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Effect of Reversible Addition−Fragmentation Transfer (RAFT) Reactions on (Mini)emulsion Polymerization Kinetics and Estimate of RAFT Equilibrium Constant

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ABSTRACT: The Smith−Ewart equation has been modified to describe the kinetics of reversible addition−fragmentation transfer (RAFT) (mini)emulsion polymerization. Two types of radicals (propagating and intermediate) are taken into account. The influence of RAFT reactions on the (mini)emulsion polymerization kinetics is investigated using the modified Smith−Ewart theory. In a simplified zero−one case, the average number of propagating radicals per particle can be described by $\bar{n}_{\mathrm{RAFT}}^{-1} = \bar{n}_{\mathrm{blank}}^{-1} + 2K[\mathrm{RAFT}]_0$, where K is the RAFT equilibrium coefficient. It is found that the rate retardation is an intrinsic kinetic property of RAFT (mini)emulsion polymerization. The miniemulsion polymerization of styrene is also carried out with styrene oligomers of 1-phenylethylphenyl dithioacetate (PS−PEPDTA) and 2-cyanoprop-2-yl dithiobenzoate (PS−CPDB) as the RAFT agents. The experimental $\bar{n}$ data are well described by the theory. The K values are estimated to be 314 L/mol for PS−CPDB and 22 L/mol for PS−PEPDTA. The fragmentation rate coefficients appear to be on the order of magnitude of 10^4−10^5 s^{-1}.

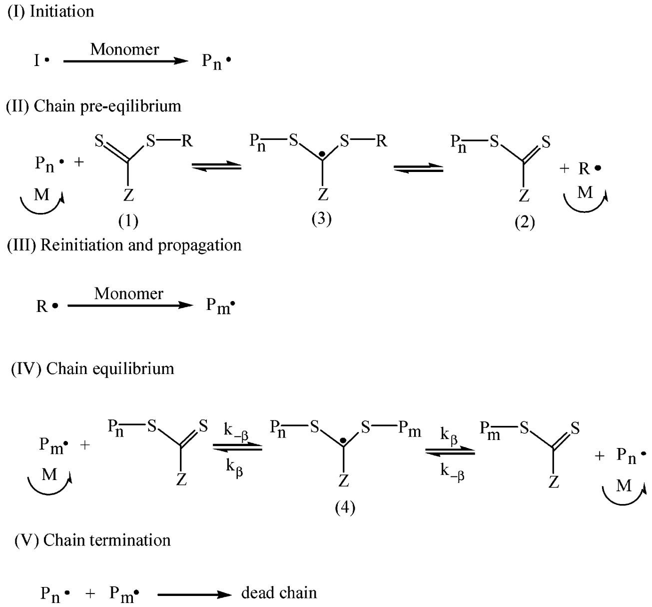
Introduction

The controlled/living radical polymerization (CLRP) technique provides a powerful tool for preparation of tailor-made polymer products.[1−3] This type of polymerization not only yields polymers with narrow molecular weight distributions but also allows generation of complex molecular architectures, such as block, star, and comb copolymers. Three major CLRP methods are nitroxide-mediated polymerization (NMP),[4−6] atom transfer radical polymerization (ATRP),[7−10] and reversible addition−fragmentation chain transfer (RAFT) polymerization.[11−14]

RAFT polymerization has attracted much attention in the recent years since it can be applied to a broad range of monomer types and can be operated at moderate conditions.[12] In the RAFT polymerization, a RAFT agent with a general structure S═C(Z)−SR is employed, where Z is an activating group and R is a leaving/initiating group.[15,16] The RAFT agent is actually a highly efficient chain transfer agent. The RAFT polymerization mechanism, as illustrated in Scheme 1, has been well accepted.[17] The RAFT process (reactions II and IV in Scheme 1) is a reversible transfer process in which free radicals exchange degeneratively with dormant species. The addition rate constant is much higher than the propagation rate constant. The appropriate choice of Z and R groups that facilitate fast fragmentation and efficient reinitiation is the key for the livingness of RAFT polymerization systems and the control of polymer molecular weights.

Compared to a bulk or a solution polymerization, an emulsion polymerization is more favored in industries as it eliminates volatile organic compounds (VOCs) and offers easy removal of reaction heat, low viscosity, ease in handling, high yield, and high molecular weight polymer products.[18] In addition, it has been argued that the compartmentalization effect in conventional emulsion polymerization is still effective in RAFT (mini)emulsion polymerization.[20] The effect separates propagating radicals into different particles, reduces radical termination, and increases the polymerization rate. Recently, many investigations on RAFT (mini)emulsion polymerization have been carried out.[19−22] However, the colloidal instability is a real issue. The particle size distribution is usually broadened.[21] The polymerization rate is unexpectedly low. The molecular weight distribution is also broad.[19,20] Luo et al.[23] attributed the instability to "superswelling" of particles in the early stage of polymerization. The problem of colloidal instability can be minimized with high levels of surfactant and hydrophobe.

Scheme 1. Mechanism of RAFT Polymerization



Some bulk RAFT polymerization systems experience inhibition or retardation in the polymerization rate.[12,24] The inhibition or retardation effect is severe in the styrene polymerization with

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2-cyanoprop-2-yl dithiobenzoate (CPDB) as the RAFT agent but is minor with 1-phenylethylphenyl dithioacetate (PEPDTA).[25] There is an ongoing debate in the community on the mechanism that causes the inhibition/retardation.[26−28] Some researchers believed that the fragmentation rate coefficient of the intermediate radicals (species (3) and (4) in Scheme 1) is on the order of magnitude of 10^{-2} s^{-1}. The intermediate radicals do not terminate with each other (self-termination) or with propagating radicals (cross-termination) and behave as a sink for propagating radicals. Other groups suggested that the fragmentation rate coefficient is on the order of magnitude of 10^4 s^{-1} and that the intermediate radicals experience significant cross-termination. Both sides are supported by some experimental data and modeling work. It is indeed very puzzling that there appears to exist a difference of 6 orders of magnitude in the reported values of the fragmentation rate coefficient for the virtually similar RAFT systems. Charleux et al. reported that in the RAFT polymerization of butyl acrylate mediated with *tert*-butyl dithiobenzoate a high apparent equilibrium constant is compatible to the observation of the induction period, but the further rate retardation is better explained by the existence of cross-termination.[29]

The inhibition/retardation effect has also been reported in RAFT (mini)emulsion polymerization.[30,31] Butte et al.[22] argued that the kinetics of RAFT (mini)emulsion polymerization is the same as that of conventional miniemulsion polymerization because there are no radicals generated or disappeared in the RAFT process. The retardation effect in an emulsion polymerization could be more severe than in a bulk countpart.[21] Some researchers attributed this retardation to the escape of the R radicals that are generated from the initial RAFT agent molecules.[21] These small-sized radicals may undergo termination in aqueous phase or reentry to particles to terminate growing chains. Others proposed that the intermediate radicals terminate with propagating radicals as in a bulk RAFT system.[14] Both explanations have invited further questions.[31]

Since RAFT is a reversible chain transfer process, it was believed that the (mini)emulsion polymerization kinetics is not affected by the addition of RAFT agent, and thus the system does not require special investigation. By a Monte Carlo simulation, Prescott[32] discussed the possible influence of RAFT agent on the chain-length-dependent termination in emulsion polymerization. Gilbert et al.[33] discussed the influence of oligomeric radicals formed in aqueous phase on the RAFT kinetics. However, to our best knowledge, there is no literature that has reported the intrinsic effect of the RAFT process on the kinetics of a (mini)emulsion polymerization system. In this paper, the intrinsic effect of RAFT reactions on the (mini)emulsion polymerization kinetics is theoretically investigated. A series of experiments of the RAFT miniemulsion polymerization of styrene are carried out to verify the theory. The RAFT equilibrium coefficients of CPDB and PEPDTA are also estimated by combining the theoretical results and experimental data.

Theoretical Development

The classical Smith−Ewart equation describes the kinetics of conventional (mini)emulsion polymerization by a population balance technique. However, in a RAFT (mini)emulsion polymerization, there are two types of radicals as shown in Scheme 1: propagating radicals and intermediate radicals. The kinetic properties of the two radical types are different. Only propagating radicals react with monomer and contribute to the polymerization. It is of high controversy whether intermediate radicals cross-terminate with propagating radicals, though the self-termination of intermediate radicals is considered to be less possible.[34] In the RAFT polymerization, we need to consider the population distribution of particles in terms of not only the number of propagating radicals but also the number of intermediate radicals. The classical Smith−Ewart equation can be modified as follows:

$$\frac{\mathrm{d}N_{i,j}}{\mathrm{d}t} = \rho(N_{i-1,j} - N_{i,j}) + k((i+1)N_{i+1,j} - iN_{i,j}) + c((i+2)(i+1)N_{i+2,j} - i(i-1)N_{i,j}) + k_{\beta}([\mathrm{RAFT}_{j-1}](i+1)N_{i+1,j-1} - [\mathrm{RAFT}_j]iN_{i,j}) + k_{-\beta}((j+1)N_{i-1,j+1} - jN_{i,j}) + \chi((i+1)(j+1)N_{i+1,j+1} - ijN_{i,j}) \qquad i, j = 0, 1, ..., \infty \quad (1)$$

where $N_{i,j}$ is the number fraction of particles that contain i propagating radicals and j intermediate radicals. The terms on the right side of the equation describe the influences of entry, exit, self-termination of propagating radicals, addition to RAFT agent, fragmentation of intermediate radicals, and cross-termination between propagating and intermediate radicals, respectively. The self-termination of intermediate radicals is ignored here since no experimental evidence supported such a reaction. ρ is the rate of entry of free radicals into particle: $= 2f_{\mathrm{in}}k_{\mathrm{d}}[\mathrm{I}]N_{\mathrm{A}}/N_{\mathrm{p}}$, where f_{in} is the initiator efficiency calculated by Maxwell−Morrison model,[35] k_{d} is the rate coefficient of initiator decomposition, [I] is the initiator concentration, N_{A} is the Avogadro number, and N_{p} is the number of particles per unit volume of aqueous phase. k is the rate coefficient for exit. c is the rate coefficient for self-termination of propagating radicals: $= k_{\mathrm{tc}}/(N_{\mathrm{A}}V_{\mathrm{p}})$, where k_{tc} is the rate coefficient for termination by recombination, and V_{p} is the swollen particle volume. k_{β} is the addition rate coefficient. $k_{-\beta}$ is the fragmentation rate coefficient. χ is the first-order rate coefficient for cross-termination: $= k_{\mathrm{ct}}/(N_{\mathrm{A}}V_{\mathrm{p}})$, where k_{ct} is the rate coefficient for cross-termination between propagating and intermediate radicals. $[\mathrm{RAFT}_j]$ is the concentration of RAFT agent molecules in the particle that contains j intermediate radicals: $= [\mathrm{RAFT}]_0 - j/(N_{\mathrm{A}}V_{\mathrm{p}})$. This set of ordinary differential equations (eq 1 with various i and j) can be numerically solved provided the values of the parameters are given. By definition, we have

$$\bar{n} = \sum_i \sum_j iN_{i,j} \quad (2a)$$

$$\bar{m} = \sum_i \sum_j jN_{i,j} \quad (2b)$$

where $\bar{n}$ and $\bar{m}$ represent the average numbers of propagating and intermediate radicals per particle, respectively.

In a zero−one system of conventional (mini)emulsion polymerization, the entry of a radical into particle that already contains a radical leads to an essentially instantaneous termination. However, when the RAFT agent is introduced to the polymerization system, the situation is very different. The propagating and intermediate radicals behave very differently in propagation and termination in the RAFT polymerization system. The polymerization remains to be a zero−one system when one of the following two conditions is satisfied: (1) the rate coefficient of cross-termination between propagating and intermediate radicals is similar to that of the self-termination of propagating radicals, or (2) the fragmentation rate coefficient is adequately high. In such a system, all particles contain either zero or one radical regardless of the radical type (propagating or intermediate). Under such conditions, a radical that enters a particle that contains either a propagating or an intermediate radical will cause instantaneous termination. Equation 1 can thus be simplified to eq 3.

$$\frac{dN_{0,0}}{dt} = -\rho N_{0,0} + \rho N_{1,0} + \rho N_{0,1} + kN_{1,0} \tag{3a}$$

$$\frac{dN_{1,0}}{dt} = -\rho N_{1,0} + \rho N_{0,0} - kN_{1,0} - k_{\beta}[\mathrm{RAFT}]_0 N_{1,0} + k_{-\beta}N_{0,1} \tag{3b}$$

$$\frac{dN_{0,1}}{dt} = -\rho N_{0,1} + k_{\beta}[\mathrm{RAFT}]_0 N_{1,0} - k_{-\beta}N_{0,1} \tag{3c}$$

$$N_{0,0} + N_{1,0} + N_{0,1} = 1 \tag{3d}$$

The steady-state solution of eq 3 is eq 4.

$$N_{0,0} = 1 - \frac{k_{\beta}[\mathrm{RAFT}]_0 + k_{-\beta} + \rho}{2((1 + k/(2\rho))(\rho + k_{-\beta}) + k_{\beta}[\mathrm{RAFT}]_0)} \tag{4a}$$

$$\bar{n} = N_{1,0} = \frac{k_{-\beta} + \rho}{2((1 + k/(2\rho))(\rho + k_{-\beta}) + k_{\beta}[\mathrm{RAFT}]_0)} \tag{4b}$$

$$\bar{m} = N_{0,1} = \frac{k_{\beta}[\mathrm{RAFT}]_0}{2((1 + k/(2\rho))(\rho + k_{-\beta}) + k_{\beta}[\mathrm{RAFT}]_0)} \tag{4c}$$

When $k_{-\beta} \gg \rho$, we have

$$\bar{r} = \frac{\rho}{2\rho + kf_n} \tag{5a}$$

$$\bar{n} = f_n\bar{r} \tag{5b}$$

where $\bar{r}$ is the average number of the total radicals per particle, i.e., $\bar{n} + \bar{m}$; f_n is the probability of a randomly selected radical that happens to be a propagating radical: $f_n = 1/(1 + K[\mathrm{RAFT}]_0)$ where K is the RAFT equilibrium constant. In such a case as styrene polymerization, the exit rate coefficient k is much smaller than the entry rate coefficient ρ ($kf_n \ll 2\rho$ in eq 5a). The value of $\bar{r}$ is close to 0.5, and $\bar{n}$ is independent of [I].

It can be noted that in a bulk RAFT polymerization, when the RAFT equilibrium is reached, we have

$$[\mathrm{P}^{\bullet}] = \frac{1}{1 + K[\mathrm{RAFT}]_0}([\mathrm{P}^{\bullet}] + [\mathrm{Y}^{\bullet}]) \tag{6}$$

where $[\mathrm{P}^{\bullet}]$ is the propagating radical concentration and $[\mathrm{Y}^{\bullet}]$ is the intermediate radical concentration. The similarity between eqs 5b and 6 reveals that the compartmentalization in a (mini)-emulsion polymerization system does not affect the RAFT equilibrium (note: $([\mathrm{Y}^{\bullet}]/[\mathrm{P}^{\bullet}])_{\mathrm{bulk}} = (\bar{m}/\bar{n})_{\mathrm{emulsion}} = K[\mathrm{RAFT}]_0$).

Since the RAFT equilibrium is still established between the propagating and intermediate radicals in a (mini)emulsion polymerization, we can apply the population balance to the total number of radicals and yield

$$\frac{dN_r}{dt} = \rho(N_{r-1} - N_r) + kf_n((r+1)N_{r+1} - rN_r) + cf_n^{\,2}((r+2)(r+1)N_{r+2} - r(r-1)N_r) + \chi f_n(1 - f_n)((r+2)(r+1)N_{r+2} - r(r-1)N_r) \tag{7}$$

where r is the number of total radicals per particle. The third and fourth terms on the right side of eq 7 describe the self-termination of propagating radicals and the cross-termination between propagating and intermediate radicals. Equation 7 is general for RAFT miniemulsion polymerization no matter whether it is a zero−one system. Let $c' = f_n^{\,2}c + f_n(1 - f_n)\chi$, eq 7 is rearranged into

$$\frac{dN_r}{dt} = \rho(N_{r-1} - N_r) + kf_n((r+1)N_{r+1} - rN_r) + c'((r+2)(r+1)N_{r+2} - r(r-1)N_r) \tag{8}$$

The physical meaning of c' is the overall termination rate coefficient. With this definition, eq 8 becomes the classic Smith−Ewart equation. Because the self-termination for intermediate radicals is prohibited in the current model (no evidence to support such a reaction to date), c' is always less than or equal to c (i.e., $c' = f_n^{\,2}c + f_n(1 - f_n)\chi \le f_n^{\,2}c + f_n(1 - f_n)c = f_nc < c$ at $\chi \le c$).

A conventional (mini)emulsion polymerization is a zero−one system if $\rho \ll c$. A RAFT polymerization is also a zero−one system if $\rho \ll c'$. Under certain conditions, for example, with very high $K[\mathrm{RAFT}]_0$ and thus very low f_n, the termination rate can be lower than the initiation rate, i.e., $\rho > c'$ even if $\rho \ll c$. When a propagating radical enters a particle that already contains a radical, the propagating radical does not terminate “instantaneously” with the existing radical and is most likely “stored” as an intermediate radical, leading to an accumulation of radicals in the particle. The polymerization may then deviate from a zero−one system. Under the condition of a large r, we have

$$\sum r^2N_r - \sum rN_r = \left(\sum rN_r\right)^2$$

The conventional zero−one system can be changed to a pseudo-bulk system. Equation 8 can be summarized into eq 9.

$$\frac{d\bar{r}}{dt} = \rho - kf_n\bar{r} - 2c'(\bar{r})^2 \tag{9}$$

If the exit of monomeric radicals is negligible ($k \approx 0$) and if the rate coefficients of initiation and termination remain constant, the following analytical solutions can be obtained from eq 9:

$$\bar{r} = \tanh(\sqrt{2\rho c'}\,t)\sqrt{\frac{\rho}{2c'}} \tag{10a}$$

$$\bar{n} = \bar{r}f_n = \tanh(\sqrt{2\rho c'}\,t)\sqrt{\frac{\rho}{2c'}}f_n \tag{10b}$$

According to the “slow-fragmentation” mechanism, as suggested by Davis et al.,[24] the cross-termination is negligible, and the c' value reaches its minimum, $f_n^{\,2}c$. Equation 10 can be rearranged as

$$\bar{r} = \frac{\tanh(\sqrt{2\rho c}\,f_nt)\sqrt{\dfrac{\rho}{2c}}}{f_n} \tag{11a}$$

$$\bar{n} = \tanh(\sqrt{2\rho c}\,f_nt)\sqrt{\frac{\rho}{2c}} \tag{11b}$$

The characteristic of eq 11b is that $\bar{n}$ approaches to a steady-state value of $\sqrt{\rho/(2c)}$ with time. This steady-state value is (1) independent of [RAFT] and (2) linearly proportional to $[\mathrm{I}]^{0.5}$.

From eqs 5 and 11, one can see how the RAFT reactions intrinsically change the kinetics of (mini)emulsion polymerization. In the case of $\rho \ll c'$ (i.e., zero−one case), the RAFT process causes a retardation in polymerization rate. On the other hand, in the case of $\rho > c'$, a zero−one system is changed to a pseudo-bulk system. No compartmentalization effect is expected in such a case.

In the above development, only the monomeric radicals are accounted for in the desorption of radicals from the particles. Very recently, Prescott et al.[33] proposed that in a RAFT (mini)emulsion polymerization a "RAFT-induced exit" could occur. According to the Mawell-Morrison model for the entry of radicals, a z-meric radical in the water phase enters irreversibly into the first particle it encounters. However, in the case of RAFT polymerization, the z-meric radical converts to a z-meric RAFT adduct after entry. This z-meric RAFT adduct can be reactivated to a z-meric radical, which is apt to exit. With the first-order rate coefficient for the desorption of the z-meric radical is an order of 10^5 s^{-1}, the rate coefficient for the loss of a radical by exit from a particle is estimated to be 4.0 s^{-1} for styrene persulfate-initiated polymerization under an assumption of one z-mer RAFT adduct per particle. When this "RAFT-induced exit" is taken into account, eq 5b is modified into (see the Appendix):

$$\bar{n} = \frac{\sqrt{(2\rho + kf_n)^2 + 8k_z f_n \rho} - (2\rho + kf_n)}{4k_z} \tag{12}$$

$$k_z = k_{\mathrm{tr,RAFT}} C_z P(\text{exit-}z) \tag{13}$$

where $k_{\mathrm{tr,RAFT}}$ is the transfer rate coefficient to the RAFT agent, C_z is the concentration of z-meric RAFT adduct in the particle, and $P(\text{exit-}z)$ is the probability of the z-meric radical exiting the particle. Equation 12 indicates that when the "RAFT-induced exit" is effective, $\bar{n}$ will be a function of the initiation rate even under the "instantaneous termination" condition.

Experimental Part

Materials. Deionized water (conductivity < 4 μS/cm) was used as received. Styrene (St) was purified by distillation. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%) was recrystallized twice from methanol. Potassium persulfate (KPS, >99%, Yixin Chemical Reagent Plant, China), sodium dodecyl sulfate (SDS, surfactant, >99%, from ABCR GmbH & Co. KG), and hexadecane (HD, costabilizer, >99%, from Aldrich) were used without further purification. 1-Phenylethylphenyl dithioacetate (PEPDTA) and 2-cyranoprop-2-yl dithiobenzoate (CPDB) were synthesized and purified according to the literature.[15,16]

Preparation of Oligomeric RAFT Agent. As an example, the mixture of St (60 g), AIBN (0.113 g), and RAFT agent (PEPDTA 3.01 g) was transferred to a 250 mL five-neck flask, equipped with a condenser, a thermometer, a nitrogen inlet, and a mechanical stirrer. The reaction solution was purged for 30 min with a nitrogen stream. After purging, the reaction vessel was placed into a water bath at 70 °C for 6 h under a nitrogen atmosphere. The reaction mixture was slowly poured with stirring into a large excess of methanol (400 mL). The precipitated polymer was washed with methanol for four times. Finally, the polymer was collected and dried at 35 °C in a vacuum oven for 16 h. Thus, 11.5 g of PS−PEPDTA with $\bar{M}_n$ = 1330 g/mol and PDI = 1.10 was obtained.

Miniemulsion Polymerization. The initial miniemulsion was prepared according to the following procedure. As an example, styrene (20.0 g) was first mixed with hexadecane (1.0 g) and RAFT agent (PS−CPDB, 0.5 g). This organic mixture was then added to an aqueous phase (75.0 g of water and 1.0 g of SDS) with stirring. The coarse emulsion mixture was ultrasonified using a KS-600 Sonifier (amplitude 70%, 600 W) for 15 min. The obtained miniemulsion was then transferred to a 250 mL five-neck flask that was deoxygenated for 60 min prior to the charge. The reactor was equipped with a condenser, a thermometer, a nitrogen inlet, and a mechanical stirrer. The miniemulsion was stirred at room temperature for 10 min before the reactor was immersed into a water bath of 75 °C. The reactor was purged with nitrogen for 20 min at the water bath temperature. The polymerization was started with the addition of KPS (0.08 g) dissolved in 5 g of water. The samples were regularly withdrawn, quenched with hydroquinone, and separated into two parts with one for conversion measurement and the other for particle size determination.

Table 1. Experimental Conditions, Particle Size, and the Number of Particles of All the Miniemulsion Polymerization Runs in This Work

expt	type of RAFT agent	[RAFT] (mol/L (St))	$[\mathrm{KPS}]_0$ (mol/L (water))	$\bar{d}_w$ (nm)	PDI	N_p (mL^{-1} (water))
1	blank	0	3.70×10^{-3}	67		9.83×10^{14}
2	PS−CPDB	1.16×10^{-2}	3.70×10^{-3}	96	1.50	3.51×10^{14}
3	PS−CPDB	2.22×10^{-2}	3.70×10^{-3}	98	1.38	3.43×10^{14}
4	PS−CPDB	4.29×10^{-2}	3.70×10^{-3}	103	1.18	3.09×10^{14}
5	PS−CPDB	2.22×10^{-2}	1.85×10^{-3}	117	1.50	1.90×10^{14}
6	PS−CPDB	2.22×10^{-2}	7.40×10^{-3}	106	1.40	3.13×10^{14}
7	PS−PEPDTA	1.70×10^{-2}	3.70×10^{-3}	90	1.56	6.54×10^{14}
8	PS−PEPDTA	3.45×10^{-2}	3.70×10^{-3}	96	1.30	5.46×10^{14}
9	PS−PEPDTA	5.62×10^{-2}	3.70×10^{-3}	98	1.17	4.77×10^{14}

Bulk Polymerization. The mixture of St (17.1 g), AIBN (1.4 × 10^{-2} g), and PS−PEPDTA (0.5 g) was transferred to glass tubes and deoxygenated with nitrogen. The tubes, sealed with septa, were then bathed in 75 °C water and removed at the preset time intervals. The reactions were quenched by cooling the tubes in an ice bath and then adding hydroquinone/tetrahydrofuran (THF) solution. The polymer materials were collected by evaporating the solvent and residual monomer.

Sample Characterization. Monomer conversion was followed gravimetrically. Each part of latex sample was diluted with 50 parts of SDS-saturated water and was kept at 50 °C under 10 mmHg for 15 h to eliminate residual monomer. The particle size was measured by a dynamic light scattering (Malvern 3000HSA) after a sonification treatment. The number of particles was calculated by

$$N_p = \frac{6M_T x}{\pi \bar{d}_w^{\,3} \rho_p} \tag{14}$$

where M_T is the monomer concentration in g/mL water, x is the monomer conversion, ρ_p is the density of polystyrene (1.06 g/mL), and $\bar{d}_w$ is the volume-average diameter. N_p was calculated at the monomer conversion >70%.

The polymer molecular weight distribution was determined at 303 K by gel permeation chromatography (Waters 2487/630C) with three PL columns (10^4, 10^3, 500 Å) and a refractive index (RI) detector. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL/min. The measurement was calibrated using low-polydispersity PS standard samples with molecular weights ranging from 580 to 710 000 g mol^{-1}.

TEM (transmission electron microscopy) measurements were performed on a JEM-1230. The samples were prepared as follows: 0.03 g of final latex was diluted by 20 g of deionized water. One drop of the dilution was dripped onto the carbon-coated copper mesh and dried at room temperature.

Results and Discussion

Three sets of experimental runs were carried out. The recipes are summarized in Table 1. In the first set (experiments 3, 5, and 6), the initiator concentration level was varied while the other conditions remained unchanged. In the second set (experiments 2, 3, and 4), the RAFT agent concentration level was varied. In these two sets, the RAFT agent was the oligomeric derivative of CPDB (PS−CPDB, M_n = 1800 g/mol, PDI = 1.05). In the third set (experiments 7, 8, and 9), the phenyl group in the RAFT agent was replaced by the benzyl group (PS−PEPDTA, M_n = 1330 g/mol, PDI = 1.10). Because of the difference in their abilities to stabilize intermediate radicals, it is believed that the fragmentation rate coefficient of PS−PEPDTA is much higher than that of PS−CPDB.

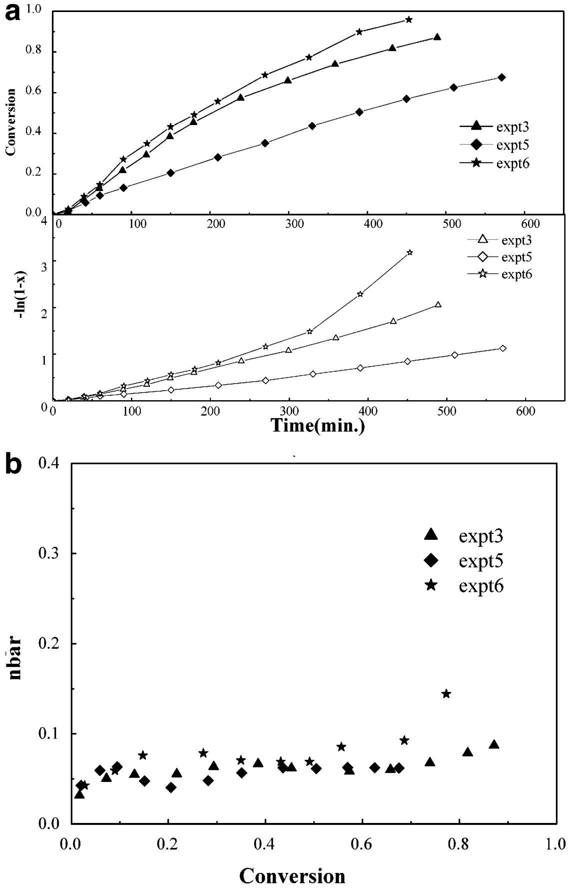

Figure 1. (a) Evolution of monomer conversion as a function of time with three initiator concentrations in the PS−CPDB (2.22×10^{-2} mol/L (St)) mediated styrene polymerization at 75 °C (experiment 3: 3.70×10^{-3} mol/L (water); experiment 5: 1.85×10^{-3} mol/L (water); experiment 6: 7.40×10^{-3} mol/L (water)). (b) Evolution of the average number of propagating radicals per particle, $\bar{n}$, as a function of conversion at three initiator concentrations in the PS−CPDB (2.22×10^{-2} mol/L (St)) mediated styrene polymerization at 75 °C. KPS (experiment 3: 3.70×10^{-3} mol/L (water); experiment 5: 1.85×10^{-3} mol/L (water); experiment 6: 7.40×10^{-3} mol/L (water)).

The experiments were designed so that the assumptions of the model could be satisfied. The use of the oligomeric RAFT agent eliminated possible inhibition or retardation effect caused by the exit of R group from particle.[21] The complication caused by the preequilibrium of step II in Scheme 1 was also eliminated because the adding and leaving radicals are the same type. The high surfactant (SDS) and costabilizer (HD) concentrations were used to limit possible monomer transport between particles and to ensure a colloidal stability.[20,23]

Influence of Initiator Concentration on RAFT Polymerization Kinetics. Figure 1a,b summarizes the conversion and $\bar{n}$ evolution curves with various initiator concentrations. It can be seen in Figure 1a that the polymerization rate increased with an increase in the initiator concentration. This influence was through the increase in the number of particles, N_p (see Table 1). As pointed out by Schork et al.[36] in a conventional miniemulsion polymerization, N_p increases with an increase in initiator concentration up to a constant N_p value that is the number of initial minidroplets. Figure 1b shows the influence of [I] on $\bar{n}$. The $\bar{n}$ value remained unchanged in the range of 20−60% conversion in all the cases. Before 20%, the $\bar{n}$ value increased with monomer conversion because more and more monomer droplets were nucleated and became particles. After 60%, the $\bar{n}$ value started to increase, probably due to a “gel effect”. This observation was in good agreement with the literature work, in which the k_{tc} value decreased sharply after 60% conversion in the bulk RAFT polymerization of styrene.[37] More importantly, $\bar{n}$ was almost constant with various initiator concentrations. This observation suggests that the polymerization was a zero−one system under the current conditions when the monomer conversion was lower than 60%. However, after 60%, the termination became diffusion-controlled and the kinetics should be pseudo-bulk. The lack of dependence of $\bar{n}$ on the initiator concentration in the range of 20−60% monomer conversion also suggests that the “RAFT-induced exit” played a negligible role in the polymerization kinetics of the current system because the “RAFT-induced exit” predicted a significant dependence of $\bar{n}$ on the initiation rate (eq 12).

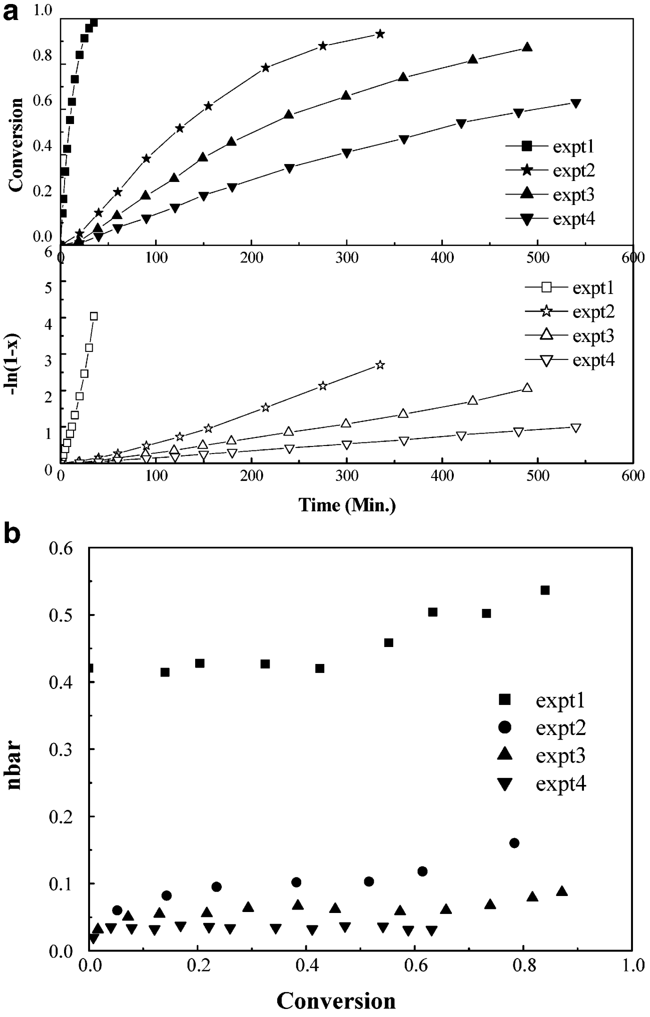

Figure 2. (a) Evolution of the monomer conversion as a function of time in the PS−CPDB mediated styrene polymerization at 75 °C. KPS: 3.70×10^{-3} mol/L (water); PS−CPDB (experiment 1: 0; experiment 2: 1.16×10^{-2} mol/L (St); experiment 3: 2.22×10^{-2} mol/L (St); experiment 4: 4.29×10^{-2} mol/L (St)). (b) Evolution of the average number of propagating radicals per particle, $\bar{n}$, as a function of conversion in the PS−CPDB mediated styrene polymerization at 75 °C. KPS: 3.70×10^{-3} mol/L (water); PS−CPDB (experiment 1: 0; experiment 2: 1.16×10^{-2} mol/L (St); experiment 3: 2.22×10^{-2} mol/L (St); experiment 4: 4.29×10^{-2} mol/L (St)).

Influence of RAFT Agent Concentration on RAFT Polymerization Kinetics. Figure 2a shows the kinetic curves of the second set of experimental runs. The polymerization rate was retarded by the RAFT agent. The rate decreased with an increase in the RAFT agent concentration. The introduction of the oligomeric RAFT agent also reduced the number of particles to ∼30% of the blank experiment (see Table 1, experiments 1

Table 2. Kinetic Parameters Used in Modeling the Miniemulsion Polymerization

parameter	value at 75 °C	remark	ref
k_d	4.35×10^{-5} s^{-1}	calculated from $k_d = 8 \times 10^{15} e^{-135/RT}$	18
$k_{t,aq}$	5×10^{8} L mol^{-1} s^{-1}	taken as $k_{t,aq} = 1 \times 10^{9} i^{-0.66}$ with $i = 2$	38, 39
$k_{p,aq}$	1.7×10^{3} mol^{-1} s^{-1}	taken as $3k_p$, because of chain length effect	40, 41
C_w	0.006 mol L^{-1}	calculated from $\ln C_w = 1.514 - 1259/T$	18
f_{ini}	0.532	$f_{ini} = \{1 + [(k_d[I]k_{t,aq})^{1/2}/(k_{p,aq}C_w)]\}^{1-z}$, z ia taken as 2	35
k	0	because of the oligomeric RAFT agent	
k_β	4×10^{6} L mol^{-1} s^{-1}	taken as the value measured at 60 °C	42
$k_{-\beta}$	0.4 to 4×10^{5} s^{-1}	changed by orders of magnitude	
k_{tc}	1.0×10^{8} or 1.0×10^{7} L mol^{-1} s^{-1}	considered as constant during conversion 20−60%	37
k_{ct}	0.4×10^{8} L mol^{-1} s^{-1}	calculated from $k_{ct} = 0.4k_{tc}$, and used only when $k_{-\beta} > 4 \times 10^{2}$, otherwise $k_{ct} = 0$	44

and 2), which caused some reduction in the rate. The decrease in the number of particles might be partly due to the higher viscosity of the oil phase that contained the oligomeric RAFT agent than that of the blank experiment[43] and partly due to the lower nucleation efficient in a RAFT system. Increasing the RAFT agent concentration did not further reduce the N_p, while the polymerization rate became further retarded. Therefore, the influence of RAFT agent addition on the N_p could not adequately explain the retardation phenomenon. The variation of $\bar{n}$ with RAFT agent concentration provided an additional explanation for the retardation effect. Figure 2b shows the $\bar{n}$ evolution curves with different RAFT agent concentrations. The dependence of $\bar{n}$ on the RAFT agent concentration led to the rate retardation.

Equations 3 and 9 were used to correlate the experimental dependence of $\bar{n}$ on [RAFT] using the parameters listed in Table 2. The solution of eq 9 agreed well with one set of the $\bar{n}$−conversion data by adjusting $k_{-\beta}$ and k_{tc} within their reasonable ranges. However, the equation could not possibly fit all the three sets of data by a single pair of $k_{-\beta}$ and k_{tc}. Figure 3 shows the results of eq 9 with two sets of parameters. When $k_{tc} = 10^{8}$ L mol^{-1} s^{-1} and $k_{-\beta} < 10$ s^{-1}, the $\bar{n}$−conversion curves with different RAFT agent concentrations overlapped and became a single line, suggesting the independence of $\bar{n}$ on the RAFT agent concentration. When $k_{tc} = 10^{7}$ L mol^{-1} s^{-1}, the curves with different RAFT agent concentrations were separated at low conversions but converged at high conversions. A wide range of the $k_{-\beta}$ (<10 s^{-1}) and k_{tc} values were tried; no single pair provided a reasonable fitting to the data with eq 9. In contrast, eq 3 with a single $k_{-\beta}$ value correlated all the three experimental $\bar{n}$−conversion curves, as seen in Figure 3. In this zero−one case, the radical termination is not a rate-determining step. The magnitude of k_{tc} does not play a role in the calculation. This allows us to estimate the K value independently, which will be demonstrated in a later part.

Influence of RAFT Agent Structure on Kinetics. Figure 4a,b shows the polymerization kinetics with the oligomeric PEPDTA. Because the Z group of the RAFT agent is benzyl instead of phenyl, the intermediate radical is believed to be less stable than that of CPDB, and a higher fragmentation rate coefficient is expected. It was reported that the bulk polymerization of styrene with PEPDTA experienced little inhibition/retardation.[25] However, in this work, we observed the retardation caused by the decrease in $\bar{n}$ in the miniemulsion polymerization. This observation suggests that the retardation in RAFT (mini)emulsion polymerization is more severe than in bulk. The general evolution trend of $\bar{n}$ with the oligomer−PEPDTA was similar to that of the oligomer−CPDB (compare Figure 2b and Figure 4b). However, the $\bar{n}$ value of the oligomer−PEPDTA was significantly higher than that of the oligomer−CPDB, which is in good agreement with the expected higher fragmentation rate coefficient.

In summary, the experimental data supported that the RAFT miniemulsion polymerization of styrene using both oligomer−CPDB and oligomer−PEPDTA were zero−one systems when the monomer conversion was less than 60%. Equation 5 gives a good description for the kinetics of such systems. We can actually estimate the equilibrium constant of the RAFT reaction using the equation. Equation 5 can be rearranged into

$$\frac{1}{\bar{n}_{\mathrm{RAFT}}} = \frac{1}{\bar{n}_{\mathrm{blank}}} + 2K[\mathrm{RAFT}]_0 \tag{15}$$

where $\bar{n}_{blank}$ is the average number of radicals per particle in a RAFT-free miniemulsion polymerization system that equals to $\rho/(2\rho + k)$. Equation 15 predicts a linear relationship between $1/\bar{n}$ and $[\mathrm{RAFT}]_0$ with the slope equal to $2K$. Figure 5 plots $1/\bar{n}$ against $[\mathrm{RAFT}]_0$ for the systems with two types of RAFT agents used in this work. The equation fitted the experimental data very well for both systems. It was estimated that $K = 314$ L/mol for PS−CPDB and $K = 22$ L/mol for PS−PEPDTA. Considering 5 nm errors in the measurement of $\bar{d}_w$ by the dynamic light scattering method, we estimated the value of K to be 314 ± 60 L/mol for the PS−CPDB system. Fukuda et al. studied the bulk polymerization of styrene at 60 °C mediated by the same RAFT agent and reported a K value of 55 L/mol that was estimated by combining kinetic and ESR data.[13] Barner-Kowollik et al. also studied a similar system but reported a K value of 10^{7} L/mol.[24] Our result in this work appeared to be much closer to Fukuda's than to Barner-Kowollik's.

The excellent agreement between the experimental data and eq 15 with different initiator concentrations, different RAFT concentrations, and different RAFT types strongly supported that the current studied systems were the zero−one emulsion polymerization systems. Equation 15 provided an independent method to estimate the RAFT equilibrium constant K. Obviously, the accuracy of the K value strongly depended on the $\bar{n}$ values and thus the diameters of the final latex. The particle sizes were measured by dynamic light scattering. Figure 6 shows the particle size distribution (PSD) of the final latex of experiment 7, which was derived from the TEM images. Although it is rather broad, the PSD is unimodal. The estimated K values were used to predict the kinetics of RAFT bulk polymerization. Figure 7 compares the theoretical predictions with the experimental observations. An excellent agreement was obtained. Such agreement strongly supports the theory and the method we developed for the estimate of K value.

Compartmentalization Effect and Rate Retardation. The RAFT miniemulsion polymerization exhibited a rate retardation effect. However, the retardation mechanism is different from that in a bulk RAFT polymerization. According to the fast fragmentation theory,[44] the retardation observed in the bulk polymerization was attributed to the cross-termination between propagating and intermediate radicals, which lowers the total

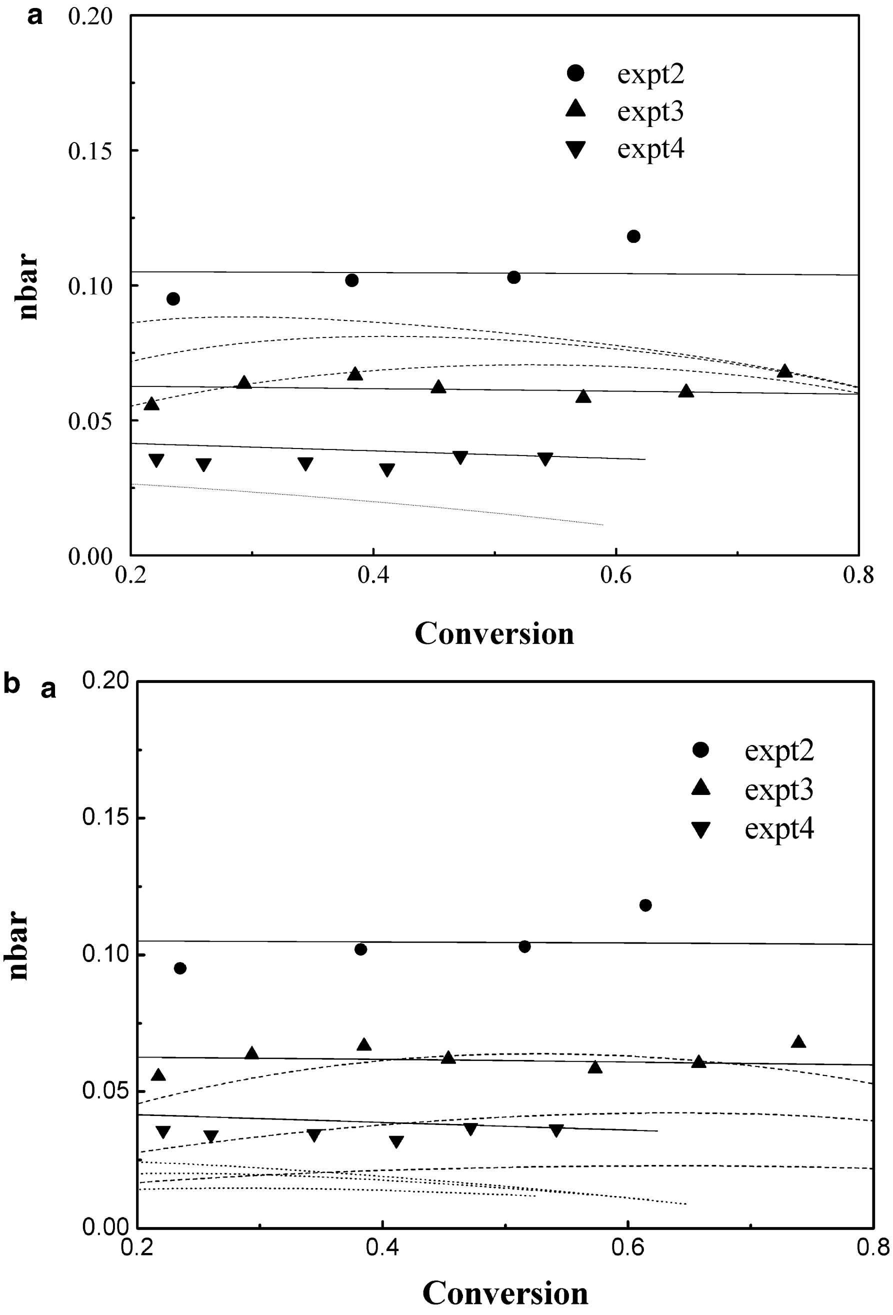

Figure 3. Evolution of the average number of propagating radicals per particle as a function of conversion in the PS−CPDB mediated styrene polymerization at 75 °C with [RAFT] = 1.16×10^{-2} mol/L (St), 2.22×10^{-2} mol/L (St), 4.29×10^{-2} mol/L (St). The solid lines are calculated by eq 3 with $k_{-\beta} = 1.1 \times 10^4$ s^{-1}. The dash lines are the results of eq 9 with (a) $k_{-\beta} = 4$ s^{-1}, $k_{tc} = 1.0 \times 10^7$ L mol^{-1} s^{-1}, and $k_{ct} = 0$ L mol^{-1} s^{-1}; (b) $k_{-\beta} = 0.4$ s^{-1}, $k_{tc} = 1.0 \times 10^7$ L mol^{-1} s^{-1}, and $k_{ct} = 0$ L mol^{-1} s^{-1}. The dotted lines are the results of eq 9 with (a) $k_{-\beta} = 4$ s^{-1}, $k_{tc} = 1.0 \times 10^8$ L mol^{-1} s^{-1}, $k_{ct} = 0$ L mol^{-1} s^{-1} (three curves overlapped); (b) $k_{-\beta} = 0.4$ s^{-1}, $k_{tc} = 1.0 \times 10^8$ L mol^{-1} s^{-1}, $k_{ct} = 0$ L mol^{-1} s^{-1}.

radical concentration. Fukuda et al.[44] derived the polymerization rate retardation factor for a bulk RAFT polymerization as

$$\frac{R_{\mathrm{p,RAFT}}}{R_{\mathrm{p,blank}}} = (1 + 2(k_{ct}/k_{tc})K[\mathrm{RAFT}]_0)^{-0.5} \qquad (16)$$

In the RAFT miniemulsion polymerization, the retardation is attributed to the reduction in both N_p and $\bar{n}$, as is evident from our experimental data. The reduction in $\bar{n}$ represents the intrinsic effect of RAFT process on miniemulsion polymerization. It should be noted that this reduction is not necessarily caused by the cross-termination. The average number of total radicals per particle approximately equals $\bar{n}_{\mathrm{blank}}$ for a zero−one system (note: $\bar{r} = [\bar{n}_{\mathrm{blank}}(1 + K[\mathrm{RAFT}]_0)]/[(1 + 2\bar{n}_{\mathrm{blank}}K[\mathrm{RAFT}]_0)]$, as derived from eqs 5a and 15, and $\bar{r} = 0.5$ at $\bar{n}_{\mathrm{blank}} = 0.5$). The reduction in $\bar{n}$ is due to the limit that is imposed on the average number of total radicals per particle by the compartmentalization effect. The magnitude of the rate retardation can be derived from eq 15 as

$$\frac{\bar{n}_{\mathrm{RAFT}}}{\bar{n}_{\mathrm{blank}}} = (1 + 2\bar{n}_{\mathrm{blank}}K[\mathrm{RAFT}]_0)^{-1} \qquad (17)$$

The differences between eq 17 and eq 16 are twofold: First, the exponent factor for the bulk RAFT polymerization is −0.5 while it is −1.0 for the miniemulsion counterpart. The rate retardation in the RAFT miniemulsion polymerization is more severe than that of the corresponding bulk system, even though the absolute rate of the former is much higher than the latter. This is in good agreement with the experimental data. Figure 7

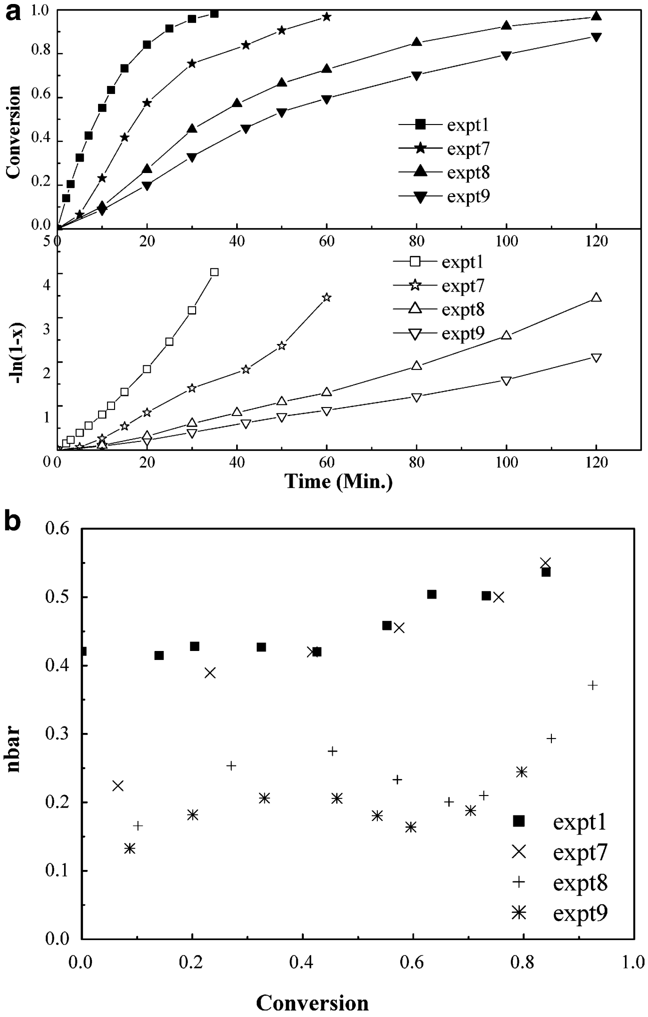

Figure 4. (a) Evolution of the monomer conversion as a function of time in the PS−PEPDTA mediated styrene polymerization at 75 °C. KPS: 3.70×10^{-3} mol/L (water); PS−PEPDTA (experiment 1: 0; experiment 7: 1.70×10^{-2} mol/L (St); experiment 8: 3.45×10^{-2} mol/L (St); experiment 9: 5.62×10^{-2} mol/L (St)). (b) Evolution of the average number of propagating radicals per particle, $\bar{n}$, as a function of conversion in the PS−PEPDTA mediated styrene polymerization at 75 °C. KPS: 3.70×10^{-3} mol/L (water); PS−PEPDTA (experiment 1: 0; experiment 7: 1.70×10^{-2} mol/L (St); experiment 8: 3.45×10^{-2} mol/L (St); experiment 9: 5.62×10^{-2} mol/L (St)).

shows that the RAFT agent concentration has little influence on the rate of the bulk RAFT polymerization, which is in good agreement with the literature.[25] The rate retardation in the bulk RAFT polymerization was mild at the low monomer conversions (<30%), much milder than the reduction of $\bar{n}$ in the RAFT miniemulsion system as seen in Figure 4b. The retardation of the bulk RAFT system became more pronounced at the higher monomer conversions, probably due to more significant gel effect. Second, the two parameters of k_{ct} and K in eq 16 are coupled. It is therefore impossible to estimate their individual values from the rate data. However, in the zero−one miniemulsion system, the radical termination is instantaneous due to the compartmentalization effect and therefore is not a rate-determining step. The only parameter that affects the rate is the equilibrium constant K, as shown in eq 15. Therefore, the K value can be readily estimated from the rate data.

Conclusions

We modified the Smith−Ewart equation for RAFT (mini)emulsion polymerization by taking into account the different kinetic properties of propagating and intermediate radicals. We also carried out the miniemulsion polymerization of styrene mediated by oligo-styrene derivatives of 1-phenylethylphenyl dithioacetate (PS−PEPDTA) and 2-cyranoprop-2-yl dithiobenzoate (PS−CPDB). On the basis of the theoretical results and experimental data, we reached the following conclusions:

(1) The effect of RAFT addition on (mini)emulsion polymerization kinetics under a zero−one condition ($\rho \ll c'$) can be adequately described by a very simple equation: $\bar{n}_{RAFT}^{-1} = \bar{n}_{blank}^{-1} + 2K[RAFT]_0$. The polymerization rate is determined by the RAFT agent concentration and the addition−fragmentation equilibrium coefficient K. This equation provides some guidance in selecting RAFT agent with smaller K's for higher polymerization rates. In the case of $\rho > c'$, a zero−one conventional (mini)emulsion system becomes to a pseudo-bulk system, and no compartmentalization effect is expected.

(2) The retardation effect is an inherent feature of RAFT (mini)emulsion polymerization under a zero−one condition of total radicals (propagating + intermediate). The reason for this peculiar kinetic behavior is that the intermediate radicals inside particles do not propagate with monomers and thus shorten the time period that is available for the radicals to propagate in the absence of a RAFT agent.

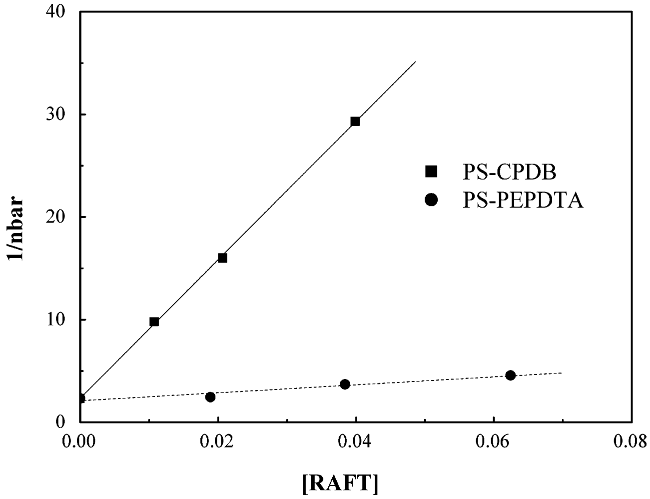

Figure 5. Plot of $1/\bar{n}$ vs [RAFT] to estimate the equilibrium constants for styrene polymerization mediated by PS−CPDB and PS−PEPDTA at 75 °C. The solid line for PS−CPDB is $y = 627.65x + 2.33$ with $R^2 = 0.999$. The dash line for PS−PEPDTA is $y = 43.19x + 1.89$ with $R^2 = 0.975$. Note: $\bar{n}$ values were obtained from the slopes of the linear section of $-\ln(1 - x) \sim t$ curves to make sure the system is under zero−one kinetics.

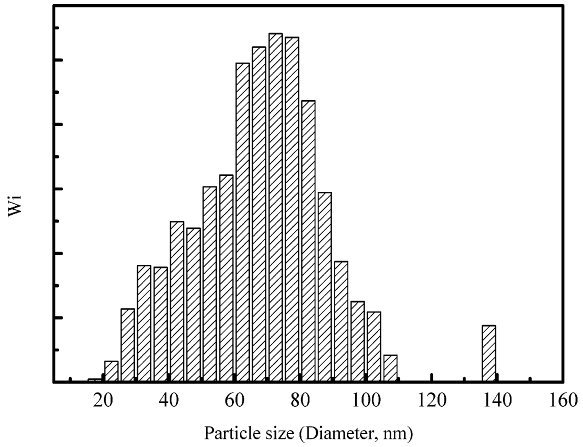

Figure 6. Particle size distribution of the final latex of experiment 7 derived from the TEM image statistics (800−1000 particles were counted).

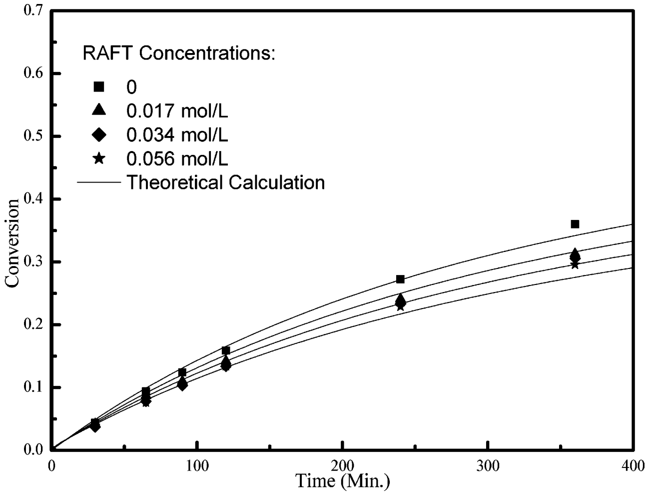

Figure 7. Bulk polymerization kinetics using PS−PEPDTA as a RAFT agent with [AIBN] = 5.0×10^{-3} mol/L at 75 °C. Theoretical calculations were made using eq 16 with $K = 22$ L mol^{-1}, $k_{ct} = 0.3k_{tc}$,[44] $k_{tc} = 1.22 \times 10^{8}$ L mol^{-1} s^{-1},[45] $k_d = 7.97 \times 10^{-5}$ s^{-1},[46] and $f = 0.4$ (estimated from the blank experiment).

(3) The experimental data verify the modified Smith−Ewart theory. The $\bar{n}$−conversion data with various initiator and RAFT agent concentrations can be well described by the theory under the zero−one condition. It appears that the pseudo-bulk model based on slow fragmentation does not fit the experimental data.

(4) The equilibrium coefficients of RAFT polymerization of styrene mediated by 1-phenylethylphenyl dithioacetate (PS−PEPDTA) and 2-cyranoprop-2-yl dithiobenzoate (PS−CPDB) are estimated to be 22 and 314 L/mol, respectively. These values suggest that the PS−PEPDTA and PS−CPDB mediated polymerizations have high fragmentation rate coefficients.

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Appendix

When the radical exit induced by the *z*-meric RAFT adduct is taken into account, eq 3 can be modified as

$$\frac{dN_{0,0}}{dt} = -(\rho + \rho_z)N_{0,0} + (\rho + \rho_z)N_{1,0} + (\rho + \rho_z)N_{0,1} + (k + k_z)N_{1,0} \tag{A1a}$$

$$\frac{dN_{1,0}}{dt} = -(\rho + \rho_z)N_{1,0} + (\rho + \rho_z)N_{0,0} - (k + k_z)N_{1,0} - k_\beta[\mathrm{RAFT}]_0 N_{1,0} + k_{-\beta}N_{0,1} \tag{A1b}$$

$$\frac{dN_{0,1}}{dt} = -(\rho + \rho_z)N_{0,1} + k_\beta[\mathrm{RAFT}]_0 N_{1,0} - k_{-\beta}N_{0,1} \tag{A1c}$$

$$N_{0,0} + N_{1,0} + N_{0,1} = 1 \tag{A1d}$$

where ρ_z is the initiation rate derived from the reentry of the *z*-meric radicals which exit out of particles; k_z is the first-order exit rate coefficient and is expressed as[33]

$$k_z = k_{\mathrm{tr,RAFT}} C_z P(\text{exit-z}) \tag{A2}$$

where $k_{\mathrm{tr,RAFT}}$ is the RAFT transfer rate coefficient, C_z is the concentration of the *z*-meric RAFT adduct, and *P*(exit-*z*) is the probability by which the *z*-meric radicals exit out of particles.

In the Maxwell−Morrison model, the *z*-meric radical was assumed to enter the first particle irreversibly it encounters.[35] It has been argued that the *z*-meric radicals cannot be terminated in the water phase since they are surface-active.[33,35] It is therefore reasonable to assume that the desorbed *z*-meric radicals derived from the *z*-meric RAFT adduct completely reenter particles. With this assumption, we have

$$\rho_z = k_z N_{1,0} \tag{A3}$$

Substituting eq A3 into eq A1 yields the steady solution of eq A1

$$\bar{n} = \frac{\sqrt{(2\rho + kf_n)^2 + 8k_z f_n \rho} - (2\rho + kf_n)}{4k_z} \tag{A4}$$

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