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Mechanism and Kinetics of Activation Processes in a Nitroxyl-Mediated Polymerization of Styrene[1]

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The recent development of the controlled or “living” radical polymerization has opened up a new and potentially wide route to well-defined, narrow-dispersity polymers.[2] Even though there are several technically or mechanistically different branches in this method, they all are based on a common mechanistic concept. Namely, a potentially reactive polymer species in such a system is supposed to go through an activated and a deactivated state alternatingly. In the activated state, it can be added by monomer, while in the deactivated state, the reactive chain end is blocked in some way or another, allowing no monomer addition. The blocking agent may be a sulfur compound,[3] a stable nitroxyl,[4,5] a halogen,[6−8] or a transition metal compound,[9,10] for example. The blocked chain remains dormant until it is reversibly deblocked by, e.g., a thermal,[4,5,9] photochemical,[3,10] or chemical[6−8] stimulus. A number of such activation−deactivation cycles and a low concentration of activated species would allow all the chains to grow slowly and simultaneously, suppressing biradical termination to a minor level. This seems to be the current, most common understanding of the basic mechanism by which well-defined polymers are produced in a radical system.[11,12]

In this regard, the knowledge about the mechanistic and kinetic details of the activation processes of individual systems is essential not only in predicting product characteristics and optimizing polymerization conditions but also in developing new and better systems. However, these details have never been disclosed on a quantitative basis in any branch of the controlled radical polymerization. This is due primarily to the lack of kinetic methods for directly studying activation processes.

We have devised a plausible method to determine the frequency or rate constant of activation reactions.[1] The purpose of this work is to apply this method to a nitroxyl-mediated polymerization of styrene and establish the activation mechanism(s) of this system. The statements given above may seem to imply that a nitroxyl-blocked polymer, for example, can be activated only by a thermal stimulus. This has been implicitly assumed in many previous studies, including those by ourselves.[12−15] Actually, it has never been proved or disproved by direct experiments. The experimental method used here will be applicable to many other systems with or without due modifications.

Definitions. For nitroxyl/styrene systems, two activation processes have been postulated:[2b,11a]

$$\mathrm{P{-}X} \underset{k_c}{\overset{k_d}{\rightleftarrows}} \mathrm{P^* + X^*} \qquad \text{(process I)} \tag{1}$$

$$\mathrm{P{-}X + P'^*} \overset{k_{ex}}{\rightleftarrows} \mathrm{P^* + P'{-}X} \qquad \text{(process II)} \tag{2}$$

In process I, the polymer−nitroxyl adduct P−X reversibly dissociates thermally into the polymer radical P* and the nitroxyl X* with rate constants of dissociation and combination k_d and k_c, respectively. Process II is the so-called “degenerative transfer”, which exchanges the active species with a second-order rate constant k_{ex} in either direction. Here all the rate constants are assumed to be independent of chain length. Since the frequency of cleavage of the P−X bond is proportional to [P−X] in process I and to [P*][P−X] in process II, the overall frequency, f_a, per unit time and unit volume, of the bond-cleaving or activation reactions, may be given by

$$f_a = k_a[\mathrm{P{-}X}] \tag{3}$$

with

$$k_a = k_d + k_{ex}\,[\mathrm{P^*}] \tag{4}$$

where k_a is the overall activation rate constant, viewed as a first-order reaction.

Method and Experiments. The experimental method used here to determine k_a is based on the observation of an early stage of the polymerization “initiated” with a polymer−nitroxyl adduct. We use a PS−TEMPO adduct, denoted P_0−X, as a “probe” polymer (PS = polystyrene; TEMPO = 2,2,6,6-tetramethylpiperidinyl-1-oxy). The compound P_0−X, prepared as described previously,[12] has a number-average molecular weight M_n of 1700 and a M_w/M_n ratio of 1.11. According to a chain-extension test, it is about 95% pure; i.e., about 5% of the chains are potentially inactive without a TEMPO moiety at the end (see Figure 1). Experimental data should be corrected for these impurities, but for the time being, we assume that P_0−X is 100% pure. We also use *tert*-butyl hydroperoxide (BHP), a radical initiator for high-temperature use. A mixture of styrene with a *fixed* amount of P_0−X and a *variable* amount of BHP, degassed and sealed in a tube under vacuum, is heated at a constant temperature for a prescribed time t to allow polymerization to proceed. The reactant mixture is directly analyzed by GPC (gel permeation chromatography) for the amount of the probe P_0−X remaining unreacted: namely, once P_0−X is activated to P_0*, it will be added by the monomer until it is blocked again by X* to form a new adduct P_1−X. Since P_0−X and P_1−X (or any other species possibly produced by, e.g., a further activation of P_1−X or the decomposition of BHP) should generally be different in chain length and its distribution, they will be resolved on the GPC elution curves by the use of the known P_0−X curve. If a fixed amount of the reactant solution is injected in the GPC column system, the area S of the thus resolved P_0−X peak will follow the first-order equation

$$\begin{aligned} \ln(S_0/S) &= \ln([\mathrm{P_0{-}X}]_0/[\mathrm{P_0{-}X}]) \\ &= k_a t \end{aligned} \tag{5}$$

from which k_a is determined. Hereafter, the subscript zero denotes the initial state ($t = 0$).

BHP plays the role of increasing [P*] and hence the polymerization rate R_p according to

$$R_p = k_p[\mathrm{P^*}][\mathrm{M}] \tag{6}$$

where k_p is the propagation rate constant and [M] is the monomer concentration. This role of BHP has been confirmed in a previous paper.[16] Incidentally, Hammouch and Catala,[17] who made a similar observation

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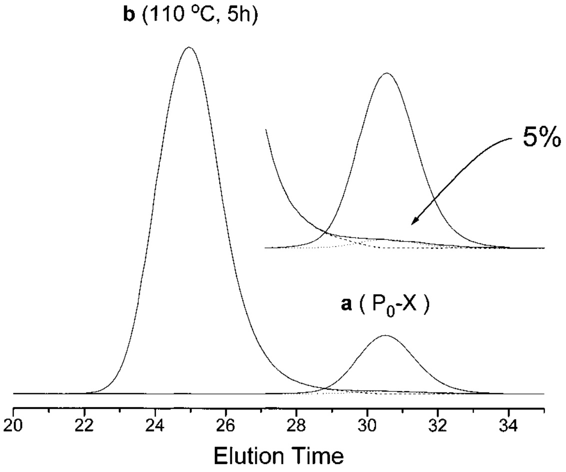

Figure 1. GPC elution curves for: (a) the PS−TEMPO adduct P_0−X and (b) the product obtained after a long enough (t = 5 h) polymerization of pure styrene "initiated" with P_0−X. The tail part of curve b contains about 5% of P_0−X remaining unreacted, which means that P_0−X originally contains this much potentially inactive species.

for a nitroxyl/styrene system with a radical initiator, have claimed the importance of process II in controlling the polymerization. On the other hand, our analysis of the M_w/M_n values of the TEMPO/styrene/BHP system (at noninitial stages of polymerization) has presented some indirect evidence against the importance of process II.[16] On the basis of the polydispersity analyses of styrene/TEMPO systems, Veregin et al.[18] have also made a similar suggestion, while Greszta and Matyjaszewski[19] have indicated a difficulty of discussing this matter because of possible side reactions. It should be stressed that the present method of k_a determination is independent of kinetic details or the behavior of all the components, other than P_0−X, possibly produced in the system, even though they may pose, in certain cases, a difficulty in the curve resolution work. Since this difficulty is a technical, not fundamental, one, it can be avoided by choosing appropriate conditions of experiment (see below). Therefore, this method is expected to provide a direct, unequivocal answer to the problem.

It may be more convenient to represent eq 4 in the form

$$k_a = k_d + (k_{ex}/k_p)(R_p/[M]) \tag{7}$$

Since the k_a in eq 5 is a time-averaged quantity, eq 7 is valid, strictly in this sense, when [P*] or R_p/[M] is independent of t. It can be shown that a general expression for the time-averaged k_a for a batch system is

$$k_a = k_d + (k_{ex}/k_p t)\ln([M]_0/[M]) \tag{8}$$

Results and Discussion. Figure 2 shows the GPC curves of the reaction mixtures with various amounts of BHP, heated at 110 °C for 10 min. Each mixture contains the same amount of P_0−X at t = 0 ($[P-X]_0$ = 23 mmol L^{-1}), as shown by the solid curve in the figure. After the heating, the curves show evident changes. When $[BHP]_0 = 0$, the curve becomes broader with the peak position shifted leftward or to the higher molecular weight side. This is commonly observed at an *early* stage of this type of controlled radical polymerization with a small R_p. When $[BHP]_0 \geq 5$ mmol L^{-1}, the curves become bimodal. The total area under each curve minus that of the t = 0 curve gives the amount of the monomer converted to polymer, i.e., the conversion. Figure 3 shows the plot of $\ln([M]_0/[M])$ vs t. In all examined cases, the plot is approximately linear, showing that R_p/[M] or [P*] is nearly stationary for each value of $[BHP]_0$ in this range of t (≤60 min).

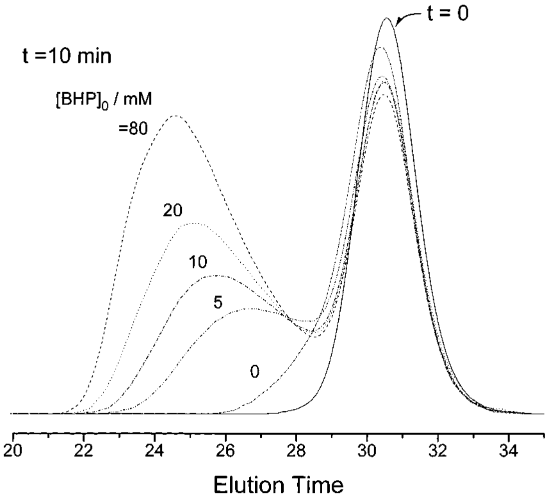

Figure 2. GPC elution curves of the styrene/PS−TEMPO (P_0−X)/BHP mixtures heated at 110 °C for 10 min. $[P_0-X]_0$ = 23 mmol L^{-1}. The number attached to each curve indicates $[BHP]_0$ in mmol L^{-1}. The solid curve is for the original (t = 0) solution, which contains only P_0−X as the polymer species. All the curves were reduced to the same original P_0−X concentration.

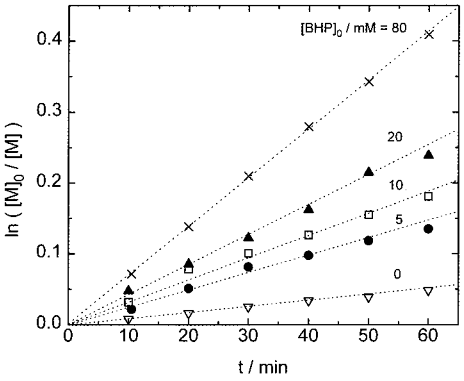

Figure 3. Plot of $\ln([M]_0/[M])$ vs t for the styrene polymerization at 110 °C with the PS−TEMPO adduct P_0−X and the radical initiator BHP: $[P_0-X]_0$ = 23 mmol L^{-1} and $[BHP]_0$ = 0 (▽), 5 (●), 10 (□), 20 (▲), and 80 (×) mmol L^{-1}.

Knowing the conversion and the overall M_n from the GPC curve, one can compute the concentration of polymer species, $[N_p]$, as a function of time, which is given in Figure 4. Within the experimental accuracy (about ±10%), $[N_p]$ is constant and equal to the initial value $[P_0-X]_0$.[20] This means that the observed changes in the GPC curves are due mainly to the dissociation (activation) of P_0−X and the subsequent polymerization starting from P_0*, rather than to the polymerization initiated by BHP. The role of BHP is to increase the stationary concentration of P* or, equivalently, to decrease the stationary concentration of X*.[16] The number of BHP-originated polymer radicals to be stationarily supplied for this purpose can be trivial, if the desired level of [P*] is not too high (note that typical values of [P*] are 10^{-8}−10^{-7} mol L^{-1}).[12,13,16] This is the main reason why the conversion and hence M_n increase with increasing $[BHP]_0$ without an appreciable increase in the number of polymers. We have made these interpretations just to avoid misunderstandings about the role of BHP and what happens at an early

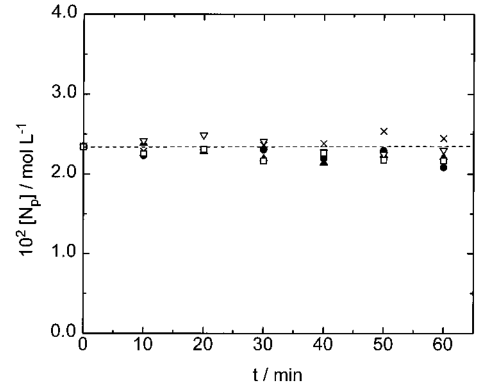

Figure 4. Total concentration [N_p] of polymer species as a function of reaction time: $[N_p]_0 = [P_0{-}X]_0 = 23$ mmol L^{-1}. For symbols and reaction conditions, see Figure 3.

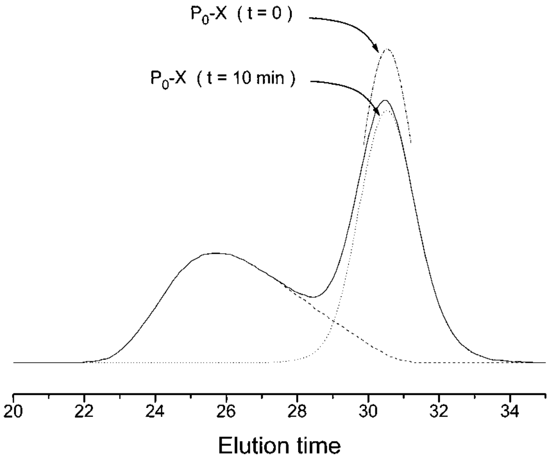

Figure 5. Resolution of the GPC elution curve (solid curve: $[BHP]_0 = 10$ mmol L^{-1}, $t = 10$ min) into the two components $P_0{-}X$ (dotted line) and the second one (broken line). The dot–dash curve indicates the $P_0{-}X$ at $t = 0$.

stage of this type of polymerization. Actually, those details are not required in the following analysis.

The bimodal GPC curves in Figure 2 clearly show that they are composed of two components, i.e., the unreacted $P_0{-}X$ and the second component to which all other species belong. As illustrated in Figure 5, these curves can be fairly accurately resolved into the two components. (The unimodal curve for $[BHP]_0 = 0$ is clearly difficult to resolve, if not impossible. The number of monomer units incorporated into the chain during one activation–deactivation cycle is too small, or [P*] is too small, in this system.)

The area (or the height) S of the resolved $P_0{-}X$ curve relative to that at $t = 0$ (S_0) is shown in Figure 6 in the first-order plot. Since the adduct $P_0{-}X$ originally contains 5% of potentially inactive species (Figure 1), this has been corrected by subtracting $0.05S_0$ from both S_0 and S in eq 5. Referring to eqs 4 and 5, one finds that

$$\ln(S_0/S) = k_d t + k_{ex}[P^*]t \qquad (9)$$

Figure 6 shows that all data points are approximately represented by a straight line, exhibiting no obvious trend with BHP concentration and hence [P*]. This suggests that k_a is independent of [P*], i.e., $k_{ex} \cong 0$. For a more quantitative discussion, one can use the data in Figure 6 to evaluate k_a as a function of [BHP] or R_p/[M]. This procedure is justified because R_p/[M] is independent of time for each value of [BHP] (Figure 3).

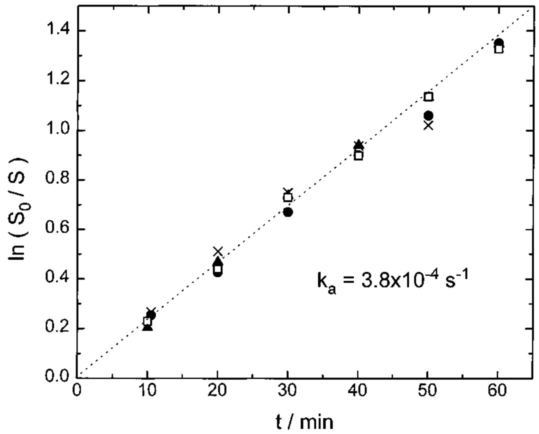

Figure 6. Plot of $\ln(S_0/S)$ vs t. The 5% correction for the inactive $P_0{-}X$ species has been made (see text). For symbols and experimental conditions, see Figure 3.

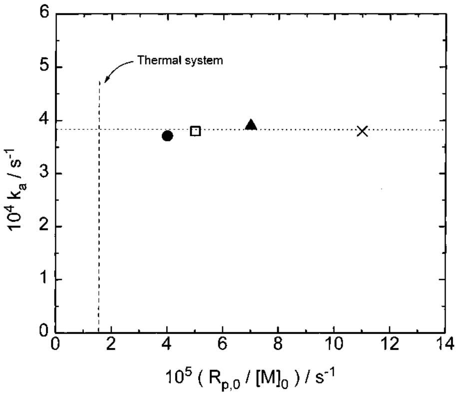

Figure 7. Plot of k_a vs t. For symbols and experimental conditions, see Figure 3. The vertical broken line indicates the value of $R_{p,0}/[M]_0$ for the thermal ($[BHP]_0 = 0$) system.

As Figure 7 shows, the plot of k_a vs $R_{p,0}/[M]_0$ (eq 7) can be represented by a horizontal straight line. The vertical dotted straight line in Figure 7 indicates the value of $R_{p,0}/[M]_0$ for the zero BHP system (thermal system), where the determination of k_a was found to be difficult (see above).

We conclude that within the present experimental conditions and the accuracy of k_a determination (about ±10%), process II, that is, the degenerative transfer, may be neglected, and k_a may be identified with k_d. This conclusion should be valid for the styrene/TEMPO polymerization at any other temperature unless R_p is increased too much by the addition of an initiator, since k_d, k_{ex}, and k_p will change with temperature more or less similarly. The method of k_a determination proposed here should be of potential use for mechanistic and kinetic studies on activation processes of “living” radical polymerizations in general. The temperature dependence of k_a ($=k_d$) in the styrene/TEMPO system studied by this and alternative methods will be reported elsewhere.[21,22]

References and Notes

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