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COMMENTS ON THE PAPER "LIVING RADICAL POLYMERIZATION: KINETIC RESULTS" (CATALA, J.M.; BUBEL, F.; OULAD HAMMOUCH, S., *Macromolecules*, 1995, 28, 8441)

by

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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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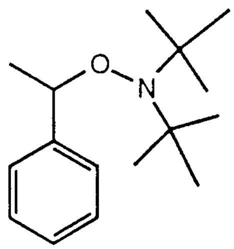
Abstract:
It has been reported that the rate of styrene bulk polymerization in the presence of various adducts of di-t-butyl nitroxides does not depend on the initial concentration of the adduct. The reported rate is very similar to thermal self-initiated polymerization of styrene at the same temperature. Therefore, it is proposed that thermal initiation controls the kinetics of nitroxide-mediated polymerization. The adduct, on the other hand, participates in either bimolecular or unimolecular exchange reactions providing control over molecular weights and polydispersities in this system. This proposal is supported by the results of computer simulations of a bulk styrene polymerization in a system with unimolecular exchange. It was determined that the equilibrium constant equals $K=k_a/k_d \leq 1 \cdot 10^{-12}$ mol$\cdot$L^{-1} and the deactivation rate constant is approximately $k_d \approx 1 \cdot 10^9$ mol$^{-1}\cdot$L$\cdot$s^{-1} in the bulk polymerization of styrene in the presence of di-t-butyl nitroxides at 90°C.

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. J.-M. Catala and coworkers have reported kinetic studies of polymerization of styrene mediated by alkoxymines **1** and **2** [1,2].



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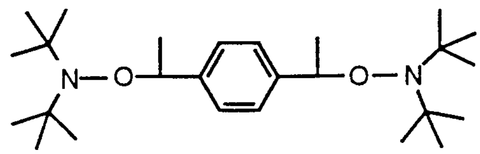

2

They made the striking observation that the polymerization rate is independent of the initial concentration of the adduct in the range $3.7 \cdot 10^{-3}$ to $4.4 \cdot 10^{-2}$ $mol \cdot L^{-1}$. 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 coworkers 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 $3 \cdot 10^{-5}$ $mol \cdot L^{-1} \cdot s^{-1}$. [3-5] 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 ($2.73 \cdot 10^{-5}$ $mol \cdot L^{-1} \cdot s^{-1}$).

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:

$$PX \underset{k_d}{\overset{k_a}{\rightleftharpoons}} P^* + X^*$$

PX - monomeric (initiating) or polymeric adduct

P* - initiating or propagating radical

X* - free nitroxyl radical

k_a - activation rate constant

k_d - deactivation rate constant

Employing the Mayo model for thermal self-initiation [3,7] and literature values for the rate constant of propagation $k_p = 892\ mol^{-1} \cdot L \cdot s^{-1}$ [8] and termination $k_t = 1 \cdot 10^7\ mol^{-1} \cdot L \cdot s^{-1}$ [9], we analyzed the dependence of $\ln([M]_o/[M])$ 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 a computer simulation program Predici[10,11]. It was established that the equilibrium constant $K=k_a/k_d$ should be equal or lower than $1 \cdot 10^{-12}\ mol \cdot L^{-1}$. 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** (Fig. 1).

The closest fit for the experimental dependence of polydispersities on conversion reported by Catala and coworkers was found for $k_d \approx 1 \cdot 10^9\ mol^{-1} \cdot L \cdot s^{-1}$ (diffusion limited) and $k_a \approx 1 \cdot 10^{-3}\ s^{-1}$ ($K=10^{-12}\ mol \cdot L^{-1}$). 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 were simulated (Figs. 2 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. 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, $M_w/M_n \geq 2$.

The purpose of this note 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 transfer [14] or by unimolecular cleavage of alkoxyamines with equilibrium constant $K \leq 10^{-12}\ mol \cdot L^{-1}$ for adduct **1** at 90 °C.

Acknowledgments.

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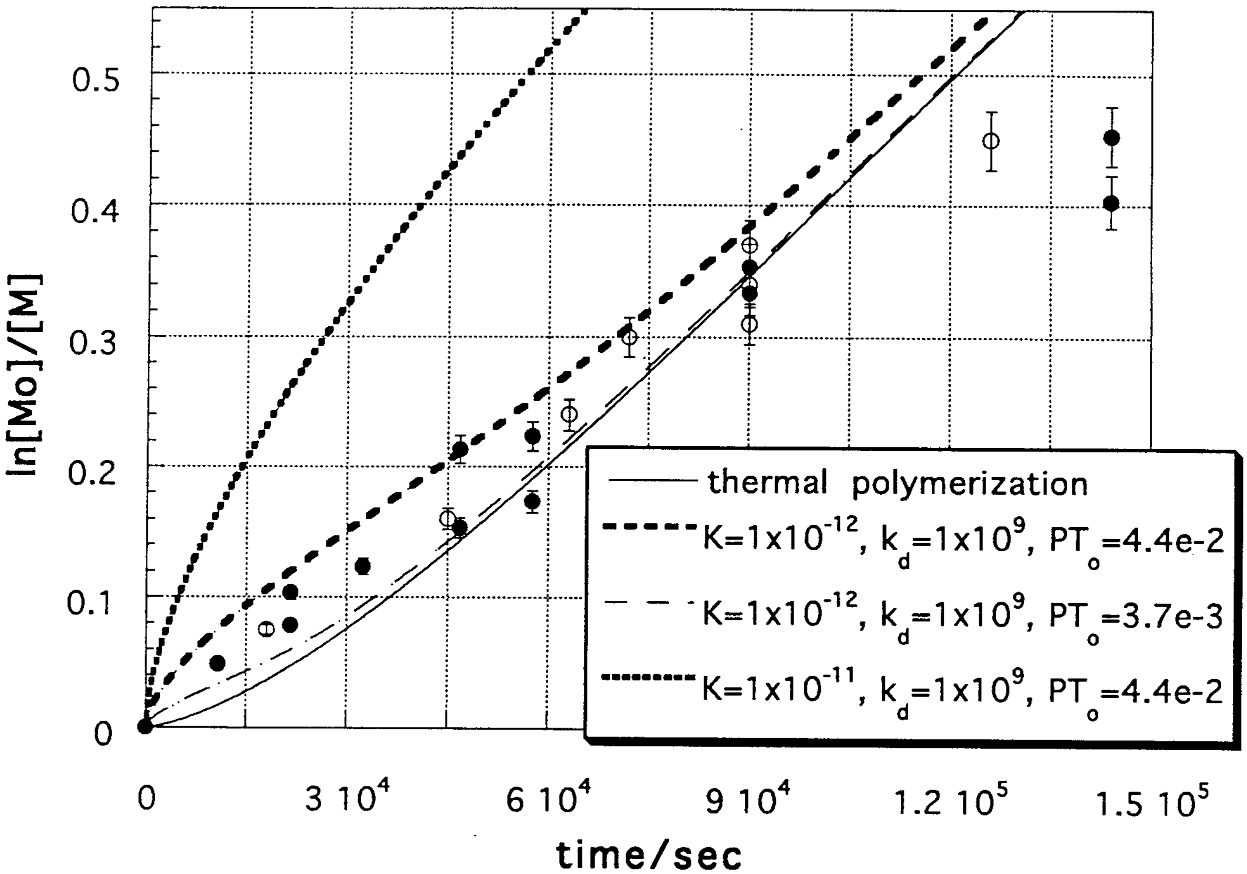
Captions for Figures:

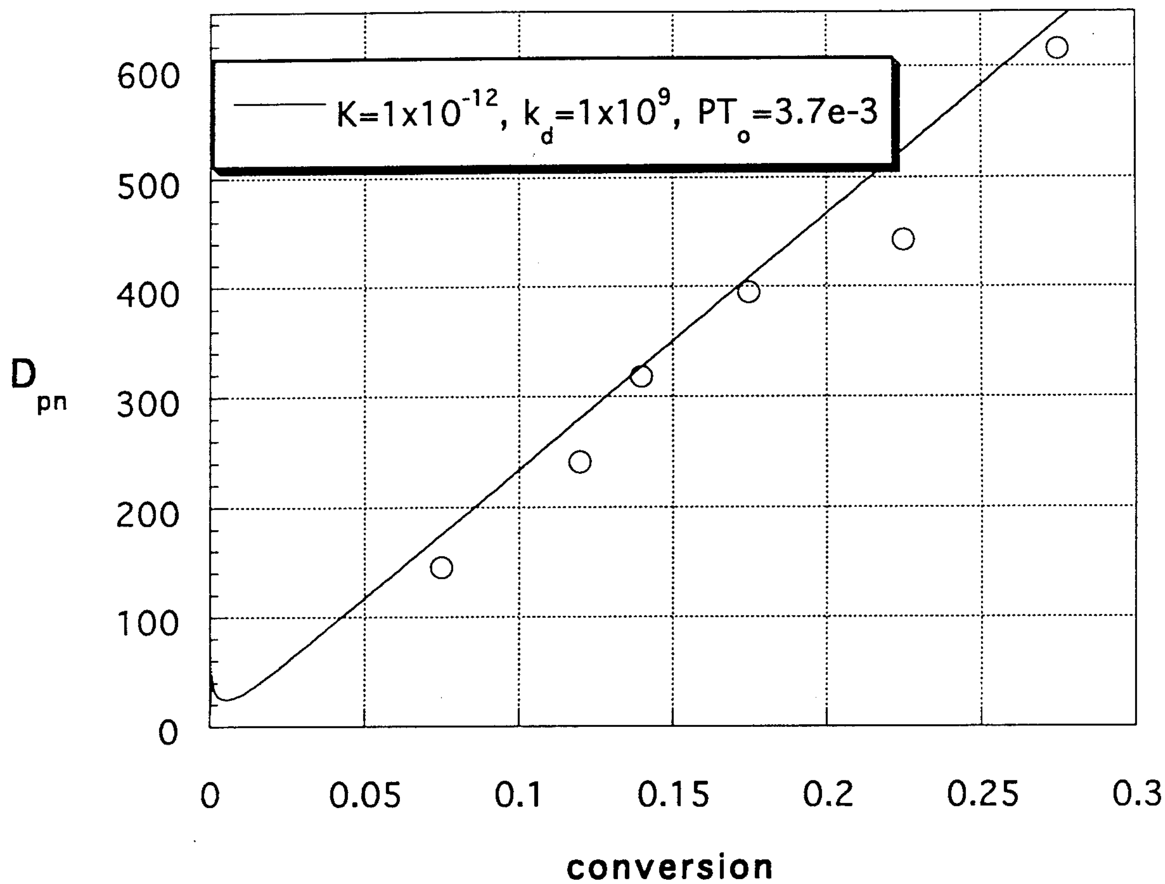
Figure 1. Dependence of $\ln([M]_o/[M])$ vs time for bulk polymerization of styrene at 90°C: lines represent simulated polymerizations (K values in $mol \cdot L^{-1}$, k_d values in $mol^{-1} \cdot L \cdot s^{-1}$, PT_o- adduct concentration in $mol \cdot L^{-1}$); open circles: experimental data for polymerization in the presence of monoadduct **1** with variable concentration $3.7 \cdot 10^{-3}$ - $4.4 \cdot 10^{-2}$ $mol \cdot L^{-1}$, closed circles: experimental data for polymerization in the presence of diadduct **2** with variable concentration $1.85 \cdot 10^{-3}$ - $2.2 \cdot 10^{-2}$ $mol \cdot L^{-1}$, data from ref. 1, 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 $K=1 \cdot 10^{-12}$ $mol \cdot L^{-1}$, $k_d=1 \cdot 10^{-9} mol^{-1} \cdot L \cdot s^{-1}$, adduct concentration$[PT]_o=3.7 \cdot 10^{-3}$ $mol \cdot L^{-1}$, open circles: experimental results for polymerization in the presence of monoadduct **1** ($3.7 \cdot 10^{-3}$ $mol \cdot L^{-1}$), data from ref. 1

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



0.5
0.4
0.3
0.2
0.1
0
ln[Mo]/[M]
0
3 10^4
6 10^4
9 10^4
1.2 10^5
1.5 10^5
time/sec
thermal polymerization
K=1x10^-12, k_d=1x10^9, PT_o=4.4e-2
K=1x10^-12, k_d=1x10^9, PT_o=3.7e-3
K=1x10^-11, k_d=1x10^9, PT_o=4.4e-2



K=1x10-12, kd=1x109, PTo=3.7e-3
Dpn
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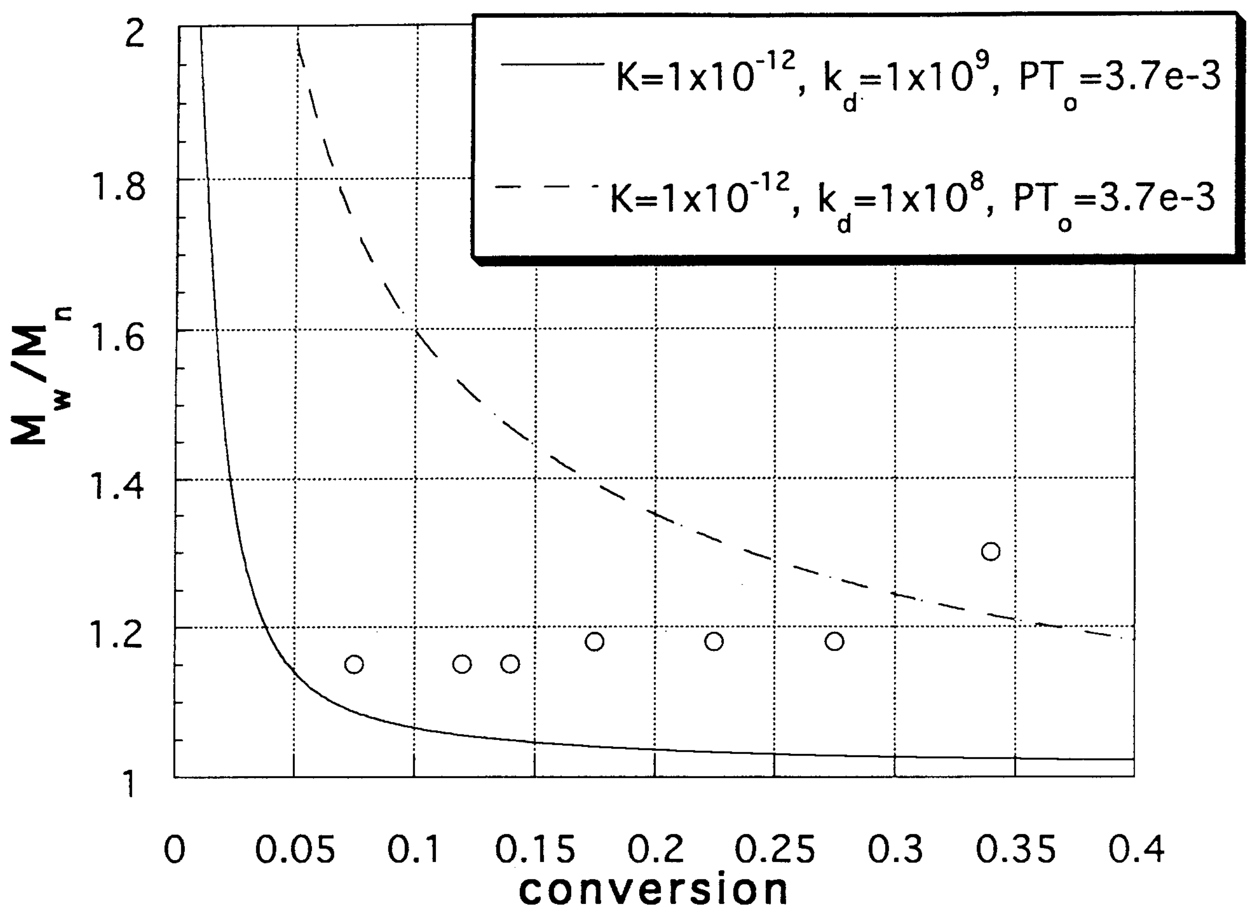
500
400
300
200
100
0
0
0.05
0.1
0.15
0.2
0.25
0.3
conversion



K=1x10-12, kd=1x109, PTo=3.7e-3
K=1x10-12, kd=1x108, PTo=3.7e-3
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1.8
1.6
1.4
1.2
1
Mw/Mn
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
conversion