of block formation is difficult. Therefore, GPEC was used to separate and quantify the various polymers formed (i.e., block copolymer, polystyrene, poly(BA−AAEMA), and PBA). This technique allowed the amount of polystyrene prepared with RAFT to be quantified. Under batch conditions the amount of polystyrene transformed to blocks is 64.5% but is increased to 76.4% under starved-feed conditions. This suggests that under batch conditions a greater amount of secondary particles of poly(BA−AAEMA) are formed compared to starved feed conditions. These particles contain no dormant RAFT species and therefore cannot form block copolymers.

The gel contents of these polymers was close to 3% in contrast to a gel content of 68% for a blend of polystyrene−poly(BA−AAEMA). The blend was prepared from a second stage polymerization of BA and AAEMA using a seed (60 nm diameter, >1 million molecular weight) prepared in the absence of RAFT agent. These data suggest that the blocks are linear with little or no branching. The particle morphology of these samples is given in Figure 9, using cryo-TEM. The use of conventional TEM was not successful since the soft PBA was not visible even after negative staining with PTA. The core−shell morphology is shown clearly, with the hard polystyrene core equal to the size of the original seed. The core−shell morphology together with the fact that 75% of blocks have formed further supports the postulate that the RAFT agent and dormant RAFT polymer species are surface-active. If this were not the case, then one would expect a much lower amount of block formation.

Conclusion

The ab initio emulsion polymerizations of styrene in the presence of RAFT agent (**1**) were carried out using conventional surfactant (SDS) and initiator (SPS). The influence of varying the concentrations of SDS, SPS, and **1** on the rate, particle size distribution, and molecular weight distribution was studied. It was found that when increased concentrations of **1** and initiator were used, the particle size distribution became narrower and the number-average diameter decreased. It is postulated that R$^•$, formed from the fragmentation of **1**, will exit the particle to reenter micelles and thus create more particles. However, if the initiator concentration is high enough, then the probability of reentry to form new particles will be low, as aqueous phase termination will be the dominant process. The rate of polymerization is also influenced by the concentrations of SDS, SPS, and **1**. When the SDS concentration is increased, so to is the rate. Increasing the concentration of **1** at a low initiator concentration and at constant SDS concentration results in significant reduction in rate prescribed to be due to exit and then reentry to terminate polymeric radicals growing in the particles. The $\bar{M}_n$ is approximately twice as high when compared to theory. The reasons for this could be resistance of diffusion from the droplets to the particles or chemical deactivation of the RAFT agent. On the basis of the rate of transportation calculations the former seems unlikely, and the postulate that the



(A)

(B)

Figure 9. Cryo-TEM of the core−shell morphologies stained with RuO_4 and PTA. (A) Block copolymer prepared with RAFT agent; seed size 30 nm. (B) Blend prepared without RAFT; core size 50 nm.

RAFT agent might undergo side reactions (e.g., hydrolysis) also seems unlikely since the $\bar{M}_n$ at high conversions converges toward theory. A tentative explanation put forth is that the RAFT agent could be surface active, and therefore the local concentration will be less than the global concentration surrounding the growing radical chains in the particles. This is also supported by the formation of a core−shell morphology containing a 75% of block copolymer. If this were not the case, then the amount of dormant species at the surface would be small and therefore one would expect a much lower amount of block formation.

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