The Role of Thermal Initiation in Nitroxide Mediated Living Free Radical Polymerizations

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(Received December 24, 1996)

The BPO initiated "living" polymerization of styrene in the presence of nitroxide is not consistent with the recently proposed steady-state mechanism, which requires constant nitroxide and polymer radical concentrations, and equal initiation and termination rates. It is shown that none of these conditions are met. The data is consistent with a polymerization rate that is dominated by nitroxide, not by the rates of thermal initiation and termination. Further, the use of agents that reduce thermal initiation shows that thermal initiation is not necessary to ensure that the polymerization proceeds, nor to ensure fast rates.

Nitroxide mediated polymerizations have generated a surge of interest,[1-10] since Georges et al.[2] showed that narrow polydispersities were possible with styrene and dienes. The established mechanism is based on an equilibrium between growing and dormant chains:[3,4,6,7,11]

$$K = k_L / k_{-L}$$

$$P_n^\bullet + T^\bullet \underset{\longleftarrow}{\xrightarrow{\qquad}} L_n \tag{1}$$

$P_n^\bullet$, $T^\bullet$ and L_n are growing polymer radicals, nitroxide radicals, and dormant polymer chains. We denote this as the *equilibrium* mechanism. Veregin et al.[3,4] showed that the rate is:

$$R_p = k_p\,[P^\bullet]\,[M] = k_p\,\frac{[L_n]}{K\,[T^\bullet]}[M] \tag{2}$$

For BPO initiated bulk styrene polymerizations $k_L = 1.5\text{x}10^7$ M^{-1} s^{-1} (ref 4) and $k_{-L} = 5.2\text{x}10^{-4}$ s^{-1} (ref 3).

Recently Fukuda et al.[9] have suggested that thermal initiation and irreversible termination are exactly balanced with eq 1:

$$R_i^\bullet + M \rightarrow P_1^\bullet \tag{3}$$

$$P_n^\bullet + P_m^\bullet \rightarrow D_{n+m} \tag{4}$$

$R_i^\bullet$ is a thermally initiated radical, and D_{n+m} is a dead chain. Using a steady-state (SS) approximation on $P_n^\bullet$, $T^\bullet$ and L_n they obtain a polymerization rate identical to that without nitroxide:

$$R_p = \left(\frac{k_p^2\,R_i}{k_t}\right)^{1/2}[M] \tag{5}$$

The SS mechanism was developed to explain the work of Catala et al.,[10] who observed that the styrene polymerization rate was independant of the amount of initiator, where the initiator was a t-butyl nitroxide trapped ethylbenzyl radical. The SS approximation requires that $P^\bullet$, $T^\bullet$ and L be constant. Thus, Fukuda et al.[9] assume that the initiation rate, R_i, must equal the termination rate, R_t:

$$2k_i\,[M]^2 = k_t\,[P^\bullet]^2 \tag{6}$$

It has been suggested that this SS mechanism is necessary for all nitroxide mediated polymerizations.[9] What evidence is there to support the SS mechanism for nitroxide mediated polymerizations? There is a large body of work on TEMPO mediated living styrene polymerizations initiated by BPO.[1-7] Clearly, there are differences between the systems described by Fukuda[9] and Catala,[10] and those initiated by BPO. Initially, there is a large excess of nitroxide in the BPO systems, which is rapidly consumed by initiated chains. Once initiation is over the polymerizations are identical, with similar levels of excess nitroxide,[3,9] except for the byproducts of BPO initiation.[5] The purpose of this letter is to test if the data with BPO initiation is consistent with the SS mechanism.

The SS mechanism does not give a consistent picture of BPO initiated polymerizations. First, neither $[P^\bullet]$ (calculated from the number of growing chains, the measured $[T^\bullet]$, the known k_p, and the observed polymerization rate), nor $[T^\bullet]$, are constant in BPO initiated systems.[3-7] Once initiation is complete (<10 min) both $[P^\bullet]$ and $[T^\bullet]$ can change 10 fold over 6 h of polymerization. Further, eq 5 of the SS model predicts a polymerization rate that is **independent** of $[T^\bullet]$. Yet, we have shown previously[3,7] that the apparent rate constant of polymerization, and thus $[P^\bullet]$, is changing with conversion, exactly in accordance with the change in $[T^\bullet]$. Further, if the ratio of nitroxide to initiator is reduced from 1.3:1 to 1.1:1, then the amount of free nitroxide is lower throughout the polymerization,[3] but the measured value of K is constant. Quantitatively, the rate is predicted by eq 2. Similar results have been found after addition of strong acids, and some salts, that consume nitroxide.[6,7] Again, the effect of reducing nitroxide levels essentially quantitatively corresponds to the rate increase.

Why does the SS model give poor agreement with experiment for styrene polymerizations? The problem is the assumption in eq 6, that the rates of initiation and termination are equal. The thermal initiation rate of styrene[12] is given by:

$$R_i = 2\,k_i\,[M]^n \qquad n=2 \text{ or } 3 \tag{7}$$

Table 1. Parameters for "Living" BPO initiated styrene polymerization with TEMPO

Parameter	115 °C	125 °C		135 °C	Literature Reference
	x=0.08 (3 h)	x=0.08(2 h)	x=0.35 (6 h)	x=0.55 (3 h)	
$[P^\bullet]$	$8.6\text{x}10^{-9}$	$3.5\text{x}10^{-9}$	$9.7\text{x}10^{-9}$	$2.6\text{x}10^{-8}$	3
R_i (2nd order)	$6.2\text{x}10^{-8}$	$1.5\text{x}10^{-7}$	$7.6\text{x}10^{-8}$	$8.3\text{x}10^{-8}$	12
R_i (3rd order)	$5.6\text{x}10^{-8}$	$1.4\text{x}10^{-7}$	$4.9\text{x}10^{-8}$	$3.7\text{x}10^{-8}$	
R_t	$6.7\text{x}10^{-9}$	$1.2\text{x}10^{-9}$	$3.8\text{x}10^{-9}$	$1.3\text{x}10^{-8}$	13
R_i/R_t	~10	~100	13-20	3-6	--

For example, after 6 h of styrene polymerization at 125 °C with BPO initiation,[3] $[P^\bullet]=1.0\text{x}10^{-9}$ M. The thermal initiation rate,[12] at x=0.35, is $R_i = 7.6\text{x}10^{-8}$ M s^{-1} (n=2), or $4.9\text{x}10^{-8}$ M s^{-1} (n=3). On the other hand, the termination rate can be described[13] as:

$$R_t = k_{t_o} g_t [P^\bullet]^2 \qquad (8)$$

Here, g_t is an exponential function with conversion. At x=0.35, k_t is $3.8\text{x}10^{-9}$ M^{-1} s^{-1}. These calculations are summarized in Table 1. At 125 °C, R_i/R_t is about 100 at x=0.03 and 13-20 at x=0.35. Thus, k_t is too small to balance thermal initiation. Further, Moad et al.[14] have found that TEMPO disappears faster than expected based on thermal initiation, as it is consumed by Mayo dimer, also generating initiating radicals.

Now, R_t and R_i might be equal under some set of conditions. However, as the dependencies of R_i and R_t, on conversion are different ($R_i \propto [M]^3$ in eq 7; g_t is exponential with conversion in eq 8), the two rates cannot continue to balance as conversion changes. Any imbalance restores eq 2 as the dominating influence for the polymerization rate. Further, the temperature dependencies of the rates are different: $\Delta H^\ddagger = 82$ kJ/mole for the NO-C bond (to release $P^\bullet$), $E_a(k_p)=37.5$ kJ/mole, $E_a(k_i)=113$ kJ/mole, and $E_a(k_t)=14.5$ kJ/mole. Thus, the SS approximation cannot hold over the range of temperatures utilized.

To illustrate this point, Table 1 shows the measured $[P^\bullet]$ at three temperatures, and calculated values of R_i, and R_t. The ratio of R_i/R_t varies from 3 to 100 with temperature and conversion. Over a larger range of temperature and conversion, this ratio will change even more dramatically. Thus, it is impossible to balance thermal initiation and termination over a range of conditions.

It should be noted that the termination rate would be expected to be lower than the literature value without nitroxide, due to narrower polydispersities and fast initiation (there are fewer short chains, the chains with the most mobility for termination). The only source of short chains will be thermal initiation.

Similarly, thermal initiation might reduce nitroxide levels, speeding up polymerization rates. It does not appear that this can be important in BPO initiated polymerizations, as there is not a strong effect of thermal initiation rates on polymerization rates. First, the amount of thermal initiation in BPO initiated living polymerizations is lower than expected. Previous work has shown that this is at least partly due to benzoic acid produced by BPO decomposition.[5] Also, additives such as CSA[5] or FMPTS[7] decrease the thermal initiation rate, while increasing the polymerization rate. For example, after 39 h at 130 °C, in the presence of TEMPO, benzoic acid reduced the number of thermally initiated chains by a factor of 2.5, while with CSA the reduction was 4 fold.[5] With FMPTS at 125 °C in the presence of TEMPO, at 4 h there is a 3 fold decrease in thermal polymerization compared to CSA. Overall, FMPTS gives about a 5 fold decrease in the thermal initiation rate compared to benzoic acid. However, for both FMPTS[7] and CSA,[6] the reduction in thermal polymerization does not result in increasing nitroxide levels, or decreasing polymer radical levels, predicted by the SS mechanism. The rate of polymerization increases substantially in both cases, as accounted for by the lower nitroxide concentration. This again argues strongly that the polymerization rate is controlled by nitroxide levels, as described by eq 2, not by thermal initiation and termination rates. Clearly, the fast polymerization with reduced thermal initiation proves that thermal initiation is not essential for the polymerizations to proceed, contrary to the suggestion of Fukuda et al.[9]

One could argue that mechanisms with BPO or nitroxide-capped initiators are fundamentally different. However, at 125 °C Fukuda observes that $[P^\bullet]$ stabilizes at $1\text{x}10^{-8}$ M after 6 h, with $K=5\text{x}10^{10}$ M^{-1}. With BPO initiation (Table 1), $[P^\bullet]$ stabilizes at an identical value of $9.7\text{x}10^{-9}$ M after 3 h, while $K=2.9$ $\text{x}10^{10}$ M^{-1} from Ref 3 is in close agreement. It does not seem reasonable to conclude that the mechanism with the two modes of initiation is dramatically different. Work is in progress to study styrene polymerization with nitroxide terminated initiator, in the presence and *total absence* of thermal initiation.

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