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Synthesis and evaluation of a new polar, TIPNO type nitroxide for "living" free radical polymerization

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ABSTRACT

The bromine–magnesium exchange of 2-bromopyridine provides an easy access to a new versatile TIPNO type nitroxide. The synthesis of four functionalized alkoxyamines have been achieved. Polymerizations of styrene and n-butyl acrylate mediated with this new nitroxide exhibited all the expected features of a controlled system. Because of its increase of polarity, this pyridine nitroxide is more efficient than TIPNO for the acrylate polymerization as no added free nitroxide is required, that confirms the strong influence of the polarity of the nitroxide on the efficiency of nitroxide-mediated radical polymerization, result already observed in the case of the polar SG1 nitroxide. Different block copolymers were synthesized. Polystyrene, poly(n-butyl acrylate) and poly(tert-butyl acrylate) blocks were successfully used as macroinitiators for the synthesis of various diblock and triblock copolymers. A representative example of such architecture is given by polystyrene-b-poly(n-butyl acrylate)-b-poly(tert-butyl acrylate) with a PDI of 1.2!

1. Introduction

Since its discovery [1,2] and development, nitroxide-mediated radical polymerization (NMP) is a powerful method to synthesize well-defined macromolecular architectures with precisely controlled topologies, compositions, microstructures and functionalities [3–5]. A significant contribution has been brought by the groups of Tordo [6], Braslau [7] and Hawker [7]. They have introduced α-hydrogen nitroxides such as TIPNO **1** (Scheme 1) and their corresponding alkoxyamines which allows the controlled polymerization of styrenes, isoprene and electron poor olefins. Recently, other groups [8–16] have also improved the efficiency in NMP.

Scheme 2 depicts a simplified NMP process, where k_d is the rate constant for C–ON bond homolysis in the macroalkoxyamine (the so-called dormant species), k_c the rate constant for the reformation of the macroalkoxyamine, k_p the propagation rate constant for the polymerization reaction and k_t the self-termination rate constant. For a well controlled [17] and living radical polymerization of a given monomer, the rate constants of the reversible cleavage k_d and k_c and the pre-equilibrium constants $K = k_d/k_c$ must fall into proper ranges. Even more, the k_d rate constant of the initiating alkoxyamine [18] is crucial for a good control of the polymerization. However, this does not always ensure successful NMP. Indeed, the NMP of the n-butyl acrylate monomer initiated with **1a** (Scheme 1) requires the addition of TIPNO to control the polymerization as a result of the large value of k_p. Moreover, Braslau [19] demonstrated that an inherent instability of the TIPNO is required for the controlled polymerization of acrylates, result recently confirmed by Georges [20].

In order to design and synthesize new nitroxides for the improvement of the NMP process, predictive relationships for k_d [21,22] and to a less extent, for k_c [23] has been developed. Factors such as polar [24,25], and steric [20,26–28] effects for nitroxide and alkyl fragments, intramolecular H-bonding [24,29,30], long-range polar effects [31], stereoelectronic [32] effect modify k_d. TIPNO is suitable for setting up such relationships because, thanks to its flexible synthesis, variation of the substituents close to the nitroxide function atom is easy: increasing steric hindrance [26] has resulted in lowering the temperature of controlled polymerization and intramolecular H-bonding [29] has increased the rate of polymerization. However few polar TIPNO type nitroxides [26,29,33,34] are described even though in a study investigated for the N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide, also known as SG1 nitroxide, a strong polar effect [22] which results in a better control of the polymerization and a shorter polymerization time has been demonstrated if the nitroxide and the radical moieties of the initiating alkoxyamine are both polar. In the same manner, a polar TIPNO type nitroxide might be more efficient than TIPNO. Therefore, we wish to report the synthesis of a new polar TIPNO type nitroxide **2** (Scheme 1) and the first results about comparative evaluation of **2** and TIPNO in radical

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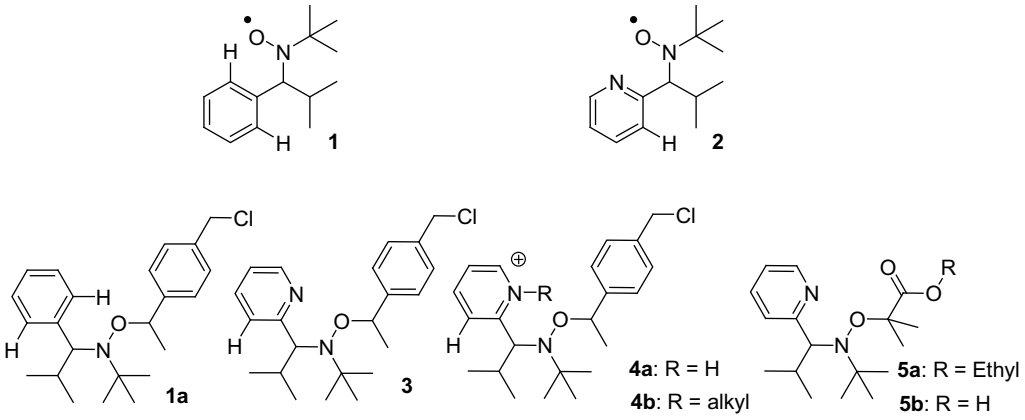


Scheme 1. TIPNO, **1**, the new pyridine nitroxide, **2** and their corresponding alkoxyamines.

polymerization. In the nitroxide **2**, the phenyl substituent of the TIPNO nitroxide **1** is replaced by the more polar pyridyl one. The pyridine group was also chosen for other reasons.

The steric hindrance and the polarity around the nitroxide O atom of alkoxyamine **3** are modulated by protonation (derivative **4a** of Scheme 1) or alkylation (derivative **4b** of Scheme 1) of the pyridyl of the alkoxyamine **3** (Scheme 1). Moreover, as the alkoxyamines **3**, **5a** and **5b** are potential nitrogen-based ligands, in the presence of copper(II) or zinc(II) halides, they should afford complexes that affect the radical polymerization initiated by such alkoxyamines. Consequently, this might be a fruitful approach to further study the relation between the structure of the initiating alkoxyamine and the polymerization rate.

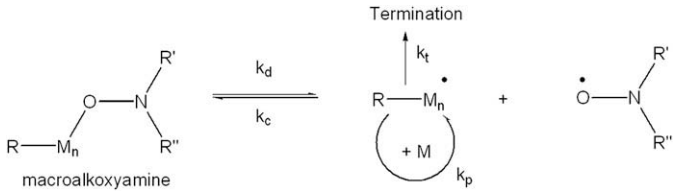
Secondly, because of their expected water solubility, the pyridinium alkoxyamines **4a**, **4b** and the carboxylic pyridine alkoxyamine **5b** (Scheme 1) might allow to further develop the NMP in pure water [33], in just water-based polymerizations emulsion [35] and in ionic liquid [36].

2. Experimental section

2.1. Analytical techniques

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on Bruker AC 200 MHz or ARX 250 MHz instruments. Proton and carbon chemical shifts are reported using the resonance of the deuterated solvent as internal standard. Elemental analyses were performed by the Service Central d'Analyses of the CNRS. Chemical ionisation (CI, ammonia or methane) and electronic ionisation (EI) mass spectra were obtained with a JMS-700 spectrometer.

Size exclusion chromatography (SEC) was performed at 40 °C with two columns (PSS SDV, linear MU, 8 mm × 300 mm; bead diameter, 5 μm; separation limits, 400 to 2×106 g mol^{-1}). The eluent was THF at a flow rate of 1 mL min^{-1}. A differential refractive index detector (LDC Analytical refracto-Monitor IV) was used and molar mass distributions were derived from a calibration curve based on polystyrene (PS) standards from Polymer Standards Service.



Scheme 2. Simplified NMP process.

2.2. Materials

All reagents and chemicals were obtained from commercial suppliers without further purification: 4-vinylbenzyl chloride (technical, 90%, Aldrich), 2-methyl-2-nitropropane (Aldrich), 2-bromopyridine (99%, ACROS) and 4-vinylpyridine (95%, ACROS). n-Butyl acrylate (nBA, Aldrich, 99%), tert-butyl acrylate (tBA) (98%, Aldrich) and styrene (S, Aldrich, 99%) monomers were distilled under reduced pressure before use. Tetrahydrofuran (THF) was distilled under N_2 from sodium benzophenone, silica gel for column chromatography was Merck Kieselgel 60. Column chromatographic separations were carried out using Merck silica gel 60 (230–400 mesh) or alumina when indicated. N-tert-butyl-α-isopropylnitrone [7], TIPNO [7] and the salen–manganese complex (Mn(salen)Cl) [38] were synthesized according to literature procedures.

2.3. Synthesis of 2,2,5-trimethyl-4-(2-pyridyl)-3-azahexane-3-nitroxide TIPNO, *2*

Under nitrogen atmosphere, isopropyl bromide (4.2 mL, 44.7 mmol) was diluted in THF (35 mL) and added dropwise to a solution of magnesium (1.48 g, 44.7 mmol) in THF (4 mL) in order to have a smooth reflux. After the addition was completed, the solution was stirred until magnesium has disappeared. To this solution was then slowly added a solution of 2-bromopyridine (4.2 mL, 44.7 mmol) in THF (20 mL) at room temperature. The solution was further stirred for 2 h at room temperature. A solution of N-tert-butyl-α-iso-propylnitrone (4.2 g, 29.3 mmol) in THF (20 mL) was added over 10 min to the solution of pyridylmagnesium bromide at 0 °C. When the addition is finished, the mixture was allowed to warm to room temperature and further stirred during one night. The excess Grignard reagent was decomposed by careful addition of a concentrated ammonium chloride solution (20 mL) followed by 20 mL of water until all solids had dissolved. The organic layer was separated, and the aqueous layer was extracted with 100 mL of diethyl ether. The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated. The residue obtained was then treated with a mixture of methanol (100 mL), of aqueous concentrated NH_4OH (5 mL), and of $Cu(OAc)_2$ (100 mg, 0.55 mmol) to give a pale yellow solution. A stream of air was bubbled for 2 h. Then the mixture was concentrated and the crude nitroxide was purified by flash column chromatography (75:25 pentane/ethyl acetate) to afford 3 g (58% yield) of **2**, as an orange oil which crystallized at temperature below −25 °C. Elemental analysis: $C_{13}H_{21}N_2O^{\bullet}$ calculated: C, 70.58; H, 9.50; N, 12.66; found: C, 69.78; H, 9.71; N, 12.05.

2.4. Synthesis of trimethyl-3-(1-(4′-chloromethyl)phenylethoxy)-4-(2-pyridyl)-3-azahexane **3**

Functionalized TIPNO **2** (1 g, 4.52 mmol) and 4-vinylbenzyl chloride (1.06 mL, 6.78 mmol) were dissolved in 10 mL of isopropyl alcohol in an open flask. The solution was vigorously stirred, and finely ground Mn(salen)Cl catalyst (202 mg, 0.567 mmol) was added, followed by $NaBH_4$ (0.278 g, 11.26 mmol) in small portions. After 24 h, the reaction mixture was evaporated to dryness. Dried Silica gel soaked with the crude product was prepared by dissolving and evaporating to dryness a mixture of the crude product with silica gel in dichloromethane. The crude product was purified by column chromatography, eluting with pure pentane gradually increasing to 25:75 ethyl acetate/pentane. The combined organic layers were then dried and evaporated to dryness and the alkoxyamine **3**, was obtained as a clear oil (1 g, 60% yield).

^{1}H NMR (250 MHz, $CDCl_3$, both diastereomers) $\delta_H = 8.30$ (dd, $J = 5.1$ Hz, 12.8 Hz, 2H); 7.60–6.91 (m, 14H); 4.80 (q + q, 2H, $J = 6.9$ Hz, both diastereomers); 4.46 and 4.43 (each s, 4H, both diastereomers); 3.67 (d, 1H, $J = 11$ Hz, minor diastereomer); 3.56 (d, 1H, $J = 11$ Hz, major diastereomer); 2.4 (two m, 2H, both diastereomers); 1.47 (d, 3H, $J = 7$ Hz, minor diastereomer); 1.40 (d, 3H, $J = 6.6$ Hz, major diastereomer); 1.18 (d, 3H, $J = 6.6$ Hz, major diastereomer); 0.90 (s, 9H, major diastereomer); 0.81 (d, 3H, $J = 6.2$ Hz, minor diastereomer); 0.62 (s, 9H, minor diastereomer); 0.44 (d, 3H, $J = 6.6$ Hz, minor diastereomer); 0.13 (d, 3H, $J = 6.6$ Hz, major diastereomer); ^{13}C NMR (50 MHz, $CDCl_3$, both diastereomers): δ_C = 162.41, 162.19, 147.67, 147.49, 145.65, 144.99, 135.76, 135.21, 135.10, 128.38, 127.24, 126.43, 125.36, 125.25, 121.69, 121.54, 83.02, 82.25, 73.80, 60.57, 60.49, 46.08, 31.68, 31.35, 28.04, 27.89, 24.36, 22.78, 21.79, 21.64, 20.28, 20.14; CIMS: *m*/*z* (%) 377 (M, 35) 375 (M, 100) 341 (M − Cl, 27.9) 222 (87.6) 207 (50); Elemental analysis: $C_{22}H_{31}ClN_2O$ calculated: C, 70.5; H, 8.27; N, 7.47, found: C, 71.16; H, 8.27; N, 7.34.

2.5. Synthesis of alkoxyamines **5a**, **5b**, **6** and **7**

2.5.1. Synthesis of the crude 2,2,5-trimethyl-3-(2-(ethyl-2-methyl-propionate)ethoxy)-4-(2-pyridyl)-3-azahexane **5a**

To a Schlenk flask were added ethyl-2-bromoisobutyrate (8.09 mL, 54.2 mmol), the functionalized TIPNO **2** (8 g, 36.2 mmol) and 50 mL of toluene. To a second Schlenk flask were added copper powder (6.89 g, 109.3 mmol), copper bromide (781 mg, 5.44 mmol), 50 mL of toluene and PMDETA (2.27 mL, 10.9 mmol)). The two reaction solutions were deoxygenated by bubbling nitrogen during 15 min. The nitroxide solution was then added to the solution of copper derivatives and the resulting solution was further stirred at room temperature. After one night, the reaction mixture was evaporated to dryness. Dried silica gel soaked with the crude product was prepared by dissolving and evaporating to dryness a mixture of the crude product with silica gel in dichloromethane. The crude product was purified by column chromatography, eluting with pure pentane gradually increasing to 5:95 ethyl acetate/pentane. The combined organic layers were then dried and evaporated to dryness and the still crude alkoxyamine **5a**, was obtained as a clear oil (8.4 g).

2.5.2. Synthesis of 2,2,5-trimethyl-3-(2-(2-methyl-propanoic acid)ethoxy)-4-(2-pyridyl)-3-azahexane **5b**

To a stirred suspension of potassium tert-butoxide (21.6 g, 193 mmol) in dry ether (200 mL), cooled to 0 °C, was added water (865 μL, 43.25 mmol) via syringe. This slurry mixture was stirred for 5 min. To this solution was added the crude alkoxyamine **5a** (8.4 g) in solution in dry ether (50 mL). The ice bath was removed and the reaction mixture was stirred at room temperature during one night. The reaction was quenched by adding a concentrated aqueous ammonium chloride (10.31 g, 193 mmol) solution (60 mL). The aqueous layer was separated and was extracted three times with 100-ml portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, and filtered. The organic phase was evaporated to give 3.96 g (35.5% yield) of **5b** as beige solid. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 8.50 (m, 1H, aromatic), 7.75 (m, 1H, aromatic), 7.30 (m, 2H, aromatic), 3.65 (d, 1H, $J = 10.6$ Hz, C**H**–N), 1.98 (m, 1H, C**H**–iPr), 1.61 (s, 3H (C**H**$_3$)$_2$–C–O), 1.47 (s, 3H (C**H**$_3$)$_2$–C–O), 1.11 (d, 3H, $J = 6.3$ Hz, C**H**$_3$–iPr), 0.96 (s, 9H, *t*Bu), and 0.30 ppm (d, 3H, $J = 6.7$ Hz, C**H**$_3$–iPr). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 180.26 (C═O), 159.18, 145.14, 137.79, 127.58, 122.57 (aromatic), 84.24 ((CH$_3$)$_2$–C–O)), 70.44 (CH–N), 60.48 (tBu–N), 30.24, 28.39 (CH–iPr), 28.19 (tBu), 22.31, 22.25, 19.76 ppm (CH$_3$). Anal. Calcd for $C_{17}H_{28}N_2O_3C$, 66.23; H, 9.09; N, 9.09. Found C, 66.33; H, 9.17; N, 8.85.

The alkoxyamines **6** and **7** were prepared using the procedure for **3**.

2.5.3. Trimethyl-3-(1-(4-pyridyl)ethoxy)-4-(2-pyridyl)-3-azahexane **6**

^{1}H NMR (250 MHz, $CDCl_3$, both diastereomers) $\delta_H = 8.51$–8.03 (m, both diastereomers); 7.57–6.96 (m, both diastereomers); 4.83 (q + q, 2H, $J = 6.6$ Hz, both diastereomers); 3.73 (d, 1H, $J = 10.6$ Hz, minor diastereomer); 3.65 (d, 1H, $J = 11$ Hz, major diastereomer); 2.22 (two m, 2H, both diastereomers); 1.52 (d, 3H, $J = 6.6$ Hz, major diastereomer); 1.45 (d, 3H, $J = 6.6$ Hz, minor diastereomer); 1.216 (d, 3H, $J = 6.6$ Hz, major diastereomer); 0.95 (s, 9H, minor diastereomer); 0.9 (d, 3H, $J = 6.6$ Hz, minor diastereomer); 0.7 (s, 9H, major diastereomer); 0.48 (d, 3H, $J = 6.6$ Hz, major diastereomer); 0.22 (d, 3H, $J = 6.6$ Hz, minor diastereomer); ^{13}C NMR (50 MHz, $CDCl_3$, both diastereomers): δ_C = 161.82, 153.96, 149.62, 147.78, 135.29, 125.18, 124.92, 121.80, 121.65, 121.03, 82.29, 81.15, 73.69, 60.71, 31.68, 31.57, 28.00, 27.82, 24.11, 22.67, 21.46, 20.21; CIMS: *m*/*z* (%) 328 (M + 1, 6.2) 222 (M − 106, 100) 207 (17.8) 108 (40.3); Elemental analysis: $C_{20}H_{29}ClN_3O$ calculated: C, 73.4; H, 8.86; N, 12.84, found: C, 72.81; H, 8.87; N, 12.61.

2.5.4. Trimethyl-3-(1-phenylethoxy)-4-(2-pyridyl)-3-azahexane **7**

^{1}H NMR (250 MHz, $CDCl_3$, both diastereomers) $\delta_H = 8.37$ (dd, $J = 4.8$ Hz, 12. Hz, 2H); 7.69–6.94 (m, 16H); 4.90 (q + q, 2H, $J = 6.6$ Hz, both diastereomers); 3.81 (d, 1H, $J = 10.6$ Hz, minor diastereomer); 3.68 (d, 1H, $J = 11.3$ Hz, major diastereomer); 2.34 (two m, 2H, both diastereomers); 1.6 (d, 3H, $J = 6.6$ Hz, minor diastereomer); 1.51 (d, 3H, $J = 6.6$ Hz, major diastereomer); 1.31 (d, 3H, $J = 6.2$ Hz, major diastereomer); 1.02 (s, 9H, minor diastereomer); 0.92 (d, 3H, $J = 6.6$ Hz, minor diastereomer); 0.75 (s, 9H, major diastereomer); 0.55 (d, 3H, $J = 6.6$ Hz, major diastereomer); 0.23 (d, 3H, $J = 6.6$ Hz, minor diastereomer); ^{13}C NMR (50 MHz, $CDCl_3$, both diastereomers): δ_C = 162.48, 162.26, 147.60, 147.45, 145.28, 135.10, 134.96, 129.00, 128.12, 127.97, 127.27, 126.83, 126.61, 125.33, 125.25, 121.58, 121.39, 83.28, 82.80, 73.83, 73.76, 60.49, 60.35, 31.60, 31.16, 28.00, 27.82, 24.33, 22.82, 21.79, 21.64, 20.25, 20.10; CIMS: *m*/*z* (%) 327 (M + 1, 100) 222 (M − 104, 8.5) 207 (7); Elemental analysis: $C_{21}H_{30}N_2O$ calculated: C, 77.3; H, 9.2; N, 8.58, found: C, 77.32; H, 9.08; N, 8.28.

2.6. Isolation of the decomposition compounds of **2**

The hydroxylamine **8** was separated from **2** by column chromatography, eluting with pure pentane gradually increasing to 10:90 ethyl acetate/pentane. The combined organic layers were then dried and evaporated to dryness and the hydroxylamine **8**, was obtained as a clear oil. Then nitrone **9** was isolated by eluting with pure ethyl acetate gradually increasing to 10:90 MeOH/ethyl acetate.

*2.6.1. N-tert-butyl-N-[(1-(2-pyridyl)-2-methyl)-propyl] hydroxylamine **8***

^{1}H NMR (300 MHz, $CDCl_3$) δ_H 10.20 (d, $J = 6.6$ Hz, 1H); 9.35 (t, $J = 11.7$ Hz, 1H); 8.91 (t, $J = 11.7$ Hz, 2H); 5.21 (d, $J = 14.6$ Hz, 1H); 4.17 (m, 1H); 2.93 (d, 1H, $J = 9.5$ Hz); 2.59 (s, 9H); 2.31 (d, 1H, $J = 10.2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 163.25, 147.31, 135.62, 123.46, 121.32, 68.85, 58.20, 30.16, 26.08, 20.48, 19.47; MS (CI, CH4): *m/z* (%) 223 (M, 100) 207 (M − 16, 18) 167 (M − 56, 20); HRMS (CI, CH4) Calcd for $C_{13}H_{23}N_2O$ (M+): 223.1810; found: 223.1816.

*2.6.2. N-tert-butyl-R-isopropyl-R-(2-pyridyl) nitrone **9***

^{1}H NMR (300 MHz, $CDCl_3$) δ_H 10.35 (d, $J = 1.5$ Hz, 1H); 9.4 (td, $J = 11.7$ Hz, 3 Hz, 1H); 8.97 (m, 1H); 8.85 (d, $J = 11.7$ Hz, 1H); 5.50 (d, $J = 10.2$ Hz, 1H); 2.94 (s, 9H); 2.61 (d, 1H, $J = 10.2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 149.13, 135.62, 125.22, 123.26, 73.39, 31.14, 29.582, 18.269; MS (EI): *m/z* (%) 220 (M, 17) 147 (M − 73, 100) 105 (M − 115, 71); HRMS (EI) Calcd for $C_{13}H_{20}N_2O$ (M+): 220.1576; found: 220.1581.

2.7. Polymerizations

The monomer conversion for styrene and n-butyl acrylate polymerizations was determined by gravimetry after drying the polymer samples under vacuum for 48 h.

2.7.1. General procedure for styrene polymerization: preparation of polystyrene

A mixture of the alkoxyamine **3** (205.5 mg, 0.548 mmol) and styrene (11.8 g, 113.4 mmol) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 125 °C for 5 h. Samples were removed at different time intervals during polymerization, and conversion and molecular weights were determined by gravimetry and SEC, respectively. The polymerization was stopped (M_n = 25,550 g mol^{-1}, M_w/M_n = 1.06, conversion = 84%) by immersing the reaction flask in an ice bath.

2.7.2. General procedure for acrylate polymerization: preparation of poly(n-butyl acrylate)

A mixture of the alkoxyamine **3** (193.3 mg, 0.516 mmol), the corresponding nitroxide, **2** (6.2 mg, 0.028 mmol), and n-butyl acrylate (16.21 g, 126.6 mmol) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 125 °C for 18 h. Samples were removed at different time intervals during polymerization, and conversion and molecular weights were determined by gravimetry and SEC, respectively. The polymerization was stopped (M_n = 11,738 g mol^{-1}, M_w/M_n = 1.18, conversion = 34%) by immersing the reaction flask in an ice bath.

2.7.3. General procedure for styrene–n-butyl acrylate random copolymerization: preparation of polystyrene-co-poly-(n-butyl acrylate)

A mixture of the alkoxyamine **3** (84.1 mg, 0.224 mmol), styrene (3.181 g, 30.58 mmol), and n-butyl acrylate (1.285 g, 10.03 mmol) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 115 °C for 8 h. The polymerization was stopped (M_n = 9776 g mol^{-1}, M_w/M_n = 1.19, conversion = 30.6%) by immersing the reaction flask in an ice bath.

2.7.4. General procedure for block copolymer formation: preparation of polystyrene-b-poly(n-butyl acrylate)

A mixture of alkoxyamine-functionalized polystyrene, (3 g, 0.36905 mmol, M_n = 8129 g mol^{-1}, PDI = 1.13, entry 1, Table 2), initially prepared by polymerizing styrene with the alkoxyamine **5**, the corresponding nitroxide, **2** (4.9 mg, 0.022 mmol) and n-butyl acrylate (12.41 g, 96.95 mmol) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 125 °C for 5 h. The polymerization was stopped (M_n = 12,865 g mol^{-1}, M_w/M_n = 1.13, entry 7, Table 2) by immersing the reaction flask in an ice bath.

2.7.5. General procedure for triblock copolymer formation: preparation of polystyrene-b-poly(n-butyl acrylate)-b-poly-(tert-butyl acrylate)

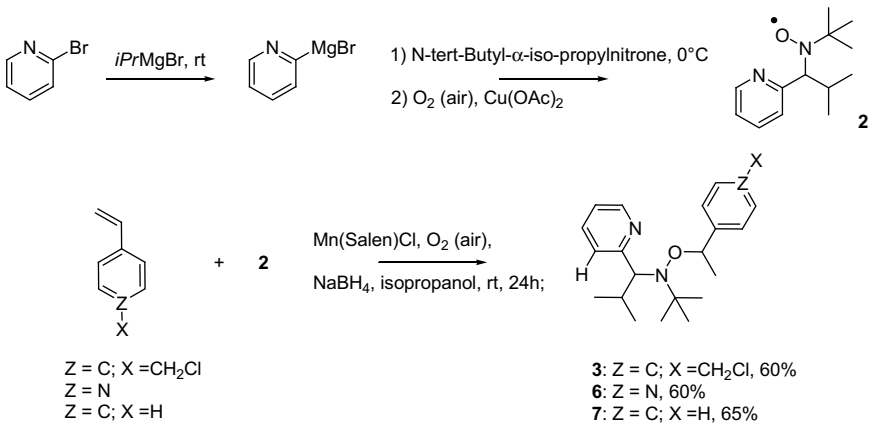
A mixture of PS–PnBA macroinitiator (2 g, 0.134 mmol, M_n = 14,916 g mol^{-1}, PDI = 1.13, entry 10, Table 2), the corresponding nitroxide, **2** (1.7 mg, 0.0077 mmol) and tert-butyl acrylate (6.55 g, 51.17 mmol) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 125 °C for 21 h. The polymerization was stopped (M_n = 22,927 g mol^{-1}, M_w/M_n = 1.24, entry 16, Table 2) by quenching the reaction in an ice bath.

Polymers were precipitated as follows: PS, PS–PnBA, PnBA–PS and PS–PnBA–PS with methanol, PtBA, PS–PtBA and PS–PnBA–PtBA were dissolved in THF and precipitated with 50% aqueous methanol.

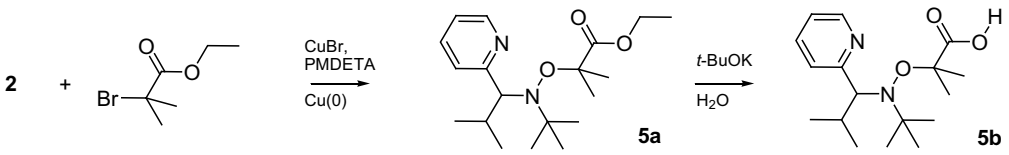
3. Results and discussion

3.1. Synthesis of the polar TIPNO **2** and of its alkoxyamines

The nitroxide **2** (Scheme 3) is synthesized in three steps. Reductive condensation of 2-methyl-2-nitropropane with i-PrCHO gave N-tert-butyl-α-iso-propylnitrone in 58% yield according to a literature procedure [7]. 2-Bromopyridine (2.2 mol/L in THF) was easily converted to its corresponding pyridylmagnesium bromide [37] by treatment with iPrMgBr (1.1 mol/L) at room temperature in THF. The resulting Grignard reagent was quenched at 0 °C by a solution of N-tert-butyl-α-iso-propylnitrone (1.5 mol/L) in THF to afford the



Scheme 3. Synthesis of functional alkoxyamines **3**, **6** and **7** by manganese coupling.



Scheme 4. Synthesis of the functionalized alkoxyamines **5a** and **5b** by atom transfer radical cross-coupling.

crude pyridine functionalised hydroxylamine which was directly converted to the nitroxide **2** (Scheme 3) in methanol at room temperature, by a copper-catalyzed oxidation [7] by air, in an overall yield of 58%.

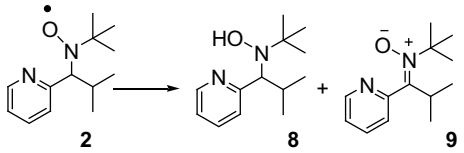
The functionalized alkoxyamine **3** (60%) (Scheme 3) was easily obtained at gram scale from 4-vinylbenzyl chloride following the procedure of Bothe [38].

The carboxy-alkoxyamine **5b**, was also synthesized by atom transfer radical cross-coupling (Scheme 4). Reaction between nitroxide **2** and ethyl 2-bromoisobutyrate in the presence of an excess of Cu(0) [32] gave the crude alkoxyamine **5a** despite several attempts to purify it by chromatography. The basic hydrolysis of **5a** has resulted, after careful acidification, in the formation of the pure carboxy-alkoxyamine **5b** in 35.5% yield. This alkoxyamine was especially designed for aqueous polymerizations, where the carboxylic acid function provides water solubility in its basic form.

Finally the functionalized alkoxyamines **6** (60%) and **7** (65%) were prepared as **3**.

Moreover, TIPNO was also prepared following the procedure of Braslau [7]. The pure nitroxides **1** and **2** were kept at −30 °C, temperature at which they are solids. Surprisingly, we observe that TIPNO is much more stable than the new nitroxide **2**. Indeed, after three days, thin layer chromatography has pointed out that **2**, unlike TIPNO undergoes decomposition. Two new products appeared and by chromatography on silica were separated from **2** and identified: as it is established for α-hydrogen nitroxides [39], **2** disproportionates to give the hydroxylamine **8** and the nitrone **9** (Scheme 5) as decomposition compounds.

A small modification of structure on TIPNO that is the replacement of a carbon–hydrogen bond by a nitrogen atom induced a strong difference of stability, which at the moment is not completely explained for us: the steric hindrance is really slightly decreased going from TIPNO to **2** and consequently this release of steric hindrance can't explain the decay of **2**. Braslau has studied in details the decomposition [19] of TIPNO in the conditions of polymerization and has proposed a mechanism for the inherent instability of TIPNO: in solution a dimer is formed between two TIPNO molecules that exchange an electron followed by a proton transfer reaction to give hydroxylamine and nitrone decomposition compounds. Nitroxides are electron donors, known to give charge-transfer [40] complexes with electron acceptors. Therefore, one can imagine that, the dimerisation of **2** is favoured as the electron acceptor pyridyl substituent of **2** interacts with the aminoxyl function of a second molecule of **2** and consequently the decay is faster for **2** than for TIPNO in the solid state but also when **2** will be tested to mediate radical polymerization. So it seems to us interesting to check if the increased degree of inherent instability [41] of this new nitroxide **2** compared to TIPNO means the improvement of controlled



Scheme 5. Disproportion of nitroxide **2**.

polymerizations mediated by nitroxides, that was theoretically predicted by Fischer [41] and observed by Mullen [42], or the lost of the control over the polymerization or not as it is well known that a too unstable nitroxide doesn't regulate radical polymerization [7]. Therefore alkoxyamine **1a** and **3** have been compared.

3.2. Polymerization of styrene

The effectiveness of the difunctional alkoxyamine **3** for the living free radical polymerization of styrene was probed at 125 °C under bulk conditions. Good control was achieved up to high conversion. A linear increase of the molecular weight with conversion as well as low PDIs was observed (Fig. 1).

Using a ratio of 200 between styrene and **3**, polystyrene with $M_n = 25{,}500\ g\ mol^{-1}$ and a polydispersity index of 1.06 was obtained after 5 h with a conversion of 84%. A linear relationship between $\ln([M]_0/[M])$ vs time was observed (Fig. 2).

Under the same conditions of polymerization, **1a** has given a polystyrene with $M_n = 16{,}400\ g\ mol^{-1}$, a polydispersity index of 1.12 with a conversion of 90%. At the same conversion, **3** afforded a polystyrene with a higher molecular weight than **1a**. However, a higher polymerization time for the same monomer conversion is needed for **2** than for TIPNO **1**. For both nitroxides **1** and **2**, $\ln([M]_0/[M]) = k_{p\ Sty}[P^\bullet]t$ where $[P^\bullet]$ is the concentration of propagating radicals that is constant during the monomer conversion (Fig. 2). At $T = 125\ °C$ $k_{p\ Sty} = 2296\ L\ mol^{-1}\ s^{-1}$ [43] and analysis of the data from the graphs of Fig. 2 gives $k_{p\ Sty}[P^\bullet]_1 = 0.0075\ min^{-1}$ and $k_{p\ Sty}[P^\bullet]_2 = 0.006\ min^{-1}$. Finally $[P^\bullet]_1 = 5.445 \times 10^{-8}\ mol\ L^{-1}$, $[P^\bullet]_2 = 4.355 \times 10^{-8}\ mol\ L^{-1}$ and $[P^\bullet]_2/[P^\bullet]_1 = 0.8$. The concentration of propagating radicals is lower with nitroxide **2** than with TIPNO **1**. Consequently, during monomer conversion, the polar nitroxide **2** less favours self-termination reaction than TIPNO. Fisher [17] has demonstrated that, when the radical polymerization is controlled and living, that is our case, (the livingness is examined further in

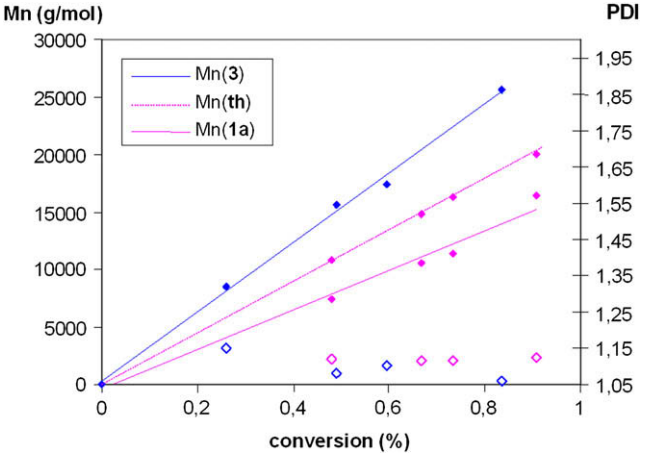


Fig. 1. Plot of the experimental molar masses (M_n, symbols), modeling M_n (unbroken lines), theoretical M_n (M_n(th), dotted lines) and polydispersity indexes (PDI, symbols) vs conversion for bulk polymerization of styrene at 125 °C with alkoxyamine **3** or **1a**. Experimental conditions: [styrene]/[**3** or **1a**] = 200; bulk; $T = 125\ °C$.

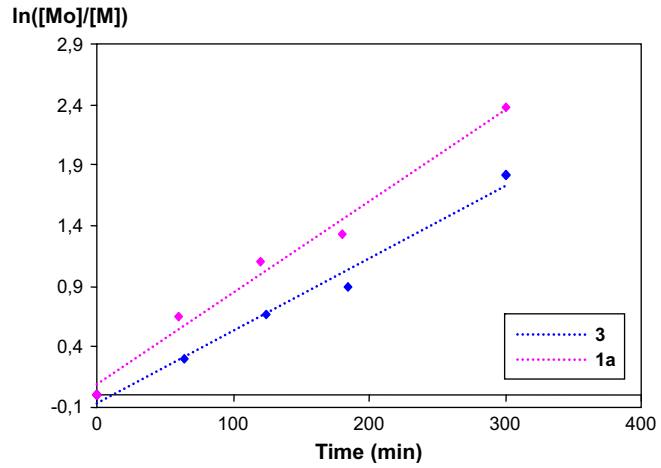


Fig. 2. Kinetic plot for bulk polymerization of styrene at 125 °C with alkoxyamine **3** or **1a**. Experimental conditions: [styrene]/[**3** or **1a**] = 200; bulk; T = 125 °C.

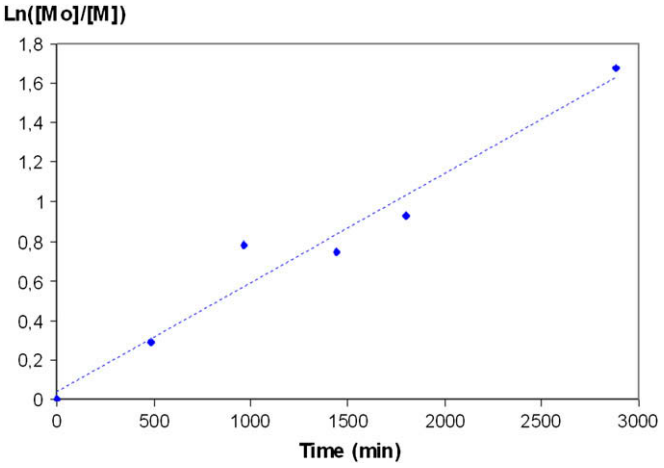


Fig. 4. Kinetic plot for bulk polymerization of styrene at 90 °C with alkoxyamine **3**. Experimental conditions: [styrene]/[**3**] = 500; bulk; T = 90 °C.

this paper), the monomer conversion is in the quasi-equilibrium stage that is established after a very short time t_0. If $t > t_0$ $[P^\bullet]_2/[P^\bullet]_1 = 0.8$. Until this quasi-equilibrium stage is reached, namely if $t < t_0$ and for low degrees of monomer conversion, $[P^\bullet]_2/[P^\bullet]_1$ might be lower or higher than 0.8 and its value might be estimated by comparison between theoretical and experimental molecular weights of polystyrene.

The alkoxyamines **1a** and **3** display the same initiating radical and differs slightly on the nitroxide structure as a carbon–hydrogen bond is replaced by a nitrogen atom. Consequently the same theoretical molecular weight M_n(th) is obtained for both **1a** and **3**. For nitroxides **1** and **2**, the number of growing chains is constant as the molecular weight increases linearly with the conversion (Fig. 1). For TIPNO **1**, M_n(th) > M_n(**1a**), and this case occurs when transfer [44] reactions take place during polymerization.

For nitroxide **2**, at 125 °C, firstly, M_n(**3**) > M_n(**1a**) and secondly, M_n(**3**) > M_n(th) what is explained usually by a efficiency of the initiating alkoxyamine **3** lower than **1**. The bulk polymerization of styrene was carried out without ramp of temperature. Under the same conditions, at 120 °C, Bertin [18] and all have observed also molecular weight higher than the predicted value because of the high lability of the initiating alkoxyamine whose fast homolysis rate induces a concentration of initiating radical large enough to favour its self-termination over reformation of alkoxyamines, that means a efficiency lower than **1**. Therefore, for the polar nitroxide **2**, before the quasi-equilibrium is reached, it is reasonable to state that $[P^\bullet]_2/[P^\bullet]_1 > 1$. If, for 0 s < t < t_0, $[P^\bullet]_2/[P^\bullet]_1 < 1$, then less self-termination for the initiating radical derived from **3** could occur and M_n(**1a**) should be higher than M_n(**3**), that is not the case. We think that the initiating alkoxyamine **3** is more labile that **1a**.

It was also possible to control the polymerization of styrene with a ratio of 1244 between styrene and **3** at 105 °C: a polystyrene with M_n = 79,800 g mol^{-1} and a polydispersity index of 1.25 was obtained after 20 h with a conversion of 83%.

The polymerization of styrene was finally investigated at 90 °C with a ratio of 500 and good control was observed (Figs. 3 and 4). As conversion increases, the PDI starting from a value of 1.45 decreases to reach a final value of 1.13 at high conversion (81%), with high molecular weight (M_n = 42,800 g mol^{-1}) after 48 h! At 90 °C, nitroxide **2** is as efficient as the best nitroxides [9,14,18] described for the controlled polymerization in bulk of styrene by NMP.

At T = 90 °C $k_{p\ Sty}$ = 890 L mol^{-1} s^{-1} [44] and analysis of the data from the graph of Fig. 4 gives $k_{p\ Sty}[P^\bullet]_2 = 0.0006$ min^{-1} and $[P^\bullet]_2 = 1.123 \times 10^{-8}$ mol L^{-1}. Moreover, the efficiency of the initiating alkoxyamine **3** is very closed to 1 (Fig. 3) at 90 °C. We observe for

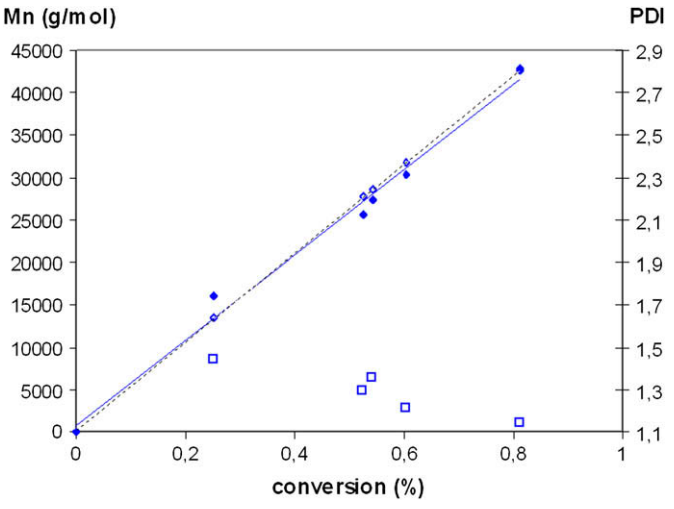


Fig. 3. Plot of the experimental molar masses (M_n, symbols), modeling M_n (unbroken lines), theoretical M_n (M_n(th), dotted lines) and polydispersity indexes (PDI, symbols) vs conversion for bulk polymerization of styrene at 90 °C with alkoxyamine **3**. Experimental conditions: [styrene]/[**3**] = 500; bulk; T = 90 °C.

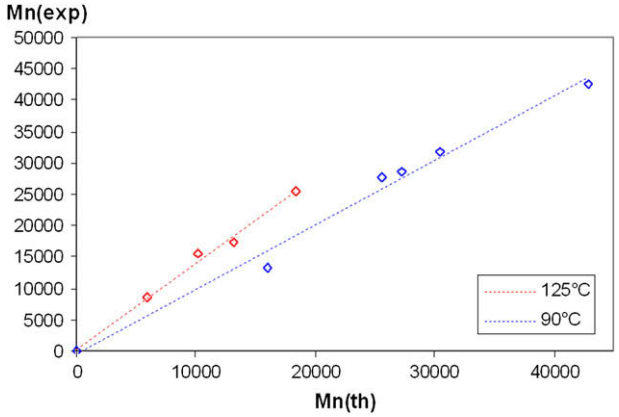


Fig. 5. Plot of experimental molecular weight vs theoretical molecular weight for alkoxyamine **3** at different temperatures.

polystyrene prepared by using **3** a much better agreement between the theoretical molecular weight and the experimental molecular weight when the temperature decreases as the slope of the straight line (Fig. 5) increases from 1.06 at 90 °C to 1.32 at 125 °C. The efficiency of the initiating alkoxyamine **3** is better at 90 °C than at 125 °C as the initiating alkoxyamine **3** is more labile at 125 °C than at 90 °C. Therefore, at 125 °C, more self-termination reaction occurs for the initiating radical derived from **3**. Moreover the concentration of propagating radicals $[P^{\bullet}]_2$ decreases with the temperature and consequently self-termination is more negligible at 90 °C than at 125 °C.

Despite an inherent instability of the polar nitroxide **2** at low temperature, its alkoxyamine **3** is an efficient initiator/regulator as good as the corresponding alkoxyamine **1a** of TIPNO for the controlled radical polymerization of styrene. Its efficiency is good over a large range of temperatures. The polymerization rates are similar for **2** and for TIPNO but the molecular weight of the polystyrene is significantly higher for **2** than for TIPNO at a given conversion. During styrene polymerization mediated by nitroxide **2** at 125 °C, the concentration of propagating radicals is kept lower than with TIPNO **1**. The determination of k_d and k_c for **3** will definitively complete the comparison between **2** and TIPNO.

3.3. Polymerization of n-butyl acrylate

It has been established that TIPNO [7], allows the control of not only styrene but also a wide range of monomers, such as acrylates, substituted acrylamides and dienes. Therefore, the effectiveness of the difunctional alkoxyamine **3** for the living free radical polymerization of n-butyl acrylate was tested at 125 °C under bulk conditions. Good control was achieved as the molecular weight is a linear increasing function of monomer conversion and as a low polydispersity index is observed (Fig. 6). Using a molar ratio [monomer]/[**3**] of 245, with 5% of free nitroxide **2**, poly(n-butyl acrylate) with $M_n = 11{,}700\ g\ mol^{-1}$ and a polydispersity index of 1.18 was obtained after 18 h (conversion 34%). A linear relationship between $\ln([M]_0/[M])$ vs time was again observed indicating that no detectable termination occurred in this system (Fig. 7). In order to compare **2** to TIPNO, **1a** was used as initiator/regulator during the n-butyl acrylate polymerization under the same conditions for **3**.

At $T = 125$ °C $k_{p\ acrylate} = 84{,}780\ L\ mol^{-1}\ s^{-1}$ [45] and analysis of the data from the graphs of Fig. 7 gives $k_{p\ acrylate}\ [P^{\bullet}]_1 = 0.0014\ min^{-1}$ and $k_{p\ acrylate}\ [P^{\bullet}]_2 = 0.0004\ min^{-1}$. $[P^{\bullet}]_1 = 2.751 \times 10^{-10}\ mol\ L^{-1}$, $[P^{\bullet}]_2 = 7.861 \times 10^{-11}\ mol\ L^{-1}$ and $[P^{\bullet}]_2/[P^{\bullet}]_1 = 0.285$. Like for styrene, the concentration of propagating radicals is lower with nitroxide **2** than with TIPNO **1**. Again, the same theoretical molecular weight M_n(th) is calculated for the alkoxyamines **1a** and **3** (Fig. 6). Moreover, for the polar nitroxide **2**, a perfect agreement is observed between the experimental molecular weight M_n(**3**) and M_n(th). During the polymerization, the excess of free nitroxide **2** keeps $[P^{\bullet}]_2$ at such low level that self-termination doesn't compete with reformation of macroalkoxyamines, which is responsible of the high efficiency of **3**. Finally with TIPNO nitroxide, $M_n(th) > M_n(\mathbf{1a})$ that could be explained like for styrene by chain transfer reactions favoured by the higher concentration of propagating radicals.

Finally, the bulk polymerization of n-butyl acrylate initiated by **3** was also investigated without adding free pyridine nitroxide **2** at 120 °C. For TIPNO **1** it was claimed that under these conditions [7] the polymerization is not living and controlled. The alkoxyamine **3** was able alone to mediate the polymerization in a controlled way.

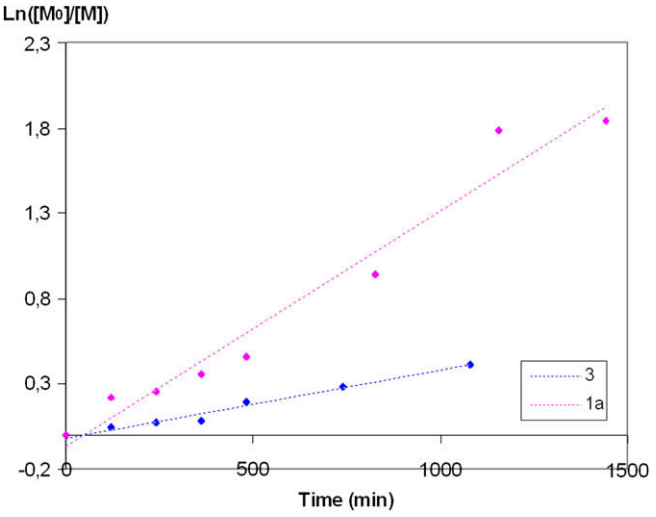


Fig. 7. Kinetic plot for bulk polymerization of n-butyl acrylate at 125 °C with alkoxyamine **1a** or **3**. Experimental conditions: [n-butyl acrylate]/[**3** or **1a**] = 245; [**2** or **1**]/[**3** or **1a**] = 0.05; bulk; $T = 125$ °C.

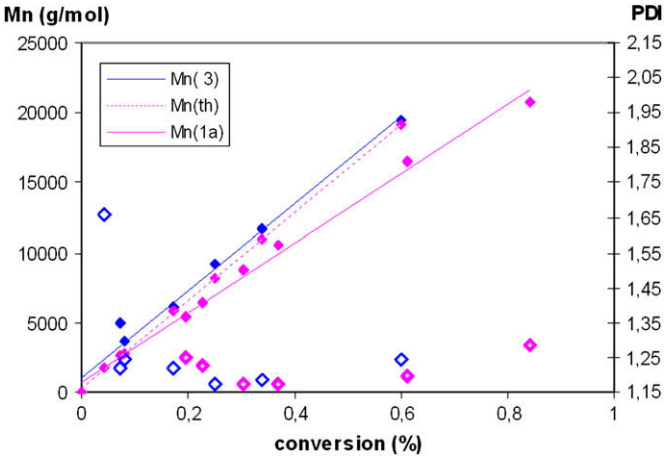


Fig. 6. Plot of the experimental molar masses (M_n, symbols), modeling M_n (unbroken lines), theoretical M_n (M_n(th), dotted lines) and polydispersity indexes (PDI, symbols) vs conversion for bulk polymerization of n-butyl acrylate at 125 °C with alkoxyamine **1a** or **3**. Experimental conditions: [n-butyl acrylate]/[**3** or **1a**] = 245; [**2** or **1**]/[**3** or **1a**] = 0.05; bulk; $T = 125$ °C.

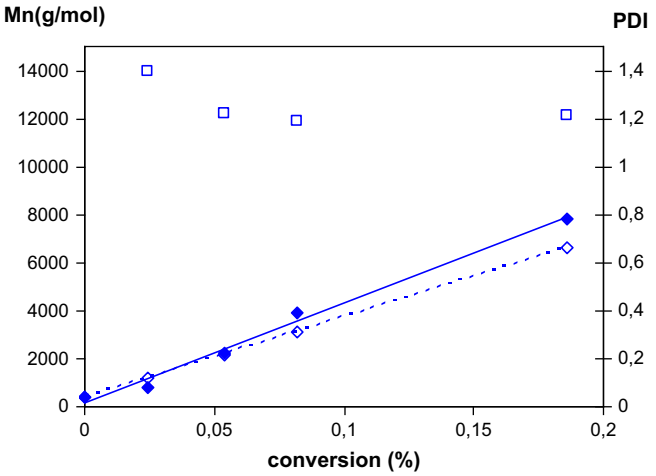


Fig. 8. Plot of the experimental molar masses (M_n, symbols), modeling M_n (unbroken lines), theoretical M_n (M_n(th), dotted lines) and polydispersity indexes (PDI, symbols) vs conversion for bulk polymerization of styrene at 120 °C with alkoxyamine **3**. Experimental conditions: [styrene]/[**3**] = 263; bulk; $T = 120$ °C.

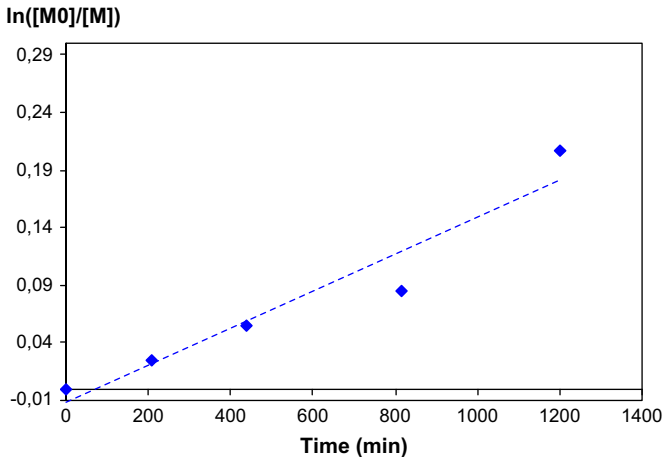


Fig. 9. Kinetic plot for bulk polymerization of styrene at 120 °C with alkoxyamine **3**. Experimental conditions: [styrene]/[**3**] = 263; bulk; T = 120 °C.

Good control was achieved with linear increase of the molecular weight and low polydispersity (Fig. 8). Using a ratio of 263 between n-butyl acrylate and **3**, poly(n-butyl acrylate) with M_n = 7840 g mol^{-1} and a polydispersity index of 1.21 was obtained after 20 h (conversion 18.6%). Moreover there is a good agreement between the experimental molecular weight and the theoretical molecular weight. The logarithmic conversion also exhibits a linear relationship with time (Fig. 9).

Very few nitroxides [9,16,18] are known to control the acrylate polymerization without adding free nitroxide. Indeed, an excess of nitroxide is required to control the polymerization of acrylate monomers because of their too fast rate of polymerization. This excess can be obtained by adding free nitroxide or with highly labile initiating alkoxyamines [18]. In this later case, at low monomer conversion, during the homolysis of the initiating alkoxyamines, termination reactions take place and meanwhile free nitroxide appears to trap reversibly the propagating radicals, which results in the control of the polymerization. Obviously the alkoxyamine **3** at 120 °C dissociates quickly enough to generate in situ free nitroxide **2** for the controlled polymerization of n-butyl acrylate and it is clear that the alkoxyamines of the pyridine TIPNO **2** are more labile than TIPNO's ones.

Of course, the polymerization rate was low at 120 °C and might increase with temperature. Therefore, a second attempt was tested at 122 °C. Using a ratio of 292 between n-butyl acrylate and **3**, poly(n-butyl acrylate) with M_n = 28,600 g mol^{-1} (M_n(th) = 26,500 g mol^{-1}) and a polydispersity index of 1.25 was obtained after 18 h (conversion 70%).

To conclude, the same differences between **1a** and **3** are observed for butyl acrylate and styrene polymerization. At the same conversion, M_n is higher with **3** than with **1a**. But at one instant, the conversion is higher for **1a** than for **3**. Moreover, the polar TIPNO **2** is more efficient than TIPNO for the acrylate polymerization and we confirm the strong influence of the polarity [22] of the nitroxide on the efficiency of the NMP process.

Table 1
Synthesis of styrene–n-butyl acrylate random copolymers, with alkoxyamine **3**.

Initial [monomer]/[**3**]	Initial r = [styrene]/[butyl acrylate]	Time (h)	Conversion (%)	M_n SEC (g/mol)	PDI
180	3	8	30.6	9700	1.19
200	0.937	8	39	10,400	1.24
180	0.32	25	55.5	18,300	1.21
200	0.1	17	43.6	18,500	1.52

Table 2
Synthesis of various copolymers and triblock polymers, R = [monomer]/[initiator], r = [initiator]/[**2**], bulk polymerization, T = 125 °C except for entry 6 for which T = 105 °C.

Entry	Polymer synthesized	Initiator	R	r	Time (min)	M_n (g/mol)[a]	PDI[a]
1	PS-1	5	196	**2** not added	105	8100	1.13
2	PS-2	3	216	**2** not added	120	8700	1.16
3	PS-3	5	206	**2** not added	300	25,550	1.08
4	PnBA-1	3	240	20.4	1140	18,100	1.13
5	PtBA-1	5	271	19	1350	7400	1.22
6	PnBA–PS1	PnBA-1	2086	**2** not added	315	100,000	1.57
7	PS–PnBA-1	PS-1	262	16.5	300	12,800	1.13
8	PS–PnBA-2	PS-1	262	16.5	1445	15,300	1.12
9	PS–PnBA-3	PS-2	254	17.6	300	11,900	1.14
10	PS–PnBA-4	PS-2	254	17.6	1445	14,900	1.13
11	PS–PnBA-5	PS-3	900	20	480	36,200	1.33
12	PS–PtBA-1	PS-1	287	16.4	180	12,500	1.12
13	PS–PtBA-2	PS-1	287	16.4	1380	18,400	1.16
14	PtBA–PS-1	PtBA-1	851	**2** not added	180	47,600	1.43
15	PS–PnBA–PtBA-1	PS–PnBA-4	381	17.35	850	20,900	1.20
16	PS–PnBA–PtBA-2	PS–PnBA-4	381	17.35	1260	22,900	1.24
17	PS–PnBA–PS-1	PS–PnBA-4	2924	**2** not added	180	80,700	1.59

[a] Apparent values for the block polymers from SEC analysis using linear PS standard calibrations except for entries 1–3.

3.4. Random copolymers

The random copolymerization of styrene and n-butyl acrylate was also investigated using **3** as initiator/regulator at 115 °C for different reaction time without adding any free nitroxide **2**.

Using a constant [monomers]/[alkoxyamine] molar ratio of around 200, well-defined copolymers, with low PDI, were obtained independently of the initial ratio r = [styrene]/[butyl acrylate] (Table 1) with the exception of low ratio r. Such behaviour has been previously observed for TIPNO [7].

3.5. Block copolymers

The livingness is essential for the synthesis of macromolecular architectures by NMP [46–59]. Therefore, to prove the living nature

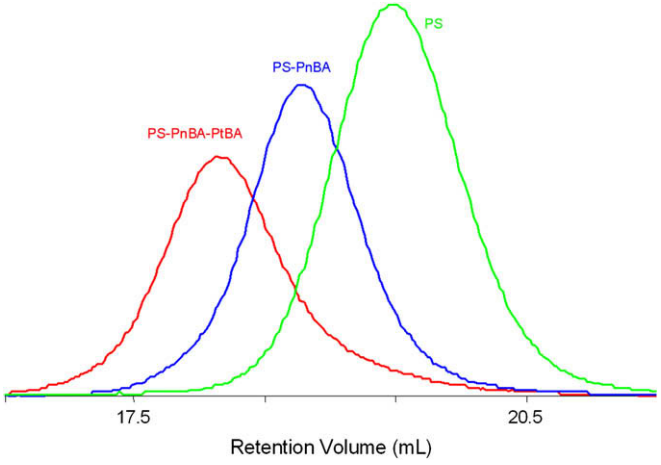


Fig. 10. SEC traces of alkoxyamine-functionalized polystyrene block PS (entry 2), block copolymer PS-b-PnBA (entry 9) and triblock polymer PS-b-PnBA-b-PtBA (entry 16), bulk; T = 125 °C.

of the radical polymerization process mediated by **2**, nitroxide-terminated PS, PnBA and PtBA homopolymers (Table 2, entries 1–5) were prepared for block polymerization studies. Table 2 summarized the results for both the initial homopolymerization step and subsequent block polymerization.

The polystyrene block, PS-1 (entry 1), was used to polymerize n-butyl acrylate, in the presence of an additional 0.06 equivalent of nitroxide **2** at 125 °C for two different reaction times: in each case, the polymerization gave block copolymers PS-b-PnBA, whose polydispersity index remained low (entries 7, 8). Furthermore, no unreacted polystyrene was detectable by SEC (Fig. 8). The same conclusions have also concerned the second polystyrene block studied PS-2 (entry 2), macroinitiator of PS-b-PnBA (entries 9, 10). Well-controlled PS-b-PtBA polymers (entries 12, 13) were also obtained by efficient initiation of the PS-1. Moreover, it was observed that the control over the molecular weight distribution is worse (entry 11) when the polystyrene macroinitiator has a higher molecular weight.

Such block copolymers can also be prepared using a PnBA macroinitiator. Usually, in NMP, chain extension of a polyacrylate block with styrene was usually accomplished without adding free nitroxide.

However, in our hands, under these conditions, the synthesis of the PnBA-b-PS (respectively PtBA-b-PS) is less controlled (entry 6 (respectively entry 14)) as the polydispersity index is around 1.57 (respectively 1.43) even though high molecular weight is reached.

But, what is more interesting is the preparation of triblock polymers PS-b-PnBA-b-PtBA (entries 15, 16) keeping a low PDI of 1.2 (Fig. 10)! A less controlled unsymmetrical triblock PS-b-PnBA-b-PS (entry 17) was synthesized by reinitiation of diblock PS-b-PnBA.

The alkoxyamine-functionalized poly(n-butyl acrylate) block synthesized without adding nitroxide **2** ($M_n = 28{,}600\ g\ mol^{-1}$, PDI = 1.25) was also used to polymerize 5408 equivalents of styrene at 115 °C for 240 min (conversion 40.3%). This gave the diblock copolymer PnBA-b-PS, which revealed the expected increase in molecular weight while the polydispersity index remained correct ($M_n(exp) = 142{,}000\ g\ mol^{-1}$, PDI = 1.52). Furthermore no unreacted poly(n-butyl acrylate) was detectable by SEC.

To conclude, different polystyrene and poly(n-butyl acrylate) blocks were successfully used as macroinitiators to prepare block copolymers, that clearly demonstrates the livingness of radical polymerization mediated by **2**.

4. Conclusions

The bromine–magnesium exchange of 2-bromopyridine provides an easy access to a new versatile TIPNO type nitroxide whose alkoxyamines, despite a more pronounced inherent instability of this new nitroxide **2** compared to TIPNO, are more efficient initiator/regulators as those of TIPNO because of the increase of polarity going from TIPNO to **2**: indeed, unlike TIPNO, no addition of free pyridine TIPNO **2** is required for the controlled radical polymerization of n-butyl acrylate. We confirm the result observed in the case of the polar SG1 nitroxide, namely, the strong influence of the polarity of the nitroxide on the efficiency of nitroxide-mediated radical polymerization. Moreover homopolymerization of styrene and butyl acrylate, **2** gives polymers with higher molecular weights than TIPNO at a given conversion and interestingly keeps propagating radicals at lower concentration than TIPNO. Finally, **2** allows to prepare efficiently different diblock and triblock copolymers. To explain the difference between **2** and TIPNO, the dissociation rate constants of the alkoxyamines of **2** will be determined. But what is of great interest is that parameters which are well known to govern the efficiency of nitroxide-mediated radical polymerization, namely the polarity and the steric hindrance around the C–O bond of these alkoxyamines might be tuned by protonation of by alkylation and this point will be published soon. We will also investigate the radical polymerization initiated by the alkoxyamines of the pyridine nitroxide in the presence of copper(II) halide as we are convinced that such alkoxyamines should be interesting initiators for atom transfer radical polymerization.

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