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## The Persistent Radical Effect in Living Radical Polymerization – Borderline Cases and Side-Reactions

Hanns Fischer\* and Marc Souaille

**Abstract:** A theoretical analysis of the basic mechanism of living radical polymerization provides criteria for the rate constants required for optimized processes. It is extended to cover borderline cases and important side reactions as cross-disproportionation, the role of an initial excess of persistent species and of additional initiation.

**Keywords:** Living radical polymerization · Radical reaction rates · Reaction kinetics

### Introduction

Living polymerizations provide polymers which are able to grow whenever additional monomer is supplied [1].

Hence, the chains are extendable, and block-copolymers can be produced. Today, this is mainly achieved by anionic and cationic processes. These suffer little from terminations [2], and, hence, the polymer chains retain reactive ion pair end groups. Initiations are fast compared to the overall polymerization time. Therefore, all chains start to grow essentially instantaneously, and the degree of polymerization increases linearly with monomer conversion and is inversely proportional to the initiator concentration. The width of the chain length distri-

bution grows slower than the degree of polymerization, *i.e.* the polydispersity index decreases with time. Besides living, such polymerizations may also be more correctly called regulated or controlled.

Conventional free radical polymerizations employ slow continuous initiation, and the polymers are formed by termination of the growing chain radicals in coupling or disproportionation reactions. These two features lead to unreactive polymers with essentially time invariant degrees of polymerization and broad molecular weight distributions [2].

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### Introduction

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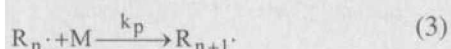
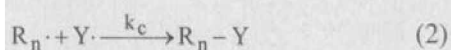
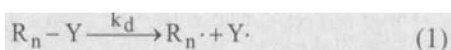
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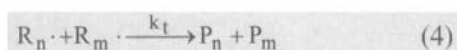
Conventional free radical polymerizations employ slow continuous initiation, and the polymers are formed by termination of the growing chain radicals in coupling or disproportionation reactions. These two features lead to unreactive polymers with essentially time invariant degrees of polymerization and broad molecular weight distributions [2].

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In recent years, ways have been found to combine the ease and robustness of radical polymerizations with the advantages of the ionic reactions. One successful scheme involves the reversible combination of growing chain radicals  $R_n\cdot$  (with  $n$  monomer units ( $M$ )) with persistent radical species  $Y\cdot$  to dormant polymer chains  $R_n-Y$ , *i.e.* the mechanism



The products of irreversible terminations, such as



are virtually absent. The concentration of the transient growing radicals  $R_n\cdot$  is low, and there is a remarkably large excess of the persistent species  $Y\cdot$ . Solomon *et al.* [3] introduced alkoxyamines  $R_0-Y$  as initiators where  $R_0$  is an alkyl and  $Y$  is a nitroxide group. Later, Georges *et al.* [4] found that the polymerization can also be started with a conventional radical initiator in the presence of a stable nitroxide  $Y\cdot$ . In this case, the alkoxyamines  $R_n-Y$  are formed *in situ*. Today, many variants are known which use different initiators, different persistent radicals and different procedures.

This radical polymerization resembles the iniferter technique of Otsu *et al.* [5] and is intrinsically related to the atom transfer radical polymerization (ATRP) of Matyjaszewski, Percec and Sawamoto [6]. In ATRP, the dormant chains are capped by halogen atoms which are reversibly transferred to metal complexes in the lower oxidation state. This generates the transient growing radicals and the complexes in the higher oxidation state, and the latter are the persistent species.

In all radical polymerizations the chain growth carriers are carbon centered free radicals. Upon encounter such radicals always disappear by the close to diffusion controlled self-termination (4). This raises the questions how in processes like (1–4) only minor amounts of dead polymer chains can be obtained and what is the reason for the large excess of the persistent over the transient radicals. For the mechanism (1–4) and for ATRP we have pointed out [7] that this is due to the operation of the Persistent Radical Effect which is known in other parts of chemistry [8].

Qualitatively, the principle is easily explained: Consider the reversible dissociation, *e.g.* of an alkoxyamine, in the absence of monomer or other radical scavenging agents into a transient and a persistent radical together with termination, *i.e.* the reactions (1, 2 and 4) with  $n, m = 0$ . If one starts only with  $R-Y$ , the radicals  $R\cdot$  and  $Y\cdot$  appear initially in equal concentrations because they are formed in one step. When their concentrations become large enough, the bimolecular processes set in. Then, the self-termination removes  $R\cdot$  irreversibly, but the group  $Y$  stays in the pool of  $R-Y$  and free  $Y\cdot$ . Hence, the self-termination of  $R\cdot$  causes, by simple stoichiometry, the build-up of excess  $Y\cdot$ . This continues as time proceeds, hence, the excess of  $Y\cdot$  increases, and cross-coupling (2) becomes more and more favored over the self-termination (4) although this never ceases. The lifetime of the radical precursor  $R-Y$  is prolonged, and there seems to be no net reaction. In polymerizing systems,  $R\cdot$  transforms to  $R_n\cdot$ , and, in the course of time,  $R_n-Y$ , the dormant chains, become the product which dominates over the dead polymers from the self-termination of  $R_n\cdot$ .

This purely kinetic effect reproduces the observed selectivity of dormant polymer formation and the features of control for the basic mechanism and for ATRP quite well [7] if the rate constants of radical formation  $k_d$  and cross-coupling  $k_c$  fulfill specific criteria. There is an intermediate quasi-equilibrium stage of the reversible bond dissociation with weakly time-dependent radical concentrations and a large excess of  $Y\cdot$ . If monomer conversion is in this quasi-equilibrium stage one obtains mainly living products, a controlled degree of polymerization and low polydispersities. Here, we first recapitulate the major analytic results for the basic process taking the nitroxide mechanism as an example and point out conditions for optimized processes and the behavior in borderline cases. Then, we briefly comment on the effects of some important side reactions without giving proofs of some important new results. These will be published in detail at a later stage.

#### The Basic Mechanism: Optimum Rate Constants and Borderline Cases

We consider reactions (1–4) with the simplification of chain length independent rate constants. This allows to sum up

all  $R_n-Y$  as  $R-Y$ , all  $R_n\cdot$  as  $R\cdot$  and all  $P_n$  as  $P$  and to drop the indices. Self-termination is by disproportionation only, but termination by combination does not change the principles, since it simply doubles the degree of polymerization of the unreactive polymers. Initially, there are only dormant molecules  $R-Y$  which are abbreviated as  $I$ . The kinetic equations for the radical concentrations (radical dots omitted)

$$\frac{d[R]}{dt} = k_d([I]_0 - [Y]) - k_c[R]\cdot[Y] - k_t[R]^2 \quad (5)$$

$$\frac{d[Y]}{dt} = k_d([I]_0 - [Y]) - k_c[R]\cdot[Y] \quad (6)$$

are simple but non-linear and have no closed analytic solutions. The validity of good approximative solutions can be proven by using the mathematical technique of phase-space analysis [9]. At early times, both radical concentrations increase linearly with time ( $[R] = [Y] = k_d[I]_0 t$ ). Then, typically in a few 100 milliseconds or seconds, a short complicated transition region is reached due to the onset of the radical-radical reactions. If the rate constants obey

$$\begin{aligned} k_d &\leq k_t[I]_0, \\ k_d &\ll k_c[I]_0 \\ \text{and } k_d/k_c &= K \ll k_c[I]_0/k_t \end{aligned} \quad (7)$$

this is followed by a long-lasting stage with very unusual features: The concentration of the persistent species increases proportional to  $t^{1/3}$ , the concentration of the transient species decreases as  $t^{-1/3}$ , and there is an equilibrium relation for the reversible dissociation.

$$\begin{aligned} [R] &= (K[I]_0 / 3k_t)^{1/3} t^{1/3} \\ [Y] &= (3k_t K^2 [I]_0)^{1/3} t^{1/3} \end{aligned} \quad (8)$$

$$\begin{aligned} k_c[R][Y] &= k_d[I]_0 \\ \text{or} \\ [R][Y] / [I]_0 &= k_d/k_c = K \end{aligned} \quad (9)$$

Eqn. (9) differs from the usual law of mass action because it contains the initial concentration  $[I]_0$  instead of the momentary value  $[I]$ . Also, the radical concentrations (8) are time dependent though this time dependence cancels out to produce a time independent expression (9). Therefore, we call the stage a *quasi-equilibrium*. If the kinetic criteria (7) are not fulfilled,  $Y\cdot$  continues to increase as in the initial phase, and  $R\cdot$  attains a constant

concentration  $[R] = (k_d[I]_0/k_t)^{1/2}$  like in a conventional radical polymerization. The process ends when  $[Y]$  approaches its final value  $[Y] = [I]_0$  with a period in which  $[R]$  decays slowly in a bimolecular fashion, and all dormant species are converted to unreactive products [9].

As known from various studies involving nitroxide radicals the rate constants are in the ranges of  $10^{-6} < k_d < 1 \text{ s}^{-1}$ ,  $10^6 < k_c < 10^8 \text{ M}^{-1}\text{s}^{-1}$  and  $k_t \approx 10^9 \text{ M}^{-1}\text{s}^{-1}$  for usual reaction temperatures around 100–120 °C [10]. The initial concentration of R–Y is usually about  $10^{-3}$  to  $10^{-1} \text{ M}$ . With these data, Eqns (7) reveal that for realistic cases the quasi-equilibrium always exists, and the  $t^{1/3}$ -dependence of  $[Y]$  was indeed observed experimentally [11]. The lifetime prolongation of the radical precursor is given by the factor  $k_c^2[I]_0/k_d k_t$  and amounts to many orders of magnitude.

To treat the polymerization one couples the Eqn for the concentration of the transient radical (8) with the usual rate law for monomer consumption ( $d[M]/dt = -k_p[M][R]$ ) and with the rate equations for the moments of the molecular weight distribution [7][9]. Livingness and control can be achieved if the monomer conversion occurs in the quasi-equilibrium but not in the other time regimes. This requires that

$$\begin{aligned} k_p &\ll 3k_t \\ \text{and} \\ k_p &\ll 3k_c \end{aligned} \quad (10)$$

and these conditions are normally also fulfilled. Then, the monomer conversion obeys

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

This dependence of  $\ln([M]_0/[M])$  on time deviates from the familiar linear dependence in conventional radical and in ionic living polymerizations [2] because the concentration of the propagating species decreases in time, and this also accounts for the factor 3/2 on the r.h.s. of Eqn (11). This Eqn was shown to accommodate experimental data [12] but we notice that a linear time dependence has been found in many living radical polymerizations. It may be caused by a decrease of the termination constant with increasing chain length and conversion [9][13] and by additional reactions which produce constant radical concentrations (see below).

For the basic mechanism the degree of polymerization and the polydispersity are given by Eqns (12) and (13) [9] where

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

$$PDI = 1 - e^{-k_d t} + \frac{1}{X_n} + \frac{[M]_0^2}{([M]_0 - [M])^2} (1 - e^{-k_d t}) \left( \frac{\pi k_p^3 [I]_0}{k_d k_c k_t} \right)^{1/2} \operatorname{erf} \left[ (3k_p)^{1/2} \left( \frac{K [I]_0}{3k_t} \right)^{1/6} t^{1/3} \right] \quad (13)$$

$\operatorname{erf}$  is the error function, and the latter Eqn. becomes Eqn (14) at long times.

$$PDI_\infty = 1 + \frac{[I]_0}{[M]_0} + \left( \frac{\pi k_p^3 [I]_0}{k_d k_c k_t} \right)^{1/2} \quad (14)$$

It is seen that both the degree of polymerization increases and the polydispersity decrease with increasing conversion as expected for a controlled process. Further, for sufficiently large  $k_d$  (12–14) reduce to formulae for a stepwise growth polymerization [2].

Eqns (11, 13, 14) show that the rate constants  $k_d$  and  $k_c$  of the reversible dissociation enter the rate of polymerization and the polydispersity in different ways: The polymerization rate and the concentration of the persistent species  $Y^\bullet$  (which by stoichiometry is practically equal to the concentration of the unreactive polymer P) are governed by the ratio  $k_d/k_c$ , i.e. the equilibrium constant  $K$ . On the other hand, the polydispersity depends on the product  $k_d k_c$  and not on  $K$ . This allows ranges to be stated for  $k_d$  and  $k_c$  for optimized living radical polymerizations from reasonable conditions:

Firstly, we demand that the fraction of the unwanted dead polymer products  $\phi = [P]/[I]_0$  at 90% monomer conversion does not exceed an upper limit  $\hat{\phi}$ . This holds if

$$K = \frac{k_d}{k_c} \leq \frac{k_p [I]_0}{2 \ln(10) k_t} \hat{\phi}^2 \quad (15)$$

Secondly, the residual polydispersity index  $PDI - 1 = [I]_0/[M]_0$  shall be smaller than or equal to an upper limit  $\hat{\delta}$ , which provides

$$k_d k_c \geq \frac{\pi k_p^3 [I]_0}{k_t} \frac{1}{\hat{\delta}^2} \quad (16)$$

Thirdly, the time for large conversion (here 90%) shall not exceed a preset time  $T$ , and this requires

$$K = \frac{k_d}{k_c} \geq \frac{(2 \ln(10))^3 k_t}{9 k_p^3 [I]_0 T^2} \quad (17)$$

Obviously, the optimum ranges of  $k_d$  and  $k_c$  depend on the monomer ( $k_p$ ) and the desired degree of polymerization ( $[I]_0$ ). Fig. 1 shows a double-logarithmic plot of  $k_d$  vs.  $k_c$  for the representative parameters  $[I]_0 = 0.1 \text{ M}$ ,  $k_p = 5000 \text{ M}^{-1}\text{s}^{-1}$  and  $k_t = 10^8 \text{ M}^{-1}\text{s}^{-1}$ . The region where all three conditions are fulfilled is marked by a heavy frame. A larger equilibrium constant  $K$  provides faster polymerizations on the expense of less living polymer, and a lower product  $k_d k_c$  leads to a larger final polydispersity.

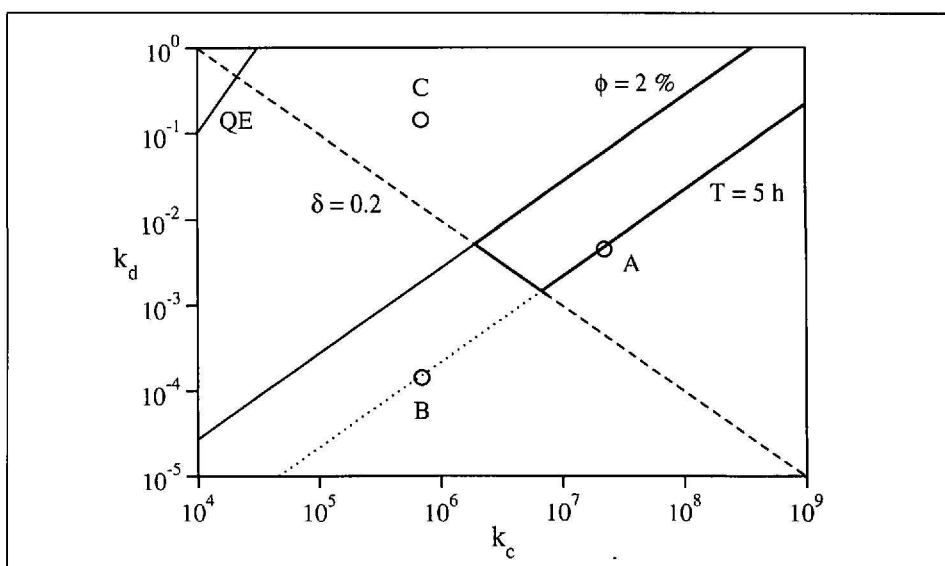


Fig. 1. Range of rate constants  $k_d$  and  $k_c$  for optimized living radical polymerizations in 5 h for 90% conversion with less than 2% unreactive polymer and a polydispersity smaller than 1.2. Other parameters, see text.

Fig. 1 also contains a line QE. Above this line the quasi-equilibrium conditions are not met, *i.e.* there can be no living and controlled radical polymerization. The points marked A, B, and C refer to the following cases: For A the rate constants are in the optimum range. B and C lie outside but in a region where the quasi-equilibrium still exists, and it is easy to predict the outcome of a polymerization for the parameters corresponding to these cases:

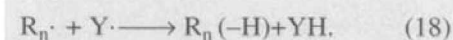
For B and A the equilibrium constants  $K$  are equal, which means equal conversion times and equal fractions of unreactive polymer. However, the product  $k_d k_c$  is smaller for B, and this leads to a larger polydispersity. Therefore, in case B one obtains a polymer which is *mainly living but not well controlled*. In fact, simulations reveal that for A and B, 90% conversion are reached within the same 5 h, and the fraction of unreactive polymer is below 2%. For A the final PDI is 1.1 but for B it increases to a high value of 3. Moreover, for case B and opposite to case A the degree of polymerization decreases with increasing conversion.

For case C the product  $k_d k_c$  is the same as for A but the equilibrium constant  $K$  is larger. Hence, one obtains a faster polymerization and a larger fraction of unreactive polymer. On the other hand, the polydispersity does not change from A to C. This means that for case C the polymer is *largely controlled but less living*. This is supported by simulations which show the same controlled behavior of the degree of polymerization and the polydispersity for A and C, but for C the final fraction of unreactive polymer amounts to about 50%. Obviously, in living radical polymerizations the properties of *livingness and control do not mutually imply each other*.

## Side Reactions

### Cross-disproportionation

Radical-radical reactions often occur not only by coupling but also by disproportionation if the  $\beta$ -hydrogen transfer is possible. Hence, for usual monomers the cross-coupling reaction (2) may be accompanied by the reaction



This removes both the transient and the persistent radicals. Products of disproportionation have been observed in model systems, and it has been speculated that (18) drastically reduces the attain-

able molecular weight and increases the polydispersity [14]. To explore this in a rigorous way we have analyzed the set of kinetic Eqns (1–4) with inclusion of (18). As long as the general conditions for the rate constants (7, 10) apply, a modified quasi-equilibrium relation

$$k_c[R][Y] = k_d([I]_0 - [YH]) \quad (19)$$

is obeyed where  $[YH]$  is the concentration of YH at time  $t$ . This increases exponentially as  $[YH] = [I]_0(1 - \exp(-f_D k_d t))$  where  $f_D$  is the fraction of disproportionation in the cross-reaction between the transient and the persistent species. When  $[YH]$  approaches  $[I]_0$  the dormant chains are mainly converted to  $[YH]$  and to the corresponding unreactive polymer with an alkene end group ( $R(-H)$ ). Then the propagation comes to a fairly abrupt end. The critical time is  $t_D = 1/f_D k_d$  and yields the maximum conversion

$$C_{\max} = 1 - \exp\left(-\frac{3}{2}k_p \left(\frac{[I]_0}{3k_c k_d k_t f_D^2}\right)^{1/3}\right) \quad (20)$$

Fig. 2 shows the degree of polymerization and the polydispersity as functions of conversion for a system with the parameters of point A in Fig. 1 except a higher  $[I]_0 = 0.005$  M for  $f_D = 0$  (broken line) and  $f_D = 2\%$ . Up to the critical time (circle) the degree of polymerization increases as if there were no disproportionation.

Except for the end of the reaction the polydispersity remains small. The theoretical degree of polymerization of 2000 is not reached but if the polymerization were stopped at about 20% conversion a living and controlled polymer would still be obtained. Eqn (20) shows that the effect of disproportionation depends strongly on the other rate parameters. We predict that 90% conversion to a living and controlled polymer is still achieved if the fraction of disproportionation obeys

$$f_D \ll 3 \left( \frac{k_p^3 [I]_0}{(2 \ln(10))^3 k_d k_c k_t} \right)^{1/2} \quad (21)$$

which allows seldom more than a very few percent. Propagating radicals of methylmethacrylates react with TEMPO mainly by disproportionation, and this explains the failure to achieve good results for this monomer by TEMPO-mediation [15].

### True Equilibria

Two situations have been analyzed by the phase-space method which may lead to steady-state radical concentrations and linear time dependencies of  $\ln([M]_0/[M])$ . They have also been treated to some extent by Fukuda *et al.* [16].

We consider first the initial presence of additional persistent species in a concentration  $[Y]_0$  for a system which also initially contains  $I = R-Y$  and obeys the conditions (7). If the initial concentration  $[Y]_0$  is very small, more specifically if

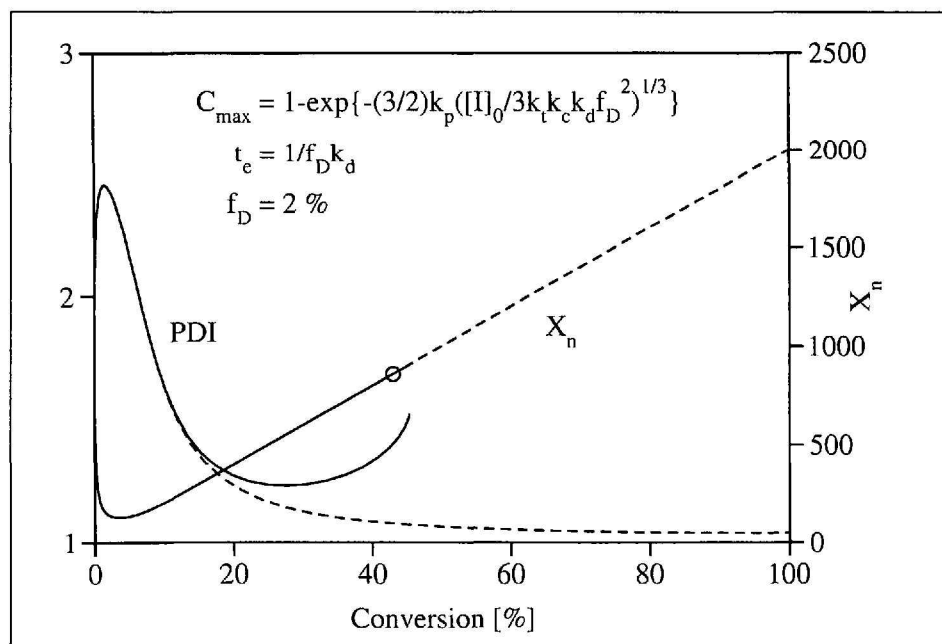


Fig. 2: Degree of polymerization and polydispersity for systems exhibiting zero (broken line) and 2% disproportionation. For parameters, see text. Circle: maximum conversion.



$[I]_0 \ll (k_d k_i [I]_0)^{1/2} / k_c$ , there is no effect, and the previous equations remain valid. For  $(k_d k_i [I]_0)^{1/2} / k_c \ll [Y]_0 < [I]_0$  relation (9) still holds but  $[Y]$  is the sum of the concentrations of persistent species initially present and those formed due to the Persistent Radical Effect. For times smaller than  $t = [Y]_0^3 / 3K^2 k_i [I]_0^2$  one has  $[Y] \approx [Y]_0$ , i.e.  $[R]$  is constant. Monomer conversion in this regime leads to a linear dependence of the conversion index  $\ln([M]_0/[M])$  on time. For larger times,  $[Y]$  is dominated by the fraction arising from the Persistent Radical Effect, and one has to apply the relations for the basic system with the quasi-equilibrium. If one has  $[Y]_0 > [I]_0$ , the quasi-equilibrium does not develop. In general, the initial persistent species slows down the polymerization but it may improve livingness and control quite significantly.

Secondly, we consider the action of a conventional initiator which is added to the basic system to speed up conversion and which produces transient radicals with a constant rate  $R_i$  during the whole polymerization process. If the constant rate is smaller than the rate of radical formation by decomposition of  $I = R - Y$ , i.e.  $R_i < k_d [I]_0$  and if the conditions (7) are fulfilled, the system first behaves as if  $R_i$  were zero and attains the quasi-equilibrium. At a time  $t = (k_i/R_i)^{3/2} k_d [I]_0^3 / k_c$ , this regime is replaced by a steady state of the radical concentrations. The concentration of the transient species is  $[R] = (R_i/k_i)^{1/2}$  as in a conventional radical polymerization, and that of the persistent follows from the equilibrium relation (9) and is constant and smaller than given by Eqn (8). Conversion in the steady state gives again a linear time dependence of the conversion index. Interestingly, even a rather small rate  $R_i \ll k_d [I]_0$  causes a considerable reduction of the polymerization time on the expense of some increase of the final unreactive polymer although the features of controlled degrees of polymerization and small polydispersities remain intact. Hence, the action of the additional initiator is less due to the initiation of new chains but to the reduction of the concentration of the persistent species.

In our opinion additional initiation is the main reason for the abundant observations of linear time dependencies of the conversion index since initiation may arise not only from deliberately added initiators but also by auto-initiation and from radical generating impurities. Moreover, a slow decay of persistent to transient species has the same effect.

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