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Mechanisms and Kinetics of Nitroxide-Controlled Free Radical Polymerization

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ABSTRACT: The bulk polymerization of styrene at 125 °C in the presence of a PS−TEMPO adduct was studied with respect to the polymerization rate and the concentration of free TEMPO as a function of time, where PS is polystyrene and TEMPO is 2,2,6,6-tetramethylpiperidinyl-1-oxy. The results were perfectly consistent with the proposed kinetic scheme which assumes the existence of a stationary state with respect to both polymeric and nitroxyl radical concentrations and predicts that the polymerization rate of the nitroxide-mediated system is independent of the adduct concentration, being equal to the polymerization rate of the adduct-free system, i.e., the rate of thermal polymerization in the case of the styrene system studied here. The equilibrium constant *K* for the PS−TEMPO reversible reaction was estimated to be 2.1×10^{-11} mol L^{-1} on the basis of the dilatometric and electron spin resonance data. This value of *K* was indicated to be large enough to set the system under control. This work thus shows that in order for the "living" radical polymerization mediated by a stable nitroxyl radical (SNR) to proceed successfully, a constant supply of initiating radicals (by, e.g., thermal initiation) to make up for the loss of polymer radicals due to irreversible termination is essential as well as the frequent reversible combination of polymeric and nitroxyl radicals. The total number of initiating radicals to be supplied in this way may be small compared with the number of polymer−SNR adducts so that they have no important influence on the molecular weight and its distribution of the product.

Introduction

Several forms of the free radical polymerization including a reversible deactivation process of growing radicals have been devised and attracted much interest as pseudoliving or "living" radical polymerizations.[1−7] Among them is the one mediated by stable nitroxyl radicals (SNRs),[2−5] which is proving to be a simple and robust method to synthesize homopolymers[5−12] and random (statistical)[5,8,13,16] and block[12,14−16] copolymers with narrow polydispersities and/or controlled chain architectures. Recent relevant topics include the synthesis of narrow-polydispersity poly(styrenesulfonate)[10] with a molecular weight as high as 9×10^5 and of well-defined block copolymers[16] comprising styrene−acrylonitrile statistical copolymer subchains with narrow polydispersities.

The key to the success of the SNR-mediated free radical polymerization is believed to be the reversible combination of a polymer radical, P*, with an SNR, N*, to form an adduct, P−N, a dormant species:

$$\mathrm{P}^* + \mathrm{N}^* \underset{k_\mathrm{d}}{\overset{k_\mathrm{c}}{\rightleftharpoons}} \mathrm{P{-}N} \tag{1}$$

$$K = k_\mathrm{d}/k_\mathrm{c} \tag{2}$$

where k_c and k_d are the rate constants of combination and dissociation, respectively. While N* is active only to P*, P* is active not only to N* and the monomer (propagation) but also to P* (irreversible bimolecular termination) and neutral molecules (chain transfer). When the last two reactions are unimportant compared with the first two, the system may be viewed as "living". The kinetic studies[17,18] conducted so far by use of electron spin resonance (ESR) were not in conflict with the mentioned mechanism.

However, the equilibrium constant *K* in eq 2 has never been successfully determined for any SNR-mediated system at any temperature. In other words, the "reversible combination" is still not based on a firm experimental basis. Another fundamental question still to be answered is as to what determines the rate of polymerization, R_p, of an SNR-mediated system. It seems to be generally believed that R_p, with other conditions fixed, increases as the adduct concentration [P−N] increases, and as the dissociation rate constant k_d increases.[4,17b] A recent report by Catala et al.[11] showed, however, that the R_p of the SNR-mediated system studied by them is independent of the adduct concentration. It must be emphasized that very little is known as yet about the true mechanisms and kinetics of SNR-mediated "living" radical polymerization.

We have examined the bulk polymerization of styrene at 125 °C mediated by 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) by means of ESR and dilatometry. As a result, we have succeeded in obtaining a plausible value of *K* of the system and, at the same time, making clear fundamental factors that control the R_p and polydispersity of the "living" radical polymerization, as will be described below. A brief account of part of this work has been presented in a short communication.[19]

Experimental Section

Materials. Commercially obtained styrene, benzoyl peroxide (BPO; Nacalai Tesque, Japan), and TEMPO (Aldrich) were purified by the standard methods described elsewhere.[20,21]

Preparation of Polystyrene (PS)−TEMPO Adduct. Freshly distilled styrene, BPO (6.1×10^{-2} mol L^{-1}), and

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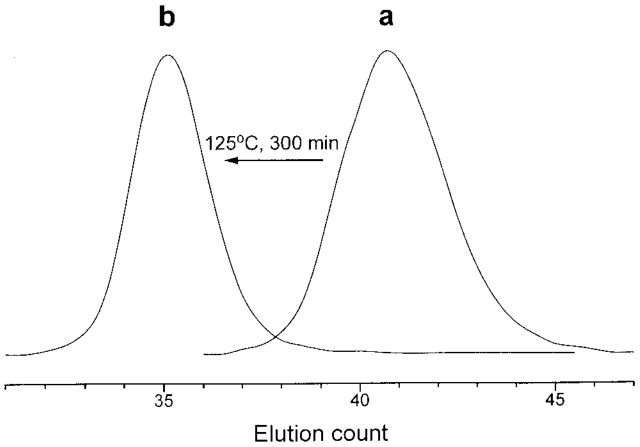

Figure 1. GPC curves for the polymerization of styrene at 125 °C in the presence of 10 wt % of a PS−TEMPO adduct (M_n = 2500, M_w/M_n = 1.13): (a) the precursor adduct; (b) the product at t = 5 h (M_n = 15 000, M_w/M_n = 1.10).

TEMPO (7.3 × 10^{-2} mol L^{-1}) were charged in a glass tube, degassed with several freeze−thaw cycles, and sealed off under vacuum. To ensure complete decomposition of BPO, the mixture was preheated for 3.5 h at 95 °C, where no appreciable polymerization proceeded.[8] Then the system was heated at 125 °C for 4 h, and the polymer was recovered as a precipitate from a large excess of methanol, purified by reprecipitation with a chloroform (solvent)/methanol (nonsolvent) system, and thoroughly dried (conversion: 14.5%). By gel permeation chromatography (see below), this polymer was found to have a M_n of 2300 and a M_w/M_n ratio of 1.14, where M_n and M_w are the number- and weight-average molecular weights, respectively. As will be shown later, this PS has a TEMPO molecule capping the active chain end and will be termed a PS−TEMPO adduct.

Polymerization Rates. The PS−TEMPO adduct (10 parts (by weight)) was dissolved in 90 parts of styrene, and the solution was charged in a dilatometer, which was degassed and sealed off as described above. The solution was heated at 125 °C, and the polymerization course was traced by observing the decrease of the system volume. The conversion factor γ was approximated by $\gamma = (v_S - v_{PS})/v_S$, where v_S and v_{PS} are the specific volumes of styrene and PS,[22] respectively. This gave γ = 0.193 at 125 °C, independently of PS molecular weight. A gravimetrically determined value of γ (for a model run) agreed to this value within a few percent.

Electron Spin Resonance (ESR). ESR measurements were made on a Bruker ESP 300.[23] The styrene/adduct mixture with the same composition as the one used for the rate study was degassed in an ESR cell, sealed off, and measured at 125 °C. The system was calibrated with a degassed styrene solution of TEMPO at room temperature. Calibration at the high temperature is not recommendable due to thermal polymerization of styrene (see below).

Gel Permeation Chromatography (GPC). GPC measurements were made on a Tosoh HLC-802 UR high-speed liquid chromatograph equipped with Tosoh gel columns G2500H, G3000H, and G4000H. Tetrahydrofuran was used as the eluent, and the temperature was maintained at 40 °C.

Results and Discussion

Before discussing the main topics of this work, some words may be due regarding the chain extension test made with a PS−TEMPO adduct (M_n = 2500 and M_w/M_n = 1.13) which has nearly the same molecular characteristics as the one used in other measurements. Figure 1 shows the GPC profiles of the adduct (precursor) and the product obtained after heating a mixture of the adduct and styrene (10/90 by weight) at 125 °C for 5 h. Clearly, the chain has grown with no appreciable amount of polymer, if any, remaining at the elution position of the precursor. In Figure 2, the M_n and M_w/M_n ratios of the polymers recovered at various polymerization times are plotted, showing that M_n increases linearly with conversion and that the M_w/M_n ratio stays close to 1.1. Moreover, the absolute values of M_n agree with the theoretical predictions (the broken line in the figure) within an experimental error. These results indicate that essentially all precursor molecules are active with a TEMPO molecule at the chain end, and the number of polymer molecules remains essentially unchanged throughout the course of polymerization.

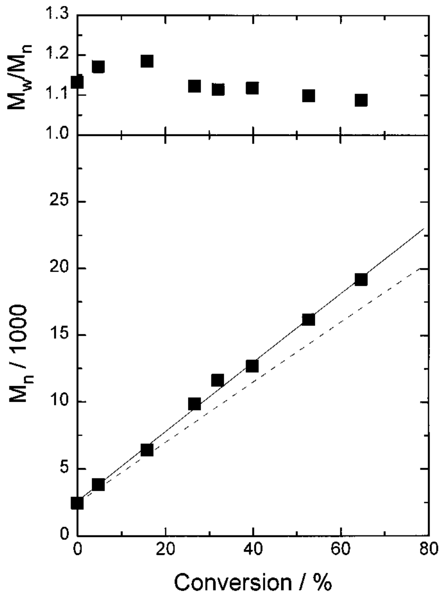

Figure 2. Values of M_n and M_w/M_n vs conversion (see the caption for Figure 1).

This remarkable feature of the styrene polymerization in the presence of such an SNR adduct[11,12] would be ascribed to (1) the essentially simultaneous initiation, (2) the reversible reaction of SNR given in eq 1, and (3) no important degree of irreversible termination, if any occurs. In this regard, one would view the system as an ideal living one, at least under limited conditions, and expect it to be described by the simple kinetic scheme valid for ideal systems. Actually, it is not the case, as already mentioned. Moreover, styrene is known to undergo a spontaneous (thermal) polymerization at high temperatures.[24,25] which seemingly complicates the situation. In what follows, we wish to show that the system in fact follows a simple kinetic scheme, *simple* in a different sense that has never been noted previously.

The free radical polymerization that includes the reversible reaction in eq 1 may generally be described by the following differential equations:

$$d[P^*]/dt = R_i - k_t[P^*]^2 + k_d[P-N] - k_c[P^*][N^*] \quad (3)$$

$$d[N^*]/dt = k_d[P-N] - k_c[P^*][N^*] \quad (4)$$

where R_i is the rate of initiation due to an initiator and/or thermal initiation and k_t is the termination rate constant between polymer radicals. Now let us consider a system composed of the adduct P−N and the monomer M *with no extra N* added*. Once the system is brought to a sufficiently high temperature where the adduct dissociation takes place, the concentrations of P* and N* will start to increase from zero up to the values determined by the equilibrium constant K. In the presence of no initiation, however, a stationary state will never be reached, since the P*−P* biradical termination will continually reduce [P*] relative to [N*] (only at the onset of polymerization; it should hold that [P*] = [N*]), and the polymerization will eventually come to an end because of the numerous N* radicals *accumulated* in the system. However, if there is an initiation reaction, the newly produced radicals will capture N*, preventing its accumulation, and a stationary state with respect to both [P*] and [N*] will be achieved. This state should be reached at a relatively early stage of polymerization, since the radical−radical reactions (P*−P* and P*−N*) are fast processes: setting $d[P^*]/dt = d[N^*]/dt = 0$ in eqs 3 and 4, we have

$$[P^*] = (R_i/k_t)^{1/2} \tag{5}$$

$$[N^*] = K[P{-}N]/[P^*] \tag{6}$$

The (stationary) rate of polymerization, $R_p = -d[M]/dt$ is given by

$$R_p = k_p[P^*][M] \tag{7}$$

$$= (k_p{}^2 R_i/k_t)^{1/2}[M] \tag{8}$$

where [M] is the monomer concentration and k_p is the propagation rate constant.

Equation 8 is just the same as the familiar equation for the conventional system (without SNR). This means that the polymerization rate is independent of the SNR concentration and equal to that of the SNR-free system.[26]

This prediction is directly evidenced by the present results given in Figure 3, which compares the $\ln([M]_0/[M])$ vs time curves in the presence and absence of the PS−TEMPO adduct, where $[M]_0$ is the concentration of the pure monomer. Since the former system originally contains 10 wt % of PS as the adduct, the origin of its curve has been shifted by that amount. The dotted curve in the figure was calculated with the relation

$$\ln([M]_0/[M]) = (2/3)\ln[1 + (3/2)A_0 t] \tag{9}$$

where A_0, the initial slope of the first-order plot or the value of $A = R_p/[M]$ at time $t = 0$, was set equal to 5.3 × 10^{-5} s^{-1} to fit the experiments. Equation 9 is based on the $[M]^3$-dependent thermal initiation[24] and the assumption of constant k_t (and k_p). The value of A_0 given above is close to the one calculated with eq 51b in ref 24 (see below).[28] As Figure 3 shows, the three curves closely coincide with one another up to $t \sim 3$ h or about 30% conversion, beyond which deviations become apparent. Thus, at low conversions, the polymerization rate of the adduct-containing system is exactly equal to that of the thermal system. The reason for the deviations at higher conversions is clear. They come from changes in k_t: as the polymer concentration increases, the polymer radicals become more difficult to diffuse to undergo bimolecular termination, hence a smaller k_t or a larger R_p (cf. eq 8). Since the average chain length in the thermal system is much larger than that in the TEMPO-mediated system, the former system should have a smaller k_t and hence a larger R_p than the latter system, which in fact was observed. The increase in R_p for this cause is still clearly observed between the TEMPO-mediated system and the hypothetical thermal system with constant k_t (the dotted curve). Incidentally, the theoretical curve (with constant k_t) based on the second-order initiation was inconsistent with our experiments, in agreement with Hui and Hamielec.[24]

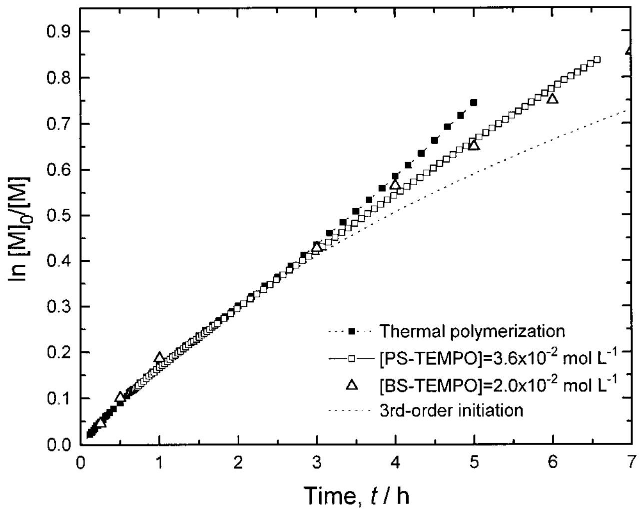

Figure 3. First-order plot for the polymerization of styrene at 125 °C in the presence of (□) and absence (■) of 10 wt % of the PS−TEMPO adduct (M_n = 2300, M_w/M_n = 1.14). The dotted curve shows eq 9. The triangles (△) show the data obtained for the batch polymerization of styrene at 125 °C with the unimer adduct BS−TEMPO (2.0 × 10^{-2} mol L^{-1}).

We have carried out further supplementary work using the low-mass model adduct [2-(benzoyloxy)-1-phenylethyl]−TEMPO (BS−TEMPO), i.e., a styrene unimer having a BPO fragment and a TEMPO molecule at the two ends. This compound was prepared according to Hawker[12] and confirmed to be of high purity.[29] Some results of the batch polymerization of styrene at 125 °C in the presence of 2.0 × 10^{-2} mol L^{-1} of BS−TEMPO are presented in Figure 3 (again, no extra TEMPO was added), which confirms that the polymerization proceeds at the same rate as in the PS−TEMPO system. Also notably, Catala et al.[11] observed that the R_p of the styrene polymerization in the presence of the model adduct S−DBN (S = 1-phenylethyl, and DBN = di-*tert*-butyl nitroxide) was independent of the adduct concentration (see Figure 4 in ref 11). Even though these authors explained their results differently,[11] they may be more simply interpreted by the present theory. In Figure 4, the initial rates of styrene polymerization $R_{p,0}$ observed by Catala et al.[11] with the S−DBN adduct and by us with the PS−TEMPO and BS−TEMPO adducts are plotted against temperature. In all cases, the value of $R_{p,0}/[M]_0$ agrees within ±10% with that of the thermal, adduct-free system.[24]

Next, we have attempted to determine the equilibrium constant K in eq 6. We made ESR measurements for the same system as was studied dilatometrically. Namely, the styrene solution of the PS−TEMPO adduct (10 wt %) was heated in an ESR cell at 125 °C and the spectrum was recorded at that temperature as a function of time. Figure 5a shows the spectrum at $t = 5$ h, which should be compared with the one for the styrene solution of TEMPO recorded at room temperature for the purpose of calibration (Figure 5b). The spectrum for the polymerization system appears to comprise two components, i.e., TEMPO and an impurity spin compound, that cannot be defined at this time. Since the concentration of the polystyryl radical is smaller by more than 2 orders of magnitude than that of TEMPO, it cannot be detected in this scale of measurements. The

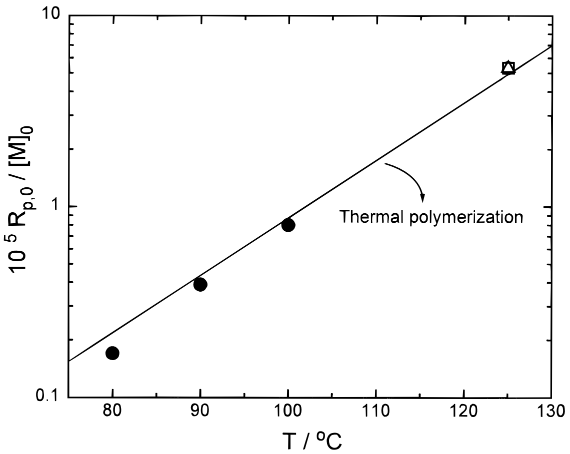

Figure 4. Plot of $R_{p,0}/[M]_0$ vs temperature for the styrene polymerization in the presence of nitroxyl adducts compared with that of the adduct-free system[24] (—): (●) [S−DBN] = 3.7 × 10^{-3} mol L^{-1} (80 and 100 °C) and 3.7 × 10^{-3}−4.4 × 10^{-2} mol L^{-1} (90 °C); (□) [PS−TEMPO] = 3.6 × 10^{-2} mol L^{-1}; (△) [BS−TEMPO] = 2.0 × 10^{-2} mol L^{-1}. The S−DBN data were taken from Figures 2 and 4 in ref 11.

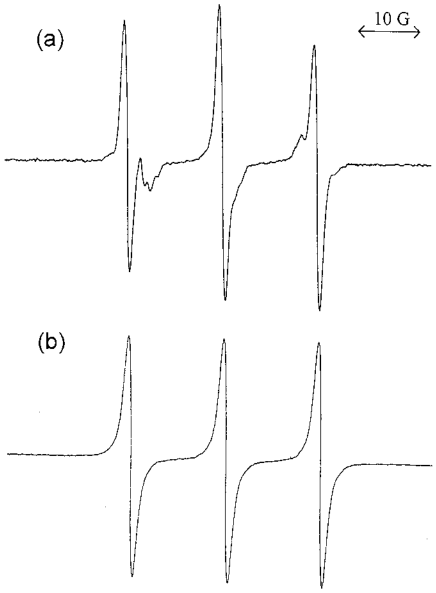

Figure 5. ESR spectra for (a) the adduct-containing polymerization system at 125 °C (t = 5 h; see the caption for Figure 3) and (b) the styrene solution of TEMPO at room temperature.

integral curve of a part of the spectrum is given in Figure 6a, which can be divided into two Lorenzian curves, as indicated in the figure. We thus estimated the concentrations of TEMPO and the impurity, which are shown in Figure 7. The TEMPO concentration increases with time, while the other component decreases, the total spin concentration staying nearly constant with time.

Using the time−conversion data for the adduct-containing system (Figure 3 or Figure 8a), we estimated the concentration of PS radicals, [P*], according to eq 7. The result is given in Figure 8b, where the value of k_p was calculated with the recently established relation[30] to be 2300 L mol^{-1} s^{-1}. A decreasing trend of [P*] with time is evident. This is essentially due to the third-order dependence of the thermal initiation rate on [M], as already discussed. With the values of [N*] and [P*] in Figures 7 and 8b, respectively, and the adduct concentration [P−N] of 3.6 × 10^{-2} mol L^{-1}, the equilibrium constant K was calculated. Since $[P^*] \ll [N^*] \ll [P-N]$, [P−N] could be regarded as constant. The results are given in Figure 9. The values of K based on the total spin concentration, [TEMPO] + [impurity], vary with time (open circles in Figure 9), whereas those based on [TEMPO] alone are independent of time (filled circles), as they should be. This would confirm the existence of an equilibrium among the PS and TEMPO radicals and their adducts and indicate that the impurity component has no important effect on their equilibration. Thus the mean value of $K = 2.1 \times 10^{-11}$ mol L^{-1} indicated by the horizontal straight line in Figure 9 may be acceptable as the equilibrium constant for the PS/TEMPO system at 125 °C,[31] with some reserve until the impurity component is better characterized.

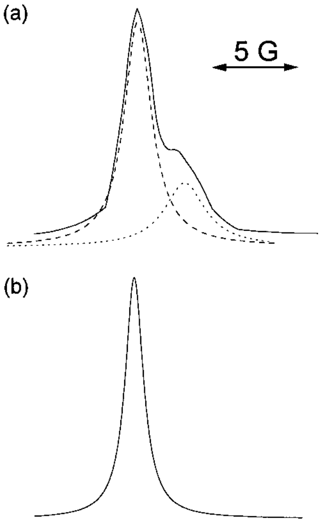

Figure 6. Integrated ESR spectra (see the caption for Figure 5).

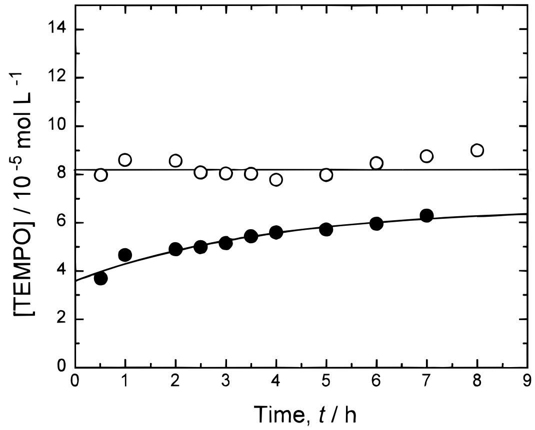

Figure 7. Plot of the TEMPO concentration vs time (filled circles). The open circles represent the total (TEMPO + impurity) concentration. The error range is estimated to be smaller than ±10% in all cases.

Concluding Remarks and Further Comments

The bulk polymerization of styrene at 125 °C in the presence of the PS−TEMPO adduct was studied with respect to the rate of polymerization and the concentration of free TEMPO, as a function time. The results were perfectly consistent with the proposed kinetic scheme, which assumes the existence of a stationary state with respect to both [P*] and [N*]: since the stationary concentration of P* is determined by the equality of the rate of thermal initiation and that of P*−P* biradical termination, the polymerization rate is always equal to that of the adduct−free system with

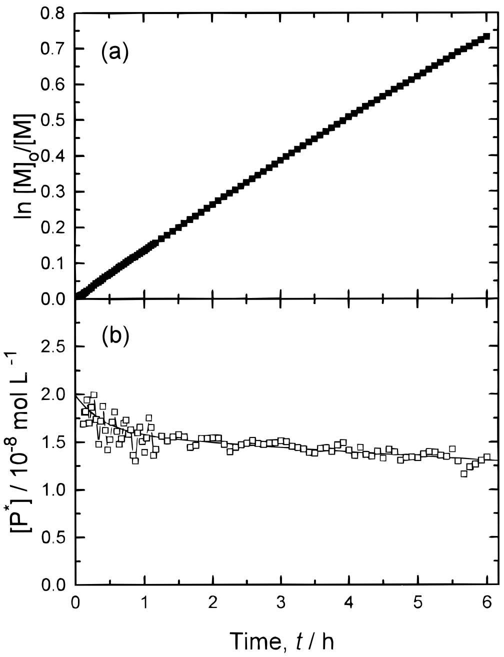

Figure 8. Plot of the polystyryl radical concentration [P*] vs time (b), estimated from the slope of the first-order plot in (a) by assuming $k_p = 2300$ L mol^{-1} s^{-1}.

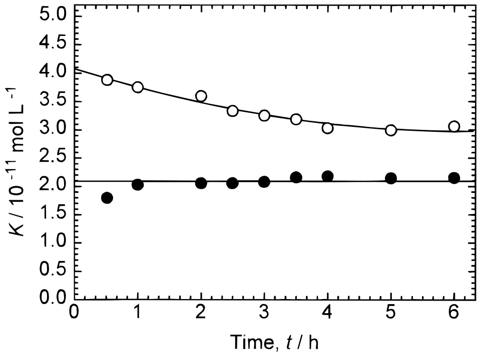

Figure 9. Plot of the equilibrium constant K vs time (filled circles). The open circles are based on the total (TEMPO + impurity) radical concentration.

the same monomer concentration (and the same k_t). This was in fact observed here and elsewhere.[11] On the basis of the free TEMPO concentration determined by ESR, the relevant equilibrium constant K was determined to be 2.1×10^{-11} mol L^{-1}. This is the first plausible value of K so far reported for this type of system.

If we assume the k_c in eq 2 to range from 10^8 to 10^9 L mol^{-1} s^{-1} in order of magnitude,[32,33] the above-noted value of K suggests that $k_d = 2 \times 10^{-2}$ to 2×10^{-3} s^{-1}. It follows that in the studied system, each adduct dissociates once every 50−500 s, and at an early stage of polymerization, about 0.6−6 styrene units are added to the PS radical before it recombines with TEMPO about 30−300 μs after the dissociation. Very recently, we devised a method to directly determine k_d, with which we hope to report relevant figures with a smaller range of uncertainty.[34] In any case, these arguments indicate that this value of K is large enough to structurally control the polymerization which takes hours. The excellent control achieved by this system has been demonstrated in Figures 1 and 2 and elsewhere.[5−12]

One might then wonder why such a high degree of control is achievable in the presence of the thermal initiation and irreversible termination. Figure 10 may answer the question schematically: the thermal and adduct systems follow the same stationary-state kinetics, which means that during a given time interval, the two systems have the same number of radicals thermally produced, the same number of radicals thermally produced, the same number of radicals deactivated to dead polymers, and the same number of monomers incorporated into the polymers. A difference is in the number of polymers among which the monomers are to be shared. In the thermal system, this number is obviously equal to the number of thermally produced polymer radicals, while in the adduct system, it is equal to the number of adduct polymers plus the thermal ones. The number of adduct polymers remains constant, since thermally produced radicals will, shortly after their birth, combine with N* to give new adducts, while as many P*s are deactivated to give dead polymers (in the stationary state). Thus, if the number of the thermal species is small enough compared with that of the adducts, and if the adduct dissociation occurs frequently enough, the system should closely follow Poisson's statistics. Under the assumptions on which eq 9 is based, it can be shown that the cumulative number $[\mathrm{P_{therm}}]$ of the polymer radicals thermally produced per unit volume is given by

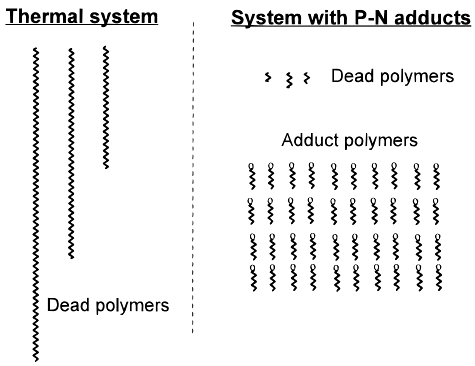

Figure 10. Illustration schematically showing the difference in chain length and its distribution between the polymers produced in the thermal and the adduct-containing systems.

$$[\mathrm{P_{therm}}] = \frac{2R_i^\circ}{3A_0}\left[1 - \frac{1}{1+(3/2)A_0 t}\right] \qquad (10)$$

or by using eq 9

$$[\mathrm{P_{therm}}] = (2R_i^\circ/3A_0)[1-([\mathrm{M}]/[\mathrm{M}]_0)^{3/2}] \qquad (11)$$

Here R_i° is the initiation rate at $t = 0$, and $A_0 = (R_i^\circ k_p^2/k_t)^{1/2}$, as before. For styrene at 125 °C,[24,28] $R_i^\circ = 1.8 \times 10^{-7}$ mol L^{-1} s^{-1} and $A_0 = 4.8 \times 10^{-5}$ s^{-1}, which means that $[\mathrm{P_{therm}}]$ exceeds in no case 2.5×10^{-3} mol L^{-1} or 7% of the PS−TEMPO concentration in the system studied here. A simple calculation suggests that with other conditions assumed to be ideal, an M_w/M_n ratio smaller than 1.1 could be achieved, if $[\mathrm{P_{therm}}]$ is smaller than about 15% of [P−N].

As shown above, the occurrence of sufficiently frequent dissociation of the P−N adduct *and* thermal initiation are essential for the "living" radical polymerization to proceed. Styrene at high temperatures meets both of these requirements. There possibly could be unknown systems in which adduct dissociation does occur but thermal polymerization does not. Such a system has been simulated by Johnson et al.[4] As shown by them, there is no stationary state in there: a rapid increase of N* brings about a rapid decrease of P* and hence R_p. Thus, it is difficult to obtain a high conversion or a high M_n, unless k_p is very large. However, a large k_p with an insufficient frequency of adduct dissociation would not guarantee a narrow polydispersity. In fact, the simulation of Johnson et al.[4] did not produce polymers with a very narrow polydispersity within the simulated "time". Our work thus gives the important suggestion that those systems can be set under control, like the styrene system, by supplying an appropriate number of radicals by use of an initiator. Moreover, the polymerization rate of a styrene-type system could itself be controlled by the same principle. Such a study is in progress in our laboratory.

In this work, the discussion has been confined to systems containing a purified P−N adduct and styrene with no excess SNR added. Kinetic descriptions of styrene systems containing excess SNR or those started with an initiator and SNR are complicated by the acceleration of thermal initiation[27] and possible effects of the byproducts from the reaction of SNR with the initiator[17] or thermally produced species.[27] This matter will be discussed elsewhere.

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