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Kinetic Studies of the Polymerization of *p-tert*-Butylstyrene and Its Block Copolymerization with Styrene through Living Radical Polymerization Mediated by a Nitroxide Compound

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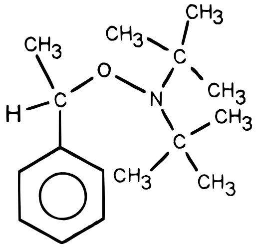
Introduction. The recent development in radical polymerization of a new concept[1] based on a thermal reversible termination of the growing species by stable nitroxide radicals (SNR) led different laboratories to focus their research on the synthesis of well-defined polymers,[2] random copolymers,[3] random grafted copolymers,[4] dendrimers,[5] and block copolymers[6] by this process. Currently, most studies are relative to free radical polymerization using TEMPO, or a substituted TEMPO, as the stable counter radical. However, the bond formed between the polymer radical and these nitroxides becomes labile around 120 °C. This high temperature favors thermal polymerization but also side reactions, such as transfer or termination by dismutation between the growing chain and the stable radical. To minimize these reactions, we have studied in our laboratory[7] a more hindered radical, namely di-*tert*-butyl nitroxide. It allows free radical polymerization of styrene at 90 °C with complete control of the molecular weight and monomer consumption. This study was achieved by carrying out the polymerization of styrene in the presence of an alkoxyamine with the same chemical structure as that of the corresponding dormant species:



(A-T)

It was then interesting to check whether this process could be extended to substituted styrene monomers and to their block copolymerization. For these reasons, kinetic studies were carried out on the homopolymerization of *p-tert*-butylstyrene monomer and on its block copolymerization with styrene. This monomer was chosen to examine the effect of the electron-donating substituent on the kinetic parameters due to a modification of the bond strength between the macroradical and the di-*tert*-butyl nitroxide.

Results and Discussion. Polymerization of *p-tert*-butylstyrene. Experimentally, several tubes, containing *p-tert*-butylstyrene[8] and A-T were degassed and sealed under vacuum before being submitted to heat (90 °C) for given times. The corresponding polymers were isolated by precipitation and the conversion yields calculated from the weight of the samples obtained. We controlled that no low molecular weight polymer was dissolved in the nonsolvent. The molecular weight and the polydispersity of the polymers obtained were determined by gel permeation chromatography using a device equipped with a light scattering detector. A poly(*p-tert*-butylstyrene) calibration curve was established.

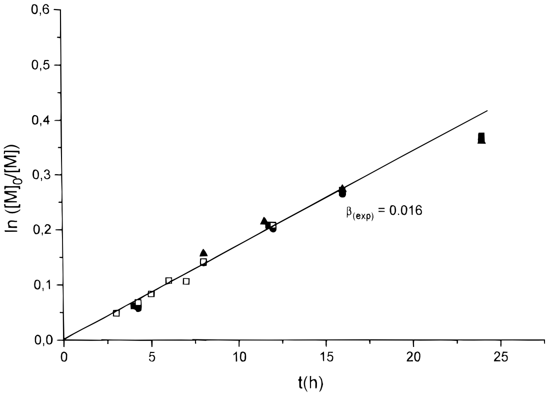


Figure 1. Conversion−time plot for polymerization of *p-tert*-butylstyrene in bulk at 90 °C, with different A-T concentrations: (□) control; (■) 2.45 × 10^{-3} mol·L^{-1}; (●) 4.0 × 10^{-3} mol·L^{-1}; (▲) 8.0 × 10^{-3} mol·L^{-1}.

To study the influence of A-T concentration on the propagation rate and molecular weight, different experiments were carried out with three A-T concentrations: 2.45 × 10^{-3}, 4.0 × 10^{-3}, and 8.0 × 10^{-3} mol·L^{-1}. In Figure 1, it can be observed that all the data fit on one single straight line. The slope of this straight line is equal to k_p[P°], k_p being the propagation rate constant of *p-tert*-butylstyrene at 90 °C and [P°] the concentration of active species. It implies that the concentration of active species remains constant during the reaction and that the polymerization rate is independent of the A-T concentration. This behavior was first observed during the polymerization of styrene in the presence of di-*tert*-butyl nitroxide as counter radical.[7] An interpretation of this phenomena was proposed by Fukuda[9] and extended to TEMPO-based polymerizations: it was suggested that the constant concentration of active radicals comes from the establishment of a stationary state due to the competition between generation of thermal radicals and termination of the growing chains. It has to be noted that, in our experiments with styrene, the stationary radical concentration due to thermal polymerization is always lower than those observed for A-T-mediated polymerizations. In a previous study,[10] we have shown that the generation of radicals in the medium (through the addition of a radical initiator) controls the rate of polymerization while the amount of the alkoxyamine controls the molecular weight. In the present case, thermal polymerization of *p-tert*-butylstyrene alone (Figure 1) takes place at the same rate as in experiments carried out in the presence of A-T. This observation and the independence of the polymerization rate with [A-T] can be explained by a constant concentration of radicals resulting from the competition between the formation of thermal radicals and the termination reaction between two growing species.

In Figure 1, one can observe that the control yield is limited to 15% soluble polymer and that beyond that a fast precipitation takes place with insoluble network formation (the resulting polymer is insoluble whatever the solvent used). The secondary reaction involved in this reticulation has not been identified. For experiments carried out in the presence of A-T, a coupling reaction of 7% of the growing chains is observed at a 30% monomer conversion.

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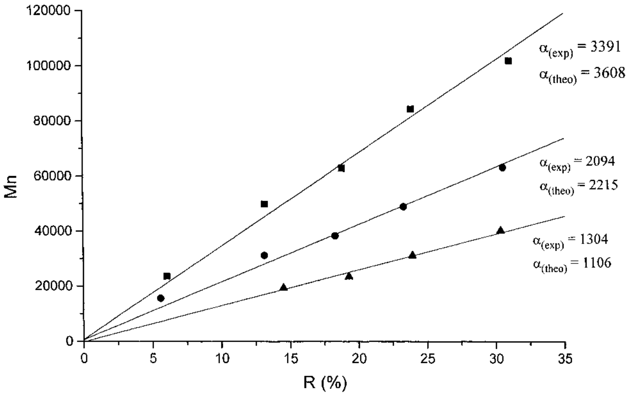

Figure 2. M_n as a function of *p*-*tert*-butylstyrene conversion polymerized at 90 °C, in bulk with different A-T concentrations: (■) 2.45 × 10^{-3} mol·L^{-1}; (●) 4.0 × 10^{-3} mol·L^{-1}; (▲) 8.0 × 10^{-3} mol·L^{-1}.

In Figure 2, the variation of the molecular weight versus yield is represented. For each A-T concentration the molecular weight increases linearly with yield. This indicates that the number of macromolecules formed remains unchanged during the process. A comparison of the theoretical slopes of these straight lines with those of the experimental ones can be done from the following expressions:

$$M_n = ([M]_o - [M])m/[A\text{-}T] = Rm[M]_o/(100[A\text{-}T]) \quad (1)$$

$$M_n = \alpha R$$

with *m* the molar mass of *p*-*tert*-butylstyrene and R the yield in percent

$$\alpha = m[M]_o/(100[A\text{-}T]) \quad (2)$$

The agreement between α_{exp} and α_{theor} (Figure 2) implies that each A-T molecule provides one macromolecule. At the same time, the polydispersity index lies between 1.2 and 1.3.

These results suggest that the same mechanism is involved for styrene and *p*-*tert*-butylstyrene. Consequently, a block copolymer should be achieved by replacing A-T by polystyrene chains bearing a di-*tert*-butyl nitroxide moiety at the chain end (P-T).

Block Copolymer Synthesis: Polystyrene−Poly(*p*-*tert*-butylstyrene). The polystyrene chain (P-T) was prepared at 90 °C, in bulk, according to the procedure described elsewhere.[7] The conversion was limited in order to get a molecular weight close to 40 000. The characteristics of the polystyrene (P-T) were $M_n = 40\,800$ and $M_w/M_n = 1.15$. This polymer was dissolved in benzene (1.1 mol·L^{-1}) containing *p*-*tert*-butylstyrene (2.5 mol·L^{-1}). From this solution and after degassing, four sealed tubes were prepared under vacuum and submitted to heat (90 °C) for given times. The copolymers were isolated by precipitation, and the yield was evaluated from the weight of the dried samples. In a similar way, controls of the *p*-*tert*-butylstyrene solution were evaluated to monitor thermal polymerization. The copolymer molecular weight was determined by GPC coupled with a light scattering detector. The GPC chromatograms of the different samples present no trace of unreacted polystyrene chain even at low conversion. This shows that poly(*p*-*tert*-butylstyrene) chains grow on all the polystyrene chains, and that the initiation is fast compared to propagation. Therefore the polydispersity remains low, i.e., 1.2−1.3.

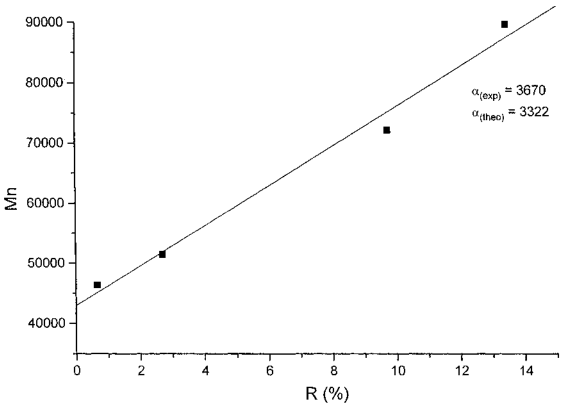

Figure 3. M_n as a function of *p*-*tert*-butylstyrene conversion polymerized at 90 °C, in solution in the presence of polystyrene chains bearing a di-*tert*-butyl nitroxide (P-T).

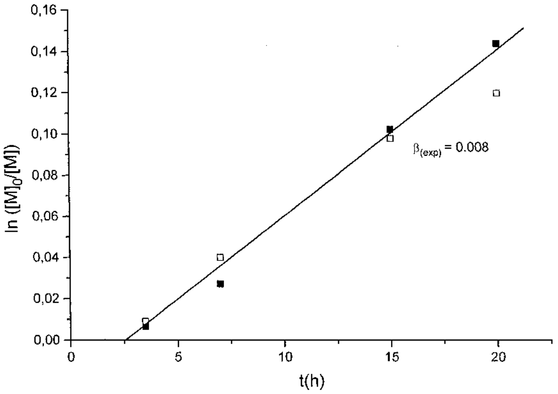

Figure 4. Conversion−time plot for polymerization of *p*-*tert*-butylstyrene in solution, at 90 °C: (□) control; (■) in the presence of polystyrene chains bearing a di-*tert*-butyl nitroxide (P-T).

Table 1. Calculated and Experimental Molecular Weight of Block Copolymers: Polystyrene−Poly (*p*-*tert*-butylstyrene)

R (%)	1.65	2.68	9.70	13.4
M_n (experimental)	46 300	51 500	72 200	89 800
M_n (calculated)	43 200	50 600	77 100	89 500

Since the refractive index of the two blocks is very close, and since the polydispersity in composition remains low, the apparent molecular weight corresponds indeed to the true average molecular weight. This was confirmed by a good agreement between the experimental molecular weight and those calculated from the monomer conversion (Table 1). In Figure 3 one observes a linear increase of M_n versus yield. The intercept of this straight line corresponds to the polystyrene molecular weight. The value of the experimental slope (Figure 3) is similar to the theoretical one; it implies a constant number of growing macromolecules, equal to that of the polystyrene chains.

Concerning the monomer consumption, an inhibition period is observed before polymerization starts (Figure 4). A similar rate of monomer consumption is then obtained for the control and for the solution containing A-T, in accordance with the previous study. The slope of the straight line (β), equal to $k_p[P°]$, is lower than that obtained in bulk (Figure 1). This decrease of the radical concentration ([P°]) cannot be due to a decrease of the A-T concentration since we have shown that $k_p[P°]$ is independent of the alkoxyamine concentration. It has then to stem from a lower rate of thermal radical formation because of a decrease of the monomer concentration. This fact confirms the role of thermal radicals in the mechanism.

In summary, we have shown that the radical polymerization of *p*-*tert*-butylstyrene in the presence of di-*tert*-butyl nitroxide, can be carried out at 90 °C while controlling the molecular weight. As with styrene, the polymerization rate is independent of A-T concentration. This behavior stems from the establishment of a stationary state in active species due to the generation of thermal radicals and to their termination. We have also demonstrated that a well-defined block copolymer can be achieved by replacing the alkoxyamine by a polystyrene chain capped with a di-*tert*-butyl nitroxide.

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