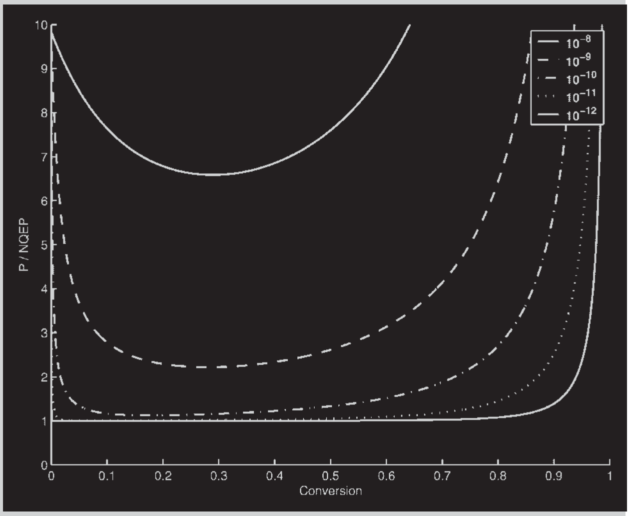
Summary: The range of validity of two popular versions of the nitroxide quasi-equilibrium (NQE) approximation used in the theory of kinetics of alkoxyamine mediated styrene polymerization, are systematically tested by simulation comparing the approximate and exact solutions of the equations describing the system. The validity of the different versions of the NQE approximation is analyzed in terms of the relative magnitude of (dN/dt)/(dP/dt). The approximation with a rigorous NQE, $k_c[P][N] = k_d[P{-}N]$, where P, N and $P{-}N$ are living, nitroxide radicals and dormant species respectively, with kinetic constants k_c and k_d, is found valid only for small values of the equilibrium constant K (10^{-11}–10^{-12} mol·L^{-1}) and its validity is found to depend strongly of the value of K. On the other hand, the relaxed NQE approximation of Fischer and Fukuda, $k_c[P][N] = k_d[P{-}N]_0$ was found to be remarkably good up to values of K around 10^{-8} mol·L^{-1}. This upper bound is numerically found to be 2–3 orders of magnitude smaller than the theoretical one given by Fischer. The relaxed NQE is a better one due to the fact that it never completely neglects dN/dt. It is found that the difference between these approximations lies essentially in the number of significant figures taken for the approximation; still this subtle difference results in dramatic changes in the predicted course of the reaction. Some results confirm previous findings, but a deeper understanding of the physicochemical phenomena and their mathematical representation and another viewpoint of the theory is offered. Additionally, experiments and simulations indicate that polymerization rate data alone are not reliable to estimate the value of K, as recently suggested.



Validity of the rigorous nitroxide quasi-equilibrium assumption as a function of the nitroxide equilibrium constant.

On the Nitroxide Quasi-Equilibrium in the Alkoxyamine-Mediated Radical Polymerization of Styrene

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Introduction

In the last few years living radical polymerization has attracted considerable interest from academia and industry. We believe that many industrial processes will be transformed or generated with the advent of this new chemistry. Nitroxide chemistry is one of the most relevant versions of this concept from both the industrial and scientific points of view. In this context, mechanistic and fundamental aspects related to nitroxide-mediated polymerization acquire special relevance.

The kinetics of living radical polymerization of styrene initiated by alkoxyamines has been studied by several authors.[1–18] Most of the early work was done with TEMPO (2,2,6,6 tetramethylpiperidine-*N*-oxyl) or its derivatives and, for this family of alkoxyamines, Fukuda[1] and Matyjaszewski[8] groups found that the rate of polymerization was independent of the concentration of alkoxyamine and equal to the rate of thermal styrene auto-polymerization, providing some experimental evidence to support this statement.[1,8] In order to explain this, Fukuda et al.[1] assumed that in a very short time, the quasi steady state (QSS) and quasi-equilibrium in the living and persistent radicals respectively, were achieved. The quasi-equilibrium of the persistent radicals (mass action law) will be referred in this work as the nitroxide quasi – equilibrium (NQE) assumption or rigorous NQE assumption:

$$k_c[N][P] = k_d[P{-}N] \tag{1}$$

Where $[N]$, $[P]$ and $[P{-}N]$ are the persistent nitroxide radical, living radical and alkoxyamine concentrations respectively. k_c and k_d are the kinetic constants of the capping/de-capping reactions, respectively

$$P{-}N \underset{k_c}{\overset{k_d}{\rightleftarrows}} P+N$$

On the other hand, as early as 1996, Puts and Sogah[17] established that the reaction rate for alkoxyamine mediated styrene polymerizations would increase with respect to the rate resulting from pure thermal autoinitiation for alkoxyamines having larger equilibrium constants.

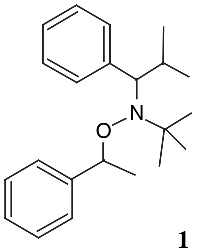
Fischer[6,7] was the first in recognize the existence of three regimes. At a very early stage living and persistent radicals appear initially in equal concentrations because they are formed at equal rate. After that, there is an intermediate quasi-equilibrium stage of the reversible bond dissociation, which in this work we shall refer as relaxed quasi equilibrium to differentiate it from the pure mass action law originally proposed by Fukuda,[1] with a weakly time dependence radical concentration. Finally, at long times the persistent radicals reach a steady state. Fischer showed that at the intermediate stage $[N] \sim t^{1/3}$ while $[P] \sim t^{-1/3}$ such that the following (relaxed) quasi equilibrium condition was satisfied:

$$k_c[N][P] = k_d[P{-}N]_0 \tag{2}$$

where $[P{-}N]_0$ is the alkoxyamine concentration at $t = 0$. At this intermediate regime, the monomer conversion shows a weak dependence on the initial alkoxyamine concentration of the form

$$\ln\left(\frac{[M]_0}{[M]}\right) = \left(\frac{3k_p}{2}\right)\left(\frac{K[P{-}N]_0}{3k_t}\right)^{1/3} t^{2/3}$$

where $[M]$ is the monomer concentration, $K = k_d/k_c$ is the equilibrium constant, k_t and k_p are the termination and propagation rate constants respectively. This law was verified experimentally by Lutz et al.[18] for styrene polymerization with an alkoxyamine having a relatively large *K*. Our group[10] together with others[11] provided additional experimental evidence showing that the rate of polymerization may be a function of the alkoxyamine concentration,[10–12] depending on the efficiency of the alkoxyamine (which is linked to its chemical nature) and its initial concentration. More recently, Schulte et al. published a systematic study[12] in which it is clearly shown that the rate of living polymerization of styrene depends on the concentration of alkoxyamine for efficient alkoxyamines (such as **1** and **2**[19]), at least in some concentration ranges. Schulte et al. attribute this fact to the magnitude of the equilibrium constant (*K*) of the efficient alkoxyamines which is rather large ($K \approx 10^{-9}$ mol · L^{-1}), compared to the less efficient alkoxyamines ($K \approx 10^{-11}$–10^{-12} mol · L^{-1}).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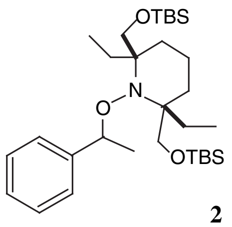

2

Following Fischer,[6] Fukuda et al.[3–5] approximated the quasi-equilibrium condition by the relaxed version Equation (2) and obtained a general solution of the kinetic equations under this approximation, arriving at Fischer's regimes as limiting cases of such solution.

Furthermore, Souaille and Fischer,[13–15] based on an elegant phase-space analysis of the differential equations that describe the evolution of the nitroxide and living radicals, developed a general theory that sets limits for the existence of the relaxed quasi-equilibrium regime for the nitroxide in alkoxyamine-mediated polymerizations. They found that a necessary and sufficient condition for this was:

$$K/[P{-}N]_0 \ll k_c/k_t$$

and

$$K/[P{-}N]_0 \ll 1 \tag{3}$$

Souaille and Fischer[15] extended their theory to the case where there is an additional source of radicals with generation rate R_i, such as the thermal autoinitiation of styrene, while Fischer [16] analyzes several practical cases showing that all of them fulfill the conditions for the validity of nitroxide quasi-equilibrium.

Although the origin of the kinetic regimes in living radical polymerization (LRP) is well established, still there are some intriguing questions about the equilibrium condition satisfied by LRP. From a purely numerical approach, Equation (1) and (2), in a practical case, differ only in the number of significant figures taken in the calculation and yet the difference in the kinetic behavior is considerable. The purpose of the present study is to compare the "exact" numerical solution of the kinetic equations with those obtained under the quasi equilibrium condition given by Equation (1) and (2), in order to obtain a physical insight of the subtle differences of the nature of these approximations. In addition, numerical bounds for the validity of both approximations will be established. These will be shown to be narrower than the analytical ones found by Fischer. Additionally, the effects not previously explored systematically of including a realistic (non-constant) R_i are considered. Finally, we provide complementary experimental data to the study of Schulte et al. and compare their results with a more thorough kinetic model.

Experimental Part

Synthesis of the Nitroxide

The 2,2,5,5-tetramethyl-4-phenyl-3-azahexane-3-nitroxide was prepared by adaptation of the method reported by Benoit et al.[20] and purified by column chromatography. It was characterized by spectroscopic methods.

Synthesis of the Alkoxyamine

The phenylethyl alkoxyamine of 2,2,5,5-tetramethyl-4-phenyl-3-azahexane-3-nitroxide (**1**) was obtained from the reaction between the nitroxide and a phenylethyl radical. (which was obtained from ethylbenzene and di-*tert*-butyl peroxyoxalate) following the procedure of Miura et al.[21] The alkoxyamine obtained, a colorless oil, was characterized by IR and ^{1}H NMR spectroscopy. The synthesis of the nitrone is described elsewhere,[22] as well as the synthesis of the di-*tert*-butyl peroxyoxalate.[23]

Polymerizations

For each reaction alkoxyamine **1** (0.1989 and 1.8496 g for the reactions with 0.012 and 0.113 M concentrations of alkoxyamine, respectively) and styrene from Aldrich (50 mL) were mixed and distributed (5 mL) in 10 vials. The vials were capped with septa and ultra high purity nitrogen was sparged in each vial for 3 min in order to remove oxygen via needles inserted through the septa. The vials were introduced in a thermostated oil bath previously heated at 120 °C. After 10 min of thermal stabilization, time zero for reaction was set and one vial was removed every 30 min and immersed in cold water (1 °C). Immediately after removal of each vial, 1 g of sample was removed from it and inhibited with drops of a solution of hydroquinone (1%) in THF for conversion and molecular weight measurements.

Conversion was measured by dry solids and molecular weight was determined using gel permeation chromatography (Waters Styragel columns HR3 and HR4, Waters 410 differential refractometry detector).

Theory

It is reasonably well established[1–8,12] that the mechanism for alkoxyamine-mediated styrene polymerization can be written as shown in Scheme 1.[24]

where M means monomer, D dead polymer and the other symbols have been defined before. P can be primary or polymeric living radicals and P–N can be either the initiator itself or a polymeric alkoxyamine. When this mechanism is translated into differential equations the following system of equations results:

$$\frac{d[M]}{dt} \approx -k_p[M][P] \tag{4}$$

$$\frac{d[P]}{dt} = R_i - k_t[P]^2 - k_c[N][P] + k_d[P\text{–}N] \tag{5}$$

$$\frac{d[N]}{dt} = k_d[P\text{–}N] - k_c[N][P] \tag{6}$$

$$\frac{d[P\text{–}N]}{dt} = k_c[N][P] - k_d[P\text{–}N] \tag{7}$$

with initial conditions $[P\text{–}N](t=0) = [P\text{–}N]_0; [N](t=0) = [P](t=0) = 0$; $[M](t=0) = [M]_0$, where R_i is the radical generation rate and subscript 0 denotes the charge conditions. The independence of the polymerization rate of the initial alkoxyamine concentration ($[P\text{–}N]_0$) was previously explained by Fukuda[1] et al. and Greszta and Matyjaszewski[8] by arguing that: i) the (rigorous) quasi equilibrium for nitroxide radicals and alkoxyamine moieties, Equation (1), is reached almost immediately, so the last two terms in Equation (5) vanish, and ii) since the quasi steady state approximation (QSSA) holds for the free radical concentration in Equation (5), then $[P] = (R_i/k_t)^{1/2}$ and the rate of polymerization in (4) is given by:

$$\frac{d[M]}{dt} \approx -k_p[M]\left(\frac{R_i}{k_t}\right)^{1/2} \tag{8}$$

Thermal Initiation:

$$3M \xrightarrow{k_{th}} 2P$$

Propagation:

$$P + M \xrightarrow{k_p} P$$

Capping / de-capping

$$P\text{-}N \underset{k_c}{\overset{k_d}{\rightleftarrows}} P + N$$

Irreversible Termination:

$$P + P \xrightarrow{k_t} D$$

Scheme 1.

where R_i for thermal autoinitiation is usually estimated as $2k_{th}[M]^3$.[24] Later Fukuda et al.[3–5] derived a more general implicit equation for the evolution of the concentrations of P and N radicals. They started from Equation (5) assuming a constant rate of initiation R_i and solved it together with Equation (6) by assuming:

$$i)\ \frac{d[P]}{dt} \ll \frac{d[N]}{dt} \qquad (9)$$

and ii) nitroxide quasi-equilibrium (relaxed version), expressed by Equation (2), which also uses the approximation $[P–N] \approx [P–N]_0$. The only difference of this formulation with respect to the first theory is that in the quasi-equilibrium (2) the initial concentration $[P–N]_0$ is used instead of the instantaneous concentration $[P–N]$, making the derivative of N different from zero. The result is a differential equation for $[N]$ that has an implicit analytical solution:

$$\ln\frac{1+x}{1-x} - 2x = at \qquad (10)$$

with

$$x = \left(\frac{R_i}{k_{tc}}\right)^{1/2}[N]/(K[P–N]_0) \qquad (11)$$

$$a = 2\left(\frac{R_i^3}{k_{tc}K^2[P–N]_0^2}\right)^{1/2} \qquad (12)$$

where it is assumed that $[N](t=0)=0$. Fukuda et al.[3–5] showed that Equation (8) is a special case of the approximate general solution represented by Equation (10–12) for the limiting condition $x \rightarrow 1$. This is valid for relatively long times and corresponds to a true stationary state for the radical concentrations, resulting from the assumption of constant R_i.

Fukuda et al. performed an initial analysis of the range of validity of the approximation (1) and its relaxed version (2),[25,26] basing the interpretation of their results in concepts such as the cross-over time, defined as the time at which the kinetic law changes from a power law to stationary state kinetics. This quantity, however, is only hypothetical for alkoxyamines showing a relatively large value of the equilibrium constant K as it is never reached in a practical situation.

Results and Discussion

First, it is important to realize that the terms quasi-steady state and quasi-equilibrium are used with different meanings by different authors. True steady states, represented by zero-time derivatives of all species are of no interest, therefore only quasi-steady-states (for P) or quasi-equilibria in a dynamic sense (for N) are attainable. For the QSSA of living radicals P we will use here the concept generally accepted by kineticists (see e.g. Hill[27]) that indicates that a species is at a QSS when its rates of generation and consumption are approximately equal, allowing to vanish the very small derivative of that species. This does not necessarily imply the constancy of concentration of that species, but implies instead that the change in its concentration is driven by the change of concentration of species exhibiting slower dynamics.

In what follows we will try to answer two specific questions:

1) Under what conditions the rigorous quasi-equilibrium of Equation (1) is valid. This condition must be understood as a dynamic one in which the time derivative of N is so small that can be canceled for the calculations without significantly altering the results.
2) What are more precise bounds for the validity of the relaxed quasi-equilibrium[4,13] given by Equation (2) (relaxed version).

Numerical Calculations

The solution of the system of differential Equation (4)–(7) was implemented in a Fortran program by using a very efficient algorithm (DDASL[28]) for the solution of stiff systems of equations (such as this one) and tested critically and independently the different assumptions using very strict numerical tolerances. The calculations were also checked independently with Matlab™. Although the effective values of the kinetic constants may be chain-length dependent and affected at some polymer concentration by diffusion control effects, we decided to keep all the kinetic parameters constant, even at high conversions, in order to understand the salient features of these systems.

For all the calculations in this work (except where noted) we used the same set of values for the kinetic parameters of styrene polymerization at 125 °C: $k_{th} = 1.86 \times 10^{-10}$ $(mol/L)^{-2} \cdot s^{-1}$,[24] $k_p = 2\,314$ $L \cdot mol^{-1} \cdot s^{-1}$,[29] $k_t = 2.03 \times 10^8$ $L \cdot mol^{-1} \cdot s^{-1}$.[30] In order to check the range of validity of different assumptions the kinetic parameters associated with the alkoxyamine were varied in wide ranges: for the equilibrium constant K (10^{-12}–10^{-8} $mol \cdot L^{-1}$) and for the de-capping constant k_d (10^{-2}–10^{-4} s^{-1}).

Validity of Rigorous NQE

In order to answer the first question, one before has to make sure that the QSSA for P is valid. This should not be taken for granted as indicated by early authors.[31,32] Once this assumption is validated, then any difference in polymerization rate must be ascribed to the failure of the rigorous quasi equilibrium Equation (1), since the simultaneous application of Equation (1) and the QSSA for P leads necessarily to a polymerization rate independent of the concentration of alkoxyamine. The QSSA of polymeric radicals P was tested by solving the system of Equation (4–7) making zero the derivative $d[P]/dt$ in Equation (2), and comparing this approximate solution to that of the system of Equation (4–7) without any simplification (“exact” solution keeping intact the derivative of P and all other derivatives). The approximate and exact solutions were identical for all practical purposes for the wide range of values of K and k_d tested, with the curves describing the evolution of each chemical species overlapping for the two cases, confirming the validity of the QSSA for P. In order to test the rigorous quasi-equilibrium assumption for the nitroxide radicals, we performed a comparison similar to that of the previous test, solving again the system of Equation (4–7), but in this case the exact solution was contrasted to an approximate solution calculated by making zero the derivative of N in Equation (6). Depending on the value of the equilibrium constant and the conversion, either no difference or important differences were observed for the evolution of conversion and the concentrations of P, N and $N\text{–}P$ between the approximate and the exact solutions. In order to show graphically how the validity of the NQE assumption depends on the value of the equilibrium constant we decided to use the ratio of the radical concentration $[P]$ to *NQEP*, where $[P]$ is given by the differential Equation (5) calculated with the exact solution of the system (4)–(7), and *NQEP* (Nitroxide Quasi-Equilibrium P concentration) is the hypothetical concentration of the polymeric radicals obtained when the derivative of Equation (6) is made zero. If the nitroxide quasi equilibrium holds, the ratio $[P]/NQEP$ should be unity. The larger the difference of that ratio with unity, the larger the deviation from Equation (1). Figure 1c and 1d show that the value of this ratio is always greater than 1 for relatively large equilibrium constants ($\approx 10^{-9}$–10^{-8} mol · L^{-1}). On the other hand, the value of the ratio $[P]/NQEP$ is nearly 1 for most of the conversion range when the equilibrium constant is low, in the order of 10^{-12} mol · L^{-1}. For small equilibrium constants (10^{-12} mol · L^{-1}), the concentrations of polymeric and nitroxide radicals required to reach the nitroxide equilibrium are relatively low and much higher with larger values of K (10^{-9} mol · L^{-1}). Notice that *NQEP* turns out to be $(2k_{th}[M]^3/k_{tc})^{1/2}$ given that the QSSA for P always holds.

Sensitivity Analysis for Rigorous NQE

Using the tools just described, a sensitivity study was performed in order to present in a more systematic way under what conditions the rigorous NQE assumption holds in this kind of systems. Some illustrative results are shown in Figure 1 and 2. In this study we varied: i) the initial concentration of alkoxyamine, ii) the value of the equilibrium constant for a fixed value of the de-capping

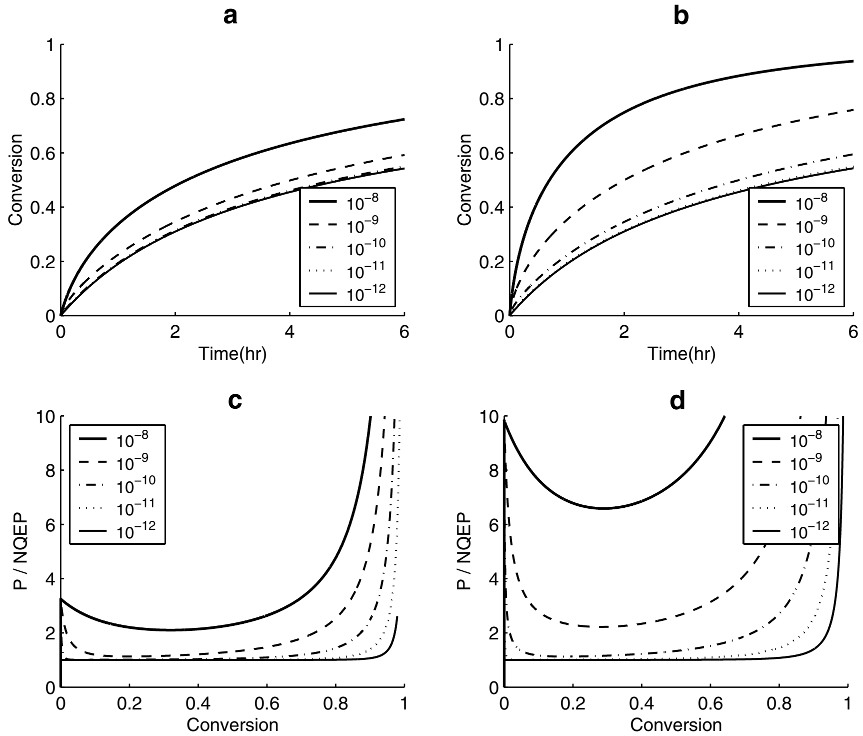

Figure 1. Effect of nitroxide equilibrium constant (K) on the rate of reaction and on the ratio *P/NQEP*. When this ratio is 1, the NQE assumption holds. Plots (a) and (c) were calculated with $[P\text{–}N]_0 = 0.1$ mol-% and plots (b) and (d) were calculated with $[P\text{–}N]_0 = 1$ mol-%. The values of kinetic constants (125 °C) are $k_d = 2.2 \times 10^{-4}$ s^{-1}, $k_{th} = 1.86 \times 10^{-10}$ (mol/L)$^{-2}$ · s^{-1}, $k_p = 2\,314$ L · mol^{-1} · s^{-1} $k_t = 2.03 \times 10^8$ L · mol^{-1} · s^{-1}. Numerical values in the legend refer to the value of K in L · mol^{-1} · s^{-1}. The value of k_c was calculated from the values of k_d and K.

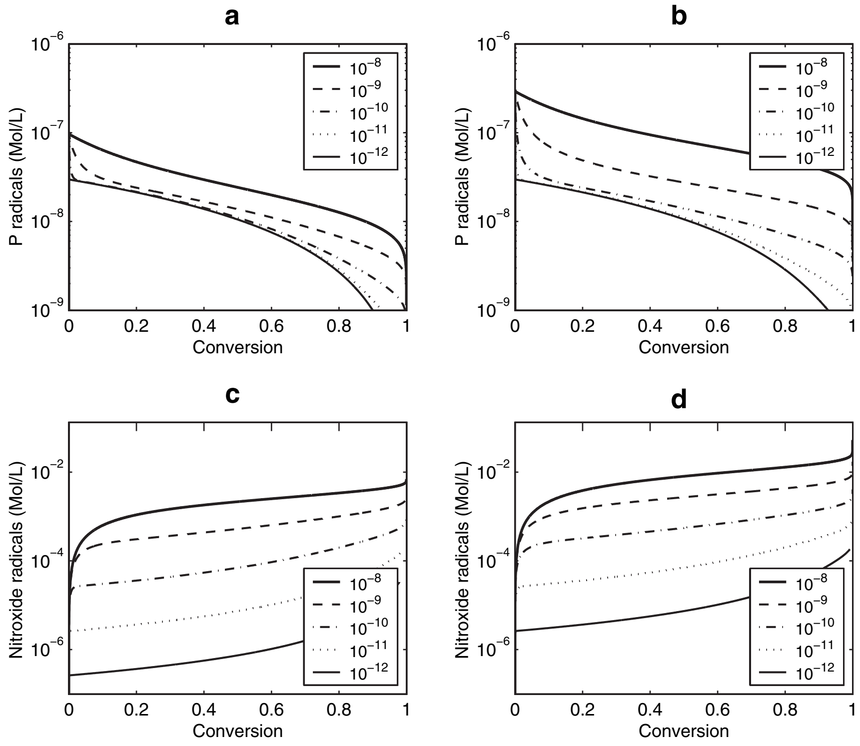

Figure 2. Effect of nitroxide equilibrium constant (K) on P and N concentrations. Plots (a) and (c) were calculated with $[P\text{–}N]_0 = 0.1$ mol-% and plots (b) and (d) were calculated with $[P\text{–}N]_0 = 1$ mol-%. The values of the kinetic constants are the same as those in Figure 1. Numerical values in the legend refer to the value of K in $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. The value of k_c was calculated from the values of k_d and K.

constant, and iii) the value of the de-capping constant for fixed values of the equilibrium constant. From these calculations we estimated the effects of the parameter variation on the ratio *P/NQEP* to test the validity of the NQE assumption. This study shows that: i) the validity of the NQE assumption is almost insensitive to variations of the de-capping constant k_d in the interval 10^{-2}–10^{-4} s^{-1}, for a given combination of values of the equilibrium constant (within 10^{-12}–10^{-8} $\text{mol} \cdot \text{L}^{-1}$) and concentrations of initial alkoxyamine in a range of 0.1 to 1 mol-% (that is 0.0078 M to 0.078 M); ii) the validity of the NQE assumption is very sensitive to the value of the equilibrium constant when everything else is fixed (Figure 1–2), this effect being more marked the higher the concentration of alkoxyamine.

Considering all the calculations (see for example Figure 1c and d), one can conclude that for a value of the equilibrium constant K of 1×10^{-12} $\text{mol} \cdot \text{L}^{-1}$ the NQE assumption holds true from zero conversion to around 80–90% conversion, depending on the values of the other parameters. When $K = 1 \times 10^{-11}$ $\text{mol} \cdot \text{L}^{-1}$ deviations from the NQE assumption start from around 60–70% conversion, or even earlier, depending on the other parameters. Neglecting diffusion effects (not considered either in previous calculations[1,8]) that may also play a role at medium and higher conversions, this last result is somewhat surprising since the value of K for TEMPO has been reported in this order of magnitude. For $K = 1 \times 10^{-10}$ $\text{mol} \cdot \text{L}^{-1}$ the validity of the NQE depends strongly on the values of the other parameters, but there may be deviations starting from 40–50% conversion or even during the whole conversion range. Finally, the rigorous NQE assumption does not hold true for any of the conditions tested when $K \geq 1 \times 10^{-9}$ $\text{mol} \cdot \text{L}^{-1}$; and the deviations of the rigorous solution from the ''exact'' solution are stronger at very low or very high conversions.

Numerical Aspects and Analysis of Time Derivatives

From the previous results it is clear that the system of interest falls in one of two regimes:

i) Systems with relatively low values of the equilibrium constant (around 10^{-11}–10^{-12} $\text{mol} \cdot \text{L}^{-1}$) operating at low to moderate conversions, in which the rigorous NQE, Equation (1) holds.
ii) Systems with relatively high values of the equilibrium constant or operating at high conversions, in which the rigorous NQE fails.

For the latter, the exact and approximate solutions differ grossly for the evolution of conversion, *P*, *N* and *N–P* concentrations. However, as Fischer demonstrated, in both cases the relaxed NQE Equation (2) holds. Surprisingly, even for relatively large values of K the ratio of concentrations $[P][N]/[P{-}N]$ at very early reaction times (less than 36 s in all cases) reaches the value of the equilibrium constant and stay constant throughout the rest of the polymerization. This means that the difference between the NQE criteria given by Equation (1) and (2) is a subtle one and has to do with the number of significant figures involved in the approximation. This apparently minor fact has, however, dramatic consequences. Numerically, it means that if not enough precision is used in the calculation, the cases with relatively large K will apparently and erroneously satisfy the criterion of Equation (1); a fact which is remarkable. More physical insight can be gained by analyzing the time derivatives of Equation (4)–(7) under the two different regimes, associated with different magnitudes of K. Without losing any generality, and subtracting Equation (6) from Equation (5), the following equation can be written:

$$\frac{\mathrm{d}[P]}{\mathrm{d}t} = k_{\mathrm{th}}[M]^3 - k_{\mathrm{t}}[P]^2 + \frac{\mathrm{d}[N]}{\mathrm{d}t} \qquad (13)$$

Under the QSSA the time derivative of P (from here on $\dot{P}$) is very small and can be neglected for the numerical solution of the equation. Also, if the time derivative of N (from here on $\dot{N}$) is sufficiently small, this derivative term can also be neglected, which is the case for relatively small values of K. On the other hand, for larger values of K, $\dot{N}$ is not sufficiently small to be neglected and it must be kept in all numerical calculations.

Figure 3a and 3c show the comparison of the magnitudes of $\dot{P}$ and $\dot{N}$ vs. conversion for the exact solution in the case of low concentration of nitroxide (0.1 mol-%). For these same conditions, Figure 4a shows the ratio of $\dot{N}$ to the absolute value of $\dot{P}$ (since it is negative) vs. conversion (the ordinate is labeled as dN/dP by the chain rule). It can be seen that for low values of K the two derivatives differ by about 1–3 orders of magnitude, while for large values of K they differ by about 4–5 orders of magnitude up to about 80% conversion. A similar situation occurs for the calculations with a high nitroxide concentration (1 mol-%) for the region up to about 80% conversion (Figure 3b and 4b). In this case the derivatives differ by 2–4 orders of magnitude for small K's, while for large K's they differ by 4–5 orders of magnitude. For small K's, both derivatives can be numerically neglected; however, for larger values of K (10^{-8} mol · L^{-1}) $\dot{P}$ can be neglected but $\dot{N}$ cannot.

Also, notice that if Equation (6) is rearranged, it can be written as follows:

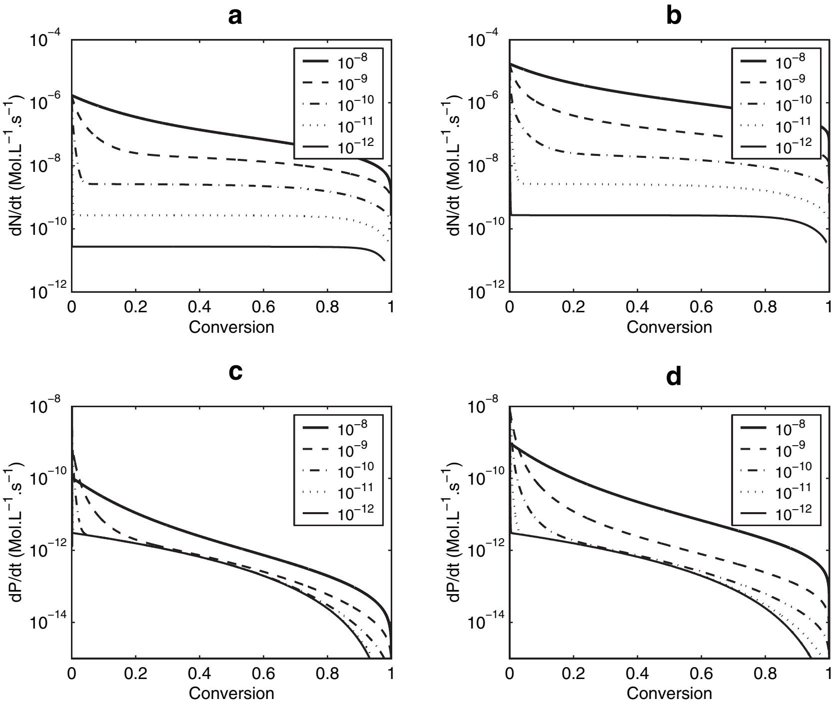

Figure 3. Effect of nitroxide equilibrium constant (K) on the time derivatives of P and N concentrations vs conversion. Plots (a) and (c) were calculated with $[P{-}N]_0 = 0.1\%$ mol and plots (b) and (d) were calculated with $[P{-}N]_0 = 1\%$ mol. The values of the kinetic constants are the same as those in Figure 1. Numerical values in the legend refer to the value of K in L · mol^{-1} · s^{-1}. The value of k_c was calculated from the values of k_d and K.

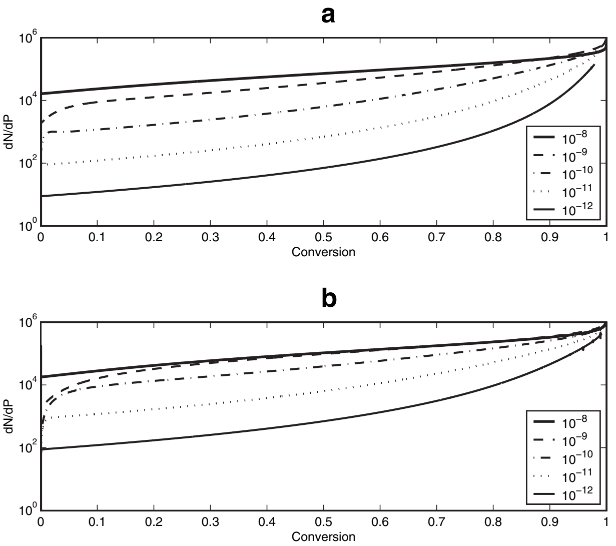

Figure 4. Effect of nitroxide equilibrium constant (K) on the ratio of derivatives of P and N concentrations vs conversion. Plot (a) was calculated with $[P\text{–}N]_0 = 0.1\%$ mol and plot (b) was calculated with $[P\text{–}N]_0 = 1\%$ mol. The values of the kinetic constants are the same as those in Figure 1. Numerical values in the legend refer to the value of K in $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. The value of k_c was calculated from the values of k_d and K.

$$\frac{d[N]}{dt} = k_c[P\text{–}N]\left(K - \frac{[N][P]}{[P\text{–}N]}\right) \tag{14}$$

The term $k_c[P\text{–}N]$ lies in the range 10^3–10^{10} for most practical cases and therefore, even when the two terms inside the parenthesis are equal up to several significant figures, $\dot{N}$ will be much larger, which explains the observations made during the calculations.

Physical Interpretation

Let us look now for a physical interpretation of the magnitude of $\dot{N}$ in the two regimes. For this analysis let us assume a fixed value of k_d and let us consider that variations in K are only due to variations in k_c. For low values of K corresponding to a relatively large k_c and very small $\dot{N}$, even a relatively small instantaneous deviation from equilibrium is enough to provide the driving force to return to a quasi-equilibrium condition. This is due to the smaller build-up of radicals necessary to reach that condition with a large k_c. In the opposite case, with a relatively large K (small k_c) the return to a quasi-equilibrium condition is slower; that is, the necessary build-up of radicals for quasi-equilibrium is larger than in the other case and this results in a larger instantaneous deviation from equilibrium, yielding a larger $\dot{N}$.

Also, at low values of K, the concentration of polymeric radicals is dominated by the generation of radicals due to the styrene thermal autoinitiation and this concentration is enough to maintain the capping–de-capping equilibrium with relatively low concentrations of nitroxide radicals, so the nitroxide quasi-equilibrium applies up to high conversions. On the contrary, at intermediate and high values of K, and even at low values of K but in the regime of high conversions, the NQE Equation (1) is not valid and relatively high concentrations of both, polymeric and nitroxide radicals are needed in order to maintain the equilibrium; in these conditions, the hypothetical concentration of P (*NQEP*) is not high enough to maintain equilibrium and more radicals (of both types) are released by decomposition of the alkoxyamine. In this case the concentration of P is always larger than *NQEP* and the polymerization rate is faster than the corresponding to auto-polymerization since the concentration level of P is dominated by the nitroxide drive to equilibrium rather than by the thermal autoinitiation.

Note that in the case of relatively large K, since $\dot{P} \ll \dot{N}, \dot{P}$ can be neglected in Equation (13) and the resulting equation can be used instead of Equation (5) for the solution of the system (4)–(7), which means that in this case the concentration of P depends on the dynamics of the nitroxide equilibrium.

Simplified Equations

In the regime of low K the behavior of the system can be represented simply by Equation (15) and (16) instead of (5) and (6).

$$\frac{d[P]}{dt} = 2k_{\text{th}}[M]^3 - k_t[P]^2 \approx 0 \tag{15}$$

$$[N][P] \approx K' \tag{16}$$

where $K' = K[P\text{–}N]$. In these conditions the concentration of active radicals is dominated by thermal autoinitiation and Equation (8) with the cubic dependence of R_i of $[M]$ can be used instead of Equation (4). The system of Equation (8), (15) and (16) has an analytical explicit solution given by:

$$[M] = ([M]_0^{-3/2} + (3/2)k_p(2k_{th}/k_t)^{1/2}t)^{-2/3} \tag{17}$$

$$[P] = \left(\frac{2k_{th}[M]^3}{k_t}\right)^{1/2} \tag{18}$$

$$[N] = K'/[P] \tag{19}$$

where the approximation $[P\text{–}N] \approx [P\text{–}N]_0$ can be used. Notice that, due to the use of a realistic expression for R_i, Equation (17) differs considerably from previous power law expressions, which helps to explain why the behavior simulated in Figure 1 and 2 is not easy to classify into the three time regimes given by Fischer. It was verified that Equation (17–19) reproduce very well the solution of the complete system (4)–(6) for low values of K (10^{-12} mol · L^{-1}) for most of the conversion range.

Conversion Effects on Rigorous NQE

It is well established[5,7] that at very low reaction times and conversions the NQE Equation (1) does not hold since in this regime the alkoxyamine decomposes until some form of quasi-equilibrium is reached. However we show that Equation (1) stops applying at high conversions, even for the lowest values of the equilibrium constant. This is due to the decreasing importance of the thermal styrene autoinitiation as a source of fresh radicals (radical flux) as the conversion increases. Taking for example the case with $K = 1 \times 10^{-12}$ mol · L^{-1}, as the conversion increases, the rate of thermal generation of radicals decreases rapidly (empirically as $[M]^3$) and in these conditions the reduced radical flux will correspond to gradually lower values of the hypothetical P concentration $NQEP = (2k_{\text{th}}[M]^3/k_t)^{1/2}$. As the trend continues, at some critical point this results in a concentration of P which is not high enough to maintain the nitroxide equilibrium and more radicals (of both types) are released by decomposition of the alkoxyamine in order to maintain equilibrium.

Consequences of the Analysis for Rigorous NQE

It is clear that NQE Equation (1) will be satisfied as long as there is a sufficiently large radical flux R_i (from thermal autoinitiation or another added radical source) for a given value of the equilibrium constant K. In general, the radical concentration will be given by $NQEP = (R_i/k_t)^{1/2}$ as long as the NQE Equation (1) holds. The larger the value of K the higher the radical flux necessary to reach (or maintain) the NQE. Also, if the radical flux is maintained high enough during the course of the polymerization, Equation (1) will apply during the whole polymerization and the persistent radical effect will not manifest itself since all the P radicals lost due to irreversible termination will be immediately replaced (this was also verified by simulations in which a constant radical flux was maintained). Still, when the Equation (1) applies, there may be a decreasing concentration of P with conversion, but this will be due to a decreased radical flux.

Finally, the range of validity of the NQE implies a lower bound for the polymerization rate. This may have important practical implications for the control of the polymerization rate as, for a given value of K, there is no point in adding initiator if the lower bound of the rate is not exceeded. Our group and others[33,34] have found that some sequences of initiator addition in TEMPO mediated styrene polymerization can increase dramatically the reaction rate, still keeping reasonably low polydispersities. This is attributed to a compensation of the persistent radical effect by the extra initiator added. It is expected that optimal trajectories of initiator addition can be calculated and the insight gained with this work is likely to aid in the calculations and data interpretation; work is ongoing in our group in this direction. Clearly, this insight can be applied to the nitroxide-mediated polymerization of other monomers, in which the radical flux is provided by a slowly decomposing initiator or continuously added initiator. Further and more detailed experimental data as well as simulations including other side reactions will be published in a future paper.

Sensitivity Analysis for Relaxed NQE Criterion

In order to answer the second question that we posed and assess the range of validity of the relaxed NQE criterion, Equation (2), we performed simulations comparing the exact solution of Equation (4–7) with the approximate solution given by:

$$\frac{\mathrm{d}[N]}{\mathrm{d}t} = -R_i + k_t\left(\frac{K[N\text{–}P]_0}{N}\right)^2 \tag{20}$$

Equation (20) was derived by Fukuda et al.[3–5] using assumptions (2) and (9) and following a procedure described before.[15] However, instead of using the analytical solution of (20) derived for the case of constant R_i (which has been already done by Fukuda et al.[25,26]), we decided to use the more realistic variable initiation rate given by $R_i = k_{\text{th}}[M]^3$ and solved Equation (20) numerically (notice that the analytical implicit solution given by Equation (10–12) also requires numerical calculations in order to recover the actual time trajectories of the species). The results of the comparison are shown in Figure 5 and 6 respectively for conversion as well as for N and P concentrations and are similar to those presented by Fukuda et al for constant R_i.[25,26] The approximation resulting from the application of the NQE criterion of Equation (2) is remarkably good, except at high values of the equilibrium constant K. Starting at $K = 10^{-9}$ mol · L^{-1} there are some deviations for the nitroxide concentration and these become more pronounced and noticeable also for conversion and P at higher values of K (especially for the lower concentration of alkoxyamine). This is qualitatively expected from the criterion (3) given by Fischer. As k_c and $[P\text{–}N]_0$ diminish and K increases, the approximation becomes worst. However, for the values used in Figure 5, the bound set by Fischer requires K rather large, in the order of 10^{-5}–10^{-6} mol · L^{-1}, for the approximation of Equation (2) to fail. Numerically we find that even for values of K as low as $K = 10^{-8}$ mol · L^{-1} that approximation stops being accurate.

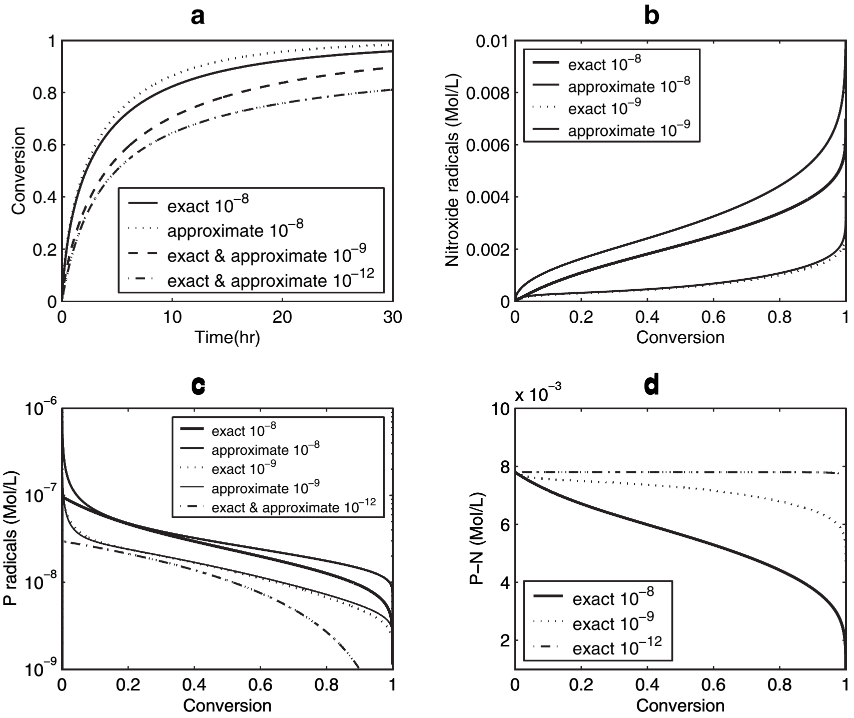

Figure 5. Comparison of approximate solution using relaxed NQE approximation with exact solution using $[P\text{–}N]_0 = 0.1\%$ mol. The numerical values in the figure legend correspond to the value of the equilibrium constant in $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. When the curves are indistinguishable only a single curve is shown. The values of kinetic constants used (125 °C) are $k_\text{d} = 2.2 \times 10^{-4}\ \text{s}^{-1}$, $k_\text{th} = 1.86 \times 10^{-10}\ (\text{mol/L})^{-2} \cdot \text{s}^{-1}$, $k_\text{p} = 2\,314\ \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $k_\text{t} = 2.03 \times 10^{8}\ \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. The value of k_c was calculated from the values of k_d and K.

Estimation of K

Finally, it is subject to discussion the proposal of Schulte et al. by which they claim that the value of K alone is enough to quantitatively explain the rate of reaction deviations from the rate of thermal styrene auto-polymerization. They even propose this as a way to estimate the value of the equilibrium constant. Although this explanation is partly true, one must be cautious in using their suggestion for quantitative purposes. On the other hand, they do not provide enough experimental data in order to show the adequacy of their data fitness for different alkoxyamine concentrations. They only show the fitting of one conversion-time curve, without exhibiting other complete conversion-time curves showing the effect on the polymerization rate of varying initial concentrations of alkoxyamine. Therefore we decided to generate our own data for alkoxyamine **1** (see experimental section). Some authors have proposed different ways of estimating K;[18,35] however, we focus here on the suggestion of Schulte et al.

In Figure 7a, the best fit of the simple model used by Schulte et al. is shown for our experimental data with alkoxyamine **1** obtained using a value of $K = 2.5 \times 10^{-9}$ $\text{mol} \cdot \text{L}^{-1}$ with the rest of the values at 120 °C fixed at $k_\text{d} = 0.022\ \text{s}^{-1}$,[12] $k_\text{th} = 1.20 \times 10^{-10}\ (\text{mol} \cdot \text{L}^{-1})^2 \cdot \text{s}^{-1}$, [24] $k_\text{p} = 2\,000\ \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, [8] $k_\text{t} = 1.46 \times 10^{8}\ \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.[24] As one sees from Figure 7a, Schulte et al. model does not fit the data adequately, which points out to the possible existence of other reactions that are not taken into account by this simple model. At least two reactions which generate additional radicals may be in part responsible for the deviations observed. One of them is the reaction of the dimer adduct with nitroxide radicals,[10,36,37] which is known to rapidly generate radicals. The other one is the decomposition of the nitroxide radical[38] which can generate additional radicals too. Some preliminary calculations are shown in Figure 7b when the reaction of the dimer adduct with nitroxide is included in the kinetic scheme. In order to include this additional reaction, we used a extended kinetic scheme previously published[10] in which the thermal initiation scheme is replaced by the following reactions:

Thermal initiation:

Reaction of dimer with the nitroxide radical:

$$D + N \xrightarrow{k_H} P + HN$$

where D is an adduct (dimeric) and HN an hydroxyl amine. In the original extended model we also included the decomposition reaction of the monomeric alkoxyamine (that also generates HN) and other side reactions, but all of

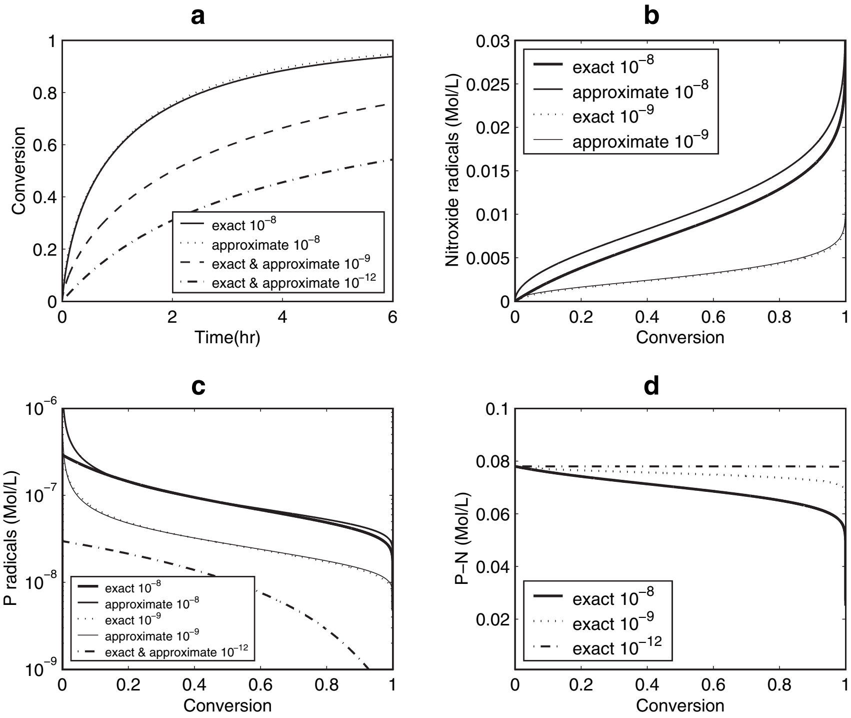

Figure 6. Comparison of approximate solution using relaxed NQE approximation with exact solution using $[P\text{–}N]_0 = 1\%$ mol. The numerical values in the figure legend correspond to the value of the equilibrium constant in $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. When the curves are indistinguishable only a single curve is shown. The values of kinetic constants used (125 °C) are $k_d = 2.2 \times 10^{-4}$ s^{-1}, $k_{th} = 1.86 \times 10^{-10}$ $(\text{mol/L})^{-2} \cdot \text{s}^{-1}$, $k_p = 2\,314$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $k_t = 2.03 \times 10^8$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. The value of k_c was calculated from the values of k_d and K.

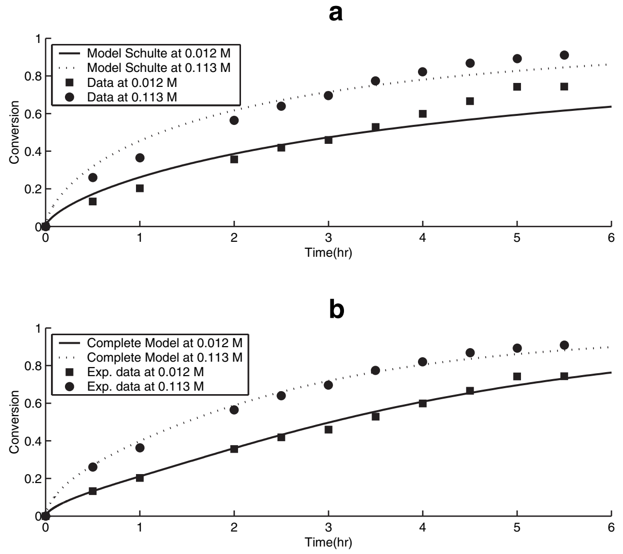

Figure 7. Best fit of: a) Schulte et al. model for conversion – time data (this work) at 120 °C using $K = 2.5 \times 10^{-9}$ $\text{mol} \cdot \text{L}^{-1}$, $k_d = 0.022$ s^{-1}, $k_{th} = 1.20 \times 10^{-10}$ $(\text{mol} \cdot \text{L}^{-1})^2 \cdot \text{s}^{-1}$, $k_p = 2\,000$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $k_t = 1.46 \times 10^8$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$and b) our extended model at same conditions. Values of kinetic constants used in our model $K = k_d/k_c = 1.08 \times 10^{-9}$ $\text{mol} \cdot \text{L}^{-1}$, $k_d = 0.022$ s^{-1}, $k_{dim} = 1.8 \times 10^{-8}$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $k_i = 5 \times 10^{-8}$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $k_p = 2\,000$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $k_t = 1.46 \times 10^8$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $k_H = 0.045$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.

them were turned off (the corresponding kinetic constants were set as zero) for the calculations in this paper. When this extended kinetic scheme is used the fitting is better (see Figure 7b), although there still seems to be a small systematic error of yet unknown origin. The set of values used was: $K = k_d/k_c = 1.08 \times 10^{-9}$ $\text{mol} \cdot \text{L}^{-1}$, $k_d = 0.022$ s^{-1},[12] $k_{dim} = 1.8 \times 10^{-8}$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$,[39] $k_i = 5 \times 10^{-8}$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$,[8] $k_p = 2\,000$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$,[8] $k_t = 1.46 \times 10^8$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$,[24] $k_H = 0.045$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. Notice that, besides the equilibrium constant K, the only fitted parameter is k_H, which has not been measured with precision, but whose value falls well in the range of values previously estimated for this parameter.[10,37] The other values were taken from literature sources. The value for k_d was reported by Schulte et al.[12] at 125 °C and here it is used at 120 °C, although we have discussed that the simulations are almost insensitive to the value of this parameter. With respect to the fit of the polydispersity data (Figure 8b), from previous results [8,10] it is known that the inclusion of the monomeric alkoxyamine decomposition reaction would have improved the match between the trend shown by the model (towards increasing polydispersity at high conversions) and the experimental values, but we decided to let this reaction out in order to emphasize the main point of this discussion.

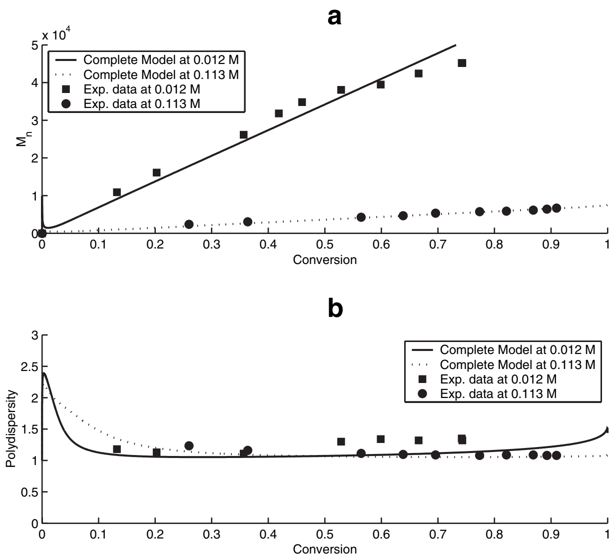

Figure 8. Comparison of extended model and experimental data (this work) for polydispersity and $\overline{M}_n$ at 120 °C. Values of kinetic constants used are the same as in Figure 7.

Finally, Figure 8a shows that the behavior of molecular weight vs conversion can be well predicted by both models, (predictions by the other model are distinguishable), as it is not very sensitive to subtle mechanistic features.

Conclusion

Two criteria for the approximation of nitroxide quasi-equilibrium have been used in the theory of alkoxyamine mediated radical polymerization. In the case of styrene, the rigorous dynamic criterion of $k_c[P][N] = k_d[P{-}N]$ Equation (1), is valid for low values of K (10^{-11}–10^{-12} $\text{mol}\cdot\text{L}^{-1}$) in low to moderate conversions. It implies that $\dot{N}$ can be neglected in the solution of the equations describing the dynamics of the system. In these conditions the rate of polymerization is identical to that of the auto-initiated styrene polymerization. On the other hand, at larger values of K, or at high conversions, this approximation fails since the value of $\dot{N}$ is relatively larger, no longer comparable to $\dot{P}$, so it cannot be neglected during the solution of the equations. As a result, the polymerization rate, controlled by the nitroxide quasi-equilibrium rather than by the rate of auto-initiation, is higher than that of styrene auto-polymerization and the concentration of P is correspondingly higher. Another relaxed criterion for the NQE has been demonstrated to be valid in some regimes by Fischer and used by Fukuda, $k_c[P][N] = k_d[P{-}N]_0$ Equation (2). This approximation preserves the dependence of the rate of polymerization of the alkoxyamine concentration and the approximate solution of the equations using this simplification turns out to be remarkably good, in part due to the fact that $\dot{N}$ is not completely neglected, deviating from the exact solution only at high values of K(10^{-9}–10^{-8} $\text{mol}\cdot\text{L}^{-1}$). These deviations start occurring at significantly smaller K's than those expected from the broad bounds given by the original work of Fischer (in the order of 10^{-5}–10^{-6} $\text{mol}\cdot\text{L}^{-1}$). The difference between the approximations given by Equation (1) and (2) is a subtle one and its essence lies on the number of significant figures taken for the approximation; still, this subtle difference has a dramatic impact in the prediction of the course of the polymerization, a fact which is remarkable. Also, the system was studied with a realistic expression for R_i and this imparts to its behavior important features not previously discussed. The physical insight gained by the analysis of these approximations has practical consequences that will be explored in future work. Finally, it is concluded that the suggestion of Schulte et al., of estimating the equilibrium constant K based solely on conversion-time data, must be taken with caution due to the presence of side reactions that may influence the polymerization rate in addition to the value of K.

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