Synthesis of a New Stable β -Sulfinyl Nitroxide and the Corresponding Alkoxyamine for Living/Controlled Radical Polymerization of Styrene: Kinetic and ESR Studies

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ABSTRACT: The syntheses of a new nitroxide bearing a sulfoxide group at the β -position (with respect to nitrogen) and the corresponding N- β -sulfinyl alkoxyamine are reported. Styrene was polymerized in bulk in the presence of this new alkoxyamine. The polymerization satisfies the usual criteria of a living/ controlled radical polymerization, with a linear increase of molecular weight vs yield and a constant transient radical concentration with time. However, the polymerization rates were independent of alkoxyamine concentration but much higher than the thermal polymerization ones: $R_p/R_{th} = 2.6$ at 90 °C, 3.7 at 100 °C, and 3.5 at 110 °C. Kinetic and ESR studies showed that both transient and persistent radical concentrations do not follow the corresponding theoretical evolutions with time but reach stationary states. The different rate constants (k_d and k_c) and corresponding activation energies were estimated, showing that the sulfoxide group has a large effect mainly on the combination reaction, the value of which is unusually low for such system ($k_c \approx 10^5$ L mol⁻¹ s⁻¹).

Introduction

Since original report of Rizzardo and Solomon¹ on the ability of nitroxides to control the radical polymerization of styrene, living/controlled radical polymerizations mediated by nitroxides have been of special interest as an alternative method to synthesize well-defined architectures. During the past 15 years, the mechanism has been studied,^{2,3} and this new synthetic route has been extended to a wide range of monomers.⁴ This process is mainly based on the equilibrium between dormant and active species (Scheme 1).

The dormant species (P-X), in the form of an alkoxyamine, carry a thermoreversible bond which produces, upon heating, a nitroxyl radical (X[•]) and the corresponding alkyl radical (P[•]). These transient alkyl radicals undergo several monomer additions before combining with free nitroxide to regenerate the dormant species. If the equilibrium constant and the product k_dk_c are high enough, cycles between the active and the dormant forms proceed sufficiently fast to ensure a narrow chain distribution.

Because of the instability of nitroxides bearing an α -hydrogen atom, the nitroxides have been restricted to *tert*-alkylated nitroxides such as di-*tert*-butyl nitroxide, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), or TEMPO derivatives.⁵ These compounds allowed the synthesis of well-defined polymers and copolymers of styrene derivatives but were unable to control the polymerization of other vinylic monomers. Moreover, polymerization rate is generally independent of the alkoxyamine concentration⁶ due to the low dissociation rate compared to the rate of thermal radicals generation.⁷ Under these conditions, nitroxide and alkyl radical concentrations soon reach a stationary state and are related by relation 1, with $[P-X]_0$ the initial alkoxyamine concentration.

$$K = k_{\rm d}/k_{\rm c} = [\mathbf{P}^{\bullet}]_{\rm stat}[\mathbf{X}^{\bullet}]_{\rm stat}/[\mathbf{P}-\mathbf{X}]_0 \tag{1}$$

Therefore, new persistent radicals are sought that lead to a high rate constant of dissociation in order to Scheme 1

$$P-X \xrightarrow{k_d} \stackrel{k_p}{\frown} + \cdot X$$

lower the temperature of polymerization and thus to minimize thermal polymerization. One nitroxide that achieves this goal is the *N*-tert-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)) nitroxide (DEPN)^{8,9} synthesized by Tordo et al. with a phosphonylated group at the α -position to the nitrogen atom. This compound leads to a controlled polymerization of styrene at 120 °C and a polymerization rate that depends on the alkoxyamine concentration and remains higher than the rate of thermal polymerization. The basic features of this process and its persistent radical effect were described in detail by Fischer² and Fukuda.³ A power-law analysis predicts the evolution of persistent radical concentration and monomer conversion according to eqs 2 and 3.

$$[\mathbf{X}^{\bullet}] = (3k_{\rm t}K^2[\mathbf{P}-\mathbf{X}]_0^{-2})^{1/3}t^{1/3}$$
(2)

$$\ln([M]_0/[M]) = (3k_p/2)(K[P-X]_0/3k_t)^{1/3}t^{2/3}$$
(3)

The persistent radical concentration should increase following the $t^{1/3}$ dependence, whereas the monomer consumption should have a $t^{2/3}$ dependence and a $[P-X]_0^{1/3}$ dependence. This kinetic behavior should be observed if the process is dominated by dissociation of the alkoxyamine. To enhance the homolysis of C–O bond, we synthesized an alkoxyamine bearing a strongly polar sulfoxide group. We used this alkoxyamine in the polymerization of styrene at different temperatures; the results of kinetic and ESR studies are presented in this paper.

Experimental Section

Characterizations. ¹H NMR (CDCl₃, 200 MHz) and ¹³C NMR (CDCl₃, 50 MHz) measurements were performed on a

Bruker AC 200 spectrometer at room temperature. 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 concentrations were determined by integration of the ESR spectra and calibration with a TEMPO solution in benzene. Size exclusion chromatography (SEC) was carried out at room temperature on a Shimadzu 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⁻¹). A calibration curve obtained from polystyrene standards was used to determine the molecular weights.

Materials. Diethyl sulfide (Aldrich, 98%) was oxidized to diethyl sulfoxide using 3-chloroperoxybenzoic acid (Aldrich, 75%) in methylene chloride and then distilled under reduced pressure.¹⁰ *n*-BuLi (1.6 M in hexanes) was purchased from Aldrich. Di-*tert*-butyl peroxalate¹¹ and *tert*-butylhydroxy-lamine¹² were synthesized as described previously. Tetra-hydrofuran (THF) was distilled from sodium benzophenome dianion. Ethylbenzene (Aldrich, 99%) was distilled twice from calcium hydroxide. Styrene (Aldrich, 99%) was distilled twice from calcium hydride prior to use. All other materials were used as received.

N-tert-Butyl-α-*tert*-butyl Nitrone (1). A solution of *tert*butylhydroxylamine (9.98 g, 0.112 mol), trimethylacetaldehyde (13.4 mL, 0.123 mol), and a catalytic amount of *p*-toluenesulfonic acid (PTS) (0.01 g, 0.5 mmol) in ether (100 mL) was stirred for 48 h at room temperature. After evaporation of the solvent, the residue was placed under dynamic vacuum overnight in order to remove excess hydroxylamine by sublimation. After crystallization in pentane 9.1 g of pure nitrone was obtained (52%) as white crystals. ¹H NMR: δ 1.27 (s, (CH₃)₃CCH, 9H), 1.48 (s, (CH₃)₃CN, 9H), 6.57 (s, CH, 1H). ¹³C NMR: δ 26.1 (s, (CH₃)₃CCH, 3C), 28.2 (s, (CH₃)₃CN, 3C), 32.4 (s, (CH₃)₃CN, 1C), 69.6 (s, (CH₃)₃CCH, 1C), 139.7 (s, CH, 1C). Anal. Calcd for C₉H₁₉NO: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.67; H, 11.92; N, 8.73.

N-tert-Butyl-N-(1-tert-butyl-2-ethylsulfinyl)propylhydroxylamine (2). A solution of *N*-tert-butyl-a-tert-butyl nitrone (1.51 g, 9.6 mmol) in THF (45 mL) was added dropwise to a cooled (-78 °C), stirred solution of α -lithiated sulfoxide prepared from n-BuLi (6 mL, 9.6 mmol) and diethyl sulfoxide (1.1 mL, 9.6 mmol) in THF (45 mL) at -20 °C. The mixture was stirred for 4 h at -78 °C and quenched with a saturated solution of ammonium chloride (20 ${\rm mL}$). The mixture was then allowed to warm to room temperature and extracted twice with dichloromethane (2 \times 40 mL). The combined organic layers were washed with water, dried over magnesium sulfate, filtered, and evaporated to give 1.67 g of crude hydroxylamine (66%) which was used without further purification in the oxidation step. ¹H NMR: δ 1.10 (s, (CH₃)₃CCH, 9H), 1.19 (s, $(CH_3)_3CN$, 9Ĥ), 1.37 (t, J = 7.5 Hz, CH_3CH_2SO , 3H), 1.43 (d, J = 7.5 Hz, CH₃CHSO, 3H), 2.53 (m, CH₃CHHSO, 1H), 2.88 (m, CH₃CHHSO, 1H), 3.53 (s, (CH₃)₃CCHN, 1H), 3.60 (q, J =7.5 Hz, CH₃CHSO, 1H), 4.82 (s, NOH, 1H).

N-tert-Butyl-*N*-(1-*tert*-butyl-2-ethylsulfinyl)propyl Nitroxide (3). A solution of hydroxylamine 2 (1.67 g, 6.4 mmol) and copper(II) acetate monohydrate (0.02 g, 0.1 mmol) in methanol (50 mL) was stirred at room temperature under O₂ (optional) for 2 h. The solvent was evaporated without heating, and the pure nitroxide was separated by column chromatography on silica gel eluting with a 1:9 cyclohexane/ethyl acetate mixture ($R_r = 0.2$). After evaporation of the solvents, 0.82 g of pure nitroxide was obtained (49%) as a red liquid and stored at -20 °C. ESR (benzene) triplet, $a_N = 14.7$ G, g = 2.0064. Anal. Calcd for C₁₃H₂₈NO₂S: C, 59.50; H, 10.75; N, 5.34. Found: C, 59.75; H, 10.86; N, 5.18.

2-Phenyl-2-(*N***-tert-butyl-***N***-(1-tert-butyl-2-ethylsulfinyl)propyl nitroxide)ethane (4).** A solution of nitroxide **3** (1.60 g, 6.09 mmol) and di-*tert*-butyl peroxalate (2.86 g, 12.2 mmol, explosive when scratching crystals!) in ethylbenzene (15 mL) was stirred at 35 °C under argon for 15 h. Excess ethylbenzene was removed under vacuum, and the residue was chromatographed on silica gel eluting with a 7:3 cyclohexane/ethyl acetate mixture ($R_f = 0.4$). After evaporation of the solvents, 663 mg of pure alkoxyamine was obtained (28%) as a colorless oil. ¹H NMR: δ 0.92, 1.16 (2s, (CH₃)₃CCH, 9H), 1.21, 1.27 (2s, (CH₃)₃CN, 9H), 1.31-1.58 (m, CH₃CH₂SO, CH₃CHSO, CH₃-CHO, 9H), 2.30-3.05 (m, CH₃CH₂SO, 2H), 3.76-3.97 (m, CH₃CHSO, (CH₃)₃CCHN, 2H), 5.00 (dq, CH₃CHO, 1H), 7.15-7.40 (m, aromatics, 5H). ¹³C NMR: δ 8.6 (s, CH₃CH₂SO, 1C), 13.0, 13.9 (2s, CH₃CHSO, 1C), 26.0, 27.9 (2s, (CH₃)₃CCH, 1C), 29.2, 29.8 (2s, (CH₃)₃CCH, 3C), 30.5, 31.1 (2s, (CH₃)₃CN, 3C), 32.0, 84.9 (2s, CH₃CHO, 1C), 36.4, 36.8 (2s,(CH₃)₃CCH, 1C), 46.0 (s, CH₃CHO, 1C), 57.8 (s, (CH₃)₃CN, 1C), 62.3 (s, CH₃CH₂-SO, 1C), 62.9 (s, CH₃CHSO, 1C), 127.2 (s, m-aromatics, 2C), 127.6, 128.1 (2s, p-aromatic, 1C), 128.8, 129.1 (2s, o-aromatics, 2C), 144.7, 147.4 (2s, CCHO, 1C). Anal. Calcd for C₂₁H₃₇-NO₂S: C, 68.61; H, 10.15; N, 3.81. Found: C, 68.35; H, 9.95; N, 3.72. HRMS (EI, 70 eV): exact mass calculated for C₂₁H₃₇-NO₂S: [M]⁺ 367.60, found: 367.75.

Typical Polymerization Experiment. A solution of alkoxyamine **4** (0.06 g, 0.16 mmol) in neat styrene (17.66 g, 170 mmol) was distributed among 10 glass tubes. The contents were degassed by freeze–pump–thaw cycles, and the tubes were sealed off under vacuum. One tube was heated to 100 °C for 12 h, and after cooling, the polymerization medium was dissolved in THF. After evaporation of excess monomer and solvent, the polymer was freeze-dried in benzene. Conversion was evaluated gravimetrically; molecular weight and polydispersity index were determined by SEC (yield = 61.8%, M_n = 73100 g mol⁻¹, PDI = 1.23).

Determination of the Rate Constant of Dissociation (k_d) by ESR Spectroscopy. Benzene solutions containing alkoxyamine 4 (0.18×10^{-3} and 0.38×10^{-3} mol L⁻¹) and excess galvinoxyl (1×10^{-3} mol L⁻¹) were degassed and then heated at temperatures between 70 and 100 °C. The release of persistent radicals was monitored by ESR spectroscopy, and their concentrations were estimated from the integration of the first peak of nitroxide **3** spectrum centered at 3360 G.

Results and Discussion

Synthesis of β -Sulfinyl Nitroxide (3) and Corresponding *N*- β -Sulfinylalkoxyamine (4). The new alkoxyamine bearing a sulfoxide function was prepared as outlined in Scheme 2.

The first step involves the synthesis of *N*-tert-butyl- α -tert-butyl nitrone (1) by acid-catalyzed condensation of trimethylacetaldehyde and *tert*-butylhydroxylamine in ether. The nitrone was then submitted to nucleophilic addition of α -lithiated diethyl sulfoxide to yield β -sulfinylhydroxylamine (2). Such compounds have been widely studied since they are easily accessible intermediates for the synthesis of enantiomerically pure amines after reduction of the sulfinyl function.¹³ In the third step, the hydroxylamine function was oxidized to obtain the corresponding β -sulfinyl nitroxide **3**.

A triplet appeared in the ESR spectrum shown in Figure 1, revealing the usual nitrogen coupling ($a_{\rm N} =$ 14.7 G), whereas β -hydrogen coupling $a_{\rm H}$ was not resolved. The absence of hydrogen coupling can be attributed to the steric hindrance introduced by the tertalkyl substituents; the α -hydrogen atom is eclipsed by a bulky tert-butyl group. For a better understanding of polymerization kinetics, the corresponding alkoxyamine 4 was synthesized. The low-temperature initiator di*tert*-butyl peroxalate was used to make the spin trap reaction mild.14 Di-tert-butyl peroxalate decomposes cleanly at 35 °C to give two carbon dioxide molecules and two tert-butoxy radicals. tert-Butoxy radicals abstract a benzylic hydrogen from ethylbenzene to form tert-butyl alcohol and 2-phenylethyl radicals. These radicals can either couple or react with nitroxides to form the alkoxyamine. The final mixture was composed of the alkoxyamine and a nonnegligible amount of side reaction products. The pure alkoxyamine was obtained



Figure 1. ESR spectrum of nitroxide 3 in benzene.



by purification by column chromatography and stored then at -20 °C.

Kinetic and ESR Studies. Bulk polymerization of styrene mediated by alkoxyamine **4** was studied at three temperatures: 90, 100, and 110 °C. To check whether the polymerization satisfies the criteria of a living/ controlled radical polymerization, the molecular weight, yield, and conversion were determined as a function of time. Figure 2 shows that the experimental values of M_n obtained for $[\mathbf{4}] = 8.2 \times 10^{-3}$ mol L⁻¹ fall on the same theoretical straight line passing through the origin. There is a small deviation at high conversions due to unavoidable termination reactions. This phenomenon is more pronounced at the lower concentration of



Figure 2. Evolution of average molecular weights as a function of conversion for the bulk polymerization of styrene in the presence of alkoxyamine **4**: (lines) theoretical values; (**A**) 110 °C; (**O**) 100 °C; (**I**, \Box) 90 °C; (**A**, **O**, **I**) [**4**] = 8.2 × 10⁻³ mol L⁻¹; (\Box) [**4**] = 4.0 × 10⁻³ mol L⁻¹.



Figure 3. Evolution of polydispersity indexes (PDI = M_w/M_n) as a function of conversion for the bulk polymerization of styrene in the presence of alkoxyamine **4**: (\blacktriangle) 110 °C; (\bigoplus) 100 °C; (\blacksquare , \square) 90 °C; (\blacktriangle , \bigoplus , \blacksquare) [**4**] = 8.2 × 10⁻³ mol L⁻¹; (\square) [**4**] = 4.0 × 10⁻³ mol L⁻¹.

alkoxyamine ([**4**] = 4.0×10^{-3} mol L⁻¹); the fraction of dead chains is therefore higher and leads to higher polydispersity indexes which increase from 1.2 to 1.35 with increasing conversion (Figure 3).

The linear increases of $\ln([M]_0/[M])$ vs time in Figure 4 shows that the concentration of the growing radicals remains constant during all of the experiments. At each temperature, the polymerization rate (R_p) is clearly higher than the thermal polymerization rate (R_{th}) of pure styrene, $R_p/R_{th} = 2.6$ at 90 °C, 3.7 at 100 °C, and 3.5 at 110 °C. This has never been reported for styrene at temperatures below 120 °C. These results suggest that the polymerization rate is not dominated by thermal radicals generated in the medium but mainly by radicals from the alkoxyamine end group of polymer chains. Therefore, the conversion should follow the theoretical relation (3).

The double-logarithmic plot of $\ln([M]_0/[M])$ vs time (Figure 5) confirms that monomer conversion follows a first-order time dependence; the slopes are equal to 1 instead of $^{2}/_{3}$ as suggested by relation 3. This first-order time dependence of monomer conversion associated with high values of the polymerization rates (compared to



Figure 4. Monomer conversion vs time for the bulk polymerization of styrene in the presence of alkoxyamine **4**: (+) thermal polymerizations of neat styrene; (**A**) 110 °C; (**O**) 100 °C; (**D**, \Box) 90 °C; (**A**, **O**, **D**) [**4**] = 8.2 × 10⁻³ mol L⁻¹; (\Box) [**4**] = 4.0 × 10⁻³ mol L⁻¹.



Figure 5. Double-logarithmic plot of conversion as a function of time for the bulk polymerization of styrene in the presence of alkoxyamine **4**: (**A**) 110 °C; (**O**) 100 °C; (**I**, \Box) 90 °C; (**A**, \bullet , **I**) [**4**] = 8.2 × 10⁻³ mol L⁻¹; (\Box) [**4**] = 4.0 × 10⁻³ mol L⁻¹.

the corresponding thermal ones) are generally observed when an additional radical initiator is added in the medium.¹⁵ It implies theoretically that the nitroxide concentration does not depend on the alkoxyamine concentration. To check this hypothesis, we carried out experiments with two different alkoxyamine concentrations (8.2×10^{-3} and 4.0×10^{-3} mol L⁻¹) at 90 °C. Figure 4 shows that the monomer conversion follows the same straight line in both cases; i.e., the polymerization rate is not related to the alkoxyamine concentration. However, no additional initiator was added in our experiments and to better understand this kinetic phenomenon, we followed the persistent radical concentrations by ESR experiments at the three temperatures (Figure 6).

Surprisingly, the evolution of nitroxide concentration does not follow the $^{1}\!/_{3}$ -order time dependence variation described by eq 2. The nitroxide concentration increases rapidly with time and reaches a maximum or a pseudo plateau that depends on temperature; its length varies from 3 h at 100 °C to 10 h or more at 90 °C. Moreover, increasing the alkoxyamine concentration from 4.0 \times 10⁻³ to 8.2 \times 10⁻³ mol L⁻¹ doubles the nitroxide concentration. Coupled with the previous kinetic result,



Figure 6. Variation of nitroxide **3** concentration as a function of time for the bulk polymerization of styrene in the presence of alkoxyamine **4**: (**A**) 110 °C; (**O**) 100 °C; (**I**, \Box) 90 °C; (**A**, **O**, **I**) [**4**] = 8.2 × 10⁻³ mol L⁻¹; (\Box) [**4**] = 4.0 × 10⁻³ mol L⁻¹.



Figure 7. Temperature dependence of the equilibrium constant (*K*) for the bulk polymerization of styrene in the presence of alkoxyamine **4**: (**II**) [**4**] = 8.2×10^{-3} mol L⁻¹; (O) [**4**] = 4.0×10^{-3} mol L⁻¹.

Table 1. Kinetic Parameters for the Bulk Polymerizationof Styrene in the Presence of Alkoxyamine 4 (k_p Valuesfrom Ref 16)

Т (°С)	$k_{\rm p}$ (L mol ⁻¹ s ⁻¹)	[4] (mol L ⁻¹)	K (mol L ⁻¹)	$k_{\rm d} ({ m s}^{-1})$	$k_{\rm c} ({ m L} { m mol}^{-1} { m s}^{-1})$
110	1563	8.2×10^{-3}	$3.3 imes10^{-9}$	2.6×10^{-3}	$7.9 imes10^5$
100	1188	$8.2 imes 10^{-3}$	$1.5 imes 10^{-9}$	$9.9 imes10^{-4}$	$6.6 imes 10^5$
90	890	$8.2 imes 10^{-3}$	$5.2 imes10^{-10}$	$3.6 imes10^{-4}$	$6.9 imes 10^5$
90	890	$4.0 imes 10^{-3}$	5.1×10^{-10}	$3.6 imes 10^{-4}$	$7.1 imes10^5$

this suggests that transient radical and nitroxide reach stationary states in the process, both concentrations being correlated by relation 1. Therefore, the equilibrium constant (*K*) was evaluated at each temperatures from the transient radical concentrations, calculated from the slopes of the plot of $\ln([M]_0/[M])$ vs time and k_p values¹⁶ (Table 1) and the nitroxide concentrations taken at the maximum of the pseudo plateau. From the van't Hoff plot (Figure 7) of the equilibrium constant, the following Arrhenius equation was established:

$$K/\text{mol } L^{-1} = 1.3 \times 10^6 \exp(-107/RT)$$
 (4)

According to eq 4, *K* extrapolates to 8.0×10^{-9} mol L⁻¹ at 120 °C. This value is slightly higher than the one



Figure 8. First-order plot of nitroxide **3** concentration vs time in benzene: $(\bullet, \bigcirc) 100 \,^{\circ}C$; $(\blacktriangle, \triangle) 90 \,^{\circ}C$; $(\diamondsuit, \diamondsuit) 80 \,^{\circ}C$; $(\blacksquare, \square) 70 \,^{\circ}C$; $(\bullet, \blacktriangle, \blacklozenge, \blacksquare) [4] = 0.18 \times 10^{-3} \text{ mol } L^{-1}$; $(\bigcirc, \triangle, \diamondsuit, \square) [4] = 0.38 \times 10^{-3} \text{ mol } L^{-1}$; $[\text{galvinoxyl}] = 1 \times 10^{-3} \text{ mol } L^{-1}$.



Figure 9. Temperature dependence of alkoxyamine **4** rate constant of dissociation (k_d) in benzene: (**1**) $[\mathbf{4}] = 0.18 \times 10^{-3}$ mol L⁻¹; (\bigcirc) $[\mathbf{4}] = 0.38 \times 10^{-3}$ mol L⁻¹; [galvinoxyl] = 1×10^{-3} mol L⁻¹.

determined for styrene polymerization mediated by DEPN⁹ ($K^{120} = 6 \times 10^{-9} \text{ mol L}^{-1}$) and is 40 times higher than that estimated for styrene–TEMPO¹⁷ ($K^{120} = 2 \times 10^{-11} \text{ mol L}^{-1}$). Since the equilibrium constant reflects the competition between the dissociation and combination reactions ($K = k_{\text{d}}/k_{\text{c}}$), it was interesting to determine both rate constants in order to evaluate their respective role in the process.

Determination of Dissociation (k_d) and Combination (k_c) Rate Constants. The rate constant of dissociation (k_d) was evaluated at different temperatures from the Fischer et al.¹⁸ method by determining the nitroxide concentration formed during the thermolysis of an alkoxyamine in the presence of excess galvinoxyl. The galvinoxyl radical traps 2-phenylethyl radicals, thereby suppressing the backward reaction that leads to initial alkoxyamine. We carried out the experiments in benzene solutions of galvinoxyl ($1 \times 10^{-3} \text{ mol L}^{-1}$), at temperatures between 70 and 100 °C for two alkoxyamine concentrations ($0.18 \times 10^{-3} \text{ and } 0.38 \times 10^{-3} \text{ mol L}^{-1}$).

The dissociation rate constant was determined from the slope of the first-order plot of nitroxide concentration evolution vs time (Figure 8) according to relation 5,



Figure 10. Temperature dependence of therate constant of combination (*k*_c) for the bulk polymerization of styrene in the presence of alkoxyamine **4**: (**II**) [**4**] = 8.2×10^{-3} mol L⁻¹; (O) [**4**] = 4.0×10^{-3} mol L⁻¹.

where $[NO^{\bullet}]$ denotes the nitroxide **3** concentration and $[ALK]_0$ the initial alkoxyamine **4** concentration.

$$\ln(([ALK]_0 - [NO^{\bullet}])/[ALK]_0) = -k_d t$$
 (5)

As expected, the alkoxyamine concentration has no effect on the dissociation rate constant values. From the van't Hoff plot represented in Figure 9, the variation of the rate constant of dissociation with temperature was determined (eq 6).

$$k_{\rm d}/{\rm s}^{-1} = 1.6 \times 10^{13} \exp(-116/RT)$$
 (6)

The low value of the frequency factor is in the range found in the literature for various alkoxyamines ($A \approx 10^{13}-10^{15} \text{ s}^{-1}$).¹⁹ The activation energy ($E_a = 116 \text{ kJ} \text{ mol}^{-1}$) is also within the range $110-140 \text{ kJ} \text{ mol}^{-1}$ for alkoxyamines that release 2-phenylethyl radicals.²⁰ From *K* and k_d values (Table 1), the combination rate constant was calculated using relation 1. The van't Hoff plot of k_c , represented in Figure 10, leads to the Arrhenius equation

$$k_c/L \text{ mol}^{-1} \text{ s}^{-1} = 4.0 \times 10^6 \exp(-6/RT)$$
 (7)

The low activation energy is not surprising for this reaction, although the value of k_c (7 × 10⁵ L mol⁻¹ s⁻¹ at 90 °C) is low in comparison to the one obtained for sterically encumbered nitroxides like di-tert-butyl nitroxide $(k_c^{90} = 1.2 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}).^{21}$ For such nitroxides, it is known that rate constants for the homolysis and the reversible coupling reactions show a corresponding dependence on nitroxide structure and mainly in steric factors.²² As the di-tert-butyl alkoxyamine has a k_d slightly higher (2-phenylethyl radical, $k_d^{90} =$ $6.4 \times 10^{-4} \text{ s}^{-1})^{20}$ than the k_{d} of alkoxyamine **4**, it was expected that the k_c values should be of the same order of magnitude. This not observed, and it seems reasonable to relate the strong difference between the k_c values to a better stabilization of the canonical form (2) of the nitroxide 3, by the sulfoxide group (Scheme 3).

Nevertheless, these rate constant values cannot explain why the polymerization rate is independent of the alkoxyamine concentration and higher than the thermal polymerization rate. The theoretical analysis relates this



behavior to radicals generated by a source other than the alkoxyamine; experimentally, this was observed by addition of an initiator in the medium.¹⁵ However, in our experiment no initiator is added; the formation of this "excess" of active species can be related to the mechanism of thermal radicals formation. It was shown, from a study of thermal polymerization of styrene,²³ that the number of primary radicals formed in the medium was higher than the number of radicals engaged in styrene initiation. Our hypothesis is based on the trapping of these intermediate radicals and the formation of alkoxyamines presenting a thermoreversible bond. Another hypothesis can also be suggested; it implies the nitroxide decomposition in active species. This type of reaction occurs with a sterically encumbered phosphonylated nitroxide used in styrene polymerization.²⁴ By an intramolecular homolysis of the C-N bond, a nitrone and an active radical (able to initiate styrene) are formed. If this reaction is applied in our process, it implies that the concentration of these new active species depends on the nitroxide concentration in the stationary state. Therefore, for experiments that double the persistent radicals concentration (Figure 6), an increase of the polymerization rate should have occurred, and this is not observed (Figure 4).

Conclusion

This study shows that introduction of a strong polar group such as sulfoxide, in β -position to an alkoxyamine nitrogen, has a pronounced effect on the dissociation and combination rate constants of the C-O bond. This new alkoxyamine allows the synthesis, at low temperature, of polystyrenes with polydispersity close to 1.2. The polymerization rate was found higher than the thermal polymerization of styrene but independent of alkoxyamine concentration. This particular kinetic phenomenon is currently under study.

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