Living Free Radical Polymerizations Mediated by the Reversible Combination of Transient Propagating and Persistent Nitroxide Radicals. The Role of Hydroxylamine and Alkene Formation

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ABSTRACT: A kinetic analysis of living polymerizations controlled by persistent nitroxide radicals is extended to cover the formation of hydroxylamines and alkene macromonomers. This reaction can occur by radical disproportionation during the cross-reaction of the carbon-centered propagating and the nitroxide radicals and/or by a direct fragmentation of the dormant alkoxyamines. For equal extents, both pathways cause nearly indistinguishable upper limits of the monomer conversion and a very similar increase of the polydispersity in the final stages of polymerization, but they do not markedly affect the linear increase of the degree of polymerization with conversion

Introduction

Living free radical polymerizations (LFRP) provide polymers with highly regulated structures. The number-average molecular weight is proportional to the conversion and is inversely proportional to the initiator concentration, and the polydispersity index is usually close to 1. Moreover, the polymer chains are living; i.e., they are capable of growing upon addition of new monomer. This allows the construction of diverse block copolymers. One successful scheme relies on the reversible cleavage of ‘dormant’ polymer chains $R_n{-}Y$ into propagating radicals $R_n^\bullet$ and persistent radicals $Y^\bullet$ (eqs 1 and 2) coupled to propagation (eq 3), n being the number of incorporated monomer units.

$$R_n{-}Y \xrightarrow{k_d} R_n^\bullet + Y^\bullet \tag{1}$$

$$R_n^\bullet + Y^\bullet \xrightarrow{k_c} R_n{-}Y \tag{2}$$

$$R_n^\bullet + M \xrightarrow{k_p} R_{n+1}^\bullet \tag{3}$$

The products of irreversible terminations, such as

$$R_n^\bullet + R_m^\bullet \xrightarrow{k_t} P_n + P_m \tag{4}$$

are often virtually absent, the concentrations of the transient growing radicals $R_n^\bullet$ are low, and there is a remarkably large excess of the persistent species $Y^\bullet$.

Rizzardo et al.[1] introduced alkoxyamines $R_0{-}Y$ (trialkylhydroxylamines) as initiators where R_0 is an alkyl and Y is a nitroxide group. Later, Georges et al.[2] found that the polymerization can also be started with a conventional radical initiator in the presence of a stable nitroxide $Y^\bullet$. In this case, the alkoxyamines $R_n{-}Y$ are formed in situ. Following this seminal work, many variants of the method were developed using different initiators, different persistent radicals and different procedures.[3]

In systems consisting initially only of the alkoxyamine and the monomer, the virtual absence of self-termination has a purely kinetic reason, the persistent radical effect (PRE):[4] the decomposition (eq 1) of a dormant chain produces a transient radical that can self-terminate (eq 4) and a persistent one that cannot. Each self-termination act increases the amount of $Y^\bullet$ with respect to $R_n^\bullet$, thus favoring the cross-termination reaction 2 with respect to self-termination. By this self-inhibition, the self-termination reaches a very low level in a short time, although it never stops.

In earlier theoretical work[5,6,7] we have analyzed the kinetics of polymerizations based solely on reactions 1−4 for chain-length independent rate constants, the absence of any additional initiation and systems initially composed of alkoxyamine $R_0{-}Y$ and monomer M only. To be controlled and living, the polymerization must occur in the time regime where the PRE operates. This regime is characterized by a quasi-equilibrium relation for reactions 1 and 2, by an extremely prolonged effective lifetime of the dormant species and by radical concentrations that vary only slowly with time. The establishment of the PRE regime requires that the rate constants k_d and k_c of reactions 1 and 2 fulfill conditions that depend solely on the termination constant k_t and the initial alkoxyamine concentration. However, to obtain large conversions, low polydispersities and small fractions of unreactive (dead) polymer, k_d and k_c must obey additional conditions which contain the propagation constant and the monomer concentration.[7] Several of our conclusions are supported by related theoretical work of Fukuda et al.[8,9]

Obviously any process that interferes with the reversible dissociation (eqs 1 and 2) has important consequences for the polymerization process. One of these is the formation a terminally unsaturated polymer (macromonomer) and a hydroxylamine by a usual radical disproportionation which competes with the cross-coupling (2).

$$R_n^\bullet + Y^\bullet \xrightarrow{k_{cD}} P_n + YH \tag{5}$$

In simulations, we and others[5,10−12] have found that

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even minor fractions of disproportionation $f_D = k_{cD}/(k_c + k_{cD})$ in the cross-reaction lead to incomplete monomer conversion and increase the final polydispersities. Deficiencies of experimentally attempted polymerizations have been attributed to this process.[10−15]

The alkene macromonomer and the hydroxylamine may also be formed in a reaction 6 competing with the alkoxyamine cleavage (1).

$$R_n{-}Y \xrightarrow{k_{dD}} P_n + YH \qquad (6)$$

Mechanistically, this could involve an (unlikely)[13,14] radical cage reaction following a normal bond cleavage or a direct fragmentation of the alkoxyamine.[8,9,16−19] With the present experimental means these two possibilities are indistinguishable.[14] However, for polymerizations, the formation of the alkene and the hydroxylamine by reactions 5 and/or 6 should to lead to very similar effects, and it is clear from the available experimental data that their extent strongly depends on the nature of both the nitroxide and the monomer.[3,8−22]

In this work, we extend our previous kinetic analysis[5,6,7] of living free radical polymerizations based on the reversible coupling of propagating and persistent radicals to account for reactions 5 and 6. In particular, we aim at equations that predict the maximum attainable conversion, the polymerization time, and the time evolutions of the degree of polymerization and of the polydispersity. Further, we investigate whether the fractions of reactions 5 and 6 can be determined from polymerization studies and whether their effects can be distinguished. Our specific examples refer to nitroxide mediated polymerizations only, but the conclusions will be valid for all radical polymerizations involving the PRE equilibrium.

Disproportionation Competing with Cross-Coupling

As before,[5,6,7] we assume chain-length independent rate constants. This allows us to consider only the sums of the concentrations [R] of all propagating radicals $R_n^\bullet$, [I] of all dormant alkoxyamine species $R_n{-}Y$, [P] of all unreactive polymer products P_n from reaction 4, [P(−H)] of all alkenes $P_n(-H)$ besides the concentrations [Y] of the persistent radical $Y^\bullet$ and [YH] of the hydroxylamine. We also assume that the irreversible termination of the propagating radicals is by disproportionation only (eq 4). Termination by combination would simply increase the degree of polymerization of the unreactive polymer fraction P but does not change the kinetics. Further, we exclude initiation other than by the alkoxyamine cleavage (1) and also exclude the presence of the persistent species at the beginning of the process.

To facilitate the comparison, it seems useful to state some earlier results[7] first which are valid in the absence of reactions 5 and 6. The reactions reach the PRE quasi-equilibrium if the rate constants of the reversible cleavage obey

$$K/[I]_0 \ll k_c/k_t \text{ or } \frac{k_c^{\,2}}{k_d} \gg \frac{k_t}{[I]_0} \qquad (7a)$$

$$K/[I]_0 \ll 1 \quad \text{or } k_d \ll k_c[I]_0 \qquad (7b)$$

and

$$k_d \le k_t[I]_0 \qquad (7c)$$

Here, $K = k_d/k_c$ is the equilibrium constant of reactions 1 and 2, and $[I]_0$ is the initial alkoxyamine concentration. The quasi-equilibrium relation is

$$k_c[R][Y] = k_d[I]_0 \qquad (8)$$

[R] denotes the total concentration of the propagating radicals $R_n^\bullet$, and [Y] is the concentration of the persistent species $Y^\bullet$. The radical concentrations obey[6−9]

$$[R] = (K[I]_0/3k_t)^{1/3}t^{-1/3} \text{ and } [Y] = (3k_tK^2[I]_0^{\,2})^{1/3}t^{1/3} \qquad (9)$$

More than 90% conversion to dormant chains will be obtained in the quasi-equilibrium regime if

$$K < \frac{k_p[I]_0}{(2\ln(10))k_t} \quad \text{and} \quad k_p \ll 3\,k_c \qquad (10)$$

and the conversion index of the monomer is then given by

$$\ln\frac{[M]_0}{[M]} = \frac{3}{2}k_p\left(\frac{k_d[I]_0}{3k_ck_t}\right)^{1/3}t^{2/3} \qquad (11)$$

The number-average degree of polymerization develops as

$$X_n = \frac{[M]_0 - [M]}{[I]_0(1 - e^{-k_dt})} \qquad (12)$$

and the polydispersity index tends to a final minimum of

$$\mathrm{PDI}_\infty = 1 + \frac{[I]_0}{[M]_0} + \left(\frac{\pi k_p^{\,3}[I]_0}{k_dk_ck_t}\right)^{1/2} \qquad (13)$$

We now combine reactions 1−4 with reaction 5 and cover only cases explicitely for which conditions 7 and 10 would be fulfilled in the absence of reaction 5. The initial conditions for the concentrations are

$$[I](t=0) = [I]_0 \neq 0, \quad \text{and} \quad [Y]_0 = [R]_0 = [P]_0 = [YH] = [P(-H)] = 0 \qquad (14)$$

By stoichiometry, the concentrations are related by

$$[I]_0 - [I] = [Y] + [YH] = [R] + [P] + [P(-H)] \qquad (15)$$

Hence, one may select [R], [Y] and [YH] = [P(−H)] as the only relevant time dependent variables. The kinetic equations for these species read for homogeneous reaction conditions

$$\frac{d[R]}{dt} = k_d([I]_0 - [Y] - [YH]) - (k_c + k_{cD})[R][Y] - k_t[R]^2 \qquad (16a)$$

$$\frac{d[Y]}{dt} = k_d([I]_0 - [Y] - [YH]) - (k_c + k_{cD})[R][Y] \qquad (16b)$$

$$\frac{d[YH]}{dt} = k_{cD}[R][Y] \qquad (16c)$$

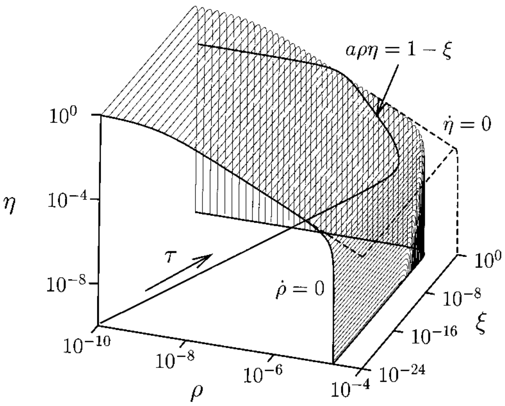


Figure 1. Time evolution of the reduced concentrations ρ, η and ξ of the radicals R$^\bullet$, Y$^\bullet$ and the hydroxylamine YH in the three-dimensional phase space and dividing surfaces. Parameters $a = 5 \times 10^8$ and $b = 2 \times 10^9$.

Because of physical reasons all rate constants and concentrations are positive or zero. The kinetic equations contain five parameters, namely k_t, k_d, k_c, k_{cD}, and $[I]_0$.

As before,[7] we find it convenient to use a set of reduced quantities that underline the kinetically relevant ratios. These are defined by eq 17a and eq 17b.

$$a = \frac{(k_c + k_{cD})[I]_0}{k_d} \; b = \frac{k_t[I]_0}{k_d} \; f_D = \frac{k_{cD}}{k_c + k_{cD}} \quad (17a)$$

$$\rho = \frac{[R]}{[I]_0} \; \eta = \frac{[Y]}{[I]_0} \; \xi = \frac{[YH]}{[I]_0} \; \tau = k_d t \quad (17b)$$

With the notation $\dot{x} = dx/d\tau$, parts a–c of eq 16 become

$$\dot{\rho} = 1 - \eta - \xi - a\rho\eta - b\rho^2 \quad (18a)$$

$$\dot{\eta} = 1 - \eta - \xi - a\rho\eta \quad (18b)$$

$$\dot{\xi} = f_D a\rho\eta \quad (18c)$$

and the conditions 7 read $a^2/b \gg 1$, $a \gg 1$, and $b \geq 1$.

The study of these coupled nonlinear differential equations is simplified[7] by considering the general behavior of the trajectory of the point $(\rho(\tau), \eta(\tau), \xi(\tau))$ in the three-dimensional phase space spanned by the possible values of the variables that, by stoichiometry, are limited to $0 \leq \rho \leq 1$, $0 \leq \eta \leq 1$, $0 \leq \xi = 1$. Figure 1 shows a trajectory computed for the parameters $a = 5 \times 10^8$, $b = 2 \times 10^9$, and $f_D = 0.02$ in a log–log–log-plot. As expected from equations (18), at first ρ and η increase in the same way while ξ remains very small. Then ρ attains a maximum and thereafter decreases to its final value $\rho = 0$, whereas η and ξ continue to increase.

Also shown in Figure 1 are two surfaces that are defined by setting the left-hand side of the eq 18, parts a and b to zero, that is by

$$\eta_l = \frac{1 - \xi - b\rho^2}{1 + a\rho} \quad (19a)$$

and

$$\eta_u = \frac{1 - \xi}{1 + a\rho} \quad (19b)$$

respectively. Insertion of $\eta = \eta_l + \delta$ and $\eta = \eta_u + \delta$ into (18a,b) reveals that these surfaces divide the phase space into three subspaces: ξ increases in all regions, and ρ and η both increase in time in the subspace below η_l. ρ decreases but η increases in the subspace between η_l and η_u, and both ρ and η decrease in the subspace above η_u. The trajectory starts below η_l. Hence, it will cross the lower surface η_l once in an upward direction, but it cannot recross it again. It cannot cross the upper surface η_u because it must do so in the downward direction but approaches it from below. Consequently, after crossing η_l the trajectory is confined to the space between the two surfaces, and accordingly, after the initial stage of increasing ρ, η, and ξ, the computed trajectory in Figure 1 evolves between the surfaces. As found by comparison, it follows eq 20.

$$a\rho\eta = 1 - \xi, \text{ or } (k_c + k_{cD})[R][Y] = k_d([I]_0 - [YH]) \quad (20)$$

In the earlier complete treatment for $k_{cD} = 0$,[7] the initial stage of the time evolution was of little importance for polymerization. Therefore, we consider here only the time regime after the first crossing where relation 20 holds. It is nothing else but the earlier PRE quasi-equilibrium relation 8 modified to account for the cross-disproportionation in a quite natural way, namely by the addition of k_{cD} to k_c on the left-hand side and by the reduction of the concentration of dormant species on the right-hand side. However, whether the time-dependent concentrations will satisfy relation 20 or not depends on kinetic conditions for the parameters a and b. They are easily derived following the procedures given earlier[7] as

$$a^2/b \gg 1 - \xi, \quad a \gg 1 - \xi, \quad \text{and} \quad b \geq 1 - \xi \quad (21)$$

These relations contain the variable ξ which is confined to values $0 \leq \xi \leq 1$. Hence, they are obviously fulfilled if the conditions 7 hold. They do not impose direct limits on the fraction of disproportionation f_D for which (20) may not be valid so that these are explored later on.

Inserting relation 20 into eq 18c gives after integration

$$\xi = 1 - e^{-f_D\tau} \quad \text{or} \quad [YH] = [I]_0(1 - e^{-f_D k_d t}) \quad (22a)$$

which also implies

$$[I] = [I]_0 e^{-f_D k_d t} \quad (22b)$$

At first glance, this result is surprising because the dormant species decay exponentially as if the dissociation (eq 1) was accompagnied by a direct decomposition to alkoxyamine and alkene, i.e., by reaction 6, and not by the disproportionation (eq 5) considered in this section. However, the interpretation is rather simple. In the quasi-equilibrium stage, there is very little self-termination. For $k_{cD} = 0$, the concentration of dormant chains [I] is practically equal to $[I]_0$ because every decomposition (eq 1) is followed by the rapid cross-termination (eq 2). But for finite disproportionation, a fraction of the dormant chains that have decomposed is lost by this irreversible process, and this loss is equivalent to a loss by the direct decomposition (eq 6). Hence, the two processes (5) and (6) will be hardly distinguishable.

With (22b) the quasi-equilibrium relation 20 becomes

$$a\rho\eta = e^{-f_D\tau} \text{ or } (k_c + k_{cD})[R][Y] = k_d[I]_0 e^{-f_D k_d t} \qquad (23)$$

From eq 18a,b, one has

$$\dot{\eta} = \dot{\rho} + b\rho^2 \qquad (24)$$

By use of (23) this reduces to an equation for η which can be integrated. Neglecting terms that arise from $\dot{\rho}$ in (24) and are important only in the transition from the initial stage to the PRE regime,[7] we obtain the radical concentrations

$$\eta = \left(\frac{3b}{2f_D a^2}\right)^{1/3}[1 - \exp(-2f_D\tau)]^{1/3} \qquad (25a)$$

or

$$[Y] = \left(\frac{3k_d k_t [I]_0^2}{2f_D(k_c + k_{cD})^2}\right)^{1/3}[1 - \exp(-2f_D k_d t)]^{1/3} \qquad (25b)$$

and using (23)

$$\rho = \left(\frac{2f_D}{3ab}\right)^{1/3}\exp(-f_D\tau)/[1 - \exp(-2f_D\tau)]^{1/3} \qquad (26a)$$

or

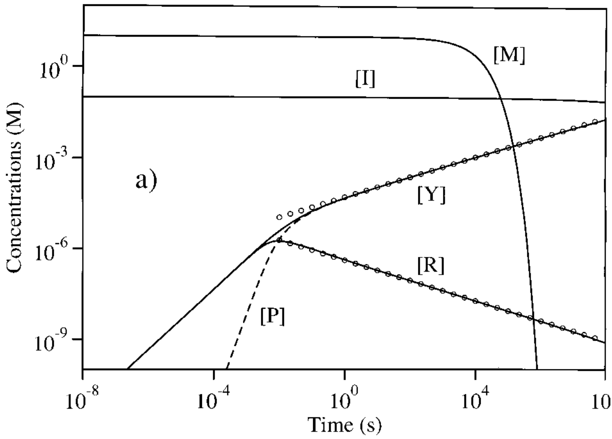
$$[R] = \left(\frac{2f_D k_d{}^2[I]_0}{3(k_c + k_{cD})k_t}\right)^{1/3}\exp(-f_D k_d t)/[1 - \exp(-2f_D k_d t)]^{1/3} \qquad (26b)$$

For $k_{cD} \to 0$, these solutions reduce to the earlier results, eqs 8 and 9.

Figure 2 displays computed concentrations of all species in a log–log representation, (a) without and (b) with a partial cross-termination by disproportionation. The parameters are $k_d = 4.5 \times 10^{-3}$ s^{-1}, $k_t = 10^8$ M^{-1} s^{-1}, $k_c = 2.2 \times 10^7$ M^{-1} s^{-1}, $k_p = 5000$ M^{-1} s^{-1}, $[I]_0 = 10^{-1}$ M, and $[M]_0 = 10$ M, and for (b) $f_D = 2\%$. The circles represent the concentrations of R$^\bullet$, Y$^\bullet$ and YH as calculated from expressions 9, 22a, 25, and 26.

Obviously, for small times the radical concentrations [R] and [Y] develop as if there were no disproportionation. This is generally true and emerges from the following consideration. For $k_c < k_t$, which is true for most living polymerizations, the quasi-equilibrium regime is entered at the time $t \approx \sqrt{k_d k_t / 9 k_c{}^2 [I]_0} / k_d$.[7] Because of condition 7a, this time is much smaller than $k_d{}^{-1}$, and with $f_D \leq 1$ it is also smaller than the time $t \approx (f_D k_d)^{-1}$ for which the exponential terms in eqs 22–26 noticeably deviate from unity. Hence, initially and for all possible values of f_D the reactions will always first reach the quasi-equilibrium (8) which is valid for zero disproportionation. However, at the time $t \approx (f_D k_d)^{-1}$ the dormant chains are effectively converted to hydroxylamine YH and alkene P(–H). Equations 23, 25, and 26 account for this reaction, and they hold for all possible values of f_D; i.e., there is no real restriction for this quantity.

At large times $t \gg (f_D k_d)^{-1}$, the persistent radicals Y$^\bullet$ form only a small product fraction so that the stoichiometry relations 15 are fulfilled. The amount of Y$^\bullet$ is equal to the amount of termination products P, so one can state a lower limit of f_D above which disproportionation becomes important before product formation is governed by self-termination.[7] For infinite time (25b) yields



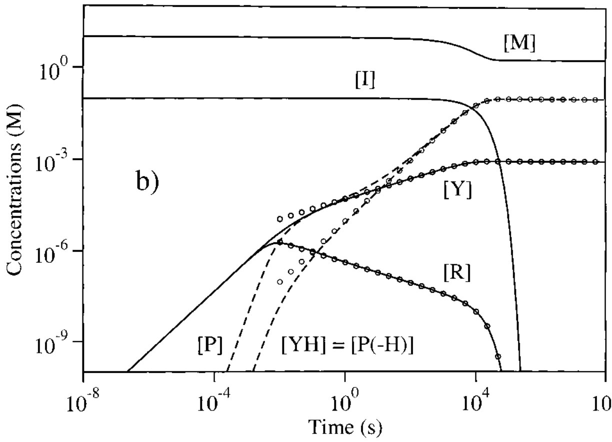


Figure 2. Time evolution of the concentrations of radicals [R], [Y], dormant species [I], self-termination [P] and disproportionation products [YH] = [P(–H)], and monomer [M], (a) without and (b) with a partial cross-termination by disproportionation: solid lines numerically computed; circles according to the analytic eqs 9, 22, and 26. Parameters: $k_d = 4.5 \times 10^{-3}$ s^{-1}, $k_t = 10^8$ M^{-1} s^{-1}, $k_c = 2.2 \times 10^7$ M^{-1} s^{-1}, $k_p = 5000$ M^{-1} s^{-1}, $[I]_0 = 10^{-1}$ M, and $[M]_0 = 10$ M and for (b) $f_D = 2\%$.

$$[Y]_\infty = \left(\frac{3k_d k_t [I]_0^2}{2f_D(k_c + k_{cD})^2}\right)^{1/3} \qquad (27)$$

and this is much smaller than $[I]_0$ if

$$f_D(1 - f_D)^{-2} \gg \frac{3k_d k_t}{2k_c{}^2[I]_0} \qquad (28)$$

In nitroxide-mediated living polymerizations, one usually has[7-9,16-21,24-30] $k_c \geq 10^6$ M^{-1} s^{-1}, $[I]_0 \geq 10^{-2}$ M, $k_d \leq 10^{-2}$ s^{-1}, and $k_t \leq 10^9$ M^{-1} s^{-1}. For the extreme values of $k_d = 10^{-2}$ s^{-1}, $k_t = 10^9$ M^{-1} s^{-1}, $k_c = 10^6$ M^{-1} s^{-1}, and $[I]_0 = 10^{-2}$ M the RHS of expression 28; i.e., the lower limit of f_D is equal to 1.5×10^{-3} or 0.15%. Below this limit, disproportionation effects are negligible.

For sufficiently large f_D, the exponential terms in the concentration of transient radicals have a striking effect on the polymerization rate. According to Figure 2a, 90% monomer conversion is reached in about 5 h in the absence of disproportionation. In Figure 2b the concentration of transient radicals first decreases as in Figure

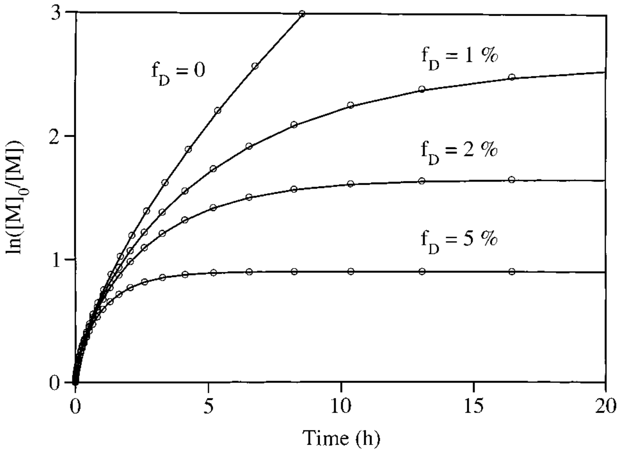


Figure 3. ln([M]$_0$/[M]) vs time for different fractions of disproportionation. Solid lines from numerical calculations and circles according to eq 30. Other parameters are as used for Figure 2.

2a, and this decrease accellerates dramatically after $t = (f_D k_d)^{-1} \approx 10^4$ s because of disproportionation. The direct consequence of this faster depletion is that the monomer conversion stops at about 80%.

Integration of the polymerization rate equation

$$\frac{d[M]}{dt} = -k_p[R][M] \tag{29}$$

using (26b) and some manipulations, gives

$$[M] = [M]_0 \exp\left(-\frac{3}{2}k_p\left(\frac{[I]_0}{3k_t(k_c + k_{cD})k_d f_D{}^2}\right)^{1/3} F(t)\right) \tag{30}$$

where

$$F(t) = \frac{2^{5/3}}{3}\int_0^{X/2} x^{-\frac{1}{3}}(1-x)^{-\frac{1}{3}}dx = \frac{2^{5/3}}{3}B\left(\frac{2}{3},\frac{2}{3}\right)I_{X/2}\left(\frac{2}{3},\frac{2}{3}\right) \tag{31}$$

with $X = 1 - \exp(-f_D k_d t)$. $B(a,b)$ and $I_x(a,b)$ are the beta and the incomplete beta functions.[23] When f_D tends to zero, eq 11 is reobtained by using in (31) the series expansion[23]

$$I_x(a,b) = \frac{x^a(1-x)^b}{aB(a,b)}[1 + O(x)]$$

where $O(x)$ are terms on the order of x. At infinite time (30) yields the maximum conversion

$$C_{max} = 1 - [M]_\infty/[M]_0 = 1 - \exp\left(-\frac{3}{2}k_p\left(\frac{[I]_0}{3k_t(k_c + k_{cD})k_d f_D{}^2}\right)^{1/3} F(\infty)\right) \tag{32}$$

with $F(\infty) = 2^{2/3}(\Gamma(^2/_3))^2/3\Gamma(^1/_3) \approx 1.08$.

Figure 3 shows polymerization indices ln([M]$_0$/[M]) computed for the same parameters as used for Figure 2 and different fractions of disproportionation. At the beginning of the process, all curves are superimposed and follow eq 11. For nonzero f_D or k_{cD} they then level off and reach a plateau of the maximum conversion which is 93% for $f_D = 1\%$, 81% for $f_D = 2\%$, and 59% for $f_D = 5\%$.

From expression 30, one can calculate the time where the fraction p of the maximum value of the polymerization index ln([M]$_0$/[M]) is reached

$$p = \frac{\ln([M]_p/[M]_0)}{\ln([M]_\infty/[M]_0)} = \frac{F(t_p)}{F(\infty)}$$

For large p, this time t_p markes essentially the end of the polymerization. With known relations for the incomplete β function[23] and the series expansion for times where $\exp(-f_D k_d t) \ll 1$, we arrive at

$$t_p = \frac{1}{f_D k_d}\ln\left[\left(\frac{2}{1-p}\right)/B\left(\frac{1}{2},\frac{2}{3}\right)\right] \tag{33}$$

and $B(^1/_2, {}^2/_3) \approx 2.59$.[23] Interestingly, t_p does not depend on the initial alkoxyamine concentration. For $p = 0.9$, (33) gives $t_p \approx 2/f_D k_d$ and corresponds to approximately 6 h for the case of $f_D = 2\%$ in Figure 3. At this time about 87% of the dormant chains are converted to hydroxylamine YH and alkene macromonomer P(−H).

The lower limit of f_D (28) above which disproportionation becomes important for product formation refers both to polymerizing and nonpolymerizing systems because it includes disproportionation between Y$^\bullet$ and $R_0{}^\bullet$. Therefore, it is also useful to find an upper limiting value of f_D that allows a large monomer conversion to dormant species before these are converted to hydroxylamines and alkenes. Requiring that the fraction of disproportionation and alkene products should be smaller than 10%, i.e., $[YH]/[I]_0 < 0.1$ at 90% monomer conversion leads with eq 22b and the time for 90% conversion following from (11) to

$$f_D < \frac{\ln(1/0.9)}{(2\ln 10)^{3/2}}3k_p{}^{3/2}\sqrt{\frac{[I]_0}{k_d k_c k_t}} \tag{34}$$

For larger f_D one will obtain mainly hydroxylamine and alkene macromonomer at large conversion. Obviously, for the production of mainly dormant chains at large conversions, monomers with larger k_p tolerate larger fractions of disproportionation. Also, larger fractions of disproportionation are tolerated if only low degrees of polymerization are attempted. Thus, for a bulk polymerization with $[M]_0 \approx 10$ M aiming at a final $X_N \approx 100$, i.e., $[I]_0 = 10^{-1}$ M the limit (eq 34) becomes for typical values of[7−9,16−21,24−30] $k_d = 10^{-3}$ s^{-1}, $k_c = 10^7$ M^{-1} s^{-1}, and $k_t = 5 \times 10^8$ M^{-1} s^{-1}, $f_D < 0.22\%$ for $k_p = 2000$ M^{-1} s^{-1}, $f_D < 0.86\%$ for $k_p = 5000$ M^{-1} s^{-1}, and $f_D < 6.9\%$ for $k_p = 20\,000$ M^{-1} s^{-1}. If $X_N \approx 10$ is attempted, these limits increase to $f_D < 0.70\%$, $f_D < 2.72\%$, and $f_D < 21.8\%$, respectively.

To characterize the chain-length distribution, we calculate the number-average degree of polymerization

$$X_n = \frac{m_1}{m_0}$$

and the polydispersity index

$$\mathrm{PDI} = \frac{m_0 m_2}{m_1{}^2}$$

from the moments[24]

$$m_k = \sum_{n=1}^{\infty} n^k([\mathrm{I}]_n + [\mathrm{R}]_n + [P_n] + [P_n(-H)]) \qquad k = 0, 1, 2$$

The exclusion of $n = 0$ in the summation ensures that only monomer-containing species are counted. Assuming that every radical $R_0^{\bullet}$ released from the regulator I_0 undergoes at least one monomer addition before recoupling,[7] gives for the zeroth moment

$$m_0 = [\mathrm{I}]_0(1 - \mathrm{e}^{-k_d t}) \tag{35}$$

For the moments m_1 and m_2, we have the kinetic equations

$$\frac{\mathrm{d}m_1}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} \tag{36a}$$

$$\frac{\mathrm{d}m_2}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} + 2k_p[\mathrm{M}]m_1(\mathrm{R}) \tag{36b}$$

Integration of (36a) gives with (35) as before[7]

$$X_n = \frac{[\mathrm{M}]_0 - [\mathrm{M}]}{[\mathrm{I}]_0(1 - \mathrm{e}^{-k_d t})} \tag{12}$$

where the exponential term comes from the finite decomposition time of the initiator. The degree of polymerization does not depend explicitely on the fraction of disproportionation. However, if this fraction is large enough the polymerization ends at the maximum conversion $C_{\max}$, and X_n attains a final value that is smaller than the usual theoretical limit $[\mathrm{M}]_0/[\mathrm{I}]_0$. From eq 33, the limiting conversion is reached at a time long compared to $(k_d)^{-1}$, so that the maximum degree of polymerization becomes

$$X_{n,\max} = \frac{[\mathrm{M}]_0}{[\mathrm{I}]_0} C_{\max} \tag{37}$$

The solid lines in Figure 4 show the development of the number-average degree of polymerization computed for the parameters used for Figure 2b and various initial concentrations of the alkoxyamine regulator. The filled circles indicate the behavior in the absence of disproportionation as given by eq 12, and the large empty circles give the maximum degrees of polymerization. As follows from eq 32, in the presence of disproportionation the polymerization ends at lower conversion for larger ratios of monomer to alkoxyamine, i.e., for larger attempted final degrees of polymerization. However, the time needed for the maximum conversion (eq 33) does not depend on $[\mathrm{I}]_0$. Moreover, we notice that disproportionation does not affect the linear increase of the number-average degree of polymerization X_n. This linear increase begins after the characteristic time $(k_d)^{-1}$ for the alkoxyamine cleavage[7] and ends at the maximum conversion where only unreactive macromonomer chains and hydroxylamine remain. It cannot be affected by disproportionation because X_n is proportional to conversion by definition, and disproportionation does not change the total number of chains.

To calculate the polydispersity index, the kinetic equation, eq 36b, of the total second moment m_2 must be solved. It involves the first moment of the radical chain length distribution $m_1(\mathrm{R})$ which is coupled to the first moment of the dormant species $m_1(\mathrm{I})$. The kinetic equations of these individual first moments are

$$\frac{\mathrm{d}m_1(\mathrm{R})}{\mathrm{d}t} = k_d m_1(\mathrm{I}) - (k_c + k_{cD})[\mathrm{Y}]m_1(\mathrm{R}) + k_p[\mathrm{M}][\mathrm{R}] - k_t[\mathrm{R}]m_1(\mathrm{R}) \tag{38a}$$

$$\frac{\mathrm{d}m_1(\mathrm{I})}{\mathrm{d}t} = -k_d m_1(\mathrm{I}) + k_c[\mathrm{Y}]m_1(\mathrm{R}) \tag{38b}$$

Insertion of (26a,b) and (30) into (38a,b) provides a set of coupled first-order differential equations with time dependent coefficients for which we did not find analytic solutions. Therefore, the polydispersity index was calculated numerically.

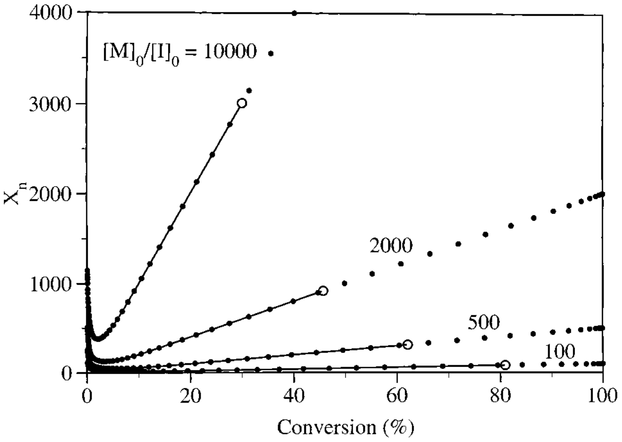


Figure 4. Number-average degrees of polymerization as a function of conversion for 2% disproportionation and various initial alkoxyamine concentrations: solid lines from numerical calculation, filled symbols according to eq 12, and empty circles according to eq 37. Other parameters as used for Figure 2.

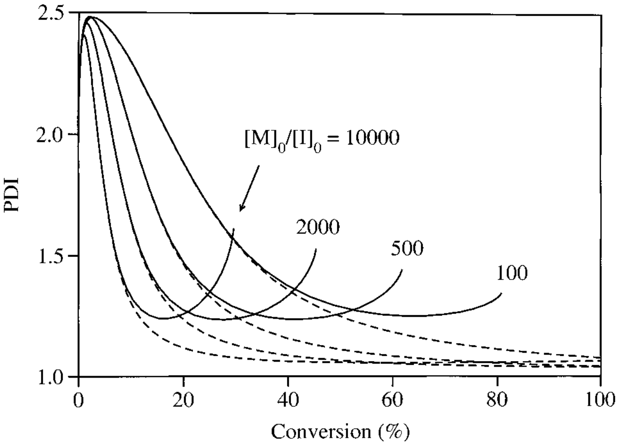


Figure 5. Polydispersity indices as a function of conversion for 2% disproportionation and various initial alkoxyamine concentrations. Solid lines from numerical calculation, broken lines from numerical calculations for $f_D = 0$. Other parameters as used for Figure 2.

Figure 5 displays the results for the fraction of disproportionation of 2% and all other parameters as used for Figure 4 as solid lines. For comparison, the behavior of the PDI in the absence of disproportionation is indicated by the broken lines. As often claimed,[3,5,8−22] disproportionation increases the polydispersity. More precisely, Figure 5 shows that the upward deviations from the ideal behavior occur only above about 50% of the maximum conversion. They are linked to the leveling off of the polymerization index seen in Figure 3. For $f_D = 2\%$ and $k_d = 4.5 \times 10^{-3}$ s^{-1} this behavior sets in after about 2 h, i.e., at about $0.6(f_D k_d)^{-1}$, and is nearly complete after $t_p \approx 6$ h. The considerable duration of the operation of the disproportionation reaction explains the final increase of the PDI in Figure 5: the dormant chains are successively converted to alkene and alkoxyamine while they still grow.

Alkoxyamine Decomposition to Hydroxylamine and Alkene

In this section, we combine reactions 1–4 with reaction 6 and again use chain-length independent rate constants, assume that the irreversible termination (eq 4) of the propagating radicals is by disproportionation only, exclude initiations other than by the alkoxyamine cleavage, exclude the presence of the persistent species at the beginning of the process, and cover explicitely only cases where conditions 7 for the operation of the PRE would be fulfilled in the absence of reaction 6. The initial conditions for the concentrations are given by (14) and the stoichiometry relations by (15). Hence, one may again select [R], [Y], and [YH] as the only relevant time dependent variables. The kinetic equations for these now read for homogeneous reaction conditions

$$\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}t} = k_\mathrm{d}([\mathrm{I}]_0 - [\mathrm{Y}] - [\mathrm{YH}]) - k_\mathrm{c}[\mathrm{R}][\mathrm{Y}] - k_\mathrm{t}[\mathrm{R}]^2 \tag{39a}$$

$$\frac{\mathrm{d}[\mathrm{Y}]}{\mathrm{d}t} = k_\mathrm{d}([\mathrm{I}]_0 - [\mathrm{Y}] - [\mathrm{YH}]) - k_\mathrm{c}[\mathrm{R}][\mathrm{Y}] \tag{39b}$$

$$\frac{\mathrm{d}[\mathrm{YH}]}{\mathrm{d}t} = k_\mathrm{dD}([\mathrm{I}]_0 - [\mathrm{Y}] - [\mathrm{YH}]) \tag{39c}$$

Now the appropriate reduced parameters are

$$a = \frac{k_\mathrm{c}[\mathrm{I}]_0}{k_\mathrm{d}}, \quad b = \frac{k_\mathrm{t}[\mathrm{I}]_0}{k_\mathrm{d}}, \quad f_\mathrm{D} = \frac{k_\mathrm{dD}}{k_\mathrm{d}} \tag{40a}$$

$$\rho = \frac{[\mathrm{R}]}{[\mathrm{I}]_0}, \quad \eta = \frac{[\mathrm{Y}]}{[\mathrm{I}]_0}, \quad \xi = \frac{[\mathrm{YH}]}{[\mathrm{I}]_0}, \quad \tau = k_\mathrm{d}t \tag{40b}$$

Using these and $\dot{x} = \mathrm{d}x/\mathrm{d}\tau$, the kinetic equations read

$$\dot{\rho} = 1 - \eta - \xi - a\rho\eta - b\rho^2 \tag{41a}$$

$$\dot{\eta} = 1 - \eta - \xi - a\rho\eta \tag{41b}$$

$$\dot{\xi} = f_\mathrm{D}(1 - \eta - \xi) \tag{41c}$$

Parts a and b of eq 41 are formally identical to parts a and b of eq 18. Hence, the earlier discussion of the behavior of the trajectory in the phase space applies also for the formation of hydroxylamine and alkene via reaction 6, and the only difference is the different definition of the parameter a.

The quasi-equilibrium relation is now

$$a\rho\eta = 1 - \xi, \quad \text{or} \quad k_\mathrm{c}[\mathrm{R}][\mathrm{Y}] = k_\mathrm{d}([\mathrm{I}]_0 - [\mathrm{YH}]) \tag{42}$$

and the conditions for its existence are again given by (21) and, hence, (7).

The standard derivation of these conditions[7] implies $\eta < \epsilon$, where ϵ is arbitralily small. Hence, η can be neglected in eq 41c. Integration provides

$$\xi = 1 - \mathrm{e}^{-f_\mathrm{D}\tau} \text{ or } [\mathrm{YH}] = [\mathrm{I}]_0(1 - \mathrm{e}^{-f_\mathrm{D}k_\mathrm{d}t}) \tag{42a}$$

and

$$[\mathrm{I}] = [\mathrm{I}]_0\mathrm{e}^{-f_\mathrm{D}k_\mathrm{d}t} \tag{42b}$$

Parts a and b of 42 are formally identical to parts a and b of eq 22, but now one has quite naturally $f_\mathrm{D}k_\mathrm{d} = k_\mathrm{dD}$ whereas before one had $f_\mathrm{D}k_\mathrm{d} = k_\mathrm{cD}k_\mathrm{d}/(k_\mathrm{c} + k_\mathrm{cD})$.

With (59a) the quasi-equilibrium relation becomes

$$a\rho\eta = \mathrm{e}^{-f_\mathrm{D}\tau} \text{ or } k_\mathrm{c}[\mathrm{R}][\mathrm{Y}] = k_\mathrm{d}[\mathrm{I}]_0\mathrm{e}^{-f_\mathrm{D}k_\mathrm{d}t} \tag{43}$$

and $k_\mathrm{c} + k_\mathrm{cD}$ in (23) is now naturally replaced by k_c. Therefore, by this simple replacement, we obtain from the previous results without further derivations the equations for the radical concentrations

$$[\mathrm{Y}] = \left(\frac{3k_\mathrm{d}k_\mathrm{t}[\mathrm{I}]_0^{\,2}}{2f_\mathrm{D}k_\mathrm{c}^{\,2}}\right)^{1/3}[1 - \exp(-2f_\mathrm{D}k_\mathrm{d}t)]^{1/3} \tag{44a}$$

$$[\mathrm{Y}]_\infty = \left(\frac{3k_\mathrm{d}k_\mathrm{t}[\mathrm{I}]_0^{\,2}}{2f_\mathrm{D}k_\mathrm{c}^{\,2}}\right)^{1/3} \tag{44b}$$

$$[\mathrm{R}] = \left(\frac{2f_\mathrm{D}k_\mathrm{d}^{\,2}[\mathrm{I}]_0}{3k_\mathrm{c}k_\mathrm{t}}\right)^{1/3}\exp(-f_\mathrm{D}k_\mathrm{d}t)/[1 - \exp(-2f_\mathrm{D}k_\mathrm{d}t)]^{1/3} \tag{44c}$$

for the monomer conversion

$$[\mathrm{M}] = [\mathrm{M}]_0\exp\left(-\frac{3}{2}k_\mathrm{p}\left(\frac{[\mathrm{I}]_0}{3k_\mathrm{t}k_\mathrm{c}k_\mathrm{d}f_\mathrm{D}^{\,2}}\right)^{1/3}F(t)\right) \tag{45}$$

and its maximum

$$C_\mathrm{max} = 1 - [\mathrm{M}]_\infty/[\mathrm{M}]_0 = 1 - \exp\left(-\frac{3}{2}k_\mathrm{p}\left(\frac{[\mathrm{I}]_0}{3k_\mathrm{t}k_\mathrm{c}k_\mathrm{d}f_\mathrm{D}^{\,2}}\right)^{1/3}F(\infty)\right) \tag{46}$$

and for the time where the polymerization ceases

$$t_p = \frac{1}{f_\mathrm{D}k_\mathrm{d}}\ln\left[\left(\frac{2}{1-p}\right)\Big/B\left(\frac{1}{2},\frac{2}{3}\right)\right] \tag{47}$$

The number-average degree of polymerization now obeys

$$X_\mathrm{n} = \frac{[\mathrm{M}]_0 - [\mathrm{M}]}{[\mathrm{I}]_0(1 - \mathrm{e}^{-(k_\mathrm{d}+k_\mathrm{dD})t})}(1 + f_\mathrm{D}) \tag{48}$$

and for the second moment (36b) holds but parts a and b of (38) are modified to

$$\frac{\mathrm{d}m_1(\mathrm{R})}{\mathrm{d}t} = k_\mathrm{d}m_1(\mathrm{I}) - k_\mathrm{c}[\mathrm{Y}]m_1(\mathrm{R}) + k_\mathrm{p}[\mathrm{M}][\mathrm{R}] - k_\mathrm{t}[\mathrm{R}]m_1(\mathrm{R}) \tag{49a}$$

$$\frac{\mathrm{d}m_1(\mathrm{I})}{\mathrm{d}t} = -k_\mathrm{d}(1 + f_\mathrm{D})m_1(\mathrm{I}) + k_\mathrm{c}[\mathrm{Y}]m_1(\mathrm{R}) \tag{49b}$$

These results obtained for inclusion of reaction 6 are not identical but are very similar to the earlier ones, and as pointed out already before, this leads essentially

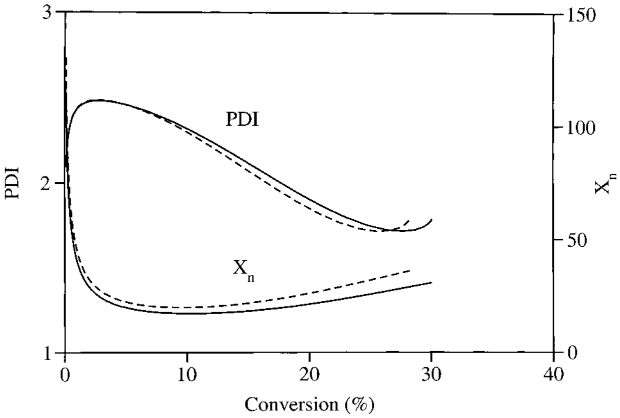


Figure 6. Number-average degree of polymerization and polydispersity index, computed including 20% of hydroxylamine and macromonomer formation during the cross-termination (solid line) or during alkoxyamine decomposition (broken line). Other parameters as used for Figure 2.

to the same behavior whether there is direct alkoxyamine decomposition (eq 6) or disproportionation (eq 5) during the cross-termination. This is even true for substantial fractions of the reactions as illustrated in Figure 6 which shows computed polydispersities and number-average degrees of polymerization for large fractions $f_D = 20\%$ and both reactions. Experimentally, the subtle differences would hardly be discriminated.

Concluding Remarks

As mentioned in the Introduction, the detrimental influences of the formation of hydroxylamine and alkene macromonomer on nitroxide mediated living radical polymerizations were recognized earlier both in numerical simulations and from experimental results though not all kinetic effects were explored, and explanations of the details often remained vague.[8-20,22] The clearest experimental evidence for the validity of our analytical results is found in publications by Fukuda et al. on the polymerization of a sugar-carrying styrene[8] and of *tert*-butyl acrylate[19] regulated by 2-(benzoyloxy)-1-(phenyl)-1-(di-*tert*-butylnitroxyl)ethane. In the absence of additional initiator, both systems exhibit the leveling off of the conversion index as in Figure 3, the linear dependence of X_n on conversion and the premature end of the polymerization as in Figure 4, and the increase of the polydispersity caused by disproportionation in the final stage of conversion as in Figure 5. Moreover, for the sugar-carrying styrene[8] the end of the conversion occurred at smaller conversions for smaller initial alkoxyamine concentrations as predicted here and shown in Figure 4.

Fukuda et al. also noticed[8,16] that the side reactions 5 and 6 lead to an exponential decrease of the concentration of the dormant chains and to the corresponding increase of the macromonomer concentration, as given by eqs 22 and 42. From this they extracted a rate constant k_{dec} which we now identify as $f_D k_d$, where $f_D = k_{cD}/(k_c + k_{cD})$ for disproportionation (eq 5) and $f_D = k_{dD}/k_d$ for the direct decomposition of the alkoxyamine (eq 6). They also established experimentally that k_{dec} did not change upon the deliberate addition of free nitroxide radicals before the reaction, although the disproportionation (eq 5) is a second-order reaction. To prove this, we define $\eta_{\text{exc}} = [Y]_0/[I]_0$ and $\eta_{\text{int}} = [Y]_{\text{int}}/[I]_0$ where $[Y]_0$ is the concentration of the initially added persistent radical, and $[Y]_{\text{int}}$ denotes the concentration of this radical which is caused by the alkoxyamine decay. For a disproportionation reaction 5, eq 18 becomes

$$\dot{\rho} = 1 - \eta_{\text{int}} - \xi - a\rho(\eta_{\text{int}} + \eta_{\text{exc}}) - b\rho^2 \qquad (58a)$$

$$\dot{\eta} = 1 - \eta_{\text{int}} - \xi - a\rho(\eta_{\text{int}} + \eta_{\text{exc}}) \qquad (58b)$$

$$\dot{\xi} = f_D a\rho(\eta_{\text{int}} + \eta_{\text{exc}}) \qquad (58c)$$

and lead to the quasi-equilibrium relation

$$a\rho(\eta_{\text{int}} + \eta_{\text{exc}}) = 1 - \xi, \quad \text{or}$$
$$(k_c + k_{cD})[R]([Y]_{\text{int}} + [Y]_0) = k_d([I]_0 - [YH]) \qquad (59)$$

Insertion into eq 58c and integration reproduces exactly eq 22, and that completes the proof. Actually, for negligible disproportionation but added nitroxide the quasi-equilibrium relation (eq 73) has been formulated earlier by Fukuda.[9] A rigorous derivation along the lines of the present work and a general discussion of the effects of added nitroxide will be published in due course.

From the kinetics of the decay of the dormant alkoxyamines, a distinction between reactions 5 and 6 is not possible because it is governed by formally the same product $f_D k_d$. This also governs the time where the polymerization ceases. Further, Figure 6 reveals only small differences for the time evolutions of the degrees of polymerization and the polydispersity index for the two cases even for a large fraction of the side reaction. To establish whether reaction 5 takes place it will be necessary to examine the formation of the hydroxylamine and alkene products under conditions where the nitroxide and the carbon-centered radicals are produced independently and where the coupling to alkoxyamine is irreversible. Reaction 6 can be identified from the products of alkoxyamine decays under conditions where the carbon-centered are completely scavenged. Such studies were initiated for model sytems.[25,26] Once the pathway of the side reaction is identified, it should be straightforeward to obtain f_D from $f_D k_d$ because methods for determining k_d are available.[14,18,20,25-29]

Unfortunately, at present it seems impossible to predict the extent of reactions 5 and 6 to any degree of certainty, because the influencing factors are not clearly established. However, there is a clear dependence on the structure of the nitroxide and of the monomer,[11,22] and for some nitroxides the side reactions seem to be virtually absent.[21]

Finally, we wish to comment on the hydrogen abstraction reaction of the propagating radicals with the hydroxylamine formed by reaction 5 or 6

$$R_n^\bullet + YH \xrightarrow{k_H} R_n\,H + Y^\bullet \qquad (60)$$

This reaction operates during the thermal and uncontrolled radical polymerization of styrene.[30] For the hydroxylamines 2,2,6,6-tetramethyl-1-piperidinol (TEMPOH) and 1-hydroxy-2,2,5,5-tetramethyl-4-imidazolidinone (TEMIOH), Gridnev[30] has reported $k_H = 35$ M^{-1} s^{-1} and $k_H = 15$ M^{-1} s^{-1} at 90 °C. Obviously, reaction 60 could enhance the effect of reactions 5 and 6 and end the polymerization *n* even earlier. However, it is likely to play only a minor role. In model systems involving the reversible alkoxyamine cleavage (eqs 1 and 2), i.e., transient carbon-centered radicals $R_0^\bullet$, the hydroxylamine YH was stable under oxygen free conditions at 100−120 °C,[15,26] and after polymerizations it was converted to nitroxide only after admission of air.[11] Further, there are kinetic reasons. Reaction 60 can operate only at the end of the polymerization when YH accumulates, and the maximum concentration of YH cannot exceed the reasonable maximum $[\mathrm{I}]_0 = 0.5$ M. From Gridnev's data,[30] an upper limit of $k_{\mathrm{H}} = 200\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ for the higher polymerization temperatures seems reasonable. Hence, the time required for a propagating radical to undergo the hydrogen abstraction will normally exceed 10^{-2} s considerably. On the other hand, during the living polymerization the concentration of the persistent radical [Y] increases to the order of 10^{-3} M (Figure 2), and cross-termination constants are usually larger than $k_{\mathrm{c}} = 10^{6}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.[27] This gives the propagating radical a maximum time of about 10^{-3} s before it deactivates to the alkoxyamine, so that many propagation steps will occur before reaction 60 can interfere.

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