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Intermediate Radical Termination as the Mechanism for Retardation in Reversible Addition−Fragmentation Chain Transfer Polymerization

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The reversible addition−fragmentation chain transfer (RAFT) process[3−5] has emerged as an important living radical technique for preparing polymer architectures with controlled composition (e.g., blocks and stars) for a wide range of monomers (e.g., NIPAM[6] and maleic anhydride[2]) and experimental conditions. The mechanism is given in Scheme 1; it first relies on the chain transfer of active species, $P_n^{\bullet}$, to the RAFT agent **(1)**, followed by fragmentation to liberate the leaving group $R^{\bullet}$, which then reinitiates polymerization. Once the RAFT agent has been consumed, chain equilibrium is established between the active and dormant species.

NMR, UV/vis spectroscopy, and MALDI spectrometry have provided much of the evidence for the mechanism shown in Scheme 1 through end group analysis,[3] while ESR studies showed the presence of the intermediate radical (**4**).[1] Accordingly, the number of propagating species and therefore the rate should be unaffected by the presence of the RAFT agent. However, it has been found that retardation in rate is proportional to the concentration of RAFT agent. The possible explanations[7] given were (a) slow fragmentation of adducts **2** and **4**, (b) slow reinitiation by the expelled radical **3**, and (c) specificity of **3** and the propagating radical to add to the RAFT agent rather than to monomer. In this paper, we postulate an additional and overriding mechanism to explain the retardation in rate, namely intermediate radical termination of the radicals **2** and **4** as shown in Scheme 2.

To obtain experimental evidence for this terminated intermediate species, we carried out UV experiments with polymeric RAFT agents (M_w of 7500)[2] in solvent, which was irradiated in the absence of monomer. UV irradiation cleaves the S−C bond, producing a polymeric radical that reacts with the polymeric RAFT agent to form the intermediate radical species **4** (where *m* and *n* are equal), which is then further terminated by another polymeric radical to give **6** with a M_w 3 times greater than the original polymeric RAFT agent. This product can only be formed through termination of the intermediate species. More compelling evidence comes from preliminary results in this laboratory through trapping of the intermediate radical with a nitroxide radical to give **5.** That is, *tert*-butoxyl radicals in cyclohexane at 60 °C are reacted with the RAFT agent, S═C(Ph)S**C(CH$_3$)$_2$Ph**, in the presence of the nitroxide trap, 1,1,3,3-tetramethyl-1,3-dihydro-1*H*-isoindol-2-yloxyl, in which these radicals add to the S═C bond and the intermediate radical is trapped.

Figure 1 shows the conversion−time plots for styrene (STY) polymerization in the presence of **1**, initiated by 2,2′-azobis(2-cyanopropane) (AIBN) in toluene at 80 °C. It is clearly shown that as the concentration of **1** is increased, the retardation in rate becomes increasingly greater. The polydispersities were below 1.2 at the two concentrations of RAFT agent, 4×10^{-2} and 6×10^{-2} mol L^{-1}. **3** was chosen as the leaving group such that slow reinitiation (mechanism b above) can be neglected as a possible explanation for retardation, since the rate coefficient for the addition of **3** to styrene[8] is orders of magnitude greater than $\langle k_p \rangle$ (STY).[9] This also lowers the specificity for **3** to **1** compared to monomer. The only other mechanisms to explain our results are slow fragmentation and primary radical termination of the intermediate radical **4**.

Simulations[10] were first carried out for the polymerization without RAFT agent, using rate constants found in the literature (k_d = rate coefficient for decomposition of AIBN;[11] k_p = rate coefficient for propagation of styrene[9]) and an adjustable parameter for thermal initiation. This value was then used in the simulations for the RAFT polymerizations. The termination rate coefficient, k_t, was estimated by the expression[12,13]

$$k_t^{ij} = 2\pi \mathbf{p}_{ij}(D_i + D_j)\mathbf{r}N_A \qquad (1)$$

where D_i and D_j are the diffusion coefficients of polymeric radicals of chain lengths *i* and *j*, respectively, *r* is the sum of the van der Waals radii of the monomer, and p_{ij} is the probability that two spins will be antiparallel to form a covalent bond (used in these simulations as 0.25). The diffusion coefficient, D_i, can be calculated at varying weight fractions of polymer, w_p, according to the relationship[14]

$$D_j(w_p) = \frac{D_{mon}(w_p)}{j^{0.66+2w_p}} \qquad (2)$$

where D_{mon} is the diffusion coefficient for monomer. Termination for normal free-radical polymerizations is dominated by short−long termination, where the long chains are considered to be immobile and can only be terminated by short mobile radical species. However, for the RAFT process where the chain lengths of the radical species are the same and grow linearly with conversion (eq 3),[15] termination is a combination of active species with chain length *v* either to another active species ($k_{tv,v}$) or to short radicals formed from either fragmentation of initiator or thermal initiation (k_{tv},short).

$$v = \frac{x[\mathrm{M}]}{[\mathrm{RAFT}]} \qquad (3)$$

where *v* is the chain length, *x* conversion, [M] the monomer concentration and [RAFT] the initial RAFT agent concentration.

When thermal initiation is set to zero, the simulations of the conversion−time profiles show good agreement with experimental data below a reaction time of 350 min. After this time most of the initiator has decomposed and polymerization ceases in the simulation (but not in the experiment); thus, the rate of thermal

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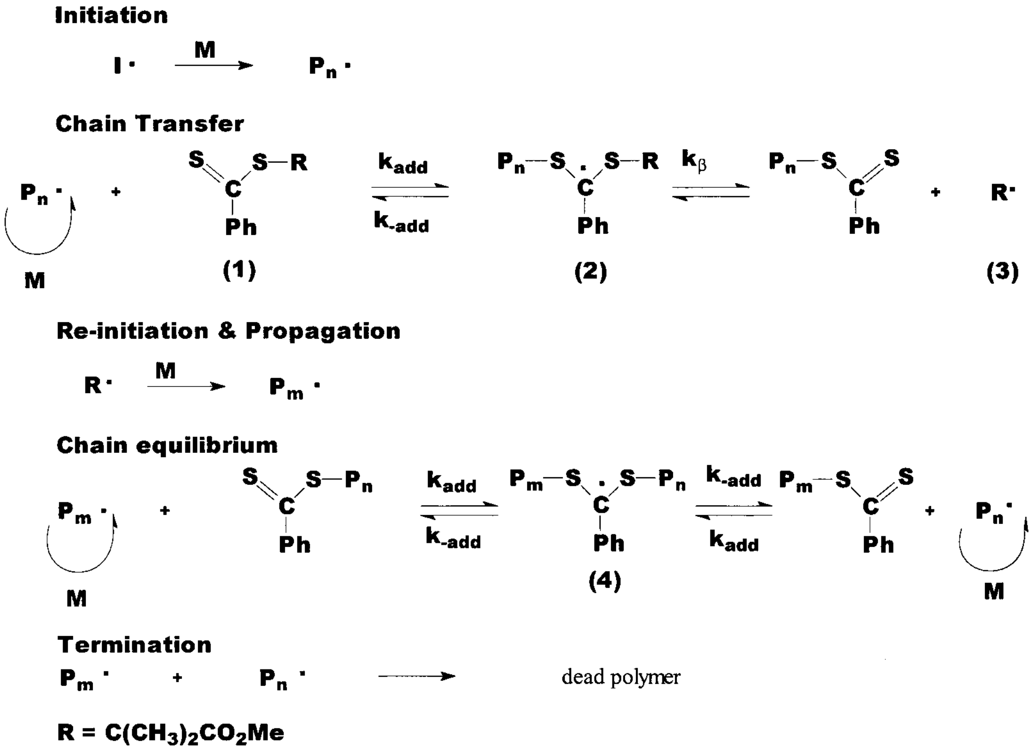
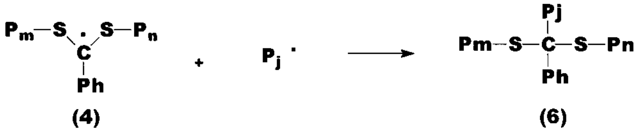
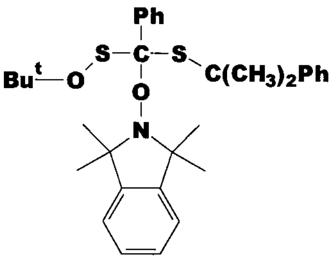
Scheme 1. Proposed Mechanism for the RAFT Process without Primary Radical Termination



Scheme 2. Additional Intermediate Radical Termination Mechanism Used To Explain Retardation





(5)

initiation is a necessary parameter. A value of 2×10^{-8} mol dm^{-3} was fitted to the experimental data points of curve a in Figure 1.

Simulations using this thermal initiation value together with the added termination step (Scheme 2) were carried out at RAFT agent concentrations of 4×10^{-2} mol L^{-1} (Figure 1, curves b). k_{add} used was that determined by Goto et al.[16] ($C_{tr,RAFT}$. = 6000), such that $k_{add} = 2 \times 6000 \times k_p$—the factor of 2 is determined by assuming k_β equals k_{-add} (see ref 3), and k_{-add} was fitted to the data points using a value of 1×10^5 s^{-1}. A k_{-add} value was found from some preliminary results in this laboratory using the nitroxide-trapping technique,[17] in which *tert*-butoxyl radicals add to the S=C bond on the RAFT agent, and the intermediate radical is trapped (compound **5**) and so to the cumyl radical (after fragmentation), allowing one to estimate a value for k_{-add} of ca. 1×10^6 s^{-1}. However, this value is expected to be greater than for our system since the **$C(CH_3)_2Ph$** group is a much better leaving group than either **$C(CH_3)_2CO_2Me$** (leaving group from the RAFT agent used in this work) or polystyrene (leaving group from the dormant species).

Using the two fitted parameters above (i.e., thermal initiation and k_{-add}), the agreement between the conversion−time profiles of the simulation and experimental data at a RAFT concentration of 6×10^{-2} mol L^{-1} (Figure 1, curves c) is remarkably good, even after long polymerization times (greater than 400 min). The simulated fraction of dead chains formed through Scheme 2 at the end of the polymerization was approximately 0.07 with a broad molecular weight distribution for both RAFT polymerizations. This suggests that trying to identify these terminated species by NMR or any other analytical technique (GPC) could prove to be quite difficult.

Simulations also showed that the concentration of **4** was approximately 5×10^{-9} mol dm^{-3} for both RAFT agent concentrations and is approximately an order of magnitude greater than the active radical concentration. Therefore, it is expected that the probability of termination of **4** is going to be far greater than conventional termination. To determine whether our simulations give realistic concentrations of **4**, we simulated (using our primary radical termination mechanism) the Rizzardo et al.[1] experimental conditions for styrene at 90 °C. The concentration of **4** found by Rizzardo et al. [1] from ESR measurements was approximated to 0.8 μmol L^{-1} and is in a similar range to our simulated value of 0.2 μmol L^{-1} (at very low conversions).

On the other hand, if the termination mechanism of **4** is neglected and we only consider the main cause of retardation as slow fragmentation, it can be seen from Figure 2 at a RAFT agent concentration of 6×10^{-2} mol L^{-1} that varying the rate coefficient for fragmentation does not affect the rate except when an unrealistic value (i.e., $k_{-add} = 0.1$ s^{-1}) is used.

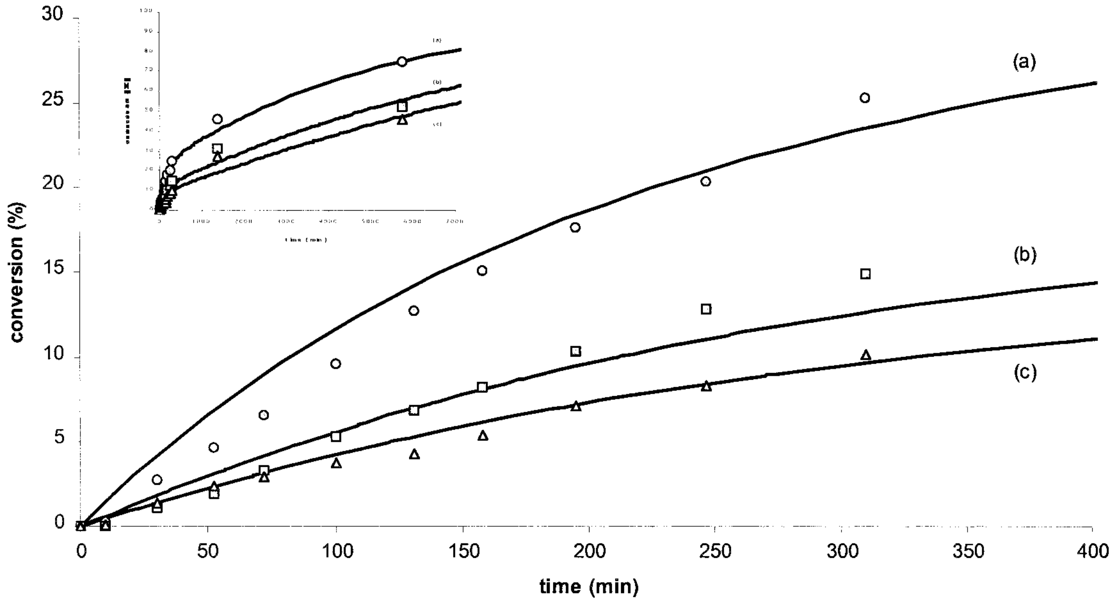


Figure 1. Simulations of styrene polymerizations in the presence of RAFT with primary radical termination, using k_p = 660 mol^{-1} dm^3 s^{-1}, k_d = 1.39 × 10^{-4} s^{-1}, k_{add} = 2 × 6000 × k_p mol^{-1} dm^3 s^{-1}, and k_{-add} = 1 × 10^5 s^{-1}. Curve a is without RAFT, curve b 4 × 10^{-2} mol dm^{-3}, and curve c 6 × 10^{-2} mol dm^{-3}. The points are the corresponding experimental data. The inset is a graph at longer polymerization times.

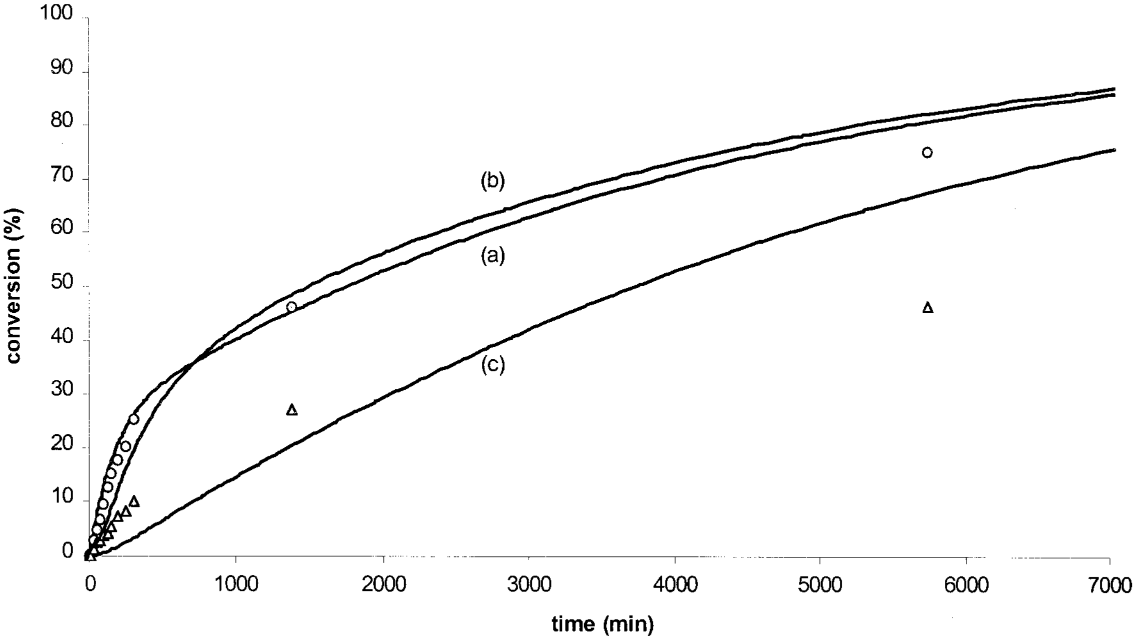


Figure 2. Simulations of styrene polymerization without primary radical termination. Curve a: k_{-add} = 1 × 10^{-5} s^{-1}; curve b: k_{-add} = 1 s^{-1}; curve c: k_{-add} = 0.1 s^{-1}. The experimental data points are the same as in Figure 1.

In conclusion, we postulate on the basis of a combination of simulations and experimental evidence that the most likely mechanism for retardation is through termination of the intermediate radical **4**. It seems that only a few percent of dead chains with a broad molecular weight distribution are formed through this process, making their identification difficult. Consequently, the loss of RAFT (dormant) species is only a few percent such that there will be little or no effect on the molecular weight distribution, and controlled polymer architecture with low polydispersity will be maintained. We have also used this mechanism to fit the retardation for methyl methacrylate, butyl acrylate, and butyl mechacrylate RAFT polymerizations, which is the subject of a future publication.

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