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Rate Retardation in Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization: Further Evidence for Cross-Termination Producing 3-Arm Star Chain

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ABSTRACT: New pieces of experimental evidence were presented showing that the rate retardation in the polymerization of styrene with polystyryl dithiobenzoate (PSt-SCSPh) at 60 °C is caused by the irreversible cross-termination between the polystyryl radical (PSt$^\bullet$) and the intermediate radical produced by the addition of PSt$^\bullet$ to PSt-SCSPh. The polymerization rate R_p decreased with an increase of [PSt-SCSPh] such that a plot of $1/R_p^2$ vs [PSt-SCSPh] was linear, as the irreversible cross-termination mechanism demands. The cross-termination rate constant k_t' was estimated to be about $0.5k_t$, where k_t is the self-termination rate constant of PSt$^\bullet$. The formation of a 3-arm star, a possible product of cross-termination, was evidenced by a model experiment involving the analysis by GPC-MALLS (gel permeation chromatography equipped with a multiangle laser-light scattering detector). The concentration of the 3-arm star relative to that of the doubled molecular weight linear chain produced by self-termination of PSt$^\bullet$ was proportional to [PSt-SCSPh], and the value of k_t' deduced by this model experiment well agreed with that determined by the kinetic (rate retardation) experiment mentioned above. The 3-arm star was perfectly stable in the time scale of the experiments at 60 °C, confirming that cross-termination is irreversible at this temperature.

Introduction

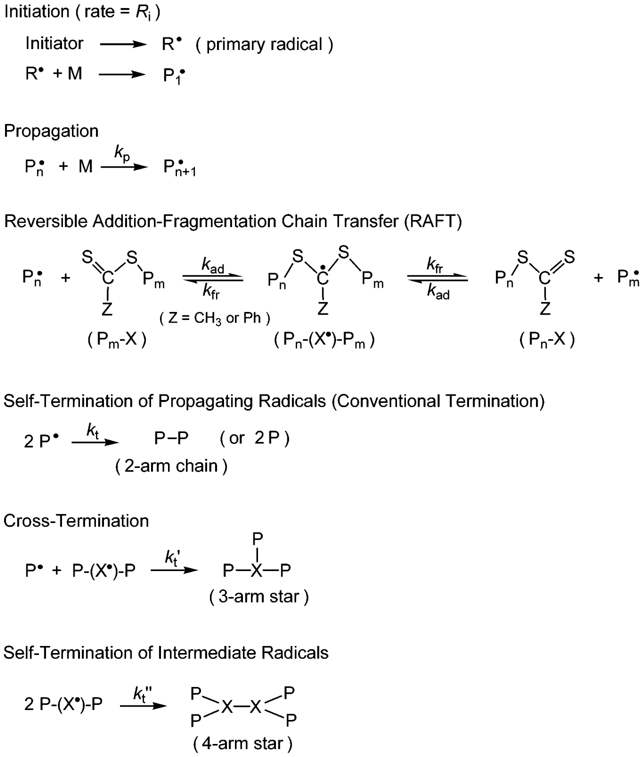
The dithioester-mediated radical polymerization is known as a particularly useful branch of living radical polymerization.[1,2] It involves a reversible addition−fragmentation chain transfer (RAFT) process, in which the propagating radical $P_n^\bullet$ undergoes addition (rate constant k_{ad}) to the dormant species P_m-X to form the intermediate adduct radical P_n-(X$^\bullet$)-P_m followed by the fragmentation (rate constant k_{fr}) into $P_m^\bullet$ and P_n-X (see Scheme 1). When P_n and P_m are kinetically identical polymers, as in the case discussed in this work, P_n and P_m need not be distinguished, but both may be written P. If fragmentation occurs fast enough accompanying no side reaction, the RAFT process should have no significant influence on polymerization rate R_p, and R_p may be equated to $R_{p,0}$, the rate for the conventional (RAFT agent-free) polymerization given by

$$R_{p,0} = k_p(R_i/k_t)^{1/2}[M] \qquad (1)$$

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.[3,4] Two opposing explanations, among others,[3] have been proposed for the rate retardation. One was slow fragmentation. The CAMD research group[5] assumed that the intermediate radical is stable enough to cause no termination with P$^\bullet$ (no cross-termination) and, under this assumption, made a computer simulation with their experimental data on the rate and polydispersity to estimate k_{fr} to be typically on the order of 10^{-2} s^{-1}. On the other hand, Monteiro et al.[6] noted the production of a tripled molecular weight species in a monomer-free model experiment with a UV-irradiated polystyryl dithiobenzoate. These authors[7] then assumed that the intermediate radical undergoes cross-termination with a rate constant k_t' equal to k_t[8] and also made a computer simulation with their rate data to deduce k_{fr} to be about 10^5 s^{-1}. Between the k_{fr} values estimated by the two groups is a difference of 6−7 orders of magnitude. Since the rate data for the styrene/dithiobenzoate system used by the two groups are more or less similar, the huge difference in k_{fr} stems from the difference in the as-

Scheme 1. Possible Elementary Reactions in the RAFT Polymerization



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sumption for the cross-termination rate constant, i.e., $k_t' = 0$ (CAMD group) vs $k_t' = k_t$ (Monteiro et al.). Apparently, computer simulations can bring no solution to this controversy. Both k_{fr} and k_t' should be determined experimentally.

Under these circumstances, we previously made an experimental study on the polymerization of styrene at 60 °C with a polystyryl dithiobenzoate (PSt-SCSPh) as a RAFT agent and azobis(isobutyronitrile) (AIBN) as a conventional initiator.[9] We followed the time evolution of intermediate radical by electron spin resonance (ESR) and of R_p (and hence the radical concentration [P•]) by dilatometry and deduced that $k_{fr} = 7 \times 10^4$ s^{-1} and $k_t' \cong k_t$. By an independent model experiment, we also showed evidence for the production of tripled molecular weigh species that could be ascribed to cross-termination.[9] This work was based on a well-established, standard approach of stationary-state (steady-state) kinetics, and in our view, there is no obvious experimental, theoretical, or logical flaw in it (except that the numerical factor 2 was erroneously omitted in the previously used theoretical relations, which requires no essential modification of the previous conclusions: cf. eqs 13 and 15 and the statements following them). Unexpectedly, however, this work was claimed not to be reliable enough to establish that the fragmentation in the mentioned system is a fast process or the intermediate radical is short-lived and that the rate retardation is caused by cross-termination.[10,11] We find the ground for this claim weak,[12] but we will not go into detail here.

Instead, in this paper we will try to reinforce our previous conclusions by presenting new experimental data and comprehensively interpreting the new and previous data on the basis of the stationary-state kinetic theory which takes account of all possible termination reactions among propagating and intermediate radicals.

Model and Theory

Scheme 1 shows the elementary reactions in the RAFT polymerization considered in this work, which include conventional initiation, propagation, RAFT reactions, the termination between propagating radicals to produce a linear chain, the termination between propagating and intermediate radicals to produce a 3-arm star chain (cross-termination), and the termination between intermediate radicals to produce a 4-arm star chain (intermediate−intermediate termination).

Here we are interested in the stationary (steady) state in which all reversible reactions are in an equilibrium (or a quasi-equilibrium) state, and the concentrations of all radical species are (approximately) invariant with time. If the intermediate−intermediate termination, for example, is not a real termination but a reversible reaction, as suggested by the CAMD group,[10] it will take a certain time before the equilibrium (or quasi-equilibrium) is reached, but after it has been reached, the radical concentrations will be in a stationary state, and in this regard, the system would look as if there were no reversible termination. In other words, the reversible termination has no effect on the stationary-state concentrations of the intermediate and propagating radicals. Of course, this discussion presupposes that the concentration of the reversibly terminated product is trivial compared with the RAFT agent concentration. If it is nontrivial exceeding, say, several or tens of percents of the RAFT agent concentration, we need to modify the stationary-state analysis by modifying the RAFT agent concentration accordingly. However, before such a large amount of RAFT agent is trapped to reach the equilibrium of reversible termination, the system has to spend a long time of nonstationary state, and therefore it can be detected experimentally by following the concentration of the intermediate radical and/or that of the propagating radical (the rate of polymerization). In any case, the stationary-state analysis of the radical concentrations will give the answer that $k_t'' = 0$ in our model. A possible analysis of the reversible termination will involve the observation of the preequilibrium stage and/or the in situ determination of the concentration of the 4-arm transient species, which is not the topic of this work. In the system discussed in this work, both the intermediate and propagating radical concentrations quickly reach the stationary-state values, which means that the concentration of the reversibly terminated product, if any present, is trivial (see below).

When the polymerization system defined in Scheme 1 is in a stationary state and viewed in a relatively short time scale, the following two equations should hold with respect to the propagating and intermediate radical concentrations:

$$0 = d[P^\bullet]/dt$$
$$= R_i - k_{ad}[P^\bullet][P\text{-}X] + k_{fr}[P\text{-}(X^\bullet)\text{-}P] - k_t[P^\bullet]^2 - k_t'[P^\bullet][P\text{-}(X^\bullet)\text{-}P] \quad (2)$$

$$0 = d[P\text{-}(X^\bullet)\text{-}P\ ]/dt$$
$$= k_{ad}[P^\bullet][P\text{-}X] - k_{fr}[P\text{-}(X^\bullet)\text{-}P] - k_t'[P^\bullet][P\text{-}(X^\bullet)\text{-}P] - k_t''[P\text{-}(X^\bullet)\text{-}P]^2 \quad (3)$$

The sum of eqs 2 and 3 reads

$$R_i - k_t[P^\bullet]^2 - 2k_t'[P^\bullet][P\text{-}(X^\bullet)\text{-}P] - k_t''[P\text{-}(X^\bullet)\text{-}P]^2 = 0 \quad (4)$$

Now let us assume that the addition−fragmentation equilibrium approximately holds:

$$k_{ad}[P^\bullet][P\text{-}X] - k_{fr}[P\text{-}(X^\bullet)\text{-}P] = 0 \quad (5)$$

This is a quasi-equilibrium valid when the rates of termination reactions (e.g., the k_t' and k_t'' terms in eq 3) are negligibly small compared with those of addition and fragmentation (the k_{ad} and k_{fr} terms in eq 3). (It will be easily confirmed that this condition for the quasi-equilibrium is met in the system to be experimentally studied below.) In terms of the equilibrium constant defined by

$$K = k_{ad}/k_{fr} \quad (6)$$

eq 5 gives the concentration of the intermediate radical:

$$[P\text{-}(X^\bullet)\text{-}P] = K[P^\bullet][P\text{-}X] \quad (7)$$

Equation 4 with eq 7 is solved for [P•], and the use of the relation $R_p = k_p[P^\bullet][M]$ along with eq 1 gives

$$R_p = \frac{R_{p,0}}{\{1 + 2(k_t'/k_t)K[P\text{-}X] + (k_t''/k_t)K^2[P\text{-}X]^2\}^{1/2}} \quad (8)$$

The rate of formation of the 3-arm star relative to that of the linear (2-arm) chain is given by

$$\frac{\mathrm{d}[\text{3-arm}]/\mathrm{d}t}{\mathrm{d}[\text{2-arm}]/\mathrm{d}t} = \frac{k_t'[\mathrm{P}^\bullet][\mathrm{P}\text{-}(\mathrm{X}^\bullet)\text{-}\mathrm{P}]}{(k_t/2)[\mathrm{P}^\bullet]^2} \qquad (9)$$

where we have assumed that termination is accompanied by no disproportionation. The factor $^1/_2$ appearing in the denominator on the right-hand side of eq 9 derives from the fact that a molecule of 2-arm chain (linear dead chain of doubled molecular weight) is formed by two polymer radicals. Equations 7 and 9 give

$$\frac{\mathrm{d}[\text{3-arm}]/\mathrm{d}t}{\mathrm{d}[\text{2-arm}]/\mathrm{d}t} = 2(k_t'/k_t)K[\text{P-X}] \qquad (10)$$

Similarly, the rate of formation of the 4-arm star relative to that of the 2-arm chain is

$$\frac{\mathrm{d}[\text{4-arm}]/\mathrm{d}t}{\mathrm{d}[\text{2-arm}]/\mathrm{d}t} = (k_t''/k_t)K^2[\text{P-X}]^2 \qquad (11)$$

Experimental Section

Materials. Styrene (99%, Nacalai Tesque, Japan) and *tert*-butylbenzene (99%, Nacalai) were purified by fractional distillation. AIBN (98%, Nacalai) was purified by recrystallization from methanol. PSt-SCSPh[13] and polystyrene bromide (PSt-Br)[14] were prepared as described previously. Tris[2-(dimethylamino)ethyl]amine ($\mathrm{Me_6TREN}$) was prepared according to Matyjaszewski et al.[15] CuBr (99.9%, Wako Pure Chemical, Japan), Cu(0) (99.85%, Wako), and tetramethylpiperidinyl-1-oxy (TEMPO) (99%, Aldrich) were used without purification.

Polymerization Rates. The mixture of styrene, AIBN (10 mM), PSt-SCSPh ($M_n = 1100$, $M_w/M_n = 1.08$: 14−71 mM), and PSt-Br ($M_n = 1100$, $M_w/M_n = 1.09$: 14−71 mM) was charged in a glass tube, degassed, sealed off under vacuum, and heated at 60 °C for a prescribed time t. The reaction mixture was then diluted with tetrahydrofuran (THF) to a known concentration and analyzed by gel permeation chromatography (GPC).

Model Experiments To Study Termination Reactions. PSt-Br (1−13 mM: $M_n = 2400$, $M_w/M_n = 1.07$), PSt-SCSPh (0−66 mM: $M_n = 2450$, $M_w/M_n = 1.09$), CuBr (82.5 mM), Cu(0) (400 mM), $\mathrm{Me_6TREN}$ (165 mM), and *tert*-butylbenzene were charged in a glass tube, degassed, and sealed off under vacuum, where $[\text{PSt-Br}]_0 = 1$ mM for $[\text{PSt-SCSPh}]_0 = 0$ and $[\text{PSt-SCSPh}]_0/[\text{PSt-Br}]_0 = 5/1$ for $[\text{PSt-SCSPh}]_0 > 0$. The mixture was heated at 60 °C for 3 h with stirring and then analyzed by GPC.

Stability Test of the Star. The polymer formed in the model experiment was purified by reprecipitation from methanol. The polymer was dissolved again into *tert*-butylbenzene to a dilute concentration (see below), degassed, heated at various temperatures for 25 h, and analyzed by GPC.

GPC. The GPC analysis was made on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L polystyrene mixed gel columns (300 × 8.0 mm; bead size = 7 μm; pore size = 20−200 Å). THF was used as eluent (40 °C). The flow rate was 0.8 mL/min. The column system was calibrated with standard polystyrenes. Sample detection and quantification were made with a Shodex differential refractometer RI-101 (equipped with tungsten lamp) calibrated with known concentrations of polystyrenes in THF. Sample detection was also made with a multiangle laser light-scattering (MALLS) detector, a Wyatt Technology DAWN EOS (Santa Barbara, CA), equipped with a Ga−As laser ($\lambda = 690$ nm). The refractive index increment dn/dc was determined to be 0.187 mL $\mathrm{g^{-1}}$ by a Wyatt Technology OPTILAB DSP differential refractometer ($\lambda = 690$ nm).

Results and Discussion

In the previous paper,[9] we used dilatometry and ESR spectroscopy to follow the polymerization of styrene at 60 °C with 100 mM of PSt-SCSPh ($M_n = 1100$, $M_w/M_n = 1.08$) and 300 mM of AIBN and showed that the system reaches a stationary state within a few minutes after the onset of polymerization. Namely, the values of $[\mathrm{P}^\bullet]$ (estimated with the dilatometrically determined R_p and the known value of k_p) and of $[\mathrm{P}\text{-}(\mathrm{X}^\bullet)\text{-}\mathrm{P}]$ (determined by the standard ESR analysis using a stable radical calibration and correcting the result for the minor contribution of $[\mathrm{P}^\bullet]$) were approximately independent of time during the experiments ($t \le 150$ min) and equal to 4.2×10^{-8} and 2.3×10^{-7} M, respectively (see Figures 2 and 3 in ref 9). With these $[\mathrm{P}^\bullet]$ and $[\mathrm{P}\text{-}(\mathrm{X}^\bullet)\text{-}\mathrm{P}]$ data, the equilibrium constant in eqs 6 and 7 were determined:

$$K = 55\ \mathrm{M^{-1}} \quad (\text{at } 60\ ^\circ\mathrm{C}) \qquad (12)$$

In this and the following analyses related to eq 8, we may approximate [P-X] by the initial RAFT agent concentration $[\text{P-X}]_0$, since $[\mathrm{P}\text{-}(\mathrm{X}^\bullet)\text{-}\mathrm{P}]$ and the number of terminated chains are negligibly small compared to $[\text{P-X}]_0$ (= 14−100 mM). Incidentally, the K value in eq 12 combined with the k_{ad} value[13] of $4 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ led to the estimate $k_{fr} = 7 \times 10^4\ \mathrm{s^{-1}}$.[9]

Coote and Radom studied low-mass intermediates by a high-level molecular orbital calculation.[16] They predicted that the benzoate intermediate R-S-C$^\bullet$(Ph)-S-R is long-lived for R = $\mathrm{CH_3}$ at 60 °C ($k_{fr} = 1.3 \times 10^{-1}\ \mathrm{s^{-1}}$).[11] They mentioned that this result supports the long-lived intermediate for R = polystyrene.[11,16] However, their calculation for the acetate intermediate R-S-C$^\bullet$($\mathrm{CH_3}$)-S-R suggests that k_{fr} rather strongly depends on the R group: k_{fr} can be different by orders of magnitude among differing R groups.[17] It is also important to consider a polymer effect on k_{fr}, as suggested for a methacrylate: the fragmentation of a poly(methyl methacrylate) PMMA radical is about 160 times (or more) faster than that of the model unimer radical for the benzoate intermediate (60 °C).[18] Thus, the mentioned k_{fr} ($1.3 \times 10^{-1}\ \mathrm{s^{-1}}$) for R = $\mathrm{CH_3}$ would not measure that for R = polystyrene.

Analysis of Polymerization Rate. Now the present work starts from this point. We tested eq 8 against the polymerization of styrene with various amounts (14−71 mM) of PSt-SCSPh ($M_n = 1100$, $M_w/M_n = 1.08$) and a fixed amount of AIBN (10 mM) at 60 °C. To minimize possible effects of polymer concentration (e.g., viscosity) on R_p, we added the model polystyryl bromide PSt-Br ($M_n = 1100$, $M_w/M_n = 1.09$) as an adjusting matrix polymer and set the sum of the concentrations of PSt-SCSPh and PSt-Br to be 71 mM in all examined cases. As Figure 1 shows, the first-order plot of [M] is approximately linear in all cases, and from the slope of the linear line, R_p was estimated. Clearly, R_p decreases with increasing concentration of the RAFT agent.

Now let us assume that the cross-termination is the main cause for the retardation in R_p. Setting $(k_t''/k_t) = 0$ and $[\mathrm{P{-}X}] = [\mathrm{P{-}X}]_0$ (see above) in eq 8, we have[9,19,20]

$$R_p^{-2} = R_{p,0}^{-2}\{1 + 2(k_t'/k_t)K[\text{P-X}]_0\} \qquad (13)$$

As shown in Figure 2a, the plot of R_p^{-2} against $[\text{PSt-SCSPh}]_0$ gives a straight line, confirming the validity of eq 13. From the slope and intercept of the plot, we have $k_t'/k_t = 0.5 \pm 0.1$, showing that k_t' is similar to k_t in magnitude. We note that the equations given in our previous papers (eqs 4 and 5 in ref 9 and eqs 7 and 8 in ref 19) are incorrect: the numerical factor 2 before the

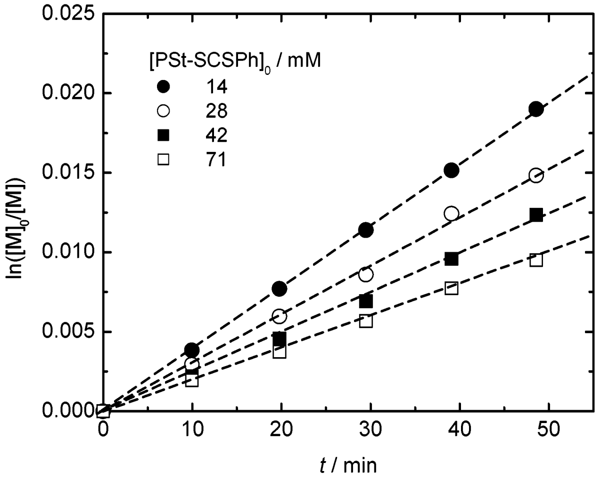

Figure 1. Plot of $\ln([M]_0/[M])$ vs t for the styrene/AIBN/PSt-SCSPh/(PSt-Br) systems (60 °C): $[AIBN]_0 = 10$ mM; $[PSt\text{-}SCSPh]_0$ as indicated in the figure; PSt-Br was added to keep the total polymer concentration constant, i.e., $[PSt\text{-}Br]_0 + [PSt\text{-}SCSPh]_0 = 71$ mM in all cases.

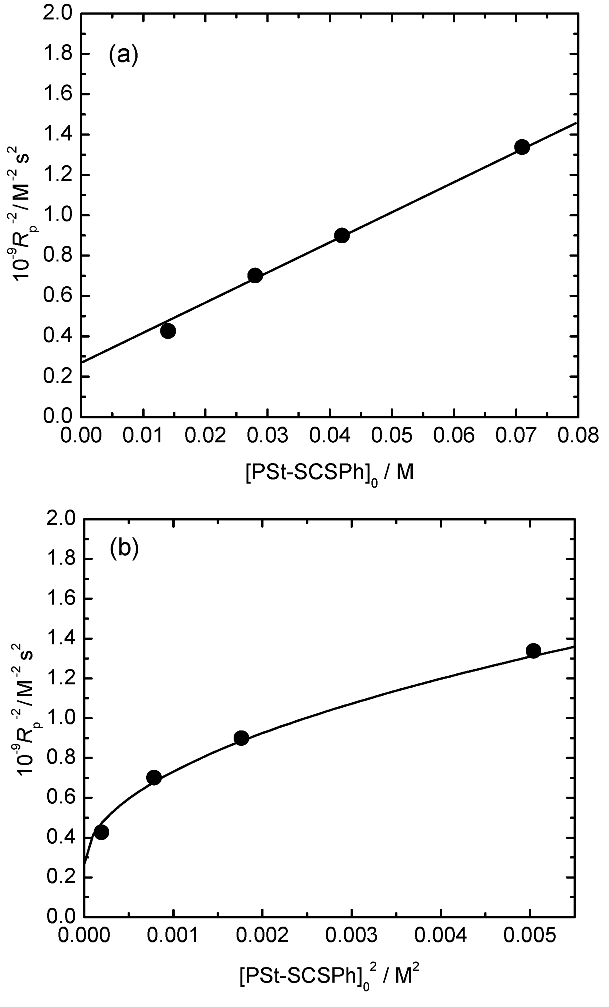

Figure 2. Plot of R_p^{-2} vs (a) $[PSt\text{-}SCSPh]_0$ and (b) $[PSt\text{-}SCSPh]_0^2$ for the styrene/AIBN/PSt-SCSPh/(PSt-Br) systems (60 °C). For experimental conditions, see Figure 1.

k_t' terms in eqs 4, 8, and 13 is missing in the previous equations. Accordingly, the approximate estimate of the k_t'/k_t ratio of 0.8 given in those papers[9,19] should be corrected to 0.8/2 = 0.4.

Termination can occur between two intermediate radicals to form a 4-arm star. If this termination predominates, we may set $k_t'/k_t = 0$ in eq 8 to have

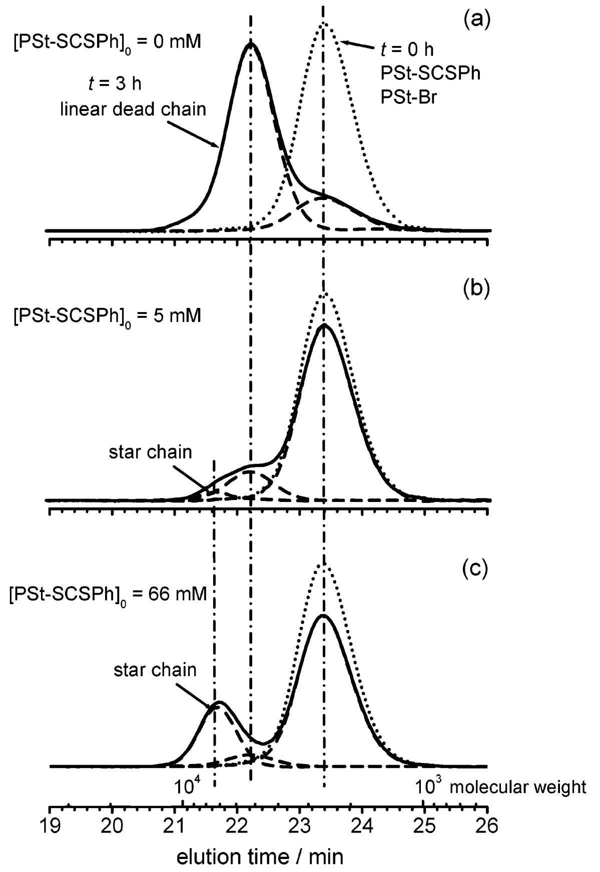

Figure 3. GPC chromatograms for the mixture of *tert*-butylbenzene, PSt-SCSPh, PSt-Br, CuBr, Cu(0), and Me$_6$TREN heated for 3 h (60 °C): $[PSt\text{-}SCSPh]_0 =$ (a) 0, (b) 5, and (c) 66 mM ($M_n = 2400$ and $M_w/M_n = 1.07$), $[PSt\text{-}Br]_0 =$ (a) 1, (b) 1, and (c) 13 mM ($M_n = 2450$ and $M_w/M_n = 1.09$), $[CuBr]_0 = 82.5$ mM, $[Cu(0)]_0 = 400$ mM, and $[Me_6TREN]_0 = 165$ mM. The vertical dot−dash lines show the peak maxima of the individual components. The peak resolution was made by using the known chromatograms of the prepolymer (PSt-SCSPh plus PSt-Br) and the linear dead chain. The chromatogram of the linear dead chain was obtained by the run with $[PSt\text{-}SCSPh]_0 = 0$, as shown in (a). The smaller decay of the prepolymer in (b) and (c) than in (a) is ascribed to the remaining PSt-SCSPh (see the note in ref 23).

$$R_p^{-2} = R_{p,0}^{-2}\{1 + (k_t''/k_t)K^2[P\text{-}X]_0^2\} \qquad (14)$$

Figure 2b shows the plot of R_p^{-2} vs $[P\text{-}X]_0^2$ according to eq 14. The plot shows a marked curvature, suggesting failure of eq 14. Thus, the contribution of intermediate−intermediate termination to R_p is, if there is any, minor in this system.

Analysis of Star Formation. We have extended the model experiment proposed previously:[9] PSt-SCSPh ($M_n = 2400$, $M_w/M_n = 1.07$: 0−66 mM) and PSt-Br ($M_n = 2450$, $M_w/M_n = 1.09$: 1−13 mM) of nearly the same chain length dissolved in *tert*-butylbenzene were heated at 60 °C in the presence of a CuBr/Me$_6$TREN complex (82.5 mM) and Cu(0) (400 mM). The PSt radical produced from PSt-Br by the catalytic reaction of the Cu(I) complex will add to PSt-SCSPh to yield an intermediate radical, which will subsequently be combined with another PSt radical, forming a star chain. Figure 3 shows the examples of the GPC chromatograms before (dotted line) and after (solid line) the heat treatment for 3 h. The chromatograms obtained at $t =$

3 h for the runs with $[\text{PSt-SCSPh}]_0 = 5$ and 66 mM (Figure 3, b and c, respectively) can be divided into three components (broken lines), i.e., PSt-SCSPh plus PSt-Br for the lowest molecular weight component ($M_n = 2450$, $M_w/M_n = 1.08$), a linear dead chain of doubled molecular weight for the middle component ($M_n = 5100$, $M_w/M_n = 1.06$), and (3- or 4-arm) star chain(s) for the highest component ($M_n = 7000$, $M_w/M_n = 1.03$). The chromatogram for the linear doubled molecular weight chain used in this peak resolution was obtained by the run with $[\text{PSt-SCSPh}]_0 = 0$, in which only self-termination between PSt radicals can occur (Figure 3a). The noted M_n value of 7000 for the star chain(s) is an apparent value obtained by the GPC calibrated with *linear* polystyrenes. The absolute molecular weight at the peak maximum for the star chain(s) was determined by GPC-MALLS to be 7800. This value is close to the M_w value expected for a 3-arm star, i.e., $M_{w,3-\text{arm}} = 2450 \times 3 \times (M_w/M_n)_{3-\text{arm}} = 7600$, but much smaller than that for a 4-arm star, i.e., $M_{w,4-\text{arm}} = 2450 \times 4 \times (M_w/M_n)_{4-\text{arm}} = 10\,000$, where the theoretical predictions[21] $(M_w/M_n)_{3-\text{arm}} = 1.03$ and $(M_w/M_n)_{4-\text{arm}} = 1.02$ for $(M_w/M_n)_{1-\text{arm}} = 1.08$ were used. Thus, the predominant component of the star is 3-armed.

Now let us assume that the cross-termination is accompanied by no disproportionation. Since recombination predominates in styrene polymerization, the concentration ratio of the 3-arm star to the linear (2-arm) chain may be approximately given by

$$\frac{[\text{3-arm}]}{[\text{2-arm}]} = 2(k_t'/k_t)K[\text{P-X}]_0 \qquad (15)$$

This equation derives from eq 10 by setting $[\text{P-X}] = [\text{P-X}]_0$ (constant).[22] We estimated the ratio [star chain]/[linear chain] from the GPC peak areas, when all stars are assumed to be 3-arm ($M_{n,\text{star}} = (3/2)M_{n,2-\text{arm}}$). Figure 4a shows the plot of this ratio as a function of $[\text{PSt-SCSPh}]_0$. The plot is approximately linear, and the slope of the line gives $k_t'/k_t \cong 0.4$ according to eq 15. This value, even though it may be subject to small errors,[23] well agrees with the above-reported value obtained by the kinetic analysis of the polymerization system ($k_t'/k_t = 0.5 \pm 0.1$).

If a 4-arm star is assumed to be a main product, its concentration relative to the linear (2-arm) chain may be approximately given by the right-hand side of eq 11 with $[\text{P-X}] = [\text{P-X}]_0$. Figure 4b shows the plot of [star chain] to [linear chain] ratio as a function of $[\text{PSt-SCSPh}]_0^2$, when all stars are assumed to be 4-arm ($M_{n,\text{star}} = 2M_{n,2-\text{arm}}$). Clearly, the linearity predicted by the theory does not hold, confirming, again, that the main component of the star chain is 3-armed, not 4-armed.

The main criticism against the cross-termination mechanism is that there has been no direct observation of the star in the actual polymerization system.[10] However, the good agreement of the k_t'/k_t values obtained in the model and actual systems is strong evidence that *the cross-termination does occur in the actual polymerization system as well as in the model system*. In the actual RAFT polymerization, the living polymers (with a RAFT moiety) usually have a narrow distribution in chain length, and hence they can be relatively easily analyzed by various methods. On the other hand, terminations will occur throughout from the beginning to the end of the polymerization, so that the terminated chains are far more widely distributed along the molecular weight axis and thus much more difficult even to detect. Undetectability of the star in the actual RAFT polymerization will not guarantee its absence.

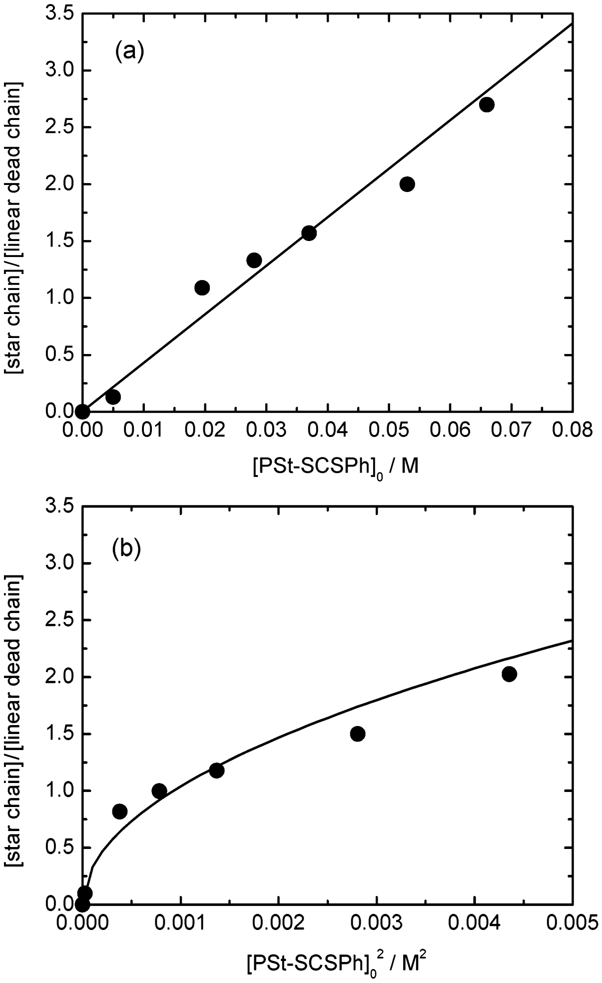

Figure 4. Plot of [star chain]/[linear dead chain] vs (a) $[\text{PSt-SCSPh}]_0$ and (b) $[\text{PSt-SCSPh}]_0^2$ (60 °C). The ratio was estimated by the GPC analysis demonstrated in Figure 3, where all produced stars are assumed to be (a) 3-arm ($M_{n,\text{star}} = (3/2)M_{n,\text{linear}}$) and (b) 4-arm ($M_{n,\text{star}} = 2M_{n,\text{linear}}$).

Stability of the 3-Arm Star. To examine the stability of the 3-arm star, the polymer species formed at 3 h in Figure 3c was purified by reprecipitation to remove the copper species, dissolved again into *tert*-butylbenzene to give a dilute solution ([polymer] = 0.5 mM) and heated for 25 h at various temperatures. If cross-termination is reversible, the star will undergo degradation to give PSt-SCSPh and PSt radical. Because the PSt-SCSPh concentration is very low, the cross-termination will hardly occur again (cf. eq 10), and most of the PSt radical will undergo self-termination or chain transfer to solvent. Figure 5 shows the GPC charts of the products. At 60 °C, no decay of the 3-arm star concentration was observed, indicating that cross-termination is virtually irreversible at this temperature. Degradation may occur by other paths, e.g., by the C−S bond cleavage of the star.[24] Thus, we carried out the same experiment in the presence of TEMPO (5 mM) to capture possibly produced radicals. The star concentration did not decay in this experiment, either, showing no degradation at this temperature. On the other hand, a slight decay of the star concentration was observed at 90 and 120 °C (Figure 5), even though the reaction was very slow. The first-order rate constant of decom-

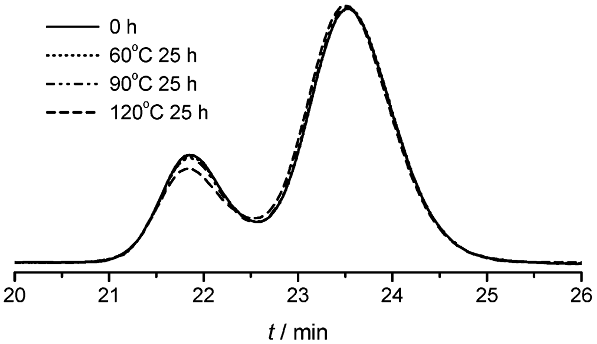

Figure 5. GPC chromatograms for the mixture of *tert*-butylbenzene and the polymer species shown in Figure 3c: [polymer]$_0$ = 0.5 mM. The mixture was heated at 60, 90, and 120 °C for 25 h.

position was estimated to be about 2.0×10^{-6} s^{-1} at 120 °C by chasing the time evolution of the GPC chart. This suggests that the star chain will work as a radical generator (initiator) with a half-life of about 100 h at 120 °C.

Conclusions

The polymerization of styrene at 60 °C mediated by polystyryl dithiobenzoate and initiated by AIBN reaches a stationary (steady) state within a few minutes after the onset of polymerization. The rate retardation observed for this system was analyzed in light of the stationary-state kinetic theory in which the cross-termination (between the intermediate and propagating radicals) to form a 3-arm star as well as the self-termination (between the intermediate radicals) to form a 4-arm star were modeled. The dependence of R_p on the RAFT agent concentration clearly favored the cross-termination rather than the self-termination, and the relevant rate constant was shown to be similar in order of magnitude to that between the propagating radicals ($k_t'/k_t = 0.5 \pm 0.1$).

The model experiment, in which the reactions of polystyryl radicals in the absence of styrene were followed by GPC equipped with a multiangle laser light scattering detector, also showed clear evidence for the formation of a 3-arm star (but not a 4-arm star), and its formation rate relative to that of the linear dead chain gave a crude estimate of $k_t'/k_t \cong 0.4$, in good agreement with the value obtained for the actual polymerization. The 3-arm star was shown to be perfectly stable at this temperature in the time scale of the experiments.

Thus, the pervious conclusion that the rate retardation of this system is caused by the irreversible formation of a 3-arm star chain has been reinforced by this study. The actual chemical structure of the star is still to be explored, however.

A *reversible* reaction leading to the transient formation of a 4-arm star may or may not exist, but it is essentially irrelevant to stationary-state kinetics.

Equation 8, for example, clearly shows that the rate retardation phenomenon depends on many factors. Comprehensive and careful experiments are primarily important in ruling out irrelevant factor(s) and approaching correct answer(s). Rate constants such as k_{ad} and k_{fr} (and hence K) can largely differ for different systems. They can significantly depend also on chain length, especially for short chains, as a body of experimental evidence for other LRP systems suggests.[25,26] Accordingly, the conclusions obtained in this work specifically apply to the polymerization of *styrene* mediated by *polystyryl dithiobenzoate* and should not be easily extended to systems with other monomers and/or other dithio compounds and *vice versa*. For example, even the polymerization of styrene mediated by 1-phenylethyl dithiobenzoate, a low-mass homologue of polystyryl dithiobenzoate, can look very different from those of the polymer homologues because of largely different parameter values. Comprehensive and accurate studies to establish the kinetic parameters of individual systems are essential to systematically understand RAFT processes and possibly accompanying side reactions.

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Note Added after ASAP Posting

This article was released ASAP on 1/30/2004. In the fifth paragraph of the Conclusions section, poly(styryl dithiobenzoate) was changed to polystyryl dithiobenzoate. The correct version was posted on 2/06/2004.

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(17) For the fragmentation of the alkyl radical R$^\bullet$ from the intermediate CH_3-S-C$^\bullet$(CH_3)-S-R, the activation enthalpy differed by 16.7 kJ mol^{-1} between R = CH_3 and $CH_2CO_2CH_3$ (primary group) and 40.9 kJ mol^{-1} between R = CH_3 and $C(CH_3)_2CN$ (tertiary group).[16] The differences of 16.7 and 40.9 kJ mol^{-1} in activation enthalpy correspond to the differences of 3 and 7 orders of magnitude in k_{fr}, respectively (60 °C).

(18) The exchange chain transfer rate constant k_{ex} (1.2×10^5 M^{-1} s^{-1}) for the polymer RAFT agent PMMA-SCSPh[13] is about 80 times larger than that (1.4×10^3 M^{-1} s^{-1}) for the corresponding unimer model ($C(CH_3)_2COOCH_3$-SCSPh),[28] when PMMA$^\bullet$ undergoes the addition to the two RAFT agents (60 °C). The addition rate constant k_{ad} of PMMA$^\bullet$ to the polymer PMMA-SCSPh would not exceed that to the unimer model $C(CH_3)_2COOCH_3$-SCSPh. Thus, these k_{ex} values mean that the probability of PMMA$^\bullet$ to be released from the intermediate radical PMMA-S-C$^\bullet$(Ph)-S-$C(CH_3)_2COOCH_3$ is about 160 times larger than the probability of $^\bullet C(CH_3)_2$-$COOCH_3$ to be released from the intermediate radical: this is so because for PMMA-SCSPh attacked by PMMA$^\bullet$, an exchange occurs by the probability of 1/2.[13] The fact that for the unimer model attacked by PMMA$^\bullet$ k_{ex} is 1/80 of that for the polymer[28] means, therefore, that this probability of exchange for the unimer model is 1/160, assuming the same k_{ad} for the two RAFT agents. (This probability is less than 1/160, if k_{ad} is larger for the unimer model.) It follows that the fragmentation of PMMA$^\bullet$ is about 160 times (or more) faster than that of the unimer model radical.

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(22) The factor 2 appearing on the right-hand side of eq 15 is erroneously missing in our previously proposed equation (eq 6 in ref 9).

(23) We may have slightly underestimated the k_t'/k_t value due to the decrease of [PSt-SCSPh] during the experiment. However, since $[\text{PSt-SCSPh}]_0/[\text{PSt-Br}]_0 = 5$ in this experiment (see Experimental Section), [PSt-SCSPh] cannot decrease by more than 10% even when all PSt-Br has been converted to the star. On the other hand, the self-termination of PSt radicals is known to be accompanied by some (~7%[27]) disproportionation. This fact alone suggests so much of overestimation of k_t'/k_t ratio. In any event, the error associated with the estimated k_t'/k_t value should not be large.

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