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Nitroxide mediated polymerization using diphenyl azabutane *N*-oxides. A study of electronic effects and of the [nitroxide]/[initiator] ratio on the polymerization control

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Abstract

3,3-dimethyl-1,1-diphenyl azabutane-*N*-oxides with electron-releasing and electron-withdrawing substituents in one of the aromatic rings were synthesized and their effect on styrene polymerization was assessed. Styrene polymerization kinetic experiments were carried out in bulk at 100 and 120 °C with BPO or AIBN as initiators and diphenyl-azabutane type nitroxides as mediators. Results were compared with the kinetics using the preformed alkoxyamine. Different [nitroxide]/[initiator] ratios were evaluated at 100 °C and the optimum ratio = 1.75 was found. Polydispersities between 1.2 and 1.4 were obtained for polystyrene of M_n up to 25,000. Experiments to obtain molecular weights around 120,000 were also carried out using oligomeric alkoxyamines as mediators. The calculated equilibrium constant (K) of the styrene polymerization at 120 °C with diphenyl azabutane as mediator is larger than the previously reported for TEMPO **1**, and similar to the reported for TIPNO **2** and DEPN **3**, The polymerization with these nitroxides is faster than the polymerization using other nitroxides and substituents on the aromatic ring have no important effect on the control of polymerization; these experimental results agree with some electronic parameters obtained from molecular modeling of the nitroxides through semiempirical methods.

Keywords: Living free radical polymerization; Nitroxide; Nitroxide mediated polymerization

1. Introduction

After the initial work with TEMPO **1** (Scheme 1) by Rizzardo and Solomon [1], Georges et al. [2] used a bicomponent system: BPO as initiator and TEMPO, to obtain polystyrene with high molecular weight and narrow polydispersity; this method was unsuccessful for processing acrylates. They observed that the addition of camphorsulfonic acid and other additives increases the polymerization rates [3]. Recently, the use of 2,2,5-trimethyl-4-phenyl-3-azahexane nitroxide (TIPNO) **2** [4] and of *N*-*t*-butyl-diethyl-posphono-2,2-dimethyl propyl nitroxide (DEPN) **3** [5] (Scheme 1) were proposed to polymerize polystyrene, acrylates and other monomers in the searching of advanced materials [6].

According to the proposed mechanism for the controlled radical polymerization [7], the success of the control by nitroxides depends on the coupling (k_c) and on the dissociation constants (k_d) (Scheme 2) which are determined by the nitroxide and the propagating radical structures [9,10]: the dissociation constant increases by enlarging the ring size of cyclic nitroxides and by using open chain nitroxides.

The stability of a nitroxide radical depends on its electronic structure: delocalization of the unpaired electron over the N–O bond ($=\text{N–O}\cdot \leftrightarrow =\text{N}^{+\cdot}\text{–O}^-$) provides thermodynamic stability to the radical and the steric hindrance of bulky substituents attached to the nitrogen atom inhibit the nitroxide from participating in decomposition reactions [11]. On the other hand, according to Keana [12], the stability of a nitroxide radical decreases when one or more hydrogen atoms are linked to the α carbon to the nitrogen, for the possibility of a bimolecular decomposition.

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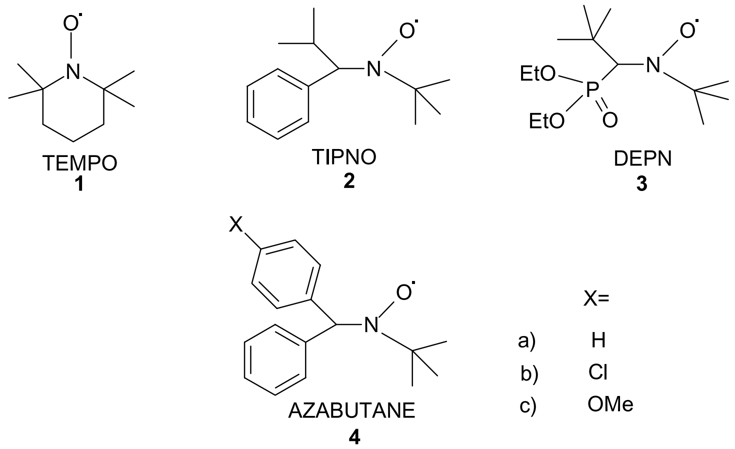
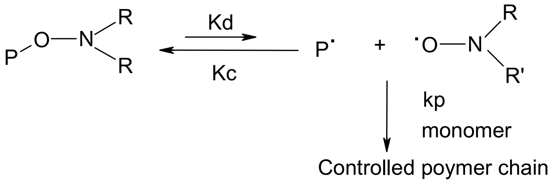


Scheme 1.

The effect of changing the TIPNO's isopropyl group for a substituted or non-substituted aromatic ring, on the nitroxides performance as polymerization mediators was studied in this work. To this end, nitroxides of diphenyl azabutane type (**4**) [13] with different substituents in one of the aromatic rings were synthesized, with the intention to assess the influence of the ring substituents on the dissociation energy of the C–O bond of polymeric alkoxyamines, on the stability of the produced radicals and on the control of polymerization carried out in their presence. A study of the optimum [nitroxide]/[initiator] ratio in a bicomponent system was also carried out.



Scheme 2.

2. Experimental section

Chemicals were acquired from commercial sources. Benzaldehyde and substituted benzaldehydes were distilled before using. THF was distilled from metallic sodium for drying. Hydrogen and carbon nuclear magnetic resonance spectroscopy were carried out in a Varian Unity 300 spectrometer. Pentafluorophenyl hydrazine [4] was used for the characterization of nitroxides by ^{1}H and ^{13}C NMR. FT-IR spectra were determined in a 1605 Perkin Elmer spectrometer. Mass spectrometry in a JEOL SX-102-A spectrometer with a direct inlet using FAB + method with 3-nitrobenzyl alcohol as matrix. Polymer molecular weights were determined by gel permeation chromatography in a liquid chromatographer equipped with a Waters 410 refractometer and styragel HR3,HR4 and HR5 columns, using THF as eluent.

Molecular modeling was performed using the standard Hyperchem package [14]. Molecular mechanics (MM +) and the semiempirical methods AM1 and PM3 were used as supplied by Hypercube. Calculations were performed initially with MM + and then with AM1 and PM3. All geometries were completely optimized to 0.01 convergence.

2.1. General procedure for the synthesis of imines

Freshly distilled *t*-butylamine (1 equiv.) and benzaldehyde or a substituted benzaldehyde (1 equiv.) was stirred without solvent in the presence of sodium sulfate (1 equiv.) during 8 h at room temperature. Diethyl ether was added to isolate the products. After filtration, the products were distilled. Yields, boiling points and spectroscopic constants are reported.

2.1.1. *t-Butyl-benzylidene-amine (**7a**)*

From 15 g (0.2 mol) of *t*-butylamine, 22.3 g (0.2 mol) of benzaldehyde and 30 g. (0.2 mol) of sodium sulfate. 87% yield. Colorless liquid. Bp 46 °C/4 mmHg. FT-IR (film) cm^{-1}: 3062, 2968, 1642, 1451, 1202, 1072 and 754. ^{1}H NMR (δ, ppm) (90 MHz CDCl$_3$) (ppm): 1.3 (s, 9H, *t*-but), 7.4 (m, 3H, arom.), 7.8 (m, 2H, arom.), and 8.3 (s, 1H, N=C–H).

2.1.2. *t-Butyl-(4-chloro)-benzylidene-amine (**7b**)*

From 0.94 g (12.8 mmol) of *t*-butylamine and 1.5 g (10.7 mmol) 4-chloro-benzaldehyde. 85% yield. Colorless liquid. Bp 77 °C/2 mmHg. FT-IR (film) cm^{-1}: 2967, 1642, 1593, 1488, 1359, 1202, 1084 and 821. ^{1}H NMR (90 MHz CDCl$_3$) (δ, ppm):1.28 (s, 9H, *t*-but), 7.3 (d, 2H, $J = 8$ Hz, arom.), 7.7 (d, 2H, $J = 8$ Hz, arom.) and 8.2 (s, 1H, N=C–H).

2.1.3. *t-Butyl-(4-methoxy)-benzylidene-amine (**7c**)*

From 6.0 g (82.2 mmol) of *t*-butylamine and 11.19 g (82.2 mmol) of 4-anisaldehyde. 80% yield. Colorless liquid. Bp 116 °C/5 mmHg. FT-IR (film) cm^{-1}: 2966, 2836, 1640, 1250, 1034 and 831. ^{1}H NMR (90 MHz $CDCl_3$) (δ, ppm): 1.24 (s, 9H, *t*-but), 3.8 (s, 3H, O–Me), 6.9 (d, 2H, $J = 8$ Hz, arom.), 7.75 (d, 2H, $J = 8$ Hz, arom.), and 8.25 (s,1H, N=C–H).

2.2. General procedure for the reduction of imines to amines [15]

Sodium borohydride (0.5 equiv.) was slowly added to a 5–10% methanol solution of *t*-butyl-benzylidene-amine (1 equiv.), in a flask fitted with stirrer and reflux condenser. After the addition, the mixture was refluxed for 30 min. Cold water was added with stirring to the reaction mixture. After methanol evaporation, the aqueous layer was extracted with ether, the extracts dried with sodium sulfate and the solvent evaporated. The amine was used without further purification.

2.2.1. t-Butyl-benzyl amine (**8a**)

From 1.64 g (51.9 mmol) of *t*-butyl-benzylidene-amine and 0.5 g (13.5 mmol) of $NaBH_4$. Yield: 84%. Colorless liquid. Bp 80 °C/5 mmHg. FT-IR (film)(cm^{-1}): 3308, 3027, 2963, 1494, 1452, 1362, 1230, 1217, 1026, 731, 606. ^{1}H NMR (90 MHz $CDCl_3$) (δ, ppm): 1.2 (s, 9H, *t*-but), 3.75 (s, 2H, N–C–H), 4.65 (s, 1H, N–H) and 7.25 (m, 5H, arom.).

2.2.2. t-Butyl-(4-chloro)-benzyl amine (**8b**)

From 1.64 g (8.90 mmol) of *t*-butyl-(4-chloro)-benzylidene-amine and 0.1 g (2.7 mmol) of $NaBH_4$. Yield: 85%. Colorless liquid. Bp 74 °C/2 mmHg. FT-IR (film) (cm^{-1}): 2965, 2868, 1491, 1364, 1216, 1092, 1015 and 808. ^{1}H NMR (90 MHz $CDCl_3$) (δ, ppm): 1.15 (s, 9H, *t*-but), 3.68 (s, 2H, N–C–H), 4.66 (s, 1H, N–H), 7.3 (s, 4H, arom.).

2.2.3. t-Butyl-(4-methoxy)-benzyl amine (**8c**)

From 4.2 g (22.0 mmol) t-butyl-(4-methoxy)-benzylidene-amine and 0.2 g (5.4 mmol) of $NaBH_4$. Yield: 82%. Colorless liquid. Bp 71 °C/2 mmHg. FT-IR (film) (cm^{-1}): 2961, 2833, 1613, 1512, 1245, 1172, 1037, 822 and 734. ^{1}H NMR (90 MHz $CDCl_3$) (δ, ppm): 1.2 (s, 9H, *t*-but), 3.7 (s, 2H, N–C–H), 3.8 (s, 3H, O–Me), 4.5 (s, 1H, N–H) 6.8 (d, 2H, $J = 8$ Hz, arom.) and 7.25 (d, 2H, $J = 8$ Hz, arom.).

2.3. General procedure for the synthesis of t-butyl-phenyl-nitrones

A 30% aqueous hydrogen peroxide (3 equiv.) was added dropwise to an ice cooled methanol solution of *t*-butyl-benzyl amine (1 equiv., 0.34 mol) and 0.2 equiv. sodium tungstate dihydrate. The mixture was stirred for 3 h at room temperature. Methanol was evaporated and substituted by dichloromethane. This solution was washed twice with brine and dried with sodium sulfate. After solvent evaporation, the residue was purified by column chromatography in alumina using hexane/ethyl acetate 97/3 as eluant; the afforded *t*-butyl phenyl nitrone was recrystallized from hexane.

2.3.1. t-Butyl-phenyl nitrone (**9a**)

From 1.50 g (9.20 mmol) of *t*-butyl-benzyl-amine, 0.1 g (0.34 mmol) of sodium tungstate dihydrate and 2.6 ml (27.6 mmol) of 30% hydrogen peroxide. Yield: 89%. White crystals. Mp 73–74 °C. IR (KBr pellet) (cm^{-1}): 3081, 2972, 1579, 1444, 1365, 1193, 1117, 759 and 696. ^{1}H NMR (300 MHz $CDCl_3$)(δ, ppm)): 1.62 (s, 9H, *t*-but), 7.54 (s, 1H, N=C–H), 7.4 (m, 3H, arom.) and 8.29 (m, 2H, arom.).

2.3.2. t-Butyl-(4-chlorophenyl) nitrone (**9b**)

From 1.8 g (9.1 mmol) *t*-butyl-(4-chloro)-benzyl-amine, 0.10 g (0.32 mmol) of sodium tungstate dihydrate and 3.1 ml (27.3 mmol) of 30% hydrogen peroxide solution. Yield: 92%. White crystals. Mp 70–72 °C. IR (KBr pellet) cm^{-1}): 3071, 2975, 1548, 1454, 1361, 1126, 830 and 507. ^{1}H NMR (300 MHz $CDCl_3$) (δ, ppm): 1.6 (s, 9H, *t*-but), 7.33 (s, 1H, N=C–H), 7.5 (d, 2H, $J = 7.5$ Hz, arom.) and 8.25 (d, 2H, $J = 7.5$ Hz arom.)

2.3.3. t-Butyl-(4-methoxyphenyl) nitrone (**9c**)

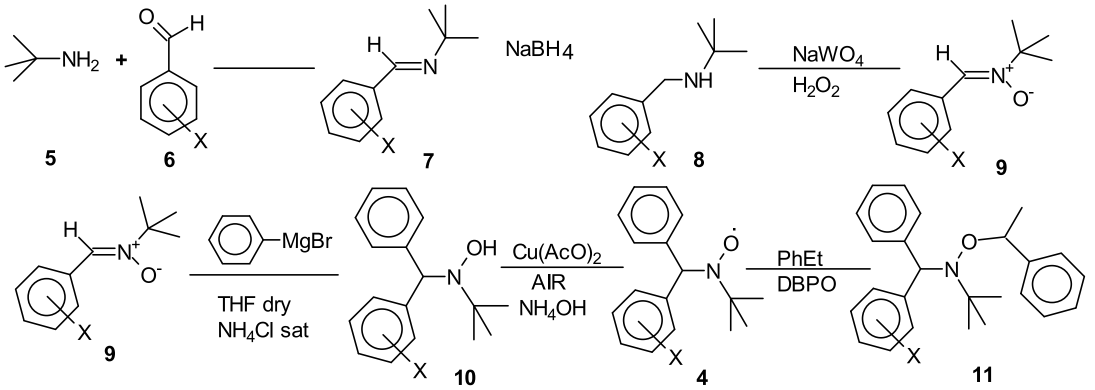
From 4.0 g (20.7 mmol) of *t*-butyl-4 methoxy-benzyl amine, 0.27 g (0.80 mmol) of sodium tungstate dihydrate and 7.0 ml (62.1 mmol) of 30% hydrogen peroxide solution. Yield: 80%. White crystals. Mp 80–82 °C. IR (KBr pellet) cm^{-1}: 2975, 2837, 1603, 1562, 1463, 1361, 1170, 1030, 841 and 530. ^{1}H NMR (300 MHz $CDCl_3$) (δ, ppm): 1.6 (s, 9H, *t*-but), 3.83 (s, 3H, O–Me), 6.9 (d, 2H $J = 9$ Hz, arom.), 7.46 (s, 1H, N=C–H) and 8.2 (d, 2H, $J = 9$ Hz, arom.).

2.4. General procedure for the synthesis of azabutane nitroxide radicals

Magnesium (1 equiv.) and a crystal of iodine were placed in a dry round three necked flask, with reflux system and nitrogen atmosphere. A dry 0.2 M THF solution of the aromatic bromide (1 equiv.) was added with stirring until the disappearance of the magnesium. This reagent was dropped through a cannula into a solution of *t*-butyl phenyl nitrone (0.33 equiv. 2 M) in THF. The stirring was continued 2 h after the addition. The reaction product was poured on ice and treated to pH 6 with saturated ammonium chloride solution, maintaining the temperature below 30 °C. Ether extraction, drying with sodium sulfate and solvent evaporation produced the corresponding hydroxylamines. The method reported by Hawker [4] was used to oxidize the hydroxylamine to the nitroxide radical.

2.4.1. 3,3-dimethyl-1,1-diphenyl-2-azabutane-N-oxide (**4a**)

From 12.7 g (81.0 mmol) bromobenzene and 4.8 g (27.1 mmol) *t*-butyl-phenyl-nitrone. Yield: (80%). Yellow crystals. Mp 95–96 °C. FT-IR (KBr pellet) (cm^{-1}): 3025, 2976, 1596, 1494, ^{1}H NMR (ppm): 1.15 (s, 9H, *t*-but), 5.25 (s, 1H, N–C–H), 7.3 (m, 5H, arom.) and 7.55 (m, 5H,



X= a) H, b) Cl, and c) MeO.

Scheme 3.

arom.). ^{13}C NMR (75.5 MHz $CDCl_3$, (δ, ppm): 142.90, 129.19, 128.05, 126.72, 69.09, 59.97, 26.99). MS *m/z* (dimer): 507 (M + , 2), 254 (20), 198 (35), 167 (100).

2.4.2. 3,3-Dimethyl-1-phenyl-1-(4-chlorophenyl)-azabutane-N-oxide (**4b**)

From 8.9 g (56.6 mmol) bromobenzene and 4 g (18.9 mmol) of *t*-butyl-(4-chlorophenyl)-nitrone. Yield: (85%). Yellow crystals. Mp 97–98 °C. FT-IR: (KBr pellet) (cm^{-1}): 3025, 2979, 1599, 1490, 1366, 1190, 749, 701, 574). ^1H NMR (300 MHz $CDCl_3$, in the presence of pentafluorophenyl hydrazine). (δ, ppm): 1.05 (s, 9H, *t*-but), 5.15 (s, 1H, N–C–H) and 7.3 (m, 9H, arom.). ^{13}C NMR (75.5 MHz ($CDCl_3$)(δ, ppm) 142.36, 141.47, 132.51, 130.57, 129.10, 128.15, 126.93, 68.23, 59.99, 26.98. MS *m/z* (dimer): 578 (M + , 1), 288 (10), 232 (5), 201 (100).

2.4.3. 3,3-Dimethyl-1-phenyl-1-(4-methoxyphenyl) azabutane-N-oxide (**4c**)

From 5.9 g (37.6 mmol) bromo-benzene and 2.6 g (12.6 mmol) *t*-butyl (4-methoxyphenyl)-nitrone. Yield 83%. Yellow crystals. Mp 92–93 °C. FT-IR (KBr pellet) (cm^{-1}): 3063, 2975, 1610, 1511, 1244, 1179, 817 and 693. ^1H NMR (300 MHz $CDCl_3$, (δ, ppm): 1.1 (s, 9H, *t*-but), 3.8 (s, 3H, O–Me), 5.15 (s, 1H, N–C–H), 7.15 (dd, 4H, arom.) and 7.35 (m, 5H, arom.). ^{13}C NMR (75.5 MHz $CDCl_3$ (ppm): 158.42, 143.37, 134.71, 130.44, 128.94, 128.00, 126.57, 113.39, 68.27, 59.84, 55.12, 26.99. MS *m/z* (: 481 (M + , 1) (nitroxide bonded to the most stable fragment) 285 (1), 228 (2), 197 (100).

2.4.4. O-(1-Phenyl-ethyl)- 3,3-dimethyl-1,1-diphenyl-2-azabutane-N-oxide (**10**)

This alkoxyamine was obtained by the Miura procedure [16] from 0.20 g (0.80 mmol) of nitroxide **1** and 0.20 g (8.5 mmol) *t*-butyl peroxyoxalate [17] and 5 ml (44.3 mmol) ethyl benzene. The alkoxyamine was purified on a silica gel column, using hexane: ethyl acetate as eluent. Colorless oil. Yield 67%. FT-IR (film) (cm^{-1}): 2973, 1451, 1362, 1208, 1077, 3085, 735, 698. ^1H NMR (CDCl3) (δ, ppm): 0.95 (s, 9H), 1.4 (d, 3H), 4.4 (q, 1H), 5.4 (s, 1H), 7.25 (wide band 5H). MS *m/z* 360 (M + , 1) (1) 302 (M − , 57) (1.5) 255 (14), 197 (100), 105 (24.5).

2.5. Styrene-oligomeric alkoxyamines

Purified styrene (9.1 g, 87.4 mmol), a diphenyl azabutane (0.53 mmol) and AIBN (35.0 mg, 0.21 mmol) were placed in a 20 ml flask. Oxygen was evacuated by bubbling nitrogen through a septum with another needle as gas exit. The flask was placed in an oil bath at 120 ± 5 °C during 4.5 h, reaching 20% of conversion. The oligomer was purified by precipitation with an excess of methanol, dried and analyzed by GPC. (Mn: 4047, PD: 1.15)

2.6. Styrene polymerization kinetics

Purified styrene (45.3 g. 0.435 mol), a diphenyl azabutane, and BPO or AIBN in different ratios were placed in a 100 ml flask for bicomponent systems. When an alkoxyamine was used as mediator, the amount of alkoxyamine was calculated according to the required molecular weight. Samples of 5 ml of this mixture were placed in ten 10 ml Wheaton glass vials, which were sealed with silicon septa and aluminum seals. Oxygen was evacuated from the samples after closing the vials, by bubbling nitrogen for 2 min through a syringe needle. Another needle was used as gas exit. Vials were placed in an oil bath at 100 or 120 ± 0.5 °C. Each vial was taken out of the bath at predetermined times, cooled in water and quenched with three drops of 1% hydroquinone solution. Samples of the polymer were analyzed to determine percent of conversion by evaporation of the residual monomer at atmospheric pressure. Molecular weights of the purified residual polymer were determined by gel permeation chromatography.

3. Results and discussion

3.1. Synthesis of phenyl azabutanes

Diphenyl azabutane nitroxides were obtained through a Grignard reaction on a 4-substituted phenyl *t*-butyl nitrone **9**. The resulting benzhydryl-*t*-butyl-hydroxyl amines were oxidized by air in the presence of copper acetate and ammonium hydroxide according to Hawker [4].

The synthesis of substituted and non-substituted nitrone intermediates **9** (Scheme 3) was carried out by a modification of the Murahashi [18] method with yields above 80%, from benzyl-*t*-butyl amines **8** which were obtained by sodium borohydride reduction [15] from the correspondent imines **7**. Sodium sulfate allowed the shifting of equilibrium toward the production of imines **7** by addition of substituted benzaldehydes **6** to *t*-butylamine **5**.

Nitroxides were characterized by spectroscopic methods. ^{1}H NMR in the presence of pentafluorphenyl hydrazine [4] shows, besides the aromatic and aliphatic protons, a singlet at 5.15–5.25 ppm corresponding to the proton α to the aromatic rings of the azabutane. ^{13}C NMR in the same conditions shows the expected signals: one signal for the methyl groups, two signals between 59.8 and 69.09 for the carbons bond to nitrogen, and the aromatic carbons between 143.36 and 113.49, depending of the substituents. Mass spectra using the FAB method, shows the molecular ion for each nitroxide at higher than the expected molecular weight: (507 and 578 for **4a** and **4b**, which have molecular weights 254 and 288, respectively), this ion results of the coupling of two molecules of nitroxide [8]. The molecular ion for **4c** (481) is the addition of a molecule of nitroxide with a *p*-methoxy-benzhydryl radical, the most stable fragment from decomposition of the nitroxide ($m/z = 201$).

Three different methods were tested for the preparation of the *O*-phenyl ethyl alkoxyamine **11** [8c,17] which was finally prepared using *t*-butyl peroxyoxalate, ethyl benzene and the diphenyl azabutane in the absence of oxygen. The ^{1}HNMR spectra of this alkoxyamine shows two signals at 4.05 and 4.25 ppm for the benzyl hydrogen, which were assigned to the possible diastereoisomers of the molecule [4] [19]. It is also noticeable in the HNMR spectra the presence of four different signals for methyl groups at 1.46, 1.18, 0.87 and 0.56 ppm [19]. The mass spectra of the alkoxyamine presents the fragment at 225 (the nitroxide), at 105 the phenyl ethyl group and at 167 the benzydryl group.

3.2. Styrene polymerization kinetics

4-Substituted-diphenyl azabutane nitroxides were evaluated in styrene polymerization in bulk at 100 and 120 °C. The study was initially carried out with a bicomponent system using AIBN or BPO as initiators with different [nitroxide]/[initiator] ratios and then with the preformed alkoxyamines.

3.3. Bicomponent systems

3.3.1. Benzoyl peroxide (BPO) as initiator

Nitroxides **4a** and **4b** (Scheme 1) were used as mediators in styrene polymerization at 120 °C with BPO as initiator in a 1.5 [nitroxide]/[BPO] ratio. Fig. 1 shows two slopes in the conversion plot, with a higher rate at low conversions; from 80 min onwards, the trend corresponds to a controlled polymerization. Although different curves were expected, due to the presence of groups that might stabilize the possible decomposition products, both have the same behavior. Fig. 2 shows the evolution of the molecular weight (M_n) and the polydispersity with the conversion. The dotted line in the figure corresponds to the theoretical molecular weight (M_n), with a 70% initiator's efficiency. The expected behavior for a controlled polymerization was observed, but the curve does not start from the origin as in

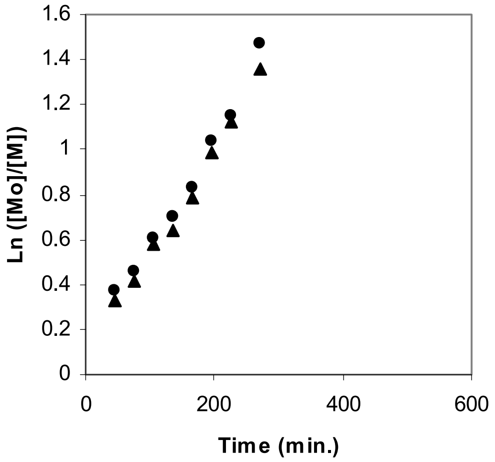


Fig. 1. Kinetics plot of bulk styrene polymerization at 120 °C using BPO as initiator and **4a** (●) and **4b** (▲) as controllers. [nitroxide$_o$]/[BPO$_o$] = 1.5, [nitroxide]$_o$ = 3.57 × 10^{-2} M.

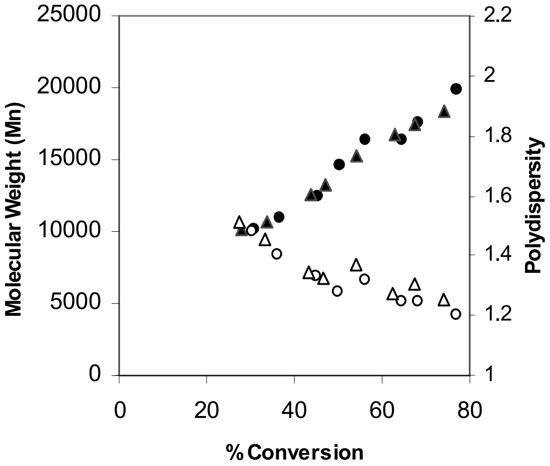


Fig. 2. Evolution of the number average molecular weight and polydispersity with the conversion in styrene polymerization at 120 °C using BPO as initiator and azabutane **4a** (●) and **4b** (▲) as controllers [nitroxide]$_o$/[BPO] = 1.5. [nitroxide]$_o$ = 3.57 × 10^{-2} M. MW (● ▲) polydispersity (○ △). (−−) Theoretical M_n.

an ideal living polymerization system. Polydispersities are high at the beginning and decrease up to 1.2 when time advances. These results indicate that azabutanes **4a** and **4b** have a good control of styrene polymerization in these conditions.

A new experiment in similar conditions but at 100 °C was carried out, in order to test the performance of the nitroxides at lower temperatures. Results showed a complete lack of control on the polymerization. These results were rationalized in terms of the long half life time of BPO at 100 °C [20].

3.3.2. Azo bis-isobutyronitrile (AIBN) as initiator

Nitroxides **4a**, **4b** and **4c** and AIBN in a [nitroxide]/[AIBN] = 1.5 ratio at 100 °C produced the results shown in Fig. 3. No significant difference in behavior among the nitroxides was found. Conversions of 43, 45 and 40% in 10 h for non, chloro and methoxy-substituted nitroxides, respectively were achieved. All curves show the same behavior of the nitroxides than in the experiment with BPO at 120 °C (Fig. 3).

The changes of molecular weight and polydispersity with the conversion are shown in Fig. 4 polydispersity decreases as the process advances, but higher polydispersity values and a larger deviation of the theoretical molecular weight curve than those at 120 °C were observed.

In order to improve the control at the beginning of the process, which might be due to a low nitroxide/initiator ratio, an increment of this ratio was increased.

At 120 °C conversions of 56, 63 and 59% were obtained in 5 h for the non, methoxy and chloro substituted nitroxide, respectively using a 1.8 [nitroxide]/[AIBN] ratio. Again, the progress of polymerization with the three nitroxides is similar (Fig. 5). There are, however, some differences in the polymerization control, as indicated by the slight unlikeness of the curves which do not overlap, but the curves show the same slope.

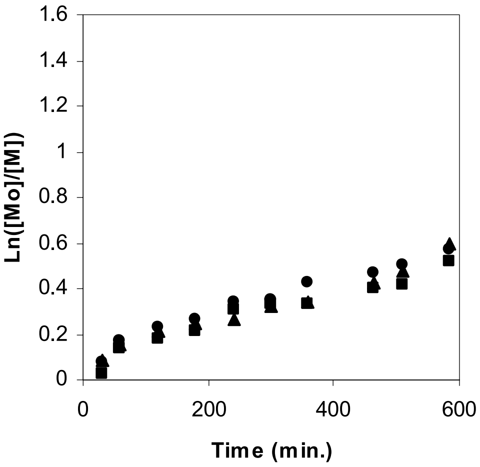


Fig. 3. Kinetics plot of styrene polymerization in bulk at 100 °C using AIBN as initiator and **4a** (●), **4b** (▲) and **4c** (■) as controllers. [nitroxide]/[AIBN] = 1.5, [nitroxide]$_o$ = 3.56 × 10^{-2} M.

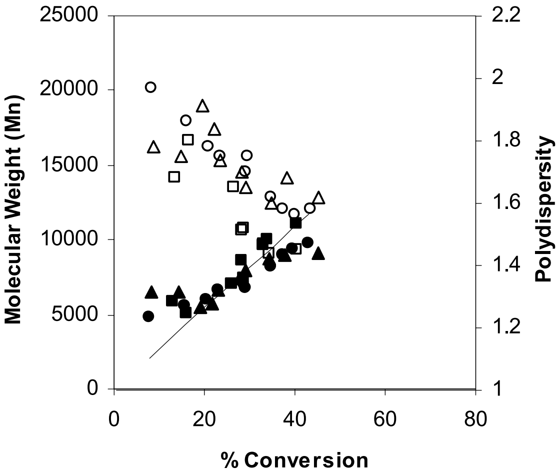


Fig. 4. Evolution of the number average molecular weight and polydispersity with the percentage of conversion in styrene polymerization at 100 °C using AIBN as initiator and azabutane **4a** (●), **4b** (▲) and **4c** (■) as controllers [nitroxide]/[AIBN] = 1.5. [nitroxide]$_o$ = 3.56 × 10^{-2} M. MW (● ▲ ■), polydispersity (○ △ □).Theoretical M_n (—).

Fig. 6 shows a linear dependence of molecular weight on the conversion and a polydispersity between 1.2 and 1.4. These data show a significant improvement of the control, relative to the experiments with a 1.5 ratio nitroxide/ initiator.

An attempt to also improve the control at 100 °C, increasing the [nitroxide]/[AIBN] ratio at 1.8, showed a long induction period (7 h), with only 8% of conversion in 10 h.

A study of the polymerization kinetics in bulk at 100 °C using different [nitroxide]/[AIBN] ratio showed that a small variation in the initiator concentration produces a large difference in the control (see Fig. 7). A gradual improvement was achieved by using higher ratios up to 1.75. Slopes of the curves in Fig. 7 are similar after about 2 h.

Fig. 8 shows the molecular weight evolution and Fig. 9 the evolution polydispersity during the kinetic study at

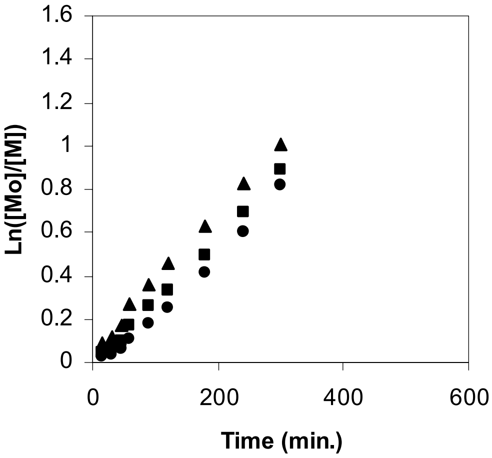


Fig. 5. Kinetics plot of styrene polymerization in bulk at 120 °C using AIBN as initiator and **4a** (●), **4b** (▲) and **4c** (■) as controllers. [nitroxide]/[AIBN] = 1.8, [nitroxide]$_o$ = 3.56 × 10^{-2} M.

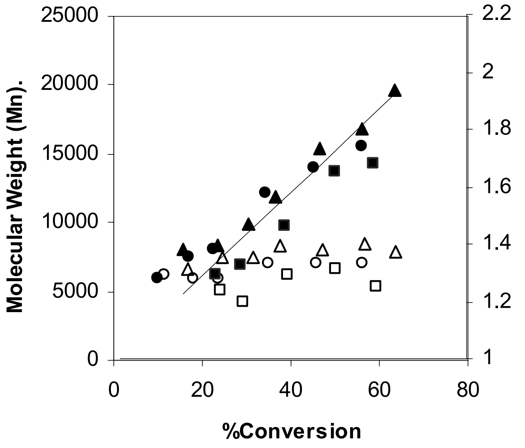


Fig. 6. Evolution of the number average molecular weight and polydispersity with the percentage of conversion in styrene polymerization at 120 °C using AIBN as initiator and azabutane **4a** (●), **4b** (▲) and **4c** (■) as controllers. [nitroxide]/[initiator] = 1.8, $[\text{nitroxide}]_o = 3.56 \times 10^{-2}$ M. MW (● ▲ ■), polydispersity (○ △ □).Theoretical M_n (—).

100 °C using different [nitroxide]/[AIBN] ratios. The process with a 1.75 ratio yields a curve closer to the ideal; however, the curve does not accurately start in the origin and looses linearity. Fig. 9 shows an almost constant 1.4 polydispersity.

These results can be rationalized considering that the initiator inefficiency in a bicomponent polymerization process does not produce two transient radicals which would be trapped by two moles of nitroxide to be controlled. Besides, part of the generated radicals might be lost by side reactions [21], therefore only 1.75 mol of nitroxide for 100 °C and 1.8 mol for the process at 120 °C are necessary. The theoretical advance of the molecular weight shown in the figures was calculated considering 70% efficiency of the initiator.

The differences between theoretical and experimental molecular weights at the beginning of the polymerization might be the result of controlled and non controlled chains suffering disproportion of coupling when a low ratio nitroxide/initiator is used. Transient radicals react faster with the nitroxide excess than with a monomer generating dormant species because coupling constants (k_c) (Scheme 2) are always larger than propagation constants (k_p) [22–24]. Above 100 °C, styrene transient radicals are spontaneously produced by thermal initiation according to the Mayo's mechanism [25], and the polymerization starts only when the nitroxide and dormant species have reached the equilibrium concentration. This might produce the different induction times in polymerization.

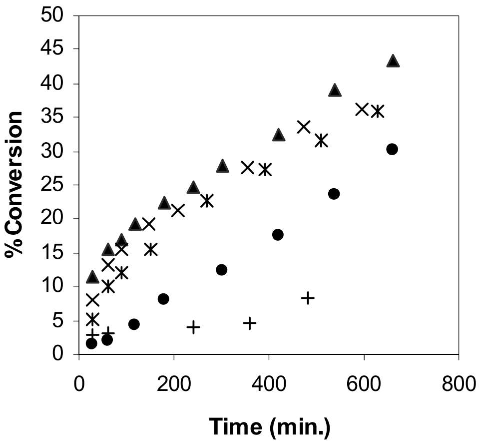


Fig. 7. Kinetics plot of styrene polymerization at 100 °C using AIBN as initiator and **4a** as controller. For $[\text{nitroxide 4a}]_o = 3.56 \times 10^{-2}$ M varying the initiator concentrations, (▲) stands for [N]/[I] = 1.5; (×) stands for [N]/[I] = 1.65; (∗) stands for [N]/[I] = 1.7; (●) stands for [N]/[I] = 1.75 and (+) stands for [N]/[I] = 1.8. [N]/[I] = $[\text{nitroxide}]_o/[\text{initiator}]_o$.

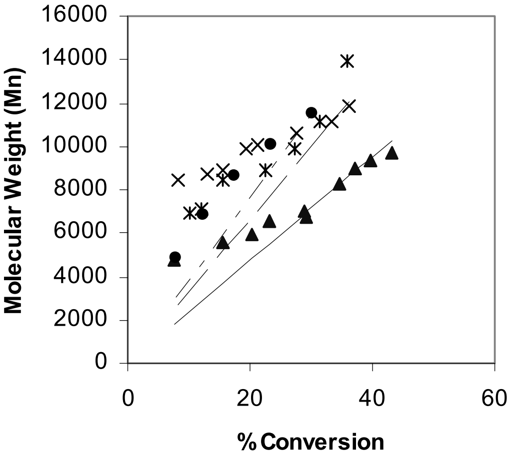


Fig. 8. Evolution of the number average molecular weight (M_n) with the percentage of conversion in styrene polymerization at 100 °C using AIBN as initiator and 4a $[3.56 \times 10^{-2}\ \text{M}]_o$ as controller, varying the initiator concentrations, (▲): [N]/[I] = 1.5, (— stands for theoretical M_n); (×): [N]/[I] = 1.65, (---) stands for theoretical M_n; (⇔): [N]/[I] = 1.7, (−−stands for theoretical M_n) and (●): [N]/[I] = 1.75 (— — stands for theoretical M_n). [N]/[I] = $[\text{nitroxide}]_o/[\text{initiator}]_o$.

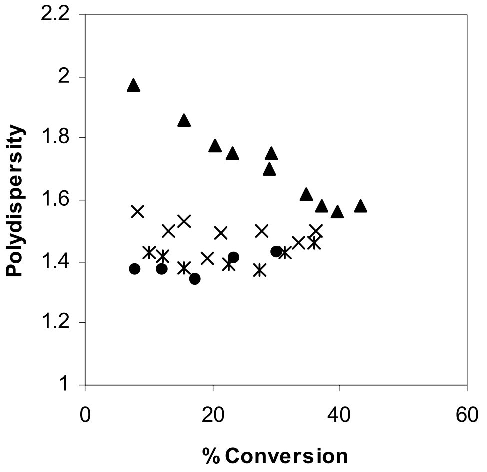


Fig. 9. Evolution of the polydispersity with the percentage of conversion in styrene polymerization at 100 °C using AIBN as initiator and $[\text{nitroxide 4a}]_o = 3.56 \times 10^{-2}$ M as controller. varying the initiator concentrations, (▲): [N]/[I] = 1.5, (– stands for theoretical M_n); (×): [N]/[I] = 1.65, (--- stands for theoretical M_n); (⇔): [N]/[I] = 1.7, (−−) stands for theoretical M_n) and (●): [N]/[I] = 1.75 (— stands for theoretical M_n). [N]/[I] = $[\text{nitroxide}]_o/[\text{initiator}]_o$.

3.4. Monocomponent system

A comparison of the performance of the preformed *O*-phenyl-ethyl-alkoxyamine with the bicomponent system [azabutane]/[AIBN] = 1.8 in a kinetic experiment at 120° is shown in Fig. 10. Both systems show the same rate, being the curve's slopes identical. The molecular weight evolution compared with the theoretical molecular weight is shown in Fig. 11. A lower than the theoretical molecular weight was observed at the end of the polymerization, although the polydispersity diminishes until 1.33–1.4 at the end. Le Mercier [26] explains this behavior in terms of the thermal generation of transient radicals and a certain number of polymer dead chains due to dimerization or coupling at the beginning of the process.

Molecular weights up to 120,000 were obtained by using a styrene oligomeric alkoxyamine ($M_n = 4047$, PD 1.15) as mediator at 120 °C. In these experiments conversions up to 60% and polydispersities of 1.4 were achieved. The lack of stirring in these experiments which introduces new diffusion factors which probably produce the slight increment of polydispersities.

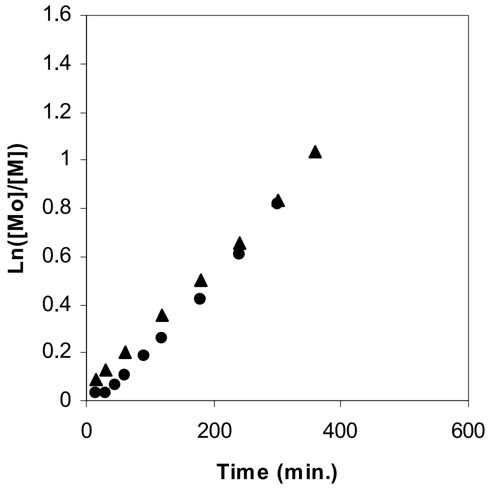


Fig. 10. Comparison between polymerization rates of a bicomponent system using a [nitroxide]/[AIBN] = 1.8 (●) and monocomponent system using an azabutane-based alkoxyamine (▲) at 120 °C.

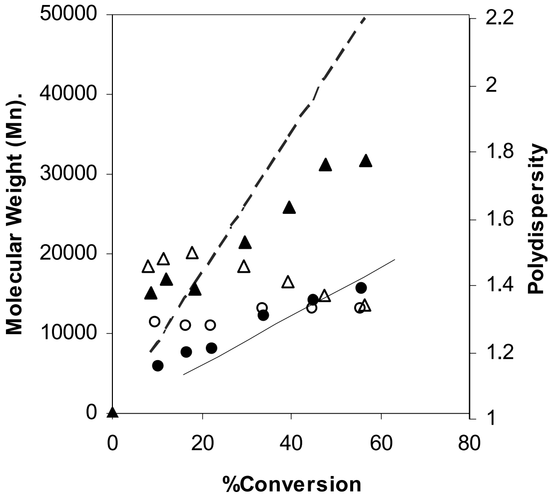


Fig. 11. Evolution of molecular weight of a bicomponent system [nitroxide]/[AIBN] = 1.8 (●) Theoretical M_n (—) and monocomponent system with azabutane-based alkoxyamine (▲) theoretical M_n (– –). Polydispersities (○ △).

Table 1
Equilibrium constant K for different nitroxides in styrene polymerization at 120 °C

Nitroxide	$K = k_d/k_c$ (mol l^{-1})
TEMPO **1**	2.1×10^{-11a} 2.1×10^{-12b}
TIPNO **2**	4.02×10^{-9a} 4.01×10^{-10b}
DEPN **3**	1.15×10^{-9a} 9.8×10^{-10b} 1.20×10^{-8c}
AZABUTANE **4**	8.6×10^{-8d}

[a] According to H. Fischer [9].
[b] According to Le Mercier [26].
[c] According to Lacroix–Desmazes [27].
[d] Calculated in this work according to Lacroix–Desmazes's method [27].

3.5. Equilibrium constant

The equilibrium constant $K = k_d/k_c$ for the styrene polymerization controlled by the nitroxide **4** was estimated according to the Lacroix–Desmazes et al. method [27] who proposed the following expression to obtain K for a bicomponent system:

$$\mathrm{Ln}([\mathrm{M}]_o/[\mathrm{M}]) = k_p K(2f[\mathrm{I}_2]_o)/([\mathrm{N}\cdot]_o - 2f[\mathrm{I}_2]o)t$$

Where $[\mathrm{M}]_o$ = initial monomer concentration. [M] = final monomer concentration, k_p = propagation constant, f = initiator efficiency, $[\mathrm{N}\cdot]_o$ = initial nitroxide concentration, $[\mathrm{I}_2]_0$ = initial initiator concentration.

Table 1 shows the reported [9,26,28] equilibrium constants K of styrene polymerization using different previously reported alkoxyamines, compared with the calculated constant for the nitroxide **4a**. As seen in Table 1, K for the azabutane type nitroxide is higher than the TEMPO's constant, and similar to the TIPNO and DEPN constants.

3.6. Molecular modeling

The C–O bond dissociation energies (BDE) of three different reported nitroxides (**1**, **2** and **3**) bonded to 1-phenyl ethyl radical were calculated, using molecular modeling with the AM1 and PM3 semiempirical methods. The geometry optimization of the different radical compounds was carried out through the open-shell method UHF (Unrestricted Hartree–Fock), the configuration interaction method (CI) was used after UHF for calculating the

Table 2
Calculated C–O bond dissociation energy for different nitroxide-phenyl ethyl alkoxyamines. Geometry optimization was carried out at a convergence limit of 0.01

Nitroxide	AM1 (kJ mol^{-1})	PM3 (kJ mol^{-1})
TEMPO **1**	95.89	122.42
TIPNO **2**	91.37	114.14
DEPN **3**	98.88	109.16
AZABUTANE **4**	89.85	115.38

formation heats (H_f). Moad and Rizzardo [23] have reported that the obtained values are closer to the experimental results using the CI method than the values obtained only with UHF. The BDE values obtained in this work (Table 2) using the PM3 method are closer to the experimental [23,26] than those obtained using the AM1, in accordance with Kazmaier [24a].

Some C–O BDE values obtained in this work by PM3 method are similar to those obtained by Le Mercier et al. [26], although they report 129.3 kJ mol^{-1} for the TEMPO-phenyl ethyl alkoxyamine. Our result: 122.42 kJ mol^{-1} is closer to the experimental value reported by Scaiano [29] (118.83 kJ mol^{-1}).

Results in Table 2 show that the azabutane-based alkoxyamine and the corresponding to DEPN and TIPNO have similar dissociation energies, but lower than TEMPO-based alkoxyamines. Phenyl ethyl alkoxyamines with electron-releasing or electron-withdrawing substituents in one of the aromatic rings of the azabutane type nitroxide do not give significantly different BDEs (Table 3). These data are in accordance with our experimental results on polymerization control.

Comparing calculated C–O BDE for both, the different reported alkoxyamines and the diphenyl azabutane-based alkoxyamine, with the reported equilibrium constant K of the processes, an inverse relationship can be observed. A higher equilibrium constant K correspond to a lower dissociation energy as suggested by Le Mercier [26].

Fig. 12 shows the correlation between the C–O bond dissociation energies calculated in this work with the PM3 method and the dissociation constants used by Le Mercier [26]. As seen in the figure, calculated BDEs are good parameters for predicting the behavior of a nitroxide in ‘living’ free radical polymerization. The dissociation constant k_d of al alkoxyamine might be estimated from the line equation.

Table 3
C–O bond dissociation energy of azabutane-O-phenyl ethyl alkoxyamines calculated by Hyperchem 5 program, using the PM3 method at 0.01 of limit of convergence

Azabutane-*O*-phenyl ethyl alkoxyamine	AM1 (kJ mol^{-1})	PM3 (kJ mol^{-1})
Non substituted **4a**	89.85	115.38
p-Chloro **4b**	89.92	115.55
p-Methoxy **4c**	89.37	115.17
p-Methyl **4d**	89.37	115.24
o-Chloro **4e**	88.87	115.34
m-Chloro **4f**	89.58	114.40

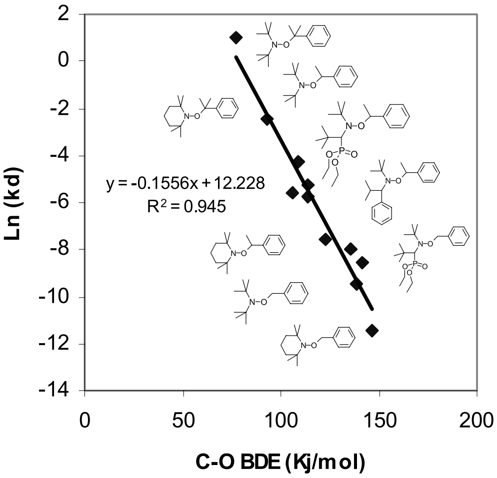


Fig. 12. C–O Bond dissociation energies of different alkoxyamines calculated by PM3 semiempirical methods in this work vs. dissociation constant (k_d) taken from ref. [9].

From all previous experiments it is possible to conclude that 3,3,-dimethyl 1,1-diphenyl azabutane-N-oxide **4** and its substituted analogs are good mediators of polystyrene radical ‘living’ polymerization. The best control at 120 °C achieved polydispersities in a range of 1.2 and 1.4, and substituents on the aromatic ring do not sensibly affect the control. This bicomponent system had a similar performance than the preformed phenyl ethyl-alkoxyamine and the oligomeric alkoxyamines. With the last mediator, slightly higher polydispersities were obtained for molecular weights up to 120,000. The [nitroxide]/[initiator] ratio in a bicomponent system is a critical parameter for the control. This parameter was better studied in polymerizations at 100 °C. At this temperature the control is moderate. Azabutane-based alkoxyamines have similar energy and equilibrium constant in comparison with other alkoxyamines.

Studies are continuing on the polymerization of other monomers using the nitroxide **4** and on the mechanism of control, mainly during the initiation process.

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