Molecular Weight Distributions in Nitroxide-Mediated Living Free Radical Polymerization: Kinetics of the Slow Equilibria between Growing and Dormant Chains

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ABSTRACT: A kinetic approach, recently developed to calculate the effect of exchange between a dormant and an active species in group transfer polymerization (GTP), has been applied to living free radical polymerization moderated by nitroxide stable free radicals. A general solution for the molecular weight distribution as a function of conversion has been derived. The solution depends only on the rate constants for propagation, the trapping of the growing chains by nitroxide radical, and the release of the growing chain. The general form of the solution is the same in GTP and the stable free radical-mediated polymerization (SFRP), except for the definition of the constants. Using the measured and known experimental rate constants for SFRP and fitting to the only unknown rate constant, that for reversible chain termination by the nitroxide radical, allow a quantitative prediction of the molecular weight distribution with conversion for bulk free radical living polymerization of polystyrene. In this way a good fit to the experimental polydispersity is obtained over a wide range of polymerization conditions. The calculated rate for the reversible termination is reasonable compared to known nitroxide-trapping reactions but is over 3 orders of magnitude slower than for a diffusion-controlled reaction, on the same order as the rate constant for polystyrene radical−radical termination. Nevertheless, because of the excess nitroxide present, trapping is fast enough to ensure a high rate of exchange of growing and dormant chains, resulting in narrow polydispersities at high conversion. The very good fit to this model indicates that neither initiation nor termination are important to the conversion dependence of the molecular weight distribution, as neither were taken into account in the kinetic model. This is further support for the current understanding of the mechanism and kinetics of the SFRP process. The polydispersity in the bulk living free radical polymerization mediated by nitroxide is controlled by the exchange rate between the growing and dormant chains. At high conversion where the rate of polymerization is high, there can be some irreversible chain termination and some autopolymerization.

Introduction

In a series of recent publications,[1−3] the rapid progress in the development of a nitroxide-mediated free radical polymerization (*s*table *f*ree *r*adical *p*olymerization or SFRP) has been elucidated. Using this polymerization system, it has been possible to achieve narrow polydispersities (PDs) by bulk, suspension, or emulsion polymerization, producing homopolymers and block copolymers with PD ≤ 1.3 and random copolymers with PD ≤ 1.5. Despite the narrow polydispersities of the resultant polymers and the calculated slow rate of termination and transfer, the molecular weight distributions (MWD) are considerably broader than a Poisson distribution, in common with many other living polymerization systems. The molecular weight distributions are particularly broad at low conversions but fall dramatically as conversion increases, typically reaching a polydispersity of 1.3−1.4, below the minimum possible value of 1.5 for free radical polymerization that terminates by combination. Since initiation of chains is very rapid, this would suggest that either termination is higher than expected based on our kinetic analysis,[2,3] or equilibrium interconversion between growing polymer chains and chains reversibly terminated by nitroxide is not fast enough to give narrow polydispersities.[4,5] The key steps of the reaction mechanism, as we currently understand it, are shown in Scheme 1. Here, $P_i^\bullet$ is the growing, or active, polymer chain, $T^\bullet$ is the nitroxide radical, L_i is the reversibly capped, or dormant, polymer chain, which we have previously denoted as the *living chain*, and *M* is monomer. While it has not been possible to prove conclusively that the dormant living chain does not add monomer, there is no evidence to suggest that it does. Indeed, below temperatures of 100 °C, where there is an insignificant amount of uncapped polymer chains, there is no observed polymer formation.[1] Thus, Scheme 1 describes a system where one species, $P_i^\bullet$, polymerizes while the other species, L_i, does not.

Scheme 1

$$P_i^\bullet + T^\bullet \overset{K_L}{\rightleftharpoons} L_i$$

$$P_i + M \overset{k_p}{\rightarrow} P_{i+1}^\bullet$$

As shown theoretically by Figini,[4] an equilibrium between two species of different reactivities can lead to broadening of the molecular weight distribution if the interconversion is slow. The history of the development of the current understanding of these slow equilibria has been recently discussed by Muller *et al.*,[5] who have extended this idea to the degenerate transfer between active and dormant chain ends in group transfer polymerization (GTP), whose key steps are shown in Scheme 2. Here $P'_{i,j}$ are dormant chains, and $P^*_{i,j}$ are active chains. Muller *et al.*[5] note that their work is of special interest to other living systems with reversible termination, such as SFRP. Indeed, it is easy to see the analogy between the systems described by Schemes 1 and 2, in

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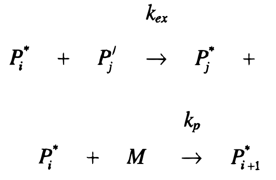
Scheme 2



$$P_i^{\bullet} + P_j^{l} \xrightarrow{k_{ex}} P_j^{\bullet} + P_i^{l}$$

$$P_i^{\bullet} + M \xrightarrow{k_p} P_{i+1}^{\bullet}$$

that the trapping of a chain of length i by nitroxide is followed by the release of another chain of length j. Thus, while the individual steps and species are different for the SFRP process, the overall result is formally the same (in terms of exchanging active and dormant chains) as in Scheme 2 for GTP. The difference is that the nitroxide is involved in Scheme 1 and not in Scheme 2. Interestingly, it has been suggested that SFRP can proceed by a mechanism much like Scheme 2, where any growing polymer chain actually attacks the dormant species (a nitroxide-terminated chain), resulting in the direct exchange of the dormant and growing chain.[6] However, there is no evidence, or precedent to date, that a polymer radical could directly attack a nitroxide-terminated chain.

The purpose of this paper is to adopt the approach of Muller *et al.*[5] for degenerative transfer in GTP, to determine the effect of degenerative transfer in the living polymerization mediated by nitroxide radicals.

Derivation of Molecular Weights and Polydispersity in SFRP

The derivation below follows very closely that of Muller *et al.*[5] Indeed, the constants have been defined here to give the same functional form as derived in that work, allowing easy comparison. The growth of polymer chains in the living free radical polymerization, as shown in Scheme 1, can be expressed by a set of differential equations describing the growth of the *growing* polymer chains, $P_i^{\bullet}$, and of the TEMPO-terminated *dormant* chains, L_i:

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = k_{\mathrm{P}}M(P_{i-1} - P_i) - k_L TP_i + k_{-L}L_i \tag{1}$$

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = k_P M(P_{i-1} - P_i) - k_L TP_i + \frac{k_L TP}{L}L_i \tag{2}$$

$$\frac{\mathrm{d}L_i}{\mathrm{d}t} = k_L TP_i - \frac{k_L TP}{L}L_i \tag{3}$$

Equations 2 and 3 make use of the equilibrium between capped and uncapped species, which is given by:

$$K_L = \frac{k_L}{k_{-L}} = \frac{L}{TP} \tag{4}$$

Here $T = [T^{\bullet}]$, $P_i = [P_i^{\bullet}]$, $P = \sum_{i=1}^{\infty} P_i$, and $L = \sum_{i=1}^{\infty} L_i$.

The initiation of the polymerization, typically by BPO or AIBN, as described in detail previously,[1-3] has been ignored, in that eqs 1–4 assume that all chains start at once, from $P_0^{\bullet}$ and L_0 in equilibrium (where $P_0^{\bullet}$ and L_0 together equal the total number of chains). In fact the equilibrium steady-state values for the growing and dormant chains are only achieved after all of the initiator is consumed, except in the case where the dormant chain L_1 is used as an initiator. Nevertheless, this approximation is reasonable for three reasons. First, under the typical SFRP conditions, initiation is done at or above 100 °C and thus is typically complete in <15 min.[1-3] Second, due to the high initial nitroxide concentration, which drops rapidly during initiation as the nitroxide reversibly caps the initiated chains, the rate of polymerization during initiation is very low, as determined by the equilibrium in eq 4 and Scheme 1.[1-3] Finally, as will be discussed later, the evolution of the PD with conversion that will be derived here is not very sensitive to the rate of initiation. Thus a relatively slow initiation of 15 min gives similar results to the infinitely fast initiation assumed here.

The above set of equations also ignore irreversible termination of two polymer chains. In previous work, this is shown to be a reasonable assumption in many SFR polymerizations.[1-3] The reason for the low rate of irreversible termination is the control of the concentration of growing polymer chain radicals by the nitroxide and the high temperatures, which favor $k_{\mathrm{p}}/k_{\mathrm{t}}$, as the rate constant for termination, k_{t}, has a lower activation energy than that for propagation.

The nth moment of the MWD is given as the sum of the distribution of the growing chains, $P_i^{\bullet}$, and TEMPO-terminated chains, L_i:

$$\mu_n = \mu_n^L + \mu_n^P \tag{5}$$

which are defined by the sums

$$\mu_n^L = \sum_{i=0}^{\infty} i^n L_i \text{ and } \mu_n^P = \sum_{i=0}^{\infty} i^n P_i \tag{6}$$

The zeroth moment is the concentration of all chains:

$$\mu_0 = \mu_0^L + \mu_0^P = \sum_{i=0}^{\infty} L_i + \sum_{i=0}^{\infty} P_i = L + P \cong L \tag{7}$$

In the living free radical polymerization, P is always $\ll L$, allowing the above approximation. Since initiation is typically by BPO and AIBN, initiation is not 100% efficient in creating polymer chains. In fact, we have shown previously that the number of chains that grow in the SFR polymerizations is equal to the number of nitroxide molecules.[3] Thus, each chain is terminated by a nitroxide molecule. In practice, $L = T_{\mathrm{o}}$, where T_{o} is the initial nitroxide concentration.

The first moment of the MWD is just the concentration of polymer, $M_0\,x$, where x is the monomer conversion:

$$x = \frac{M_0 - M}{M_0} = 1 - \mathrm{e}^{k_P P t} \tag{8}$$

Here, P can also be defined as αL. Taking the derivative of eq 8 with respect to time and conversion gives:

$$\frac{\mathrm{d}}{\mathrm{d}t} = \alpha k_P L(1 - x)\frac{\mathrm{d}}{\mathrm{d}x} \tag{9}$$

The derivative in eq 9 has been taken with the assumption that P is constant throughout the polymerization. This assumption has been found to not be strictly correct[3] and will be dealt with later in this paper. For the moment, this is a necessary approximation to allow an analytical solution of the problem at hand. In addition, initiation has been ignored. While initiation lasts only a few minutes, P, L, and T change very dramatically during those few minutes. The effect of this assumption will also be discussed later in this paper.

Equation 9 can be used to replace time by conversion in writing a set of differential equations involving the conversion dependence of μ_2^P and μ_2^L. Multiplying eqs 2 and 3 by i^2 and then taking the summation over all chains, i, and making the substitution with eq 9 give the following two simultaneous differential equations:

$$(1 - x)\frac{\mathrm{d}\mu_2^P}{\mathrm{d}x} = \frac{\gamma}{\alpha}(1 - x)(2\mu_1^P + P) - \frac{\beta}{\alpha}(\mu_2^P - \alpha\mu_2^L) \tag{10}$$

$$(1 - x)\frac{\mathrm{d}\mu_2^L}{\mathrm{d}x} = \frac{\beta}{\alpha}(\mu_2^P - \alpha\mu_2^L) \tag{11}$$

Here the terms $\alpha = P/L$, $\gamma = M_0/L$, and $\beta = k_L T/k_P L$ have been defined in writing eqs 10 and 11. The terms α and γ are essentially equivalent to those used by Muller *et al.* for GTP.[5] However, for GTP β was k_{ex}/k_p. Or, to put it another way, the constant k_{ex} is now $k_L T/L$ or, equivalently, k_{-L}/P (using eq 4). Summing eq 10 and 11 gives the differential equation for the second moment of the total amount of polymer:

$$\frac{d\mu_2}{dx} = \frac{\gamma}{\alpha}(2\mu_1^P + \alpha L) \tag{12}$$

Similarly, multiplying eq 2 by i, again using eq 9, and taking the summation over i give:

$$(1 - x)\frac{d\mu_1^P}{dx} = \frac{\gamma}{\alpha}(1 - x)\mu_0^P - \frac{\beta}{\alpha}(\mu_1^P - \alpha\mu_1^L) \tag{13}$$

Since $\mu_1 = \mu_1^P + \mu_1^L = M_0\, x$, eq 13 can be written as:

$$(1 - x)\frac{d\mu_1^P}{dx} = M_0[1 - x(1 - \beta)] - \frac{\beta}{\alpha}\mu_1^P \tag{14}$$

The approximation $\alpha \ll 1$ has been made in writing eq 14. This is always true for a living nitroxide-mediated polymerization. The integration of eq 14, with the initial condition that $\mu_1^P = 0$, gives:

$$\mu_1^P = \alpha M_0\left[1 + \frac{\beta - 1}{\alpha - \beta}(1 - x) + \frac{1 - \alpha}{\alpha - \beta}(1 - x)^{\beta/\alpha}\right] \tag{15}$$

Again, it has been assumed that L, T, and P are constants. Only L is truly a constant, except for a few minutes during initiation when L changes substantially. Substituting eq 15 into eq 12 and integrating, with the initial condition that $\mu_2^P = 0$, give:

$$\mu_2 = M_0\left\{x + \gamma x\left[2 + \frac{\beta - 1}{\alpha - \beta}(2 - x)\right] - \frac{2\alpha\gamma(1 - \alpha)}{(\beta^2 - \alpha^2)}[1 - (1 - x)^{1+\beta/\alpha}]\right\} \tag{16}$$

Since $P_n = \mu_1/\mu_0 = \gamma x$, *and* $P_w = \mu_2/\mu_1 = \mu_2/M_0\, x$, we can write eq 17:

$$P_w = 1 + \gamma\left[2 + \frac{\beta - 1}{\alpha - \beta}(2 - x)\right] - \frac{2\alpha\gamma(1 - \alpha)}{(\beta^2 - \alpha^2)x}[1 - (1 - x)^{1+\beta/\alpha}] \tag{17}$$

Thus,

$$\mathrm{PD} = \frac{P_w}{\gamma x} = \frac{1}{\gamma x} + \frac{1}{x}\left[2 + \frac{\beta - 1}{\alpha - \beta}(2 - x)\right] - \frac{2\alpha(1 - \alpha)}{(\beta^2 - \alpha^2)x^2}[1 - (1 - x)^{1+\beta/\alpha}] \tag{18}$$

The form of the description of the conversion dependence of the molecular weight distributions for GTP and the living nitroxide-mediated polymerization is identical. However, the constants are defined differently. Nevertheless, there is no fundamental difference in the effect of slow exchange with the dormant species in GTP and SFRP. The only difference is in defining the three constants, α, β, and γ. Thus the functional form does not distinguish between a mechanism that involves an attack of a growing polymer chain on a dormant chain, similar to Scheme 2, or release of nitroxide from the dormant chain, as in Scheme 1. It has been suggested that a scheme involving attack of the growing radical on the dormant nitroxide-terminated chain is necessary to obtain narrow polydispersities.[6] The work herein clearly shows that if α, β, and γ have the same values, then either mechanism will give identical values of polydispersity. To distinguish the two mechanisms from the observed PD, one must be able either to show that the values of α, β, and γ are unreasonable for one of the mechanisms or to calculate them *a priori*, or change them by varying the experimental conditions. Thus, using the latter approach, a mechanism that depends on the release and trapping of the growing polymer radical, as shown in Scheme 1, has an exchange rate that is proportional to $[T^\bullet]$, that is, $\beta \propto [T^\bullet]$. On the other hand, any mechanism that depends on the direct attack of the active species on the dormant species, as in Scheme 2, has $\beta = k_{ex}/k_p$ and is independent of $[T^\bullet]$. We will use this difference later in this paper to show that the observed data are not consistent with a significant contribution from a direct exchange mechanism as in Scheme 2.

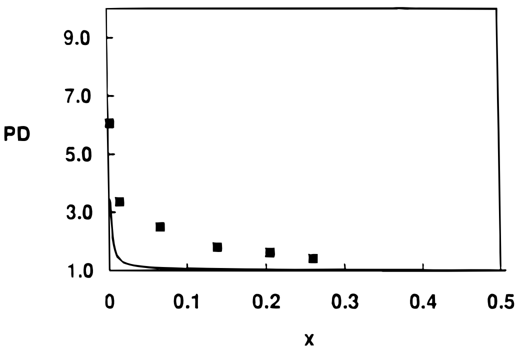


Figure 1. Polydispersity plotted as a function of conversion for bulk styrene SFR polymerization. Initial [TEMPO] = 0.040 M and [BPO] = 0.036 M at 115 °C. The curve is predicted from eq 18, where these constants have been calculated from the known rate constants in ref 3. The data were calculated with $\alpha = 1.25 \times 10^{-7}$, $\beta = 2330$, and $\gamma = 208$, assuming $k_L = 1 \times 10^9$ M^{-1} s^{-1} and a constant TEMPO concentration of 5×10^{-3} M.

Muller *et al.*[5] give an excellent detailed discussion of some of the fine points of eq 18, which will not be repeated here. In the next section, eq 18 will be utilized to understand the conversion dependence of the MWD in some SFR polymerization experiments.

Molecular Weight Distributions in SFRP Processes

Experimental details of the SFRP processes that will be discussed here have been published previously.[3] Data were obtained for four different bulk styrene polymerizations [using benzoyl peroxide (BPO) as the initiator and TEMPO as the nitroxide mediator] at three different temperatures, from 115 to 135 °C, and for two different TEMPO:BPO molar ratios at 125 °C. These different conditions give a wide range of polymerization rates and conversion dependence and cover much of the range of conditions that will give a living free radical polymerization. Some of this experimental data is shown in Figures 1–8, along with the predicted polydispersities based on eq 18.

The conversion rate data for these SFR polymerizations has been shown previously in ref 3. The data in that work have also shown that M_n is linear with conversion, as expected for $P_n = \gamma x$. Figure 1 shows one of these SFR polymerizations, with an initial high PD at low conversion which rapidly decreases with conversion. The values of α, β, and γ were calculated based on the derived rate constants from ref 3. However, only the value of k_L/k_{-L} is known, not the individual values of k_L and k_{-L}. From our previous ESR work,[2] we do know that k_L is large, as capping of the growing chains by nitroxide is much faster than propagation, $k_L T \gg k_p M$. When necessary, we have previously assumed a value of k_L that is expected for the trapping of an *unhindered* radical by a nitroxide (about 1×10^9 M^{-1} s^{-1} with an activation energy of 4 kJ/mol).[7] However,

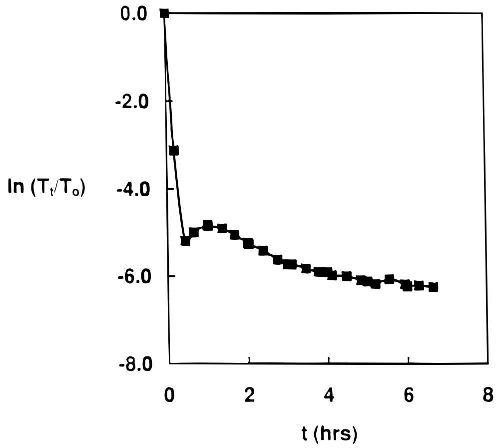


Figure 2. Measured TEMPO concentration as a function of polymerization time as determined by ESR for bulk styrene SFR polymerization at 115 °C, with initial [TEMPO] = 0.040 M and [BPO] = 0.036 M.

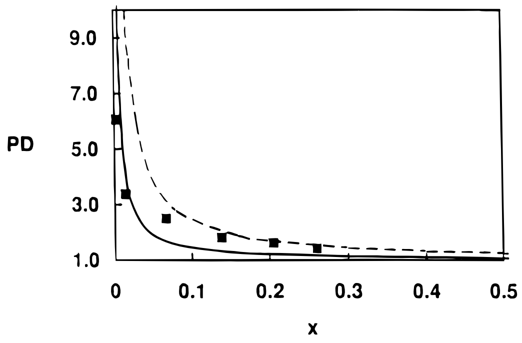


Figure 3. Polydispersity plotted as a function of conversion for bulk styrene SFR polymerization. Initial [TEMPO] = 0.040 M and [BPO] = 0.036 M at 115 °C. The curves are predicted from eq 18, where these constants have been calculated from the known rate constants in ref 3. The curves show data calculated with $\gamma = 208$ and $k_L = 1.5 \times 10^7$ M^{-1} s^{-1}, the solid line calculated with the TEMPO concentration at 1 h, 7×10^{-3} M, with $\alpha = 8.92 \times 10^{-8}$ and $\beta = 48.9$, and the dashed line with the TEMPO concentration at 6 h, 2×10^{-3} M, with $\alpha = 3.12 \times 10^{-7}$ and $\beta = 13.98$.

the polystyrene radical that is trapped in not an unhindered radical. Furthermore, as the growing polymer radical becomes increasingly sterically hindered, it is likely that this value increasingly overestimates k_L. Figure 1 shows the resultant prediction of eq 18, based on this assumed rate constant, where the concentration of the TEMPO radical has been assumed to be constant. As shown in Figure 2, the TEMPO concentration actually decreases rapidly initially by 2 orders of magnitude, as TEMPO traps the initiated chains. Once initiation is over, after about 15 min, the TEMPO concentration still changes but only by a factor of about 3 over the next 5 h. In the calculated curve in Figure 1, the TEMPO concentration is taken to be 5×10^{-3} M, an average of the TEMPO concentration once initiation is over, from Figure 2. As Figure 1 shows clearly, the predicted PD is far below the experimental values at all conversions. While the predicted curve is very sensitive to the TEMPO concentration, as shown in Figure 3, it is clear that the observed TEMPO concentration in Figure 2 cannot come close to the prediction of the experimental PD in Figure 1, if k_L is taken to be that for trapping an unhindered radical.

There are two possibilities to explain the large initial observed PD. The first possibility is that, at low conversion, there is a high initial *irreversible* chain termination rate, which is not included in the derivation of eq 18. Although we have calculated that irreversible termination is not significant once initiation is complete (based on the relevant rate parameters),[3] termination could be a factor during initiation, as there is a very high rate of production of growing chains due to the very fast initiation with BPO at these temperatures. One can try to account for an irreversible termination occurring during initiation by adding an initial μ_2 (at t = 0). However, initiation is short, and the rate of polymerization is slow during most of the initiation due to the high initial TEMPO concentration (the polymerization rate is inversely proportional to TEMPO concentration). Thus, it does not appear that it is possible to obtain a high enough initial μ_2 to bring the fit of eq 18 to the high PD observed.

The more likely possibility is that k_L is considerably smaller than that for a sterically *unhindered* radical. As will be shown later in this paper, all of the PD data are well fit only by a k_L of 1.5×10^7 M^{-1} s^{-1}, about 100 times slower than that for an unhindered radical. While this value is on the same order as the termination of two polystyrene radicals,[8] this still is sufficient to result in narrow polydispersity resin, as shown in Figures 3−7. The reason for this is that while the rate constants for reversible trapping of a growing polymer radical by nitroxide and for irreversible reaction of two polymer radicals are similar, the concentration of nitroxide radical is more than 4 orders of magnitude greater than the polymer radical concentration.

There are some relevant rates known for the trapping of hindered radicals by nitroxides, in particular, the TEMPO radical used here, although the rate is solvent dependent.[10] Thus, the benzyl radical in benzene is trapped at a rate of 1.8×10^8 M^{-1} s^{-1} at 18 °C by TEMPO. While this is about 10 times slower than the rate for an unhindered radical, it is still 10 times higher than the value we use here for trapping a polystyrene radical, although the benzyl radical is clearly less hindered. A better comparison is the trapping of TEMPO by the ethylbenzyl radical, C_6H_5-$CH^•$-CH_3, which is known in isooctane. The ethylbenzyl radical is trapped about 3 times slower than the benzyl radical in isooctane. Assuming a similar rate decrease in benzene would give an approximate rate of 6×10^7 M^{-1} s^{-1} for this radical, about 4 times faster than the value used here. This radical is still, however, less hindered than the polystyrene radical. In extremely hindered radicals, rates below 10^6 M^{-1} s^{-1} have been reported for trapping of TEMPO in isooctane.[10] In all cases where activation energies have been measured for these nitroxide-tapping reactions, the values are <4 kJ/mol, even with hindered radicals! This low activation energy is ascribed to entropic and steric effects and enables one to assume that these trapping rates are essentially temperature independent. Thus, the trapping rate used to fit the data here appears to be reasonable in view of the available trapping data for nitroxides.

Figure 3 shows the fit of the PD from an SFR polymerization to eq 18 calculated at two different TEMPO concentrations: the TEMPO concentration immediately after initiation and the TEMPO concentration at the end of 6 h polymerization as shown in Figure 2. The fit to eq 18 in Figure 3 is generally consistent with the observed dependence of PD with conversion, with the former TEMPO concentration fitting low conversions quite well and the latter concentration fitting the high conversions, with intermediate conver-

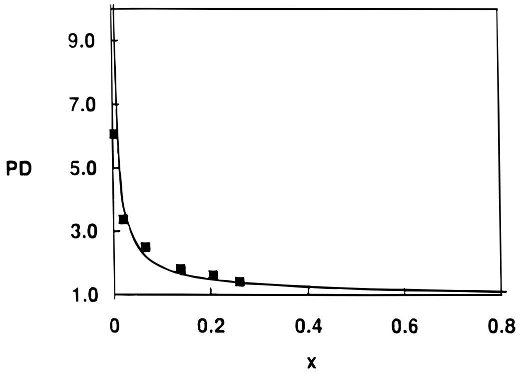


Figure 4. Polydispersity plotted as a function of conversion for bulk styrene SFR polymerization, with initial [TEMPO] = 0.040 M and [BPO] = 0.036 M at 115 °C. The curves are predicted from eq 18, with a variable [TEMPO] calculated on 1 h intervals, the rate constants and [TEMPO] from ref 3 (shown in Figure 2). $\alpha = 7.95 \times 10^{-8}$, $\beta = 55.0$, $\gamma = 208$, and $k_L = 1.5 \times 10^7$ M^{-1} s^{-1}.

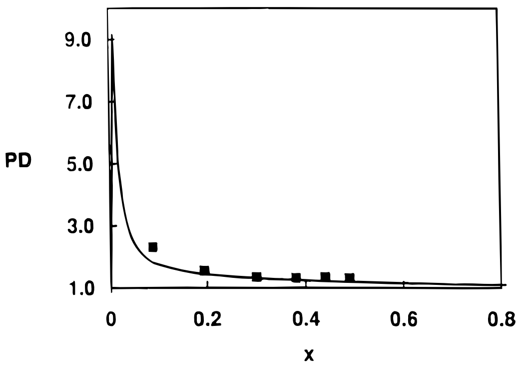


Figure 5. Polydispersity plotted as a function of conversion for bulk SFR styrene polymerization, with initial [TEMPO] = 0.040 M and [BPO] = 0.036 M at 125 °C and [TEMPO]/[BPO] = 1.1. The curves are predicted from eq 18, with a variable [TEMPO] calculated on 1 h intervals, the rate constants and [TEMPO] from ref 3, $\alpha = 1.69 \times 10^{-7}$, $\beta = 23.2$, $\gamma = 208$, and $k_L = 1.5 \times 10^7$ M^{-1} s^{-1}.

sions showing polydispersities between the two predicted curves. However, it is also clear that the changing TEMPO concentration must be taken into account in eq 18 if good quantitative agreement with experiment is to be obtained.

While it is possible to numerically integrate eqs 12 and 13, an alternate approach, which is easier to calculate, is simply to evaluate eq 18 over a series of intervals, where TEMPO is constant in each interval but varies from interval to interval, and then take the summation. Over each inteval the TEMPO concentration was taken as the initial value for that interval, and α, β, and γ are recalculated based on the TEMPO concentration in the interval. Figures 4–7 show the fit of the curves estimated in this way, where the polymerization is taken as the sum over six equal time intervals (each hour of the polymerization). Note that aside from k_L, there are no adjustable parameters in this fit and that the fit depends both on the accuracy of the relevant rate parameters and on our current understanding of the mechanism and kinetics of the SFRP process. Clearly, using a slower rate of capture of the growing chains with the nitroxide gives a good fit with experiment. The good fit, for the entire series of data shown here, suggests that the slower rate of capture is the correct rate and that chain termination during initiation does not impact the observed polydispersity. Note that this is not the same as assuming that termination does not occur, just that it does not lead to an observable increase in polydispersity.

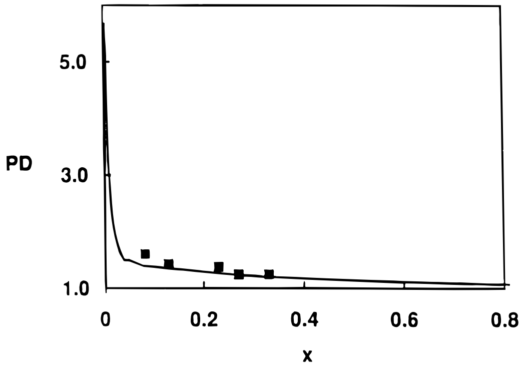


Figure 6. Polydispersity plotted as a function of conversion for bulk styrene SFR polymerization, with initial [TEMPO] = 0.047 M and [BPO] = 0.036 M at 125 °C and [TEMPO]/[BPO] = 1.3. The curves are predicted from eq 18, with a variable [TEMPO] calculated on 1 h intervals, rate constants and [TEMPO] from ref 3, $\alpha = 3.02 \times 10^{-8}$, $\beta = 138$, $\gamma = 177$, and $k_L = 1.5 \times 10^7$ M^{-1} s^{-1}.

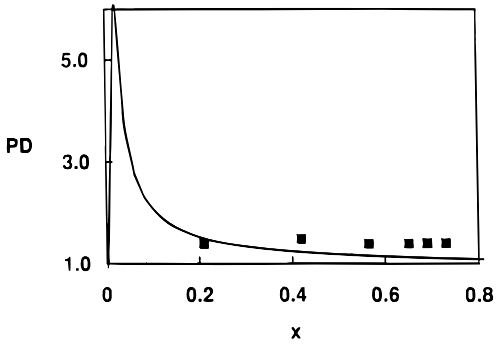


Figure 7. Polydispersity plotted with conversion for bulk styrene SFR polymerization, with initial [TEMPO] = 0.040 M and [BPO] = 0.036 M at 135 °C. The curves are predicted from eq 18, with variable [TEMPO] calculated on 1 h intervals, rate constants and [TEMPO] from ref 3, $\alpha = 4.43 \times 10^{-7}$, $\beta = 18.2$, $\gamma = 208$, and $k_L = 1.5 \times 10^7$ M^{-1} s^{-1}.

However, at high conversion at 135 °C and 1.1 TEMPO to BPO, shown in Figure 7, which has the fastest rate of polymerization of the data shown here, the PD does not decrease with conversion as expected at high conversions. Instead, the PD remains constant. This suggests that either some termination or autopolymerization is occurring, or both. While previous experimental work shows that the nitroxide radical, as well as benzoic acid, the byproduct of initiation by BPO, inhibits autopolymerization under these conditions,[9] some autopolymerization is possible, particularly at longer reaction times and higher temperatures. Figure 8 shows the TEMPO concentration with reaction time for the polymerization in Figure 7. Unlike the other polymerizations shown in Figures 4–6, the polymerization in Figure 7 shows a slow increase in TEMPO concentration at high conversions (compared to Figure 2, for example). If autopolymerization occurs, then Scheme 1 requires that TEMPO be consumed to trap the thermal initiated chains. On the other hand, if *irreversible* termination occurs, Scheme 1 requires that TEMPO be released, one molecule of TEMPO for each chain end that is irreversibly terminated.[3] Thus, the increase in TEMPO concentration suggests that there is some irreversible chain termination under these conditions, resulting in the observed increase in TEMPO concentration. On the basis of the amount of TEMPO released, this corresponds roughly to a few chains out

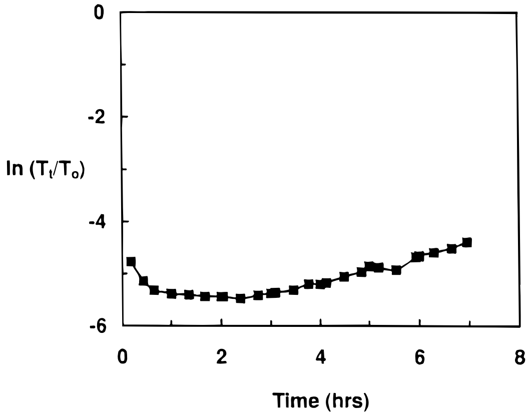


Figure 8. Measured TEMPO concentration with polymerization time as determined by ESR for bulk styrene SFR polymerization at 135 °C, with initial [TEMPO] = 0.040 M and [BPO] = 0.036 M. The curve is shown as a guide to the eye only.

of 100 terminating during the last few hours of the polymerization. However, a rough estimate of the second moment resulting from chain termination by combination, which results in a chain molecular weight equal to the molecular weights of the two chains terminated, suggests that the additional second moment for this irreversible termination is insufficient to completely account for the higher polydispersity. It is possible, however, that irreversible termination is somewhat higher than this, if some TEMPO is being consumed by some other mechanism. This could result in an observed rate of TEMPO increase that is lower than expected from the irreversible chain termination alone. For example, autopolymerization would produce more chains, which would consume TEMPO. Not only would the autopolymerization increase the PD, it would also cause an underestimation of the irreversible termination suggested by Figure 8 by compensating for some of the expected increase in TEMPO concentration from the irreversible termination.

Figures 5 and 6 show the effect of changing the initial concentration of the nitroxide, from 1.1:1 [TEMPO]:[BPO] to 1.3:1 [TEMPO]:[BPO], respectively. As shown by ESR measurements in ref 3, this difference in initial TEMPO concentration corresponds to a 2−10 times lower TEMPO concentration during the polymerization shown in Figure 5 than in Figure 6, once initiation is complete (initiation consumes most of the initial TEMPO to trap the initiated polymer chains). At the lower TEMPO concentration for the polymerization in Figure 5, the exchange rate is slower (the exchange rate constant, β, is equal to $k_L T/k_p L$) resulting in a broader polydispersity at any particular conversion. The differences are greatest at low conversions. Comparison of experimental PD's in Figures 5 and 6 shows clearly the higher polydispersity at lower TEMPO concentration, in agreement with the predicted curves. As discussed above, this is consistent with the proposed mechanism in Scheme 1, where the exchange of dormant and active chains is controlled by the release and trapping of TEMPO. It is not consistent with the direct exchange mechanism, with attack of the dormant chain by an active chain,[6] as in Scheme 2.

Conclusions

Following the approach of Muller *et al.*[5] to calculate the effect of exchange between a dormant and an active species in group transfer polymerization, it has been possible to calculate the effect of a similar exchange in living free radical polymerizations moderated by nitroxide radicals. The general form of the solution of the different moments of the distribution, and thus of the molecular weight distribution, as a function of conversion is the same in GTP and SFRP, if the approximation is made that the concentrations of nitroxide and growing polymer are constant. However, in order to obtain the same form for the general solution, two of the three constants that define the solution (the relative rates of the various kinetic steps) are different for SFRP compared to those for GTP. Using this general solution allows qualitative prediction of the molecular weight distribution with conversion, but only with a trapping rate of about 1.5×10^7 M^{-1} s^{-1} is it possible to fit any of the experimental data.

A solution that gives a better quantitative fit to the data could be obtained by using a numerical integration, which takes into account the changing nitroxide concentration and thus growing polymer chain concentration. However, a good match to experiment is obtained by using the general solution, which requires a constant TEMPO concentration and growing polymer radical concentration, and dividing the polymerization into a fixed number of intervals, one for each hour of the polymerization, where the concentrations of nitroxide and polymer radical are assumed constant over each interval but differing between intervals. Using this approach a very good quantitative fit to the experimental polydispersity is obtained over a wide range of polymerization conditions, again only by using a rate of trapping of the polymer chain by nitroxide that is considerably slower than that for trapping an unhindered radical. However, this lower rate of trapping is still consistent with our previous studies, which require that the rate of trapping be much faster than the rate of polymerization, and is comparable to the known rates of trapping of similar hindered radicals by nitroxides. While this reversible termination rate constant is on the same order as the rate constant of polystyrene radical−radical termination, the 4 orders of magnitude higher nitroxide concentration, compared to the active growing polymer radical, ensures that irreversible polymer radical recombination is minimized.

The good fit to the experimental data is further support for our current understanding of the mechanism and kinetics of SFRP. The general form of the solution of the molecular weight dependence on conversion is the same for a mechanism that is controlled by release of the nitroxide radical from the polymer chain and by a mechanism that is controlled by an attack on the nitroxide-terminated dormant chain by a growing chain, as has been suggested elsewhere.[6] The only difference is the way in which the three constants are defined in the general solution. However, a mechanism based on attack of the dormant polymer chains by the active chains does not predict the observed increase in the rate of exchange with increased TEMPO and thus a decreased PD at comparable conversion, but it is perfectly consistent with the mechanism presented here, where exchange depends on release and trapping of the polymer chains by nitroxide radicals.

It is concluded that the polydispersity in the bulk living free radical polymerization mediated by nitroxide is controlled by the exchange rate between the growing and dormant chains. At high conversion where the rate of polymerization is high, there is also perhaps a small amount of irreversible chain termination and some autopolymerization.

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