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The Persistent Radical Effect In “Living” Radical Polymerization

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ABSTRACT: A kinetic analysis is presented of “living” polymerizations initiated and controlled by reactions involving persistent radicals. It is shown how a simple self-regulation operates which is known as the persistent radical effect in other areas of radical chemistry. Predictive analytical formulas are derived for the time dependent concentrations of the radical intermediates and the dormant and the final polymer products. They are supported by numerical simulations and agree with experimental findings. In particular, we consider the initiation by homolysis of a stoichiometric initiator into a transient and a persistent radical in the absence and in the presence of self-initiation and the use of conventional initiators together with a persistent species.

Introduction

Since the first report[1] of “living” high polymers with low polydispersities and controllable molecular weights formed in thermal radical reactions, the field of “living” radical polymerization has been advanced tremendeously[2−8] both in science and industry. It seems to be generally understood that successful mechanisms involve a coupling of the usual radical initiation, propagation, and termination steps to the simultaneous and reversible formation of transient propagating radicals and persistent radicals or radicaloids as in the reversible bond dissociation reaction

$$R_i{-}Y \rightleftharpoons R_i + Y$$

Here, $R_i{-}Y$ denotes dormant chains of *i* monomer units ($i = 0, 1, 2, ...$), R_i are the initiating and propagating radicals, and Y is the persistent species which reacts with the transient radicals but does not undergo self-termination. In practice, Y is a nitroxide radical,[1,3] for instance 2,2,6,6,-tetramethyl-1-piperidinyloxy (TEMPO) or a derivative thereof, a borinate radical,[4] or a Co^{II} complex[5]. The polymerization is initiated by homolysis of the stoichiometric initiator $R_0{-}Y$, or of $R_1{-}Y$ which is formed *in situ* by radicals from an external source, the monomer, and the deliberately added persistent species.

Alternatively, in atom transfer polymerization one applies the reversible process

$$R_i{-}Hal + Me \rightleftharpoons R_i + MeHal$$

where Hal is a halogen atom. Me is a complex of e.g. Cu,[6] Ni,[7] or Ru,[8] and its halogenated form behaves as Y.

Necessarily, in the reversible reactions the transient and the persistent partners form and disappear with equal rates. This sets the stage for a self-regulation of the reaction system which we have analyzed earlier[9] to explain very unusual selectivities of several radical reactions, following a suggestion of K. U. Ingold. The principle is simple: If the reversible processes were the only reactions and if at zero time no radicals are present, then the concentrations of R_i and Y increase equally in time and reach equal steady state values in the equilibrium. However, the transient radicals also decay by the unavoidable irreversible bimolecular self-terminations, whereas, ideally, there is no such reaction of Y. Hence, the concentration of the transient species reaches a maximum and decreases thereafter. In contrast, the concentration of the persistent radical increases steadily because it must balance the self-termination loss of R_i. No steady state of R_i and Y will exist except for infinite time when Y reaches the initial initiator concentration and R_i is fully converted to the self-termination products.

As time proceeds the decreasing concentration of the transient radicals also renders the product formation by their self-termination less and less likely. Instead, the cross-reaction of the transient with the persistent species becomes the dominant product formation pathway. This leads to an increased precursor lifetime and to a dominance of chemically distinguishable side products of the cross-reaction. If the transient radicals transform into other transient radicals, for instance by rearrangement, fragmentation or addition to unsaturated compounds[9], the cross-products of the persistent species with the radicals formed by the secondary processes dominate.

Besides the examples discussed earlier[9] a variety of selective reactions involving fully or reasonably persistent radicals have more recently been explained[10] by this self-regulation. It has been phrased the persistent radical effect (PRE) by Finke et al.[10b] which is a proper description. Its operation in “living” radical polymerization has been recognized,[3b,5,6a] but as far as we are aware of, the details have not yet been explored, though some features can be recognized in recent[3b,h] and earlier[11] simulations.

Here, we present a kinetic analysis of the persistent radical effect and of its role in “living” polymerizations especially for the case of initiation by radicals from reversible bond homolysis. The atom transfer variant is not explicitely considered but leads to similar results. Aiming at a deeper understanding of the phenomena, we reduce the number of reactions and rate constants to the absolute minimum, i.e. consider somewhat idealized systems only. This facilitates the numeric calculations, and, moreover, allows us to derive analytical formulas from which the essential features of the PRE and of “living” polymerizations emerge. We do not aim

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at simulations of reported experimental data, yet we use rate constants which should hold approximately for bulk polymerizations of styrene at 120 to 125 °C, so that comparisons with experiments are possible.

Analysis and Discussion

Initiation by Reversible Homolysis of a Stoichiometric Initiator. The polymerization begins with the reversible dissociation of an initiator $R_0{-}Y$. The transient radicals R_0 start the propagating chains by addition to the monomer M, the transient adduct radicals repeat this, and all transient species R_i combine reversibly with Y to dormant chains $R_i{-}Y$. For brevity, these are called I_i in the following. In addition, the transient radicals undergo the irreversible self-termination to final polymer products P, which are unable to react further on. To simplify the calculation of moments we assume termination by disproportionation only. Hence, the reactions are

$$I_i \xrightarrow{k_I} R_i + Y$$

$$R_{i-1} + M \xrightarrow{k_p} R_i$$

$$R_i + Y \xrightarrow{2k_t} I_i$$

$$R_i + R_j \xrightarrow{2k_t} P_i + P_j$$

with $i \geq 0$. All rate constants are taken independent of the chain length i, and those for the two radical–radical reactions are set equal. This leads to the kinetic equations

$$\frac{d[R_i]}{dt} = k_I[I_i] - 2k_t[R_i](\sum_0^\infty [R_j] + Y) + k_p[R_{i-1}][M] - k_p[R_i][M] \quad (1a)$$

$$\frac{d[Y]}{dt} = k_I \sum_0^\infty [I_i] - 2k_t[Y]\sum_0^\infty [R_j] \quad (1b)$$

$$\frac{d[I_i]}{dt} = -k_I[I_i] + 2k_t[R_i][Y] \quad (1c)$$

$$\frac{d[P_i]}{dt} = 2k_t[R_i]\sum_0^\infty [R_j] \quad (1d)$$

$$\frac{d[M]}{dt} = -k_p[M]\sum_0^\infty [R_i] \quad (1e)$$

We write $2k_t$ in the termination terms explicitely to display the stoichiometry and the statistical factors instead of k_t as customary in polymer kinetics. The initial conditions are $[I_0]_0 \neq 0$ and $[M]_0 \neq 0$, $[I_i]_0 = 0$ for $i > 0$ and $[R_i]_0 = [Y]_0 = [P_i]_0 = 0\ \forall\ i$.

Summing the equations over all i, assuming $[R_\infty] = 0$ and denoting the sums of concentrations by R, I, and P one obtains

$$\frac{dR}{dt} = k_I I - 2k_t R(R + Y) \quad (2a)$$

$$\frac{dY}{dt} = k_I I - 2k_t RY \quad (2b)$$

$$\frac{dI}{dt} = -k_I I + 2k_t RY \quad (2c)$$

$$\frac{dP}{dt} = 2k_r R^2 \quad (2d)$$

$$\frac{dM}{dt} = -k_p MR \quad (2e)$$

Parts a–d of eq 2 are quite general for systems exhibiting the PRE and are not restricted to polymerizing systems. From (2c) and (2d) it is obvious that $I = I_0 - Y$ and $P = Y - R$, so that one has to find solutions for R and Y only.

At very short times the radical concentrations increase linearly, $R = Y = k_I I_0 t$. Inserting this expression into (2), integrating, and repeating the procedure give a power series solution. Up to terms linear in t^3 it is

$$R = k_I I_0 t\left(1 - \frac{1}{2}k_I t\left(1 - \frac{1}{3}k_I t(1 - 8k_t I_0/k_I)\right)\right) \quad (3a)$$

$$Y = R + \frac{2k_t}{3}k_I{}^2 I_0{}^2 t^3 = R + P \quad (3b)$$

Similar equations hold for I and M. They are not given here because these concentrations are practically constant at early times. The first derivative of R is zero at $\hat{t} = (2k_I 2k_t I_0)^{-1/2}$; i.e. R reaches the predicted maximum, whereas Y continues to increase. The series can be extended, but it diverges.

More useful approximate solutions are found by converting eq 2a–c to second-order differential equations for R and/or Y with the parameters k_I, $2k_t$, and I_0. Using the ansatz $R = at^b$ or $Y = at^b$ and the experimentally justified assumption of $2k_t I_0 \gg k_I$, one sees[12] after straightforward manipulations that the second-order equations are fulfilled in different time ranges by specific values of b.

For very short times $t \ll (k_I{}^2(2k_t I_0/k_I - 1))^{-1/2} \approx (k_I 2k_t I_0)^{-1/2}$ before the maximum of R one finds

$$R = Y = k_I I_0 t \quad (4)$$

which is the first term of the power series in (3a). The other species keep their initial concentrations.

For the next time range $(k_I 2k_t I_0/3)^{-1/2} << t << 2k_t I_0/24k_I{}^2$ one obtains

$$R = I_0(k_I/3(2k_t I_0)^2)^{1/3} t^{-1/3} \quad (5a)$$

$$Y = I_0(3k_I^2/2k_t I_0)^{1/3} t^{1/3} \quad (5b)$$

$$I = I_0 - Y \approx I_0 \quad (5c)$$

$$P = Y - R \approx Y \quad (5d)$$

$$M = M_0 \exp\left(-\frac{3}{2}k_p I_0(k_I/3(2k_t I_0)^2)^{1/3} t^{2/3}\right) \quad (5e)$$

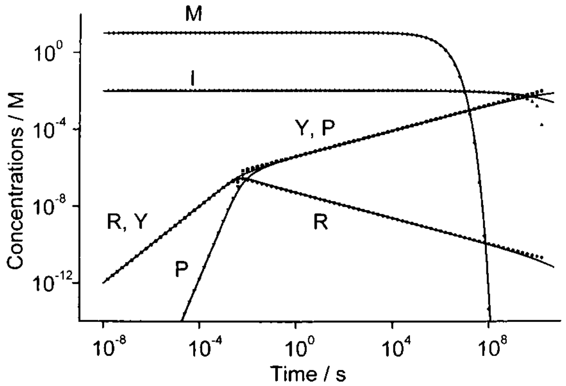

Figure 1. Concentrations of the transient (R) and the persistent (Y) radicals, the dormant (I) and the final (P) polymer chains, and the monomer M vs time for a "living" polymerization initiated by homolysis of an initiator R−Y. Key: symbols, analytical results; lines, numerical results.

Finally, for long times $t >> 4k_t I_0/k_I^2$ one has

$$R = I_0/k_It \tag{6a}$$

$$Y = I_0(1 - 2k_tI_0/k_I^2t) \approx I_0 \tag{6b}$$

$$I = I_0 2k_tI_0/k_I^2t \tag{6c}$$

$$P = Y - R \approx Y \approx I_0 \tag{6d}$$

To judge the practical significance of the three solutions, we now evaluate their time limits by inserting rate constants and initial conditions which seem reasonable for styrene polymerizations at 120−125 °C. We adopt $I_0 = 10^{-2}$ M as the initial initiator concentration and $2k_t = 5 \times 10^8$ M^{-1} s^{-1} for the termination constant. The latter value is set higher than the room temperature data for the coupling of carbon centered radicals with TEMPO[13] and is in the midrange of values used in other kinetic treatments.[3b,e] The initiator 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane is implied which has been used several times, and from available reaction rates[3e,14] one estimates $k_I = 10^{-2}$ s^{-1}.

With these parameters R reaches a maximum at $\hat{t} =$ 3.16 ms. Equation 5 with the very peculiar third root time dependencies holds between $t >>$ 7.75 ms and $t << 2.083 \times 10^7$ s, i.e up to about 579 h. The solution for long times (eq 6) has no practical relevance since for our parameters it is valid only after 3170 years.

In the usual observation time of up to 100 h the concentration of the persistent species Y increases, and that of the transient radicals R decreases continuously. However, their product is constant, $RY = k_II_0/2k_t$; i.e. there is an equilibrium relation between the dormant chains I and the radicals though the concentrations of the latter are not constant in time. As long as equation 5 is valid the conversion of I to P is negligible, Y does not approach its final value I_0, and the dormant chains contain most of the consumed monomer units. The conversion of the monomer is not exponential in time but is characterized by an increase which slows down as time proceeds.

Figure 1 shows a plot of the concentrations of R, Y, I, P, and M as functions of time calculated with the analytical formulas for the initial time range (eq 3) and the following period (eq 5). They are presented by symbols and overlay the results of a numerical integration[15] of eq 2. In addition to the parameters given above, the initial monomer concentration was set to M_0 = 10 M and the propagation constant to $k_p = 2000$ M^{-1} s^{-1} as valid for styrene at 120 to 125 °C.[16] Except for times close to their validity limits, the analytical solutions agree with the numerical results. For the parameters chosen the conversion of monomer to polymer occurs within these limits, and during polymerization the concentration of the dormant chains I is still much larger than P; i.e. the polymerization is in fact "living". At the upper end of the considered time range Figure 1 indicates the onset of the very long time behavior.

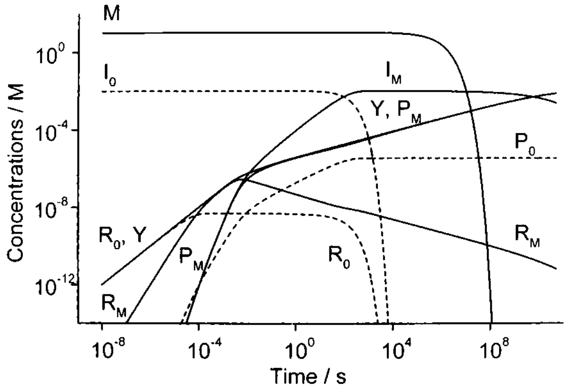

Figure 2. Concentrations of the transient (R_0, R_M) and the persistent (Y) radicals, the dormant (I_0, I_M) and the final (P_0, P_M) polymer chains, and the monomer M vs time for a "living" polymerization initiated by homolysis of an initiator R_0−Y. Key: index 0, species without monomer units; index M, species with monomer units.

The total concentrations used in Figure 1 do not reveal the inner working of the process. To obtain additional insight we separate eq 1 into two sets for (a) monomer containing species $R_M = \sum_1^\infty R_i$, $I_M = \sum_1^\infty R_I$, and $P_M = \sum_1^\infty P_i$, and for (b) the species without monomer units R_0, I_0, and P_0 and discuss their numeric solutions. Since the kinetic equations are very similar to (2) they are not given here. The subdivision also allows the calculation of moments of the chain length distribution. The first $m_1^R = \sum_1^\infty iR_i$, $m_1^I = \sum_1^\infty iI_i$, and $m_1 = \sum_1^\infty i(R_i + I_i + P_i)$ and the second $m_2 = \sum_1^\infty i^2(R_i + I_i + P_i)$ moments yield the number and the weight average of the degree of polymerization $P_n = m_1/(R_M + I_M + P_M)$ and $P_w = m_2/m_1$, the polydispersity index P_w/P_n, and the standard deviation of the distribution $\sigma = (P_wP_n - P_n^2)^{1/2}$. They obey the differential equations

$$\frac{dm_1^R}{dt} = k_Im_1^I - 2k_t(R + Y)m_1^R + k_pMR \tag{7a}$$

$$\frac{dm_1^I}{dt} = -k_Im_1^I + 2k_tYm_1^R \tag{7b}$$

$$\frac{dm_1}{dt} = k_pMR \tag{7c}$$

$$\frac{dm_2}{dt} = 2k_pMm_1^R + k_pMR \tag{7d}$$

Numerical solutions for the concentrations were obtained with the parameters used before and are shown in Figure 2. As expected, the initial radical R_0 reaches only very low concentrations since it is converted within the time required for one monomer addition $\tau_p = (k_pM)^{-1} = 5 \times 10^{-5}$s to R_M. After $\tau_I = k_I^{-1}$, the lifetime of the initiator I_0, it dies out completely. From thereon the initiator is fully replaced by the dormant chains I_M. The behavior of Y, R_M, and P_M is self-explaining.

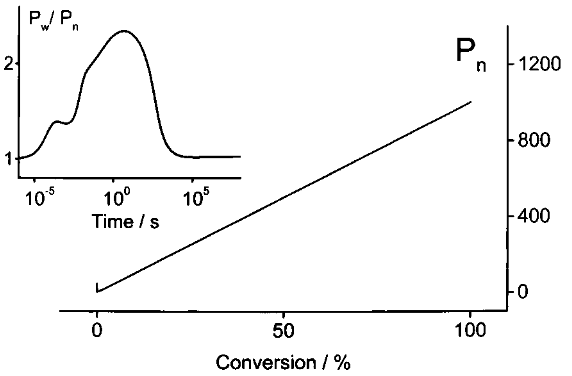

Figure 3. Number average degree of polymerization vs monomer conversion for a "living" polymerization initiated by homolysis of an initiator R−Y. Inset: Time dependence of the polydispersity index.

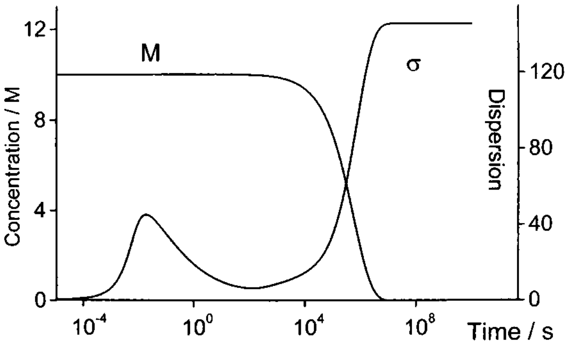

Figure 4. Dispersion of the degree of polymerization σ and monomer concentration M vs time for a "living" polymerization initiated by homolysis of an initiator R−Y.

Integration of eq 7c with R and M from eq 5 yields $P_n = (M_0 - M)/(R_M + I_M + P_M)$. Neglecting the small contributions of the species without monomer units one has from eq 5d $R_M + I_M + P_M = I_0$; i.e. one arrives analytically at the familiar relation for "living" polymerization systems

$$P_n = (M_0 - M)/I_0 \tag{8}$$

according to which the number average degree of polymerization increases linearly with monomer conversion and is controlled by the initial initiator concentration.

In Figure 3 the numerically calculated number average P_n is plotted against the monomer conversion. At very low conversions, i.e. when eq 5 is not yet valid, oligomers are formed, but thereafter eq 8 holds up to 100% conversion. The inset displays the development of the polydispersity. Before I_0 is fully converted to I_M (see Figure 2), P_w/P_n is rather high but it then decreases to values close to 1. Further, Figure 4 shows the width of the distribution σ together with the monomer concentration. The dispersion is rather large at early times, then it narrows when the monomer conversion begins, and finally it broadens again.

Qualitatively, this can be understood from the time dependence of the probability of addition of j monomer units to a propagating radical $w(j) = (k_pM\tau_1)^j \exp(-k_pM\tau_t)/j!$ during its termination lifetime $\tau_t = (2k_t\,(R + Y\,))^{-1}$. At very early times the radical concentrations are very low and termination is slow compared to propagation, $k_p\, M\tau_t >> 1$. Therefore, on the average, one radical will add many monomer units. With increasing time τ_t decreases because Y increases. Hence, the probabilities for multiple addition decrease rapidly. For our parameters they become very small when the concentration of the persistent radical Y exceeds about 4×10^{-5} M, which is after about 10 s. From Figure 2 it is evident that I_0 is consumed mainly between 10 and 1000 s, as governed by k_I. Thus, most of the chains start in this period and initially acquire about one monomer unit only. This explains why the distribution narrows and the polydispersity decreases after 10 s. The final increase reflects the further chain growth. The probabilities for addition continue to decrease but remain finite. Each dormant chain opens every 100 s, so that there are about 10^5 cycles of opening and reclosure before monomer depletion, and this is enough to ensure chain growth and to account for occasional probabilistic errors resulting in the addition of more than one monomer unit.

Most of the features derived here have been observed experimentally in "living" polymerization. The linear increase of P_n with conversion and a low polydispersity are the standard signatures.[1−8] In addition, many authors have observed the decrease of the polydispersity with time, and there are also examples for the final increase at high conversions.[3b,d,14,17] A nonlinear release of TEMPO during polymerizations with stochiometric initiators has been noted[3e,18] though the $t^{1/3}$ behavior has not yet been explored. Large conversions seem to need rather long times, and furthermore, the "living" polymerizations do not exhibit a gel effect[17a]. This is of course due to the very low concentration of transient radicals at high conversions and for long times.

To examine the ranges of kinetic parameters which can lead to satisfactory "living" radical systems extensive numerical calculations were performed, and some results are presented in Table 1. There, we list the times needed for 5, 50 and 90% conversion, the ratio of the calculated number average degree of polymerization to the theoretical one (eq 8) and the calculated polydispersity index P_w/P_n at the conversion times.

Table 1 shows that for the chosen parameters the degrees of polymerization and the polydispersities are very satisfactory. However, the calculated times for polymerization are rather long and in most cases much longer than observed.[3] They decrease with increasing I_0 as predicted from eq 5e, but this also disagrees with the experimental results for styrene[3]. The reason for both discrepancies is examined more closely in the next section. A faster homolysis of the dormant chains accelerates the polymerization, but for $k_I > 10\ \mathrm{s}^{-1}$ the "living" character is increasingly obscured because the increasing concentration of the transient radicals leads to an increased termination to unreactive chains.

We believe that a good "living" process following the mechanism treated in this section requires a monomer conversion of 90% before about 10% of the dormant are converted to unreactive chains. With this assumption eq 5b,c,e yields $200 \ln(10)k_I/k_pI_0 \leq 1$, a condition which does not involve the termination constant and was found to hold by numerical tests.

Effects of Self-Initiation. In contrast to intuitive expectation and to the results given in Table 1, the propagation rate of styrene is independent of the concentration of stochiometric initiators R_0−Y. It rather closely follows the rates observed in pure thermal polymerizations.[3b,d,e] Matyjaszewski et al.[3b,19] and Fukuda et al.[3e] have made clear that this is due to the self-initiation of styrene which occurs at high temperatures aside from the action of initiators. The self-initiation is of third order in monomer concentration, and to

Table 1. Conversion Times, Degrees of Polymerization, and Polydispersities for Initiation by a Stoichiometric Precursor

	time			P_n/P_n^{th}			P_w/P_n		
parameter/conversion	5%	50%	90%	5%	50%	90%	5%	50%	90%
$I_0 = 3 \times 10^{-3}$ M[a]	3.2 h	158 h	1016 h	1.0002	1.0002	1.0002	1.036	1.025	1.034
$I_0 = 10^{-2}$ M	1.7 h	67 h	525 h	1.0003	1.0003	1.0003	1.067	1.015	1.020
$I_0 = 3 \times 10^{-2}$ M	59 min	49 h	302 h	1.0005	1.0005	1.0005	1.138	1.014	1.014
$I_0 = 10^{-1}$ M	33 min	28 h	165 h	1.0215	1.0006	1.0006	1.308	1.026	1.017
$k_I = 3 \times 10^{-3}$ s^{-1} [b]	3.1 h	158 h	967 h	1.0002	1.0002	1.0002	1.102	1.011	1.012
$k_I = 3 \times 10^{-2}$ s^{-1}	60 min	51.h	320 h	1.0007	1.0007	1.0007	1.050	1.024	1.033
$k_I = 3 \times 10^{-1}$ s^{-1}	19 min	16.7 h	109 h	1.0029	1.0029	1.0029	1.045	1.073	1.107
$k_I = 3$ s^{-1}	7 min	6.5 h	49 h	1.012	1.012	1.012	1.079	1.256	1.412

[a] Other parameters: $k_I = 10^{-2}$ s^{-1}, $2k_t = 5 \times 10^{-8}$ M^{-1} s^{-1}, $k_p = 2000$ M^{-1} s^{-1}, [M$_0$] = 10 M. [b] $I_0 = 10^{-2}$ M; other parameters are as above.

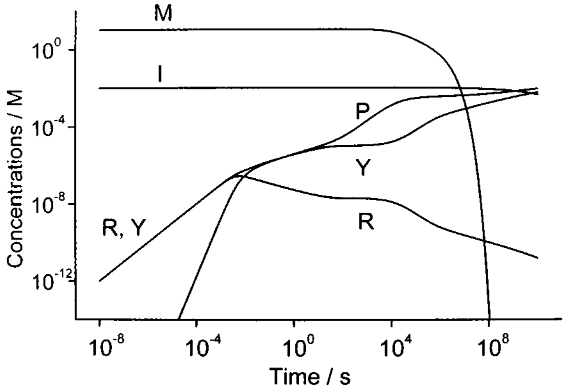

Figure 5. Concentrations of the transient (R) and the persistent (Y) radicals, the dormant (I) and the final (P) polymer chains, and the monomer M vs time for a "living" polymerization initiated by homolysis of an initiator R−Y and by self-initiation of the monomer.

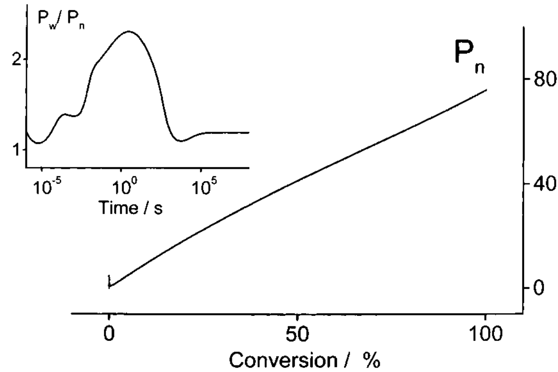

Figure 6. Number average degree of polymerization vs monomer conversion for a "living" polymerization initiated by homolysis of an initiator R−Y and by self-initiation of the monomer. Inset: Time dependence of the polydispersity index.

account for it a radical generating term r_I is added to the kinetic equations, i.e. eq 2a now reads

$$\frac{dR}{dt} = r_I + k_I I - 2k_t R(R + Y) \qquad (9)$$

If r_I is only slowly varying with time, eqs 2b-d and 9 allow the transient and the persistent radicals R and Y to reach a quasi-steady state with the radical concentrations given by $R = (r_I/2k_t)^{1/2}$ and $Y = k_I\, I_0/2k_t\, R$. In this state the propagation rate k_pMR is identical to that of a polymerization without initiator. This has been recognized,[3e] but the time range for the existence of the steady state was not examined. Therefore, we give here numerical results for the third-order initiation[3e,20] $r_I = k_s\, M^3$ with $k_s = 2 \times 10^{-10}$ M^{-3} s^{-3} in the presence of a stoichiometric initiator and all other parameters as used before.

Figure 5 displays the variation of the concentrations with time. Up to about 10 s the behavior is identical to that of Figure 1, and there is no effect of the self-initiation. This is expected since for the parameters chosen the rate of self-initiation is 500 times smaller than the initiation rate by I_0. However, after about 10 s, when R would become very low otherwise, the quasi-steady state is reached, and it exists during the first hours of polymerization. Thereafter, when the monomer depletes, the pattern of Figure 1 is followed again. Figure 6 shows that the calculated number average degree of polymerisation and the polydispersity are similar to those of Figure 2. P_n increases linearly with conversion but with a slightly smaller than ideal slope. This is due to a larger yield of unreactive chains and is compatible with several experimental data.[3b,d,e,19]

Further results are given in Table 2. When self-initiation is included the conversion times do indeed not depend on the initiator concentration at least for not too large conversions. They agree better with observations for "living" styrene polymerizations but still show tailing behavior for large conversions.

The "Xerox" Initiation Including Self-Initiation. The original recipe for the "living" polymerization of styrene[1] uses a conventional initiator, such as dibenzoylperoxide, in the presence of a persistent nitroxide radical (TEMPO). It is known that the benzoyloxy radicals add to styrene and that the adduct radical then mainly combines with TEMPO to give a 1-mer-compound in high yield which also dissociates and initiates new chains.[3] The lifetime of dibenzoylperoxide does not exceed a few minutes at 120 to 125 °C, and in our calculation we have used a first order decay constant of $k_d = 5 \times 10^{-3}$ s^{-1} neglecting the induced decomposition. The initial concentration of the peroxide was set to 4×10^{-2} M.

Figure 7 gives the results of a calculation with initially 8×10^{-2} M TEMPO. In the beginning, the concentration of the transient radicals stays extremely low since they are effectively trapped by TEMPO and lead to the formation of the styryl-1-mer. When the lifetime of the peroxide is reached, the TEMPO concentration decreases sharply and R increases. Thereafter, the concentrations develop in close analogy to the patterns given in Figures 1 and 5. We state with some pleasure that Figure 9 of ref 3a resembles our prediction for the time evolution of TEMPO. Figure 8 reveals that the "Xerox" way of initiating gives an excellent linear increase of P_n with conversion and very low polydispersities, since the formation of oligomers at early times is supressed. In this scheme it is critical to apply an optimum TEMPO concentration[1,3a] which is exactly 2:1 TEMPO/peroxide for our idealized mechanism. In practice, 1.3:1 ratios are optimal since the initiating efficiency of dibenzoylperoxide is lower than one. Table

Table 2. Conversion Times, Degrees of Polymerization, and Polydispersities for Initiation by a Stoichiometric Precursor and Self-Initiation

	time			P_n/P_n^{th}			P_w/P_n		
parameter[a]/conversion	5%	50%	90%	5%	50%	90%	5%	50%	90%
$I_0 = 3 \times 10^{-3}$ M	22 min	8.9 h	130 h	0.924	0.579	0.484	1.209	1.382	1.490
$I_0 = 10^{-2}$ M	22 min	8.6 h	115 h	0.976	0.822	0.761	1.190	1.144	1.190
$I_0 = 3 \times 10^{-2}$ M	22 min	8.6 h	98 h	0.933	0.933	0.908	1.223	1.061	1.072
$I_0 = 10^{-1}$ M	20 min	8.1 h	77 h	1.030	0.980	0.972	1.351	1.043	1.034
$I_0 = 3 \times 10^{-1}$ M	15 min	7.5 h	59 h	1.325	0.994	0.992	1.402	1.075	1.043

[a] Other parameters: $k_I = 10^{-2}$ s^{-1}, $2k_t = 5 \times 10^{-8}$ M^{-1} s^{-1}, $k_p = 2000$ M^{-1} s^{-1}, [M$_0$] = 10 M and $k_s = 2 \times 10^{-10}$ M^{-3} s^{-3}.

Table 3. Conversion Times, Degrees of Polymerization and Polydispersities for Initiation by a Conventional Initiator in the Presence of a Persistent Radical and Self-Initiation

	time			P_n/P_n^{th}			P_w/P_n		
parameter[a]/conversion	5%	50%	90%	5%	50%	90%	5%	50%	90%
$Y_0 = 6 \times 10^{-2}$ M	6 min	5.6 h	84 h	3.18	1.37	1.36	1.94	1.28	1.27
$Y_0 = 8 \times 10^{-2}$ M	31 min	8.3 h	81 h	1.54	1.46	1.45	1.38	1.05	1.04
$Y_0 = 10 \times 10^{-2}$ M	22 h	37 h	105 h	1.26	1.27	1.27	1.23	1.04	1.03

[a] Initiator concentration = 4×10^{-2} M and $k_d = 5 \times 10^{-3}$ s^{-1} ; other parameters are as above.

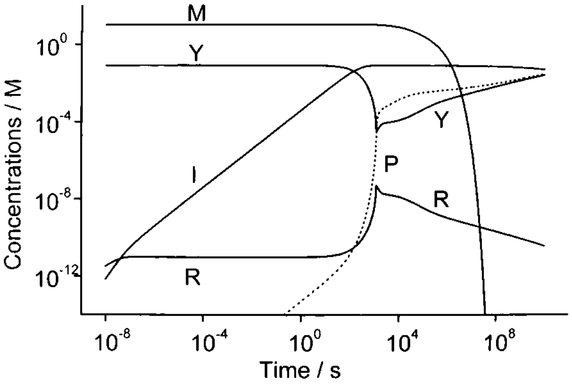

Figure 7. Concentrations of the transient (R) and the persistent (Y) radicals, the dormant (I) and the final (P) polymer chains, and the monomer M vs time for a "living" polymerization initiated by homolysis of a peroxide initiator in the presence of the persistent radical and by self-initiation of the monomer.

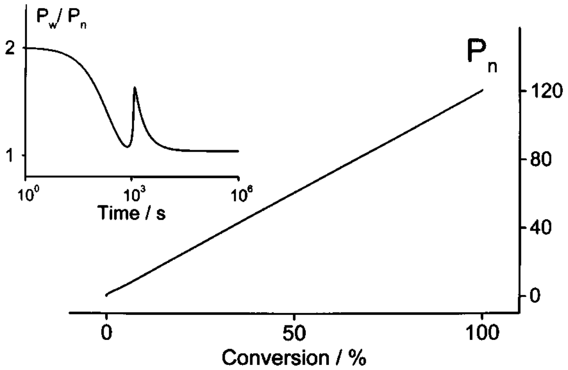

Figure 8. Number average degree of polymerization vs monomer conversion for a "living" polymerization initiated by homolysis of a peroxide initiator in the presence of the persistent radical and by self-initiation of the monomer. Inset: Time dependence of the polydispersity index.

3 shows that too little TEMPO deteriorates the "living" character, while too much prolongs the polymerization time.

In this context we would also like to comment on the possible initiation by the addition of TEMPO[21] in the absence of additional initiators but including self-initiation. Assuming a rate constant for addition to styrene of 10^{-4} M^{-1} s^{-1} as indicated by several hours for the formation of a 1-mer,[21b] TEMPO concentrations of 10^{-3} to 1 M and the other parameters as given before, we calculated the development of concentrations and the properties of polystyrene. They are very similar to those found for the "Xerox" initiation.

Concluding Remarks

This work concentrated on the understanding of the persistent radical effect and of its role in "living" radical polymerization. The mathematics underlying the basic equations (eq 2a-d) leads to rather peculiar time dependencies which are normally not encountered in chemical kinetics. Therefore, extractions of rate constants from experimental data using conventional rate laws can mislead severely if the PRE is involved.

For instance, we have mentioned above that a molecule which dissociates into a transient and a persistent radical will show an average lifetime which is much larger than the inverse of its true first-order decay constant unless it is converted to a chemically distinguishable species by scavenging of the intermediate transient radical. There is an illuminating but still unexplained example for this effect: Hawker et al.[14] found that the initiator 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane has a half-life of a few minutes at 123 °C in deuterated styrene, and under these conditions the 1-phenyl-1-ethyl radical reacts rapidly with styrene;[22] i.e. it is scavenged. On the other hand, for the same compound, Priddy et al.[23] reported a half-life of about 2.5 h at the higher temperature of 140 °C in tetrachlorobenzene and in the absence of a scavenger. Naturally, in the latter case the PRE operates, and it is possible that it even prolongs the lifetime in the former to some extent since the conversion shows a long time tail. Experiments to observe the $t^{1/3}$ release of TEMPO from 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane and other similar initiators by ESR are successfully underway in this laboratory.

The conclusions and predictions derived here from analytical and rather simple numerical calculations agree very well with those of an earlier large scale numerical integration of eq 1 by Johnson et al.,[11] who used the same rate constant approximations. These authors correctly noticed the absence of a steady state and the diverging time dependencies of the transient and the persistent radicals which are typical for the persistent radical effect. Unfortunately, their way of data presentation obscured the self-regulating feature of the reactions in the short time range. Here, we also checked our results by a large scale numerical integration of about 2000 kinetic equations (from eq 1) for chain lengths $0 < i \leq 500$. These confirm the conclusions reached above and are now being extended. Numerical results have also been published by Matyjaszewski et al.[3b] and by Fukuda et al.[3h] They allowed various side reactions which change the polymerization dynamics so that the results cannot be compared directly with our findings. An analytical treatment has been offered by Müller et al.[24a,b] It is based on the reversible degenerate exchange[24c] $R_i + I_j \rightleftharpoons R_j + I_i$ and complete neglect of the self-termination of the transient species. The exchange reaction is implicitely covered by our treatment, but the latter approximation leads to equal concentrations of transient and persistent radicals at all times which cannot hold in reality.

Of course, our analytical formulas are valid only as far as the idealized reaction scheme applies. An extension to the more realistic case of unequal rate constants for the cross- and the self-termination of the transient species leads to equations which differ in detail but not grossly from those given here. Furthermore, we have numerically studied some effects caused by changes of the reaction scheme. Inclusion of combination as formation path for the unreactive chains P increases their molecular weight and has no other particular influence. It is known that persistent nitroxide radicals (TEMPO) slowly and irreversibly abstract benzylic hydrogen atoms,[3b,23,21b,25] i.e. cause chain tranfer to polystyrene. This destroys the controlling reaction partner and causes higher polydispersities but has the favorable side effect of shorter times for large conversions and is still under regulating conditions. Further, as in the recent simulation,[3h] the disproportionation reaction between nitroxide and transient chain radicals to hydroxylamine and alkene is found to be very important. Details of these additional results will be published in due time.

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