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Free Radical Polymerizations for Narrow Polydispersity Resins: Electron Spin Resonance Studies of the Kinetics and Mechanism

Richard P. N. Veregin,* Michael K. Georges, Peter M. Kazmaier, and Gordon K. Hamer

Xerox Research Centre of Canada, 2660 Speakman Drive,
Mississauga, Ontario, Canada L5K 2L1

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ABSTRACT: Electron spin resonance (ESR) was used to follow the time-dependent concentration of stable TEMPO nitroxide radical *in situ* to understand the formation of narrow polydispersity, high molecular weight resins by a modified free radical polymerization process. This process involves the reversible termination of growing free radical chains by the TEMPO radicals. The first step is shown to involve a bimolecular reaction of nitroxide radical and benzoyl peroxide (BPO) initiator. This bimolecular reaction, which leads to peroxide radicals, is a rate-promoted decomposition having an activation energy of 40 ± 5 kJ/mol in toluene, compared to 125 kJ/mol for the thermal decomposition of BPO to its radicals. Computer simulations were used to numerically solve the reaction kinetics. ESR has shown that the rate of nitroxide radical disappearance in styrene polymerization is consistent with reversible termination of growing chains by the nitroxide radical, affording a *pseudoliving* polymer system.

Introduction

Recently, a number of workers[1,2] have postulated the idea of using reversible termination of growing polymer chain in a free radical polymerization to give a *pseudoliving* polymer that is capable of stepwise chain growth. Figure 1 shows how this might occur for the stable free radical TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy). Such nitroxides are known to react with growing free radical polymer chains, acting as strong polymerization inhibitors.[3] This is not unexpected, as nitroxides react at nearly diffusion controlled rates with carbon-centered radicals, although not with oxygen-centered radicals.[4] Further, Otsu et al. have shown that certain radicals, which they refer to as *iniferters*, can both initiate polymerization and react reversibly with a growing polymer chain. With this method polymers can be produced, but without narrow polydispersity.[1] Other workers have studied in detail the reaction of nitroxide radicals with growing polymer chains.[5] On the basis of this work, Solomon et al. have shown that a nitroxide radical adduct can be used to initiate polymerization, while the nitroxide moiety can reversibly terminate the growing polymer chain, producing low molecular weight oligomers.[2]

Independently, we have also been working with stable free radicals to control growing free radical chains, applying the concept of reversible termination. In companion papers we have demonstrated that high molecular weight polymers can be produced with controlled increases in molecular weight to produce either high or low molecular weight polymers having narrow polydispersities of ca. 1.3 or less.[6] In other work, we have shown that electron spin resonance (ESR) can monitor the various steps in the reaction *in situ*.[7] The purpose of this paper is to present further findings related to the reaction kinetics and mechanism, especially in the initial stages of reaction. ESR is used to study reaction kinetics *in situ* by following stable free radical concentrations in either toluene or styrene.

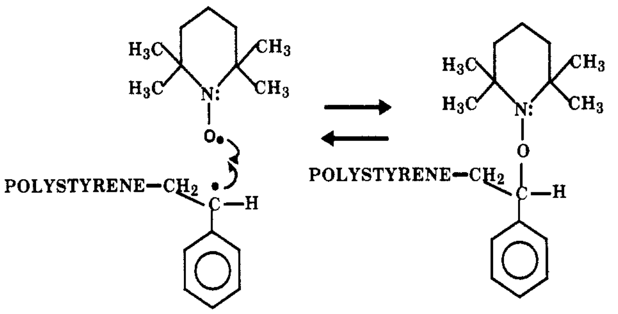

Figure 1. Reversible termination of polymer chain by TEMPO radical.

Experimental Section

As a model system, initiation reactions were performed using benzoyl peroxide (BPO) initiator and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) stable free radical in toluene without monomer. Polymerizations were done in the same manner in styrene, without toluene. All reagents were used without purification. Solutions were Ar or N_2 purged, placed in an ESR sample tube, and inserted into the variable-temperature Dewar of the ESR spectrometer at 95 °C. Spectra were collected over time using a Bruker ESP300 spectrometer and ER4111 variable-temperature accessory. The first two spectra were usually obtained at ca. 30 and 60 s. Using these two points, the natural logarithm of the TEMPO concentration was extrapolated to zero time to obtain the initial TEMPO concentration ($[\mathrm{TEMPO}]_0$, or T_0). Since the extrapolation was always within the range of concentration where the resultant $\ln([\mathrm{TEMPO}]_t/[\mathrm{TEMPO}]_0)$ was linear with time, this procedure was assumed not to add any significant systematic error in the determination of initial rate constants. Numerical computer simulations of kinetics were done using HAVCHM (similar to the QCPE GEAR iterator) on a SUN SPARC station.

Results and Discussion

In our previous work,[6] we have shown that narrow polydispersity, high molecular weight polymers can be obtained by a modified free radical polymerization in which TEMPO stable free radical has been added. In a typical polymerization, TEMPO and BPO, in a 1.2:1 molar ratio, are heated together in styrene at 95 °C for 3.5 h. At this point, there is no formation of polymer as shown by GPC. Subsequent heating at 123 °C for 69 h yields a polymer with a polydispersity of 1.27 and M_w of 10 000.[6] In this paper we will focus on the first step of the reaction, which occurs at 95 °C.

(a) Reaction of Nitroxide Radical with BPO Initiator in Toluene. While TEMPO radicals are stable in

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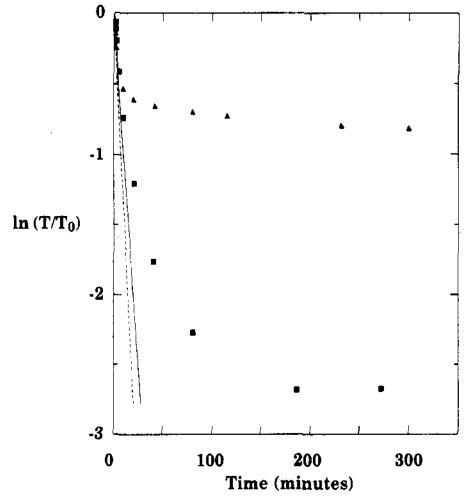


Figure 2. TEMPO radical disappearance in toluene with BPO: (▲) $[\mathrm{TEMPO}]_0 = 0.023$ M, $[\mathrm{BPO}]_0 = 0.0177$ M, $[\mathrm{TEMPO}]_0/[\mathrm{BPO}]_0 = 1.3$; (■) $[\mathrm{TEMPO}]_0 = 0.0089$ M, $[\mathrm{BPO}]_0 = 0.0177$ M, $[\mathrm{TEMPO}]_0/[\mathrm{BPO}]_0 = 0.5$. Initial rates of reaction for reaction of TEMPO and BPO are shown. For $[\mathrm{TEMPO}]_0/[\mathrm{BPO}]_0 = 1.3$, the dashed line gives $k_{\mathrm{PR}} = 0.13$ M^{-1} s^{-1}. For $[\mathrm{TEMPO}]_0/[\mathrm{BPO}]_0 = 0.5$, the solid line gives $k_{\mathrm{PR}} = 0.094$ M^{-1} s^{-1}.

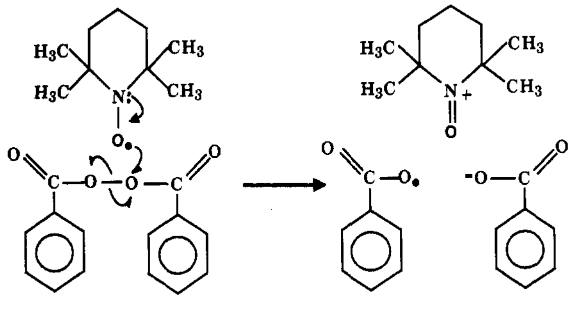


Figure 3. Mechanism proposed for reaction of BPO and TEMPO from ref 9 forming the benzoate anion and TEMPO non-radical cation intermediates.

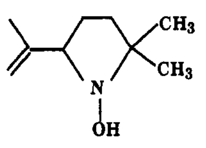
toluene at 95 °C, Figure 2 shows the drop in TEMPO radical concentration as a function of reaction time for two TEMPO/BPO ratios, 1.3:1 and 0.5:1, when BPO is added to toluene under N_2. The reaction profile is identical in air and under N_2. The reaction of TEMPO with BPO is rapid compared to BPO thermal decomposition, as BPO is completely consumed in 1 h (as shown by the constant [TEMPO]), while the thermal half-life of BPO at 95 °C is 1 h.[8] To model the kinetics of this accelerated decomposition, the following model was assumed. The thermal decomposition of BPO is

$$\mathrm{I} \xrightarrow{k_{\mathrm{D}}} 2\mathrm{R} \tag{1}$$

and the rate-promoted decomposition of BPO by TEMPO is

$$\mathrm{T} + \mathrm{I} \xrightarrow{k_{\mathrm{PR}}} \mathrm{X} + \mathrm{R} \tag{2}$$

where T = TEMPO radical, I = BPO, X = products, and R = benzoyloxy radical. The form of eq 2 is based on previous work on promotion of BPO decomposition using TEMPO in styrene at a lower temperature of 60 °C.[9] The identity of X has been suggested to be a benzoate anion and a TEMPO non-radical cation, as shown in Figure 3.[9] It was proposed that these two products are produced as a result of an oxidation–reduction reaction between TEMPO and BPO. It was further proposed that these products are intermediates, which react further to give benzoic acid and a nitrone (1). The latter was identified by NMR. Under the conditions of the current work, at 95 °C, benzoic acid and the nitrone were isolated by thin-layer chromatography. The nitrone was identified by comparison of the NMR parameters with those from ref 9.



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Although the details of this reaction are not fully understood, the kinetics are expected to be consistent with reactions 1 and 2, giving

$$\mathrm{d}I/\mathrm{d}t = -k_{\mathrm{PR}}TI - k_{\mathrm{D}}I \tag{3}$$

$$\mathrm{d}T/\mathrm{d}t = -k_{\mathrm{PR}}TI \tag{4}$$

These coupled differential equations yield a rate equation for TEMPO which may not be solvable analytically:

$$\mathrm{d}T/\mathrm{d}t = k_{\mathrm{PR}}(I_0 - T_0)T + k_{\mathrm{PR}}T^2 + k_{\mathrm{D}}T\ln(T/T_0) \tag{5}$$

However, the initial rate of disappearance of TEMPO is

$$(\mathrm{d}T/\mathrm{d}t)_{\mathrm{initial}} \simeq -k_{\mathrm{PR}}I_0T \tag{6}$$

Integration gives

$$\ln(T/T_0) = -k_{\mathrm{PR}}I_0t \tag{7}$$

Thus a plot of $\ln(T/T_0)$ vs t will have slope of $-k_{\mathrm{PR}}I_0$, showing an initial linear response close to $t = 0$ (typically, $t \leq 120$ s).

The initial linear response is shown in Figure 2. The slowing of the rate from linearity is due to the consumption of BPO (thus, $I_t < I_0$), both from the promoted decomposition by TEMPO (k_{PR}) and from BPO thermal decomposition (since k_{D} is significant). To confirm the kinetic model, $[\mathrm{BPO}]_0$ was varied from 0.005 to 0.045 M at constant $[\mathrm{TEMPO}]_0$. The slope of the line from initial rate versus $[\mathrm{BPO}]_0$ gave $k_{\mathrm{PR}} = 0.11 \pm 0.02$ M^{-1} s^{-1}. When $[\mathrm{TEMPO}]_0$ was varied from 0.003 to 0.07 M, at constant $[\mathrm{BPO}]_0$, there was no significant change in initial rate, as predicted by eq 7, and the calculated average k_{PR} was 0.10 ± 0.02 M^{-1} s^{-1}, in agreement with the BPO concentration study.

Using the computer program HAVCHM, the disappearance of TEMPO for a TEMPO:BPO ratio of 0.5:1 was simulated. The program calculates the reaction time course by calculating the effect of the differential rates of change of reactants and products with small varying time increments. An excellent fit to the reaction time profile was achieved with the values $k_{\mathrm{D}} = 0.0003$ s^{-1} and $k_{\mathrm{PR}} = 0.089$ M^{-1} s^{-1} as shown in Figure 4. The former constant is very close to the literature value,[8] and the latter is within error of the experimental value. From many simulations it was observed that increasing k_{PR} increases the initial rate of TEMPO disappearance and decreases the limiting amount of TEMPO remaining after all of the BPO has been consumed. In contrast, increasing k_{D} has the opposite effect. Thus there is a range of values for k_{PR} and k_{D} that fit the experimental data quite well, with only a small change in overall shape of the reaction time profile. In addition, small changes in the initial concentrations can have a significant effect on the limiting [TEMPO] at long reaction times. Thus the values of these simulated parameters should be taken only as an indication that this model of BPO decomposition in the presence of TEMPO and the associated rate constants are reasonable.

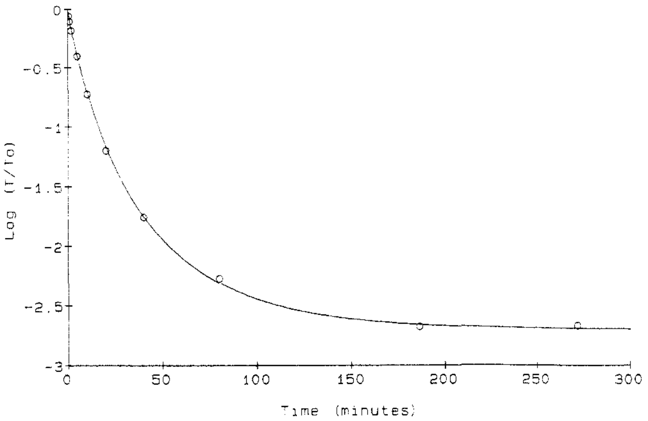

Figure 4. A HAVCHM computer simulation of reaction of BPO and TEMPO, shown by the solid line for $k_{RP} = 0.0858\ M^{-1}\ s^{-1}$ and $k_D = 3 \times 10^{-4}\ s^{-1}$. The open circles show the observed data for $[TEMPO]_0 = 0.0089$ M, $[BPO]_0 = 0.018$ M, and $[TEMPO]_0/[BPO]_0 = 0.5$.

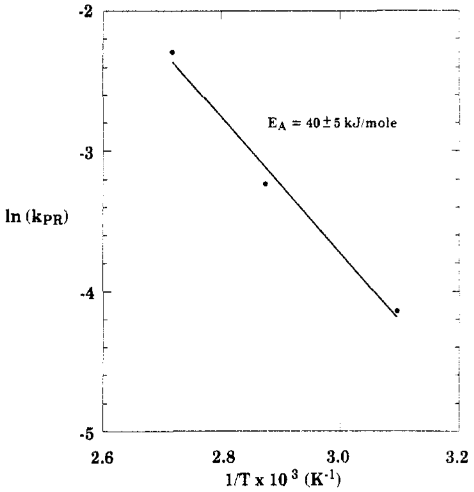

Figure 5. Activation energy determination for reaction of BPO and TEMPO. $[TEMPO]_0 = 0.023$ M, $[BPO]_0 = 0.046$ M, and $[TEMPO]_0/[BPO]_0 = 0.5$.

While the full reaction time profile can be fitted by a reasonable set of k_{PR} and k_D parameters when TEMPO/BPO is less than 1, such a fit is not possible for a 1.3:1 TEMPO:BPO ratio. While the first 40 min of this reaction is fitted very well, the predicted lower limiting concentration of TEMPO at long reaction times is about 0.75 of the observed value for any reasonable set of parameters. There are two obvious explanations for the increased overall consumption of TEMPO. The first is that TEMPO radical is reacting, presumably in an oxidation–reduction reaction, with the benzoate anion that is produced, in accordance with Figure 3. However, addition of benzoic acid to the TEMPO/BPO mixture has no effect on the disappearance of TEMPO radical, suggesting that this reaction is not important. A second possibility is that TEMPO radicals are coupling with the phenyl radicals that are produced by the decarboxylation of BPO radicals. TEMPO is well known to couple very rapidly with such carbon-centered radicals (while it does not react with oxygen-centered radicals such as BPO radicals).[4] Further simulation work is in progress to more fully understand the effect of phenyl radicals.

Reaction temperature was varied from 55 to 95 °C, yielding an activation energy of 40 ± 5 kJ/mol for rate-promoted BPO decomposition, as shown in Figure 5, compared to ~120 kJ/mol for thermal decomposition.[8] The reduction in activation energy is reasonable in terms of the oxidation–reduction reaction shown in Figure 3, in which scission of the peroxide bond is enhanced by oxidation of TEMPO radical to its non-radical cation, with a concomitant reduction of one benzoyloxy moiety to its anion and formation of one benzoyloxy radical.[9]

(b) Styrene Polymerization Using TEMPO and BPO. In styrene polymerization, the kinetics become more complex. Promoted BPO decomposition gives

$$\mathrm{T} + \mathrm{I} \xrightarrow{k_{PR}} \mathrm{X} + \mathrm{R} \tag{8}$$

Thermal BPO decomposition gives

$$\mathrm{I} \xrightarrow{k_D} \mathrm{R} \tag{9}$$

Chain initiation gives

$$\mathrm{R} + \mathrm{M} \xrightarrow{k_I} \mathrm{P}_1 \tag{10}$$

Reversible termination gives

$$\mathrm{P}_N + \mathrm{T} \overset{k_L, k_{-L}}{\rightleftarrows} \mathrm{L}_N \tag{11}$$

Chain propagation gives

$$\mathrm{P}_N + \mathrm{M} \xrightarrow{k_P} \mathrm{P}_{N+1} \tag{12}$$

Here M is monomer, L_N is a reversibly terminated, or pseudoliving polymer chain, and P_N are growing polymer chains of length N that are free rather than terminated by TEMPO radical.

To analyze the kinetics of the reaction, it is necessary to look at the initial rate of the reaction, where $I \simeq I_0$ and $M \simeq M_0$. The latter approximation means that we can ignore propagation, which only changes M. In any event, for the experiments run at 95 °C, no polymerization was observed. The equilibrium constant for the trapping of the chain end by TEMPO, eq 11, apparently strongly favors the chain-terminated species, preventing a significant polymerization rate until the temperature rises above 120 °C. Thus, eq 12 can be dropped, and eq 11 can be assumed to be well represented, at this temperature, by the rate of the forward reaction, k_L. The simultaneous equations to be solved are thus

$$\mathrm{d}T/\mathrm{d}t = -k_{PR}I_0T - k_LPT \tag{13}$$

$$\mathrm{d}R/\mathrm{d}t = k_{PR}I_0T + 2k_DI_0 - k_IRM \tag{14}$$

$$\mathrm{d}P/\mathrm{d}t = -k_LPT - k_IRM \tag{15}$$

Using the steady-state assumption on R, that is, that R reaches a small, but constant value very rapidly, $\mathrm{d}R/\mathrm{d}t = 0$

$$k_{PR}I_0T + 2k_DI_0 = k_IRM \tag{16}$$

Using eq 16, we can rewrite eq 15 as

$$\mathrm{d}P/\mathrm{d}t = -k_{PR}I_0T + 2k_DI_0 - k_LPT \tag{17}$$

Equations 13 and 17 are a set of two coupled differential equations that can be solved if P can be given as a function of T. This is done by dividing eq 17 by eq 13 to give

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{-k_{PR}I_0 + 2k_D(I_0/T_0) - k_LP}{-k_{PR}I_0 - k_LP} \tag{18}$$

To integrate this equation, we can make one of a number of assumptions. With the relative concentrations that have been used in this study and a temperature of 95 °C, the term $2k_DI_0/T$ can be approximated by setting $T \simeq T_0$ in the term, giving $2k_DI_0/T_0$. The maximum error in doing this is less than 5%, assuming the initial rate is measured while $T \geq 0.8\ T_0$. Integrating eq 18, using this approximation, gives

$$T - T_0 = \left(\frac{2k_{PR}I_0 + 2k_D(I_0/T_0)}{k_L}\right) \times \ln\left(\frac{k_{PR}I_0 + 2k_D(I_0/T_0) - k_LP}{k_{PR}I_0 + 2k_D(I_0/T_0)}\right) + P \quad (19)$$

To solve for P, the assumption is made that P is small compared to $T - T_0$, and thus the term P can be dropped. This assumption is equivalent to the assumption that the trapping of the growing polymer chain, P_N, is very fast compared to its formation. This is a reasonable assumption, as the rate of trapping of a carbon-centered radical by a stable free radical, like TEMPO, is very fast, essentially diffusion controlled.[4] In contrast, the production of P_N depends on the much slower rates of formation of initiating radical and its reaction with monomer to form the growing chain. Dropping the final term, P, and integrating eq 19 yields

$$P = \left(\frac{k_{PR}I_0 + 2k_D(I_0/T_0)}{k_L}\right) \times \left[1 - \exp\left(\frac{(T - T_0)k_L}{2k_{PR}I_0 + 2k_D(I_0/T_0)}\right)\right] \quad (20)$$

As long as $(T - T_0)k_L \gg 2k_{PR}I_0 + 2k_D(I_0/T_0)$, then the exponential term can be dropped to give

$$P = \frac{k_{PR}I_0 + 2k_D(I_0/T_0)}{k_L} \quad (21)$$

This assumption is true if $k_L \gg 2k_{PR}I_0 + 2k_D(I_0/T_0)$. This is the same assumption that was made above, that trapping of the growing chain by the TEMPO radical is fast. Substitution from eq 21 for P in eq 13 yields

$$dT/dt = [-2k_{PR}I_0 - 2k_D(I_0/T_0)]T \quad (22)$$

Integration then gives

$$\ln(T/T_0) = [-2k_{PR}I_0 - 2k_D(I_0/T_0)]t \quad (23)$$

The enhancement of the rate of disappearance of TEMPO in styrene to that in toluene, at the same temperature, I_0 and T_0, is $R_{S/T}$:

$$R_{S/T} = \frac{-2k_{PR}I_0 - 2k_D(I_0/T_0)}{-k_{PR}I_0} = 2\left(1 + \frac{k_D}{k_{PR}T_0}\right) \quad (24)$$

The assumptions that have been made to reach eq 24 are, in summary, (i) the rate of reaction is the initial rate, where $T \geq 0.8T_0$, $M \simeq M_0$, $I \simeq I_0$, and $T \leq 95$ °C, and (ii) the rate of trapping of the polymer chain is fast compared to the rate of formation of growing the polymer, $k_L \gg 2k_{PR}I_0 + 2k_D(I_0/T_0)$.

The initial rate of disappearance of TEMPO will be greater in styrene than in toluene, due to reaction 11, the formation of TEMPO-terminated living polymer chain. Figure 6 shows ESR data for [TEMPO] in a polymerization in styrene, compared to data in toluene, under otherwise identical conditions. As expected, there is a clear increase in the initial rate of disappearance of TEMPO in styrene over toluene by a factor of 2.2 ± 0.2. Using the literature value of $k_D = 0.0002$ s^{-1} and the experimental value of $k_{PR} = 0.10$ in eq 24 gives a value of 2.17. This value is relatively insensitive to the exact values of k_D and k_{PR}. Thus, a k_D of 0.0003 s^{-1} gives $R_{S/T} = 2.26$. However, as Table I shows, predicted values of $R_{S/T}$ systematically fall below the observed values as the initial concentration of TEMPO decreases. Equation 24 was fitted using the data in Table I by plotting $(R_{S/T} - 2)$ against $(1/k_{PR}T_0)$ and using the experimentally determined value, $k_{PR} = 0.10$, to find the best fitted value of k_D. This value of $k_D = (6 \pm 1) \times 10^{-4}$ s^{-1} is ca. 3 times that of the literature value in styrene. The agreement is reasonable considering the uncertainty in the calculation of k_D from ref 8 and that the addition of TEMPO to the system may change k_D from its value in styrene alone.

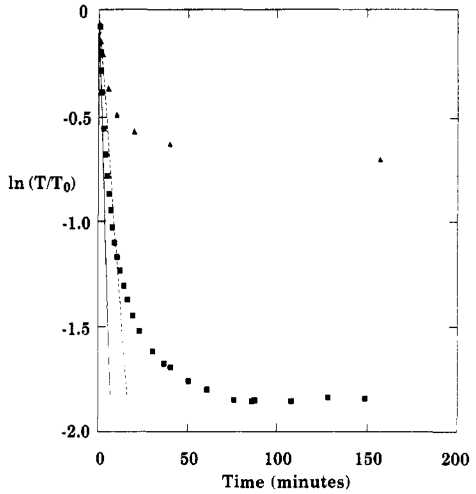

Figure 6. TEMPO radical disappearance in toluene and styrene with BPO. $[\text{TEMPO}]_0 = 0.023$ M, $[\text{BPO}]_0 = 0.0177$ M, and $[\text{TEMPO}]_0/[\text{BPO}]_0 = 1.3$. (▲) In toluene; the dashed line shows the initial rate, $-dT/dt = -0.117$ min^{-1}. (■) In styrene; the solid line shows the initial rate, $-dT/dt = -0.261$ min^{-1}. The ratio of the two initial rates, $R_{S/T}$, is 2.2 ± 0.2.

Table I. Ratio of Rate of Disappearance of TEMPO in Styrene and in Toluene[a]

		predicted $R_{S/T}$	
T_0 (M)	obsd $R_{S/T}$	$k_D \simeq 2 \times 10^{-4}$ s^{-1} (k_D from ref 8)	$k_D = (6 \pm 1) \times 10^{-4}$ s^{-1} (k_D from best fit)
0.023	2.2 ± 0.2	2.17	2.52 ± 0.05
0.0085	3.2 ± 0.3	2.45	3.41 ± 0.14
0.00442	4.9 ± 0.3	2.95	4.72 ± 0.17

[a] $I_0 = 0.0177$ M, 95 °C, under N$_2$.

The observed kinetics are consistent with the termination of the growing styrene polymer chain by TEMPO. At 95 °C there is no polymerization when TEMPO is present, suggesting that the TEMPO which has reacted with the chain end is not labile at this temperature. Thus there is no significant amount of P_N to enable the chain propagation shown in eq 12. As we have shown,[6] subsequent heating of the reaction mixture to a higher temperature of 123 °C increases the lability of the TEMPO on the chain end. Polymerization can then proceed in a relatively slow (slow for a free radical polymerization) step growth, controlled by the equilibrium in eq 11.

In practice,[6] we have shown that it is necessary to use an excess of TEMPO compared to BPO, so that there is still excess TEMPO remaining before polymerization is started at elevated temperature. In this way, not only do all chains begin to grow at the same time but also there is sufficient TEMPO throughout the polymerization to trap the growing chains. Thus, following this procedure we have shown[6] that 3.5 h at 95 °C with styrene and a TEMPO/BPO ratio of 1.2 followed by bulk polymerization for 69 h at 123 °C results in 90% conversion to polymer with $M_n = 7800$, $M_w = 10\,000$, and polydispersity of 1.27 as determined by gel permeation chromatography (GPC). The controlled growth of the polymer is shown by the incremental increase in molecular weight with reaction time and narrow polydispersities throughout the reaction.[6]

Increasing the TEMPO concentration further suppresses the free growing chain concentration, determined by eq 11, slowing the reaction, but further narrowing the polydispersity.[6]

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