

Mechanism and Kinetics of Nitroxide-Controlled Free Radical Polymerization

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In the nitroxide-mediated free radical polymerization, the rate of polymerization is determined by the balance of the rates of thermal initiation and bialkyl termination, just like in the conventional system, while the polydispersity is determined by the dissociation-combination frequency of the polymer-nitroxyl adduct and the rate of decomposition of the adduct. These mechanisms were quantitatively confirmed by both experiments and computer simulations.

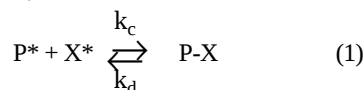
Keywords: Nitroxyl-polymer adduct / Reversible dissociation / Initiation / Termination / Decomposition / Narrow polydispersity

Introduction

Nitroxide-controlled free radical polymerization, first reported in 1985¹ and most extensively studied since 1993,² is a simple and robust method for preparing well-defined polymers. However, no unified views on the mechanism and kinetics have been established as yet. Here, we discuss the problems on the basis of our published and unpublished results.

Kinetic Schemes

A key role of the nitroxyl method is believed to be played by the reversible reaction among the polymer radical P*, the nitroxyl X*, and their adduct P-X^{1,2,3}:



while X* is active only to P*, P* should generally be active not only to X* and the monomer M (propagation) but also to other P* (termination). The concentrations of P* and X* should follow

$$d[P^*]/dt = R_i - k_t[P^*]^2 + k_d[P-X] - k_c[P^*][X^*] \quad (2)$$

$$d[X^*]/dt = k_c[P-X] - k_t[P^*][X^*] \quad (3)$$

where R_i is the rate of initiation, and k_t is the termination rate constant. If R_i is non-zero, a stationary state will be eventually reached, in which d[P*]/dt = d[X*]/dt = 0, and we have³

$$[P^*] = (R_i/k_t)^{1/2} \quad (4)$$

$$[X^*] = K [P-X] / [P^*] \quad (5)$$

Experimental Results and Discussion

For simplicity, here we confine ourselves to the polymerization of styrene in the presence of a purified adduct of polystyrene (PS) with TEMPO (2,2,6,6-tetramethylpiperidiny-1-oxy) with no extra (free) nitroxyl added.

ORGANIC MATERIALS CHEMISTRY —Polymeric Materials—

Scope of research

Basic studies have been conducted for better understandings of the structure/property or structure/function relations of polymeric materials and for development of novel functional polymers. Among those have been the studies on (1) the synthesis and properties of cellulose- and oligosaccharide-based functional polymers, e.g., biodegradable polymers, liquid crystals and polymers of well-defined structure having pendant oligosaccharides, (2) the structure of polymer gels, ultrathin films and polymer alloys, and (3) the syntheses of new types of block and graft copolymers and fullerene(C₆₀)-including polymers.



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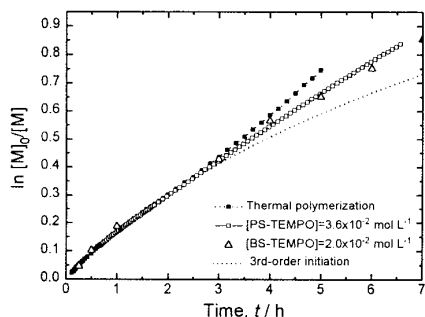


Figure 1 First-order plot for the polymerization of styrene at 125 °C in the presence (□) and absence (■) of 10 wt% of PS-TEMPO adduct ($M_n = 2300$, $M_w/M_n = 1.14$). The dotted curve shows the $[M]^3$ -dependent initiation (constant k_i): (Δ) batch polymerization with 2-benzoyloxy-1-phenylethyl adduct with TEMPO, a unimer model of PS-TEMPO ($[BS-TEMPO] = 20 \text{ m mol L}^{-1}$)

Polymerization Rate R_p . According to eq 4, the polymerization rate $R_p = k_p [P^*][M]$ is independent of $[P-X]$, being equal to that of the thermal (adduct-free) system. This has been verified experimentally, as Figure 1 shows.⁴ The deviations observed at high conversions are ascribed to changes in k_t (changes in viscosity).

Equilibrium Constant K . The same styrene/PS-TEMPO system as was dilatometrically studied in Figure 1 was in situ followed by ESR to determine the concentration of free TEMPO as a function of time. The result was combined with the dilatometrically estimated $[P^*]$ with $k_p = 2300 \text{ L mol}^{-1} \text{ s}^{-1}$ (125 °C), yielding $K = 2.1 \times 10^{-11} \text{ mol L}^{-1}$, independent of time.⁴

Dissociation Rate Constant k_d . Styrene was polymerized in the presence of a PS-TEMPO adduct and the initiator *t*-butylhydroperoxide (BHP). In this condition, a dissociated PS radical will undergo propagation until it is recombined with TEMPO, and hence it should be distinguishable from the never-dissociated species by use of GPC. BHP plays the role of capturing free TEMPO, thereby helping the chain propagate longer so that the GPC analysis becomes easier. This idea in fact worked, as shown in Figure 2. The concentration of the never-dissociated species, determined in an absolute manner independent of the grown components, was found to be first order in itself, giving $k_d = A \exp(-E/RT)$ with $A = 3.0 \times 10^{13} \text{ s}^{-1}$

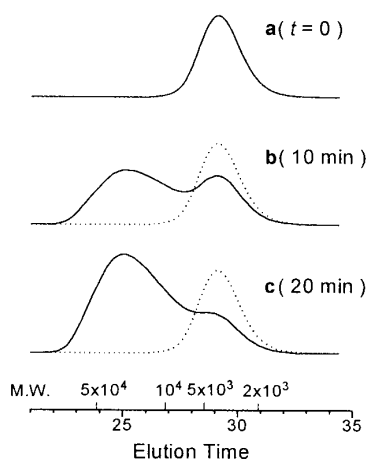


Figure 2 GPC charts for the styrene/BHP/PS-TEMPO ($M_n = 2300$, $M_w/M_n = 1.14$) mixture heated at 120 °C for varying times: $[PS-TEMPO] = 18 \text{ m mol L}^{-1}$; $[BHP] = 20 \text{ m mol L}^{-1}$.

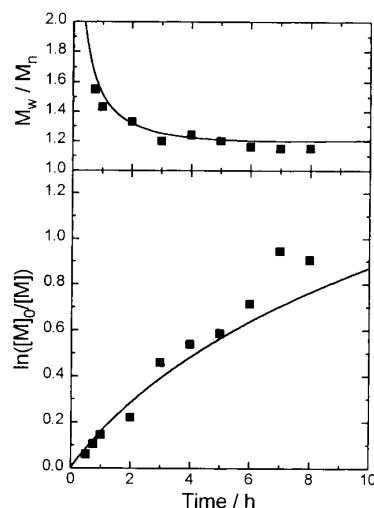


Figure 3 Plot of $\ln([M]_0/[M])$ and M_w/M_n vs. polymerization time for the styrene/BS-TEMPO/125 °C system with $[BS-TEMPO] = 50 \text{ m mol L}^{-1}$ (cf. Caption to Figure 1): (□) measured; (—) simulated.

and $E = 124 \text{ kJ mol}^{-1}$.⁵ The k_d value thus determined was independent of $[BHP]$, which indicates that the degenerative transfer to the alkoxide is not a main mechanism of the controlled polymerization in this system.

Thermal Decomposition of the Alkoxide. The 1-phenylethyl adduct with TEMPO (S-TEMPO) thermally decomposes through the β -H abstraction to give styrene and the hydroxylamine.⁶ We have made an NMR study to examine the decomposition of a PS-TEMPO ($M_n = 1100$, $M_w/M_n = 1.03$) according to a similar mechanism and evaluated the first-order rate constant of decomposition as $k_{dec} = A' \exp(-E'/RT)$ with $A' = 5.7 \times 10^{14} \text{ s}^{-1}$ and $E' = 153.3 \text{ kJ mol}^{-1}$. This result indicates that in the TEMPO-mediated polymerization of styrene, the decomposition of the active chain-end would occur less seriously than implied by the experiment with S-TEMPO.⁶

Computer Simulation. We have carried out a computer simulation on a styrene/BS-TEMPO/125 °C system, for which all the main parameters are known including k_d , $k_c (= k_p/K)$, k_{dec} , $k_p/k_t^{1/2}$, k_p , and k_i (the 3rd-order thermal initiation rate constant). The result predicts that the stationary state with both $[P^*]$ and $[X^*]$ will be reached in about 5 min for $[BS-TEMPO] = 5.0 \times 10^{-2} \text{ mol L}^{-1}$, for example. Figure 3 gives the time dependence of $\ln([M]_0/[M])$ and M_w/M_n of the same system. The experimental data are well reproduced by the simulation *without any adjustable parameters*. A main cause of the rather small deviations is the neglect of the conversion dependence of k_i in the simulation. The postulated mechanisms of the TEMPO-controlled polymerization of styrene are thus confirmed.

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