

# The QSSA of Living Radicals in Alcoxyamine – Mediated Radical Polymerization of Styrene

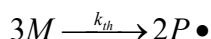
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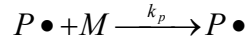
In early works, mostly done with TEMPO (2,2,6,6 tetramethyl, piperidine-N-oxyl) based alcoxyamines by the Fukuda<sup>1</sup> and Matyjaszewski<sup>2</sup> groups, it was believed that the rate of alcoxyamine mediated styrene polymerization was independent of the concentration of alcoxyamine and equal to the rate of autothermal styrene polymerization. This was based on some experimental data and Fukuda gave theoretical arguments to explain it. Recently, a growing body of evidence is being built showing that the rate of polymerization may be a function of the alcoxyamine concentration, depending on the efficiency of the alcoxyamine. Our group was among the first to provide experimental evidence showing the dependence of the rate of polymerization on the alcoxyamine concentration<sup>3</sup>. Very recently, Schulte et al. published a systematic study<sup>4</sup> in which it is clearly shown that the rate of living polymerization of styrene depends on the concentration of alcoxyamine for efficient alcoxyamines, such as aza-hexane based alcoxyamines of Hawker<sup>5</sup>(TIPNO), at least in some concentration ranges. The authors of this study attribute this fact to the magnitude of the equilibrium constant (K) of the efficient alcoxyamines which is rather large ( $K \approx 10^{-9}$  mol L<sup>-1</sup>), compared to the less efficient alcoxyamines ( $K \approx 10^{-11}$  -  $10^{-12}$  mol L<sup>-1</sup>). By simulations they show how this explanation is consistent with the experimental data. They also argue that the magnitude of the equilibrium constant correlates inversely to the relative importance of the autothermal styrene initiation: for alcoxyamines with relatively low K, the role of the autothermal initiation is more relevant, and it becomes less relevant the larger the magnitude of K. However, this explanation is somewhat vague and leaves several questions unanswered, especially when contrasted with the initial theory proposed by Fukuda, that explains the independence of the rate of polymerization on the alcoxyamine concentration, which seems rather plausible. What is wrong with Fukuda's assumptions under the light of the recent evidence ?. Here we address this problem and propose a more complete explanation based on the existence or not of the quasi-steady-state for the polymeric living radicals. A preliminary study of sensitivity is also performed in order to define boundaries for which the rate of polymerization is independent of the initial alcoxyamine concentration. Also we provide data suggesting that it may be necessary to take into account other reactions if a quantitative account of the effect of alcoxyamine concentration on the rate of polymerization is to be provided.

The mechanism proposed by Schulte et al.<sup>4</sup> is given by scheme 1

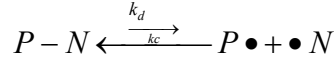
Thermal initiation:



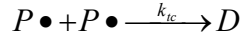
Propagation:



Capping / de-capping



Irreversible Termination:



Where  $M$  means monomer,  $P\bullet$  a free radical (either primary or polymeric),  $N\bullet$  represents the nitroxide radical,  $P-N$  an alcoxyamine (either the initiator itself or a polymeric alcoxyamine) and  $D$  dead polymer. When this mechanism is translated into differential equations the following system of equations results:

$$\frac{d[M]}{dt} \approx -k_p[M][P] \quad 1$$

$$\frac{d[P]}{dt} = k_{th}[M]^3 - k_{tc}[P]^2 - k_c[N][P] + k_d[P-N] \quad 2$$

$$\frac{d[N]}{dt} = k_d[P-N] - k_c[N][P] \quad 3$$

$$\frac{d[P-N]}{dt} = k_c[N][P] - k_d[P-N] \quad 4$$

with initial conditions  $[P-N](t=0) = [P-N]_0$

The independence of the polymerization rate on the initial alcoxyamine concentration ( $[P-N]_0$ ) was previously explained by Fukuda<sup>1</sup> by arguing that: i) equilibrium between free TEMPO and alcoxyamine moieties is reached almost immediately in these systems ( $k_d[N][P] = k_c[P-N]$ ), vanishing the last two terms in equation and, (ii) since the quasi steady state approximation holds for free radical concentration in equation (2) the rate of polymerization in (1) is given by:

$$\frac{d[M]}{dt} \approx -k_p[M] \left( \frac{k_{th}M^3}{k_t} \right)^{1/2} \quad 5$$

which is the same as the styrene polymerization rate due to the autothermal mechanism. However, as shown by the experimental evidence of Schulte et al. equation 5 does not hold true for efficient alcoxyamines in some concentration ranges; therefore at least one of the assumptions of Fukuda does not apply for these systems. We implemented the solution of the system of differential equations 1-4 in a Fortran program by using a very efficient algorithm (DDASL<sup>6</sup>) for the solution of stiff systems of equations and tested critically the two assumptions. For the same system employed by Schulte et al.<sup>4</sup> with alcoxyamine **2** and using the kinetic constants that they propose ( $K=k_d/k_c=1.4 \times 10^{-9}$  mol L<sup>-1</sup>,  $k_d=0.022$  s<sup>-1</sup>,  $k_{th}=1.86 \times 10^{-10}$  M<sup>-2</sup>s<sup>-1</sup>,  $k_p=2340$  M<sup>-1</sup>s<sup>-1</sup>,  $k_t=2.03 \times 10^8$  M<sup>-1</sup>s<sup>-1</sup>), the

equilibrium in equation 3 is reached almost instantly (less than 3 seconds) and is maintained throughout the polymerization. This is expected given the large value of the equilibrium constant. However, under this condition the QSSA does not hold at any time during the polymerization. Figure 1c shows the ratio of the radical concentration P to QSSAP, where P is calculated by the simulation (given by the differential equation 2) without any simplifying assumption and QSSAP is the hypothetical concentration of the polymeric radicals if the QSSA holds; that is  $QSSAP = (k_{th}M^3/k_{tc})^{1/2}$

If the QSSA holds true this ratio will be 1, but this is never obtained for the polymerization with a relatively large equilibrium constant ( $1.4 \times 10^{-9} \text{ mol L}^{-1}$ ). Figure 1c also shows the same ratio for different values of the equilibrium constant. The ratio is nearly one for most of the conversion range when the equilibrium constant is in the order of  $10^{-12} \text{ mol L}^{-1}$ .

At low values of the equilibrium constant ( $10^{-12} \text{ mol L}^{-1}$ ), the generation of active and nitroxide radicals is relatively low and much higher with larger values of K ( $10^{-9} \text{ mol L}^{-1}$ ). At low values of K the concentration of polymeric radicals is dominated by the generation of radicals due to the styrene autothermal initiation and this concentration is enough to keep equilibrium with relatively low concentrations of nitroxide radicals.

In these conditions the concentration of radicals given by the QSSA is enough to keep the equilibrium. On the other hand, at high values of K, relatively high concentrations of both, polymeric and nitroxide radicals are needed in order to maintain the equilibrium; in these conditions the QSSA concentration of P is not high enough to maintain equilibrium and more radicals (of both types) are released by decomposition of the alkoxyamine. This last species can be seen as an infinite reservoir of radicals (of both types), that are quickly released as needed in order to maintain equilibrium. The next question is under what conditions the QSSA for polymeric radicals holds true in this kind of systems. We performed a sensitivity study in which we vary: i) the initial concentration of alkoxyamine, ii) the value of the equilibrium constant for a fixed value of the de-capping constant, and iii) the value of the de-capping constant for fixed values of the equilibrium constant. From these calculations we estimated the effect on the ratio P/QSSAP, therefore getting a measure of the validity of the QSSA for polymeric radicals. In the meeting we will discuss these results in detail.

Finally, it is important to question the statement of Schulte et al. by which they claim that the value of K is enough to quantitatively explain the rate of reaction deviations from the rate of autothermal styrene polymerization. They even propose this as a way to estimate the value of the equilibrium constant. Although this explanation is partly true, one must exert caution at the quantitative use of this. They don't 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 the effect of the change in polymerization rate at different initial concentrations of alkoxyamine. Therefore we decided to generate our own data for an azahexane based (TIPNO) alkoxyamine. In the meeting we will present evidence showing that a more detailed kinetic mechanism with additional side reactions is necessary in order to get quantitative agreement of simulations and experimental data.

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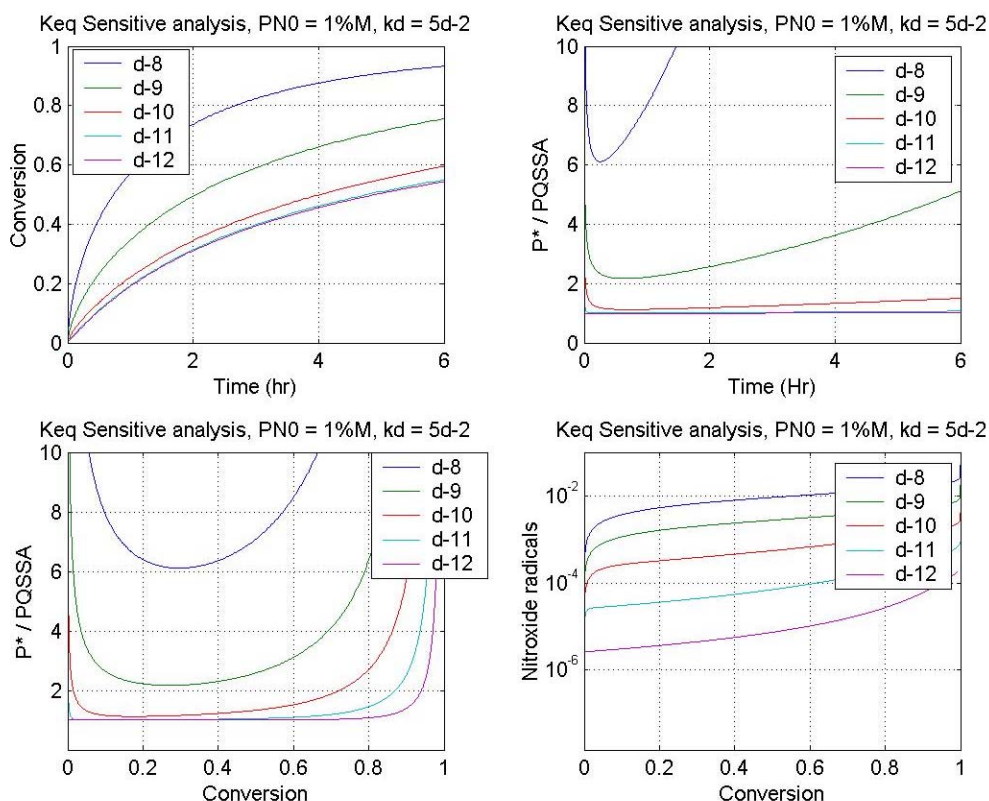


Figure 1. Sensitivity of reaction variables to the value of the alkoxyamine decomposition equilibrium constant.