

Kinetics of the Incubation Period in Nitroxide – Mediated Radical Autothermal Polymerization of Styrene

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Introduction. Considerable attention has been given to the mechanism and kinetics of nitroxide controlled radical polymerization of styrene^{1,2,3} and it seems to be reasonably understood, in spite of a still incomplete understanding of the mechanism of styrene autothermal initiation. However, most of the previous studies have been focused on the stage at which steady state kinetics for the nitroxide species has been reached, in part because most of these studies have focused on model systems in which initiation is achieved via an alcoxyamine. For these systems, equilibration of the nitroxide stable radical and alcoxyamine concentrations is reached at very early reaction times. However, the region of non-equilibrium kinetics is quite important and may last for significantly long reaction times for systems showing an inhibition period, in which the rate of initiation (R_i) is low, such as systems with pure autothermal initiation or with a low concentration of initiator, in which control is achieved by adding pure nitroxide as a radical. Although they have been qualitatively discussed in previous studies (Boutevin and Bertin⁴, Devonport et al.⁵), and their behavior could be regarded as similar to that of an inhibited system, it presents particular features and a clear and detailed kinetic analysis for them seems to be lacking in the literature. Furthermore, a paper by Kothe and Fischer (2001)⁶ confirms the quadratic dependence of the rate of nitroxide consumption during the inhibition period (which is the same rate as that of radical generation) on monomer concentration and provides the missing key element for a more quantitative description of the inhibition period.

A modeling and simulation study is presented here in which the kinetics of the relevant species are analyzed for a model system controlled by adding nitroxide radical and having the lowest possible R_i : that given only by autothermal initiation. Additionally, a link between the kinetics of styrene autothermal initiation before and after the incubation period induced by TEMPO (2,2,4,4, tetramethyl, piperidine N-oxy), is established via a computational model and simplified analytical expressions that can be extended to both regions under certain assumptions. These assumptions are critically tested in the light of available experimental evidence, resulting in further insight in the mechanism of pure styrene autothermal polymerization.

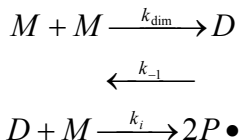
Experimental. The inhibition period for systems at 120 and 125 °C was measured in our lab in order to provide additional experimental evidence on the duration of the inhibition period. Styrene from Aldrich was used. Previous to use, styrene was washed with a. NaOH 10 % wt solution and dried up with sodium sulfate. TEMPO from Aldrich was used as received. Styrene and TEMPO were weighed and put in glass vials for a total

¹ T. Fukuda, T. Terauchi, A. Goto, K. Ohno, Y. Tsujii, T. Miyamoto, S. Kobatake and B. Yamada; *Macromolecules*, **29**, 6393-6398 (1996); ² D. Greszta and K. Matyjaszewski, *Macromolecules*, **29**, 7661-7670 (1996); ³ H. Fischer, *Macromolecules*, **29**, 7661-7670 (1996); ⁴ B. Boutevin and D. Bertin, *Eur. Polym. J.*, **35**, 815-825 (1999) ⁵ W. Devonport, L. Michalak, E. Malmström, M. Mate, B. Kurdi, C.J. Hawker, G. C. Barclay and R. Sinta, *Macromolecules*, **30**, 1929-1934 (1997); ⁶ T. Kothe and H. Fischer, *J. Polym. Sci.A: Polym. Chem.*, **39**, 4009-4013 (2001)

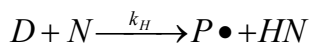
solution volume of about 4.5 ml. Ultra high purity nitrogen was sparged in the solution for several minutes in order to purge the oxygen. The vials were then submerged into a preheated oil bath at the desired reaction temperature. Samples were taken out of the bath at preset times and quenched in iced water. The conversion was measured by solids content. The induction period was estimated by extrapolating the non-zero conversion vs time data until they crossed the time axis.

Kinetics and model. A simplified kinetic model for the nitroxide mediated radical autothermal polymerization of styrene can be written as follows (see Hui & Hamielec⁷, and others^{2,6}), assuming that first propagation is fast:

Thermal initiation:



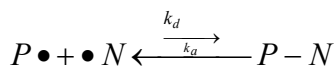
Reaction of dimer with TEMPO (Moad et al.⁸):



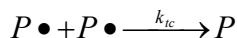
Propagation:



Deactivation / Activation



Irreversible Termination:



Where M means monomer, D a dimer adduct (dimeric styrene), HN an hydroxyl amine, $P\bullet$ a free radical (either primary or polymeric), $N\bullet$ represents a nitroxide radical, $P-N$ a polymeric alkoxyamine and P dead polymer. It has been experimentally observed that this system shows a clear induction period with no conversion, whose length is proportional to the initial amount of nitroxide in the system. After that period the polymerization rate (at least below approximately 40 % conversion) proceeds as if no nitroxide was present and the rate of autothermal initiation of styrene returns to its normal value. Enough data from literature are available to derive expressions for the rate of consumption of nitroxide radicals (already given by Kothe and Fischer⁶), the rate of radical generation (R_i) and the rate of dimer generation.

Assuming during the induction period: i) QSSA for dimer D , ii) QSSA for free radicals $P\bullet$, iii) $k_{tc} P\bullet^2 \ll k_c P\bullet N\bullet$ and iv) $k_d [P-N] \ll k_c P\bullet N\bullet$, one gets:

$$\frac{dN\bullet}{dt} = -2k_{dim}M_0^2 \left(\frac{k_i M_0 + k_H N\bullet}{k_i M_0 + k_{-1} + k_H N\bullet} \right) \quad (1)$$

This reduces to the expression given by Kothe and Fischer⁶, $\frac{dN\bullet}{dt} = -2k_{dim}M_0^2$, only if k_{-1} is much smaller than the rest of the denominator or if $k_i M_0$ and k_{-1} are both $\ll k_H$

⁷ A. W. Hui and A. E. Hamielec, *J. Appl. Polym. Sci.*, **16**, 749-769 (1972); ⁸ G. Moad, E. Rizzardo, D. H. Solomon, *Polym. Bull.*, **6**, 589-593 (1982)

N•. This last condition seems to be approximately true given the values of the kinetic constants from previously published measurements and estimations². On the other hand, the net rate of radical generation is given by:

$$R_i = 2k_iDM_0 + k_HDN\bullet \quad (2)$$

From the QSSA of D one gets:

$$k_iDM_0 + k_{-1}D + k_HDN\bullet = k_{\text{dim}}M_0^2 \quad (3)$$

$$D = \left(\frac{k_{\text{dim}}M_0^2}{k_iM_0 + k_{-1} + k_HN\bullet} \right) \quad (4)$$

Combining (3) and (4) in (2) yields

$$R_i = k_{\text{dim}}M_0^2 \left(\frac{2k_iM_0 + k_HN\bullet}{k_iM_0 + k_{-1} + k_HN\bullet} \right) \quad (5)$$

Given the order of magnitude of the constants discussed before, during the induction period it must be:

$$R_i = k_{\text{dim}}M_0^2 \quad (6), \text{ and}$$

$$\frac{dN\bullet}{dt} = -2R_i \quad (7)$$

After the period of induction, if the QSSA is still valid for the dimer D, then expression 5 is still valid but, under those conditions $N\bullet \rightarrow 0$ and given the order of magnitude of the remaining quantities, eq. 5 becomes approximately:

$$R_i = k_{\text{dim}}M_0^2 \left(\frac{2M_0}{k_{-1}} \right) = \frac{2k_{\text{dim}}k_i}{k_{-1}} M_0^3 \quad (8)$$

which is the well know cubic expression by Hui & Hamielec⁷ for styrene thermal autoinitiation. Notice that the rate of dimer generation is $k_{\text{dim}}M^2$, and for each dimer two nitroxide radicals are consumed, independently of the reaction path taken by D; therefore the rate of nitroxide consumption is twice the rate of dimer generation, that is $2k_{\text{dim}}M$. Also, under the assumption that $k_HDN \gg k_iDM$ (whose plausibility was discussed before), and using the QSSA on D,

$$R_i \approx k_HDN \approx k_{\text{dim}}M^2 \quad (9)$$

which indicates that the rate of radical generation is the same as that of dimer generation. This is because the chemical path markedly favored by D, manifested as a significant difference in kinetic rates, is the second one, that yields one radical per dimer molecule. This also explains why the rate of radical generation is much faster in the presence of TEMPO than without it. The second path is much faster than the first one and is the one prevailing in the presence of TEMPO (At $[\text{TEMPO}] > 0.05 \text{ M}$). In the absence of TEMPO the only path available for dimer reaction and radical generation is the first one which is relatively slow compared to the second one. It is worth mentioning that the four assumptions listed before for the derivation of equation (1) seem to be consistent with all available experimental evidence, as pointed out by Kothe and Fischer. However, the validity of the QSSA for the dimer D after the induction period is still not a clear matter, due to the fact that the second chemical path becomes negligible, and therefore the only significant consumption

step for D is the first one (at a relatively low reaction rate) leading to a higher QSSA D concentration (if a QSSA is indeed present). A key value for quantitative calculations and simulations, both during the induction period and afterwards, is the value of k_H ; only a gross estimation is available (Bertin & Boutevin⁴).

Summary of Results and Conclusions. The experimental results will be shown in the meeting; however, from our simulations and kinetic parameter estimations two important results (whose derivations will be explained in more detail during the meeting) are found:

1) In order to represent previously published experimental results for kinetic data including the induction period, we proceeded in two different ways: i) using the quadratic dependence on monomer concentration for the rate of radical generation (eq. 6) during the induction period and switching towards the cubic dependence on monomer concentration (eq. 8) for the rate of radical generation after the induction period (assuming QSSA for the dimer D), and ii) using a single model for both periods, in which a detailed kinetic scheme based on the Mayo dimer formation mechanism without any QSSA is applied. ***Both approaches are able to represent the kinetic data of Devonport et al using previously estimated kinetic constants. The only fitted parameter for the second approach, not available from previous estimations, is k_H .*** The fitted data for the second approach with a value of k_H of 0.05 is shown in Figure 1.

2) Using the second approach we confirmed by simulation that, as suggested by Kothe and Fischer (see Fig.2), the QSSA for the styrene dimer D is valid during the induction period (due to the fast consumption of D via its reaction with TEMPO radicals); however ***the QSSA for the styrene dimer D is not valid after the induction period. This demonstrates that the generally accepted model of Hui and Hamielec for the cubic dependence on monomer concentration (eq. 8) of the rate of radical generation is not mechanistically correct, since it is based on the QSSA for the dimer D.*** Its success in representing kinetic data is based on an empirical data fitting. ***This conclusion is very important since this model has been used for almost 30 years in the kinetics and modeling literature of styrene polymerization.***

Figure 1. Fitting of Devonport et al. data⁵ with detailed single model

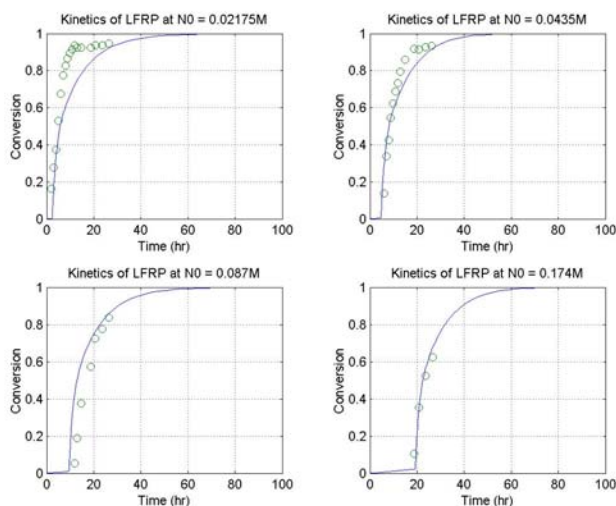


Figure 2. Concentration of dimer D for detailed single model with and without QSSA assumption for D. The curves bifurcate after the induction period (around 20 hrs.).

