Comments on the Paper "Living Radical Polymerization: Kinetic Results" (Catala, J. M.; Bubel, F.; Oulad Hammouch, S. *Macromolecules* 1995, *28*, 8441)

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The development of living/controlled radical polymerizations has been receiving increasing interest, due to its commercial and academic importance. Polymerization of styrene in the presence of various nitroxides or the corresponding adducts is among the most popular approaches. Catala and co-workers have reported kinetic studies of polymerization of styrene mediated by alkoxyamines **1** and **2**.^{1,2}



They made the striking observation that the polymerization rate is independent of the initial concentration of the adduct in the range 3.7 \times 10^{-3} to 4.4 \times 10^{-2} $mol \cdot L^{-1}$. This phenomenon was attributed by the authors to aggregation of dormant chains to a degree of 10 or higher. However, there is neither physical nor chemical precedence for such aggregation of neutral nonpolar species. Besides, aggregation could affect polymerization rates, molecular weights, and polydispersities. From the kinetic plots presented by Catala and co-workers, it seems that the rates of polymerizations in the presence of nitroxide adducts used at different concentrations are almost identical with the rate of bulk thermal polymerization of styrene. The rate of thermal polymerization of styrene at 90 °C is 3×10^{-5} $mol \cdot L^{-1} \cdot s^{-1} \cdot s^{-5}$ Converting Catala's data of $ln([M]_0/[M])$ vs time to [M] vs time, the calculated initial rate of polymerization in the presence of variable amount of the adduct is remarkably close to that for the thermal self-initiated styrene bulk polymerization (2.73×10^{-5} $mol \cdot L^{-1} \cdot s^{-1}$).

The main conclusion which can be drawn from the rate comparison is that the thermal self-initiation of styrene is responsible for maintaining reasonable rates of polymerization in the presence of nitroxides. In other words, all or a large majority of propagating radicals are produced by thermal self-initiation. The main role of the adduct is to control molecular weights and polydispersities by bimolecular and/or unimolecular exchange. Bimolecular exchange (degenerative transfer) has been discussed elsewhere.⁶ Here we focus on a possibility of control via unimolecular cleavage of alkoxyamine:

$$PX = \frac{k_a}{k_d} P^* + X^*$$

where PX is the monomeric (initiating) or polymeric adduct, P* is the initiating or propagating radical, X* is free nitroxyl radical, k_a is the activation rate constant, and k_d is the deactivation rate constant.



Figure 1. Dependence of $\ln([M]_0/[M])$ vs time for bulk polymerization of styrene at 90 °C: lines represent simulated polymerizations (*K* values in mol·L⁻¹, *k*_d values in mol⁻¹·L·s⁻¹, [PT]_0 = adduct concentration in mol·L⁻¹); open circles, experimental data for polymerization in the presence of monoadduct **1** with variable concentration $3.7 \times 10^{-3} - 4.4 \times 10^{-2}$ mol·L⁻¹; closed circles, experimental data for polymerization in the presence of diadduct **2** with variable concentration of $1.85 \times 10^{-3} - 2.2 \times 10^{-2}$ mol·L⁻¹ (data from refs 1 and 2).



Figure 2. Dependence of number-average degree of polymerization on conversion for bulk polymerization of styrene at 90 °C: solid line, simulation results for $K = 1 \times 10^{-12}$ mol·L⁻¹, $k_d = 1 \times 10^9$ mol⁻¹·L·s⁻¹, adduct concentration [PT]₀ = 3.7 × 10⁻³ mol·L⁻¹; open circles, experimental results for polymerization in the presence of monoadduct **1** (3.7 × 10⁻³ mol·L⁻¹) (data from ref 1).

Employing the Mayo model for thermal self-initiation^{3,7} and literature values for the rate constant of propagation $k_p = 892 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1} \, ^8$ and termination k_t = 1 × 10⁷ mol⁻¹ \cdot L \cdot \text{s}^{-1} \, ^9 we analyzed the dependence of ln([M]₀/[M]) vs time as well as the evolution of molecular weights and polydispersities with conversion for bulk thermal polymerization of styrene in the presence of the adduct **1** using the computer simulation program Predici.^{10,11} It was established that the equilibrium constant $K = k_a/k_d$ should be equal to or lower than 1 × 10⁻¹² mol·L⁻¹. It is evident that at low conversions the plots for both thermal polymerization and polymerizations in the presence of adducts are almost identical with the plots reported by Catala for adducts **1** and **2** (Figure 1).

The closest fit for the experimental dependence of polydispersities on conversion reported by Catala and co-workers was found for $k_d \approx 1 \times 10^9 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ (diffusion limited) and $k_a \approx 1 \times 10^{-3} \text{ s}^{-1}$ ($K = 10^{-12} \text{ mol} \cdot \text{L}^{-1}$). Using these values, low polydispersities ($M_w/M_n < 1.10$), linear dependence of molecular weights on conversion, and number-average degree of polymerization (DP_n) defined by the ratio of concentrations of reacted monomer and adduct was simulated (Figures 2

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Figure 3. Dependence of polydispersities M_w/M_n on conversion for bulk polymerization of styrene at 90 °C: lines represent simulated polymerizations for $K = 1 \times 10^{-12} \text{ mol}\cdot\text{L}^{-1}$, $k_d = 1 \times 10^9 \text{ mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$ and $k_d = 1 \times 10^8 \text{ mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$; open circles represent experimental results for polymerization in the presence of monoadduct **1** (3.7 × 10⁻³ mol}\cdot\text{L}^{-1}) (data from ref 1).

and 3). The kinetic model used for simulations includes only thermal self-initiation, propagation, termination by coupling, and reversible decomposition of the adduct, but does not include any additional side reactions^{12,13} and therefore the simulated polydispersities are lower than experimental ones. The observed polydispersities could also be fitted with $k_{\rm d} = 10^8 \, {\rm mol}^{-1} \cdot {\rm L} \cdot {\rm s}^{-1}$ in the presence of initial free nitroxide, since the deactivation rate depends on the nitroxide concentration. Thermal polymerization under similar conditions but in the absence of adducts results in polymers with DP_n \approx 300, independent of conversion and high polydispersities, $M_{\rm w}/M_{\rm n} \geq 2$.

The purpose of this communication is to report that in the polymerization of styrene mediated by nitroxides the polymerization rate is mainly governed by thermal self-initiation, but the control of molecular weights and polydispersities is achieved by exchange between propagating radicals and dormant adducts. The exchange can occur via degenerative bimolecular transfer¹⁴ or by unimolecular cleavage of alkoxyamines with equilibrium constant $K \leq 10^{-12}$ mol·L⁻¹ for adduct **1** at 90 °C. The equilibrium constant increases with temperature and depends on the nature of the nitroxide, and for example, simulations of styrene bulk polymerization with TEMPO as the nitroxide lead to $K \approx 10^{-11}$ mol·L⁻¹ and $k_{\rm d} \approx 10^8$ mol⁻¹·L·s⁻¹ at 125 °C.

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