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Mechanism of Living Free Radical Polymerizations with Narrow Polydispersity: Electron Spin Resonance and Kinetic Studies

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ABSTRACT: This work focuses on the mechanism of the *pseudoliving* free radical bulk polymerization of styrene, which produces narrow polydispersity resin, using nitroxide radicals to reversibly terminate the growing polymer chain. The polymerization kinetics and the rate of breaking of the nitroxide to polymer NO−C bond were studied. The polymerization gives an increase in molecular weight that is linear with conversion to high conversion, gives polydispersities that are narrow (<1.3) and relatively insensitive to conversion, and shows first-order kinetics in monomer concentration. Calculations demonstrate that the kinetics of polymerization greatly reduce the termination of the polymerization by the reaction of two growing chains, which is the predominant mechanism in conventional free radical polymerization. It is concluded that this nitroxide-mediated free radical polymerization is a living polymerization. To study the stability of the NO−C bond, model compounds, comprising a styrene unit terminated at either end with a benzoyloxy moiety and a nitroxide moiety, were prepared and characterized. These compounds were heated *in situ* in the ESR cavity to generate nitroxide radicals. Radical concentrations were followed as a function of time and temperature, and an activation energy for cleavage of the NO−C bond was calculated. A proposed mechanism fits the available kinetic data well, and measured activation energies for nitroxide compounds correlate with rates of polymerization.

Introduction

A number of workers[1−5] have experimented with reversible termination of growing polymer chains in free radical polymerizations, giving *pseudoliving* polymers that are capable of stepwise chain growth. In a recent article Georges et al. showed the remarkable progress that has been made in this field,[5] while Greszta et al. have reviewed some of the issues that constrain these living systems.[6] Otsu et al. have shown that *iniferters* form radicals that can both initiate polymerization and react reversibly with growing polymer chains, to produce polymers, but without narrow polydispersity.[1] Other studies have shown that nitroxide stable free radicals react with nearly diffusion-controlled rates with carbon-centered radicals[7] and with growing polymer chains[8] and act as polymerization inhibitors.[9] 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, producing low molecular weight oligomers.[2] Johnson et al.[10] have shown that computer modeling predicts narrow polydispersities using reversible termination under certain conditions. However, no experimental verification of these predictions was shown. Production of high molecular weight polymers with narrow polydispersities and high levels of conversion was not demonstrated.

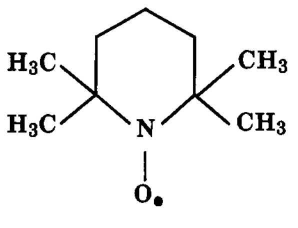
In independent work,[3−5,11,12] we have applied the concept of reversible termination, using a nitroxide stable free radical, such as TEMPO, to produce what we have described as a *pseudoliving* free radical polymerization system. This system can provide polymers having narrow polydispersities less than 1.3, with controlled stepwise growth for low molecular weight oligomers to high molecular weight polymers. This approach has been successfully applied not only to bulk homopolymerization[3−5,11] and block copolymerization[11] but also to suspension copolymerization[5] and emulsion homopolymerization.[12] This is one of only two approaches that has been successful in preparing polymers with narrow polydispersities by a free radical process. The second approach, recently shown by Mardare and Matyjaszewski,[13] makes use of a coordination catalyst, as well as TEMPO. However, the latter system requires purified reagents and strict removal of oxygen and water from the polymerization, which are not a concern in the process to be discussed.

Our previous electron spin resonance (ESR) studies have shown that the polymerization reaction kinetics are consistent with a reversible termination of the growing polymer chains by TEMPO.[4] This initial ESR work concentrated on kinetics of the first two steps of the polymerization: initiation followed by reversible termination with TEMPO.

This paper extends the *in situ* ESR studies of these pseudoliving polymerizations for the production of narrow polydispersity polymers, focusing on the reversible termination of the polymer chain and its influence on polymerization kinetics. We also show that the polymerization kinetics merit describing this polymerization process as a truly living polymerization.

Experimental Section

(a) Polymerizations. Bulk polymerizations were performed using benzoyl peroxide (BPO) initiator in styrene, with either 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO (**1**) or 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (3-carboxy-PROXYL) (**2**) stable free radicals. All reagents were used without purification, while solutions were Ar purged. The



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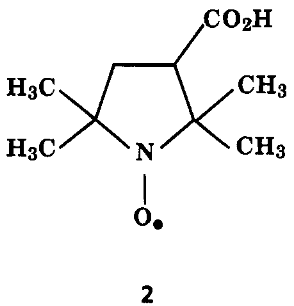

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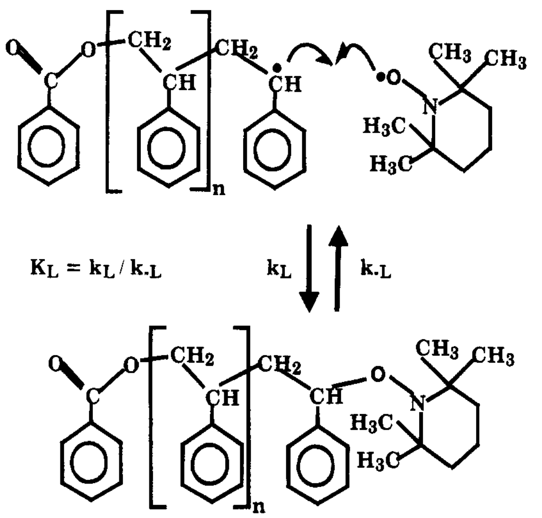
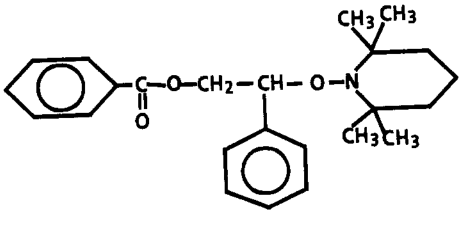


Figure 1. Reversible termination of growing polymer chain.

presence of air, however, had no observable effect on the polymerizations. Molecular weights were determined by gel permeation chromatography calibrated with polystyrene standards, using samples taken directly from the reaction mixture. Percent conversions were obtained from residual monomer analysis by gas chromatography.

(b) Preparation and Purification of Model Compounds. The model styrene 1-mers **3** and **4**, consisting of one styrene unit, terminated at one end with a benzoyloxy moiety and at the other end by a nitroxide (*n* = 0 in Figure 1), were prepared using **1** and **2**, respectively, with styrene and benzoyl peroxide (BPO). To prepare **3**, a solution of 3 g of TEMPO and 2.25 g of BPO (molar ratio of TEMPO to BPO = 1.6:1) in 11 g of styrene was heated under argon with stirring for 4 h using a 75 °C oil bath. Residual styrene was removed at room temperature with a stream of argon. The resulting mixture was first passed through a silica gel column with CH_2Cl_2 as the eluant, followed by a second column with 2% methanol in CH_2Cl_2, to give a slightly colored oil (**3**). To prepare **4**, 0.44 g of 3-carboxy-PROXYL (**2**) was dissolved in 10 g of styrene, which was heated to reflux using an oil bath at 140 °C, before adding 0.35 g of BPO (molar ratio of 3-carboxy-PROXYL to BPO = 1.6:1). After 1 min the reaction mixture was removed from the oil bath and cooled to room temperature. The excess styrene was removed in a stream of argon at room temperature. The reaction mixture was then passed through a silica gel column with 7% methanol in CH_2Cl_2 as the eluant, to give **4**.



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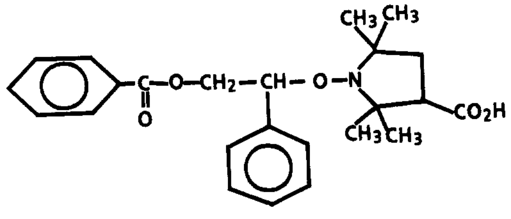

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Note added in proof. Following our preliminary publication of work with these styrene 1-mers at the American Chemical Society meeting in San Diego (published in the Division of Polymer Chemistry preprints[4]), Hawker reported the preparation of the styrene 1-mer with TEMPO, **3**, along with ^1H NMR spectra (Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185–11186).

(c) NMR Analysis. The model 1-mers were identified from their ^1H and ^{13}C NMR spectra obtained using a Bruker AMX400 spectrometer.

(d) ESR Studies. Spectra were collected using a Bruker ESP300 spectrometer and ER4111 variable temperature accessory. The model 1-mers **3** and **4** were dissolved in xylene to a concentration of 10^{-3} M and purged with Ar. Equal aliquots of these solutions were weighed into separate ESR tubes. One of the ESR tubes was then inserted into the variable temperature Dewar of the ESR spectrometer, which had been previously set to the desired temperature. At each temperature, the relative rate of formation of the nitroxide radical was measured from double integration of the ESR spectrum. Typically, 4 scans were used for each time point, and 10 points were collected over an 8 min interval. Plots of the observed concentration of nitroxide with time were linear over most of the 8 min. The linear portion of the curve was then used for a linear regression to give a best-fit line, which is the rate of nitroxide disappearance at that temperature. The procedure was then repeated using another ESR tube at a higher temperature. The experiment was repeated at 10 K intervals, from room temperature to 380 K. These relative rates were used to calculate activation enthalpies for the homolysis of the nitroxide–polymer NO–C bond. The kinetic analysis will show that there is no reason to calculate absolute rates. To achieve accurate activation energies for each of the 1-mers, the relative rate measurements were made on identical samples of the 1-mer. In order to do this, equal weight aliquots from a single standard solution of 1-mer were placed in the ESR sample tubes, using a new aliquot at each temperature.

Results and Discussion

In our previous work,[3–5,11,12] we have shown that narrow polydispersity, high molecular weight polymers can be obtained by a modified free radical polymerization in which a nitroxide stable free radical, such as TEMPO, has been added. In a typical bulk polymerization, TEMPO and BPO, in a 1:2 molar ratio, are heated together in styrene at 95 °C for 3.5 h. At this point, there is formation of neither polymer nor oligomers, as shown by GPC. Subsequent heating at 123 °C for 69 h yields a polymer with a polydispersity of 1.26 and M_w of 10 000.[5] ESR[4] was used to study the kinetics and mechanism of the first step of the living polymerization: heating at 95 °C. This work showed that TEMPO was involved in a promoted decomposition of BPO. Thus, there are two routes to initiating radical formation, given by reaction 1 for the usual thermal homolysis of BPO and reaction 2 for the promoted decomposition:

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

$$T^\bullet + I \xrightarrow{k_{pr}} X + R^\bullet \tag{2}$$

where $T^\bullet$ = TEMPO radical (more generally, $T^\bullet$ will be used to denote any nitroxide radical), I = BPO, X = intermediate products, and $R^\bullet$ = benzoyloxy radical. Through a series of intermediate steps that have not been fully studied,[14] X was identified to result in the formation of a nitrone and benzoate anion.[4] The initiation of the polymer chains then follows the usual kinetics, given by reaction 3.

$$R^\bullet + M \xrightarrow{k_i} P_1^\bullet \tag{3}$$

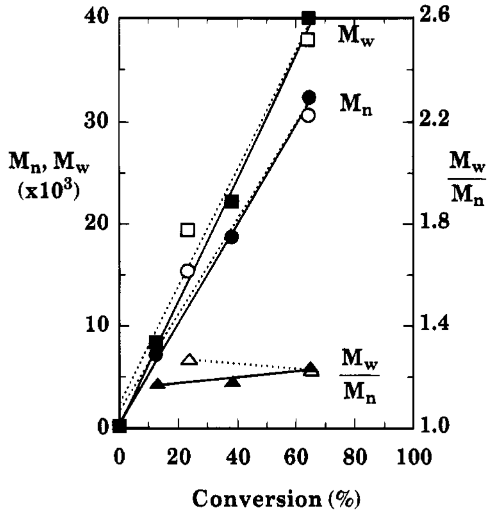

Figure 2. Polymer molecular weights (M_n and M_w) and polydispersity (M_w/M_n) plotted with conversion for bulk polymerization with $[\text{nitroxide}]_0 = 0.0186$ M, $[\text{BPO}]_0 = 0.0125$ M. Open symbols indicate 3-carboxy-PROXYL nitroxide was used; closed symbols, TEMPO nitroxide: (■, □) M_w; (●, ○) M_n; (▲, △) polydispersity = M_w/M_n.

Here, M is monomer and $P_1^\bullet$ is the polymer radical, $P_n^\bullet$, with $n = 1$. Using ESR, it was shown that the polymer chain that was initiated was trapped very rapidly by the TEMPO radical, given by reaction 4, and illustrated

$$P_n^\bullet + T^\bullet \xrightleftharpoons{K_L = k_L/k_{-L}} L_n \tag{4}$$

in Figure 1. Here L_n is the polymer chain that has been reversibly terminated by TEMPO, referred to as the "living polymer chain" to distinguish it from the growing polymer chain, $P_n^\bullet$. At 95 °C, there is little polymerization observed by GPC (there may be some oligomer formation), so that all of the chains are terminated by TEMPO as L_n, where n is on the order of 1–4. The kinetics observed by ESR are consistent with the rate of trapping being nearly diffusion controlled. Bowry et al.,[7] have suggested that the reaction of any nitroxide with a sterically unhindered radical is approximately

$$k_L = 5.03 \times 10^9 \exp\{-3772/RT\} \text{ M}^{-1} \text{ s}^{-1} \tag{5}$$

On the other hand, k_{-L} is the rate of homolytic cleavage of the NO–C bond, to give the growing chain radical and the nitroxide radical. At 95 °C this rate constant must be very small, since no polymerization is observed. We have shown that polymerization to narrow polydispersity polymer proceeds as the temperature is raised above about 120 °C,[3-5] due to the thermal activation and cleavage of the NO–C bond.

Initially, we had assumed that the two-step process (formation of the living chains at lower temperature (95 °C) where there is virtually no polymerization, followed by raising the temperature to above 120 °C to begin polymerization) was necessary for the production of narrow polydispersity polymers. This is analogous to ionic living polymerization, where the living chain is generated first, before polymerization, resulting in all chains beginning to grow at the same time. However, the BPO initiator, styrene, and the stable free radical can be mixed together at a temperature above 120 °C directly. Figure 2 shows the step-growth increase in molecular weight for two living free radical polymerizations performed using this latter method at 135 °C: one using the TEMPO stable free radical (**1**) and the other using 3-carboxy-PROXYL (**2**). Polydispersities of less than 1.3 were seen for all polymers. Reactions were stopped at about 70% conversion due to the difficulty of stirring the reaction mixtures after this point.

Key to the success of the one-step process is, firstly, that the rate of benzoyloxy radical formation and initiation is very rapid at temperatures above 120 °C. All the BPO is consumed within about 10 min at 120 °C and within about 1 min at 150 °C. As a consequence, all of the chains are initiated in a very short time period compared to the rate of polymerization. Secondly, in this short period of chain initiation, the rate of polymerization of the initiated chains is much slower than the rate after all the chains have formed. The reason for this can be seen from the kinetic analysis of the polymerization rate, as will be discussed in a later section. The result of the initial slower polymerization is that the divergence of chain lengths is small once initiation is completed.

Once a living chain L_n has been formed, the rate of polymerization at elevated temperatures will still be determined by the usual propagation steps:

$$P_n^\bullet + M \xrightarrow{k_p(n)} P_{n+1}^\bullet + 1^\bullet \tag{6}$$

This is controlled by the usual rate constants for propagation, $k_p(n)$ for each $P_n^\bullet$. The assumption here is that the presence of any free TEMPO radical does not affect reaction 6 and that monomer does not insert into the NO–C bond in a concerted reaction. If insertion does occur, then we would also have to consider reaction 7. Here $k_{p_i}(n)$ would be the corresponding

$$L_n + M \xrightarrow{k_{p_i}(n)} L_{n+1} + 1 \tag{7}$$

propagation rate constants for insertion. For the purposes of this paper, the result of including reaction 7 for insertion is only that

$$k_{p,\text{obs}}(n) = k_p(n) + k_{p_i}(n)[L_n]/[P_n^\bullet] \tag{8}$$

Since $[L_n]$ and $[P_n^\bullet]$ are constant after the first few minutes of the polymerization, once all chains have been initiated, this only results in an altered value for the rate constant. At this point, there is no evidence of a contribution of reaction 7 to the rate of polymerization.

The termination step for polystyrene is assumed to be unchanged by the addition of stable radicals and is given by

$$P_n^\bullet + P_{n'}^\bullet \xrightarrow{k_t(n,n')} \text{dead polymer} \tag{9}$$

Here $k_t(n,n')$ represents the rate constant for termination of two chain radicals with n and n' units. Data will be shown below for a bulk living free radical polymerization with TEMPO stable free radical as the reversible terminating agent. The $[P_n^\bullet]$ in this bulk polymerization, calculated from the observed rate of polymerization, is 1×10^{-8} M at 135 °C. For k_t we use k_{t_0}, the termination rate constant at low conversion for the usual bulk polymerization,[15] which is assumed to be unchanged here with a value of 1×10^8 M^{-1} s^{-1}. The rate of termination is then given by

$$-d[P_n^\bullet]/dt = k_t[P_n^\bullet]^2 \tag{10}$$

For the bulk living free radical polymerization with styrene this gives an initial value for $-\mathrm{d}[\mathrm{P}_n{}^\bullet]/\mathrm{d}t$ of about 10^{-8} M s^{-1}. Comparing this rate to the rate of propagation, given by reaction 6, using the usual value of k_p of 3790 M^{-1} s^{-1} for bulk styrene polymerization at 135 °C,[16] gives a rate of polymerization to termination ratio of 3×10^4 at the beginning of the reaction. That is, 3×10^4 monomer units add for every chain that terminates.

As the polymerization proceeds, this ratio increases, since k_t decreases rapidly with conversion, particularly above the point at which chains reach the entanglement limit. Thus at 70% conversion, k_t is on the order of 10 times smaller than k_{t_0}.[17] We can thus estimate that for an M_n of 30 000 at 70% conversion, less than 1 in 100 chains are terminated to dead polymer! Indeed, it is known that the rate of termination for polystyrene is controlled, in the entanglement limit, by the diffusion of short polymer radicals to long polymer radicals, since only the short chains have sufficient mobility for termination.[18] Since there is a much narrower polydispersity in the nitroxide-controlled polymerization, as initiation is complete in the first few minutes, and since thermal polymerization is not significant,[19] there are very few of these short chains that could terminate the long polymer chains. The rate constant for termination is thus reasonably expected to be much less important than in the conventional free radical polymerization, with a value smaller than that calculated above. In terms of the kinetics, the termination step of reaction 9 can be ignored for these free radical polymerizations mediated by stable free radicals, under these conditions. This is a direct contrast to conventional free radical polymerization, where reaction 9 dominates the termination of growing polymer chains.

The rate of polymerization in the free radical polymerization with the stable radical present can be calculated from reactions 4 and 6. The resultant rate is given by eq 12, which is derived from the usual polymerization rate given in eq 11. However, what is unique to a

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_P[\mathrm{M}]P \tag{11}$$

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_P[\mathrm{M}]L\left(\frac{1}{K_L T_\mathrm{e}}\right) \tag{12}$$

nitroxide-mediated free radical polymerization is that here $\Sigma[\mathrm{P}_n{}^\bullet]$, which we call P, is constant throughout the polymerization, once all of the living chains have been formed (in the first few minutes of the polymerization). Similarly, $\Sigma[\mathrm{L}_n]$, which we call L, is also a constant. The rate is proportional not only to the propagation rate constant k_p and to the concentration of monomer, M, but also to L, $1/K_L$, and $1/\mathrm{T}_\mathrm{e}$. T_e is the free TEMPO concentration (not the initial TEMPO concentration), after all chains have been reversibly terminated by TEMPO. Equation 12 differs from that of conventional free radical polymerization by the factor within the brackets, and with the replacement of the concentration of the growing polymer chain, P, with the concentration of the *living* chain, L.

While L is clearly much larger than P would be in the usual bulk polymerization of styrene, the term in brackets is always $\ll 1$, due to the large value of K_L. This results because bond-breaking, which produces the growing polymer chain, will always be much slower than the essentially diffusion-controlled trapping of the chain. Early in the one-step polymerization reaction, $[\mathrm{T}^\bullet]_t \simeq [\mathrm{T}^\bullet]_0$, and the rate of polymerization is very slow. As initiation proceeds, every chain that is initiated very rapidly consumes one molecule of TEMPO.[4] Thus, in the first few minutes of the reaction, $[\mathrm{T}^\bullet]_t$ rapidly decreases, dramatically increasing the rate of polymerization. For the polymerizations shown in Figure 2, $[\mathrm{T}^\bullet]_t$ drops from its initial value of about 0.02 M, to a value that is close to its equilibrium value given by K_L in eq 4, as $[\mathrm{T}^\bullet]_0 \simeq L = 2f_\mathrm{d}[\mathrm{I}]_0$. Thus, the large amount of excess TEMPO during the initiation period slows polymerization. Once initiation is completed, the TEMPO has reached a much lower concentration, which remains constant during the polymerization. Because of this, there is a short induction period at the start of the reaction (<2 min), where the large excess of TEMPO slows polymerization. This allows chains to be initiated within a period of time where the polymerization is relatively slow. In essence, this results in a low dispersion of chain lengths at the end of the initiation period, as if all chains begin polymerization at about the same time. This very short induction period would be very difficult to observe. Although the experimental data are limited, at 135 °C there is little indication of an induction period in Figures 2 and 3, within the limits of error in measurement of conversion. If there is an induction period it must be less than 30 min, which is dramatically shorter than the long induction periods that we have observed at lower temperatures.[3,4]

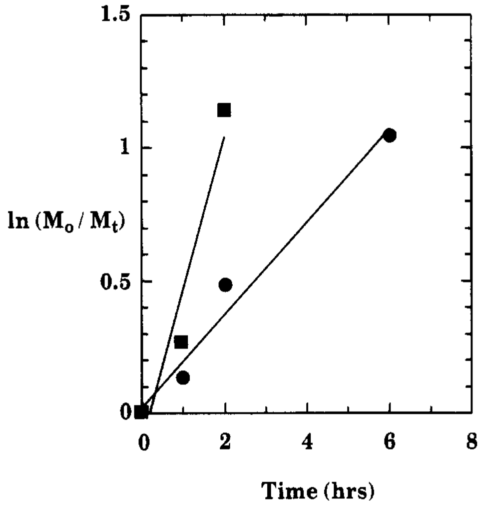

Figure 3. Polymerization with time for bulk polymerization with $[\text{nitroxide}]_0 = 0.0186$ M, $[\mathrm{BPO}]_0 = 0.0125$ M: (■) 3-carboxy-PROXYL, $k_\mathrm{obs} = 1.6 \times 10^{-4}$ s^{-1}; (●) TEMPO, $k_\mathrm{obs} = 4.9 \times 10^{-5}$ s^{-1}.

Once the short induction period is finished, the rate of polymerization becomes constant and is given by the integration of eq 12, with T_e and L as constants:

$$-\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}_0]}\right) = k_\mathrm{p}\left(\frac{L}{K_L T_\mathrm{e}}\right)t \tag{13}$$

Unfortunately, it is difficult to get an accurate value of T_e, as it is the small difference between the number of chains formed, L, and the amount of TEMPO added. The number of chains formed can be estimated from the molecular weight of the polymer, but due to uncertainties in molecular weights determined by GPC, and the sensitivity of this calculation to high or low molecular weight polymer far from M_n, it is difficult to get an accurate value. Similarly, for T_e, the amount of nitroxide added at the start of the reaction is known; however, the purity of the nitroxides in terms of the number of spins is difficult to determine to sufficient accuracy, as are the effects of side reactions of TEMPO during the polymerization. If these calculations are attempted, then the excess stable free radical varies between about 0 and 20% of the initial value for the various experiments. In the former case, the amount of TEMPO is now governed only by the small equilibrium amount from reaction 4. In this case, using the procedure outlined below, and eq 13, $k_{-L} \simeq 10^{-6}$ s^{-1} ($K_L \simeq 1.7 \times 10^{15}$ M^{-1}). In the latter case, $k_{-L} \simeq 1$ s^{-1} ($K_L \simeq 1.7 \times 10^{9}$ M^{-1}). Another alternative is to measure an absolute concentration of stable free radical during the polymerization at 135 °C, using ESR to measure the number of spins directly. This work will be the subject of a future publication.

One can, however, define a polymerization rate constant k_{obs}, as $k_pL/(K_LT_e)$, or equally as k_pP, since all of the terms in the brackets are constant after the first 10 min induction period. Typical plots of eq 13 using k_{obs} are shown in Figure 3 for polymerizations that utilize either TEMPO or 3-carboxy-PROXYL, at the same initial ratio of the nitroxide to BPO initiator. The plots are typically linear up to the highest conversion (70%) and molecular weight (about 60 000) in these two polymerizations. From the slopes of these lines k_{obs} is calculated to be approximately 4.9×10^{-5} s^{-1} for TEMPO and 1.6×10^{-4} s^{-1} for 3-carboxy-PROXYL. These rates can be used to calculate the stationary concentration of free growing polymer chains, P, which is about 1×10^{-8} M for TEMPO and 3×10^{-7} M for PROXYL. This very low concentration results in insignificant termination of growing chain to dead polymer, as was shown above.

The polymerization with 3-carboxy-PROXYL appears to be about 3 times faster than that with TEMPO in this experiment. As noted above, however, changes in L and T_e could account for some of these differences, particularly if the number of spins per mole of nitroxide were slightly different in 3-carboxy-PROXYL compared to TEMPO. Indeed, at higher nitroxide:BPO ratios of 2.5:1 the rate of polymerization is only marginally faster with 3-carboxy-PROXYL compared to TEMPO, with k_{obs} of 7.8×10^{-5} s^{-1} for the former and 7.0×10^{-5} s^{-1} for the latter. This difference, at the two different ratios could indicate a slightly different purity of 3-carboxy-PROXYL in terms of the number of spins per mole of nitroxide, which would change the amount of excess nitroxide slightly. There are also a number of side reactions that can involve nitroxides, particularly in the initiation steps of the polymerization.[4] It may be that the two radicals behave slightly differently in this respect, leading to a difference in the amount of excess nitroxide. The amount of free growing chain, controlled by the equilibrium of reaction 4, controls the rate of polymerization. If there is a difference in the amount of excess nitroxide for the two nitroxides, for the same nominal initial concentration, the rate of polymerization will change. The effect of this difference in the amount of excess nitroxide on the rate of polymerization would be sensitive to the nitroxide/BPO ratio, as observed.

In order to clarify this picture and to better understand the differences between 3-carboxy-PROXYL and TEMPO, model studies were undertaken. The rate of polymerization is controlled by K_L, k_p, and T_e. While it is clear that k_p is fixed for a particular monomer and that T_e is fixed by the initial conditions (temperature, BPO:nitroxide:monomer ratio), it should be possible to change K_L. K_L depends on k_L, which is essentially diffusion controlled, and k_{-L}, which depends on the strength of the NO−C bond. While the former might be reduced by increasing steric hindrance of the nitroxide, most nitroxides appear to give similar values for k_L.[7] On the other hand, the strength of the NO−C bond might be changed by varying the nitroxide. To study this bond strength, model compounds, consisting of one styrene unit, terminated at one end with a benzoyloxy moiety, and at the other end by a nitroxide ($n = 0$ in Figure 1), were synthesized, isolated, and characterized by NMR. These compounds provide models of a polystyrene *living* 1-mer.

The xylene solutions of the 1-mers were heated *in situ* in a sample tube in the ESR cavity, forming free nitroxide radicals. Initially, ESR showed very little free nitroxide radical. The concentration of the released nitroxide radical was followed over time using ESR to determine the rate of bond breaking for the NO−C bond. By systematically varying temperature, the activation energy for the breaking of the NO−C bond was also calculated. In this way it was possible to measure activation energies with different terminal nitroxides.

Figure 4 shows representative curves of the concentration of free TEMPO radical as a function of time. The plots are typically linear over the first few minutes, then begin to show curvature toward a slower increase in radical concentration. The kinetics of this process are governed by the release of the nitroxide, as shown in reaction 14, by the capture of the 1-mer radical by the nitroxide, given by reaction 15, by the termination by combination or disproportionation, shown by reaction 16, and by other termination processes, as for example, those governed by reactions 17−19. Here H−S is a source of H$^\bullet$, which would most likely be the solvent.

$$\mathrm{P_1{-}T} \xrightarrow{k_{-L}} \mathrm{P_1}^{\bullet} + \mathrm{T}^{\bullet} \qquad (14)$$

$$\mathrm{P_1}^{\bullet} + \mathrm{T}^{\bullet} \xrightarrow{k_L} \mathrm{P_1{-}T} \qquad (15)$$

$$\mathrm{P_1}^{\bullet} + \mathrm{P_1}^{\bullet} \xrightarrow{k_t(1,1)} \mathrm{D_1} \qquad (16)$$

$$\mathrm{P_1}^{\bullet} + \mathrm{H{-}S} \rightarrow \mathrm{P_1{-}H} + \mathrm{S}^{\bullet} \qquad (17)$$

$$\mathrm{P_1}^{\bullet} + \mathrm{S}^{\bullet} \rightarrow \mathrm{P_1{-}S} \qquad (18)$$

$$\mathrm{S}^{\bullet} + \mathrm{T}^{\bullet} \rightarrow \mathrm{S{-}T} \qquad (19)$$

Clearly, the kinetics are very complicated and include a number of rate constants that are not known. Unfortunately, due to the absence of excess TEMPO radical to trap $\mathrm{P_1}^\bullet$, these termination processes become significant. Initially, at $t = 0$, $[\mathrm{P_1}^\bullet] = [\mathrm{T}^\bullet] = 0$, $[\mathrm{P_1T}] = [\mathrm{P_1T}]_0$, and the kinetics are simple, given only by eq 14. We would thus expect initially that the rate of formation of $\mathrm{T}^\bullet$ would be given by

$$\mathrm{d}[\mathrm{T}^\bullet]/\mathrm{d}t = k_{-L}[\mathrm{P_1{-}T}]_0 \qquad (20)$$

Integration gives

$$[\mathrm{T}^\bullet] = k_{-L}[\mathrm{P_1{-}T}]_0 t \qquad (21)$$

However, as the concentration of $[\mathrm{P_1}^\bullet]$ increases, the reverse reaction (15) and the termination reactions (16)

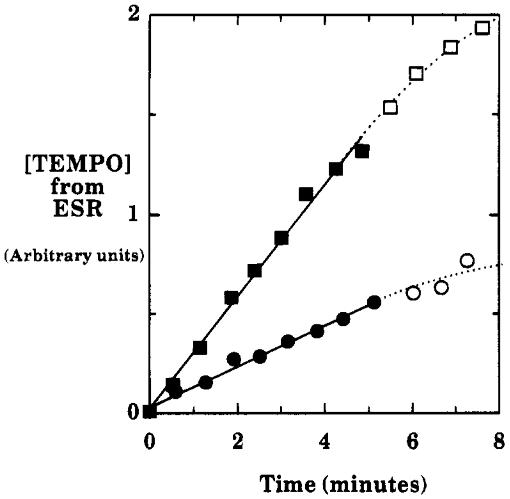

Figure 4. Release of TEMPO nitroxide radical with time from styrene 1-mer adduct (**3**): (■, □) 370 K; (●, ○) 360 K. Data represented by filled symbols were used for calculation of initial rates.

to (19) become more important. Using the above estimates of k_{-L} suggests that this simple kinetic view of eqs 20 and 21 will not be adequate over the first few minutes. For the maximum rate, $k_{-L} = 1\ \mathrm{s}^{-1}$, with $[P_1{-}T]_0 = 10^{-3}$ M, the equilibration time for reactions 14 and 15 is on the order of 10^{-3} s. For the minimum rate, $k_{-L} = 10^{-6}\ \mathrm{s}^{-1}$, it is on the order of 1 s. We observe the increase in $[T^•]$ for $>10^3$ s. Therefore, both reaction 14 and the reverse reaction, reaction 15, must be considered, as well as the coupling of two $P_1^•$, reaction 16. As we will show, to a good first-order approximation, we can ignore reactions 17–19 in analyzing the first few minutes of the release of the $T^•$ radical. However, it is likely that these reactions cause the observed curvature of the reaction profiles at longer reaction times, shown in Figure 4.

Once equilibrium is established, reactions 14 and 15 are equal in rate, ignoring reaction 16. Now, reaction 15 is known to be essentially diffusion controlled for nitroxides, as discussed above, with k_L on the order of $10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. It is not clear what $k_t(1,1)$ should be, in eq 16. At most, it too will be essentially diffusion controlled, with a rate similar to k_L. On the other hand, in the polymerization of styrene, the initial k_t is $k_{t_0} = (4{-}8) \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, in the temperature range utilized for these studies. However, k_{t_0} will likely underestimate $k_t(1,1)$, as high molecular weight polymer is always present in a typical free radical polymerization. In addition, steric hindrance to coupling should be much less important for $k_t(1,1)$ than for k_{t0} measured from a polymerization. Thus $k_t(1,1)$ likely lies between k_{t_0} and k_L. Also, as reaction 16 removes $P_1^•$ from the system, and as $[T^•]$ increases, reaction 16 becomes increasingly slower compared to reactions 14 and 15. An approximate model for the subsequent time evolution of the initial equilibrium between reactions 14 and 15 is, thus, of a slow reduction in $[P_1^•]$ compared to the fast equilibrium.

Thus

$$d[P_1^•]/dt = (k_{-L}[P_1T]_0 - k_L[P_1^•][T^•]) - k_t[P_1^•]^2 \qquad (22)$$

Since the term in brackets is a fast equilibrium compared to $k_tP_1^2$, equation 22 becomes

$$d[P_1^•]/dt = -k_t[P_1^•]^2 \qquad (23)$$

Integration of this equation gives

$$[P_1^•] = \frac{[P_1^•]_0}{[P_1^•]_0k_tt + 1} \qquad (24)$$

Here, $[P_1^•]_0$ is the initial equilibrium $[P_1^•]$ from reactions 14 and 15. Now, from the fast equilibrium, we can write

$$[T^•] = \frac{k_{-L}[P_1T]_0}{k_L[P_1^•]} \qquad (25)$$

Substitution of $[P_1^•]$ from eq 24 into eq 25, yields

$$[T^•] = \frac{k_{-L}k_t[P_1T]_0}{k_L}t + \frac{k_{-L}[P_1T]_0}{k_L[P_1^•]_0} \qquad (26)$$

The first term shows the time dependence, while the second term is just the initial $[T^•]$, before any $P_1^•$ is consumed. Thus $[T^•]$ increases linearly with time. If we set $k_t = k_L$, then we can calculate the minimum time to consume the P_1T (as $k_t \leq k_L$). For the range of $k_L = 1$ to $10^{-6}\ \mathrm{s}^{-1}$, 1% of $[P_1T]_0$ is consumed in the range of 10^{-2} s to 10^4 s, with this assumption. These times may be up to 50 times larger if k_t is equal to k_{t_0} from styrene polymerizations. Depending on temperature, we observe on the order of 1–10% $[P_1T]_0$ consumed in 10^3 s, somewhere in the middle of the calculated range.

Finally, the possibility of transfer of $P_1^•$ to solvent, reaction 17, should be considered. Using the known transfer constant to xylene and the most likely value of k_{-L}, which lies toward the middle of the range 1 to $10^{-6}\ \mathrm{s}^{-1}$, one can show that the transfer is not important, until enough $P_1^•$ is consumed so that reaction 17 becomes comparable to reaction 16. This will ultimately happen, as coupling depends on $[P_1^•]^2$, while transfer depends on $[P_1^•]$. At that point, the subsequent reaction steps (17) to (19) can reduce the amount of $T^•$, which will initially be noted as a curvature in the linear production of $T^•$, as observed. This is the most likely cause of the observed curvature, as we know that the drop in $[P_1T]$, which is the other possible cause of this curvature, is less than 10% in the linear region of the plots in Figure 4.

Using this initial rate, it was possible to measure a relative value of $k_{-L}k_t/k_L$, from eq 26 for a nitroxide-terminated 1-mer. By repeating the experiment, the relative value of this term was determined as a function of temperature. A similar procedure was used for a standard sample of 3-carboxy-PROXYL–styrene–BPO 1-mer. The relative rates for each 1-mer, as a function of temperature, do allow the calculation of the activation barrier to break the NO–C bond, in the usual manner:

$$-\ln\left(\frac{k}{T}\right) = \left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(\frac{-\Delta H^{\ddagger}}{RT}\right) \qquad (27)$$

The observed $\Delta H^{\ddagger}$ is given by equation (28).

$$\Delta H^{\ddagger} = \Delta H_{k_{-L}}{}^{\ddagger} + \Delta H_{k_t}{}^{\ddagger} - \Delta H_{k_L}{}^{\ddagger} \qquad (28)$$

Here $\Delta H_{k_{-L}}{}^{\ddagger}$, $\Delta H_{k_t}{}^{\ddagger}$, and $\Delta H_{k_L}{}^{\ddagger}$ are the activation energies for $k_{t_{-L}}$, k_t, and k_L from eq 26. Now, $\Delta H_{k_L}{}^{\ddagger} \simeq 4$ kJ/mol, as this reaction step is essentially diffusion controlled.[7] The minimum possible value of $\Delta H_{k_t}{}^{\ddagger}$ would be that where k_t is also essentially diffusion controlled, with $\Delta H_{k_t}{}^{\ddagger} \simeq 4$ kJ/mol. The maximum possible value would be that where $\Delta H_{k_t}{}^{\ddagger}$ is equal to the activation

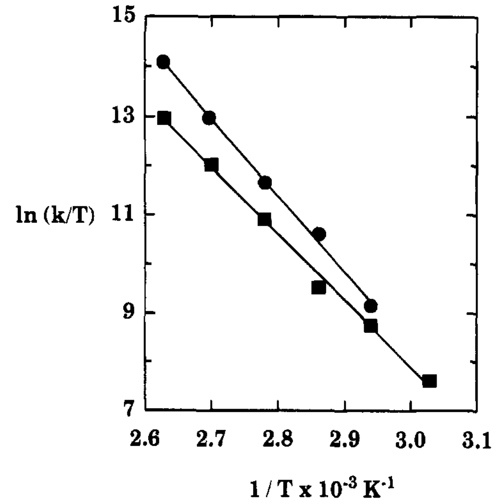

Figure 5. Activation energy plot for the breaking of the NO–C bond of the styrene 1-mer with TEMPO (**3**) and 3-carboxy-PROXYL (**4**): (■) 3-carboxy-PROXYL, $\Delta H^{\ddagger} = 113 \pm 4$ kJ/mol; (●) TEMPO, $\Delta H^{\ddagger} = 130 \pm 4$ kJ/mol.

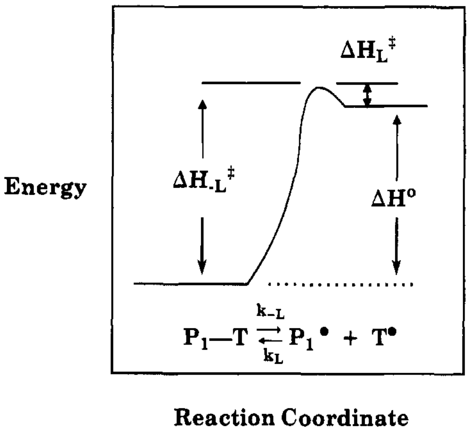

Figure 6. Energy profile for equilibrium of free growing chain with nitroxide radical (vibrational energies are not shown for clarity).

energy for k_{t_0}, or $\Delta H_{k_t}^{\ddagger} = 14.5$ kJ/mol.[15] Thus, if we assume the observed $\Delta H^{\ddagger} \simeq \Delta H_{k_{-L}}^{\ddagger}$, then the desired enthalpy of activation, $\Delta H_{k_{-L}}^{\ddagger}$, may have some systematic error:

$$\Delta H_{k_{-L}}^{\ddagger} = \Delta H^{\ddagger} - (0 \text{ to } 10.5)\ \text{kJ/mol} \qquad (29)$$

Note, however, that the systematic error will be approximately the same for the different nitroxides, even if there are changes in $\Delta H_{k_t}^{\ddagger}$ and $\Delta H_{k_L}^{\ddagger}$. Thus the difference in relative values of $\Delta H_{k_{-L}}^{\ddagger}$ for the different nitroxides will be nearly independent of this systematic error.

The linear plots of eq 27 are shown in Figure 5 for the two 1-mers. The calculated values of $\Delta H^{\ddagger}$ are 130 ± 4 kJ/mol for TEMPO and 113 ± 4 kJ/mol for 3-carboxy-PROXYL. On the basis of these measured activation energies, it is expected that the rate of styrene polymerization should be faster with 3-carboxy-PROXYL than with TEMPO, all other factors being equal, due to the weaker NO–C bond. This confirms the general trend of faster polymerization rates with 3-carboxy-PROXYL compared to TEMPO, although this does not explain why the difference in rates becomes smaller as the nitroxide to BPO ratio increases.

Figure 6 shows the relation between the calculated activation enthalpy for bond-breaking, $\Delta H^{\ddagger}$, with the bond energy $\Delta H°$ for the NO–C bond. The two values are essentially equivalent, as the reverse step, the trapping reaction of the two radicals, is nearly a diffusion-controlled process. The activation energy is estimated to be only about 4 kJ/mol for typical nitroxide trapping reactions, from experimental data.[7] This value is actually slightly smaller than the theoretical value for diffusional activation in organic solvents, which is about 8 kJ/mol for *p*-xylene, for example.[20] It is clear that the trapping reaction itself has little activation energy, except this diffusional activation.

In other work, we have shown that the bond dissociation enthalpy of nitroxides trapping benzyl radicals, structurally similar to the 1-mers described here, can be estimated from the gas-phase heats of formation determined from MOPAC semiempirical calculations.[5,21] From these calculations the bond dissociation enthalpies were estimated as 92 kJ/mol for TEMPO and 71 kJ/mol for unsubstituted PROXYL (the latter was used to simplify the calculation) by AM1, and 109 and 79 kJ/mol, respectively, by PM3.[21] The difference in the calculated value for TEMPO and PROXYL is 21 (30) kJ/mol for AM1 (PM3), compared to the observed difference of 17 ± 6 kJ/mol for TEMPO and 3-carboxy-PROXYL, in reasonably good agreement.

The calculated values are somewhat smaller than the observed values. However, there is reasonably good agreement, despite the lack of the 3-carboxyproxyl group in the calculations. The observed offset of the calculated and observed values could arise from the effect of the 3-carboxy group, from the fact that the calculations were for the gas phase at 298 K, while the measured values were in solvent (xylene) at elevated temperatures, or simply due to the difficulty in accurately predicting heats of formation for the NO$^{\bullet}$ and NOC moieties, which may not be accurately represented by the MOPAC parametrization. There is a significant difference in the calculated values depending on the type of calculation used. In addition, if there is indeed a slight systematic error according to eq 29, then this would bring the two sets of values more in agreement.

Conclusions

In nitroxide-controlled free radical polymerizations, it has been shown that polymerization is by a step-growth increase in molecular weight that is linear with conversion up to 70% conversion, polydispersities are narrow (<1.3) and relatively insensitive to conversion, and polymerizations are first-order in monomer concentration. Calculations also show that the kinetics of the reaction limit the usual irreversible termination by dead polymer, occurring by reaction of two growing chain radicals, to on the order of only 1 in 100 chains for a molecular weight of 30K. It is concluded that this free radical polymerization is a living polymerization.

The rate of polymerization is controlled by the usual rate of propagation, as well as the stationary concentration of living chains, the excess nitroxide radical, and the reversible equilibrium of the capped living polymer radical, with the growing polymer chain and free TEMPO radical. Using model styrene 1-mers capped by either TEMPO or 3-carboxy-PROXYL and ESR to follow the formation of the released nitroxide radical, it is shown that this equilibrium is controlled by the breaking of the nitroxide–polymer NO–C bond. The activation enthalpy and bond energy for breaking this bond are dependent on the structure of the nitroxide, with values of 130 ± 4 kJ/mol for TEMPO and 113 ± 4 kJ/mol for 3-carboxy-PROXYL for styrene. The bond energies are in reasonable agreement with semiempirical molecular orbital calculations. Lower bond enthalpies result in a faster polymerization rate, all other factors being equal.

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References and Notes

(1) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127–132. Endo, K.; Murata, K.; Otsu, T. *Macromolecules* **1992**, *25*, 5554–5556.

(2) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Patent 4,581,-429. Rizzardo, E. *Chem. Aust.* **1987**, *54*, 32.

(3) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Polym. Mater. Sci. Eng.* **1993**, *68*, 6–7. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. K.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987–2988. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. *Macromolecules* **1994**, *27*, 7228–7229.

(4) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Polym. Mater. Sci. Eng.* **1993**, *68*, 8–9. Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316–5320. Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (1), 797–798.

(5) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66–71.

(6) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638–644.

(7) Beckwith, A. L. J.; Bowry, V. W.; OLeary, M.; Moad, G.; Rizzardo, E.; Solomon, D. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1003–1004. Beckwith, A. L. J.; Bowry, V. W. *J. Org. Chem.* **1988**, *53*, 1632–1641. Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. H. *J. Am. Chem. Soc.* **1992**, *114*, 4983–4992.

(8) Rizzardo, E.; Solomon, D. H. *Polym. Bull.* **1979**, *6*, 529–534. Moad, G.; Rizzardo, E.; Solomon, D. H. *J. Makromol. Sci.* **1982**, *A17* (1), 51–59.

(9) Moad, G.; Rizzardo, E.; Solomon, D. H. *Polym. Bull.* **1982**, *6*, 589–593. Hallensleben, M. L.; Wibowo, T. S.; Wurm, H. *Polym. Bull.* **1990**, *24*, 59–62.

(10) Johnson, C. H.; Moad, G.; Solomon, D. H.; Spurling, T. H.; Vearing, D. J. *Aust. J. Chem.* **1990**, *43*, 1215–30.

(11) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 582. Georges, M. K.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *Macromol. Symp.* **1994**, *88*, 89–103.

(12) Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 675.

(13) Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 645–649.

(14) Moad, G.; Rizzardo, E.; Solomon, D. H. *Tetrahedron Lett.* **1961**, *22*, 1165–1168.

(15) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1345–1371.

(16) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; pp 67–79.

(17) Friis, N.; Hamielec, A. E. *ACS Symp. Ser.* **1976**, *24*, 82.

(18) O'Shaughnessy, B.; Yu, J. *Macromolecules* **1994**, *27*, 5067–5078.

(19) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 870–871.

(20) *Physico-Chemical Constants of Pure Organic Compounds*; Timmermans, J., Ed.; Elsevier Publishing: New York, 1978; p 168.

(21) Kazmaier, P. M.; Moffat, K. A.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K. *Macromolecules* **1995**, *28*, 1841–1846. Note that the AM1 and PM3 calculated values of this reference supplant the initial calculations reported in ref 5.

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