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Living Radical Polymerization: Kinetic Results

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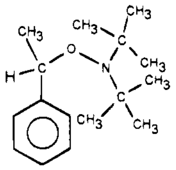
Within the last few years radical polymerization has been the object of renewed interest due to an original approach[1−4] that allows the elimination of transfer and termination reactions. This process is based on the capping of the active site with a stable nitroxy radical: this termination type reaction is thermoreversible and the polymerization presents a "living character". Though extensive work has been done recently on the influence of the chemical structure of the capping agent,[5−7] no study has been yet undertaken on the kinetics of a polymerization carried out in the presence of stable nitroxide radicals. We have therefore investigated the polymerization of styrene initiated by a well defined initiator:


(A-T)

Generally, initiation of a living radical polymerization is done by using classical initiators such as AIBN or benzoyl peroxide. These initiators are added to the monomer containing the stable radical. However, the stoichiometry between the growing radical and the capping agent is rarely respected, and consequently, no data can be obtained about the kinetic parameters. In order to use stoichiometry, we have synthesized initiator A−T using classical reactions of organic chemistry.[8] Heated, this compound leads to the formation of a di-*tert*-butyl nitroxide radical (T•) and an alkyl radical (A•) that exhibits a chemical structure similar to that of the styryl radical. The choice of this capping agent comes from its absence of reactivity toward alkenes and from the low strength of the bond formed with the active site.[9] In this paper, we suggest that the classical kinetic scheme of living polymerization should be modified. This stems from kinetic studies concerning the monomer consumption and the evolution of the molecular weight with time. Experimentally, several sealed tubes containing styrene and the initiator (A−T) were prepared and submitted to heat during given times. The corresponding polymers were isolated by freeze-drying and the conversion yield calculated from the weight of the samples obtained. The molecular weight and the polydispersity were determined by gel permeation chromatography, polystyrene standards being used for the calibration.

First, polymerizations were carried out at different temperatures in order to determine the best temperature leading to (i) a fast initiation rate as compared to the propagation rate, (ii) a fast equilibrium between the active species and the dormant ones, (iii) a low concentration of active species in order to minimize the termination and/or transfer reactions and (iv) a negligible thermal polymerization of styrene. All these conditions are necessary to obtain a low polydispersity of the samples. The reactions[10] were done at three temperatures, 80, 90, and 100 °C, with the same initiator concentration, $[A-T] = 3.7 \times 10^{-3}$ mol L^{-1}.

In Figure 1, it can be observed that the molecular weight increases linearly with the polymer yield, up to 30% conversion. The initiator concentration is equal in all cases, and the same molecular weight is obtained for the same conversion in each case. In Figure 2, the conversion-time plots are straight lines for experiments done at 80 and 90 °C. This shows that the order in monomer is equal to unity and indicates that the concentration of the active species remains constant: these polymerizations present both criteria of a living polymerization. At 100 °C, no straight line is observed: the formation of thermal radicals which recombine with the growing radicals contribute to a decrease of the number of the active sites with time. The rate of formation of the thermal radicals was evaluated from the yield and molecular weight of the polystyrene samples isolated from the blank solutions and is equal to 1.6×10^{-8} mol L^{-1} s^{-1} at 100 °C, 0.6×10^{-8} mol L^{-1} s^{-1} at 90 °C, and 0.2×10^{-8} mol L^{-1} s^{-1} at 80 °C. These results show that the thermal polymerization can be neglected at 90 and 80 °C when compared to the initiator concentration used. For this reason, it is not necessary to use camphorsulfonic acid to limit thermal polymerization.[11]

The polydispersity of the samples (Figure 3) gives evidence that 90 °C is the best temperature to study the characteristics of the system. One can observe that, at 80 °C, the initiation rate and the equilibrium exchange between the growing radical and the dormant species are not sufficiently fast to provide a good polydispersity index.

Experiments were then carried out at 90 °C to study the influence of the initiator concentration on the propagation rate and on the molecular weight: four concentrations were chosen, ranging from 3.7×10^{-3} to 4.4×10^{-2} mol L^{-1}. The plot of the monomer consumption versus time (Figure 4) shows that all data corresponding to the four kinetics experiments are located on one single straight line, which means that the polymerization rate is independent of the concentration of the initiator. This result is totally unexpected because, in a classical kinetic scheme, the polymerization rate (V_p) is proportional to the concentration of the active species ($[P^\bullet]_e$) which can be related to the initiator concentration:

$$V_p = -d[M]/dt = k_p[M][P^\bullet]_e \qquad (1)$$

By considering the equilibrium between the dormant (P−T) and the active species (P•), V_p can be correlated to the concentration of the initiator:

$$P-T \overset{K}{\rightleftharpoons} P^\bullet + T^\bullet$$

where K is the equilibrium constant. Relation (1) becomes

$$V_p = k_p[M]K^{1/2}[P-T]_e^{1/2} \qquad (2)$$

with

$$K = [P^\bullet]_e[T^\bullet]_e/[P-T]_e = [P^\bullet]_e^{2}/[P-T]_e$$

For low values of K, $[P-T]_e \cong [A-T]$, where [A−T] is

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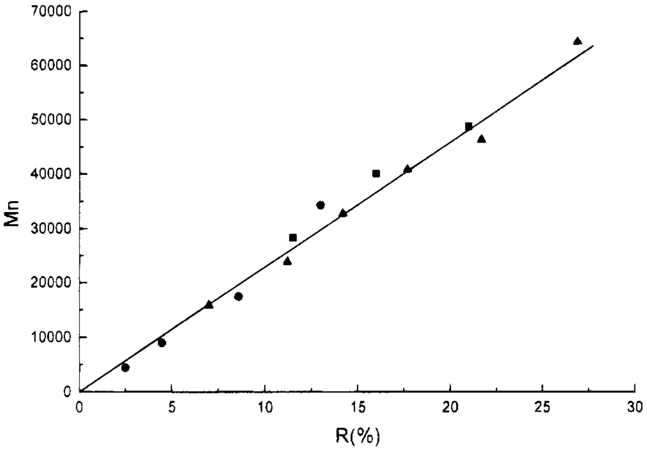

Figure 1. M_n as a function of styrene conversion at different temperatures: (●) 80 °C, (▲) 90 °C, (■) 100 °C with [A−T] = 3.7×10^{-3} mol^{-1}.

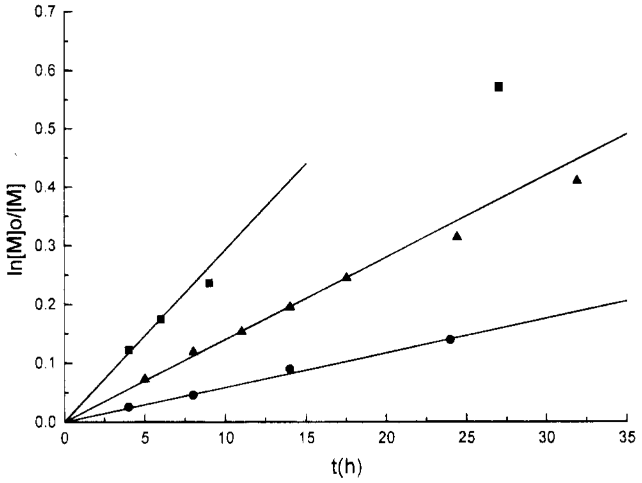

Figure 2. Conversion-time plot for polymerization of styrene in bulk at different temperatures: (●) 80 °C, (▲) 90 °C, (■) 100 °C with [A−T] = 3.7×10^{-3} mol L^{-1}.

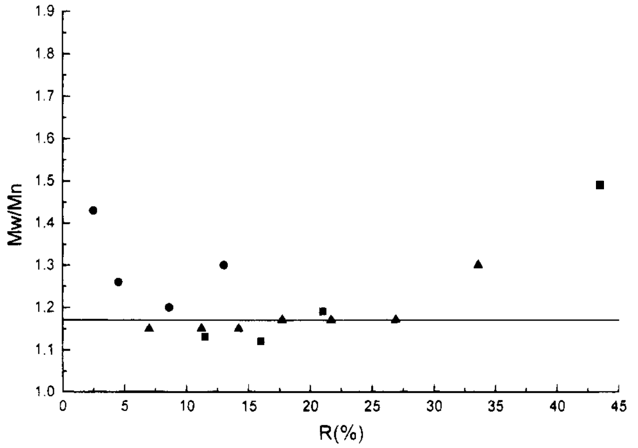

Figure 3. Polydispersity index as a function of styrene conversion at different temperatures: (●) 80 °C, (▲) 90 °C, (■) 100 °C with [A−T] = 3.7×10^{-3} mol L^{-1}.

the initiator concentration

$$V_p = k_p[M]K^{1/2}[A-T]^{1/2} \qquad (3)$$

or

$$\ln([M]_0/[M]) = k_pK^{1/2}[A-T]^{1/2}t$$

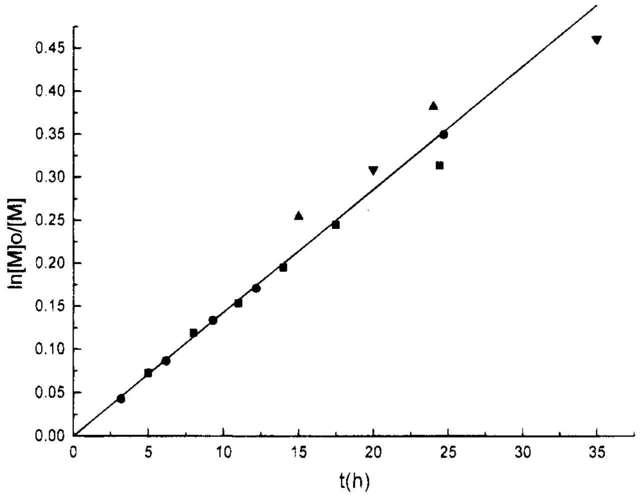

Figure 4. Conversion-time plot for polymerization of styrene in bulk, at 90 °C, with different initiator concentrations: (■) 3.7×10^{-3} mol L^{-1}, (●) 7.4×10^{-3} mol L^{-1}, (▲) 2.2×10^{-2} mol L^{-1}, (▼) 4.4×10^{-2} mol L^{-1}.

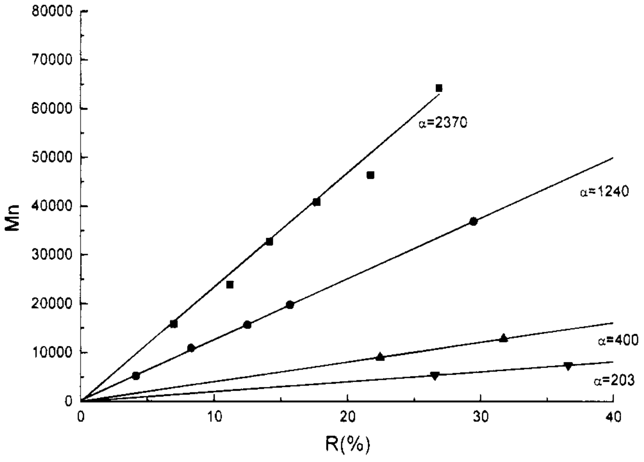

Figure 5. M_n as a function of styrene conversion polymerized at 90 °C, in bulk with different initiator concentrations: (■) 3.7×10^{-3} mol L^{-1}, (●) 7.4×10^{-3} mol L^{-1}, (▲) 2.2×10^{-2} mol L^{-1}, (▼) 4.4×10^{-2} mol L^{-1}.

Should the classical scheme apply to our case, four straight lines should be obtained with slopes proportional to the square root of the initiator concentration: the polymerization rate should represent a 3.4 factor between the lower (3.7×10^{-3} mol L^{-1}) and the higher (4.4×10^{-2} mol L^{-1}) concentration. In fact, the polymerization rate is independent of the concentration of the initiator. However, each molecule of initiator provides one macromolecule. This is evidenced by the comparison of the calculated and experimental slopes (α) for the different straight lines obtained for the molecular weight−yield plot (Figure 5). This has been done by using relation (4):

$$M_n = ([M]_0 - [M])m/[A-T] = Rm[M]_0/(100 \times [A-T])$$

where m is the molar mass of styrene and R is percentage yield.

$$\alpha = m[M]_0/100[A-T] \qquad (4)$$

The data in Table 1 exhibit a very good agreement between α_{calc} and α_{exp}. The concentration of the active sites can also be calculated from relation (4). By taking

Table 1. Calculated and Experimental Slopes of the M_n–Conversion Plots Corresponding to the Polymerization of Styrene in Bulk, at 90 °C, with Different Initiator Concentrations

[A-T] (mol L^{-1})	α_{calc}	α_{exp}
3.7×10^{-3}	2459	2370
7.4×10^{-3}	1230	1240
2.2×10^{-2}	413	400
4.4×10^{-2}	207	203

the k_p value of styrene[12] at 90 °C to be equal to 9581 L mol^{-1} s^{-1} and the concentration of styrene $[M]_0 = 8.75$ mol L^{-1}, the equilibrium concentration in radical is $[P^\circ] \cong 5 \times 10^{-9}$ mol L^{-1}, i.e. much smaller than the concentration of A–T used.

How could such a behavior be explained? One possible explanation of this phenomena is to consider an association of the dormant species with a high degree of association (n) such as

$$(P-T)_n \rightleftharpoons nP-T$$

with

$$K' = [P-T]_e^{\,n}/[(P-T)_n]_e$$

where K' is the equilibrium constant. In this case,

$$[P-T]_e = (K')^{1/n}[(P-T)_n]_e^{\,1/n} = (K')^{1/n}[A-T]^{1/n}$$

and relation (2) becomes

$$V_p = k_p[M]K^{1/2}(K')^{1/2n}[A-T]^{1/2n} \qquad (5)$$

A high degree of association (higher than 10) could explain that a 12-fold variation of initiator concentration leads to a practically constant value of the concentration of the active sites. However, the low polydispersity observed implies that very fast exchanges still exist between all the species concerned: aggregates and dormant and active species.

References and Notes

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(8) The initiator (A–T) was obtained in THF by reacting, under argon, (1-bromoethyl)benzene with the sodium salt of di-*tert*-butylnitroxyl. After filtration of the sodium bromide that formed and evaporation of the solvent, the compound (A–T) was isolated by elution on a silica column (30% yield). ^1H NMR: δ 1.09 (s, 9H, CH_3), 1.34 (s, 9H, CH_3), 1.47 (d, 3H, CH_3), 4.84 (q, 1H, CH), 7.29 (m, 5H, Ar). Elemental analysis: found, C, 77.2%; H, 10.8%; O, 6.2%; N, 5.5%; calculated, C, 77.1%, H, 10.8%; O, 6.4%; N, 5.6%.

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(10) In a typical experiment six tubes were prepared from a styrene solution containing 3.7×10^{-3} mol L^{-1} of the initiator A–T. The precise amount of solution was determined by weighing. In a similar manner six tubes were also prepared with only styrene. After degassing, all the tubes were sealed under vacuum and placed in a heating bath. At given times, two tubes (a blank and its corresponding reactive solution) were taken out and cooled to room temperature. After evaporation of the unreacted styrene, the resulting products were dissolved in benzene, freeze-dried, and their weights determined. The amount of styrene consumed was then calculated from the weight difference.

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