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Peculiar Behavior of β-Phosphonylated Nitroxides Bearing a *tert*-octyl Group during Living/Controlled Radical Polymerization of Styrene: Kinetics and ESR Studies

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ABSTRACT: Bulk radical polymerization of styrene, in the presence of new nitroxides bearing a *tert*-octyl group and various bulky phosphonate groups in β-position to the nitrogen, is reported. From kinetics studies performed at 90 °C, with or without a radical initiator, it was shown that the polymerization presents the criteria of a living/controlled polymerization. From ESR experiments carried out in the same reaction medium, it was established that the counter radical involved in the process is a new nitroxide presenting a proton in β-position to the nitrogen. This behavior is related to the steric hindrance of the *tert*-octyl group that leads to the formation of the corresponding nitroso, able to react with the styryl radicals. From kinetics and ESR studies, the equilibrium constant for this nitroxide was estimated to be 6×10^{-11} mol L^{-1}.

Introduction

The field of living free radical polymerization mediated by nitroxyl radicals has expanded rapidly during the last years[1] due to the need of well-defined macromolecules. This process is based on the association of a stable counter radical, a nitroxide X°, to the active center P°. These two radicals lead to the formation of an alkoxyamine P−X presenting a thermally reversible bond:

$$\mathrm{P{-}X} \underset{k_c}{\overset{k_d}{\rightleftharpoons}} \mathrm{P}^\bullet + \mathrm{X}^\bullet$$

Most studies have been carried out using 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO).[2] However, with this nitroxide, the equilibrium is established at a temperature close to 120 °C. Under these experimental conditions, thermal polymerization cannot be neglected, and the increase of radical concentration in the stationary state leads to an increase of irreversible termination. To overcome this problem, it was necessary to weaken the strength of the C−O bond of the dormant species. This was achieved by choosing a more hindered counter radical, di-*tert*-butylnitroxide.[3,4] The polymerization of styrene and substituted styrenes[5] in the presence of this nitroxide presents the criteria of a living/controlled radical polymerization around 90 °C. However, the polymerization rate remains controlled by the generation of thermal radicals in the medium. Recently another approach was applied, based on the introduction of a bulky electron withdrawing substituent (a phosphonate group) in β-position to the nitrogen atom.[5] Living/controlled radical polymerization of styrene and acrylates was observed at 123 °C with a polymerization rate higher than for thermal polymerization. To obtain a similar behavior at a lower temperature, we developed the synthesis of new nitroxides bearing a bulky alkyl substituent (*tert*-octyl) and various phosphonate groups. This paper deals with the effect of the nature of the phosphonate substituent toward control of the radical polymerization of styrene (alone or with AIBN) at 90 °C. The same reactions were followed by electron spin resonance (ESR) to evaluate the nitroxide concentration and its behavior vs time.

Experimental Section

Spectroscopy Measurements. IR and UV spectra were recorded on a BOMEM MB 155 and a Shimadzu UV-2101 PC spectrometer, respectively. ^{1}H, ^{31}P, and ^{13}C NMR measurements were performed on a Brucker AC 200 spectrometer at room temperature. ESR spectra were recorded on a Bruker ESP-300 X-band ESR spectrometer equipped with a frequencemeter HP 53150A and a microwattmeter BOOTON. The nitroxide concentration was measured by integration of the ESR spectrum and calibrated with TEMPO in the same medium. Molecular weight determination was done with a size exclusion chromatography (SEC) apparatus equipped with a refractometer (Shimadzu) and five columns (PL GEL, mixte B, 10^3Å, 10^5Å).

Synthesis of New Nitroxides. *N*(Cyclohexyl)-1,1,3,3-tetramethylbutylimine (1). In a flask equipped with a reflux condenser, a Dean Stark condenser, and a stirrer were placed 6.48 g (0.05 mol) of 1,1,3,3-tetramethylbutylamine, 14.74 g (0.15 mol) of cyclohexanone, 100 mg of *p*-toluensulfonic acid, and 40 mL of benzene. The mixture was stirred and heated under reflux for 48 h and water removed azeotropically. At room temperature, the mixture was saturated with solid potassium carbonate and filtered and the solvent evaporated. The crude product was purified by distillation (3 mmHg, 80−85 °C). Yield: 44% of colorless liquid. Anal. Calcd for $C_{14}H_{29}N$: C, 80.30; H, 13.00; N, 6.70. Found: C, 78.97; H, 12.96; N, 6.63. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 1.0 (s, 9H, $C(CH_3)_3$); 1.2 (s, 2H, $C(CH_2)C$); 1.33 (s, 6H, $C(CH_3)_2$); 2.2−2.4 (m, 4H, $CH_2\mathit{CH}_2C$); 1.5−1.8 (m 6H, $CH_2{-}(CH_2)_3{-}CH_2$). ^{13}C NMR (200 MHz, $CDCl_3$), δ (ppm): 170.0 (1C, $(CH_2)_5{-}C{=}N$); 34.45 and 42.64 (2C, $(\mathit{CH}_2)_2C{=}N$); 26.67; 27.80 and 28.64 (3C, $(\mathit{CH}_2){-}(\mathit{CH}_2)_2{-}C{-}N$); 58.93 (1C, $(CH_3)_2\mathit{C} = N$); 31.70 (2C, $(\mathit{CH}_3)_2C{=}N$); 56.10 (1C, $C\text{-}\mathit{CH}_2{-}C$); 32.42 (4C, $\mathit{C}(\mathit{CH}_3)_3$). FTIR spectrum (cm^{-1}): C=N (ν 1660, F).

***N*-[1-(Diethylphosphono)cyclohexyl]-*N*-(1,1,1,3-tetramethylbutyl)amine (2).** A stirred mixture of 6.0 g (0.033 mol) of *N*-(cyclohexyl)1,1,3,3-tetramethylbutylimine (**1**) and 4.2 mL (0.033 mol) of diethyl phosphite was heated at 60 °C for 14 h. The mixture was acidified with diluted hydrochloric acid, and the organic layer was washed with water. The aqueous layer was treated with potassium carbonate (pH > 7) and extracted with diethyl ether. The ethereal layer was finally washed with saturated sodium chloride solution and dried over sodium

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sulfate. Yield: 56% of colorless amine. Anal. Calcd for $C_{18}H_{38}NO_3P$: C, 62.27; H, 10.94; N, 4.03; O, 13.82. Found: C, 61.48; H, 11.06; N, 3.94; O, 13.16. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 0.75 (s, 9H, $C(CH_3)_3$); 1.00 (m, 12H, $(CH_2)_5$, CH_3-CH_2 and $C(CH_3)_2$); 1.24 (s, 2H $C-CH_2-C$); 1.50 (m, 10H, $(CH_2)_5$); 3.80 (quint, $J = 7.26$ Hz, 4H, CH_2-CH_3). ^{13}C NMR (200 MHz, $CDCl_3$), δ (ppm): 58.99 (1C, P-*C*-N), 20.73 and 20.55 (2C, CH_2-C-N); 30.57 and 30.61 (2C, CH_2-CH_2-C-N); 26.20 (1C, $CH_2-(CH_2)_2-C-N$); 57.00 and 57.15 (1C, $(CH_3)_2C$-N); 33.24 and 33.17 (2C, $(CH_3)_2C-N$); 56.22 (1C, C-CH_2-C); 31.92 (1C, $C(CH_3)_3$), 32.20 (3C, $C-(CH_3)_3$); 61.57 and 61.40 (2C, OCH_2-CH_3); 16.55 and 16.66 (2C, OCH_2-CH_3). ^{31}P NMR (200 MHz, reference $H_3PO_4/CDCl_3$), δ (ppm): 31.5. FTIR spectrum (cm^{-1}): POC (ν_a 1060, 1030 two bands, F); P═O (ν 1240, F).

***N*-[1-(Diethylphosphono)cyclohexyl]-*N*-(1,1,1,3-tetramethylbutyl)nitroxide (3).** To a stirred and cold mixture (0 °C) of the amine (**2**) (3.22 g, 0.0093 mol) in 70 mL of dichloromethane was added in small portions 2.61 g (0.015 mol) of *m*-chloroperbenzoic acid. The solution turned orange and then green, and it was stirred for 8 h while a precipitate was formed. After filtration, the organic layer was washed three times with 30 mL of saturated hydrogenocarbonate solution and then three times with distilled water and dried over sodium sulfate. The solution was concentrated under vacuum and the crude product purified by column chromatography (70/30 pentane/ethyl acetate). Yield: 17% as red oil. Anal. Calcd for $C_{18}H_{37}NO_4P$: C, 59.69; H, 10.21; N, 3.87; O, 17.67; P, 8.56. Found: C, 59.19; H, 10.27; N, 3.84. UV (CH_2Cl_2) λ, nm (ϵ in L·mol^{-1}·cm^{-1}): 224.0 (1571), 251.5 (1458), 463.5 (52). FTIR spectrum (cm^{-1}): NO$^\bullet$ (∂ 1326, f−m); POC (ν_a 1020, 1055 two bands, tF); P═O (ν 1245, F). ESR (benzene), a_N, a_P in G (*g* factor): 14.3, 55.3 (2.0070).

***N*-[1-(Diisopropylphosphono)cyclohexyl]-*N*-(1,1,1,3-tetramethylbutyl)amine (4).** This amine was prepared using the same procedure as for amine **2** from 2.0 g (0.0096 mol) of ketimine **1** and 1.65 g (0.0096 mol) of diisopropyl phosphite heated at 45 °C for 24 h. Yield: 42% of colorless oil. Anal. Calcd for $C_{20}H_{42}NO_3P$: C, 64.02; H, 11.19; N, 3.73; O, 12.79; P, 8.26. Found: C, 63.85; H, 11.08; N, 3.53. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 0.93 (s, 9H, $C(CH_3)_3$); 1.10−1.30 (m, 28H, $(CH_2)_5$, $(CH_3)_2-CH$ and $C(CH_3)_2$); 1.43 (s, 2H $C-CH_2-C$); 4.6 (m, 2H, $(CH_3)_2$-CH). ^{13}C NMR (200 MHz, $CDCl_3$), δ (ppm): 59.19 (1C, P−*C*−N), 20.86 and 21.05 (2C, CH_2-C-N); 30.87 and 30.92 (2C, CH_2-CH_2-C-N); 26.56 (1C, CH_2-$(CH_2)_2-C-N$); 57.30 and 57.35 (1C, $(CH_3)_2C-N$); 33.28 and 33.37 (2C, $(CH_3)_2C-N$); 56.35 (1C, C-CH_2-C); 32.24 (1C, $C(CH_3)_3$), 32.53 (3C, $C-(CH_3)_3$); 69.95 and 70.12 (2C, $OCH(CH_3)_2$); 24.35 and 24.65 (4C, $OCH(CH_3)_2$). ^{31}P NMR (200 MHz, reference $H_3PO_4/CDCl_3$), δ (ppm): 29.55. FTIR spectrum (cm^{-1}): POC (ν_a 975, 1000 two bands, F); P═O (ν 1240, F).

***N*-[1-(Diisopropylphosphono)cyclohexyl]-*N*-(1,1,1,3-tetramethylbutyl)nitroxide (5).** This nitroxide was prepared using the same procedure as for nitroxide **3** starting from 0.75 g (0.002 mol) of amine **4** and 0.64 g (0.0037 mol) of *m*-chloroperbenzoic acid in 17 mL of dichloromethane. The solution turned yellow and was stirred 6 h at 0 °C. The product was purified by column chromatography (70/30 pentane/ethyl acetate). Yield: 29% as red crystals. Anal. Calcd for $C_{18}H_{37}NO_4P$: C, 61.56; H, 10.50; N, 3.60; O, 16.40; P, 7.94. Found: C, 60.56; H, 10.38; N, 3.64. UV (CH_2Cl_2) λ, nm (ϵ in L·mol^{-1}·cm^{-1}): 224.0 (1560), 250.0 (1490), 464.0 (12). FTIR spectrum (cm^{-1}): NO$^\bullet$ (∂ 1329, f−m); POC (ν_a 975, 1000 two bands, tF); P═O (ν 1245, F). ESR (benzene), a_N, a_P in G (*g* factor): 14.3, 55.3 (2.0070).

***N*-[1-(Dicyclohexylphosphono)cyclohexyl]-*N*-(1,1,1,3-tetramethylbutyl)nitroxide (6).** The precursor amine of this nitroxide was prepared using the same procedure as for amine **2** from 2.0 g (0.0096 mol) of ketimine **1** and 2.35 g (0.010 mol) of dicyclohexyl phosphite heated at 45 °C for 48 h. After evaporation of the solvent and estimation of the yield (60%) by ^{31}P NMR, 1.55 g of the crude product was dissolved in 30 mL of dichloromethane and 1.45 g (0.0084 mol) of *m*-chloroperbenzoic acid was added in small portions. The solution turned yellow, then green and was stirred for 6 h (0 °C), and a precipitate was formed. After extraction, the product was purified by column chromatography (85/15 pentane/ethyl acetate). Yield: 27% as red crystals. Anal. Calcd for $C_{26}H_{49}NO_4P$: C, 66.40; H, 10.42; N, 2.97; O, 13.61; P, 6.60. Found: C, 65.80; H, 10.52; N, 2.80. UV (CH_2Cl_2) λ, nm (ϵ in L·mol^{-1}·cm^{-1}): 224.0 (2068), 250.0 (1904), 462.5 (77). FTIR spectrum (cm^{-1}): NO$^\bullet$ (∂ 1326, f−m); POC (ν_a 1020, 1055 two bands, tF); P═O (ν 1245, F). ESR (benzene), a_N, a_P in G (*g* factor): 14.2, 55.7 (2.0080).

***N*-[1-(Diethylphosphono)cyclohexyl]-*N*-(1,1-dimethylethyl)amine (8).** A mixture of 60 mL (0.57 mol) of *tert*-butylamine, 18 mL (0.17 mol) of cyclohexanone, and 60 g of molecular sieves was stirred and heated to reflux 38 h. The mixture was concentrated, and the crude ketimine **7** (yield: 85%) was used in the second step without any purification: 2.1 g (0.014 mol) of **7** and 4.0 g (0.029 mol) of diethyl phosphite was heated at 45 °C for 24 h. The mixture was treated as for the synthesis of amine **2**. Yield: 83% of colorless oil. Anal. Calcd for $C_{14}H_{30}NO_3P$: C, 57.75; H, 10.30; N, 4.81; O, 16.48; P, 10.66. Found: C, 57.67; H, 10.33; N, 4.75; O, 16.54. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 1.25 (s, 9H, $C(CH_3)_3$); 1.28−1.36 and 1.72−1.80 (m, 16H, $(CH_2)_5$, and $(CH_3)-CH_2O$); 4.11 (quint, $J = 7.30$ Hz, 4H, CH_2-CH_3). ^{13}C NMR (200 MHz, $CDCl_3$), δ (ppm): 59.08 (1C, P-*C*-N), 20.87 and 21.04 (2C, CH_2-C-N); 32.57 and 32.62 (2C, CH_2-CH_2-C-N); 26.54 (1C, $CH_2-(CH_2)_2-C-N$); 52.80 and 52.86 (1C, $(CH_3)_3C-N$); 33.05 and 33.12 (3C, $(CH_3)_3C-N$); 61.96 and 62.13 (2C, OCH_2-CH_3); 16.94 and 17.05 (2C, OCH_2-CH_3). ^{31}P NMR (200 MHz, ref: $H_3PO_4/CDCl_3$) δ (ppm): 31.01. FTIR spectrum (cm^{-1}): POC (ν_a 1025, 1060 two bands, tF); P═O (ν 1230, F).

***N*-[1-(Diethylphosphono)cyclohexyl]-*N*-(1,1-dimethylethyl)nitroxide (9).** To a stirred and cold (0 °C) mixture of 1.50 g (0.0051 mol) of **8** in 33 mL of dichloromethane, was added, in small portions, 1.87 g (0.0076 mol) of *m*-chloroperbenzoic acid. The solution turned yellow and was stirred for 8 h as a precipitate was formed. After extraction, the product was purified by column chromatography (85/15 dichloromethane/ethyl acetate). Yield: 47% as red crystals. Anal. Calcd for $C_{14}H_{29}NO_4P$: C, 54.92; H, 9.48; N, 4.57; O, 20.90; P, 10.13. Found: C, 54.00; H, 9.62; N, 4.41. UV (CH_2Cl_2) λ, nm (ϵ in L·mol^{-1}·cm^{-1}): 224.5 (2908), 250.0 (3337), 461.0 (12). FTIR spectrum (cm^{-1}): NO$^\bullet$ (∂ 1329, f−m). ESR (benzene), a_N, a_P in G (*g* factor): 14.1, 55.7 (2.0070).

Polymerization. For each nitroxide, a styrene solution was prepared and distributed in several tubes. After degassing, the tubes were sealed under vacuum and placed in a heating bath. At given times a tube was taken out and the corresponding polymer isolated by precipitation. The conversion was calculated from the weight of the sample.

Results and Discussion

Synthesis of β-Phosphonylated Nitroxides. A series of nitroxides bearing *tert*-octyl substituent and phosphonate groups was prepared according to the strategy shown in Scheme 1.

The amine was obtained by addition of a dialkyl phosphite ($HPO(OR)_2$) on the carbon−nitrogen double bond.[6] Various phosphites were used and three different nitroxides were prepared with R as ethyl (**3**), isopropyl (**5**), and cyclohexyl (**6**). The addition of di-*tert*-butyl phosphite on the ketimine failed, due to steric hindrance. For diphenyl phosphite, degradation was observed during the oxidation step due to the acidic conditions. This series was completed by the synthesis of nitroxide **9** bearing a *tert*-butyl group (Scheme 1) and diethylphosphonate group in order to compare the effect of the alkyl substituent on the process.

All these nitroxides were characterized by ESR spectroscopy using a calibration curve based on standard solutions of TEMPO in benzene. From the spectra, two coupling constants, a_N and a_P, were determined. All these constants and the *g* factor are reported in the Experimental Section.

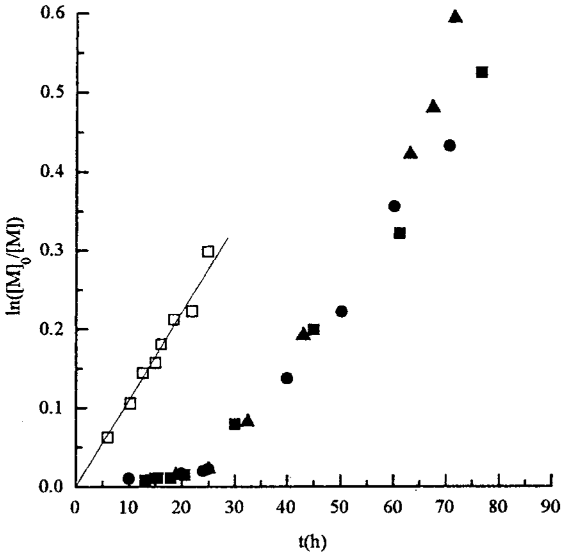
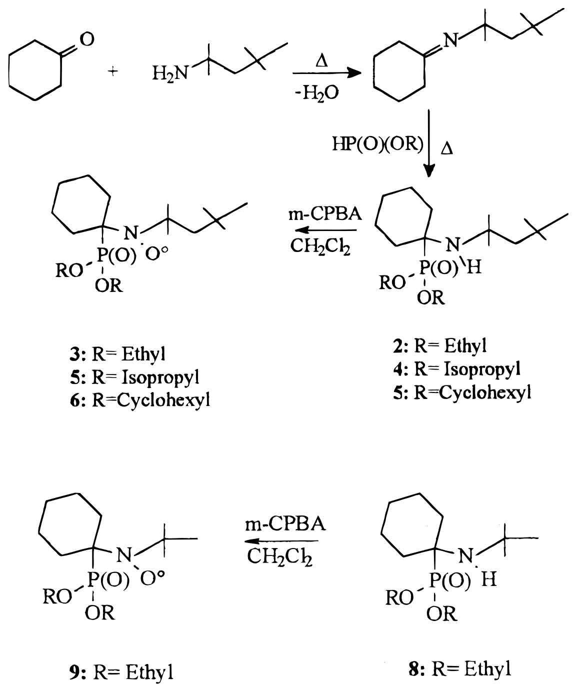


Figure 1. Conversion−time plot for polymerization of styrene in bulk at 90 °C, in the presence of nitroxide: (□) control; (■) [**3**] = 3.70 × 10^{-3} mol L^{-1}; (●) [**5**] = 3.80 × 10^{-3} mol L^{-1}; (▲) [**6**] = 3.30 × 10^{-3} mol L^{-1}.

Scheme 1



3: R= Ethyl
5: R= Isopropyl
6: R=Cyclohexyl

2: R= Ethyl
4: R= Isopropyl
5: R=Cyclohexyl

9: R= Ethyl

8: R= Ethyl

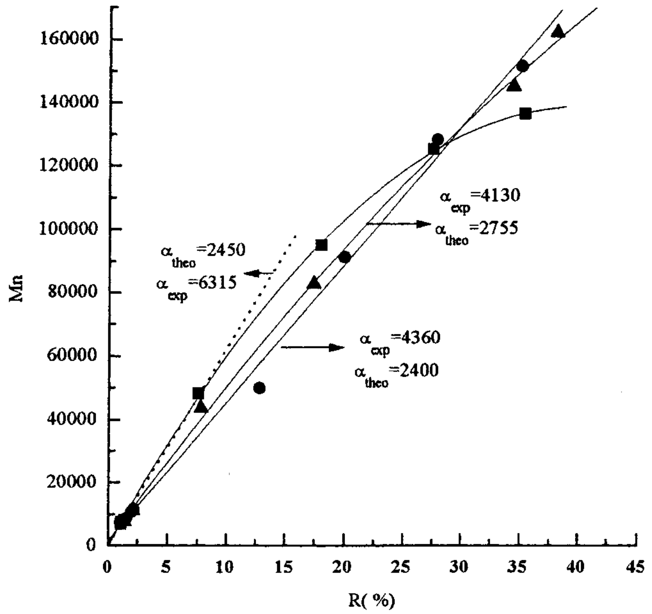


Figure 2. M_n as a function of styrene conversion polymerized in bulk at 90 °C in the presence of nitroxide: (■) [**3**] = 3.70 × 10^{-3} mol L^{-1}; (●) [**5**] = 3.80 × 10^{-3} mol L^{-1}; (▲) [**6**] = 3.30 × 10^{-3} mol L^{-1}.

Polymerization of Styrene. In a first approach, neat styrene was heated at 90 °C, in the presence of a nitroxide (**3**, **5**, or **6**). The examination of the plot $\ln([M]_0/[M])$ vs time (Figure 1) reveals an important inhibition period. This inhibition period corresponds to the time necessary for nitroxyl radicals to react with the thermal radicals. Its duration depends on the rate of thermal radical formation, and also on the nitroxide concentration. At 90 °C, thermal polymerization of styrene is low and the inhibition period extent is then of 30 h. After this induction period, the polymerization of styrene starts and the monomer consumption rate becomes close to that of thermal polymerization. It has to be noted that this behavior is generally observed when an alkoxyamine is directly introduced in the polymerization medium.[3] On the other hand, when the reaction is carried out by direct introduction of a nitroxide, as in our experiments, the styrene polymerization rate is lower than that for thermal polymerization:[8] termination reactions occur between the growing radicals and the hydroxylamine generated as a side product during the inhibition period.[9] This is not observed in the present case, and the phosphorus group on the nitroxyl radical seems to prevent this side reaction.

As can be seen in Figure 2, the evolution of the number-average molecular weight with conversion is not completely linear. The lower values (by 40−50%) of the experimental slopes ($\alpha = M_n/R$), compared to the theoretical ones, show that a large fraction of nitroxide is decomposed during the inhibition period. This implies that the number of chains uncapped by nitroxide is much lower than expected. This lower value of the growing chains concentration (1.5 × 10^{-3} M) permits one to observe a variation of the concentration of the total number of chains with time. As a matter of fact, the total number of chains present in the medium, at a given time, is equal to the sum of the growing chains and of the dead chains (irreversible termination by coupling) formed during the given time. As the number of dead chains increases with time, it becomes less and less negligible in the total sum of chains and monomer consumed is more and more distributed on a higher total number of chains: the average number molecular weight is then lower than expected. This phenomenon explains the small curvature observed for the different plots as well as the large polydispersity of aliquot samples ($M_w/M_n = 1.6$). To reduce this induction period and the related side reactions, polymerizations were carried out with an added radical initiator AIBN ([nitroxide]/[AIBN] = 2).

Under these conditions, the inhibition time is markedly reduced (Figure 3), and the monomer is then consumed with a rate close to or slightly higher than that observed during thermal polymerization. Figure 4 shows that the average number molecular weight increases linearly with yield. However, if the number of chains formed is plotted vs yield (Figure 5) it can be

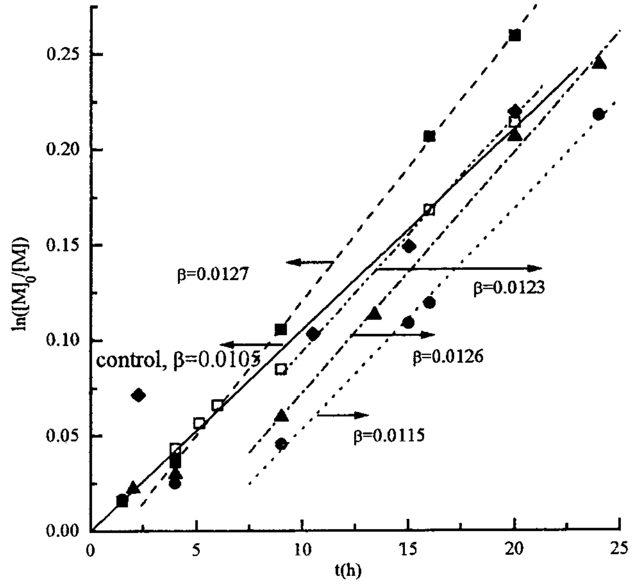


Figure 3. Conversion−time plot for polymerization of styrene in bulk at 90 °C, in the presence of nitroxide and AIBN: (□) control; (■) [**3**] = 3.70 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}; (●) [**5**] = 3.80 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}; (▲) [**6**] = 3.50 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}; (◆) [**9**] = 3.80 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}.

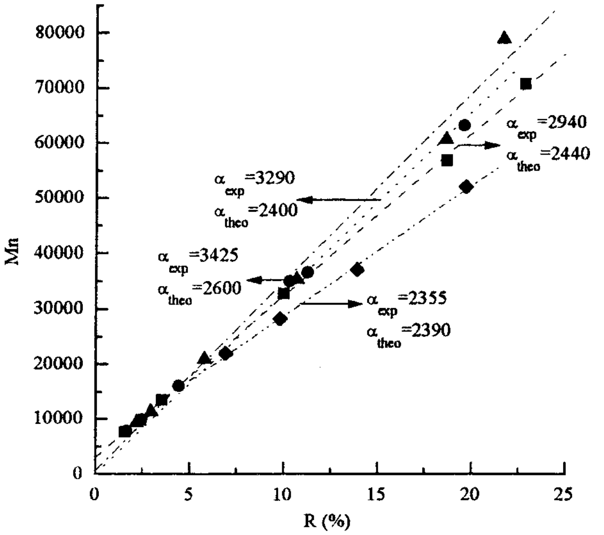


Figure 4. M_n as a function of styrene conversion polymerized in bulk at 90 °C in the presence of nitroxide and AIBN: (□) control; (■) [**3**] = 3.70 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}; (●) [**5**] = 3.80 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}; (▲) [**6**] = 3.50 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}; (◆) [**9**] = 3.80 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}.

observed that it levels off after a 5−10% conversion. Except in the presence of nitroxide **9** (*tert*-butyl group), the value corresponding to the plateau is 15−20% lower that the theoretical one. This difference could be related to the stability of the nitroxides used (**3**, **5**, and **6**) and in order to probe this hypothesis, ESR experiments were carried out on the same reaction medium.

ESR Studies. Electron spin resonance spectroscopy has been previously used to determine concentrations of free TEMPO in living/controlled radical polymerizations.[10] In the present study, all the phosphonylated nitroxides were first characterized in *benzene solution* at 90 °C and then in the polymerization medium. Since all the nitroxides bearing the *tert*-octyl group (**3**, **5**, and **6**) exhibited the same behavior, we only report the data concerning the nitroxyl radical **3** as an example.

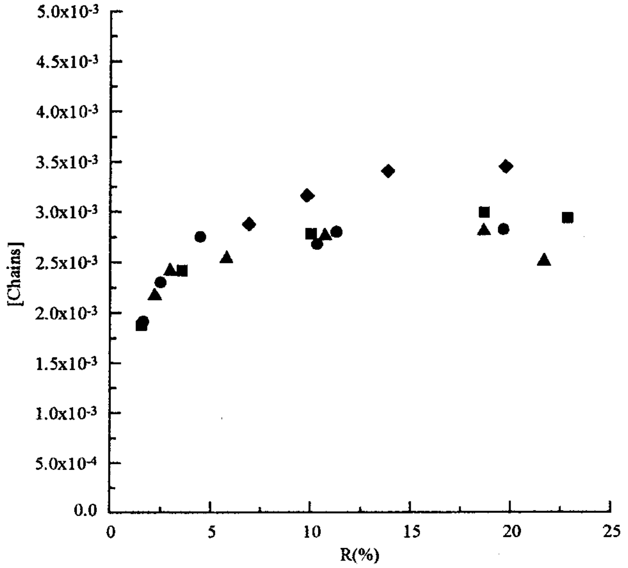


Figure 5. Evolution of chain concentration with monomer conversion: (■) [**3**] = 3.70 × 10^{-3} M; [AIBN] = 1.90 × 10^{-3} mol L^{-1}; (●) [**5**] = 3.80 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}; (▲) [**6**] = 3.50 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}; (◆) [**9**] = 3.80 × 10^{-3} mol L^{-1}; [AIBN] = 1.90 × 10^{-3} mol L^{-1}.

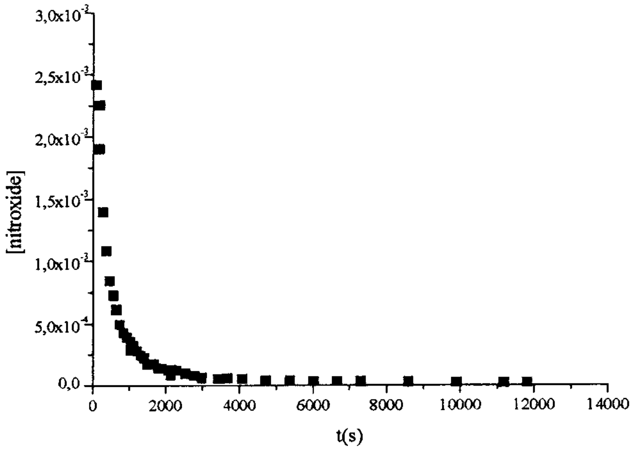


Figure 6. Evolution of the total nitroxide concentration as a function of time in benzene solution at 90 °C: (■) [**3**] = 3.70 × 10^{-3} mol L^{-1}.

In Figure 6, the variation of nitroxide concentration in benzene solution at 90 °C is presented. A degradation of the nitroxide can be observed, and less than 2% of the initial concentration is still present in the medium after 2000 s. On the spectra, the signal of a new nitroxide remains but in very small amount ($<10^{-5}$ M). This new nitroxide does not exhibit any phosphorus coupling constant but only a classical nitrogen coupling: a_N = 15.6 G and g = 2.0070. Its very low concentration shows that it does not constitute the main product issued of the phosphonated nitroxides decomposition.

When the same experiment is conducted in *styrene*, the total nitroxide concentration decreases and stabilizes (Figure 7) at a value of 2 × 10^{-4} M. This occurs in 2000 s and the resulting spectrum indicates clearly that the disappearance of the initial nitroxyl radical is accompanied by the formation of a new one, different

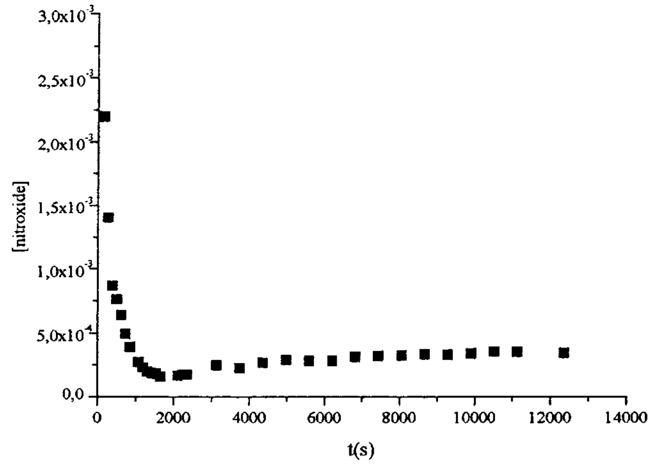


Figure 7. Evolution of the total nitroxide concentration as a function of time, in styrene at 90 °C: (■) [**3**] = 3.70 × 10^{-3} mol L^{-1}.

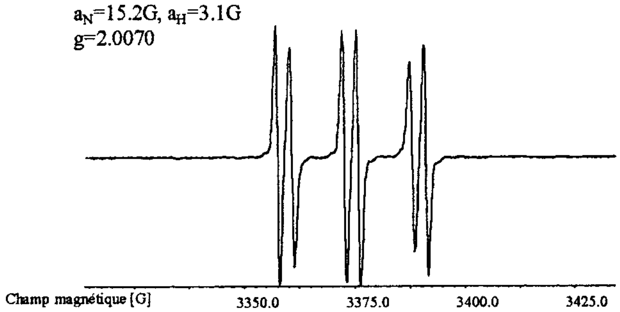


Figure 8. ESR spectrum recorded for nitroxide **3** during the polymerization of styrene in bulk at 90 °C after 3000 s.

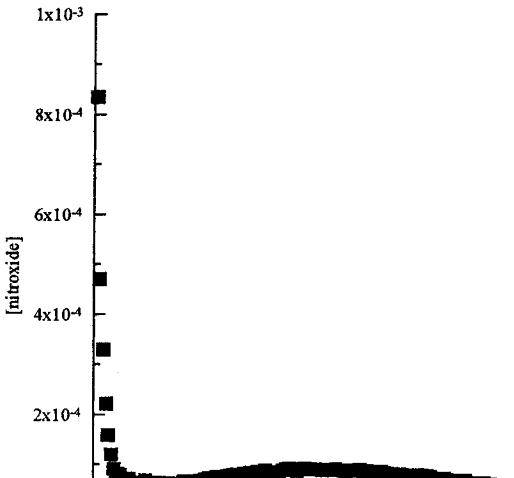


Figure 9. Evolution of the total nitroxide concentration during the polymerization of styrene in bulk at 90 °C: (■) [**3**] = 3.70 × 10^{-3} mol L^{-1}, [AIBN] = 1.90 × 10^{-3} mol L^{-1}.

from that formed in benzene and couplings are observed with the nitrogen and hydrogen atoms (Figure 8, a_N = 15.2 G and a_H = 3.1 G).

The addition of a radical initiator in the medium does not modify deeply the evolution of the nitroxide concentration with time. The signal of nitroxide **3** is also replaced, in 2000 s, by the signal of the new nitroxide described previously. As shown in Figure 9, the total radical concentration decreases with time but stabilizes at a lower concentration (5 × 10^{-5} mol L^{-1}) than the preceding experiment. This stems from the styryl radicals, generated from the initiator, which have reacted with new nitroxides. After this period, the formation of the nitroxide seems to continue since its concentration increases slightly. This is probably due to the reaction of the styryl radicals with the remaining compounds coming from the degradation of the initial nitroxide. This can explain the increase of the number of chains formed during the first events of the polymerization (Figure 5).

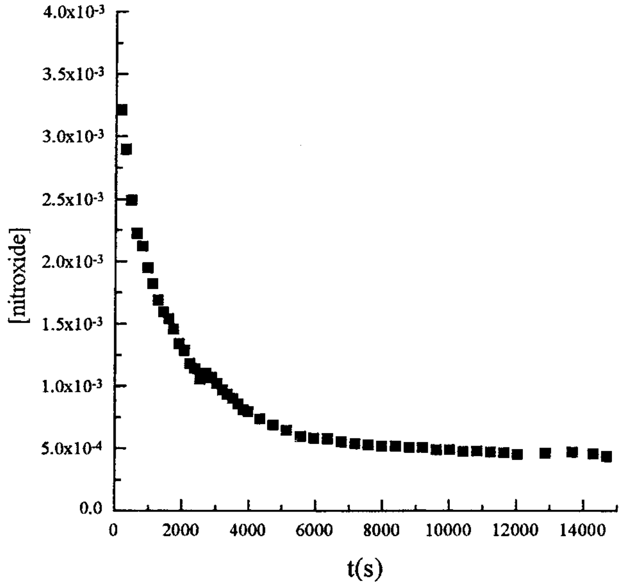


Figure 10. Evolution of the total nitroxide concentration during the polymerization of styrene in bulk at 90 °C with (■) [**9**] = 3.80 × 10^{-3} mol L^{-1}, [AIBN] = 1.90 × 10^{-3} mol L^{-1}.

By considering the graph in Figure 9, the concentration of nitroxide in the stationary state is estimated at 6 × 10^{-5} mol L^{-1}. This permits one to calculate the equilibrium constant K from the formula $K = k_d/k_c = [P^\bullet][N^\bullet]/[P-NOP]$. The concentration of active species is given by the slope of the plot $\ln[M]_0/[M] = f(t)$, $k_p[P^\bullet]$ = 3.3 × 10^{-6} s^{-1} L^2 with k_p = 958 L mol^{-1} s^{-1} $[P^\bullet]$ = 3.4 × 10^{-9} mol L^{-1}. The concentration of dormant species is issued from the plot $M_n = f(R)$, [P−NOP] = 3.1 × 10^{-3} mol L^{-1}. The value of K is 6 × 10^{-11} mol L^{-1} at 90 °C, comparable to that obtained at 120 °C for TEMPO.[11]

All the ESR studies carried out on the phophonated nitroxides (**3**, **5**, **6**) have shown that these nitroxides decomposed differently in benzene medium or in styrene medium. This involves undoubtedly the participation of styrene monomer in the formation of the new radical. On the other hand, it has to be noted that all the phosphonylated nitroxides bearing a *tert*-octyl group present the same behavior, and this suggests that the degradation is not related to the nature of the substituents of the phosphorus atom but, more probably to the alkyl group. Indeed, by changing the *tert*-octyl group to the *tert*-butyl one (nitroxide **9**), a better agreement between theoretical and experimental M_n values has been observed for the kinetic studies. It was then interesting to carry out an ESR study on the polymerization medium containing nitroxide **9**.

As expected, the concentration of the nitroxyl radicals decreases with time (Figure 10) but the rate of disappearance is lower than that observed for the *tert*-octylnitroxides, and more importantly, the spectrum remains identical during all the experiments. Only very small traces (<5% of total signal) of the new nitroxide presenting a hydrogen coupling are detected. It is then obvious that the *tert*-octyl group plays a role in the decomposition of the phophonated nitroxide and to explicit the mechanism involved, some characterization has been carried out on the resulting polymer.

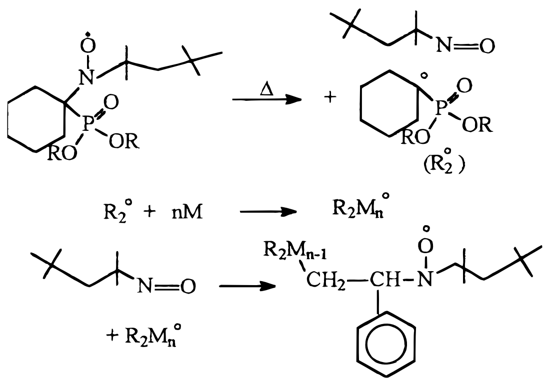
To check the presence of phosphorus on the polymer backbone, quantitative ^{31}P NMR was carried out on a precipitated sample. The phosphorus content shows that the phosphorus group is quantitatively fixed on the polymer. Furthermore, the chemical shift, 33.5−34.0 ppm for the polymer and 31−32 ppm for amine **2**, indicates that the substituents of the alkylphosphonate group have not really changed. From this statement, it was necessary to determinate whether the phosphorus atom was attached to the nitroxide site or/and to the macromolecular chain. To answer this question, we tried to separate, after chemical modification, the polymer and the nitroxide by precipitation. A sample, in benzene solution, was heated at 90 °C for 3 h with butanethiol in large excess.

$$\mathrm{PONR_1R_2} \xrightarrow[\mathrm{RSH}]{\Delta} \mathrm{PH} + \mathrm{HONR_1R}$$

The polymer was isolated, half by freeze-drying and half by precipitation and then analyzed with ^{31}P NMR and SEC. From the NMR analysis, it was observed that 85% of the phosphorus is still present on the precipitated sample. However, no conclusion can be drawn from this result because both SEC curves of freezed-dried and precipitated samples present a tail of low molecular weight oligomers, formed during the thiol treatment, which is not suppressed by precipitation. Nevertheless this last observation implies that the counter radical is not a nitroxide of low molecular weight but a styrene oligomer bearing a nitroxyl radical. This also explains the reason the number-average molecular weights of both samples are practically divided by two: the chemical modification of uncapped macromolecule leads to two molecules: one polystyrene chain (PH) and one oligomeric hydroxylamine. The formation of an oligomeric nitroxide based on styrene permits to give an interpretation to the ESR spectrum: a styryl group is directly attached on the nitrogen atom leading to a coupling with a methylene proton. The coupling constant $a_H = 3.1-3.2$ G is close to that observed for similar molecules.[12]

From these results, a mechanism can be proposed (Scheme 2): the highly sterically hindered nitroxide decomposes, by homolytic cleavage of the C−N bond, into a *tert*-octylnitroso compound and a cyclohexyl radical bearing the phosphonate group. This radical initiates the radical polymerization of styrene before reacting on the *tert*-octylnitroso. The phosphorus atom is still borne by the nitroxide but too far from the radical site to give a coupling detectable by ESR. This statement implies that the nitroxide can be formed in situ by mixing styrene and *ter*-octylnitroso. This reaction is actually under study.

Scheme 2



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