Macromolecules **1998,** *31,* 2699−2701

Kinetic Study on the Activation Process in an Atom Transfer Radical Polymerization

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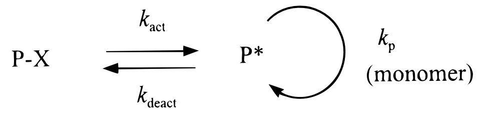
Received October 31, 1997
Revised Manuscript Received February 19, 1998

Introduction. Controlled/"living" radical polymerization techniques have attracted much attention as new and robust synthetic routes to well-defined polymers.[1−6] Mechanistically, they are commonly based on an alternating activation−deactivation process in which the potentially active (dormant) species P−X is reversibly transformed to the active species (polymer radical) P* or vice versa by thermal, photochemical and/or chemical stimuli:



(1)

Here k_p is the rate constant of propagation, and k_{act} and k_{deact} are those of activation and deactivation, respectively, with a reaction order dependent on mechanistic details. When necessary, the reaction order will be specified by a numerical subscript: for example, $k_{1,act}$ denotes that the activation reaction is, or is viewed as, first-order, and $k_{2,deact}$ implies that the overall order of deactivation reaction is second-order or so assumed. In our previous publications, no such specification of reaction order was made, but it would be clear from the context without it (e.g., in one of the papers,[7a] the symbol k_a was used for k_{act} or more specifically $k_{1,act}$). Two general methods to determine $k_{1,act}$ have been proposed and applied to nitroxide-mediated and iodide-mediated systems to disclose the mechanistic details of these techniques of "living" radical polymerization.[7,8]

In the atom transfer radical polymerization (ATRP) in which a copper(I) complex, $Cu^IX/2L$ ($X = Cl$ or Br, and L = 4,4′-disubstituted-2,2′-bipyridine, for example), is used as an activator,[9]

$$P{-}X + Cu^IX/2L \xrightleftharpoons[k_{2,deact}]{k_{2,act}} P^* + Cu^{II}X_2/2L \qquad (2)$$

the $k_{1,act}$ defined as above would take the form

$$k_{1,act} = k_{2,act}[Cu^IX/2L] \qquad (3)$$

where $k_{2,act}$ is the second-order rate constant. As has been reported,[9] the homogeneous ATRP of styrene can yield polymers with predetermined degrees of polymerization up to DP $\approx$ 100 and polydispersity indices, M_w/M_n, as low as 1.04−1.05 from an early stage of polymerization. Since an essential requirement for a low polydispersity in such a system is a sufficiently large number of activation−deactivation cycles,[8,10] the reported result indicates that the magnitude of $k_{1,act}$ of the ATRP system is exceptionally large. In what follows, we have confirmed this by directly measuring $k_{1,act}$ by the GPC (gel permeation chromatography) curve-resolution method.[7] At the same time, this work presents experimental evidence for the mechanistic scheme given by eq 2.

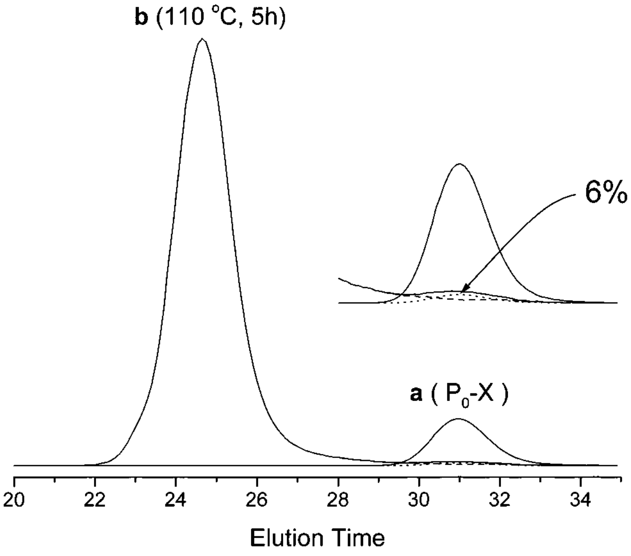


Figure 1. GPC elution curves for (a) the PS−Br adduct P_0−X and (b) the product obtained after a long enough (t = 5 h) polymerization of styrene "initiated" with P_0−X ($[PS{-}Br]_0$ = 35 mmol L^{-1} and $[Cu^IBr/2L]_0$ = 80 mmol L^{-1}). The tail part of curve b contains about 6% P_0−X remaining unreacted, which means that P_0−X originally contains this much of potentially inactive species.

Experimental Section. A polystyryl bromide (PS−Br) was prepared by the homogeneous ATRP.[9] According to the PS-calibrated GPC (see below), it has a number-average molecular weight M_n of 1400 and a M_w/M_n ratio of 1.06. This PS−Br will be used as a model adduct P_0−X. A chain-extension test has demonstrated that about 6% of the chains are potentially inactive without a halogen atom at the end (Figure 1). Styrene and *tert*-butyl hydroperoxide (BHP) were purified by fractional distillation. Cu^IBr (99.999%, Aldrich) was used without further purification.

In a typical run, a Schlenk flask was charged with a predetermined amount of $Cu^IBr/2L$ (in this work, L = 4,4′-di-*n*-heptyl-2,2′-bipyridine), to which 4 mL of styrene solution with BHP (20 mmol L^{-1}) and P_0−X (12 mmol L^{-1}) dissolved in advance was quickly added, and the flask with a glass stopper was immediately attached to a vacuum line, followed by three cycles of evacuation and dry-argon introduction. The system was then kept at 110 °C and stirred magnetically. After a prescribed time t, an aliquot (0.1 mL) of the solution was taken out by a syringe and quenched to room temperature, and a known amount of the solution was injected to a GPC apparatus for a quantitative analysis.

The GPC analysis was made on a Tosoh GPC-8020 high-speed liquid chromatograph equipped with Tosoh gel column G2500H, G3000H, and G4000H. Tetrahydrofuran (THF) was used as the eluent, and the temperature was maintained at 40 °C. Sample detection and quantification were made with a Tosoh differential refractometer RI-8020 calibrated with a known concentration of THF solution of P_0−X adduct.

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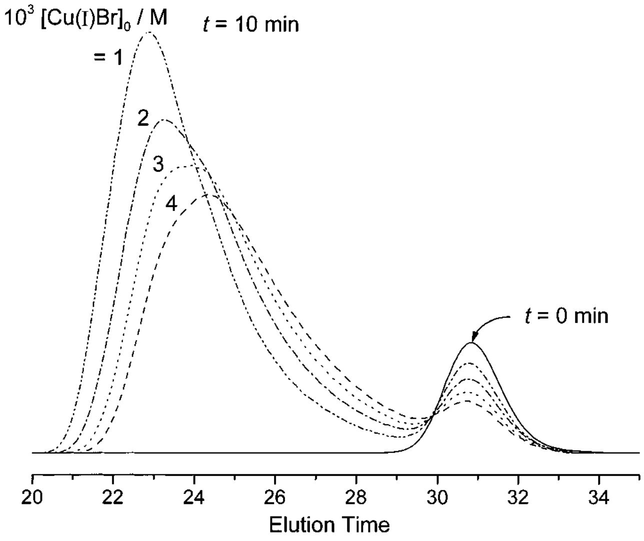

Figure 2. GPC charts for the PS−Br P_0−X/styrene/BHP mixture with different $Cu^IBr/2L$ concentrations heated at 110 °C for 10 min: $[P_0-X]_0 = 12$ mmol L^{-1}; $[BHP]_0 = 20$ mmol L^{-1}; $[Cu^IBr/2L]_0 = 1$, 2, 3, and 4 mmol L^{-1}.

Results and Discussion. The direct method for determining $k_{1,act}$ used here is based on the GPC observation of an early stage of the polymerization "initiated" with a probe adduct P_0−X:[7] when P_0−X is activated via the halogen atom transfer to $Cu^IBr/2L$, the resulting P_0* radical will take up monomer unit(s) and then be deactivated by $Cu^{II}Br_2/2L$ to give a new adduct P_1−X, where the subscript 1 denotes one redox cycle. Hence P_0−X may be distinguishable from P_1−X (or any other species possibly produced in the system) by GPC, owing to the difference in molecular weight and its distribution. Then $k_{1,act}$ may be determined according to the first-order plot:

$$\ln(S_0/S) = k_{1,act}t \qquad (4)$$

where S_0 and S are the concentrations or the peak areas of P_0−X at times 0 and t, respectively.

Accurate resolution of the GPC curve into the mentioned two components requires that a sufficiently large number of monomer units be added to the polymer radical during one activation−deactivation (redox) cycle. To meet this requirement, the ratio of $[Cu^IBr/2L]$ to $[P_0-X]$ was greatly reduced (usually,[9] this ratio is set to unity), and a small amount of the radical initiator BHP, which has a long half-life time at the reaction temperature, was added. Such radical initiators have been found to play the expected role of an accelerator in nitroxide systems.[7,8a,11]

Figure 2 shows the GPC traces of the reaction mixtures with various concentrations of $Cu^IBr/2L$, heated at 110 °C for 10 min. All curves are clearly bimodal with a lower-molecular weight component corresponding to the unactivated adduct P_0−X and a higher-molecular weight one composed of the grown chain P_1−X and other minor species possibly produced by a further activation of P_1−X, decomposition of BHP, and so on. The devolution of the P_0−X concentration with time is shown in Figure 3 in a first-order plot. At all examined concentrations of $Cu^IBr/2L$, a straight line was obtained. Since P_0−X originally contains about 6% of potentially inactive species (cf. Figure 1), it has been corrected by subtracting $0.06S_0$ from both S_0 and S in eq 4. Clearly, an increase in the concentration of $Cu^IBr/2L$ makes the slope of the straight line or the value of $k_{1,act}$ larger.

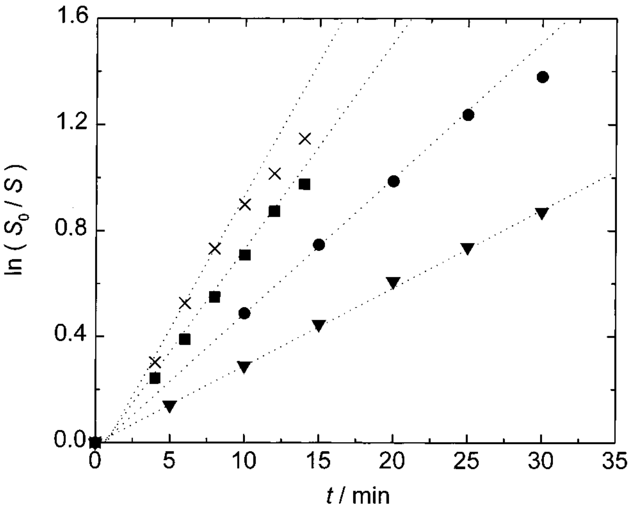

Figure 3. Plot of $\ln(S_0/S)$ vs t for the PS−Br activated by cuprous halide complex at 110 °C: $[Cu^IBr/2L]_0 = 1$ (▼), 2 (●), 3 (■), and 4 (×) mmol L^{-1}.

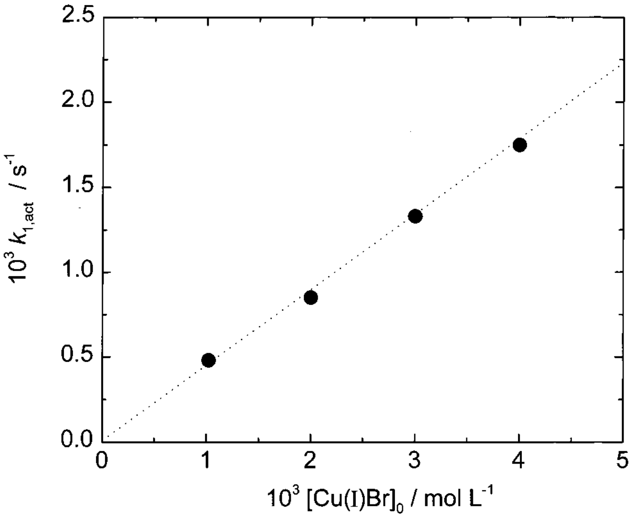

Figure 4. Plot of $k_{1,act}$ vs $[Cu^IBr/2L]_0$: data from Figure 4. The slope of the straight line gives $k_{2,act} = 0.45$ L mol^{-1} s^{-1}.

Figure 4 shows the plot of thus determined $k_{1,act}$ against $[Cu^IBr]_0$. The data points form a straight line passing through the origin, and $k_{2,act}$ can be estimated to be 0.45 L mol^{-1} s^{-1} according to eq 3. Here we have assumed that the equilibrium concentration $[Cu^IBr]$ is equal to the initial one $[Cu^IBr]_0$. This is justified as follows: the radical concentration is estimated to be $\simeq 2.0 \times 10^{-8}$ mol L^{-1} from the plot of $\ln([M]_0/[M])$ vs t (data not shown), where [M] is the monomer concentration. The equilibrium constant K $(=[P^*][Cu^{II}Br_2/2L]/[P-X][Cu^IBr/2L])$ of 3.9×10^{-8} estimated by Matyjaszewski et al.[9b] suggests that $[Cu^IBr]$ is smaller than the initial value only by approximately 5%, which is negligibly small compared with other experimental errors. Also importantly, the straight line passing through the origin, given in Figure 4, suggests that the degenerative transfer reaction[12] is negligible in this system. More direct evidence for this will be presented elsewhere.

The rate constant $k_{1,act}$ could also be estimated by analyzing the evolution of polydispersities, according to the following relation:[8]

$$[(M_w/M_n) - 1 - (1/x_n)]^{-1} = (k_{1,act}/2)t \qquad (5)$$

where x_n is the number-average degree of polymerization. This relation applies to the "grown" portion of the chain so that the contribution of "initiating" portion has to be subtracted by the method described previously.[8] The constancy of the radical and monomer concentrations and the absence of side reactions are requisites for this relation to be rigorously valid. Therefore, its applicability is limited to the initial stage of *stationary-state* polymerization where the effects of side reactions are minor. Unfortunately, the rate of polymerization (hence the radical concentration) of the present system was observed to vary seriously at an early stage of polymerization, and therefore it was not possible to determine $k_{1,act}$ rigorously by this method. However, it is possible to estimate the lower limit of $k_{1,act}$ on the basis of the polydispersities observed at relatively large conversions: for a batch system with a finite conversion C, eq 5 is modified to[8b,13]

$$[(M_w/M_n) - 1 - (1/x_n)]^{-1} = (k_{1,act}t)/[(1 - 2C^{-1})\ln(1 - C)] \qquad (6)$$

At relatively large conversions, the effect of the initial nonstationarity would be unimportant, and the contribution of the "initiating" P_0-X would be minor if P_0-X is a low-mass compound. For example, in the bulk polymerization of styrene at 110 °C with $[P_0-X]_0 = [Cu^IBr/2L]_0 = 0.087$ mol L^{-1}(P_0-X = 1-phenylethyl bromide), the polydispersity observed at 30% conversion ($t \simeq 2300$ s, and $x_n \simeq 30$) was $M_w/M_n = 1.05$.[9b] Application of these data to eq 6 gives $k_{1,act} = 0.05\ s^{-1}$ or $k_{2,act} = k_{1,act}/[Cu^IBr/2L] \simeq k_{1,act}/[Cu^IBr/2L]_0 = 0.6\ L\ mol^{-1}\ s^{-1}$, which is in remarkable agreement with the directly determined value. At higher conversions, the estimated value of $k_{2,act}$ rapidly decreases, indicating that side reactions have a more serious effect as conversion increases.

Also notably, the above cited value[9b] of the equilibrium constant $K = k_{2,act}/k_{2,deact}$ of 3.9×10^{-8} combined with the $k_{2,act}$ value of 0.45 L mol^{-1} s^{-1} gives $k_{2,deact} = 1.1 \times 10^{-7}$ L mol^{-1} s^{-1}.

In conclusion, the second-order activation rate constant $k_{2,act}$ in cuprous bromide-mediated ATRP at 110 °C was determined by the GPC peak-resolution method to be 0.45 L mol^{-1} s^{-1}. The $k_{2,act}$ value combined with a typical Cu^IBr concentration of 0.1 mol L^{-1} gives a $k_{1,act}$ value of 0.045 s^{-1}; i.e., a PS−Br adduct is activated once every 22 s. This figure is much smaller than, e.g., the $k_{1,act}{}^{-1}$ value of 45 min for a PS−TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) adduct at the same temperature[7b] and explains why the ATRP system provides low-polydispersity polymers *from an earlier stage of polymerization*.[9] The activation frequency in the TEMPO system is not so large that it takes a rather long time before the PS−TEMPO adduct experiences a sufficiently large number of activation−deactivation cycles to yield a low polydispersity.[8a] It should be remembered that for technical reasons, the experiments in this work were conducted at unusually low concentrations of $Cu^IBr/2L$. The value of $k_{2,act}$ of conventional (high-concentration) systems could be somewhat different, if the assumed kinetic linearity should break due to the potential effect of the concentration of $Cu^IBr/2L$ on its structure and reactivity. However, this difference should not be very large, since the value of $k_{2,act}$ estimated by the polydispersity analysis with a conventional system reasonably agreed with the one obtained at the low concentrations of $Cu^IBr/2L$.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan (Grant-in-Aid 09450351) and National Science Foundation.

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MA971610V