

Living/Controlled Radical Polymerization of Styrene Mediated by Nitroso Compound: Kinetic and ESR Studies

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ABSTRACT: The radical polymerization of styrene in the presence of the nitroso-*tert*-octane have been studied at 90 and 110 °C. From kinetic and ESR experiments it has been established that the process presents the criteria of a living/controlled radical polymerization up to 50% monomer conversion. This has been explained by the initial formation of a nitroxide by addition of a styryl radical on the nitroso compound.

Introduction

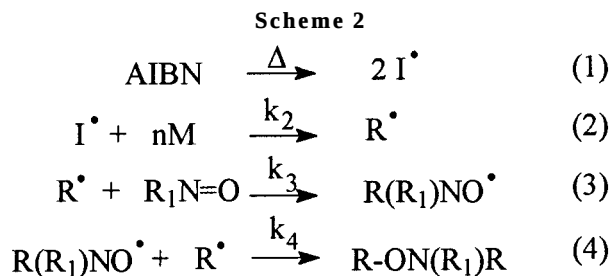
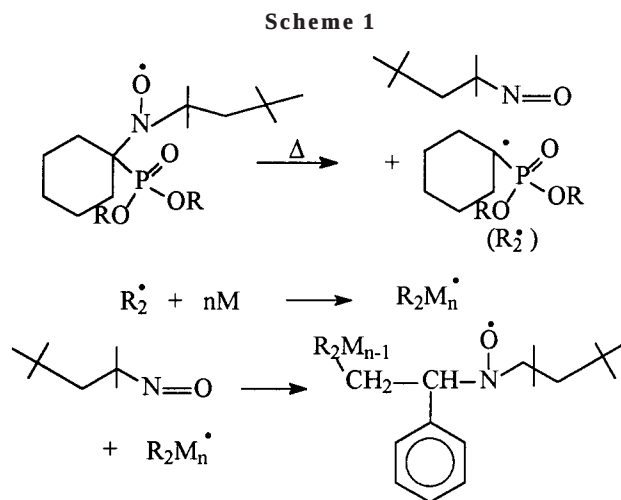
Control of the chain length in radical polymerization mediated by a nitroxide is governed by the equilibrium between active and dormant species. The position of this equilibrium and the rate of exchange of the two species depend on the polymerization temperature. Styrene-based monomers are generally polymerized at a temperature between 90 and 120 °C,¹ with lower temperature requiring modification of the chemical structure of the nitroxide. This can be achieved by changing the bulkiness or/and the chemical nature of the substituents on the nitrogen atom. In the case of styrene monomer, when the nitroxide possesses a phosphonate group in the β -position, the equilibrium is shifted toward active species at 120 °C.² To get a similar behavior at lower temperature, we synthesized β -phosphonylated nitroxides bearing a bulkier *tert*-octyl substituent.³ Kinetic studies carried out at 90 °C on styrene in the presence of these nitroxides have shown that the polymerization is living/controlled. However, ESR experiments established that the counter radical involved in the process was not the starting nitroxide, but a new one with a proton in the β -position formed by a three-step reaction. The first step is a homolytic scission of a C–N bond to form the nitroso-*tert*-octane and an alkyl radical. The second step is initiation of styrene by the alkyl radical, and the last step involves reaction of styryl radicals with the nitroso (Scheme 1).

This result suggests that the radical polymerization of styrene can be controlled by forming in situ the nitroxide counter radical from a nitroso compound introduced in the polymerization medium (Scheme 2). The addition of radicals to nitroso compound has been used to prepare alkoxyamines in living/controlled radical polymerizations.⁴

This report describes kinetic and ESR studies of styrene polymerizations in the presence of nitroso-*tert*-octane and a radical initiator.

Experimental Section

Spectroscopy Measurements. ESR spectra were recorded on a Bruker ESP-300 X-band ESR spectrometer equipped with a HP 53150A frequency meter and a BOONTON microwatt meter. The nitroxide concentration was measured by integration of the ESR spectrum and calibrated with TEMPO in the same medium. These values are accurate within $\pm 15\%$. The molecular weight was determined at room temperature, with



a size exclusion chromatography (SEC) apparatus equipped with a refractometer (Shimadzu) and five columns PL GEL (10 μ m particles) (three mixed B, 10³ Å, 10⁵ Å), using THF as eluant (flow rate: 1 mL/min). UV spectra were recorded on a Shimadzu UV-2101PC spectrometer.

Materials. 2,2'-Azobis(isobutyronitrile) (AIBN, Merck) was used after crystallization in methanol. Styrene (Aldrich) was distilled on calcium hydride before use. Nitroso-*tert*-octane was prepared according to the synthesis described in ref 5.

Polymerization. In a typical experiment 10 tubes were prepared from a styrene solution containing 7×10^{-3} mol L⁻¹ of nitroso-*tert*-octane⁵ and of AIBN. The precise amount of solution was determined by weighing. After degassing, all the tubes were sealed under vacuum and placed in a heating bath. At given times, a tube was taken out and cooled to room temperature. After evaporation of the unreacted styrene, the resulting products were dissolved in benzene and freeze-dried and their weights determined. The amount of styrene consumed was then calculated from the weight difference.

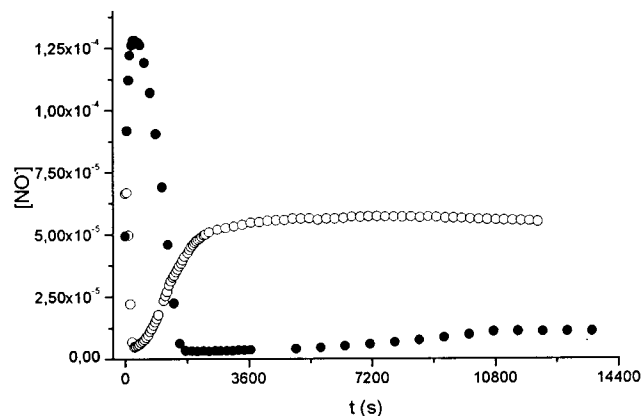


Figure 1. Evolution of the total nitroxide concentration as a function of time in bulk styrene containing nitroso-*tert*-octane and AIBN ($[AIBN] = [\text{nitroso-}tert\text{-octane}] = 7 \times 10^{-3} \text{ mol L}^{-1}$): ●, 90 °C; ○, 110 °C.

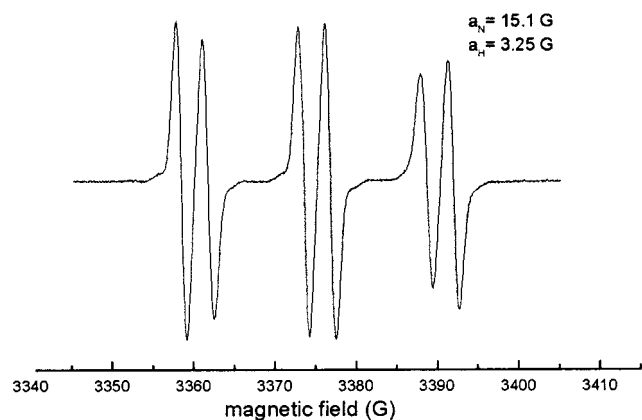


Figure 2. ESR spectrum recorded for nitroxide formed during bulk polymerization of styrene at 90 or 110 °C in the presence of nitroso-*tert*-octane and AIBN ($[AIBN] = [\text{nitroso-}tert\text{-octane}] = 7 \times 10^{-3} \text{ mol L}^{-1}$).

Results and Discussion

An initiator (AIBN) was added to all of the experiments to accelerate production of styryl radicals, which react with the nitroso compound or the resulting nitroxide (Scheme 2). This minimizes the inhibition period, which occurs if only thermally produced radicals are involved in the process. Since the formation of the alkoxyamine needs the reaction of two styryl radicals (Scheme 2), the nitroso-*tert*-octane was mixed with an equimolar amount of initiator in neat styrene. To follow the nitroxide concentration, ESR measurements were performed.

At 90 °C, the nitroxyl radicals formed instantaneously (Figure 1). The ESR signal (Figure 2) presents the characteristics of a nitroxide bearing a proton in β position: $a_H = 3.25 \text{ G}$, $a_N = 15.1 \text{ G}$, $g = 2.005$. These coupling values are identical to those for the radical generated during the decomposition of the β -phosphonylated nitroxide.³ This implies that the nitroxyl radicals formed in the two experiments have the same chemical structure, with the nitrogen atom bearing a styryl unit and a *tert*-octyl group (Scheme 1).

The evolution of the nitroxide concentration with time at 90 °C (Figure 1) displays three main stages. During the first minutes of the reaction, the nitroxide concentration rapidly increases due to the reaction of styryl radicals with nitroso compounds (reaction 3, Scheme 2). The concentration of this radical increases until the rate

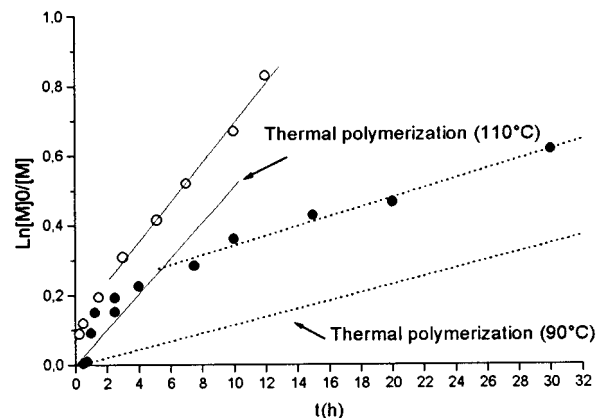


Figure 3. Conversion–time plot for the bulk polymerization of styrene in the presence of nitroso-*tert*-octane and AIBN ($[AIBN] = [\text{nitroso-}tert\text{-octane}] = 7 \times 10^{-3} \text{ mol L}^{-1}$): ●, 90 °C; ○, 110 °C.

of reaction of styryl radicals on the nitroxide (reaction 4, Scheme 2) becomes higher than the rate of reaction of styryl radicals on nitroso. Therefore, the nitroxyl radicals concentration diminishes, but a plateau is reached after 1800 s. Since initiator is still present (40%), the nitroxide concentration has no reason to level off. This stabilization corresponds to the establishment of a stationary state in nitroxide. Its concentration is close to 10^{-6} M (20% accuracy) and depends on reactions 3 and 4 and the dissociation reaction of the alkoxyamine formed (eqs 1 and 2).

$$\frac{d[\text{NO}^*]}{dt} = k_3[\text{R}^*][\text{R}_1\text{N=O}] - k_4[\text{R}^*][\text{R}(\text{R}_1)\text{NO}^*] + k_d[\text{R-ON}(\text{R}_1)\text{R}] \quad (1)$$

$$\frac{d[\text{R}^*]}{dt} = k_2[\text{I}^*][\text{M}] + k_d[\text{R-ON}(\text{R}_1)\text{R}] - k_4[\text{R}^*][\text{R}(\text{R}_1)\text{NO}^*] - k_t[\text{R}^*]^2 - k_3[\text{R}^*][\text{R, N=O}] \quad (2)$$

When the nitroso compound is consumed, the polymerization starts and the concentration of the nitroxide detected results from the equilibrium between active and dormant species: $[\text{NO}^*] = K[\text{RON}(\text{R}_1)\text{R}]/[\text{R}^*]$. This implies that as the initiator concentration slowly decreases, the concentration of persistent radical increases until the thermally generated radicals concentration $[\text{R}^*]$ becomes constant. This behavior can be observed between $t = 3600 \text{ s}$ and $t = 10\,800 \text{ s}$. The nitroxide concentration reaches 10^{-5} M and remains practically constant throughout the process; it decreases by 10% after 32 h.

This general interpretation is confirmed by the evolution of the monomer consumption with time and of the molecular weight with yield.

The plot $\log[M]_0/[M]$ vs time (Figure 3) at 90 °C shows effectively an inhibition period of 1 h corresponding to the trapping of styryl radicals by nitroso and nitroxide species. This period is followed by fast monomer consumption due to the high concentration of active species in the stationary state due to generation of radicals from the initiator. After 2 h, the initiator is totally consumed, and the polymerization rate slowly becomes equivalent to that of thermal polymerization (dotted line, Figure 3). In all the process carried out at 90 °C, the polymerization rate decreases and levels off. This behavior is consistent with a nonexcess of nitroxide in the medium.⁶ The molar mass of the samples obtained during this

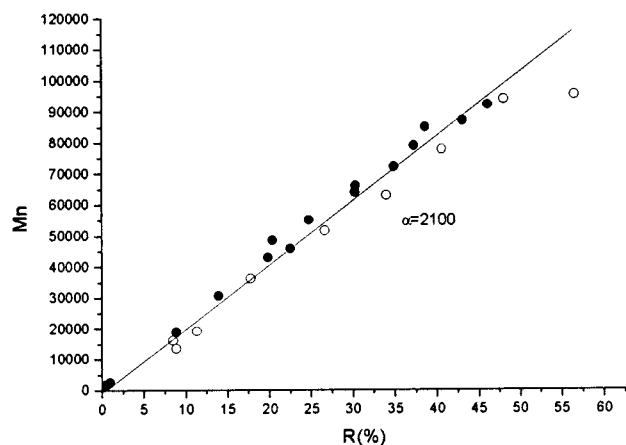


Figure 4. Number-average molecular weight (M_n) as a function of styrene conversion in bulk polymerization in the presence of nitroso-*tert*-octane and AIBN ($[AIBN] = [\text{nitroso-}tert\text{-octane}] = 7 \times 10^{-3} \text{ mol L}^{-1}$): ●, 90 °C; ○, 110 °C.

experiment increases linearly with yield up to 45% conversion (Figure 4).

The slope α is equal to 2100 and can be compared to the theoretical value derived from the following equation: $\alpha = [M]_0 m / [\text{nitroso}]$ (m = molar mass of the monomer). The theoretical value 1300 shows that 40% of nitroso decomposes or leads to a stable compound at 90 °C. The last hypothesis is based on the possibility of the initiator radical reacting with the nitroso compound or the nitroxyl, leading to an alkoxyamine with a nonthermal reversible bond.

To check the effect of temperature on the general process, the same study was performed at 110 °C. As shown in Figure 1, the variation in the nitroxide concentration determined by ESR is different (Figure 1) from that at 90 °C. The main difference is a faster rate of nitroso and nitroxide consumption due to faster decomposition of the initiator. This explains the sharp decrease in the nitroxide concentration and the absence of the first plateau observed at 90 °C (Figure 1). As the concentration of active species diminishes, the nitroxyl radical concentration increases according to the relation $[\text{NO}^\bullet] = K[\text{R-ON}][\text{P}^\bullet]$. It is stabilized when the concentration of the dormant species and active species have reached their equilibrium concentration. The value observed ($[\text{NO}^\bullet] = 6 \times 10^{-5} \text{ M}$) is higher than those obtained at 90 °C stemming from a higher value of the equilibrium constant between dormant and active species. $[\text{P}^\bullet]$ is higher at 110 °C, and $[\text{R-ON}]$ is practically the same in both experiments as will be shown later. All these observations made from ESR data can be perfectly correlated with the following kinetic results. Figure 3 shows that the monomer is rapidly consumed

the first 30 min, corresponding to the time required for the total decomposition of the initiator. After this period, the polymerization rate becomes equal to the thermal one (full line, Figure 3). Concerning the evolution of the molar mass with yield, Figure 4 shows that the chain length increases linearly up to 50% conversion. The experimental slope is similar to that obtained at 90 °C, and its value remains lower than the theoretical one. To check the stability of the nitroso compound, a solution of nitroso in toluene was heated at 110 °C, and the evolution of its absorption at 680 nm was followed with time. The total absorption decreased by 9% in 1 h; hence, this result cannot explain the preceding observation. It seems more probable that the formation of a stable alkoxyamine with the initiator is responsible for the lower number of chains formed. Nevertheless, from these results we have shown that a living controlled polymerization of styrene up to 50% conversion can be observed by introduction of a nitroso compound in a classical radical medium.

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