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The Pivotal Role of Excess Nitroxide Radical in Living Free Radical Polymerizations with Narrow Polydispersity

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ABSTRACT: The pivotal role of the nitroxide concentration in bulk living polymerization of styrene was studied between 115 and 135 °C, using *in situ* electron spin resonance spectroscopy (ESR) to follow the concentration of the TEMPO stable free radical during the polymerization. Molecular weight and conversion were also followed on the same reaction mixtures using gel permeation chromatography and thermogravimetric analysis, respectively. While molecular weights were linear with conversion, to high conversion, there was an increase in the polymerization rate with time: nonideal behavior for a living polymerization. However, the TEMPO concentration also shows a slow decay as polymerization proceeds. Using the current mechanistic model, which predicts a polymerization rate inversely proportional to TEMPO concentration, this changing concentration was incorporated into the kinetic analysis. Except for low conversion in the lowest temperature polymerization, correction for the TEMPO concentration resulted in ideal, constant polymerization rate constants. While increasing the initial TEMPO concentration decreases the rate of polymerization dramatically, the corrected rate is independent of initial TEMPO concentration, again consistent with the current mechanism. From these corrected polymerization rates, the activation energy for the release of TEMPO from the growing chain end was estimated as 82 kJ/mol, considerably less than the previously observed value of 130 kJ/mol for the release of TEMPO from styrene 1-mers. Using TEMPO as a probe of irreversible chain termination, ESR shows that irreversible chain termination up to 75% conversion is limited to less than 2 chains in a hundred. It is concluded that the TEMPO-mediated polymerization is a living polymerization under the conditions of this study. To aid in the understanding of these living polymerizations that are based on reversible termination, a new term has been defined, the germination efficiency, which describes the yield of living chains in terms of the reversible terminating agent.

Introduction

The rapid development of a living free radical polymerization has been documented in a recent series of articles.[1−5] The concept of reversible termination, using a nitroxide stable free radical, such as TEMPO (*1*), has been applied to produce the living polymers. This system can provide polymers having polydispersities less than 1.3, with controlled stepwise growth, providing low molecular weight oligomers through to high molecular weight polymers. This approach has been successfully applied not only to bulk homopolymerization[1−4] and block copolymerization,[4] but also to suspension copolymerization[3] and aqueous solution homopolymerization.[5] Other groups have also begun to use this process. Hawker[6] uses TEMPO terminated initiators to prepare narrow polydispersity polystyrene. Mardare and Matyjaszewski[7] make use of a coordination catalyst as well as TEMPO to obtain narrow polydispersities.

A number of groups[1−3,8,9] have set the ground work to understand the reversible termination of growing polymer chains in free radical polymerizations, in some cases giving stepwise chain growth. Greszta et al. have reviewed some constraints on these pseudo-living systems.[10] Otsu et al.[8] showed that iniferters form radicals that can both initiate polymerization and react reversibly with growing polymer chains, but the polymers obtained do not have narrow polydispersities.

It is now well established that nitroxide stable free radicals react very rapidly with carbon centered radicals[11] and with growing polymer chains,[12] acting as polymerization inhibitors.[13] Solomon et al. have shown that an adduct of a nitroxide and an initiator fragment can initiate polymerization, while the nitroxide moiety reversibly terminates the growing polymer chain, to yield low molecular weight oligomers.[9] Computer modeling by Johnson et al.[14] predicts that narrow polydispersities using reversible termination should be possible, but no experimental verification of these predictions was shown.

We have previously utilized electron spin resonance (ESR) to study the mechanism and kinetics of the nitroxide-mediated polymerization, using model reactions at temperatures below 100 °C. The initial polymerization steps are consistent with a reversible termination of the initiated polymer chains by TEMPO.[2] As an excess of TEMPO is used in these polymerizations, there is always some residual "free" TEMPO (TEMPO that is not attached to the end of a polymer chain). It was also shown that the bulk polymerization of styrene in the presence of nitroxides is living. Using model compounds, consisting of a styrene unit terminated at one end by a benzoyloxy moiety, and at the other end by a nitroxide moiety, the activation energy for the breaking of the styrene−nitroxide NO−C bond was determined. In this way, it was shown that this bond breaking was the rate determining step for the polymerization. If the current proposed mechanism[1−3] is correct, then the rate of polymerization should strongly increase as the inverse of the excess "free" TEMPO concentration.

This paper extends this work to *in situ* ESR studies of the living free radical polymerization process for the production of narrow polydispersity polymers, focusing on the role of the excess nitroxide radical on the kinetics of the polymerization. This has been accomplished by observing the actual polymerizations *in situ*, using ESR

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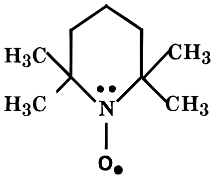
to follow the TEMPO radical concentration, while concurrently following conversion using thermogravimetric analysis, and molecular weight distributions using gel permeation chromatography (GPC).

Experimental Section

(a) Polymerizations. Bulk polymerizations were performed using benzoyl peroxide (BPO) initiator in styrene, with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO; **1**) stable free radicals. The TEMPO was purified by sublimation, while the other reagents were used as received. Solutions were purged with argon. Molecular weights were determined on samples taken every hour directly from the reaction mixture, by GPC. The GPC analysis employed THF as eluent at 0.8 mL min^{-1} through four Waters Ultrastyragel columns (100, 2 × 500, 400 Å) and a Waters 410 RI detector. The data analysis was accomplished on a Waters 860 system. Percent conversions were calculated from samples obtained similarly using a TA Instruments thermogravimetric analyzer (TGA) 2950 by comparing the weight loss due to monomer vaporization to the decomposition of polymer. The TGA conversion measurement was performed in nitrogen at a heating rate of 20 °C/min from room temperature to 520 °C. There is a clear plateau in the weight loss data between about 200 °C, at which point the monomer has volatilized, and 300 °C, at which point polymer degradation begins. Thus, the weight loss below about 200 °C gives the monomer content, while the weight loss above about 300 °C gives the polymer content. A good correlation was found between conversions determined by this method and a GC method based on residual monomer. Other than the inherent instrument error, the GC method can suffer from weighing and dilution errors, which this TGA method avoids. While the TGA method does suffer from the possibility of continued polymerization during measurement, this is minimized by the rapid heating rate utilized.



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Each polymerization was performed in an oil bath held at 115, 125, or 135 °C to ±0.1 °C. A solution of TEMPO and most of the styrene was mechanically stirred in a Morton flask at polymerization temperature, before adding the BPO, which had been previously dissolved in the rest of the styrene. Five minutes after addition of the BPO solution, an aliquot was taken into an ESR tube, which was placed in the ESR spectrometer dewar held at the polymerization temperature. While the [TEMPO] was determined as a function of time in the ESR spectrometer, the conversion and molecular weight were determined on samples taken periodically from the Morton flask. To verify that the polymerization in the ESR spectrometer was representative of that in the Morton flask, a second aliquot from the Morton flask was taken after 6 h of polymerization. This aliquot was placed in an ESR tube, and the TEMPO radical concentration was measured (at reaction temperature). The concentration of TEMPO was within ±5% to that of the original aliquot that had been polymerizing for 6 h in the ESR tube. Thus, the absence of stirring in the ESR tube has no effect on the excess TEMPO radical concentration in the polymerization.

(b) ESR Spectroscopy. Spectra of the excess TEMPO stable free radical were collected using a Bruker ESP300 spectrometer and ER4111 variable temperature accessory. The receiver gain and number of scans to acquire each spectrum were varied depending on the amount of TEMPO present. The modulation amplitude was kept constant at 0.5 G, while the microwave power was held at 10 mW. Absolute radical concentrations were determined by comparison to a secondary standard of strong pitch, which had been calibrated with a primary standard of sublimed TEMPO dissolved in styrene. These absolute values are reproducible within ±10%, and presumably accurate within the same ±10%.

Results and Discussion

In our previous work,[1−5] we have shown that narrow polydispersity, high molecular weight polymers can be obtained by a modified free radical polymerization in the presence of a nitroxide, such as TEMPO. Using a combination of kinetic analysis and ESR, the mechanism has been elucidated.[2] At the temperatures that will be discussed here (between 115 and 135 °C), initiation is essentially via reaction 1, the usual thermal homolysis of BPO (at lower temperatures, the promoted decomposition of BPO by TEMPO must also be considered[2]), and via reaction 2, the usual chain initiation.

$$\text{I-I} \xrightarrow{k_d} 2\text{I}^\bullet \tag{1}$$

$$\text{I}^\bullet + \text{M} \xrightarrow{k_i} \text{P}_1 \tag{2}$$

Here, I-I is initiator, $\text{I}^\bullet$ is the initiating radical, M is monomer, and $\text{P}_1^\bullet$ is the polymer radical, $\text{P}_n^\bullet$, where $n = 1$. ESR shows that initiated polymer chain is trapped reversibly by TEMPO, as given by:

$$\text{P}_n^\bullet + \text{T}^\bullet \overset{K_L}{\rightleftharpoons} \text{L}_n \tag{3}$$

L_n is the polymer chain that has been reversibly terminated by TEMPO, referred to as *living polymer chain*, to distinguish it from growing polymer chain, $P_n^\bullet$. K_L $(=k_L/k_{-L})$ is the equilibrium constant for the capture (with rate constant k_L) and release (with rate constant k_{-L}), of TEMPO from the growing chain end. The kinetics observed by ESR are consistent with trapping that is much faster than propagation, $k_L[\text{T}^\bullet] \gg k_p[\text{M}]$, where k_p is the usual propagation rate constant. Beckwith et al.[11] have shown that the reaction of any nitroxide with a sterically *unhindered* radical is very fast and is approximately:

$$k_L = 5.03 \times 10^9 \exp(-3772/RT) \text{ M}^{-1} \text{ s}^{-1} \tag{4}$$

The rates are slower for trapping of hindered radicals, due to a reduction in the preexponential factor in eq 4. On the other hand, k_{-L} is the rate of homolytic cleavage of the NO−C bond, to give growing chain radical and nitroxide radical. This rate was studied using a model styrene 1-mer capped by a nitroxide (I-M_1-T), L_1 in eq 3, and which consists of a single styrene unit, M_1, terminated at one end by a benzoyloxy moiety, I, and at the other end by the nitroxide, T. Using ESR to study the rate of release of the nitroxide from the capped chains, L_1, as a function of temperature, this equilibrium was shown to be controlled by the breaking of the nitroxide−polymer NO−C bond. The bond energy, ΔH_b, is dependent on the nitroxide, with a value of $\Delta H_b \simeq \Delta H^\ddagger = 130 \pm 4$ kJ/mol for TEMPO capped styrene 1-mer.[2] Confirming the ESR work, the bond dissociation enthalpies of nitroxide trapped benzyl radicals, structurally similar to the 1-mer described here, were estimated from the gas-phase heats of formation determined using MOPAC semiempirical calculations.[3,15]

Using the usual propagation step:

$$\text{P}_n^\bullet + \text{M} \xrightarrow{k_p} \text{P}_{n+1}^\bullet \tag{5}$$

and the usual termination steps, illustrated by:

$$\mathrm{P}_n^{\bullet} + \mathrm{P}_{n'}^{\bullet} \xrightarrow{k_\mathrm{t}(n,n')} \text{dead polymer} \tag{6}$$

allows a full mechanistic description, whose derivation has been discussed in detail previously.[1-3] The following are the key features of the mechanism. First, initiation with BPO at these high temperatures ensures a very rapid initiation of all chains, typically in less than a few minutes at 135 °C, after which no BPO remains. These chains are trapped very rapidly. Thus, initiation does not occur after the first few minutes (autopolymerization is also suppressed under these conditions and can be ignored[16]). The initiated chains are trapped by TEMPO, before they begin to polymerize. The rate of polymerization is still given by the usual differential equation:

$$\frac{\mathrm{d[M]}}{\mathrm{d}t} = -k_\mathrm{p}[\mathrm{M}]\sum[\mathrm{P}_n^{\bullet}] \tag{7}$$

However, because the growing polymer chains are trapped by TEMPO, the $\Sigma[\mathrm{P}_n^{\bullet}]$, is lower, at the same temperature, than in the usual free radical polymerization. Substitution for $\Sigma[\mathrm{P}_n^{\bullet}]$ in eq 7 from the equilibrium in eq 3 gives the differential rate equation for polymerization in the presence of nitroxide:

$$\frac{\mathrm{d[M]}}{\mathrm{d}t} = -\frac{k_\mathrm{p}}{K_\mathrm{L}}\frac{L}{T}[\mathrm{M}] \tag{8}$$

For simplicity, we have adopted the following conventions: $P = \Sigma[\mathrm{P}_n^{\bullet}]$, total concentration of growing chains; $L = \Sigma[\mathrm{L}_n]$, total concentration of living chains; and $T = [\mathrm{T}^{\bullet}]$, unbound TEMPO concentration. In our previous work we have assumed that all of these are constant, after living chain formation. The rate is proportional not only to the propagation rate constant k_p and to the concentration of monomer, M, but also to L, $1/K_\mathrm{L}$, and $1/T$. Equation 8 is written with the assumption that the termination of eq 6 can be ignored. This is observed to be a good assumption experimentally and can also be quantitatively predicted, due to a number of factors which have been previously discussed in detail.[2] Briefly, P is much lower than a conventional polymerization at the same temperature, so that the higher polymerization temperature gives a more favorable ratio of $k_\mathrm{p}MP/k_\mathrm{t}P^2$. In addition, since initiation is complete in the first few minutes of the polymerization, there are fewer short chains present during the polymerization than in the usual free radical polymerization. This reduces chain termination, since the rate of chain diffusion is strongly length dependent.[17]

At the start of initiation, $T \simeq T_0$, the initial TEMPO concentration, which is approximately the same as the concentration of chains initiated ($T_0 \simeq L = 2f_\mathrm{d}[\mathrm{I}]_0$, where f_d is the initiatior effiency). In the first 15 min, the initiated chains are capped by TEMPO, thus reducing the amount of free TEMPO (i.e., unbound to a polymer chain) to a very low level. In our previous studies, the measured molecular weight suggested that the amount of excess TEMPO, left after initiation is complete, is less than 5% of the initial amount.

After initiation is complete, it was assumed that neither the TEMPO concentration, nor L, changes.[2] This assumption was made to allow the integration of eq 8, giving eq 9 for the conversion of monomer to polymer in the presence of TEMPO. In that work, it was shown that plotting eq 9, as $\ln(M_0/M_t)$ versus t, gave a linear relationship at 135 °C for the polymerization of styrene by BPO. This suggested that T did not change significantly during the polymerization (after the first few minutes of initiation), up to high conversion. However, previous work at lower temperature did show an apparent induction period, which could be due to changes in TEMPO concentration. Because of the importance of the TEMPO concentration to the rate of polymerization, as shown by eq 8, we decided to follow the TEMPO concentration during the polymerization, allowing an exact integration of eq 8. Most of these polymerizations were performed at temperatures below 135 °C, where the apparent nonideality of the living polymerization is most obvious.

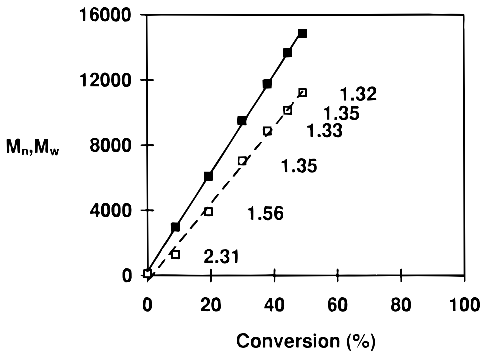


Figure 1. Polymer molecular weights (M_n and M_w) and polydispersity ($M_\mathrm{w}/M_\mathrm{n}$) plotted versus conversion for bulk polymerization with 1.1:1 TEMPO/BPO, $[\mathrm{BPO}]_0 = 0.036$ M, at 125 °C. The lines shown are best linear least-squares fits.

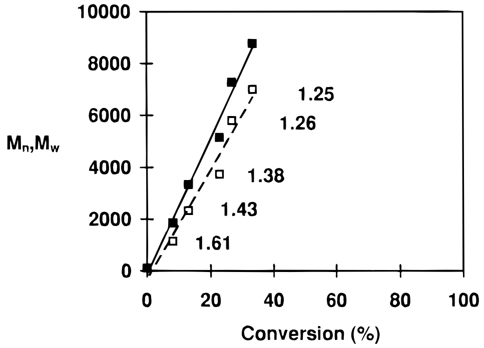


Figure 2. Polymer molecular weights (M_n and M_w) and polydispersity ($M_\mathrm{w}/M_\mathrm{n}$) plotted versus conversion for bulk polymerization with 1.3:1 TEMPO/BPO, $[\mathrm{BPO}]_0 = 0.036$ M, at 125 °C. The open symbols show M_n, while the closed symbols show M_w. The lines shown are best linear least-squares fits.

$$-\ln\left(\frac{[\mathrm{M}]_t}{[\mathrm{M}]_0}\right) = k_\mathrm{p}\left(\frac{L}{K_\mathrm{L}T}\right)t \tag{9}$$

Figures 1 and 2 show typical examples of the increase in molecular weight of bulk living free radical styrene polymerizations, using TEMPO and BPO in 1.1:1 and 1.3:1 molar ratios, respectively, at 125 °C. A linear growth of the molecular weight with conversion and narrow polydispersities (<1.4, except at very low conversion) are observed. The increased initial TEMPO concentration reduces the polydispersity at equivalent conversion, for example, from 1.35 at 1.1:1 TEMPO/BPO to 1.25 at 1.3:1 at ≈40% conversion. This is due to the increase in excess TEMPO (shown below), which results in less growing polymer radical, P, as governed by eq 3, and thus less chain termination due to coupling at the same conversion (coupling $\propto P^2$ as described by eq

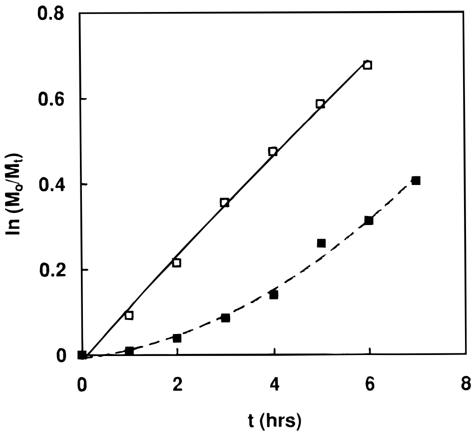


Figure 3. Semilog plot of conversion with polymerization time for bulk polymerization with a TEMPO/BPO ratio of 1.1:1 (open symbols) and 1.3:1 (closed symbols), $[BPO]_0 = 0.036$ M, at 125 °C. The lines are smoothed curves drawn as a guide to the eye only.

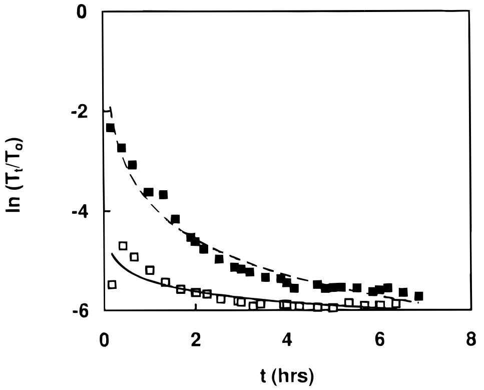
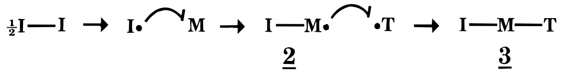


Figure 4. Semilog plot of TEMPO concentration with polymerization time for bulk polymerization with a TEMPO/BPO ratio of 1.1:1 (open symbols) and 1.3:1 (closed symbols), $[BPO]_0 = 0.036$ M, at 125 °C. The lines shown are best linear least-squares fits to eq 12.

6, while propagation ∝ P).[2] A second result of the increased TEMPO is a faster exchange rate between the active and dormant polymer chains (eq 3), which also leads to a narrowing of the PD.[19]

Figure 3 shows a semilogarithmic plot of conversion with reaction time for the two polymerizations. Figure 4 shows the corresponding TEMPO concentrations, measured *in situ* in the polymerizations, as a function of reaction time. As expected, there is initially a very rapid drop in the TEMPO concentration as the TEMPO caps the initiated chain ends (the first measurement of TEMPO is 15 min after the polymerization is started). At this temperature, the half-life of the BPO is about 3 min.[2,18] Indeed, as shown by Figure 4, the sharp drop in TEMPO concentration is complete (>99%) within 15 min, as all chains have been initiated and capped. After this initial sharp drop, there is a slower decay in TEMPO radical concentration, which will be discussed in more detail later. Thus, at 125 °C, the assumption that TEMPO concentration is constant once initiation is complete is not a good approximation.

As one might expect, the polymerization with a higher initial TEMPO to BPO ratio has a higher residual TEMPO concentration throughout the polymerization. While this is obvious qualitatively, the quantitative details illustrate a more subtle point. These narrow molecular weight distribution (MWD) polystyrenes provide a relatively accurate measurement of chain length, from M_n's obtained by GPC. Combining these data with the conversion data, we can calculate the initiator efficiency: the number of polymer chains divided by twice the number of benzoyl peroxide molecules. The initiator efficiency is determined by the yield of product **2**. The initiator efficiencies observed are typically 50–60% for BPO.



$$\tfrac{1}{2}\mathrm{I{-}I} \rightarrow \mathrm{I\bullet}\ \ \mathrm{M} \rightarrow \underset{\underline{2}}{\mathrm{I{-}M\bullet}}\ \ \mathrm{\bullet T} \rightarrow \underset{\underline{3}}{\mathrm{I{-}M{-}T}}$$

We can measure the yield of the nitroxide-capped chains, **3**, resulting from the combination of the nascent free radical terminated chain, **2**, the uncapped 1-mer unit, with the stable nitroxide free radical: the critical step in the formation of living chains. To distinguish it from initiator efficiency, we have dubbed this the *germination efficiency* and defined it as follows: the number of living polymer chains divided by the initial number of TEMPO molecules, or $f_g = L/T_0$. This definition only applies if the amount of TEMPO is less than the stoichiometric amount of initiating radicals (typical TEMPO:initiator ratios are about 1.1:1 to 1.5:1, below the stoichiometric amount of 2:1). The shortcoming of this approach is that it multiplies the error of molecular weight determination with that of the conversion measurement; at molecular weights below 2000 and conversions less than 25%, the values are highly variable, but beyond that range the data settle down. Whatever the experimental limitations in determining the germination efficiency, it remains a powerful concept in understanding the polymerization.

The concept of germination efficiency can only be properly applied to systems with the correct stoichiometry of nitroxide to initiator to provide a practical living system. Large excess of nitroxide results in very slow rates of polymerization, while a deficiency leads to a predominantly conventional free radical polymerization. Empirically, it has been found that the TEMPO to BPO ratio cannot be dropped below about 0.5:1 to 0.6:1 while maintaining the characteristic narrow MWD of a living free radical system. Within these limits, the presence of more initiator than there is TEMPO to cap the growing chain ends will result in excess chain ends that cannot be controlled by the TEMPO. There will be an excess of growing chains, which will terminate rapidly. This will result in a small amount of short dead chains, as well as a small amount of longer chains that have a wide distribution of chain lengths. These chains will not be living and may be difficult to observe in the GPC analysis, due to their low concentration. No matter how much initiator is added, the number of living chains can only be less than or equal to the number of TEMPO molecules to form the chains. As will be shown below by ESR, typically >99% of the TEMPO is consumed by termination of the growing chains. Thus, ideally the initial TEMPO concentration is equal to the number of living chains, $T_0 \simeq L$.

Using this new concept of germination efficiency, gives an f_g of 0.95 at 1.1:1 TEMPO/BPO, while at a 1.3:1 ratio f_g is 1. These calculations also show that the number of growing chains is roughly constant, to the limit of the accuracy of the conversion and molecular weight data. Conversely, the molecular weight is lower at 1.3:1 TEMPO compared to 1.1:1 TEMPO. This observation is general: the germination efficiency increases with increasing TEMPO/BPO ratio, reaching 100% at a sufficiently high ratio. The result is that increasing the TEMPO/BPO ratio does not lead to the exactly expected excess in TEMPO concentration, as adding more TEMPO makes germination somewhat more efficient, increasing the yield of living chains. Thus, with regard to TEMPO/BPO ratios, the polymerization has what one might call a negative feedback loop, in that initial differences in the TEMPO/BPO stoichiometry are translated into smaller differences in the amount of residual TEMPO. Increased [TEMPO] affords the opportunity to capture or "cap" more initiated chains, thereby increasing their number. We cannot discern whether the [TEMPO] alters the BPO initiator efficiency. Thus, the combination of the initiator efficiency of 50−60%, and the very high germination efficiency, explains the typical 1.1 to 1.3:1 ratio of TEMPO/BPO. A 100% overall efficiency would require a considerably higher 2:1 ratio.

Figure 4 shows another feedback loop operating as well, which is the slow decay in the [TEMPO] with time that ultimately brings the polymerizations, at the two different initial TEMPO/BPO ratios, to nearly the same final [TEMPO]. These feedback mechanisms are extremely important to the control of the polymerization. Without them, even minor changes in the stoichiometric ratio of the reagents would cause a large change in the overall rate, primarily controlled by a widely changing excess [TEMPO]. Indeed, if this were the case, it would be very difficult to maintain the small excess TEMPO concentration needed to give a reasonably fast rate.

The difference in the TEMPO concentration curves at the two TEMPO/BPO ratios clearly does have an effect on the rate of polymerization. The higher ratio has the most excess TEMPO, and the slowest polymerization rate, in qualitative agreement with the predictions of eqs 8 and 9. In addition, there is an observable curvature in both the semilogarithmic plot of conversion (Figure 3) and the TEMPO concentration with polymerization time (Figure 4). Comparison of the two curves suggests that the TEMPO concentration accounts for the curvature of the conversion plot. The detailed analysis below will show that this is quantitatively correct.

It is not clear what is causing the slow decrease in the TEMPO concentration, as TEMPO is stable at these temperatures. If polymer chains were terminating, then for every terminated chain, one TEMPO radical should be released from the capped polymer chain, L_n, increasing the TEMPO concentration. That is, if the number of chains terminated is a small fraction of L_n, then the decrease in $P_n^\bullet$ must be compensated by an increase in $T^\bullet$, determined by eq 3. The general form of the slow decay is typically close to second-order in TEMPO, involving two TEMPO radicals in the rate controlling step(s):

$$1/T - 1/T_0 = at \tag{10}$$

In these polymerizations, T drops rapidly from T_0 as shown in Figure 4. Thus, $T \ll T_0$, and we can rewrite eq 10:

$$T^{-1} = at \tag{11}$$

Rather than fitting eq 11, the following equation was used to allow a better fit to the data, by fitting to the exponent, s, as well as to a prefactor, T_a:

$$T = T_a t^{-s} \tag{12}$$

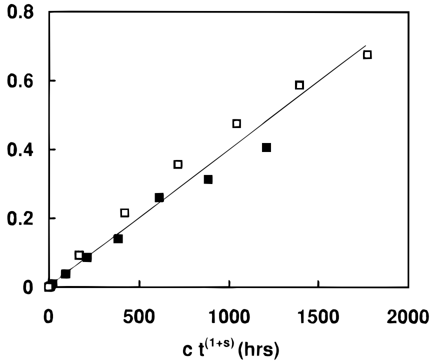


Figure 5. Semilog plot of conversion with polymerization time corrected for the TEMPO concentration and the number of living chains as given by eqs 14 and 15. Bulk polymerization with a TEMPO/BPO ratio of 1.1:1 (open symbols) and 1.3:1 (closed symbols), $[BPO]_0 = 0.036$ M, at 125 °C. The line shown is the best linear least-squares fits, as described by eq 14.

The reasonably good fit of this function to the TEMPO concentration is shown in Figure 3, with $s = 0.31$ for TEMPO/BPO = 1.1:1 and $s = 1.06$ for TEMPO/BPO = 1.3:1. Note that the initial sharp drop in TEMPO concentration, due to initiation, distorts the curve and the fit, at a 1.1:1 ratio. The decrease in TEMPO concentration described by eq 12 might be due to autopolymerization. However, in this case, it should be very strongly temperature dependent and should be present to a similar extent in all of the polymerizations, and throughout the polymerization, which is not observed in this work. Moreover, autopolymerization has been shown to be insignificant under these reaction conditions.[16]

Now that we have a functional form for the concentration of TEMPO with polymerization time, it is possible to integrate eq 8, by describing the TEMPO concentration with eq 12, to obtain:

$$\int \frac{d[M]}{[M]} = -\frac{k_p}{K_L} L \int \frac{dt}{T_a t^{-s}} \tag{13}$$

In these polymerizations $s > 0$. Integration under this constraint gives:

$$\ln\left(\frac{[M]_0}{[M]_t}\right) = c\frac{k_p}{K_L} t^{(s+1)} \tag{14}$$

where c is defined as:

$$c = \frac{L}{(s+1)T_a} \tag{15}$$

Thus, a plot of $\ln([M]_0/[M]_t)$ versus $ct^{(s+1)}$ will be linear with a slope of k_p/K_L. As discussed above, L is constant, approximated as $L = T_0$, which is a good approximation under the typical reaction conditions.

The semilogarithmic plot of conversion versus the corrected time axis, as described by eqs 14 and 15, is shown in Figure 5. The two conversion curves for the 1.1:1 and 1.3:1 TEMPO/BPO ratios, which were so different in Figure 3, are now coincident (within the 95% confidence levels), after correction for the number of growing chains and for the order of magnitude difference in TEMPO concentration. Thus, the current polymerization mechanism, and the associated kinetics predicted by eq 8, are quantitatively confirmed. The observed rate constant, which is equal to k_p/K_L, is 9.9

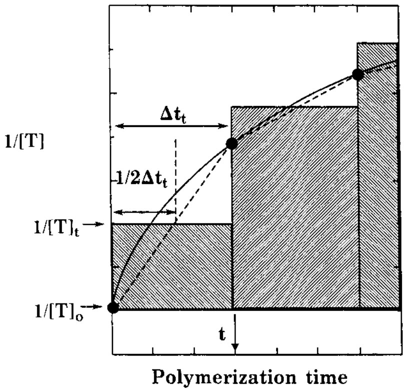


Figure 6. Schematic diagram of finite sum of inverse TEMPO concentration used in eq 17.

$\times 10^{-8}$ s^{-1}. Since k_p, which is assumed to be unchanged from the usual free radical kinetics,[21] is 2870 M^{-1} s^{-1}, $K_L = k_L/k_{-L} = 2.9 \times 10^{10}$ M^{-1}. We have recently shown that k_L for the hindered polystyrene $P_N^{\bullet}$ radicals in these polymerizations is considerably smaller than that given by eq 4, with a calculated value of 1.5×10^7 M^{-1} s^{-1}.[19] Using this value gives $k_{-L} = 5.2 \times 10^{-4}$ s^{-1}. This value is reasonable, within the range of values, $k_{-L} = 1-10^{-6}$ s^{-1}, that was roughly estimated for the release of TEMPO from the styrene 1-mer (I-M$_1$-T).[2]

While the fit of eqs 14 and 15 to the TEMPO decay is reasonably good, as shown in Figure 4, there is some deviation, particularly at short reaction times, due to ongoing initiation. Thus, there is a need for an alternate method of integrating eq 8. The method chosen was to replace the integral involving the concentration of TEMPO by a finite summation, as defined by Figure 6. The area under the curve of the function $1/T$ is estimated by dividing the area into intervals, which are defined by the time at the end of the interval, t, where the concentration of TEMPO was measured, and by the average TEMPO concentration on that interval (interpolated from the TEMPO concentration at the beginning and the end of that interval). The resulting equation, taken by replacing the integral on the right-hand side of eq 8 by the finite summation, is:

$$\int \frac{d[M]}{[M]} \simeq -L\frac{k_p}{K_L}\sum_t (\Delta t_t/T_t) \qquad (16)$$

Integration of the left-hand side gives:

$$\ln([M]_t/[M]_0) \simeq -L\frac{k_p}{K_L}\sum_t (\Delta t_t/T_t) \qquad (17)$$

A plot of $\ln([M]_0/[M]_t)$ versus $L\sum_t(\Delta t_t/T_t)$ should be linear, with a slope of k_p/K_L. The semilogarithmic plot of conversion versus the corrected time axis, as described by eq 17, is shown in Figure 7. Again, the two conversion curves for the 1.1:1 and 1.3:1 TEMPO/BPO ratios are coincident, after correction for both the number of growing chains and the TEMPO concentration. The slopes of the curves, and thus the values of the corrected rate constants from Figures 7 and 5, are nearly identical, $k_p/K_L = 9.4 \times 10^{-8}$ s^{-1} and 9.9×10^{-8} s^{-1}, respectively. Thus, the rate constant determination is robust to the method of fit.

Figure 8 shows the semilogarithmic plot of conversion with polymerization time, for identical polymerizations (1.3:1 TEMPO/BPO) at 115, 125, and 135 °C. In all cases, the molecular weight increases linearly with conversion, and polydispersities are low (<1.4, except at very low conversion) and decrease with conversion (data not shown). While the initial PD at very low conversion can be high, in all cases the initial high PD drops rapidly below 1.40 by 25% conversion.

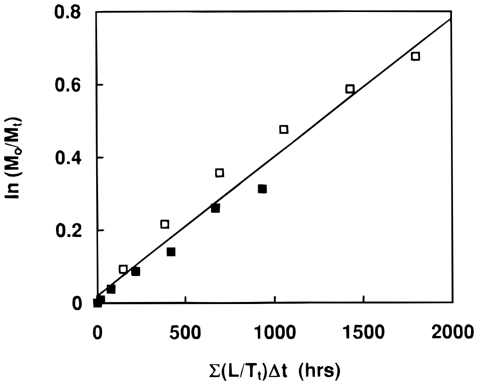


Figure 7. Semilog plot of conversion with polymerization time corrected for the TEMPO concentration and the number of living chains as given by eq 17. Bulk polymerization with a TEMPO/BPO ratio of 1.1:1 (open symbols) and 1.3:1 (closed symbols), $[BPO]_0 = 0.036$ M, at 125 °C. The lines shown are best linear least-squares fits.

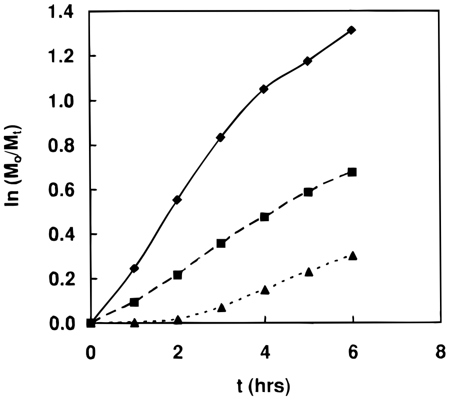


Figure 8. Semilog plot of conversion with polymerization time for bulk polymerization with 1.1:1 TEMPO/BPO, $[BPO]_0 = 0.036$ M. The lines are smoothed curves drawn as a guide to the eye only. (▲) 115 °C; (■) 125 °C; (♦) 135 °C.

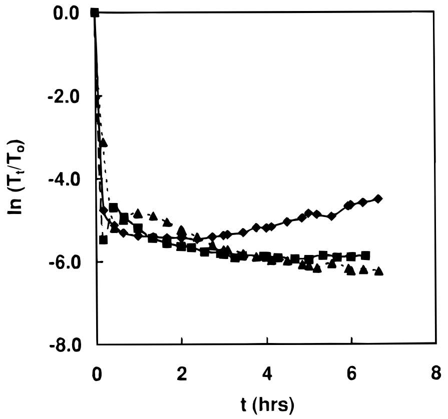


Figure 9. Semilog plot of TEMPO concentration with polymerization time for bulk polymerization with 1.1:1 TEMPO/BPO, $[BPO]_0 = 0.036$ M. The lines shown are a guide to the eye only. (▲) 115 °C; (■) 125 °C; (♦) 135 °C.

Figure 9 shows the TEMPO concentration during the polymerization at the various temperatures. In all cases, initiation is complete in about 15 min, typically where the first data point was taken. At 115 and 125

°C, after the initial decrease in free TEMPO concentration during initiation (which consumes >99% of the initial TEMPO), the TEMPO concentration then increases by a factor of 2 in an hour, before following the slow decay described by eq 12. At 135 °C, initiation is apparently so fast that it is not possible to observe if there is an initial rise.

The most likely cause of the short rise in TEMPO concentration is some irreversible termination of chains, probably by chain radical combination, or by termination of the chains with an impurity or oxygen. The latter appears unlikely, as a similar increase in [TEMPO] is observed whether solutions are left in air or purged with nitrogen. For any chain *irreversibly* terminated (each $P^\bullet$ consumed), one molecule of TEMPO will be released, determined by the equilibrium of eq 3. That is, chain termination cannot occur without releasing the corresponding stoichiometric amount of TEMPO. Since the initial TEMPO concentration is approximately equal to the number of growing chains, L, this rise in TEMPO concentration corresponds to only one chain in a hundred undergoing irreversible termination.

After the initial fast decrease in TEMPO during initiation, followed by the short increase in TEMPO concentration, and subsequent second-order decay, there is an observed increase in the TEMPO concentration at long reaction times (excepting the lowest temperature). Again, a likely mechanism for this increase is some irreversible chain termination, amounting to a maximum of 1 in 100 chains terminated after 6 h at 135 °C. While it appears that this increase is larger at higher temperature, there are a number of confounding factors. First, the second-order TEMPO decay might be less at higher temperatures, making any increase in TEMPO concentration at long reaction times more obvious. Second, at higher temperatures the rate of polymerization is higher, about a factor of 5 difference between 115 and 135 °C. The latter is important, as both k_p and k_t increase with temperature. At higher temperatures, k_t will be larger, resulting in more chain termination per unit time (and thus a bigger apparent rise in TEMPO concentration per unit time), but there will be a lower rate of chain termination per monomer unit polymerized (per monomer conversion), as determined by the k_p/k_t ratio. The latter ratio, per unit conversion, determines the final polymer PD. Nevertheless, the PD does not continue to decrease at 135 °C, while it does at lower temperatures, supporting some chain termination at higher temperatures.

Figure 10 shows the semilog plot of the conversion at the three different temperatures, after correction for the [TEMPO] and the number of living chains, based on eq 17. The resulting curves are linear, except for the lowest temperature, which does still show some induction period. Part of the induction period can be attributed to the assumption, made in the integration of eq 17, that there is no initiation period (the number of chains is constant). Correcting for this lower number of chains during the initiation period, by incorporating an initial exponential increase in the number of living chains, L_i, into eq 17, does account for some, but not all, of this induction time.

On the basis of decomposition studies with a model TEMPO terminated styrene 1-mer in various solvents, Li et al.[20] have suggested that a substantial fraction of polymer chains terminated by TEMPO decompose at 140 °C, resulting in a dead chain and a reduced TEMPO (reduced to the corresponding hydroxylamine). The data shown here, once corrected for the changing TEMPO concentration, show no sign of a large amount of termination. Extensive chain termination by this mechanism would result in a slowing of the rate of the polymerization, due to the loss of growing chains. This would also result in a substantial increase in PD with conversion. The data shown here typically show constant polymerization rates and PD's that narrow with conversion. At higher temperatures, PD's do broaden somewhat at the high conversions, but with an increase in free TEMPO, due to a small amount of termination due to chain coupling, as discussed. Since the process proposed by Li et al. results in loss of both a $P_n^\bullet$ and $T^\bullet$, or equivalently, one capped chain, L_n, the equilibrium in eq 3 would result in a drop in both $T^\bullet$ and $P_n^\bullet$, inconsistent with our observations. The reason for the different behavior in our work and that of Li et al. is not clear; however, their work was a model study using TEMPO terminated styrene 1-mer as an initiator in a nonpolymerizable solvent, whereas our work used BPO initiator in styrene.

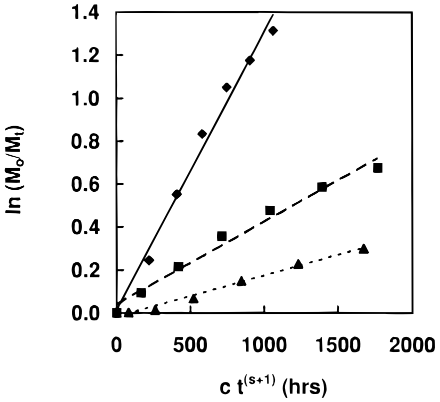


Figure 10. Semilog plot of conversion with polymerization time, corrected for the number of living chains and the TEMPO concentration as given by eq 17. Bulk polymerizations with 1.1:1 TEMPO/BPO, $[BPO]_0 = 0.0036$ M. The lines shown are best linear-squares fits. (▲) 115 °C; (■) 125 °C; (◆) 135 °C.

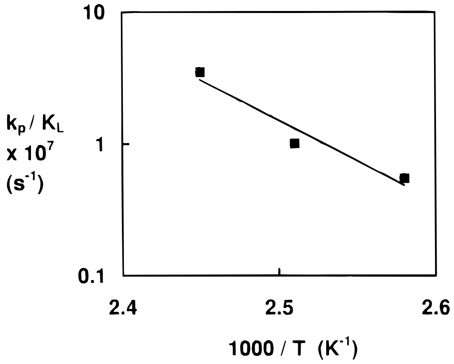


Figure 11. Activation energy plot for bulk polymerization of styrene using rate constants corrected for the number of living chains and the TEMPO concentration (eq 17). The line shown is the best linear least-squares fit.

Figure 11 shows the activation energy plot for the rate constants from Figure 10 corrected according to eq 17. The activation enthalpy, $\Delta H^\ddagger$, for k_p/K_L is 115 kJ/mol. Now,

$$\Delta H^\ddagger(k_p/K_L) = \Delta H^\ddagger(k_p) + \Delta H^\ddagger(k_{-L}) - \Delta H^\ddagger(k_L) \quad (18)$$

Here, the $\Delta H^\ddagger$'s are the activation enthalpies for the respective rate constants, k_p/K_L, k_{-L}, and k_L, which are related to the more commonly calculated E_a's by $\Delta H^\ddagger =$

$E_a + RT$. For the usual free radical bulk polymerization of styrene, $E_a(k_p) = 37.5$ kJ/mol,[21] while $E_a(k_L) = 4$ kJ/mol[11] for the reaction of TEMPO with an unhindered or hindered radical.[22] Thus $\Delta H^{\ddagger}(k_{-L})$ is about 82 kJ/mol for the release of TEMPO from the polymer chain end. This value is considerably less than the value of 130 ± 4 kJ/mol observed[2] for the release of TEMPO from the styrene 1-mer (I-M_1-T). While some of this difference could be due to experimental uncertainty, taken at face value, this difference indicates that the release of TEMPO is easier as the polymer chain becomes longer. Indeed, if the release of TEMPO, and thus the release of growing chains, is slower for short chains, this might explain the induction period observed at low temperatures (Figure 10), where conversion is low and the chains are short.

If it is assumed that this induction period is due to a slower release of TEMPO for shorter chains, then this slower release occurs only for chains that are less than about 10 monomer units long, as the apparent induction period is finished by the time the molecular weight reaches about 1000. This decrease in activation enthalpy as the chain grows to about 10 units may be due to a decrease in conformational freedom about the chain end. It is not unreasonable that a 1-mer has much more conformational freedom, and less steric hindrance, about the chain end, than does a 10-mer, due to the steric interaction of mer units. Both a decrease in conformational freedom and an increase in steric hindrance could lead to a weaker NO−C bond and/or a slower rate of trapping of the chain end by nitroxide.[11] The latter could result in a smaller apparent activation enthalpy, as eq 18 assumed that the rate of trapping is the same in all cases.

This difference in bond enthalpy is too large to be explained either in terms of an inverted configuration for the styrene unit (about 7% of the 1-mer is inverted according to NMR) or in terms of phenyl initiation in the 1-mer (about 7% of the 1-mer is phenyl initiated according to NMR). Based on the observed abundance, both phenyl initiated and inverted configuration 1-mers would need to have activation enthalpies of 440 kJ/mol to account for the observed activation enthalpy differences. If the activation enthalpy were this high for some of the 1-mer, then it would be inert at the temperatures used here, and its contribution to the observed rate would be negligible compared to the bulk of the 1-mer, which has a much lower activation enthalpy.

Conclusions

While the nitroxide controlled free radical polymerizations show a linear increase in molecular weight with conversion to high conversion, with narrow polydispersities (<1.4), the semilogarithmic conversion−time plots show an increase in the polymerization rate, nonideal behavior for a truly living polymerization. *In situ* ESR has been used to actually follow the excess "free" TEMPO stable free radical concentration during the polymerization. The TEMPO concentration shows a slow, typically second-order decay as the polymerization proceeds. Our current mechanistic and kinetic model predicts a polymerization rate that is inversely proportional to excess TEMPO. Using either an integral or finite summation method, the decay in TEMPO concentration has been incorporated into the kinetic model. Except for the lowest temperature, the effect of the TEMPO concentration totally accounts for the observed rate increase with time.

At the lowest temperature, there is slight induction period that cannot be explained by slower initiation at the lower temperature. However, the induction could be due to a slower rate of release of TEMPO from very short chains, compared to that from longer polymer chains. The higher proposed activation energy for release of TEMPO is limited to chain lengths less than about 10 monomer units.

Increasing the initial TEMPO concentration decreases the polymerization rate dramatically. Using the ESR data to correct for differences in the excess TEMPO concentration during polymerization gives identical polymerization rate constants, quantitatively consistent with our polymerization mechanism. Using the corrected polymerization rates at different temperatures, the activation enthalpy for the release of TEMPO during the polymerization was estimated to be about 82 kJ/mol, considerably less than the observed for the release of TEMPO from the styrene 1-mer, 130 ± 4 kJ/mol. This is consistent with an increase in steric hindrance and a decrease in chain conformational freedom as the polymer chain lengthens. It is also consistent with the slight induction period at the lowest temperature.

The TEMPO concentration is a probe of any irreversible chain termination, as every chain terminated releases one molecule of TEMPO. It is shown that irreversible chain termination is limited to less than about 2 chains in a hundred, at the highest temperature, and even less at lower temperatures. It is concluded that the predominant chain growth mechanism is indeed living under these conditions.

To aid in the understanding of living polymerizations that are based on reversible termination, a new term has been defined, the germination efficiency, which describes the yield of living chains in terms of the reversible terminating agent. It is defined as follows: the number of living polymer chains divided by the initial number of terminating molecules. This is a powerful new concept, which emphasizes the role of the reversible terminating agent in controlling the number of living chains.

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(22) While the activation enthalpy for trapping could be greater than 4 kJ/mol, as the value for the polystyrene radical has not been measured, this value was also used in calculating the enthalpy of activation, $\Delta H^{\ddagger}(k_{-\mathrm{L}}) = 130 \pm 4$ kJ/mol, for the styrene 1-mer in ref 2. Thus the comparison of the enthalpy for TEMPO release from the styrene 1-mer and the styrene polymer is not affected by the value of $\Delta H^{\ddagger}(k_{\mathrm{L}})$.

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