Mechanism and Kinetics of Iodide-Mediated Polymerization of Styrene

Atsushi Goto, Kohji Ohno, and Takeshi Fukuda*

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

Received August 7, 1997; Revised Manuscript Received February 23, 1998

ABSTRACT: The kinetics of the bulk polymerization of styrene in the presence of a model ω-polystyryl iodide ($M_n \approx 2000$, and $M_w/M_n \approx 1.26$) as mediator and benzoyl peroxide as initiator was studied. The rate of polymerization, R_p, was found to be independent of the iodide concentration, showing that the stationary concentration of polymer radicals, [P*], is determined by the balance of initiation and termination rates, as in the conventional (iodide-free) system. The pseudo-first-order activation rate constant k_{act} of the model iodide was determined as a function of BPO concentration and temperature (50−80 °C) by both the GPC curve-resolution and polydispersity-analysis methods. The results showed that k_{act} is directly proportional to [P*], which means that degenerative transfer (active species-exchanging transfer) is the only important mechanism of activation in this system. The activation energy for the transfer rate constant k_{ex} was found to be 27.8 kJ mol^{-1}, somewhat smaller than the known activation energy for the styrene propagation rate constant k_p of 32.5 kJ mol^{-1}. This indicates that lowering, rather than raising, the reaction temperature will be more effective in preparing polystyrenes with a narrower polydispersity by the iodide-mediated polymerization. This is because the most important parameter for determining the polydispersity of a degenerative-transfer-type system is the k_{ex}/k_p ratio, as has been known for some time.

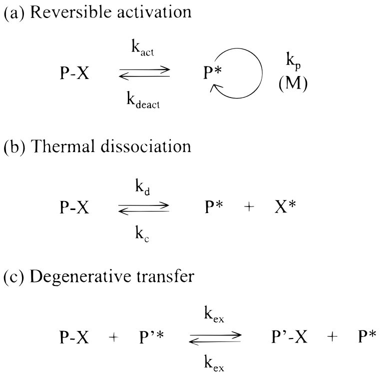
Introduction

The past few years have witnessed explosive growth of the synthesis of well-defined polymers by controlled or "living" radical polymerization techniques.[1] Mechanistically, these techniques are commonly characterized by activation−deactivation reversible processes (Scheme 1). Namely, the active chain (P*) will, in the presence of the monomer M, undergo polymerization with a mean rate k_p[M] until it is deactivated by a capping agent X. Examples of X include sulfur compounds,[2] stable nitroxyls,[3,4] halogens,[5−9] transition metal complexes,[10,11] and others.[1,12] The chain remains inactive, or dormant, until it is decapped by thermal, photochemical, and/or chemical activation. A number of such activation−deactivation cycles and a low concentration of the active species (relative to that of the dormant species) will allow all the chains to grow slowly and simultaneously with a minor effect of alkyl−alkyl bimolecular termination. This seems to be the most common understanding of the basic mechanism by which well-defined polymers are produced in radical polymerization systems.[13,14]

In this regard, the reversible activation process is the "heart" of "living" radical polymerizations. Since the frequency of deactivation is basically equal to that of activation, the pseudo-first-order rate constant of activation, k_{act} (in units of s^{-1}), is the essential parameter that controls the polydispersity of a given polymerization system. In previous publications,[15,16] we proposed two mutually related but basically different methods for determining k_{act} by the use of gel permeation chromatography (GPC) and used them to show that the main mechanism of activation in the TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) mediated polymerization of styrene is the thermal dissociation of the polystyrene (PS)−TEMPO adduct (Scheme 1b) rather than degenerative transfer[1c,13a] (Scheme 1c).

We have applied the GPC methods to the iodide-mediated polymerization of styrene to examine its activation process. According to Matyjaszewski et al.,[7] the control of chain length and chain length distribution is achieved by the mechanism of degenerative transfer, but no direct experimental evidence for it has been obtained as yet. In what follows, we will make a detailed study on this problem by determining the pseudo-first-order rate constant of activation, k_{act}, as a function of polymerization rate and temperature and discuss the possibility and limitation of the iodide-mediated polymerization of styrene.

Scheme 1. (a) Reversible Activation, (b) Thermal Dissociation, and (c) Degenerative Transfer



Experimental Section

Synthesis and Characterization of *ω*-Polystyryl Iodide. 1-Phenylethyl iodide (PEI) was prepared as described elsewhere[7a] and confirmed to be virtually 100% pure by ^{1}H NMR (proton nuclear magnetic resonance spectroscopy). A styrene solution of PEI (0.20 mol L^{-1}) and benzoyl peroxide (BPO; 0.030 mol L^{-1}) in a glass tube was degassed by several freeze−thaw cycles, sealed off under vacuum, and heated at 80 °C for 70 min. After purification,[14] there was obtained a polymer which had number- and weight-average molecular weights M_n and M_w of 1500 and 1890, respectively, according to PS-calibrated GPC.[14] These values of M_w and M_n are not necessarily reliable on an absolute scale because of the differences in the end groups between this sample and the anionically prepared standard PSs used for the GPC calibration.

S0024-9297(97)01200-X CCC: $15.00

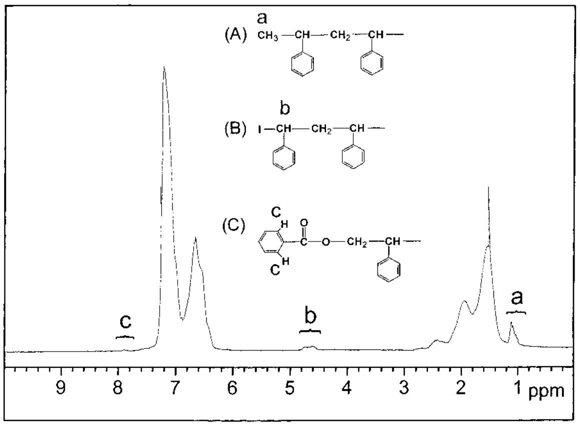


Figure 1. ^{1}H NMR spectrum of the model polystyryl iodide P_o−X. A, B, and C are the three major possible structures of the chain ends, and a, b, and c denote the assignments of the signals.

^{1}H NMR analysis may give more reliable results in this particular case. The spectrum given in Figure 1 (taken at ambient temperature with flip angle 45°, spectral width 3001 Hz, acquisition time 2.666 s, and pulse delay 2.0 s) clearly shows the signals due to the methyl protons at the initiating chain end (0.9−1.2 ppm; peak a), the methine proton at the iodine end (4.5−4.8 ppm; peak b), and the ortho protons of the benzoyloxy ring at the BPO-initiated chain end (7.9 ppm; peak c). From the peak areas of the protons at the initiating chain ends (peaks a and c) relative to that of the methylene and methine protons in the main chain (1.2−2.8 ppm) and to that of the terminal methine (peak b), we estimated the M_n of the PS moiety of the sample and the number fraction f_I of the iodine-capped chains to be 1900 and 0.98, respectively. Since peak a is slightly overlapped by the tail part of the main-chain protons, appropriate curve resolution was made in reference to the spectrum of a free-radically prepared PS with a high M_n ($>10^5$), which showed no detectable chain-end signals. We also note that an elemental analysis showed that the sample contained 6.16 wt % of iodine, which, along with the M_n value of 1900, gives $f_I = 0.98$, in agreement with the NMR value. On the other hand, the number fraction of the chains with a benzoyloxy chain end, f_B, is about 0.04 according to the above-mentioned NMR analysis. This value of f_B is consistent with the decomposition rate constant of BPO in styrene (see below) and the experimental conditions given above. Since the number of initiated chains is equal to that of the terminated (dead) chains (see below), and since the rate of thermal (spontaneous) initiation of styrene at this temperature (80 °C) is negligibly small compared to that of the BPO initiation, we can estimate that the fraction f_B of chains were terminated (mostly by combination in the case of styrene). This indicates that the fraction of active chains (f_I) does not exceed $1 - f_B = 0.96$, approximately.[17]

From all these results, we may conclude that the prepared polystyryl iodide sample, which will be designated P_o−X, is 96−98% pure. In the following analysis, we will correct experimental data assuming that P_o−X includes 3 wt % of inactive species (without an iodine moiety). This correction, however, was generally small compared with other experimental errors. Even though the absolute values of molecular weights estimated by GPC may not be very accurate, as suggested above, they can be used probably with less error for the purpose of comparative studies such as are made in the determination of the activation rate constant by polydispersity analysis (see below). For example, the M_w/M_n ratio of 1.26 for P_o−X estimated by GPC should be a good approximation.

Kinetic Analysis of Polymerization. A fixed amount of P_o−X (1.7×10^{-2} mol L^{-1}) and a variable amount of BPO ($(0-3.0) \times 10^{-2}$ mol L^{-1}) were dissolved in styrene, degassed, sealed off under vacuum, and heated at 80 °C for a prescribed time t. The mixture was then quenched to room temperature, diluted by tetrahydrofuran (THF) to a known concentration, and directly analyzed by GPC with THF as eluent (40 °C).[14−16]

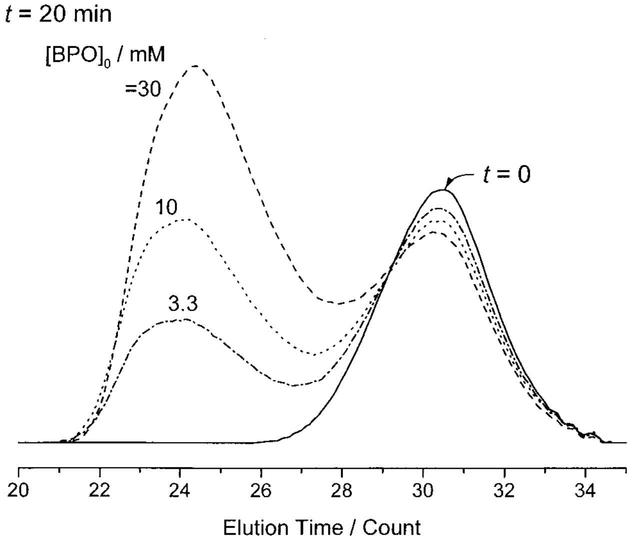


Figure 2. Examples of GPC chromatograms of the raw polymerization products: $[P_o\text{−X}]_0 = 17$ mmol L^{-1}; $[BPO]_0$ as indicated in the figure (80 °C).

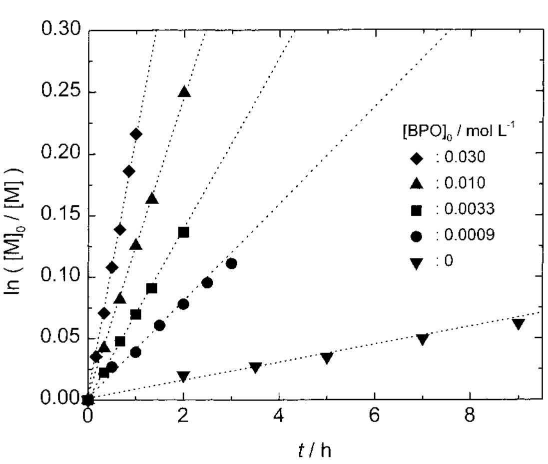


Figure 3. Plot of $\ln([M]_0/[M])$ vs t: $[P_o\text{−X}]_0 = 17$ mmol L^{-1}; $[BPO]_0$ as indicated in the figure (80 °C).

Results and Discussion

Polymerization Rates. We first examine the rate of polymerization, R_p, of this system. Figure 2 shows examples of the GPC curves of the reaction mixtures obtained after 20 min of heat treatment of the system with $[P_o\text{−X}]_0 = 1.7 \times 10^{-2}$ mol L^{-1} and varying values of $[BPO]_0$, where the subscript 0 denotes the initial state ($t = 0$). (The actual chromatograms have a huge monomer peak at around 40 counts, which, being irrelevant to the present analysis, is not included in the figure.) Since a constant amount of each reaction solution was injected to the column system, the total area under each curve relative to that of the $t = 0$ curve shows how much monomer was converted to polymer. By independent experiments, it was confirmed that the RI (refractive index) detector response of polystyryl iodides does not depend on chain length (for $M_n \geq 2000$), being the same as that of standard PSs within 1 or 2%. Figure 3 gives the first-order plot of the monomer concentration [M]. In these relatively small conversion ranges, the plot is approximately linear, indicating that the system is in a stationary state with respect to the ratio $R_p/[M]$ (the slope of the $\ln([M]_0/[M])$ vs t) or the

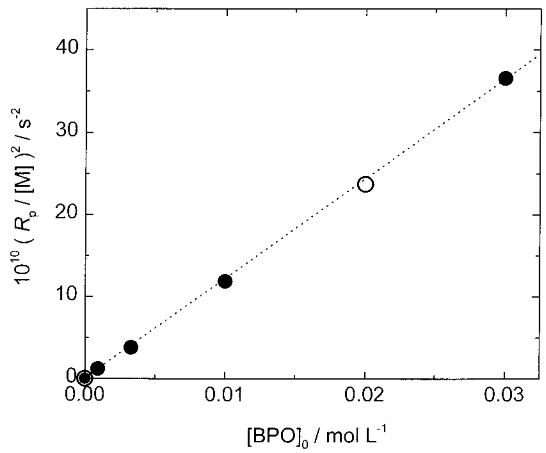


Figure 4. Plot of $(R_p/[M])^2$ vs $[BPO]_0$ for the polymerization of styrene at 80 °C in the presence of P_o-X ($[P_o-X]_0$ = 17 mmol L^{-1}, filled circles) and the absence of it (open circles).

polymer radical concentration [P*]

$$[P^*] = k_p^{-1}(R_p/[M]) \qquad (1)$$

where k_p is the rate constant of propagation.

Figure 4 gives the values of $(R_p/[M])^2$ as a function of $[BPO]_0$, indicating that $[P^*]^2$ is linear in $[BPO]_0$. The open circles in the figure for the conventional system (without the iodide P_o-X) fall on the same straight line as for the iodide system. This means that the iodide has no effect on the stationary rate of polymerization, and R_p, whether the iodide exists or not, may be given by the relations

$$(R_p/[M])^2 = (k_p^2/k_t)R_i \qquad (2)$$

$$R_i = R_{i,th} + 2f'k_{BPO}[BPO] \qquad (3)$$

with $R_{i,th} = 2.2 \times 10^{-9}$ mol L^{-1} s^{-1}, and $2f'k_{BPO} = 7.2 \times 10^{-5}$ s^{-1}. In eqs 2 and 3, k_t is the termination rate constant and R_i is the total rate of initiation, which is the sum of the thermal initiation $R_{i,th}$ of styrene and the initiation due to the decomposition of BPO with a rate constant k_{BPO} and an efficiency f'. The values of $R_{i,th}$ and $2f'$ k_{BPO} obtained here are reasonably comparable to the literature values: $R_{i,th} = 2.5 \times 10^{-9}$ mol L^{-1} s^{-1} [18] and $k_{BPO} = 3.5 \times 10^{-5}$ s^{-1}.[19] In this work, use is made of the k_p value recommended by IUPAC[20] and the k_p^2/k_t value due to Hui and Hamielec[18] (k_p = 660 and $k_p^2/k_t = 1.71 \times 10^{-3}$ L mol^{-1} s^{-1}, respectively).

Determination of k_{act} by GPC Peak Resolution. The GPC curves given in Figure 2 are composed of two peaks. Clearly, the first, lower-molecular-weight (larger-elution-count) component corresponds to the undissociated P_o-X.[15] This peak was observed to become smaller with an increase in BPO concentration when t was fixed (Figure 2) and with an increase in t when $[BPO]_0$ was fixed (not shown in the figure). The second, higher-molecular-weight component is ascribed mainly to the activated, grown chains. This component can also include those species, albeit small in fraction, that originate from BPO, thermal initiation, and/or a further activation of P_1-X, where P_1-X is the polystyryl iodide produced from P_o-X after one cycle of activation–propagation–deactivation (cf. Scheme 1a). Actually, the number density of polymer chains, $[N_p]$, estimated by the GPC curves such as given in Figure 2 is nearly constant and equal to $[P_o-X]_0$ within ±10% in the studied ranges of $[BPO]_0$ and t (Figure 5). This means that the cumulative number of BPO- (and thermally) originating chains is small compared with the number of P_o-X molecules. These details, however, are not required, since we are concerned here with the time evolution of $[P_o-X]$ or the intensity S of the first peak. As was the case with the polystyryl nitroxide system,[15] the resolution of the bimodal GPC curves into the two components could be accurately made, which is the basic requirement of this analysis, and the quasi-first-order activation rate constant k_{act} was determined from the slope of the plot of $\ln(S_0/S)$ vs t:

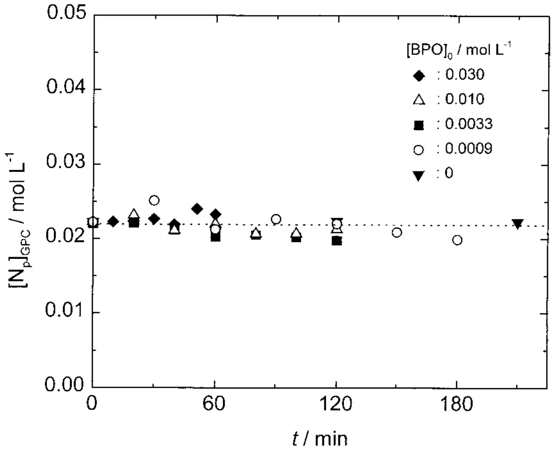


Figure 5. Plot of the number density $[N_p]_{GPC}$ of polymer vs t: $[P_o-X]_0$ = 17 mmol L^{-1}; $[BPO]_0$ as indicated in the figure (80 °C). $[N_p]_{GPC}$ denotes the value of $[N_p]$ estimated by GPC.

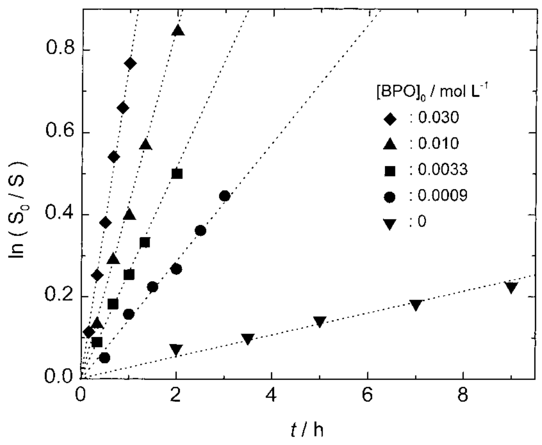


Figure 6. Plot of $\ln(S_0/S)$ vs t (80 °C): $[P_o-X]_0$ = 17 mmol L^{-1}; $[BPO]_0$ as indicated in the figure.

$$\ln(S_0/S) = k_{act}t \qquad (4)$$

Figure 6 shows this plot for various values of $[BPO]_0$. The plot is linear in all cases, giving a well-defined value of k_{act}.

Determination of k_{act} by Polydispersity Analysis. The above-described method for determining k_{act} is free from any kinetic details, other than the existence of activation and propagation processes, and it was termed the "direct" method. The alternative approach, the "indirect" method, is based on the analysis of the evolution of polydispersities at an early stage of polymerization by using the relations[16]

$$Y = w_A^2 Y_A + w_B^2 Y_B \qquad (5)$$

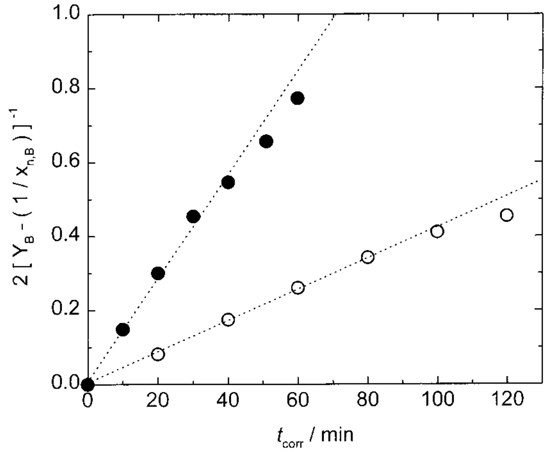


Figure 7. Plot of $2[Y_B - (1/x_{n,B})]^{-1}$ vs t_{corr} (80 °C): $[P_o\text{-}X]_0$ = 17 mmol L^{-1}; $[BPO]_0$ = 3.3 mmol L^{-1} (○) and 30 mmol L^{-1} (●).

$$2[Y_B - (1/x_{n,B})]^{-1} = k_{act}t \tag{6}$$

Here the polymerization product at time t is viewed as an A−B diblock copolymer with subchains A and B referring to P_o−X and the incremental part of the molecule, respectively: $Y = (x_w/x_n) - 1$, $Y_K = (x_{w,K}/x_{n,K}) - 1$, $w_A = 1 - w_B = x_{n,A}/x_n$, $x_n = x_{n,A} + x_{n,B}$, and x_n and x_w are the number- and weight-average degrees of polymerization with K = A or B. Since we know the overall degrees of polymerization (x_n and x_w) and those of the subchain A or P_o−X ($x_{n,A}$ and $x_{w,A}$), we can estimate Y_B and $x_{n,B}$ according to eq 5. Among the important conditions for this method to be valid[16] are the constancy of the number of polymers, N_p, and the constancy of the rate of polymerization, R_p. For a batch system with a constant $R_p/[M]$, t in eq 6 should be replaced by t_{corr}, a function of conversion C:[21,22]

$$t_{corr} = 2Ct/[(C - 2)\ln(1 - C)] \tag{7}$$

The constancy of both $R_p/[M]$ and $[N_p]$ is approximately met in the present systems, as Figures 3 and 5 show.[23]

Two examples of the plot of $2[Y_B - x_{n,B}^{-1}]^{-1}$ vs t_{corr} are presented in Figure 7. The values of k_{act} estimated from the initial slopes of these curves are 7.1 × 10^{-5} and 2.3 × 10^{-4} s^{-1} for $[BPO]_0$ = 3.0 × 10^{-2} and 3.3 × 10^{-3} mol L^{-1}, respectively, which well agree with the values 7.2 × 10^{-5} and 2.2 × 10^{-4} s^{-1}, respectively, obtained by the direct method (Figure 6).

Mechanism of Activation. The activation, i.e., the cleavage of the C−I bond in this system, can possibly occur by a thermal (or photochemical) stimulus (homolytic cleavage: Scheme 1b) and/or a chemical stimulus by a propagating radical P* (degenerative transfer: Scheme 1c). Since the former reaction is first order and the latter is second order, the pseudo-first-order coefficient k_{act} defined by eq 4 takes the form[15]

$$k_{act} = k_d + k_{ex}[P^*] \tag{8}$$

Thus the plot of k_{act} against [P*] will make a straight line with its intercept at [P*] = 0 and slope giving k_d and k_{ex}, respectively.

This plot is shown in Figure 8. It is evident that the data points obtained by the direct (curve-resolution) method (filled circles) form a straight line passing through the origin, showing that k_d = 0 (within the accuracy of the present analysis) and k_{ex} = 2400 L mol^{-1} s^{-1}. The values of k_{act} obtained by the indirect method (open circles) are somewhat more scattered but give almost the same results. These experiments have established that degenerative transfer is virtually the only mechanism of activation in the iodide/styrene system.

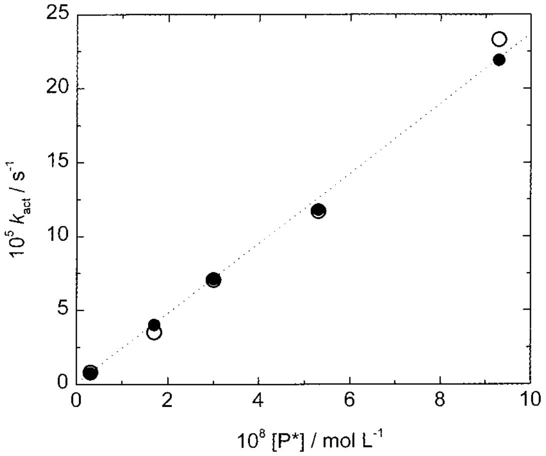


Figure 8. Plot of k_{act} vs [P*] (80 °C): (●) by the direct (curve-resolution) method, and (○) by the indirect (polydispersity-analysis) method.

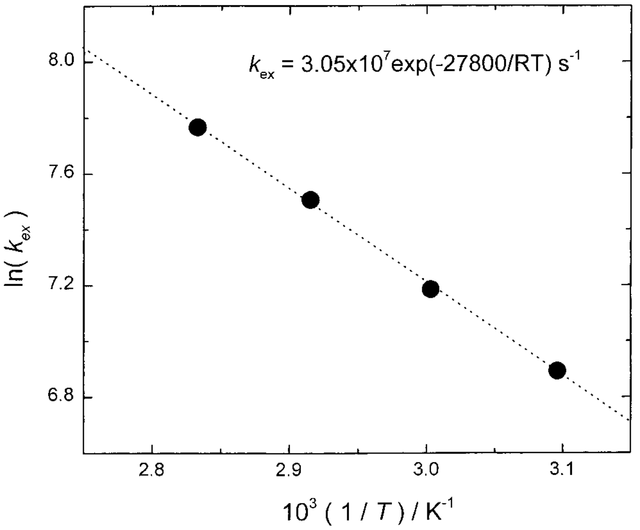


Figure 9. Plot of $\ln(k_{ex})$ vs $1/T$ for the iodide-mediated polymerization of styrene.

Temperature Dependence of k_{ex}. Figure 9 shows the rate constant of degenerative transfer, k_{ex}, determined by the direct method at various temperatures. The result can be represented by the Arrhenius formula

$$k_{ex}/s^{-1} = 3.1 \times 10^7 \exp(-27.8 \text{ kJ mol}^{-1}/RT) \tag{9}$$

The activation energy of 27.8 kJ mol^{-1} obtained here is very small compared with those of homolytic bond-cleavage reactions, e.g., the PS−TEMPO dissociation reaction (124 kJ mol^{-1}),[15b] but it seems reasonable in the order of magnitude for a transfer reaction. An increase in temperature does not give the iodide system such a large increase in activation rate as it gives the TEMPO system. The iodide-mediated polymerization at high temperatures (≥100 °C) is not recommended because of the possible isolation of iodine molecules.

Comments on the Narrowest Possible Polydispersity. In an ideal living system where side reactions

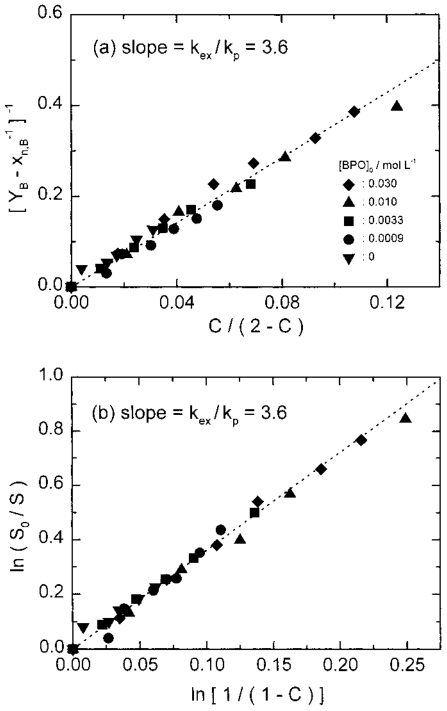


Figure 10. (a) Plot of $2[Y_B - (1/x_{n,B})]^{-1}$ vs $C/(2 - C)$ and (b) of $\ln(S_0/S)$ vs $\ln[1/(1 - C)]$ for the iodide-mediated polymerization with varying values of $[BPO]_0$, as indicated in Figure 10a (80 °C).

such as initiation, termination, and transfer reactions (other than degenerative one) have negligible effects on polydispersity, the polydispersity factor Y_B of the incremental portion of the chain in a batch system (with constant R_p/[M]) is given by eq 6 with t replaced by t_{corr} in eq 7:

$$[Y_B - (1/x_{n,B})]^{-1} = (Ctk_{act})/[(C - 2)\ln(1 - C)] \quad (10)$$

In a nitroxide/styrene system, for example, $k_{act} = k_d =$ constant at a given temperature, and therefore Y_B can be manipulated by changing t for a given value of C. The smallest possible value of Y_B, which is equal to $x_{n,B}^{-1}$, is expected for $t = \infty$ for any value of $C < 1$. Even though this limiting value of Y_B is difficult to realize due to side reactions, we have demonstrated in a previous paper[16a] that qualitatively the Y_B of a nitroxide/styrene system became smaller as t was increased while C was fixed.

The behavior of an iodide/styrene system is expected to be quite different from this, since $k_{act} = k_{ex}[P^*]$ in this system. In reference to eqs 1 and 10, we have

$$[Y_B - (1/x_{n,B})]^{-1} = (k_{ex}/k_p)[C/(2 - C)] \quad (11)$$

Namely, the polydispersity of this system is a function of C only (if side reactions are not considered). Similarly, eq 4 with $k_{act} = k_{ex}[P^*]$ reads

$$\ln(S_0/S) = (k_{ex}/k_p)\ln[1/(1 - C)] \quad (12)$$

Again, this is a function of C only. Equations 11 and 12 are tested in Figure 10a,b, respectively. In both cases, experimental points differing in BPO concentration and hence P* concentration fall on a straight line, whose slope (k_{ex}/k_p) is 3.6 in both cases. With the aforementioned value of k_p of 660 L mol^{-1} s^{-1}, we recover the k_{ex} value of 2400 L mol^{-1} s^{-1}.

As this discussion suggests, the polydispersity of the iodide system is determined essentially by conversion, and the smallest possible value of Y_B is expected for full conversion ($C = 1$), where eq 11 gives

$$Y_B = x_{n,B}^{-1} + (k_p/k_{ex}) \quad (\text{at } C = 1) \quad (13)$$

When the "initiating" A subchain and the $x_{n,B}^{-1}$ term are negligibly small, eq 5 with eq 13 simplifies to $Y = k_p/k_{ex}$ (at $C = 1$).[13b,21] At 80 °C, $k_{ex}/k_p = 3.6$ (see above), and therefore the smallest value of M_w/M_n possibly achievable at 80 °C would be 1.28.[24] More generally, combination of the Arrhenius equations for k_{ex} (eq 9) and k_p[20] gives

$$k_p/k_{ex} = 1.38\exp(-4.7\text{ kJ mol}^{-1}/RT) \quad (14)$$

The value of -4.7 kJ mol^{-1} may be subject to a considerable error, but it makes a striking contrast to, e.g., the large activation energy of the dissociation rate constant of a PS–TEMPO adduct (124 kJ mol^{-1}).[15b] Taking eq 14 at its face value, it suggests that with respect to polydispersities, the iodide system would somewhat benefit from lowering the reaction temperature. At 20 °C, for example, the smallest possible value of M_w/M_n would be 1.20. Of course, side reactions would inevitably broaden the polydispersity over these limiting values. At lower temperatures, R_p is smaller and it takes more time to achieve the desired conversion. Optimization of experimental conditions based on the detailed kinetic information obtained here and elsewhere will be primarily important.

Conclusions

The bulk polymerization of styrene in the presence of a model polystyryl iodide as mediator and BPO as initiator was kinetically studied with respect to the rate of polymerization, the rate of activation of the mediator, and the evolution of polydispersity of the polymerization product. It was found that (1) as in the conventional (iodide-free) system, the rate of polymerization, R_p, is determined by the balance of initiation and termination rates. In other words, the iodide has no direct effect on the stationary concentration [P*] of the polymer radical. (However, as in a nitroxide-mediated polymerization,[14] the iodide can have some indirect effect on [P*] by, for example, lowering the average molecular weight of the product, which may be reflected on k_t and hence on [P*] through the stationary-state relation $[P^*] = (R_i/k_t)^{1/2}$.) (2) Both the GPC curve-resolution and polydispersity-analysis methods allowed us to determine the pseudo-first-order activation rate constant k_{act} of the polystyryl iodide accurately, showing that k_{act} is directly proportional to [P*], namely, degenerative transfer is the only important mechanism of activation in this system. (3) The fact that the k_{act} in the iodide system is proportional to [P*] hence R_p means that the polydispersity of this system is determined by conversion only (if effects of side reactions are disregarded), which is a unique feature that is not a characteristic of, e.g., a nitroxide system. (4) The minimum possible value of the M_w/M_n ratio, achievable in a degenerative-type system with a high M_n, at a full conversion, and with negligible effects of side reaction, is equal to $1 + (k_p/k_{ex})$,[13b,21] which, for the iodide/styrene system, has turned out to be 1.28 at 80 °C. This limiting value becomes somewhat smaller by lowering the temperature. Since details of elementary reactions including the activation (deactivation), initiation, and termination processes are known, details of the evolution of the chain length and its distribution of the polymers produced in the iodide system can now be predicted.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research, the Ministry of Education, Science, Sports, and Culture, Japan (Grant-in-Aid 09450351), and also by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

References and Notes

(1) For recent reviews, see: (a) Moad, G.; Rizzardo, E.; Solomon, D. H. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.: Pergamon: London, 1989; Vol. 3, p 141. (b) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (c) Matyjaszewski, K.; Gaynor, S.; Greszta, D.; Mardare, D.; Shigemoto, T. *J. Phys. Org. Chem.* **1995**, *8*, 306. (d) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Pergamon: Oxford, U.K., 1995; p 335. (e) Davis, T. P.; Haddleton, D. M. In *New Methods of Polymer Synthesis*; Ebdon, J. R., Eastmond, G. C., Eds.; Blackie: Glasgow, U.K., 1995; Vol. 2, p 1. (f) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365. (g) Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183. (h) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371. (i) Sawamoto, M.; Kamigaito, M. In *Polymer Synthesis*; Materials Science and Technology Series; VCH (in press). (j) Fukuda, T.; Goto, A.; Ohno, K.; Tsujii, Y. In *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series No. 685; American Chemical Society: Washington, DC, 1998; Chapter 11.

(2) (a) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127. (b) Doi, T.; Matsumoto, A.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 2911.

(3) (a) Solomon, D. H.; Rizzardo, E.; Cacioli, P. Eur. Pat. Appl. 135280, 1985. (b) Rizzardo, E. *Chem. Aust.* 1987, *54*, 32. (c) Moad, G.; Rizzardo, E. *Macromolecules* **1995**, *28*, 8722.

(4) (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987. (b) Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1997**, *30*, 2232. (c) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185. (d) Catala, J. M.; Bubel, F.; Hammouch, S. O. *Macromolecules* **1995**, *28*, 8441. (e) Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T.; Shimizu, Y. *Macromolecules* **1996**, *29*, 3050. (f) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323. (g) Greszta, D.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 7661. (h) Howell, B. A.; Priddy, D. B.; Li, I. Q.; Smith, P. B.; Kastl, P. E. *Polym. Bull.* **1996**, *37*, 451.

(5) Yutani, Y.; Tatemoto, M. Eur. Pat. Appl. 048937OA1, 1991.

(6) (a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Polym. Prepr., Jpn.* **1994**, *43*, 255. (b) Ueda, N.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr., Jpn.* **1996**, *45*, 1267.

(7) (a) Matyjaszewski, K.; Gaynor, S.; Wang, J.-S. *Macromolecules* **1995**, *28*, 2093. (b) Gaynor, S.; Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 8051.

(8) (a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (b) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2249.

(9) (a) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (b) Grimaud, T.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 2216.

(10) (a) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943. (b) Wayland, B. B.; Mukerjee, S.; Poszmik, G.; Woska, D. C.; Fryd, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 742.

(11) Arvanitopoulos, L. D.; Grenel, M. P.; Harwood: H. J. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 549.

(12) Kristina, J.; Moad, G.; Rizzardo, E.; Winzor, C. L. *Macromolecules* **1995**, *28*, 5381.

(13) (a) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638. (b) Matyjaszewski, K. *Macromol. Symp.* **1996**, *111*, 47.

(14) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. *Macromolecules* **1996**, *29*, 6393.

(15) (a) Goto, A.; Fukuda, T. *Macromolecules* **1997**, *30*, 5183. (b) Goto, A.; Terauchi, T.; Fukuda, T.; Miyamoto, T. *Macromol. Rapid Commun.* **1997**, *18*, 673.

(16) (a) Goto, A.; Fukuda, T. *Macromolecules* **1997**, *30*, 4272. (b) Fukuda, T.; Goto, A. *Macromol. Rapid Commun.* **1997**, *18*, 682.

(17) More strictly, if the dead chains are produced by combination only, the *number* fraction f_I does not exceed $1 - (f_B/2) = 0.98$.

(18) Hui, A. W.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1972**, *16*, 749.

(19) Molnar, S. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2245.

(20) Gilbert, R. G. *Pure Appl. Chem.* **1996**, *68*, 1491.

(21) Müller, A. H. E.; Zhuang, R.; Yan, D.; Litvinenko, G. *Macromolecules* **1995**, *28*, 4326.

(22) The factor -2 appearing in eq 4 in ref 16b is a misprint for $C - 2$.

(23) The values of $[N_p]$ estimated by GPC can include a systematic error, since the large end-group effect observed for P_o-X (see the text) would become less and less significant as the chain length increases. Therefore, the condition of constancy of $[N_p]$ may not be so well met as the figure suggests.

(24) The M_w/M_n ratio of the PS$-$I adduct (P_o-X) used for this study is 1.26 (see the **Experimental Section**), which is smaller than the limiting value. This is because some lower-mass components have been removed during the purification process. The raw product must have had a larger M_w/M_n ratio.

MA9712007