# Effects of Radical Initiator on Polymerization Rate and Polydispersity in Nitroxide-Controlled Free Radical Polymerization

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ABSTRACT: The free radical polymerization of styrene "initiated" by a 2,2,6,6-tetramethyl-1-poly(styroxypiperidine) (PS-TEMPO: $M_n = 1700$ and $M_w/M_n = 1.11$) was studied to examine the effect of *tert*-butyl hydroperoxide (BHP), a radical initiator, on the polymerization rate and molecular weights. It was demonstrated that, by the addition of BHP, the rate can be increased by a factor of up to about 3 without causing any appreciable increases of the number of chains and the polydispersity index $M_w/M_n$ (at 114 °C). These results are consistent with the kinetic schemes proposed previously (Fukuda, T.; et al. *Macromolecules* **1996**, *29,* 6393) and suggest a general method to manipulate the polymerization rate of such systems. A simple analytical equation was presented showing how the polydispersity is narrowed by alternating activation−deactivation processes, and it allowed us to evaluate the frequency of activation independently of other reactions. This equation consistently interpreted the experimental results.

## Introduction

The development of controlled/"living" radical polymerization has been attracting much attention due to its practical and academic importance. The polymerization of styrene mediated by stable nitroxyls like TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) is among the most extensively studied systems.[1−18] A key reaction in this system is believed to be the reversible dissociation of the polymer-nitroxyl adduct P−X (a dormant species) into the polymer radical P* and the stable nitroxyl X*

$$\mathrm{P{-}X} \underset{k_c}{\overset{k_d}{\rightleftharpoons}} \mathrm{P^* + X^*} \tag{1}$$

where $k_d$ and $k_c$ are the rate constants of dissociation and combination, respectively. In situ ESR (electron spin resonance) measurements have been conducted to follow the nitroxyl concentration and deduce the equilibrium constant $K$.[6,7,16]

$$K = k_d/k_c \tag{2}$$

More recently, we succeeded in determining the $k_d$ of the PS/TEMPO system by a direct method using GPC (gel permeation chromatography).[17] Thus the existence of the reversible reaction in eq 1 has been experimentally confirmed.

However, there have been established no perfectly unified views of the exact mechanisms by which the chain length, the chain length distribution, the rate of polymerization, and other details are controlled. One of the largest differences among the mechanisms proposed by different research groups[4−18] is in the treatment of the initiation and termination reactions. In a series of papers by Veregin et al.,[4−7] for example, those reactions were considered unimportant. On the other hand, in view of the existence of significant thermal (spontaneous) initiation in styrene at high temperatures,[19] Matyjaszewski and co-workers[10,11] and we[15,16] have stressed the importance of those reactions in characterizing the nitroxyl-mediated polymerization of styrene.

More specifically, we have introduced the idea of stationary-state concentrations of P* and X*, which read[15,16]

$$[\mathrm{P^*}] = (R_i/k_t)^{1/2} \tag{3}$$

$$[\mathrm{X^*}] = K[\mathrm{P{-}X}]/[\mathrm{P^*}] \tag{4}$$

Namely, the stationary concentrations of P* and X* are determined by different mechanisms: [P*] is determined by the balance of the initiation rate $R_i$ and the termination rate $k_t[\mathrm{P^*}]^2$, just like in a conventional free radical system, while [X*] is determined by the equilibration in eq 1, and therefore it depends on the equilibrium constant $K$ as well as on the adduct concentration [P−X] and [P*]. The typical values of [P*] and [X*] referred to from ref 16 are about $10^{-8}$ mol L$^{-1}$ and $10^{-5}$ mol L$^{-1}$, respectively. (This relatively large value of [X*] means that it takes a certain time before this amount of X* is accumulated in the system as a result of bialkyl termination.) Other possible reactions include the thermal decomposition of P−X adducts[12,18] and transfer reactions.[8,9] They are important in the discussion of polydispersities, for example, but not so in the discussion of $R_p$, the stationary rate of polymerization, which, according to eq 3, is given by

$$\begin{aligned} R_p &= k_p[\mathrm{P^*}][\mathrm{M}] \\ &= (k_p/k_t^{1/2})R_i^{1/2}[\mathrm{M}] \end{aligned} \tag{5}$$

Thus $R_p$ should be *independent* of the adduct concentration, being equal to that of the adduct-free system (if $k_t$ and other parameters are the same). This prediction was experimentally verified by the styrene polymerizations with a PS-TEMPO[16] or a low-mass model adduct[13,16] (but with no extra nitroxyl added: see ref 20).

The initiation rate $R_i$ in the mentioned experiments refers to the thermal initiation of styrene. In this framework, $R_p$ is a fixed parameter for a fixed temperature. A purpose of this work is to test eq 5 more generally by examining systems including a radical initiator. If eq 5 and the underlying mechanism are correct, $R_p$ should increase with $R_i$ or initiator concentration, just like in the conventional polymerization,

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without causing appreciable broadening of the chain length distribution at least in a limited range of $R_p$.[16] This has been fragmentarily observed by experiments,[14,17] but no systematic studies have been conducted. This work therefore includes an important clue to manipulate one of the main parameters of nitroxyl-controlled polymerization. The only possible method, known so far, to increase the $R_p$ of nitroxyl-controlled polymerization at a fixed temperature is to use a strong organic acid like camphorsulfonic acid.[7b]

Another purpose of the work is to make clearer the role of the reversible reaction in eq 1 in controlling the polydispersity of the system. To this end, we will derive a simple analytical equation describing how the polydispersity is narrowed by this (or equivalent) reaction, and test it by the experiments carried out with and without a radical initiator. If the above-mentioned role is in fact played by the initiator, we can thereby manipulate the stationary concentration of P* or X*. Then we will be able to see the effects of, e.g., chain length and transfer reactions on the polydispersity, if there are any.

## Experimental Section

A PS-TEMPO adduct was prepared and purified as described previously.[16] In brief, a mixture of benzoyl peroxide (0.072 mol $L^{-1}$), TEMPO (0.086 mol $L^{-1}$), and styrene, degassed and sealed off under vacuum, was heated at 90 °C for 1 h and at 125 °C for 4.5 h to yield a polymer with $M_n = 1700$ and $M_w/M_n = 1.11$ (by GPC; see below), where $M_n$ and $M_w$ are the number- and weight-average molecular weights. Both nitrogen elemental analysis and proton magnetic resonance spectroscopy indicated that a high fraction of this polymer had a TEMPO moiety at the chain end, but its molecular weight was a little too high for these analyses to be quantitative enough. A chain-extension test,[17] namely, the polymerization of styrene with this sample used as an "initiator", indicated that the fraction of TEMPO-capped molecules is never smaller than about 94% of the total molecules. *tert*-Butyl hydroperoxide (BHP) was purified by fractional distillation. This radical initiator was chosen because of its desirable rate of decomposition at the temperature of the experiments. It could potentially add complications due to the possible transfer reaction to itself. However, this is presumably negligible because of the relatively low concentrations of the initiator and the high concentration of the potentially reactive polymer chains, i.e., the adduct molecules, used in these experiments.

In each experimental run, 10 parts (by weight) of the PS-TEMPO adduct and 90 parts of styrene were charged in a Pyrex tube, to which a known amount of BHP was dissolved. After being degassed by several freeze−thaw cycles and sealed off under vacuum, the mixture was heated at 114 °C for a predetermined time *t*, quenched to room temperature, and diluted to a known concentration with tetrahydrofuran (THF) to be directly studied by GPC for the conversion and molecular weights.

The GPC analysis was made on a Tosoh HLC-802 UR high-speed liquid chromatograph equipped with Tosoh gel columns G2500H, G3000H, and G4000H (Tokyo, Japan). THF was used as eluent (40 °C). The column system was calibrated with Tosoh standard PSs. Sample detection and quantification were made with a Tosoh differential refractometer RI-8020 calibrated with known concentrations of PS-TEMPO adducts in THF.

## Results and Discussion

**Polymerization Rate.** Figure 1 shows the $\ln([M]_0/[M])$ vs *t* plot for the polymerization of styrene containing 10 wt % (0.049 mol $L^{-1}$) of the PS-TEMPO adduct and varying amounts of the initiator BHP. Here the subscript "0" denotes the initial state ($t = 0$). Even in the absence of BHP, styrene undergoes thermal polymerization, the rate of which is given by $R_{p,0}/[M]_0 = 2.4 \times 10^{-5}\ s^{-1}$ at 114 °C according to the literature.[19] On the other hand, the initial slope of the curve for $[BHP]_0 = 0$ (Figure 1) gives $R_{p,0}/[M]_0 = 1.8 \times 10^{-5}\ s^{-1}$. This value is increased to $2.1 \times 10^{-5}\ s^{-1}$ after being corrected for the difference in $[M]_0$ between the two systems (note that the thermal initiation rate of styrene is proportional to the third power of monomer concentration,[19] and our system originally contains 10 wt % of polymer as the adduct). Thus, $R_p$ is essentially unchanged by the presence of such an adduct, as verified previously.[16]

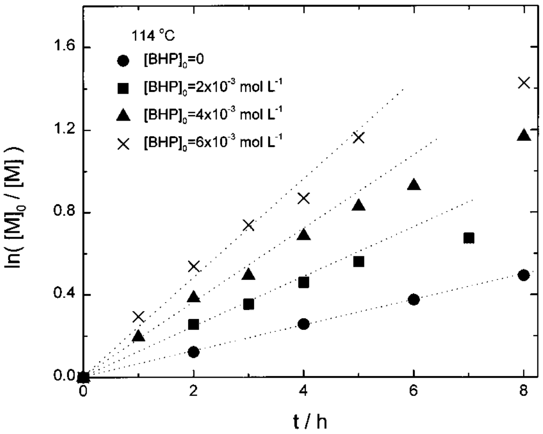

**Figure 1.** Plot of $\ln([M]_0/[M])$ vs polymerization time for the styrene polymerization at 114 °C with $[\text{PS-TEMPO}] = 4.8 \times 10^{-2}$ mol $L^{-1}$: $[BHP] = 0$ (●), $2.0 \times 10^{-3}$ mol $L^{-1}$ (■), $4.0 \times 10^{-3}$ mol $L^{-1}$ (▲), and $6.0 \times 10^{-3}$ mol $L^{-1}$ (×).

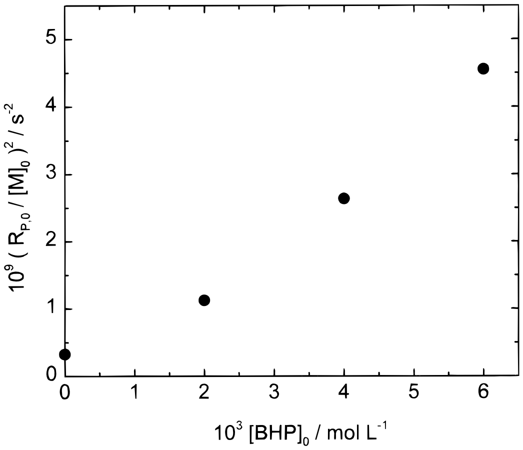

**Figure 2.** Plot of $(R_{p,0}/[M]_0)^2$ vs $[BHP]_0$: data from Figure 1.

Figure 1 clearly shows that $R_p$ increases with increasing concentration of BHP. For a more quantitative discussion, we are tempted to recast eq 5 into

$$(R_p/[M])^2 = (k_p{}^2/k_t)(R_{i,th} + R_{i,BHP}) \tag{6}$$

by assuming that the thermal initiation rate $R_{i,th}$ and the initiation rate due to the decomposition of BHP, $R_{i,BHP}$, independently contribute to the total rate $R_i$. The BHP term may be written

$$R_{i,BHP} = k_d'[BHP] \tag{7}$$

where $k_d'$ is the decomposition rate constant including the efficiency factor. The plot of $(R_{p,0}/[M]_0)^2$ vs $[BHP]_0$ for the data in Figure 1 is presented in Figure 2, which shows the suggested linearity to hold as a crude approximation.[22]

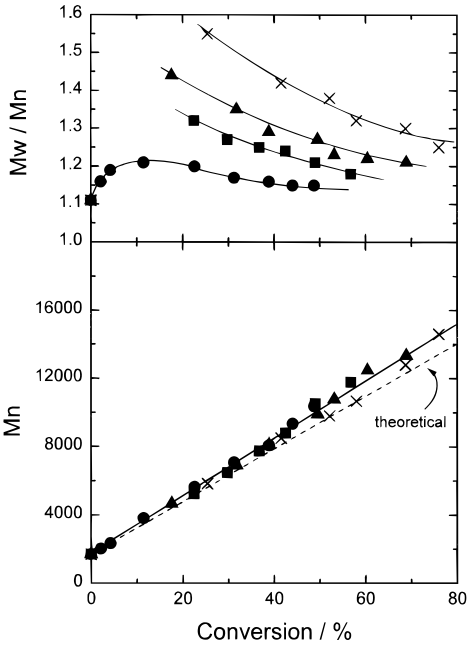

**Figure 3.** Plot of $M_w/M_n$ and $M_n$ vs monomer conversion. The broken line is theoretical, and the solid lines are just for the eyes: for symbols and experimental conditions, see Figure 1.

**Number-Average Molecular Weight.** Figure 3 shows the $M_n$ of the produced polymers as a function of conversion. Clearly, $M_n$ increases linearly with conversion and is independent of the initiator concentration. All the data points are close to the theoretical line that is based on the assumption of a constant number of polymer molecules throughout the course of polymerization. Thus, these systems seem to meet a criterion of living polymerization at least approximately.

More quantitatively, the initiation rate at $t = 0$ can be estimated from eq 5, namely, $R_{i,0} = (R_{p,0}/[M]_0)^2(k_{p,0}{}^2/k_{t,0})^{-1}$ with[19] $k_{p,0}{}^2/k_{t,0} = 0.880 \times 10^5\exp(-6270/T)$ and $R_{p,0}/[M]_0$ given in Figure 2. Thus the value of $[N_i] = R_{i,0}t$ gives a maximum estimate (*maximum* because $R_i$ can decrease with time) of the cumulative number of chains initiated up to time $t$ per unit volume. These values of $[N_i]$ never exceed 10% of [PS-TEMPO]$_0$ in the studied range of $t$ for $[BHP] \leq 4 \times 10^{-3}$ mol L$^{-1}$. For the highest BHP concentration studied here ($[BHP] = 6 \times 10^{-3}$ mol L$^{-1}$), $[N_i]$ amounts to about 20% of [PS-TEMPO]$_0$ at the largest $t$ studied, for which deviations from other groups of data become appreciable at high conversions or large $t$ in both $M_n$ (Figure 3) and $M_w/M_n$ (Figure 4; see below). According to the present stationary-state kinetics, the number of initiated chains is essentially equal to the number of terminated chains. Since PS radicals are terminated predominantly by combination rather than by disproportionation, the net increase in the total number of chains would be about half that of the initiated chains. Thus the lowering of $M_n$ observed for the high-[BHP] runs (about 8% at maximum) are in a predictable range.

**Polydispersity.** The $M_w/M_n$ ratio shown in Figure 3 strongly depends on the initiator concentration. At a given conversion, $M_w/M_n$ increases with increasing [BHP]. At a first sight, this may appear to indicate that the control of the polydispersity becomes more and more difficult, as [BHP] and hence $R_p$ increase. However, this is not true: the polydispersity of the present system is determined by the polydispersity of the PS chain in the initiator adduct (subchain A) and that of the grown part of the chain (subchain B), if other contributions such as thermal initiation are neglected. Since the molecular weight distributions of the two subchains should be uncorrelated, it holds that[24]

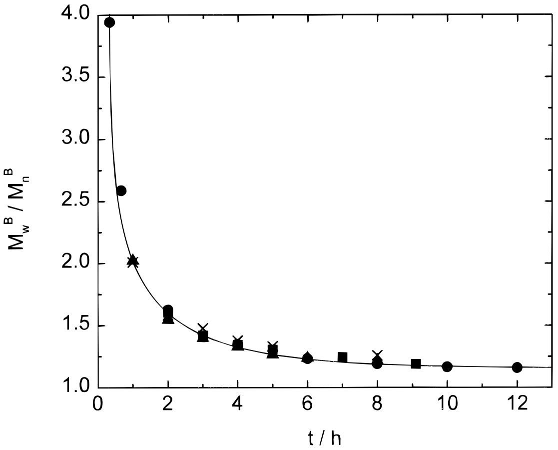

**Figure 4.** Plot of $M_w^B/M_n^B$ vs polymerization time. For symbols and experimental conditions, see Figure 1.

$$M_w/M_n = 1 + w_A{}^2Y_A + w_B{}^2Y_B \tag{8}$$

where $w_K = M_n{}^K/(M_n{}^A + M_n{}^B)$, and $Y_K = (M_w{}^K/M_n{}^K) - 1$ with $M_n{}^K$ and $M_w{}^K$ referring to the K subchain (K = A or B; $M_n = M_n{}^A + M_n{}^B$). Given $M_n{}^A$ (=1700), $M_w{}^A/M_n{}^A$ (=1.11), $M_w$, and $M_n$ (Figure 3), we can thus calculate the polydispersity index of subchain B, $M_w{}^B/M_n{}^B$, which is presented in Figure 4 as a function of time. All the data points fall approximately on the same curve. The value of $M_w{}^B/M_n{}^B$ is large (>2.0) for small $t$ (<1 h) but rapidly decreases with increasing $t$. These results indicate that the polydispersity is controlled essentially by the number of the activation−deactivation cycles and that the $R_p$ or the number of monomer units incorporated into the chain per such cycle has no or little effect on the polydispersity. Moreover, the effect of initiated and/or terminated chains on the polydispersity is rather minor in the examined range of [BHP] or $R_p$. It is thus clear that the differences among the $M_w/M_n$ vs conversion curves in Figure 3 are ascribed predominantly to the differences in polymerization time and the chain length of subchain B relative to that of subchain A.

For a more quantitative discussion on the polydispersity, we consider a model system in which a P−X adduct is activated once every $k_d{}^{-1}$ s (on average) and incorporates an average of $x_n{}^o$ monomer units into the chain before it is deactivated again. Assuming that $x_n{}^o$ is independent of time (constant $R_p$) and neglecting all other reactions, one can derive by a probabilistic approach the following simple expression for the polydispersity index (see the Appendix):

$$M_w/M_n = x_w/x_n = 1 + (2/y_n) + (1/x_n) \tag{9}$$

Here $x_w$ and $x_n$ are the weight- and number-average degrees of polymerization, $y_n$ is the average number of activation−deactivation cycles that an adduct experiences during time $t$

$$y_n = k_dt \tag{10}$$

and $x_n = y_n\, x_n{}^o$. Equation 9 is valid when $[P^*] \ll [P{-}X]_0$. This condition is met in most radical polymerization systems. We also note that eq 9 is based on the averaging process in which *all* of the initiating segments (the A subchains in the present problem), each having

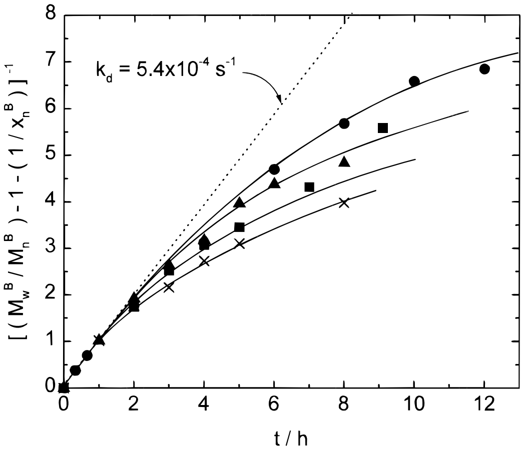

**Figure 5.** Plot of $[(M_w^B/M_n^B) - 1 - (1/x_n^B)]^{-1}$ vs $t$ for the data in Figure 4 ($x_n^B = M_n^B/M_0$ with $M_0$ being the molecular weight of the monomer unit). For symbols, see Figure 1.

*zero* mass, are taken into account. This is a reason for the simplicity of eq 9. (To take account of the initiator mass and evaluate the overall $M_w/M_n$ ratio in general, use should be made, in turn, of eq 8 along with eq 9.) By a kinetic approach, Müller et al.[25a] have derived analytical expressions which are equivalent to eqs A-9 and A-10 (in the Appendix) for $[P^*] \ll [P-X]_0$. However, their equation for $M_w/M_n$ is more complicated and more difficult to compare with experiments, particularly in a small $t$ region. This is because they took an average over the initiator species that have been added by more than one unit. In this regard, eq 9 and the relevant method of analysis (see below) are new.

Since in the present experiments, $x_n^{-1} \cong 0$ in all cases, eqs 9 and 10 predict that $M_w/M_n$ is independent of $x_n^o$ or $R_p$ if $t$ is fixed. This has been observed to hold approximately (Figure 4).

Rearrangement of eqs 9 and 10 gives

$$[(M_w/M_n) - 1 - (1/x_n)]^{-1} = (k_d/2)t \qquad (11)$$

This linearization allows us to determine $k_d$ by a graphical method. The relevant plot is given in Figure 5. The nonlinearity of the experimental curves is ascribed partly to the decrease of $R_p$ or $x_n^o$ with $t$: namely, $R_p$ is proportional to [M] which is a decreasing function of $t$, and [M] decreases more rapidly for larger $R_p$. In addition, the ratio $R_p$/[M] is not always a constant but decreases at large $t$, and this trend is more evident for higher-$R_p$ runs (see Figure 1). Since no propagation gives no narrowing of the polydispersity, the curves in both Figures 4 and 5 would eventually level off at large $t$, and this would occur at an earlier stage as $R_p$ increases. This agrees with what Figure 5 shows. A method to correct for the inconstant $R_p$ is given elsewhere.[26]

Very importantly, all the curves in Figure 5 appear to coincide with each other at small $t$. This is consistent to the prediction that effects of inconstant $R_p$ and all side reactions such as initiation, termination, and decomposition will become minor at small $t$. Namely, the initial slope of this plot gives a *model-independent* value of $k_d$. In a strict sense, this $k_d$ is the mean frequency of adduct dissociation (per unit time), to which not only the spontaneous dissociation in eq 1 but also any other reactions causing the dissociation can contribute in general (see below). From Figure 5, there is obtained an estimate of $k_d$ (at 114 °C) of $5.4 \times 10^{-4}$ s$^{-1}$, which should be compared with the value of $3.8 \times 10^{-4}$ s$^{-1}$ at 110 °C determined by a direct assay.[17b,c] If the temperature difference is taken into account, the agreement is indeed remarkable. Discussion on the polydispersity in a large $t$ region requires considerations of all other factors that were neglected here, and it will be best performed by computer simulations.[11,27,28]

## Conclusions

It was demonstrated that by adding BHP, a radical initiator, the $R_p$ of styrene polymerization at 114 °C in the presence of an oligomeric PS-TEMPO adduct can be increased by a factor of up to about 3 without causing any appreciable broadening of the molecular weight distribution and lowering of $M_n$ below the theoretical value. The polydispersity of the product is determined essentially by the polymerization time, and not the rate $R_p$, at least in a limited range of $R_p$. This suggests a practically useful method to synthesize narrow-polydispersity large molecular weight polymers. Namely, they can be produced by carrying out the polymerization for a sufficiently long time at an increased rate by the use of a radical initiator. Continuous or occasional addition of the monomer should be effective to maintain a high rate of polymerization.

As has been pointed out,[15,16] there possibly can be systems in which the dissociation of P−X adduct does occur but a thermal or spontaneous initiation does not, and for this reason, controlled polymerization does not proceed successfully. This work demonstrates a possibility of "awaking" those dormant systems by using a radical initiator.

A simple analytical expression was presented describing how the polydispersity is narrowed by alternating activation−deactivation processes and permitting the determination of the frequency of activation. It described the experimental results in a small $t$ region almost quantitatively. The observation that the polydispersity is independent of $R_p$ (strictly at small t) suggests that the degenerative transfer[8,9] (the active species-exchanging transfer reaction) may not be among main mechanisms of activation in this system. If it is a main one, an increase in $R_p$ and hence [P*] would increase the frequency of activation, which should be reflected in the polydispersity. The need is apparent, however, for more precise and direct experimental studies to establish this on a more quantitative basis. This will be a topic of a separate publication.[17b]

After the submission of this paper, we were informed that Greszta and Matyjaszewski[29] reached nearly the same conclusions regarding the roles of initiation and initiator in a nitroxide/styrene system. This work is distinguished from theirs by the fact that the discussion of the polymerization rate here is based on the analytical eq 5, which will give a deeper and more transparent insight into the problem. The linearization method based on eqs 8 and 11 and its first application to experimental data are pure original features of this work.

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## Appendix: Chain Length Distribution in Polymers Produced via Alternating Activation−Deactivation Processes

We consider polymerization processes in which the propagating species experiences an activated and a deactivated state alternatingly. In the deactivated state, the active chain end is blocked in some way or another, and no propagation occurs. In the activated state, the chain can be added by a monomer unit with a probability $p$ or deactivated with a probability $1 - p$. The transition from the deactivated to activated state occurs with a probability density of $y_n/t$, so that $y_n$ is the mean number of such transitions during time $t$. Here we have assumed that the time during which the chain is in the activated state is much shorter than the total time or $\tau y_n \ll t$, where $\tau$ is the "transient" lifetime, i.e., the mean time in the activated state per activation–deactivation "cycle". We neglect all other reactions.

Clearly, the length distribution of the chain fragment produced in a cycle is the most probable one

$$f_1(x) = p^x(1 - p) \tag{A-1}$$

where $x$ is the degree of polymerization and it can take integers from 0 to $\infty$.[30] If the chain experiences $y$ such cycles, the number density distribution of the chain with length $x$ is

$$f_y(x) = (1 - p)^y p^x \binom{x + y - 1}{x} \tag{A-2}$$

The last factor in the right-hand-side of eq A-2 denotes the number of ways to distribute $x$ units over $y$ groups, and it holds that

$$\sum_{x=0}^{\infty} p^x \binom{x + \mathrm{y} - 1}{x} = (1 - p)^{-y} \tag{A-3}$$

That is, eq A-2 is normalized to unity. The probability that the chain has $y$ cycles is given by a Poisson distribution

$$g(y) = \mathrm{e}^{-y_n} {y_n}^y / y! \tag{A-4}$$

where $y_n$ is the mean value of $y$. Finally, the number density of the chain characterized by the two parameters $x$ and $y$ is given by

$$N(x,y) = g(y) f_y(x) \tag{A-5}$$

which is normalized to unity ($x$, $y = 0, 1, 2, ...$).

Moments of the distribution may be calculated by defining the function $N_s(x,y)$ of a dummy variable $s$

$$N_s(x,y) = ({y_n}^y/y!)(1 - p)^y (ps)^x \binom{x + y - 1}{x} \tag{A-6}$$

Referring to eqs A-2 through A-5, the zeroth moment of $N_s$ reads

$$\begin{aligned} Z_0(s) &= \sum_{y=0}^{\infty}\sum_{x=0}^{\infty} N_s(x,y) \\ &= \exp[y_n(1 - p)/(1 - ps)] \end{aligned} \tag{A-7}$$

Higher moments are obtainable by successively differentiating $Z_0$ according to

$$\begin{aligned} Z_k(s) &= \sum_{y=0}^{\infty}\sum_{x=0}^{\infty} x^k N_s(x,y) \\ &= s[\partial Z_{k-1}(s)/\partial s] \quad (k = 1, 2, ...) \end{aligned} \tag{A-8}$$

The number- and weight-average degrees of polymerization are calculated as

$$x_n = Z_1(1)/Z_0(1) = py_n/(1 - p) \tag{A-9}$$

$$x_w = Z_2(1)/Z_1(1) = (1 + p + py_n)/(1 - p) \tag{A-10}$$

which give eq 9 in the text.

Obviously, this model applies to any types of polymerization characterized by an alternating activation–deactivation process with $p$ and $y_n/t$ independent of $t$ and $\tau y_n \ll t$. The correlations to the nitroxyl system discussed in the text are $p/(1 - p) = x_n^{\circ}$, $y_n/t = k_d$, and $[P^*] \ll [P{-}X]_0$. For more general discussion, the readers are referred to ref 25, in which polymerizations with a constant $R_p$ and those with a constant $R_p/[M]$ ratio (batch systems) are theoretically analyzed by a kinetic approach.

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(20) As eqs 3 and 4 show, the stationary concentrations of P* and X* are different. According to a typical result on a PS-TEMPO/styrene system,[16] $[\mathrm{PS}^*] \sim 10^{-8}$ mol L$^{-1}$ and [TEMPO] $\sim 10^{-5}$ mol L$^{-1}$ in the stationary state. Since both [P*] and [X*] should be zero at the onset of polymerization, it takes a certain time before a sufficient number of termination reactions occur leaving the stationary concentration of free TEMPO and dead polymers in the system. This time is estimated to be 5–10 min, typically.[25] If there is an extra TEMPO added to the system, the stationary state will not be reached until the excess TEMPO molecules are "consumed" by combining with thermally initiated species forming as many new adducts. If this process is viewed by ESR, the TEMPO concentration will gradually decrease, approaching the stationary level. The time required for this process can be long, if the excess TEMPO concentration is high, e.g.,

$>10^{-3}$ mol $L^{-1}$. After the stationary state is reached, [TEMPO] can gradually increase in some cases because of a decrease in $R_i$, for example.[16] We believe that the observations made by Veregin et al. (e.g., Figures 4 and 9 in ref 6) can be qualitatively interpreted in this way, while the authors ascribed the changes of [TEMPO] to an unclear cause. As has been pointed out,[16] however, kinetic descriptions of styrene systems containing excess TEMPO or those started with an initiator and TEMPO may be complicated by the acceleration of thermal initiation[21] and possible effects of the byproducts from the reaction of TEMPO with the initiator[4] or thermally produced species.[21] For this reason, the stationary state in these systems may not be exactly the same as that in the system including a purified adduct and the monomer only.

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