A Kinetic Study on the Rate Retardation in Radical Polymerization of Styrene with Addition−Fragmentation Chain Transfer

Yungwan Kwak, Atsushi Goto, Yoshinobu Tsujii, Yasujiro Murata, Koichi Komatsu, and Takeshi Fukuda*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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ABSTRACT: The polymerization of styrene mediated by a polystyryl dithiobenzoate was studied by electron spin resonance spectroscopy to determine the concentration of the intermediate radical produced by the addition of polystyryl radical to the dithiobenzoate. The polymerization was also followed by dilatometry to estimate the concentration of the growing radical. The results showed that the fragmentation of the intermediate radical is a fast process with a relevant rate constant on the order of 10^4 s^{-1} (at 60 °C) and that the intermediate radical undergoes the cross-termination with polystyryl radical to form a 3-arm star chain, thus causing a retardation in the rate of polymerization. The rate constant of cross-termination was estimated to be similar to (somewhat smaller than) that of the termination between polystyryl radicals. The formation of the star was evidenced by an independent model experiment.

Introduction

Among the most versatile techniques of living radical polymerization (LRP)[1] is the one mediated by dithioester compounds.[2−4] This polymerization involves a reversible addition−fragmentation chain transfer (RAFT) process,[2−4] in which a propagating radical P$^\bullet$ adds to the dormant species P′−X to form an intermediate radical P′−(X$^\bullet$)−P followed by the fragmentation into P′$^\bullet$ and P−X (Scheme 1). When P′ and P are kinetically identical polymers, as in the case discussed in this work, we will not distinguish P′ and P and write both of them P. If fragmentation occurs fast enough accompanying no side reaction, a RAFT process should have no significant influence on the rate of polymerization R_p, as was observed for the iodide-mediated LRP[5] and also for most conventional polymerizations with a chain-transfer agent. In these systems, the stationary state kinetics, eq 1, holds shortly after the onset of polymerization:[5]

$$R_p = k_p(R_i/k_t)^{1/2} \qquad (1)$$

where R_i is the rate of (conventional) initiation, [M] is the monomer concentration, and k_p and k_t are the rate constants of propagation and termination, respectively.

In some dithioester-mediated polymerizations, however, significant retardation in R_p has been observed.[4,6−10] Two opposing opinions, among others, to explain this phenomenon have been proposed. One is the slow fragmentation of the intermediate P−(X$^\bullet$)−P. Davis et al.[6−8] assumed that the intermediate is stable enough to cause no polymerization or no termination and carried out a computer simulation to estimate the fragmentation rate constant k_{fr} to be typically on the order of 10^{-2} s^{-1}. On the other hand, Monteiro et al.,[9] who noted that the UV irradiation of a polystyryl dithiobenzoate in the absence of monomer produces polymer species with a tripled molecular weight, assumed that the cross-termination, i.e., the termination between P$^\bullet$ and P−(X$^\bullet$)−P, occurs with a rate constant k_t' similar in magnitude to k_t and carried out a computer simulation to deduce k_{fr} to be about 10^5 s^{-1}.[10] Between the k_{fr} values reported by these two groups is a difference of 7 orders of magnitude, which is quite uncommon in science.

In this work, we studied the polymerization of styrene with a polystyryl dithiobenzoate (PSt−SCSPh) as a RAFT agent and azobis(isobutyronitrile) (AIBN) as a conventional initiator. We determined the concentration of the intermediate radical by electron spin resonance (ESR) and R_p by dilatometry to estimate the polymer radical concentration, both as a function of time. In this way, we were able to estimate k_{fr} on the basis of experimental data alone. Moreover, by a model reaction of PSt radical with the PSt−SCSPh adduct, we explored the production of the 3-arm star chain, a possible product of the cross-termination.

Experimental Section

Materials. Commercially available styrene and AIBN were purified by fractional distillation and recrystallization from methanol, respectively. PSt−SCSPh[11] and polystyryl bromide (PSt−Br)[12] were prepared as described previously. Tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN) was prepared according to Matyjaszewski et al.[13] All other reagents were commercially obtained and used without purification.

Dilatometry. The mixture of styrene, AIBN (300 mM), and PSt−SCSPh (M_n = 1100, M_w/M_n = 1.08: 100 mM) was charged in a dilatometer, degassed, sealed off under vacuum, and heated at 60 °C. The monomer conversion was traced dilatometrically, in which the contraction factor γ was approximated by $\gamma = (v_S - v_{PS})/v_S = 0.171$ at 60 °C.[14] Here v_S and v_{PS}[15] are the specific volumes of styrene and PSt of sufficiently high molecular weight, respectively. A gravimetrically determined γ (for a model run) agreed with this value within a few percent.

Electron Spin Resonance (ESR) Spectroscopy. The mixture of styrene, AIBN, and PSt−SCSPh with the same composition as the one used for the dilatometry was degassed in an ESR tube, sealed off, and place in the preheated ESR cavity. The spectra were recorded at 60 °C on Bruker EMX with 100 kHz magnetic field modulation at microwave output of 5.0 mW. Figure 1 shows an example of an ESR spectrum, which is essentially the same as the one reported elsewhere.[16] The system was calibrated with a degassed toluene solution of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) at 60 °C. Calibration in the styrene solution is not recommendable due to the thermal initiation of styrene.

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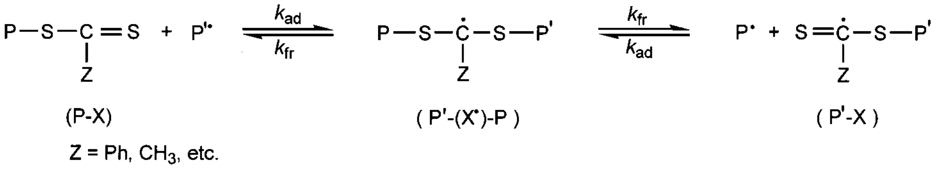
Scheme 1. Reversible Addition−Fragmentation Chain Transfer



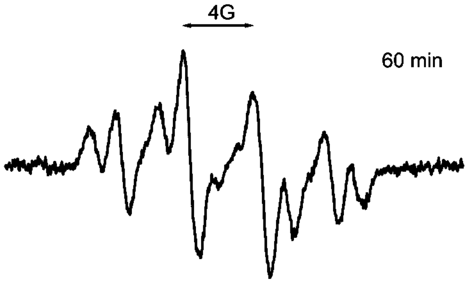


Figure 1. ESR spectrum obtained for the styrene/AIBN/PSt-SCSPh system at 60 min. For the experimental conditions, see the caption to Figure 2.

Model Reaction of PSt Radical with PSt−SCSPh. PSt−Br (130 mM: $M_n = 2000$, $M_w/M_n = 1.05$), PSt−SCSPh (65 mM: $M_n = 1990$, $M_w/M_n = 1.07$), CuBr (125 mM), Cu(0) (600 mM), and Me_6TREN (250 mM) were dissolved in *tert*-butylbenzene, degassed, and sealed off under vacuum. The mixture was then heated at 60 °C for 2 h and analyzed by gel permeation chromatography (GPC).

GPC. The GPC analysis was made on a Tosoh HLC-802 UR high-speed liquid chromatograph equipped with Tosoh gel columns G2500H, G3000H, and G4000H (Tokyo, Japan). THF was used as eluent (40 °C). The column system was calibrated with Tosoh standard PSts. Sample detection was made with a Tosoh differential refractometer RI-8020.

Results and Discussion

The polymerization of styrene at 60 °C including 100 mM of PSt−SCSPh ($M_n = 1100$, $M_w/M_n = 1.08$) and 300 mM of AIBN was studied. An equivalent RAFT agent-free system was also studied for comparison. Figure 2a shows the logarithmic change of the monomer concentration with time *t* followed dilatometrically. The slope of the curve for the RAFT agent-free system (open squares) is about twice as large as that for the RAFT system (filled squares), meaning that the latter system suffers a serious retardation. To minimize the difference in chain length and the resultant effect on R_p between the two systems, we added CBr_4 (400 mM) as a chain transfer agent to the RAFT agent-free system, which reduced M_n to 2000, i.e., to nearly the same M_n level as in the RAFT system. The slope of the line connecting each pair of adjacent experimental points gives [P•] around that time, according to

$$\Delta \ln([M]_0/[M])/\Delta t = k_p[P^\bullet] \qquad (2)$$

with $k_p = 340\ M^{-1}\ s^{-1}$ at 60 °C.[17] The [P•] estimated in this way is nearly constant independent of time (Figure 2b).

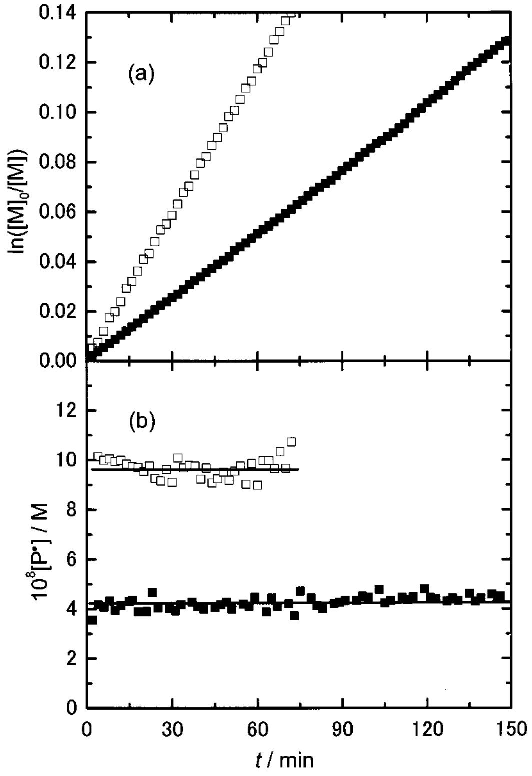


Figure 2. Plot of (a) $\ln([M]_0/[M])$ and (b) [P•] vs *t* for the styrene/AIBN/(PSt−SCSPh or CBr_4) systems (60 °C): $[AIBN]_0 = 300$ mM; $[PSt-SCSPh]_0 = 100$ mM ($M_n = 1100$, $M_w/M_n = 1.08$; filled square) or $[CBr_4]_0 = 400$ mM (open square). [P•] was calculated with the known k_p of 340 $M^{-1}\ s^{-1}$.

The concentration of the intermediate radical was determined by doubly integrating the ESR spectra, such as given in Figure 1.[18] The integral values indicated that [P−(X•)−P] is on the order of 10^{-7} M. Since [P•] is on the order of 10^{-8} M and is not perfectly negligible compared to [P−(X•)−P], we corrected this by subtracting the [P•] given by Figure 2b from the integral value at each time *t*. The correction did not exceed 16% in any case. Figure 3a shows the plot of the corrected intermediate radical concentration against *t* in the RAFT system. [P−(X•)−P] also stays nearly constant from an early stage of polymerization. With these [P•] and [P−(X•)−P] data, we computed the equilibrium constant K ($= k_{ad}/k_{fr}$) from

$$K = [P-(X^\bullet)-P]/([P^\bullet][P-X]) \qquad (3)$$

where [P−X] may be approximated by the concentration of the initial RAFT agent $[P-X]_0$, since [P−(X•)−P] is negligibly small (2.3×10^{-7} M, see Figure 3a) compared to $[P-X]_0$ (= 100 mM). The value of K thus calculated is independent of *t* (Figure 3b), clearly showing that the addition−fragmentation equilibrium holds from an early stage of polymerization, and we have $K = 55\ M^{-1}$.

The exchange constant $C_{ex} = k_{ex}/k_p$ of this system was found to be too large to be accurately determined by the currently available methods, and we previously presented a roughly estimated value: $C_{ex} = 6000 \pm 2000$ at 40 °C.[11] Since C_{ex} is not sensitive to temperature,[11] we use this value to estimate k_{ad} ($= 2k_{ex}$) to be about $4 \times 10^6\ M^{-1}\ s^{-1}$ and then $k_{fr} = k_{ad}/K$ to be about $7 \times 10^4\ s^{-1}$. Even though the error range associated with the reported value of C_{ex} is not small, the estimated k_{fr} should be definitely correct at least in the order of

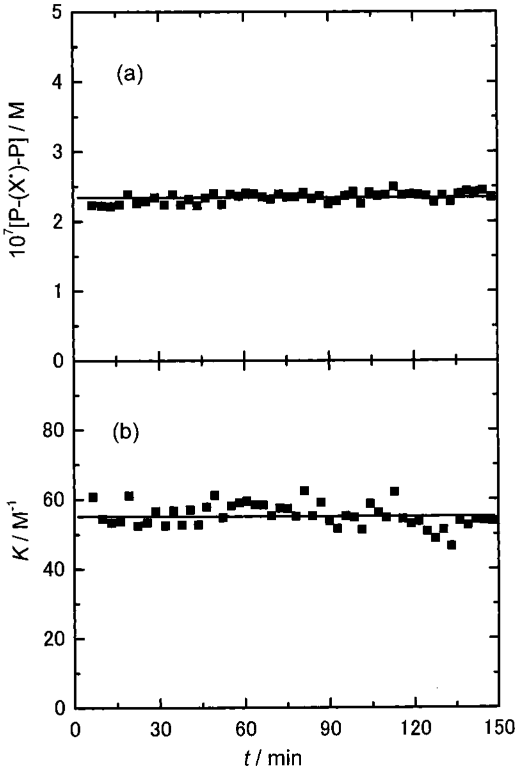


Figure 3. Plot of (a) $[P{-}(X^{\bullet}){-}P]$ and (b) K $(= [P{-}(X^{\bullet}){-}P]/([P^{\bullet}][P{-}X]))$ vs t for the styrene/AIBN/PSt−SCSPh system (60 °C): For the experimental conditions, see the caption to Figure 2.

magnitude. (Incidentally, the RAFT process in the styrene polymerization with polystyryl dithioacetate (PSt-SCSCH$_3$), which can be accurately studied because of the much smaller C_{ex} in this system, has a C_{ex} value of 197 at 60 °C.[11] If we adopt this obviously too small value to the benzoate system, we still get a k_{fr} value of 2×10^3 s^{-1}.) Hence, we conclude that the fragmentation is a fast process, fast enough to bring about a quick equilibrium with the addition, and that the reason for the R_p retardation in the styrene/dithiobenzoate system is *not* a slow fragmentation.

Thus, it is likely that the retardation is caused by the cross-termination. The existence of the addition−fragmentation equilibrium allows us to calculate the stationary-state concentration of P• from the equality of the initiation and termination rates:

$$R_i = k_t[P^{\bullet}]^2 + k_t'[P^{\bullet}][P{-}(X^{\bullet}){-}P] \qquad (4)$$

with $[P{-}(X^{\bullet}){-}P]$ given by eq 3. Hence we have

$$[P^{\bullet}] = (R_i/k_t)^{1/2}\{1 + K(k_t'/k_t)[P{-}X]_0\}^{-1/2} \qquad (5)$$

Since $[P^{\bullet}]$ is proportional to R_p, and $(R_i/k_t)^{1/2}$ gives the $[P^{\bullet}]$ of the conventional system ($[P{-}X]_0 = 0$), the RAFT system suffers a retardation of R_p by a factor $\{1 + K(k_t'/k_t)[P{-}X]_0\}^{-1/2}$. From the already-noted experimental data on K, $[P{-}X]_0$ and R_p's (or $[P^{\bullet}]$'s) in the presence and absence of P−X (Figure 2), we estimate k_t'/k_t to be about 0.8. Namely, k_t' is similar to k_t in magnitude. A more accurate value of k_t' will be reported in a forthcoming paper.[19]

If the cross-termination is recombination rather than disproportionation, it will produce a 3-arm star chain. The concentration ratio of the star to the linear chain (of doubled chain length) produced by the recombination of polystyrene radicals should be

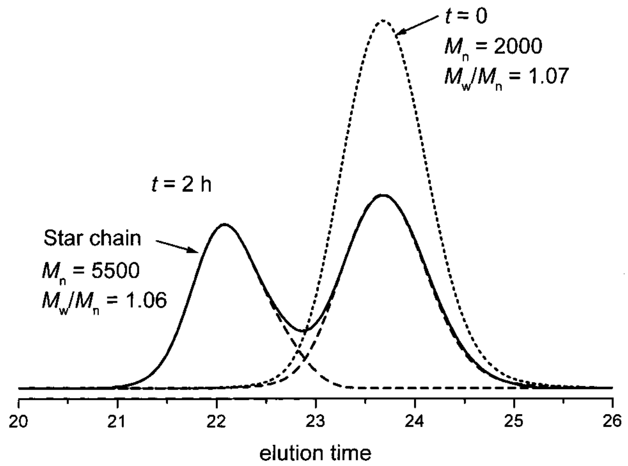


Figure 4. GPC chromatogram for the mixture of *tert*-butylbenzene, PSt−SCSPh, PSt−Br, CuBr, Cu(0), and Me$_6$-TREN heated for 2 h (60 °C): $[\text{PSt−SCSPh}]_0 = 65$ mM ($M_n = 1990$ and $M_w/M_n = 1.07$), $[\text{PSt−Br}]_0 = 130$ mM ($M_n = 2000$ and $M_w/M_n = 1.05$), $[\text{CuBr}]_0 = 125$ mM, $[\text{Cu(0)}]_0 = 600$ mM, and $[\text{Me}_6\text{TREN}]_0 = 250$ mM.

$$\frac{[\text{3-arm star}]}{[\text{linear chain}]} = \frac{k_t'[P{-}(X^{\bullet}) - P][P^{\bullet}]}{k_t[P^{\bullet}]^2} = K(k_t'/k_t)[P{-}X]_0 \qquad (6)$$

This predicts that we will have dead chains composed of a large fraction of the 3-arm star, when $[P{-}X]_0$ is large. It will be difficult to observe this in the GPC of a polymerization system, since the amounts of dead chains are usually small, for one thing, and the chain lengths of dead chains will be widely distributed and overlapped with those of active chains, for another.

To confirm the prediction of eq 6, we heated a *tert*-butylbenzene solution of PSt−SCSPh ($M_n = 1990$, $M_w/M_n = 1.07$: 65 mM), PSt−Br ($M_n = 2000$, $M_w/M_n = 1.05$: 130 mM), CuBr (125 mM), Cu(0) (600 mM), and Me$_6$TREN (250 mM) at 60 °C. In this system, PSt−Br is activated by the CuBr/Me$_6$TREN complex to give the polymer radical P•.[20] P• will add to the RAFT agent P′−X to form P′−(X•)−P, which subsequently will be attacked by another P•, where P and P′ are almost identical, as already noted. In this way, this system will mimic the RAFT polymerization without chain growth. Metallic copper Cu(0) is known to prevent the accumulation of the deactivator, CuBr$_2$.[21]

Figure 4 shows the GPC chromatograms of the polymer species before (the dotted curve) and after (the solid curve) the heat treatment for 2 h. After the heat treatment, two well-separated peaks appeared, which can be divided into the indicated two components (the broken curves), one of which corresponds to the original polymers and the other is a new one. The new component has a M_n of 5500, which suggests the formation of the 3-arm star in a high fraction. (As a matter of fact, the figure 5500 is somewhat smaller than $3 \times 2000 = 6000$, but a star polymer will have a larger GPC elution volume than the linear chain with the same molecular weight, and the GPC calibration here is based on linear polystyrenes.) Equation 6 with the present value of $[P{-}X]_0$ predicts [star]/[linear] $\cong 3$, and since the star's molecular weight is 1.5 times larger than that of the linear chain, the weight ratio will be about 4.5. Therefore, the mentioned model experiments confirms the predominant formation of the star predicted by eq 6. The theory implies the formation of about 18 wt % of the linear chain. A model calculation shows that the observed GPC curve (Figure 4) is not in conflict with the presence of this much of the linear chain, but it is difficult to quantify the amount of the linear chain on the basis of this GPC curve.

The intermediate radical can possibly undergo disproportionation with $P^\bullet$ to produce the linear chain P−(XH)−P and the terminally unsaturated species $P_=$. It is also possible that the intermediate radicals react among themselves to form a 4-arm star chain. However, these reactions, if any present, should be minor, as already indicated by Figure 4.

As eq 5 indicates, the importance of cross-termination on the polymerization rate depends on k_t' and K. These parameters differ for different monomers and different dithioester groups, and thus all RAFT polymerizations do not necessarily show significant retardation. On the contrary, we believe that in most systems K is much smaller than in the styrene/dithiobenzoate system. In this sense, strong rate retardation is a rather exceptional phenomenon. The recent finding[22] that the use of a (phenyl)dithioacetate group for Z, which less stabilizes P−($X^\bullet$)−P (a smaller K) than the dithiobenzoate group, alleviates retardation can be explained in the same way.

Conclusions

This work has shown that the cause for the R_p retardation observed in the dithiobenzoate-mediated polymerization of styrene is the reaction of the intermediate radical with the polystyryl radical to form a 3-arm star chain. The rate constant of this cross-termination is similar to k_t in order of magnitude, and the fragmentation process is a fast one with k_{fr} of the order of 10^4 s^{-1}.

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