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Unique Behavior of Nitroxide Biradicals in the Controlled Radical Polymerization of Styrene

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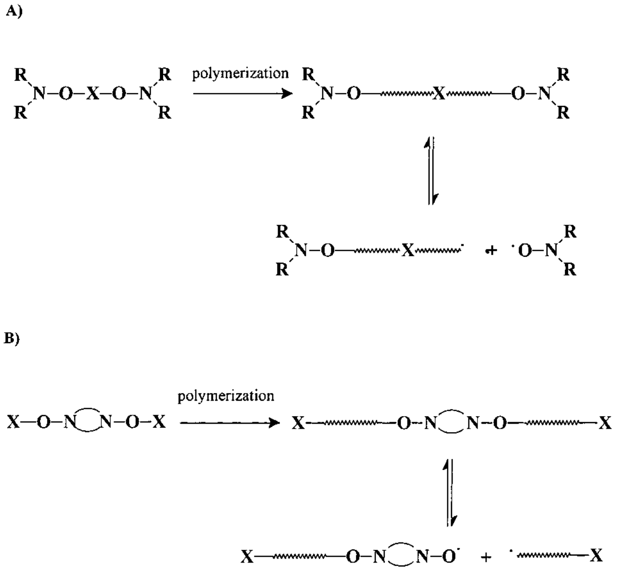
ABSTRACT: The use of various binitroxides, with both radical sites of similar reactivity, as mediator in the controlled radical polymerization of styrene was examined and the rate constants of the reactions involved were determined at 130 °C. Typical features of a controlled radical polymerization were observed in the early stage of the polymerization, leading to the formation of two-arm macromolecules containing the binitroxide at the core. At higher conversion, however, continuous decomposition reaction resulted in a break of the two-arm macromolecules into a dead chain having an unsaturation end group and a living chain capped by a modified binitroxide. The latter had the free nitroxide site inactivated by conversion into hydroxylamine. The extent of this side reaction was much larger than in classical nitroxide-mediated controlled radical polymerization of styrene. This feature was assigned to the structure of the growing chains. As they contain the binitroxide at the core, the activation reaction produces a propagating chain and a nitroxide to which another polymeric chain remains attached by the second alkoxyamine bond. Thus, deactivation of the propagating radical by nitroxide is a bimolecular process between two macromolecular species. This unique situation had no significant effect on the rate constant of the alkoxyamine homolytic dissociation, but more importantly decreased the rate constant of recombination. The latter was 30 times lower than that determined for the recombination of TEMPO with polystyryl radical at 130 °C. The slow recombination was assigned to steric hindrance and resulted in an unusually high concentration of nitroxide in the polymerization medium, together with a large concentration of propagating radicals. A consequence of the high concentration of both radicals was the enhanced rate of hydrogen transfer from the active species to the persistent radical, leading to alkoxyamine bond breaking and, hence, to arm separation.

Introduction

Nitroxide-mediated controlled free-radical polymerization (CRP) is based on an equilibrium between propagating macromolecular radicals and dormant chains that have an alkoxyamine end functionality.[1−4] Providing the nitroxide is carefully selected so as to allow the homolytic cleavage of the NO−C bond under acceptable conditions, polymerization yields well-defined polymers with predictable molar mass and narrow molar mass distribution. The chains formed exhibit an end functionality close to 1 and are able to further grow upon new addition of monomer at the polymerization temperature. Many types of complex architectures have been created, as an additional proof of the "livingness" of the system.[1,5] For this goal, preformed alkoxyamines were used as well-defined mono, bi or multifunctional initiators, leading respectively to single-arm, biarm, or multiarm structures (Scheme 1A). The most studied nitroxide, TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl), provides good control for the polymerization of styrenic monomers at elevated temperatures ($T > 110$ °C).[1] Other cyclic nitroxides have been examined, not behaving differently from TEMPO.[1] A new generation of acyclic nitroxides bearing a hydrogen on the carbon α to the nitroxide function are more efficient at controlling a broader range of monomers at significantly lower temperatures and with faster kinetics.[6,7] Among all the studies in the field, the use of nitroxide biradicals or multiradicals (as previously, we distinguish multiradicals, small molecules containing several nitroxide groups, from polyradicals, polymers made of monoradical mono-

Scheme 1. (A) Alkoxyamine Multifunctional Initiator (R = Alkyl Group; X = Initiator Fragment; ∿∿ = Polymer Chain) and (B) Alkoxyamine Based on a Multifunctional Nitroxide (Multifunctional Coupling Agent)



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mers)[8] as control agents in radical polymerization has never been reported. Such species, and more particularly binitroxides, have long been known[9] and used as spin probes[10] and more recently as magnetic material[11] or spin-labeled spin traps.[12] In addition to their ability to control radical polymerizations, nitroxide multiradicals with sites of similar reactivity can be seen as reversible multifunctional coupling agents. Compared with the usual alkoxyamine multifunctional initiators, these nitroxides and the derived alkoxyamines might offer different synthetic capabilities (Scheme 1). The arms would grow as single chains, independent of the structure and size of the overall macromolecule, preventing star-star coupling via propagating radical terminations. They would exchange from one macromolecule to another, ensuring a narrow molar mass distribution of the final polymer. The resulting multiarm macromolecules would not be thermally stable and therefore able to release the arms under selected conditions. For instance, methacrylic- and styrenic-based monomers with a nitroxide function were used as both comonomers and mediators in the CRP of styrene.[13] The resulting polymeric nitroxide led to branched structures, whose formation is thermally reversible. In contrast, if a nitroxide with very low reactivity to carbon radical existed, combining this inert group with a reactive nitroxide in the same molecule would permit monitoring of the chain growth and end group purity by ESR[12] during the controlled polymerization.

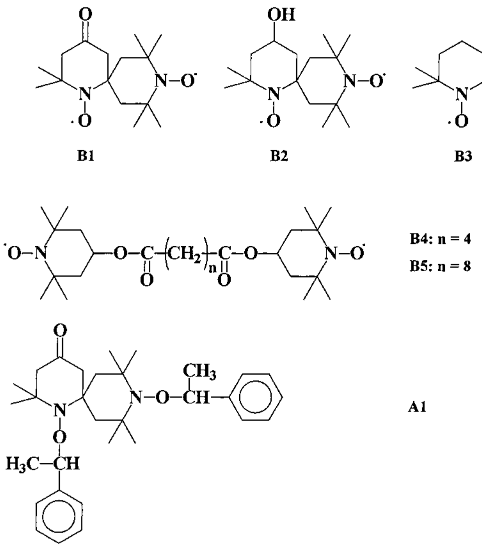
The purpose of this work was to study the behavior of various binitroxides with sites of similar reactivity in the radical polymerization of styrene, and to examine their ability to act as both coupling and control agents.

Experimental Section

Materials. Styrene (S; 99% from Aldrich) was distilled under reduced pressure before use. Benzoyl peroxide (BPO; 97% from Aldrich) was recrystallized at room temperature from a chloroform/methanol mixture. TEMPO (98% from Aldrich) was purified by sublimation. *m*-Chloroperbenzoic acid (*m*CPBA; 77% from Aldrich, remainder 3-chlorobenzoic acid and water) was purified as described.[14] *m*-Xylene (Aldrich) and *tert*-butylbenzene (Aldrich) were stirred three times with 15 vol % of concentrated H_2SO_4 for 30 min; then they were washed twice with H_2O, then with 10% aqueous Na_2CO_3 and finally with H_2O; after drying over Na_2SO_4, they were distilled, and stored over molecular sieves (3 Å).[15] Tetrahydrofuran (THF) was distilled first from potassium hydroxide and then from Na−benzophenone immediately before use. Unless otherwise specified, other materials were purchased from commercial suppliers and used without further purification. Organic solutions were dried over Na_2SO_4 and evaporated using a rotary evaporator. For synthesis of the binitroxides, the sentence "the oxidation was monitored by ESR" means that, after each addition of oxidant, a sample was taken from the reaction mixture and its ESR spectrum was recorded; when the intensity of the radical signal (measured by double integration) reached a plateau, the addition of *m*CPBA was discontinued.

Analytical Techniques. Thin-layer chromatography (TLC) was performed on commercial Merck plates coated with SiO_2 or neutral Al_2O_3 ($60F_{254}$; 0.25 mm thick). Preparative column chromatography was carried out using SiO_2 60 (0.063−0.2 mm) or activated neutral Al_2O_3 III (from Merck). For some samples, preparative chromatography was performed on plates coated with SiO_2 ($60F_{254}$; 2 mm thick) or with neutral Al_2O_3 ($60F_{254}$; 1.5 mm thick). EI (electrical impact) and CI (chemical impact, ammonia) mass spectra were obtained with a Nermag R10-10C spectrometer or a JEOL MS 700 spectrometer. Melting points were measured on a Büchi 535 melting point apparatus. Elemental analyses (C, H, and N) were performed at the Service of Microanalysis, University Pierre and Marie Curie (Paris). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AC spectrometers operating at 200 or 250 MHz for ^1H and 62.9 MHz for ^{13}C, using deuterated chloroform as the solvent and the internal solvent peak as the reference. Size exclusion chromatography (SEC) was carried out using a Waters apparatus working at room temperature with stabilized tetrahydrofuran eluent at a flow rate of 1 $mL \cdot min^{-1}$ and equipped with four PL-gel 10μ columns (100, 500, 10^3, and 10^4 Å). A differential refractive index detector was used and molar masses were derived from a calibration curve based on polystyrene standards. The concentration of chains in the polymerization medium was calculated according to the following formula

Scheme 2. Nitroxide Biradicals B1−B5 and Bisalkoxyamine A1



$$[\text{chains}]\ (\text{mol} \cdot \text{L}^{-1}) = \frac{x d_S}{M_n} \qquad \text{(I)}$$

with d_S = the styrene density (909 $g \cdot L^{-1}$), x = the conversion of monomer and M_n = the number average molar mass ($g \cdot mol^{-1}$).

Electron spin resonance (ESR) spectra were recorded on a Bruker ESR300 spectrometer operated in continuous wave (CV) mode with a TE_{102} rectangular cavity. The modulation amplitude was kept constant at 1 G, while the microwave power was held at 10 mW. For the ESR studies at 130 °C, the tube was heated in an oil bath and then cooled by cold water and analyzed at room temperature in the cavity of the spectrometer. The relative concentration of nitroxide radicals was measured by double integration of the ESR spectrum. The number of spin **s** in the solution (absolute radical concentration) was calculated by comparing the spectrum of a solution of sublimed TEMPO of known concentration, recorded under strictly the same experimental conditions. Under these conditions, traces of residual biradical, although not visually apparent in the spectrum,[12] would contribute to this number of spin.

Synthesis of the Nitroxide Biradicals and of the Bisalkoxyamine (Scheme 2). 1,9-Dioxy-2,2,8,8,10,10-hexamethyl-1,9-diazaspiro[5.5]undecane-4-one (B1) was prepared as described, from the diaminoketone 2,2,8,8,10,10-hexamethyl-1,9-diazaspiro[5.5]undecane-4-one (**1**).[16] R_f = 0.75 (Al_2O_3, Et_2O); MS (EI) *m/z* 282 (M), 267 (M − CH_3), 237 (M − $3CH_3$), 222 (M − $4CH_3$); mp 112.5−114 °C (lit.:[16] 111−113 °C). Anal. Calcd for $C_{15}H_{26}N_2O_3$ (282.4): C, 63.80; H, 9.28; N, 9.92. Found: C, 63.77; H, 9.30; N, 9.80. ESR: a single broad line (27 G) at room temperature in Et_2O (*M*/1000).

1,9-Dioxy 2,2,8,8,10, 10-hexamethyl-1,9-diazaspiro[5.5]-undecan-4-ol (B2). A solution of the diaminoketone **1** (1.54

g, 6.1 mmol) in anhydrous THF (75 mL) was added dropwise to a solution of $LiAlH_4$ (465 mg, 12.2 mmol) in anhydrous THF (110 mL). After the mixture was stirred at room temperature for 4 h, H_2O (0.45 mL), 15% aqueous NaOH (0.45 mL), and H_2O (1.35 mL) were successively added dropwise while stirring. The resulting suspension was filtered through Celite, rinsed with a mixture of CH_2Cl_2/MeOH (99/1) and the filtrate was dried and evaporated to give the diaminoalcohol **2** (2,2,8,8,10,10-hexamethyl-1,9-diazaspiro[5.5]undecan-4-ol) (1.45 g, 5.7 mmol) as a yellow solid (93%). ^{13}C NMR (62.9 MHz): δ 28.5, 30.6, 34.1, 34.3, 34.8 (CH_3); 45.7, 48.2, 51.1, 53.3 (CH_2); 50.1, 50.3, 51.5, 54.0 (C); 63.1 (CH). A solution of *m*CPBA (3.01 g, 17.6 mmol) in CH_2Cl_2 (50 mL) in 5 mL fractions was added to a solution of **2** (1.45 g, 5.7 mmol) in CH_2Cl_2 (300 mL). After complete oxidation (monitored by ESR), the solution was treated with aqueous $NaHCO_3$ (5%); the organic phase was separated, dried, and evaporated. The crude product was purified by column chromatography on Al_2O_3, using first Et_2O then Et_2O/MeOH (98/2) as an eluent, to give **B2** (810 mg, 2.9 mmol) as an orange-red solid (50%). $R_f = 0.53$ (Et_2O/MeOH, 98/2); MS (EI) *m*/*z* 284 (M), 269 (M − CH_3), 239 (M − 3 CH_3), 224 (M − 4 CH_3); mp 110.0−111.5 °C. Anal. Calcd for $C_{15}H_{28}N_2O_3$ (284.4): C, 63.35; H, 9.92; N, 9.85. Found: C, 63.31; H, 10.11; N, 9.70. ESR: a single broad line (27 G) at room temperature in Et_2O (*M*/1000).

1,9-Dioxy-2,2,8,8,10,10-hexamethyl-1,9-diazaspiro[5.5]undecane (B3). Hydrazine hydrate (1 mL) was added to a solution of diaminoketone **1** (1.5 g, 6.0 mmol) in diethylene glycol (5 mL) in a flask equipped with a reflux condenser with variable takeoff. The mixture was refluxed for 2 h. After cooling to room temperature, KOH pellets (1.96 g) were added and H_2O distilled off. When the distillation temperature rose above 100 °C, the takeoff was disconnected and the mixture was refluxed for 1.5 h. The mixture was allowed to cool to room temperature, H_2O (5 mL) was added and the reflux condenser replaced by a distillation bridge. Water was distilled off, and the distillate was extracted with Et_2O (3 × 5 mL). The organic phases were combined, dried and evaporated to give crude diamine **3** (2,2,8,8,10,10-hexamethyl-1,9-diazaspiro[5.5]undecane) (460 mg) as a bright yellow liquid. This product was oxidized directly without further purification. A solution of *m*CPBA (250 mg, 1.5 mmol) in CH_2Cl_2 (5 mL) in 0.5 mL fractions was added to a solution of crude diamine **3** (107 mg, 0.5 mmol) in CH_2Cl_2 (20 mL). After complete oxidation (monitored by ESR), the solution was treated with aqueous $NaHCO_3$ (5%). The organic phase was separated, dried, and evaporated. The crude product was purified by chromatography with a SiO_2 plate, using Et_2O/pentane (50/50) as an eluent to give the biradical **B3** (50 mg, 0.18 mmol) as an orange-red solid (13% yield for two steps). $R_f = 0.50$; MS (EI) *m*/*z* 268 (M), 253 (M − CH_3), 237 (M − 2 CH_3 − 1); mp 43−44 °C. Anal. Calcd for $C_{15}H_{28}N_2O_2$ (268.4): C, 67.13; H, 10.52; N, 10.44. Found: C, 67.27; H, 10.56; N, 10.24; ESR: a single broad line (27 G) at room temperature in Et_2O (*M*/1000).

Hexanedioic acid bis(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl) ester (B4) and **decanedioic acid bis(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl) ester (B5)** were prepared as described.[17]

2,2,8,8,10,10-Hexamethyl-1,9-bis(1-phenylethoxy)-1,9-diazaspiro[5.5]undecan-4-one (A1). The synthesis of alkoxyamines in the presence of Jacobsen's reagent was described by Dao et al.[18] and this method was used here to prepare **A1**. [*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino]manganese(III) chloride (Jacobsen's catalyst) (280 mg, 0.4 mmol) was added to a solution of biradical **B1** (284 mg, 1.0 mmol) and styrene (419 mg, 4.0 mmol) in 1/1 toluene/ethanol (15 mL). This step was followed by the addition of di-*tert*-butyl peroxide (0.54 mL, 3.0 mmol) and sodium borohydride (228 mg, 6.0 mmol). The reaction mixture was then stirred at room temperature for 4 h, evaporated to dryness, and partitioned between CH_2Cl_2 (15 mL) and H_2O (20 mL). The aqueous layer was further extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, dried, and evaporated. The crude product was purified by column chromatography on Al_2O_3 (pentane/ether, 50/50) to give the bisalkoxyamine **A1** (444 mg, 0.9 mmol) as a white solid (89%). $R_f = 0.45$; ^1H NMR (200 MHz) δ 0.2−3 (m, 8 CH_3 and 4 CH_2; 32 H), 3.83 and 4.6 (m, 2 CH; 2 H), 7.0−7.5 (m, aromatic protons; 10 H). Anal. Calcd for $C_{31}H_{44}N_2O_3$ (492.70): C, 75.57; H, 9.00; N, 5.68. Found: C, 75.08; H, 9.29; N, 5.41. MS (CI): *m*/*z* 495 (M + 2), 496 (M + 3), 391 (M + 3 − C_8H_8), 375 (M + 3 − C_8H_8 − O).

2,2,6,6-Tetramethylpiperidine-*N*-(1-phenethyloxy) (S-TEMPO) was prepared in the presence of Jacobsen's reagent according to literature.[18] Complete characteristics of this molecule have already been reported.[18,19]

Bulk Polymerization of Styrene. The solutions of BPO (73 mg; 0.030 mol·L^{-1}) and binitroxide (0.018 mol·L^{-1}, [nitroxide group, NO$^\bullet$] = 0.036 mol·L^{-1}) in styrene (9.1 g; 10 mL) were degassed by three freeze−pump−thaw cycles. The tubes were sealed off under vacuum and then immersed in an oil bath thermostated at 110 or 130 °C. After polymerization, the content of each tube was poured while stirring into an excess of methanol (200 mL). The polymers were isolated by filtration, washed with methanol and dried. Styrene conversion (x) was determined by gravimetry. The same procedure was applied for alkoxyamine initiated polymerizations. Results are reported in Tables 1 and 2.

The methanol filtrates and the purified polymers (dissolved in a solution of THF or CH_2Cl_2) were analyzed by ESR. In all cases, a spectrum characteristic of that of a mononitroxide was observed (see below). The concentration of nitroxide present in the filtrates was always very small because of dilution and was not used for further calculation. The number of spin **S** (mol·L^{-1}) of nitroxide attached to a polymer chain in the polymerization reaction medium was calculated from the number of spin **s** of a solution of 10 mg of polymer dissolved in 2 mL of THF (or CH_2Cl_2), according to the following relationship

$$\mathbf{S} = \frac{W_{\mathrm{PS}}\cdot\mathbf{s}\cdot\frac{2}{10}}{\frac{W_{\mathrm{S}}}{d_{\mathrm{S}}}} = \mathbf{s}\cdot x d_{\mathrm{S}}\frac{2}{10} \qquad \text{(II)}$$

with W_{PS} and W_S, the respective weight of polystyrene and initial weight of styrene in the polymerization medium. The ESR results are reported in Table 3.

Direct ESR Monitoring of the Nitroxide Radicals Formed during the Course of Polymerization. As described above, the quantity of nitroxide radicals attached to a polymer chain and formed during polymerization can be estimated from a solution of the precipitated polymer, obtained at different polymerization times. To get an accurate overall value (including the polymeric and the small nitroxides) and avoid side reactions (such as spontaneous transformation of hydroxylamine into nitroxide in air), a direct ESR analysis was made on the reaction mixture. A known concentration of a solution of bisalkoxyamine **A1** in styrene (1.0 × 10^{-2} and 2.0 × 10^{-2} mol·L^{-1} for the two respective experiments) was introduced in an ESR tube. The tube was thoroughly degassed by three freeze−pump−thaw cycles and sealed off under vacuum. It was then heated at 130 °C in a thermostated oil bath. At regular time intervals, the tube was removed from the bath and the concentration of nitroxide radicals produced during the course of the reaction was monitored by ESR at room temperature. Figure 1 shows the spectra obtained after heating during (a) 15 min, (b) 2.5 h, (c) 5 h, and (d) 10 h. At the beginning of the experiment (a and b), the three-line spectra characteristic of a mononitroxide in solution were observed with a rotational correlation time[20] $\tau_c = 0.5 \times 10^{-10}$ s after 15 min, increasing to $\tau_c = 5 \times 10^{-10}$ s after 2.5 h. After 5 h (c), a broad shoulder is detected on the low-field line, indicating the presence of two species: the three-line spectrum corresponds to a mononitroxide with $\tau_c = 5 \times 10^{-10}$ s, while the broad shoulder may be attributed by comparison with reference spectra, to a mononitroxide with a τ_c of the order of 5−7 × 10^{-9} s. After 10 h (d), a new signal appeared at the lower field. Again two species are present, one with $\tau_c = 5 \times 10^{-10}$ s and the other one with τ_c of the order of 10^{-8} s. No

Table 1. Bulk Polymerization of Styrene at 130 and 110 °C (∗), Initiated by BPO (0.030 mol·L^{-1}) in the Presence of Various Nitroxide Biradicals ([NO$^•$] = 0.036 mol·L^{-1}): SEC Analysis of the Polymers

					raw polymer[a]					heated polymer[b]	
			theoretical		experimental[c]					experimental	
binitroxide	time (h)	convn	$M_{n,th}$ (g·mol^{-1})	$M_{n,th}/2$ (g·mol^{-1})	M_n (g·mol^{-1})	M_{p1} (g·mol^{-1})	M_{p2} (g·mol^{-1})	M_w/M_n	[chain] (mol·L^{-1})	M_n (g·mol^{-1})	M_w/M_n
B1	2.5	0.38	19000	9500	17300		27900	1.34	0.020	11100	1.25
	5.0	0.60	30200	15100	23900	26500	46600	1.44	0.023	13900	1.37
	14.0	0.89	44800	22400	31200	45200		1.48	0.026	21400	1.69
B1*	2.5	0.12	6060	3030	7400		9500	1.31	0.015	3840	1.55
	5.0	0.29	14640	7320	14200		22000	1.40	0.019	9000	1.41
	14.0	0.74	37500	18750	32000		57000	1.56	0.021	21600	1.45
B2	2.5	0.22	11300	5650	10500		15700	1.29	0.019	6500	1.22
	5.0	0.61	30900	15400	24000	23400	46200	1.43	0.023	14500	1.29
	14.0	0.84	42300	21160	26000	35100	73000	1.42	0.029	21000	1.51
B3	2.5	0.43	21900	10950	19000	16100	32000	1.41	0.021	12500	1.32
	5.0	0.64	32470	16240	24300	25800	55200	1.55	0.024	19300	1.32
	14.0	0.85	42670	21340	24900	34200	75300	1.62	0.031	19800	1.51
B4	2.5	0.53	26800	13400	22200			1.37	0.022		
	5.0	0.72	36400	18200	25300			1.44	0.026		
	14.0	0.88	44500	22250	26000			1.57	0.031		
B5	2.5	0.53	26500	13250	20600			1.68	0.023		
	5.0	0.76	38400	19200	26300			1.60	0.026		
	14.0	0.86	43400	21700	25000			1.72	0.031		

[a] Polymer recovered after precipitation in methanol, washed and dried under vacuum. [b] Polymer heated at 130 °C for 24 h. [c] M_{pi}: mass at the maximum of the *i*th peak.

Table 2. Bulk Polymerization of Styrene at 130 °C, in the Presence of the Bisalkoxyamine A1: SEC Analysis of Polymers

			theoretical		experimental		
[**A1**] (mol·L^{-1})	time (h)	convn	$M_{n,th}$ (g·mol^{-1})	$M_{n,th}/2$ (g·mol^{-1})	M_n (g·mol^{-1})	M_w/M_n	[chain] (mol·L^{-1})
0.016	0.5	0.18	10300	5150	10200	1.58	0.016
	1.0	0.32	17900	8950	15300	1.43	0.019
	1.5	0.40	22800	11400	21300	1.28	0.017
	2.5	0.54	30600	15300	23000	1.42	0.021
	5.0	0.65	36700	18350	23400	1.45	0.025
	14.0	0.79	45000	22500	19100	1.60	0.039
0.010	0.5	0.19	17300	8650	16800	1.50	0.010
	1.0	0.29	26100	13050	23700	1.43	0.011
	1.5	0.37	33200	16600	30400	1.35	0.011
	2.5	0.47	42400	21200	35500	1.38	0.012
	5.0	0.63	57000	28500	38000	1.45	0.015
	14.0	0.77	70400	35200	31500	1.55	0.022

Table 3. Bulk Polymerization of Styrene at 130 and 110 °C (∗), Initiated by BPO (0.030 mol·L^{-1}) in the Presence of Various Nitroxide Biradicals ([NO$^•$] = 0.036 mol·L^{-1}): ESR Analysis of the Raw Polymer before and after Oxidation with PbO$_2$ at Room Temperature in CH$_2$Cl$_2$

				number of spins of raw polymer solution[a] (10^{-4} mol·L^{-1})		
bini-troxide	time (h)	convn	[chain] (mol·L^{-1})	before oxidn	after oxidn	concn of hydroxylamine (mol·L^{-1})[a,b]
B1	0.5	0.18	0.018	1.4	3.6	2.2
	1.0	0.34	0.022	3.2	9.5	6.3
	1.5	0.48	0.024	3.7	12.2	8.5
	2.5	0.63	0.025	4.9	10.3	5.4
	5.0	0.73	0.032	5.9	10.3	4.4
	14.0	0.95	0.032	6.8	9.9	3.1
B1*	2.5	0.12	0.015	1.1	2.6	1.5
	5.0	0.29	0.019	2.7	5.1	2.4
	14.0	0.74	0.021	5.1	8.5	3.4
B4	2.5	0.53	0.022	8.7		
	5.0	0.72	0.026	12.8		
	14.0	0.88	0.031	10.2		
B5	2.5	0.53	0.023	5.4		
	5.0	0.76	0.026	7.8		
	14.0	0.86	0.031	10.9		

[a] Calculated with respect to the reaction medium volume. [b] Calculated from the difference between the spin number of the raw polymer before and after oxidation.

change was observed in the hyperfine splitting ($a_N = 15.4$ G) of the three-line spectra, indicating an isotropic motion and thus validating the previous calculation of τ_c.[20] The above 10-fold increase of the smaller τ_c with the time of heating may be attributed either to an increase of the (microscopic) viscosity, the volume of the species with the smaller τ_c being constant, or to a small increase of this volume, the viscosity being constant, or to a simultaneous occurrence of both changes. In any case, the approximately 200-fold increase of the larger τ_c has to be attributed mainly to an increase in the volume of the corresponding molecule.[21]

Polymer Oxidation. The purified polymers (50 mg) (see Table 3) obtained in the bulk polymerization were dissolved in CH$_2$Cl$_2$ (10 mL) and a large excess of PbO$_2$ was added. The mixture was stirred at room temperature and the oxidation was monitored by ESR. When the intensity of the radical signal reached a plateau, the number of spin of the solution **s** was measured and converted to the number of spin of the polymerization medium **S** after oxidation. The ESR signal of the purified polymer samples (in CH$_2$Cl$_2$ solution) before and after oxidation was characteristic of that of a mononitroxide, and after oxidation the intensity of the ESR signal increased (see Figure 2).

Polymer Heating. The purified polystyrene (10 mg), placed in a tube open to air, was heated at 130 °C in a thermostated oven for 24 h. The polymer was then dissolved in THF (2 mL) for measurement of the molar mass by SEC.

Kinetic Study of the Homolytic Dissociation of A1 in the Presence of Galvinoxyl. A procedure similar to that in previous literature was used.[22] A large excess of galvinoxyl radical (1 × 10^{-3} mol·L^{-1}) was added to a solution of 2 × 10^{-5} mol·L^{-1} of **A1** in *tert*-butylbenzene, to instantaneously scavenge all the carbon-centered radicals formed upon alkoxyamine dissociation. The solution was then introduced into an ESR tube, which was degassed by three freeze−pump−thaw cycles and sealed off under vacuum. The tube was then heated to 130 °C, and the concentration of nitroxide radicals produced during the course of the reaction was monitored by ESR: the evolution of the peak at low field of the nitroxide, which distinguished itself from the large peak of galvinoxyl, was followed and measured.

Kinetic Study of Homolytic Dissociation of PNNP Chains in the Presence of Galvinoxyl. Two PNNP polystyrenes (**P1** and **P2**) were prepared in bulk at 130 °C, using BPO (0.030 mol·L^{-1}) as the initiator and **B1** (0.018 mol·L^{-1};

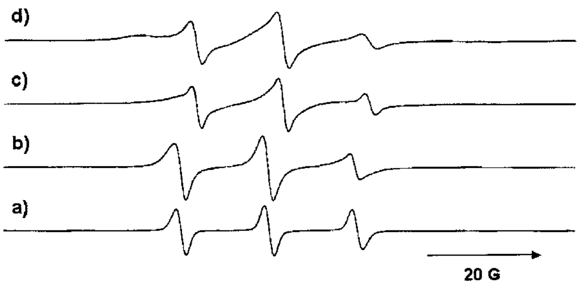


Figure 1. ESR spectra of nitroxide radicals formed at different time intervals in the bulk polymerization of styrene at 130 °C, in the presence of the bisalkoxyamine **A1** (0.02 mol·L^{-1}): (a) 15 min; (b) 2.5 h; (c) 5 h; (d) 10 h.

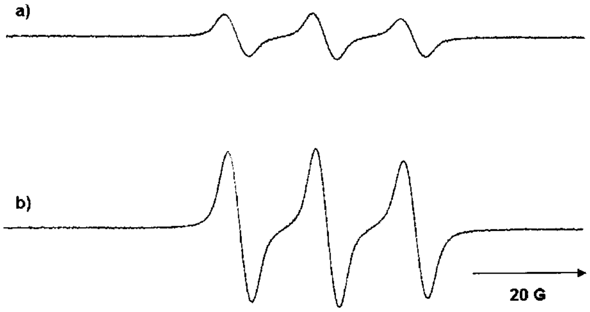


Figure 2. ESR signal of a purified polymer sample in CH_2Cl_2 solution, polystyrene prepared in bulk at 130 °C (0.5 h polymerization time), using BPO as the initiator and **B1** as the mediator: (a) before and (b) after oxidation.

$[NO^\bullet] = 0.036$ mol·L^{-1}) as the mediator. To avoid chain-end decomposition, polymerization was stopped at low monomer conversion, namely 5.1% after 20 min for **P1** and 7.6% after 40 min for **P2**. The polymers were recovered, purified, and analyzed as described above. The number average molar mass of **P1** was $M_n = 3840$ g·mol^{-1}, with $M_w/M_n = 1.26$; for **P2**, $M_n = 5230$ g·mol^{-1} and $M_w/M_n = 1.24$. Dissociation of the alkoxyamine end group was monitored by ESR using the same procedure as for **A1**.

Irreversible Decomposition of the Bisalkoxyamine A1 and of the Monoalkoxyamine S-TEMPO. Thermal decomposition of bisalkoxyamine **A1** and alkoxyamine S-TEMPO was studied by ^{1}H NMR, following the same procedure for both compounds. A solution of the alkoxyamine in benzene (0.06 mol·L^{-1}) was introduced in a NMR tube. The tube was thoroughly degassed by three freeze−pump−thaw cycles and sealed off under vacuum. It was then immersed into an oil bath at 130 °C. At regular time intervals, the tube was cooled to room temperature and ^{1}H NMR analysis was performed. The precise protocol has already been reported.[23] For the decomposition of S-TEMPO, two byproducts, styrene and the *N*-hydroxylamine derivative of TEMPO, were formed, as was previously observed in the absence of oxygen.[23] With the heating time, the peaks corresponding to the three vinylic protons of styrene at δ 5.3 (d), 5.7 (d), and 6.7 (dd) ppm and the peak corresponding to the twelve methyl protons of the hydroxylamine of TEMPO at δ 1.3 ppm (s) increased in intensity, while the peak of the methine proton of S-TEMPO at δ 5.0 (q) ppm decreased in intensity. For decomposition of the bisalkoxyamine **A1**, the spectrum was much more complicated; however, it clearly showed an increase of the vinylic styrene protons at δ 5.3, 5.7, and 6.7 ppm, as well as a decrease of the methine protons of the alkoxyamine at δ 3.9 (m) and 4.9 (m) ppm. Although the production of styrene and hydroxylamine should occur simultaneously and in the same quantity, the corresponding hydroxylamine could not be detected with certainty, probably because its spectrum was too close to the alicyclic part of the alkoxyamine.

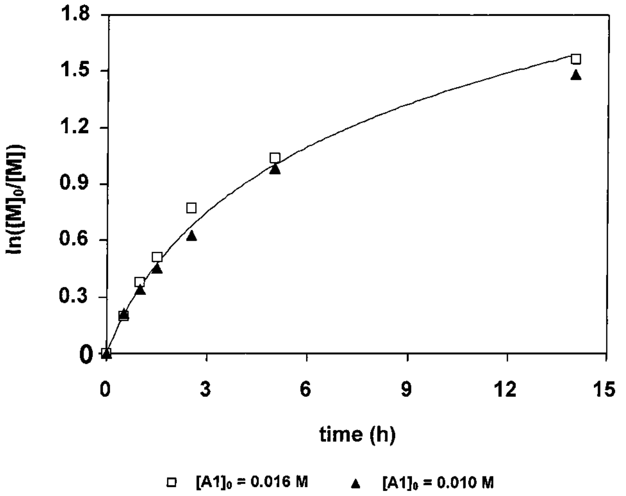


Figure 3. ln[M]$_0$/[M] vs time for the bulk polymerizations of styrene at 130 °C in the presence of the bisalkoxyamine **A1**. Equation of calculated curve taken from Fukuda et al.[24] applied for thermal auto-initiation, with third-order kinetics with respect to monomer. $\ln[M]_0/[M] = {}^2/_3 \ln(1 + {}^3/_2 A_0 t)$ with $A_0 = 1.3 \times 10^{-4}$ s^{-1} (to fit the experimental data).

Results and Discussion

1. Bulk Polymerizations of Styrene Initiated either by BPO in the Presence of the Various Binitroxides or by the Bisalkoxyamine A1. Five biradicals with their nitroxide groups having an environment similar to that of TEMPO were chosen and were thus expected to exhibit similar reactivity. The polymerizations were performed in bulk at 130 or 110 °C using the experimental conditions described in the literature for TEMPO-mediated polymerizations, either with BPO as a radical initiator in the presence of various binitroxides[3] or initiated by **A1** as a unimolecular initiator.[4,5] As shown in Tables 1 and 2, the binitroxides examined behaved in a similar way, regardless of their structure. Some typical features of nitroxide-mediated controlled polymerizations were displayed, such as slow polymerization, increase in M_n with monomer conversion and polydispersity indices below 1.5 (at least in the early stage of the polymerization). Polymerization kinetics were slower at 110 °C than at 130 °C. At the higher temperature, the same kinetics were observed for the various binitroxides and for both **A1** concentrations (Figure 3), indicating the occurrence of thermal auto-initiation and its strong influence on the concentration of propagating radicals as demonstrated for TEMPO-mediated CRP of styrene in bulk.[24] Contrary to conventional mononitroxide-mediated polymerizations, the purified polymer samples were paramagnetic and their ESR spectra in THF or CH_2Cl_2 solvent were characteristic of that of a mononitroxide in fluid solution ($\tau_c < 10^{-11}$ s) (Table 3 and Figure 2). This implies first that the binitroxides were involved in the polymerization reaction and second that part of them remained attached to polymer chains by one side only. The concentration of chains increased throughout the reaction (this effect being more pronounced at 130 °C, see Table 1) in such a way that it could not be explained by thermal auto-initiation only (thermal auto-initiation of styrene in the absence of added nitroxide led to the formation of no more than 0.0022 mol·L^{-1} polymer chains, after 14 h in bulk at 130 °C).[25] As a consequence, the polydispersity indices also increased, instead of progressively decreasing. The SEC traces

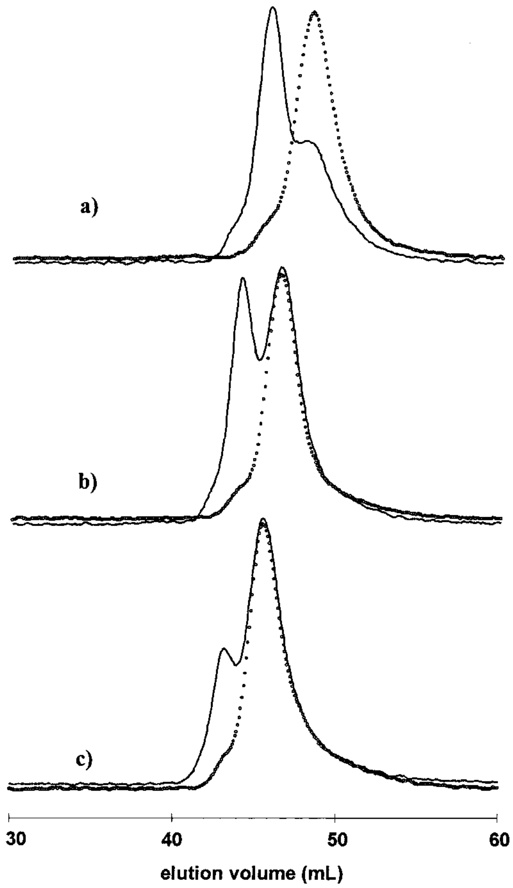


Figure 4. SEC traces (differential refractive index) of raw (—) and heated (○○○○○○) polymers obtained from bulk polymerization of styrene at 130 °C in the presence of BPO and **B3** nitroxide biradical ([BPO] = 0.030 mol·L^{-1}; [NO$^\bullet$] = 2 [**B3**] = 0.036 mol·L^{-1}): (a) conversion = 43%; (b) conversion = 64%, (c) conversion = 85%.

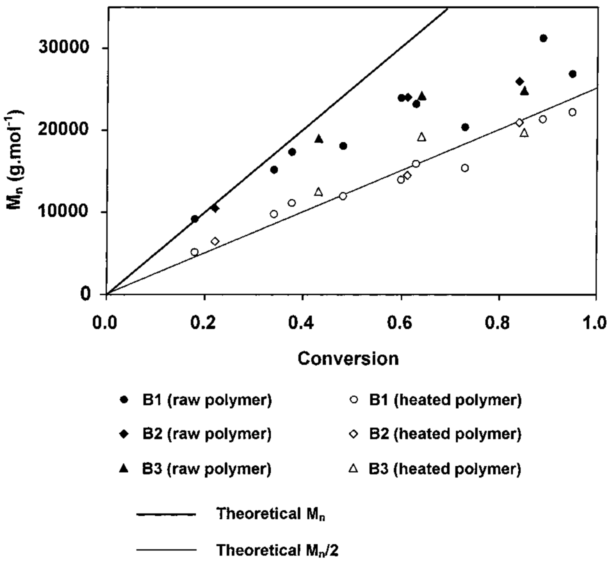


Figure 5. M_n vs monomer conversion for bulk polymerizations of styrene at 130 °C in the presence of BPO and **B1**, **B2**, or **B3** nitroxide biradicals ([BPO] = 0.030 mol·L^{-1}; [NO$^\bullet$] = 2 [**B1**] = 2 [**B2**] = 2 [**B3**] = 0.036 mol·L^{-1}).

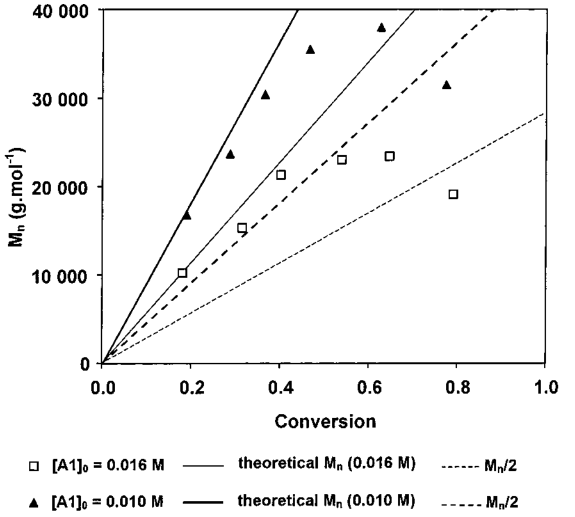


Figure 6. M_n vs monomer conversion for bulk polymerizations of styrene at 130 °C in the presence of bisalkoxyamine **A1**.

were particularly unusual, as illustrated in Figure 4. Indeed, while the overall peak shifted with conversion toward the lower elution volumes (larger molar masses) a bimodal distribution was observed. The molar mass values at the maximum of the two peaks were systematically in a ratio of 2 (see Table 1). However, the proportions of both peaks changed dramatically with the progress of monomer conversion: the relative area of the low molar mass peak increased whereas that of the high molar mass peak decreased. As a result, the M_n vs conversion displayed in Figures 5 and 6 was not linear. Initially, the M_n values followed the theoretical line corresponding to polymers with two growing chains attached to a central bisalkoxyamine core. Then the M_n values steadily deviated from linearity to reach another theoretical line referred to as M_n/2 and corresponding to branches that have disconnected from the core. After the dried polymer was heated at 130 °C for 24 h, the SEC traces considerably changed to display a single peak, which perfectly overlayed the lower molar mass one in the initial distribution (Figure 4). Moreover, M_n of such modified polymer increased linearly with monomer conversion, following the M_n/2 line (Figure 5). Indeed, when the polymer was heated to 130 °C, the alkoxyamine C—O bonds in the polymer chains were broken (producing unsaturation or ketone end group): [26] the two-arm macromolecules broke in the middle, supporting both segments having the same length owing to fast exchange. This result, together with the bimodal distribution of the SEC traces, showed very clearly that the alkoxyamine bonds were not perfectly stable during the course of the polymerization but underwent side reaction leading to irreversible arm separation.

Two possible reactions can account for separation of the arms. The first one (reversible, PNNP $\rightleftharpoons$ PNN$^\bullet$ + P$^\bullet$) is the homolytic cleavage of one alkoxyamine bond leading to a propagating chain and a nitroxide terminated polymer. The second one (irreversible, PNNP → PNNH + P$^=$) is the decomposition of one alkoxyamine bond into an unsaturated polymer (dead) and a macromolecular hydroxylamine (still living, because the other alkoxyamine function is still present). The first reaction necessarily exits, as it allows polymerization to proceed. Moreover, the concentration of free nitroxide was rather high compared to TEMPO-mediated CRP of styrene (see Table 3), in the range 10^{-4}–10^{-3} mol·L^{-1} instead of 10^{-5}–10^{-4} mol·L^{-1}.[24] Such a result was also observed for the polymeric nitroxides obtained by copolymerizing styrene with a nitroxide-bearing comonomer.[13] However, it was not sufficiently high (< 5 mol % of the total chain concentration) to completely explain the large proportion of divided chains. Thus the second mechanism was also supposed to occur to a large extent at 130 °C. At a lower temperature, namely 110 °C, a better control of the two-arm structure was observed, since experimental molar masses remained close to the theoretical values, even at 74% conversion (Table 1). To ascertain the occurrence of this second reaction, the polymer was analyzed by ESR after mild oxidation with PbO_2. If present, the hydroxylamines would be oxidized into nitroxides, and the number of spin would increase after oxidation, which was indeed observed (Figure 2; Table 3).

On the basis of all the experimental observations, the major reactions involved are summarized in Scheme 3. They lead to a mixture of polymer chains mainly composed of PNNP, PNNH (turned into PNN$^\bullet$, after mild oxidation), PNN$^\bullet$, and P$^=$ in proportions that vary with conversion. To fully understand the mechanisms that govern the behavior of the studied nitroxide biradicals in the CRP of styrene, a thorough kinetic study of the main reactions depicted in Scheme 3 (namely the activation−deactivation equilibrium of the polymeric species and the alkoxyamine decomposition) has been undertaken and is presented.

2. Determination of the Rate Constant of Dissociation, $k_{d,0}$, of the Bisalkoxyamine A1. The kinetics of the homolytic cleavage of **A1** were monitored by real-time quantitative ESR analysis of the concentration of released nitroxide. The dissociation reaction was performed at 130 °C in the presence of galvinoxyl and the concentration of nitroxide vs time is plotted in Figure 7. Providing that the carbon-centered radicals produced were instantaneously trapped by the galvinoxyl radical in order to prevent the back reaction, the initial rate of appearance of the nitroxide gave the value of $k_{d,0}$ of reaction 1 in Scheme 3, according to eq III.

$$k_{d,0} = \frac{\left(\frac{d[SNN^\bullet]}{dt}\right)_{t=0}}{[\mathbf{A1}]_0} \tag{III}$$

Although the reaction was allowed to proceed for a long period of time, for a better accuracy of the result only the initial slope was used to determine $k_{d,0}$. The structure of the nitroxide formed evolved progressively from SNN$^\bullet$ (reaction 1) to $^\bullet$NN$^\bullet$ (reaction 2). The latter exhibited a very broad ESR spectrum which was not taken into consideration for the quantitative analysis (only the peak at low field of the SNN$^\bullet$ nitroxide was followed and measured). In addition, **B1**, **B2** and **B3** nitroxide biradicals $^\bullet$NN$^\bullet$ were quite unstable at 130 °C:[27] **B1** completely decomposed within 2 h, and **B2** and **B3**, within 4 h. Hence, only the concentration of the monoradical SNN$^\bullet$ was quantitatively monitored in the applied procedure. Thus, the measured nitroxide concentration did not reach the maximum value of 4×10^{-5} mol·L^{-1} (corresponding to twice the initial concentration of **A1**), but passed through a maximum at a lower value and then continuously decreased. The calculated value of $k_{d,0}$ at 130 °C was 6.6×10^{-4} s^{-1}. It can be compared with data reported for the analogous monoalkoxyamine S-TEMPO. Dissociation of the latter was studied by Skene et al.[28] in cyclohexanol in a temperature range of 75−120 °C: the activation energy was $E_a = 128$ kJ·mol^{-1}, the preexponential factor was $A = 5.0 \times 10^{13}$ s^{-1}, and calculated $k_{d,130°C} = 1.1 \times 10^{-3}$ s^{-1}. It was also studied by Marque et al.[29] who obtained $k_{d,130°C} = 1.4 \times 10^{-3}$ s^{-1} in *tert*-butylbenzene. Another alkoxyamine with structure very close to S-TEMPO, the 2-*tert*-butoxy-1-phenyl-1-(1-oxy-2,2,6,6-tetramethylpiperidinyl)ethane, was examined by Bon et al.[30] in toluene

Scheme 3. Reaction Scheme for Bulk Polymerization of Styrene Initiated by the Bisalkoxyamine A1

Considered species and nomenclature:

styrene unit:	**S**	
polymer chain:	**P**	
styryl radical:	**S•**	
polystyryl radical:	**P•**	
A1:	**SNNS**	
nitroxide biradical:	**•NN•**	
living polymers:	**PNNS, PNNP, PNNH, PNN•**	
mononitroxides:	**SNN•, PNN•, HNN•**	
hydroxylamines:	**HNNP, HNN•**	
dead polymers:	**P-P**	(saturated; formed by radical-radical coupling)
	P$^=$	(unsaturated; formed by decomposition of the chain end)

Activation-deactivation equilibrium of the bisalkoxyamine **A1**:

$$\mathbf{A1} \xrightleftharpoons{k_{d,0}} SNN\bullet + S\bullet \quad \text{(equilibrium constant } K_0) \tag{1}$$

$$SNN\bullet \rightleftharpoons \bullet NN\bullet + S\bullet \quad \text{(equilibrium constant } K_0) \tag{2}$$

if $K_0 << [S\bullet]$ (which is the case for TEMPO-mediated CRP of styrene), then $[\bullet NN\bullet] << [SNN\bullet]$ and the second equilibrium can be neglected.

Initiation, propagation, and reversible termination:

$$S\bullet + n\,S \xrightarrow{k_p} P\bullet \circlearrowleft k_p \tag{3}$$

$$P\bullet + SNN\bullet \rightleftharpoons PNNS \rightleftharpoons PNN\bullet + S\bullet \circlearrowleft k_p \tag{4}$$

$$PNNP \xrightleftharpoons[k_c]{k_d} PNN\bullet + P\bullet \circlearrowleft k_p \quad \text{(equilibrium constant } K = k_d/k_c) \tag{5}$$

The second equilibrium leading to •NN• was neglected because $[\bullet NN\bullet]/[PNN\bullet] = K/[P\bullet]$ would be much smaller than 1.

$$HNNP \xrightleftharpoons[k'_c]{k'_d} HNN\bullet + P\bullet \circlearrowleft k_p \quad \text{(equilibrium constant } K' = k'_d/k'_c) \tag{6}$$

Although hydroxylamine group is rather unstable,[37] for simplicity, the reaction is not considered here. Hence, HNNP and HNN• refer to both species with the hydroxylamine end-group and their decomposition products identified as XNP and XN•.

Thermal auto-initiation:

$$2\,S \rightleftharpoons \text{Diels-Alder dimer} \xrightarrow{S} P\bullet \tag{7}$$

Rate[41]: $R_i = k_i.[S]^3 = k_i.[S]_0^3.(1-x)^3$

Irreversible termination reaction:

$$P\bullet + P\bullet \xrightarrow{k_t} P\text{-}P \quad \text{(mainly by coupling)} \tag{8}$$

Irreversible decomposition reactions:

$$\begin{tikzcd} PNN\bullet + P\bullet \arrow[dr, "k_{tr}"] & & (9) \\ & PNNH + P^= & \\ PNNP \arrow[ur, "k_{dec}"] & & (10) \end{tikzcd}$$

$$\begin{tikzcd} HNN\bullet + P\bullet \arrow[dr, "k'_{tr}"] & & (11) \\ & HNNH + P^= & \\ HNNP \arrow[ur, "k'_{dec}"] & & (12) \end{tikzcd}$$

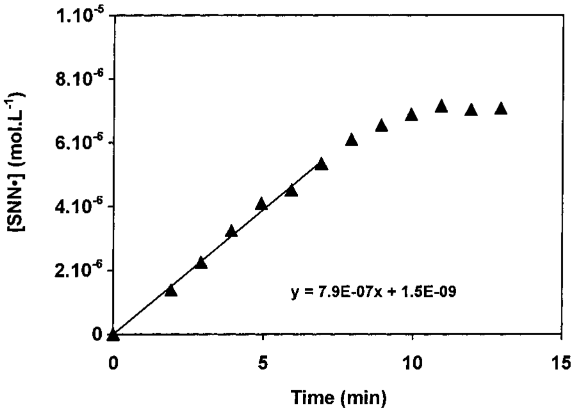


Figure 7. Decomposition of bisalkoxyamine **A1** at 130 °C in *tert*-butylbenzene solutions, in the presence of galvinoxyl. The formation of SNN$^\bullet$ nitroxide radicals is followed by ESR analysis. [**A1**] = 2 × 10^{-5} mol·L^{-1}; [galvinoxyl] = 1 × 10^{-3} mol·L^{-1}.

in a temperature range of 60−100 °C. They reported $E_a = 133$ kJ·mol^{-1} and $A = 1.1 \times 10^{14}$ s^{-1} and calculated $k_{d,\,130\,°C} = 6.0 \times 10^{-4}$ s^{-1}. In the case of the bisalkoxyamine **A1**, the measured $k_{d,0}$ value at 130 °C is not very different from those obtained for similar monoalkoxyamines, indicating no effect of the binitroxide structure on the dissociation reaction.

3. Determination of the Rate Constant of Dissociation, $k_{d,0}$, of Polymeric Bisalkoxyamines PNNP. Concerning the TEMPO-based polystyryl alkoxyamine (P-TEMPO), Goto et al.[31] determined $E_a = 124$ kJ·mol^{-1}, $A = 3.0 \times 10^{13}$ s^{-1} and $k_{d,130°C} = 2.5 \times 10^{-3}$ s^{-1} while Bon et al.[30] reported $E_a = 141$ kJ·mol^{-1}, $A = 1.0 \times 10^{16}$ s^{-1} and $k_{d,130°C} = 5.6 \times 10^{-3}$ s^{-1}. These observed 2- to 9-fold larger k_d values for the polymeric species with respect to the small molecules were ascribed to a larger steric strain on the breaking bond,[29,30] but the difference was generally considered as rather marginal.[29,31,32] To compare with the styryl-based bisalkoxyamine **A1**, the dissociation of two PNNP polymeric bisalkoxyamines **P1** and **P2** was examined at 130 °C, using the same experimental procedure. The rate constant of dissociation, $k_{d,0}$, was 1.5×10^{-3} s^{-1} for **P1** and 1.4×10^{-3} s^{-1} for **P2**. The values were only slightly larger than that determined for **A1**, indicating no strong effect of the chain length. In addition, the rate constant of dissociation was not very different from that of P-TEMPO, indicating that the presence of a polymeric chain attached to the leaving nitroxide had no significant influence on the homolytic cleavage of the alkoxyamine bond.

4. Determination of the Apparent First-Order Rate Constant of Decomposition (k_{dec}). The proton NMR analysis of the bisalkoxyamine **A1** in benzene solution at 130 °C showed the existence of a decomposition reaction leading to styrene and supposedly hydroxylamine in the absence of oxygen in the NMR tube. When oxygen was present, small fractions of acetophenone and 1-phenyl-1-ethanol were also detected. The results were not different from those also observed for the S-TEMPO alkoxyamine and already described in the literature.[23] A kinetic study concerning the decomposition of S-TEMPO alkoxyamine in toluene at 130 °C, gave $k_{dec} = 5.0 \times 10^{-5}$ s^{-1} ($t_{1/2} = 3.9$ h).[33] Surprisingly, the rate constant found by Ohno[34] for the 2-benzoyloxy-1-phenylethyl TEMPO-based alkoxyamine was 1 order of magnitude lower ($k_{dec} = 2.1 \times 10^{-6}$ s^{-1} at 130 °C in toluene solution), which was explained by the deactivating effect of the carbonyl group in the molecule. Concerning P-TEMPO, the same authors found $k_{dec} = 8.4 \times 10^{-6}$ s^{-1} at 130 °C in toluene solution ($t_{1/2} = 22.9$ h). Again the rate constant of decomposition was found to be below that of S-TEMPO, which was not clearly explained. The decomposition of P-TEMPO in styrene during polymerization was also studied by Zhu et al.[35] and Hawker et al.[36] They found that alkoxyamine end functionality decreased with increasing monomer conversion and target molar mass. An end group purity larger than 90% was obtained for low molar mass polystyrene only ($M_n < 10\,000$ g·mol^{-1}). In the polymerization of styrene initiated by a styryl-based alkoxyamine with a chromophore attached to the nitroxide group (TEMPO type), the chain-end purity was approximately 60% after 16 h polymerization time at 120 °C.[35] This leads to a rate constant of decomposition of approximately 9×10^{-6} s^{-1}, which is not very different from the value obtained in an inert solvent.

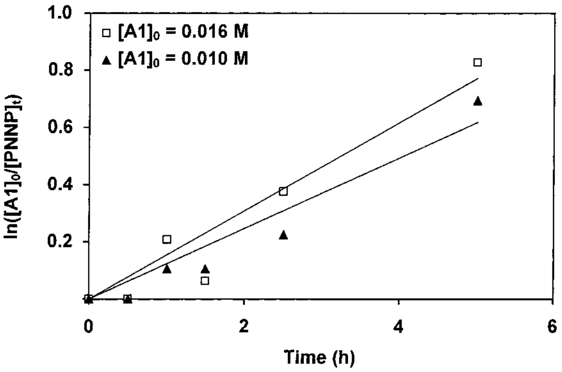


Figure 8. ln([**A1**]$_0$/[PNNP]$_t$) vs time for the bulk polymerizations of styrene at 130 °C in the presence of bisalkoxyamine **A1**. The slope gives the apparent first-order rate constant $k_{dec} = 3.8 \times 10^{-5}$ s^{-1}.

In this work, the decomposition rate of polystyryl-based bisalkoxyamine PNNP was not studied directly from NMR analysis in an inert solvent but was deduced from the proportion of dead chains formed during the course of the polymerization. As mentioned in the first paragraph, hydroxylamine simultaneously formed, the concentration of which was calculated from ESR measurements after mild oxidation of the polymer samples (see Table 3). The concentration went however through a maximum, indicating the slow degradation of the hydroxylamine under the polymerization conditions.[37] Therefore, this technique was not appropriate for an accurate determination of the rate constant of formation of the hydroxylamine, and hence k_{dec}. Assuming that the chain-end decomposition was the principal chain-breaking reaction in the system (as also supposed and well argued by Ohno et al.),[34] the extent of this reaction could be estimated from the concentration of chains derived from conversion and M_n data (see Table 2, polymerizations initiated with **A1**). The first step of the decomposition reaction producing PNNH and P$^=$ led to an increase in the chain concentration, with $[P^=]_t = [\text{chains}]_t - [\mathbf{A1}]_{t=0}$ and $[\text{PNNP}]_t = [\mathbf{A1}]_0 - [P^=]_t = 2[\mathbf{A1}]_{t=0} - [\text{chains}]_t$. Considering decomposition as an apparent first-order reaction, $\ln([\mathbf{A1}]_{t=0}/[\text{PNNP}]_t)$ is plotted vs time in Figure 8 for two **A1** initial concentrations, namely 0.010 and 0.016 mol·L^{-1}. The slope gave $k_{dec} = 3.8 \times 10^{-5}$ s^{-1} at 130 °C ($t_{1/2} = 5.1$ h; 85 mol % of chains have decomposed within 14 h), under polymerization conditions, i.e., in styrene solution. This value is four to five times larger than the k_{dec} previously reported for P-TEMPO in toluene at 130 °C,[34] or than the k_{dec} calculated from published polymerization data.[35] The strong discrepancy with TEMPO-mediated polymerization of styrene might be related to the unique structure of the nitroxide counterradical, PNN$^\bullet$. Indeed, as long as the chains grow, overall size of this nitroxide increases accordingly. This effect will be discussed more thoroughly in the last part of this article, in light of the full set of rate constants.

5. Determination of the Equilibrium Constants *K* and *K′* of Reactions 5 and 6 at 130 °C. The binitroxide-mediated polymerization of styrene cannot be regarded as a simple system, regulated by only one activation–deactivation equilibrium. Indeed, when monomer conversion progresses and PNNP chains decompose into HNNP (and eventually X-NP, as the hydroxylamine group is not stable), the activation–deactivation equilibrated reactions 5 and 6 occur simultaneously. Then, two different nitroxides, PNN$^\bullet$ and HNN$^\bullet$ in continuously changing proportions, actually control the polymerization. As shown in Scheme 3, the probability of formation of the binitroxide $^\bullet$NN$^\bullet$ is too low to consider this species in the kinetics. The way both equilibrium relationships can be written depends on the very mechanism of the decomposition reaction (see appendix). However, it is still not clear in the literature whether such irreversible decomposition follows a true first order kinetics (reactions 10 and 12; Scheme 3) or a second order one (i.e., hydrogen transfer from propagating radical to nitroxide, reactions 9 and 11) because it was demonstrated that they cannot be kinetically differentiated.[38] In the case of a first-order decomposition reaction, k_{dec} is a true first-order rate constant, while in the case of a second-order decomposition reaction, the rate constant is k_{tr}, and an apparent first-order rate constant k_{dec} can be calculated as $k_{dec} = k_{tr}k_d/(k_c + k_{tr})$. When k_{tr} is small with respect to k_c (in such a case k_{dec} becomes Kk_{tr}) (see Appendix), then both mechanisms lead to the same formula for the overall nitroxide concentration (eq IV), from which an apparent equilibrium constant can be deduced (eq V).

$$[\mathrm{N}^\bullet] = [\mathrm{PNN}^\bullet] + [\mathrm{HNN}^\bullet] = \frac{K[\mathrm{PNNP}]_t + K'[\mathrm{HNNP}]_t}{[\mathrm{P}^\bullet]} = \frac{(K - K')[\mathbf{A1}]_0 \exp(-k_{dec}t) + K'[\mathbf{A1}]_0}{[\mathrm{P}^\bullet]} \quad \text{(IV)}$$

$$K_{app} = \frac{[\mathrm{N}^\bullet][\mathrm{P}^\bullet]}{[\mathbf{A1}]_0} = (K - K')\exp(-k_{dec}t) + K' \quad \text{(V)}$$

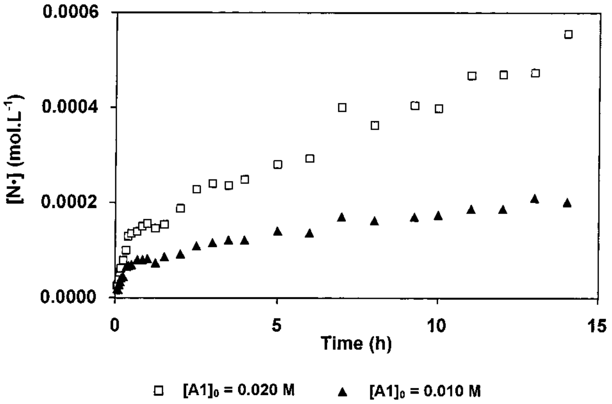


Figure 9. Overall concentration of nitroxide, $[\mathrm{N}^\bullet] = [\mathrm{PNN}^\bullet] + [\mathrm{HNN}^\bullet]$, vs time followed by in situ ESR analysis for bulk polymerizations of styrene at 130 °C in the presence of bisalkoxyamine **A1** at two initial concentrations.

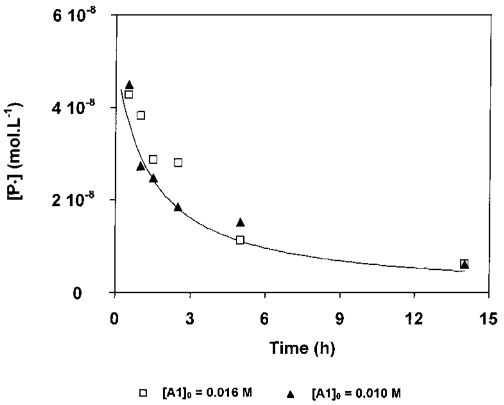


Figure 10. [P$^\bullet$] vs time for the bulk polymerizations of styrene at 130 °C in the presence of the bisalkoxyamine **A1**. Calculated curve (derivative of the curve given in Figure 3): $[\mathrm{P}^\bullet] = A_0/k_p(1 + {}^3/_2A_0t)$ with $k_p = 2600$ L·mol^{-1}·s^{-1} [39] and $A_0 = 1.3 \times 10^{-4}$ s^{-1}.

Variation of the concentration of free nitroxide with polymerization time was determined in situ by real-time ESR analysis (see Experimental Section) for two **A1** initial concentrations, namely, 0.010 and 0.020 mol·L^{-1} at 130 °C (Figure 9). Measurements gave an overall concentration, $[\mathrm{N}^\bullet] = [\mathrm{PNN}^\bullet] + [\mathrm{HNN}^\bullet]$. This was supported by the ESR spectra showing two mononitroxides with different rotational correlation time; in addition two different mononitroxides were detected after purification of the polymer, respectively in the recovered polymer (PNN$^\bullet$) and in the filtrate (HNN$^\bullet$ or a derivative). The experimental concentration of P$^\bullet$ (Figure 10) was calculated from the tangent of the $\ln[\mathrm{M}]_0/[\mathrm{M}]$ vs time plot given in Figure 3, using the propagation rate constant $k_p = 2600$ L·mol^{-1}·s^{-1} at 130 °C.[39] To facilitate the calculation and take advantage of the large number of data points of [N$^\bullet$], the [P$^\bullet$] vs time plot was fitted with a mathematical curve (the same for both initial concentrations of initiator, which had no significant effect on the rate) from which [P$^\bullet$] was calculated for each time an experimental value of [N$^\bullet$] was available. The apparent equilibrium constant $K_{app} = [\mathrm{N}^\bullet][\mathrm{P}^\bullet]/[\mathbf{A1}]_0$ was plotted as a function of polymerization time for both **A1** initial concentrations 0.010 and 0.020 M (Figure 11a). Interestingly, K_{app} continuously decreased with polymerization time, from 3.0×10^{-10} mol·L^{-1} (corresponding to K in eq A9 or to $k_d/(k_c + k_{tr})$ in eq A24) to a value around 1×10^{-10} mol·L^{-1} (corresponding to K' or to $k'_d/(k'_c + k'_{tr})$ at infinite time). Considering eq A9, one can calculate $K = 3.0 \times 10^{-10}$ mol·L^{-1} and $k_c = k_d/K = 4.7 \times 10^6$ L·mol^{-1}·s^{-1} using $k_d = 1.4 \times 10^{-3}$ s^{-1} for PNNP. With equation (A24), the ratio $k_d/(k_c + k_{tr})$ equals 3.0×10^{-10} mol·L^{-1}; with $k_d = 1.4 \times 10^{-3}$ s^{-1}, one has $k_c + k_{tr} = 4.7 \times 10^6$ L·mol^{-1}·s^{-1}; and finally, with eq A15 and $k_{dec} = 3.8 \times 10^{-5}$ s^{-1}, it is possible to calculate $k_{tr} = 1.3 \times 10^5$ L·mol^{-1}·s^{-1}; $k_c = 4.6 \times 10^6$ L·mol^{-1}·s^{-1} and $K = 3.0 \times 10^{-10}$ mol·L^{-1}. In the latter case, equation (A15) simplifies into $k_{dec} = Kk_{tr}$ and both situations (first or second-order decomposition reaction) lead to the same results for K and k_c, respectively. All the data are gathered in Table 4 with those already reported for P-TEMPO. It is quite interesting to note that K is very

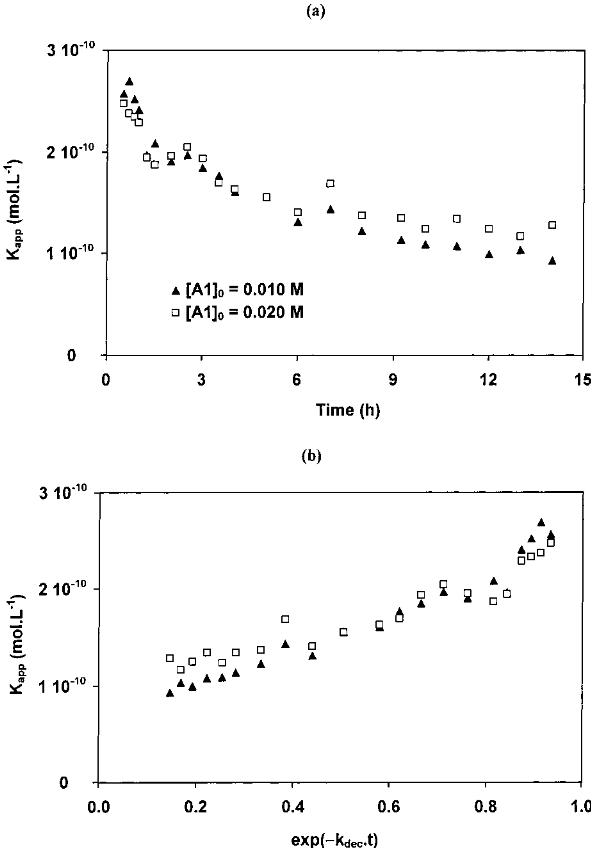


Figure 11. Apparent equilibrium constant K_{app} as a function of time (a) and of exp($-k_{dec}t$) (b) for the bulk polymerization of styrene at 130 °C initiated by bisalkoxyamine **A1** at two initial concentrations (0.010 and 0.020 M), using $k_{dec} = 3.8 \times 10^{-5}$ s^{-1}.

Table 4. Kinetic Parameters at 130 °C for PNNP and P-TEMPO Alkoxyamines

	P-TEMPO	PNNP
k_d (s^{-1})	2.5×10^{-3}, ref 31 5.6×10^{-3}, ref 30	1.4×10^{-3}
k_c (L·mol^{-1}·s^{-1})	1.2×10^{8}, ref 31	4.6×10^{6}
K (mol·L^{-1})	2.1×10^{-11}, ref 31	3.0×10^{-10}
k_{dec} (s^{-1})	8.4×10^{-6}, ref 34	3.8×10^{-5}
k_{tr} (L·mol^{-1}·s^{-1})	$k_{dec}/K = 4.0 \times 10^{5}$	1.3×10^{5}

large in this system and k_c is very small in comparison with the values reported for P-TEMPO ($K = 2.1 \times 10^{-11}$ mol·L^{-1} and $k_c = 1.2 \times 10^{8}$ L·mol^{-1}·s^{-1}).[31] This result can be explained by steric hindrance of the nitroxide counterradical PNN$^•$, which is a polymeric species. The same trend was previously observed for the polymeric nitroxides, which were shown to be less efficient at trapping propagating radicals than the classical mono-nitroxides.[13]

When plotting K_{app} as a function of exp($-k_{dec}t$), one cannot get a perfectly linear evolution (Figure 11b) as anticipated by eq V. This makes it difficult to accurately determine K' according to this equation. The trend however indicates that K' is quite smaller than K, which is actually not unexpected. Indeed, equilibrium 6 concerns the small nitroxide HNN$^•$, which should not behave very differently from TEMPO, as it has a similar structure. The imperfect linearity of K_{app} with exp($-k_{dec}t$) might be the consequence of a change in the value of K (coming from a change in k_c) with the progress of monomer conversion and the increase in viscosity. Indeed, recombination is a bimolecular reaction between two macromolecules of the same size, namely PNN$^•$ and P$^•$, and, also admitted for k_t,[40] k_c might be chain-length dependent (k_c would decrease and K would increase with the increase of chain length, and hence with conversion).

6. Effect on Polymerization Kinetics of the Existence of Two Simultaneous Equilibria. It was shown in Figure 3 that the polymerization rate was almost independent of the initial concentration of **A1**. This was not surprising as polymerization was conducted at 130 °C, where thermal auto-initiation of styrene cannot be neglected. However, the concentration of P$^•$ significantly decreased throughout the polymerization reaction, whereas Fukuda demonstrated that only a slight decrease could be observed in TEMPO-mediated polymerization of styrene, owing to the decrease of R_i with monomer consumption (reaction 7, Scheme 3).[24,41] The pronounced decrease in our system is concomitant with an increase in the concentration of free nitroxide (Figure 9). Such a continuous increase in the concentration of the persistent radical with time is the signature of the so-called persistent radical effect (PRE),[42] which is usually concealed when only thermal auto-initiation governs the kinetics.[24,32] Indeed, the continuous thermal generation of radicals contributes to the creation of new chains, which in turn are capped by free nitroxide molecules released upon termination of propagating radical. This effect levels off the nitroxide concentration, while the natural trend would be a continuous built up. In our system, however, the behavior is somewhat different. Figure 9 illustrates the continuous increase in nitroxide concentration with polymerization time. Furthermore, it proves it was dependent on the initial concentration of **A1**. This could be anticipated from eq IV which points out that a direct proportionality should exist between [N$^•$] and the concentration of living chains, providing that [P$^•$] is independent of this concentration. Actually, the concentration of released nitroxide approximately doubled when the initial concentration of **A1** was multiplied by 2. All these results show quite clearly that the kinetics of our system can be perfectly described neither by the PRE (the polymerization rate does not depend on [**A1**]$_0$, [N$^•$] is not proportional to [**A1**]$_0^{2/3}$)[42] nor by the simple steady state induced by thermal auto-initiation ([P$^•$] and [N$^•$] are not constant). It is also noticeable in Figure 9 and Table 3 that the concentration of released nitroxide was approximately 1 order of magnitude larger than that usually observed in TEMPO-mediated polymerization of styrene.[24] This last result can be explained by a larger value of the equilibrium constant K of reaction 5, with respect to that observed in the P-TEMPO system. However, as the apparent equilibrium constant, K_{app}, decreases from K to K' throughout the reaction owing to the existence of equilibrium 6 (Scheme 3), the system is shifted toward the formation of a larger proportion of dormant species. The buildup of free nitroxide is not as large as it would have been in a simple system with a single activation−deactivation equilibrium. The behavior of our system is between that observed for the polymerization of styrene mediated by the acyclic nitroxide SG1 (*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide), for which the kinetics was shown to be regulated by the PRE owing to a large equilibrium constant[43] and TEMPO-mediated polymerization, the kinetics of which is governed by thermal auto-initiation.[24]

7. Discussion on the Mechanism of the Decomposition Reaction of the Alkoxyamine End Group. In the binitroxide-mediated polymerization of styrene studied in this work, one of the main features is the fast decomposition of the alkoxyamine end group, as compared with TEMPO-mediated polymerization. From a kinetic viewpoint, this decomposition reaction can be seen either as a first-order reaction or as a second-order one, without any possible distinction.[38] If formation of the dead chains followed a unimolecular mechanism, because chemical structure of the polymeric bisalkoxyamines studied is similar to that of P-TEMPO, the rate constants of decomposition, k_{dec}, would not be so different. For comparison, the rate constants of homolytic dissociation, k_d, for both alkoxyamines were quite similar. If, in contrast, decomposition is a bimolecular reaction between propagating radical and nitroxide, then the reason for different kinetics can be more easily explained. Indeed, the large activation–deactivation equilibrium constant of reaction 5 allows in the system the simultaneous existence of a high concentration of both $P^\bullet$ and $PNN^\bullet$. Thus, even if the rate constant k_{tr} of the hydrogen abstraction reaction is not different in this system from that observed in the P-TEMPO system (it is even lower; see Table 4), the apparent first-order rate constant k_{dec}, which equals $k_{tr}.K$ can be significantly larger if K is larger. At 110 °C, the two-arm structure is more stable, because of a lower value of $k_{tr}K$.

Conclusion

The use of binitroxides, with both radical sites of similar reactivity, as mediator in the controlled radical polymerization of styrene was examined and the rate constants of the variously involved reactions were determined at 130 °C. The typical features of a controlled polymerization were observed in the early stage of the polymerization, leading to the formation of two-arm macromolecules containing the binitroxide at the core. Then a deviation occurred owing to continuous irreversible termination leading to unsaturated polymer and hydroxylamine. This behavior was particularly observed in the SEC traces, with a bimodal distribution assigned to a mixture of two-arm and one-arm macromolecules. After irreversible separation, the one-arm macromolecules formed were of two kinds: $P^{=}$ (dead chains with terminal unsaturation) and PNNH (living chains with a hydroxylamine attached to the nitroxide moiety). The apparent first-order rate constant of the decomposition reaction was much larger than in TEMPO-mediated polymerization of styrene. In contrast, the rate constants of the reversible dissociation of the low molar mass model bisalkoxyamine (SNNS, **A1**) and of the polymeric bisalkoxyamines (PNNP) were not very different from each other, and not very different from those determined for S-TEMPO or P-TEMPO, indicating no strong effect of chain length, neither from the alkyl radical ($P^\bullet$), nor from the nitroxide ($PNN^\bullet$). In contrast, the rate constant of recombination between a propagating radical $P^\bullet$ and a macromolecular counterradical $PNN^\bullet$ was shown to be much lower than with the modified counterradical $HNN^\bullet$ and lower than with TEMPO, indicating a strong effect of the nitroxide size. This resulted in a large activation–deactivation equilibrium constant and a high concentration of free nitroxide in the system. As a consequence, chain-end decomposition was supposed to be a second-order reaction, i.e., β-hydrogen transfer from $P^\bullet$ to $PNN^\bullet$, rather than a first-order decomposition of PNNP. The strong enhancement of this reaction in binitroxide-mediated CRP of styrene was assigned to the large concentrations of both propagating and persistent radicals. For these reasons, the use of multinitroxides in radical polymerization does not allow the synthesis of well-defined multiarm macromolecules at large monomer conversion. The quality of the structure can however be improved when polymerization is performed at a temperature of 110 °C, instead of 130 °C.

Appendix. Overall Nitroxide Concentration and Apparent Activation–Deactivation Equilibrium Constant for Two Different Cases

(i) Case of a First-Order Irreversible Decomposition Reaction. Consider reactions 5, 6, 7, 8, 10, and 12 depicted in Scheme 3. The rate of evolution of the concentration of propagating radicals is

$$\frac{d[P^\bullet]}{dt} = R_i + k_d[PNNP] + k'_d[HNNP] - (k_c[PNN^\bullet] + k'_c[HNN^\bullet])[P^\bullet] - k_t[P^\bullet]^2 = 0 \quad (A1)$$

according to the kinetic treatment proposed by Fukuda when thermal initiation takes place.[24]

The true first-order decomposition of the alkoxyamine leads to the following rate and concentration equations:

$$\frac{d[PNNP]}{dt} = -k_{dec}[PNNP]_t \quad (A2)$$

$$[PNNP]_t = [\mathbf{A1}]_0 \exp(-k_{dec}t) \quad (\text{with } [\mathbf{A1}]_0 = [PNNP]_0) \quad (A3)$$

$$[HNNP]_t = [\mathbf{A1}]_0 - [PNNP]_t = [\mathbf{A1}]_0 (1 - \exp(- k_{dec}t)) \quad (A4)$$

For simplicity, the decomposition reaction of HNNP into HNNH (reaction 12) was neglected, assuming that it would decompose very slowly, such as P-TEMPO.

Owing to thermal auto-initiation, the concentration of propagating radicals is

$$[P^\bullet] = \sqrt{\frac{R_i}{k_t}} \quad (A5)$$

independent of the initial concentration of alkoxyamine initiator in the system, providing that both equilibria 5 and 6 are established:

$$[PNN^\bullet] = \frac{K[PNNP]_t}{[P^\bullet]} = \frac{K[\mathbf{A1}]_0 \exp(-k_{dec}t)}{[P^\bullet]} \quad \text{equilibrium 5} \quad (A6)$$

and

$$[HNN^\bullet] = \frac{K'[HNNP]_t}{[P^\bullet]} = \frac{K'[\mathbf{A1}]_0(1 - \exp(- k_{dec}t))}{[P^\bullet]} \quad \text{equilibrium 6} \quad (A7)$$

The overall concentration of free nitroxide reads then

$$[\mathrm{N}^\bullet] = [\mathrm{PNN}^\bullet] + [\mathrm{HNN}^\bullet] = \frac{K[\mathrm{PNNP}]_t + K'[\mathrm{HNNP}]_t}{[\mathrm{P}^\bullet]} = \frac{(K - K')[\mathbf{A1}]_0 \exp(-k_{\mathrm{dec}}t) + K'[\mathbf{A1}]_0}{[\mathrm{P}^\bullet]} \quad (\mathrm{A8})$$

An apparent equilibrium constant can be deduced:

$$K_{\mathrm{app}} = [\mathrm{N}^\bullet][\mathrm{P}^\bullet]/[\mathbf{A1}]_0 = (K - K') \exp(-k_{\mathrm{dec}}t) + K' \quad (\mathrm{A9})$$

(ii) Case of a Second-Order Irreversible Decomposition Reaction. Consider now reactions 5, 6, 7, 8, 9, and 11. The hydrogen transfer reaction affects the rate of evolution of [P•] and the concentration of nitroxide in the following way:

$$\frac{\mathrm{d}[\mathrm{P}^\bullet]}{\mathrm{d}t} = R_i + k_{\mathrm{d}}[\mathrm{PNNP}] + k'_{\mathrm{d}}[\mathrm{HNNP}] - (k_{\mathrm{c}} + k_{\mathrm{tr}}) [\mathrm{PNN}^\bullet][\mathrm{P}^\bullet] - (k'_{\mathrm{c}} + k'_{\mathrm{tr}})[\mathrm{HNN}^\bullet][\mathrm{P}^\bullet] - k_t[\mathrm{P}^\bullet]^2 = 0 \quad (\mathrm{A10})$$

$$\frac{\mathrm{d}[\mathrm{PNN}^\bullet]}{\mathrm{d}t} = k_{\mathrm{d}}[\mathrm{PNNP}] - (k_{\mathrm{c}} + k_{\mathrm{tr}})\,[\mathrm{PNN}^\bullet][\mathrm{P}^\bullet] = 0 \quad (\mathrm{A11})$$

$$[\mathrm{PNN}^\bullet]_t = \frac{k_{\mathrm{d}}[\mathrm{PNNP}]_t}{(k_{\mathrm{c}} + k_{\mathrm{tr}})[\mathrm{P}^\bullet]} \quad (\mathrm{A12})$$

In this case, the decomposition rate of the PNNP alkoxyamine is a true second-order reaction, which can be written as an apparent first-order reaction

$$\frac{\mathrm{d}[\mathrm{PNNP}]}{\mathrm{d}t} = -k_{\mathrm{tr}}[\mathrm{PNN}^\bullet][\mathrm{P}^\bullet] = \frac{-k_{\mathrm{tr}}k_{\mathrm{d}}}{(k_{\mathrm{c}} + k_{\mathrm{tr}})}[\mathrm{PNNP}]_t \quad (13)$$

$$[\mathrm{PNNP}]_t = [\mathbf{A1}]_0 \exp(-\,k_{\mathrm{dec}}t) \quad (\mathrm{A14})$$

with the apparent rate constant

$$k_{\mathrm{dec}} = \frac{k_{\mathrm{tr}}k_{\mathrm{d}}}{(k_{\mathrm{c}} + k_{\mathrm{tr}})} \quad (\mathrm{A15})$$

Then, eq A12 reads as follows:

$$[\mathrm{PNN}^\bullet]_t = \frac{k_{\mathrm{d}}[\mathbf{A1}]_0 \exp(-k_{\mathrm{dec}}t)}{(k_{\mathrm{c}} + k_{\mathrm{tr}})[\mathrm{P}^\bullet]} \quad (\mathrm{A16})$$

The evolution with time of the other nitroxide, HNN•, is given by

$$\frac{\mathrm{d}[\mathrm{HNN}^\bullet]}{\mathrm{d}t} = k'_{\mathrm{d}}[\mathrm{HNNP}] - (k'_{\mathrm{c}} + k'_{\mathrm{tr}})[\mathrm{HNN}^\bullet][\mathrm{P}^\bullet] = 0 \quad (\mathrm{A17})$$

$$[\mathrm{HNN}^\bullet]_t = \frac{k'_{\mathrm{d}}[\mathrm{HNNP}]_t}{(k'_{\mathrm{c}} + k'_{\mathrm{tr}})[\mathrm{P}^\bullet]} \quad (\mathrm{A18})$$

$$\frac{\mathrm{d}[\mathrm{HNNP}]}{\mathrm{d}t} = k_{\mathrm{tr}}[\mathrm{PNN}^\bullet][\mathrm{P}^\bullet] - k'_{\mathrm{tr}}[\mathrm{HNN}^\bullet]\,[\mathrm{P}^\bullet] = \frac{k_{\mathrm{tr}}k_{\mathrm{d}}}{(k_{\mathrm{c}} + k_{\mathrm{tr}})}[\mathrm{PNNP}]_t - \frac{k'_{\mathrm{tr}}k'_{\mathrm{d}}}{(k'_{\mathrm{c}} + k'_{\mathrm{tr}})}[\mathrm{HNNP}]_t \quad (\mathrm{A19})$$

As previously, for simplicity, the second term was finally neglected, considering that the decomposition of HNNP was sufficiently slow in the system so as not to interfere. This gives then

$$[\mathrm{HNNP}]_t = [\mathbf{A1}]_0\,(1 - \exp(-\,k_{\mathrm{dec}}t)) \quad (\mathrm{A20})$$

and

$$[\mathrm{HNN}^\bullet]_t = \frac{k'_{\mathrm{d}}[\mathbf{A1}]_0(1 - \exp(-k_{\mathrm{dec}}t))}{(k'_{\mathrm{c}} + k'_{\mathrm{tr}})[\mathrm{P}^\bullet]} \quad (\mathrm{A21})$$

This situation does not change the concentration of propagating radicals, which remains as given in eq A5.

The overall concentration of free nitroxide reads then

$$[\mathrm{N}^\bullet] = [\mathrm{PNN}^\bullet] + [\mathrm{HNN}^\bullet] = \frac{k_{\mathrm{d}}[\mathbf{A1}]_0 \exp(-k_{\mathrm{dec}}t)}{(k_{\mathrm{c}} + k_{\mathrm{tr}})[\mathrm{P}^\bullet]} + \frac{k'_{\mathrm{d}}[\mathbf{A1}]_0(1 - \exp(-k_{\mathrm{dec}}t))}{(k'_{\mathrm{c}} + k'_{\mathrm{tr}})[\mathrm{P}^\bullet]} \quad (\mathrm{A22})$$

and the apparent equilibrium constant is

$$K_{\mathrm{app}} = [\mathrm{N}^\bullet][\mathrm{P}^\bullet]/[\mathbf{A1}]_0 = \frac{k_{\mathrm{d}} \exp(-k_{\mathrm{dec}}t)}{(k_{\mathrm{c}} + k_{\mathrm{tr}})} + \frac{k'_{\mathrm{d}}(1 - \exp(-k_{\mathrm{dec}}t))}{(k'_{\mathrm{c}} + k'_{\mathrm{tr}})} \quad (\mathrm{A23})$$

$$K_{\mathrm{app}} = \left(\frac{\mathrm{K}}{1 + \dfrac{k_{\mathrm{tr}}}{k_{\mathrm{c}}}} - \frac{K'}{1 + \dfrac{k'_{\mathrm{tr}}}{k'_{\mathrm{c}}}}\right) \exp(-k_{\mathrm{dec}}t) + \frac{K'}{1 + \dfrac{k'_{\mathrm{tr}}}{k'_{\mathrm{c}}}} \quad (\mathrm{A24})$$

which is the same as eq A9 when k_{tr} is small with respect to k_{c} (in such a case eq A15 becomes: $k_{\mathrm{dec}} = Kk_{\mathrm{tr}}$) and k'_{tr} is small with respect to k'_{c}.

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