A Styryl TIPNO-Based Nitroxide as Efficient Mediator for the Synthesis of Multiblock Polystyrenes and Well-Grafted Polymers

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ABSTRACT: The chloromagnesium exchange of 4-chlorostyrene provides an easy access to a new versatile polymerizable 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO)-based nitroxide. Indeed, first, its alkoxyamine based on the α-methyl benzyl radical fragment efficiently mediates the polymerization of styrene (respectively *n*-butyl acrylate) to yield branched polystyrene [respectively poly(*n*-butyl acrylate)] with alkoxyamine function as branch point and well-defined branches. Second, the self-condensing of this polymerizable nitroxide by manganese coupling affords a mixture of oligomeric linear polyalkoxyamines. Polymerization of styrene mediated with these polyalkoxyamines gives multiblock polystyrenes with alkoxyamine group as linker between polystyrene blocks and exhibits the following features: the synthesis of the polystyrene blocks is controlled as their average molecular weight M_n(block) increases linearly with conversion and their average dispersity M_w/M_n(block) decreases with it. At a given temperature, the molecular weight and the dispersity of the polyalkoxyamines weakly impact M_n(block) and M_w/M_n(block). In contrast, the molecular weight of the multiblock polystyrene increases linearly with conversion until reaching a constant value. The number of block is independent of the molecular weight of the polyalkoxyamines. These unusual results can be explained by the fact that during polymerization, mediating TIPNO-based polymeric nitroxides with different lengths are generated and are exchanged. Finally the dispersity of the multiblock polystyrene is quite broad and lies between 1.7 and 2.8. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: alkoxyamines; block copolymers; branched; branched polymer; graft copolymers; inimer; living radical polymerization (LRP); multiblock polystyrene; nitroxide-mediated radical polymerization; polystyrene; radical polymerization

INTRODUCTION Controlled radical techniques (CRTs) such as nitroxide-mediated radical polymerization (NMRP),[1,2] radical addition fragmentation transfer (RAFT)[3] polymerization, atom transfer radical polymerization (ATRP),[4] and single electron transfer living radical polymerization (SET-LRP)[5] are versatile tools in macromolecular synthesis. Indeed, because of their living character, they allow to prepare well-defined[6,7] macromolecular architectures with complex structure. Especially, NMRP, RAFT, ATRP, and SET-LRP processes were used for the preparation of architectures whose synthesis is difficult or impossible by conventional radical polymerization. Multiblock[7] copolymers and highly branched[8] polymers are typical examples of such architectures.

Highly branched[9,10] and hyperbranched[11] polymers are the subject of increasing attention because of their unique[12] properties in solution (low viscosity) and in the solid state when compared with linear polymers and the presence of functional groups at their periphery as well as their potential applications in surface modification,[13] coatings,[14] and drug-delivery systems.[15] As a result, tremendous efforts have been devoted to their controlled[16,17] synthesis. Indeed, ATRP,[18–21] RAFT,[22,23] and NMRP[24,25] have been successfully applied to the preparation of these branched and tree-like macromolecules. All these synthetic approaches are based on the use of inimers,[26] molecules that contain a vinyl monomer and an initiator (halogenated alkane for ATRP or alkoxyamine for NMRP) or controller (dithioester group for RAFT) site. The self-condensation vinyl polymerization of inimers affords hyperbranched polymers.

As branched polymers, multiblock copolymers have also attracted attention because of their self-assembly morphologies in solution[27] and in the solid state[28] and their

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promising applications as compatibilizers,[29] materials with improved mechanically properties,[30] and proton[31,32] exchange fuel cells. Until the discovery of CRT, most of the multiblock copolymers were synthesized by condensation[7] of telechelic building blocks. As a radical process tolerates many functional groups, new well-defined telechelic building blocks with various structures[7,27,33] are now available by capitalizing on CRT, which widens the range of accessible multiblock copolymers. A second approach is to prepare step by step the multiblock using sequential ATRP[34] or RAFT[35] or more interestingly to build it in one pot using SET-LRP,[36] which by keeping its livingness until very high conversion makes the purification after the growing of each block nonessential. Finally, in third general approach, RAFT[37–41] agents or alkoxyamines,[42–44] initiator/controllers in NMRP, are incorporated in a linear polymer chain, which after monomer insertion affords multiblock polymers.

In this report, a polymerizable nitroxide was easily synthesized in few steps and good overall yield and was essential in the synthesis of branched and multiblock polymers. Indeed, its alkoxyamine based on 1-phenyl-ethyl radical has appeared as an efficient initiator/controller in NMRP of styrene and *n*-butyl acrylate (*n*BA) as well-defined branched polystyrenes and poly(*n*-butyl acrylates) were obtained. In both cases, the molecular weight and the dispersity of their linear backbones and their branches were nearly identical. Finally, this nitroxide underwent its self-condensation by manganese coupling to afford linear polyalkoxyamines, which on heating have inserted styrene to give multiblock polystyrenes with broad dispersity and whose molecular weight first increases linearly with conversion and finally becomes constant. In contrast, the synthesis of the polystyrene blocks was controlled in terms of molecular weight and dispersity.

EXPERIMENTAL

General Considerations

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on Bruker AC 200 MHz, 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 analysis was performed by the Service Central d'Analyses of the CNRS. Chemical ionization (CI, ammonia or methane) and electronic ionization mass spectra were obtained with a JMS-700 spectrometer.

All reagents and chemicals were obtained from commercial suppliers without further purification excepted when indicated. *n*BA (99%; Aldrich) and styrene (S, 99%; Aldrich) monomers were distilled under reduced pressure before use and stored at −4°C. 4-Chlorostyrene (technical, 90%) was purchased from Aldrich and used without further purification. Magnesium turnings (99%), sodium borohydride (>98%), copper powder (99%), copper(I) bromide (98%), *N,N,N′,N″,N‴*-Pentamethyldiethylenetriamine (PMDETA) (99%), (1-bromoethyl)-benzene, 2-methyl-5-*tert*-butylthiophenol (93%), chlorobenzene (99%), and ammonia solution (20% solution in water) were all obtained from Acros Organics. Methanol (MeOH), isopropanol, dichloromethane (CH_2Cl_2), and toluene (>99%) were purchased from VWR.

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 it is indicated.

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 2×10^6 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 standards from Polymer Standards Service. The monomer conversion for styrene and *n*BA was determined by gravimetry after drying the polymer samples under vacuum for 48 h.

N-tert-Butyl-α-iso-propylnitrone[45] and the salen–manganese complex[46] were synthesized according to literature procedures.

Synthesis of 2,2,5-Trimethyl-4-(4-vinylphenyl)-3-azahexane-3-nitroxide (2)

Under nitrogen atmosphere, 4-chlorostyrene (2.6 mL, 18.8 mmol) was diluted in THF (25 mL) and added dropwise for 20 min to a solution of magnesium (750 mg, 22.6 mmol) and of dibromo-1,2 ethane (0.1 mL, 1.15 mmol) in THF (4 mL) in order to have a smooth reflux. After the addition was completed, the solution was further heated at 65°C for 195 min. A solution of *N-tert*-butyl-α-*iso*-propylnitrone (2 g, 14 mmol) in THF (20 mL) was added for 10 min to the solution of styryl magnesium chloride 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 an aqueous ammonium chloride solution (7 g of NH_4Cl in 50 mL of water). Then 100 mL of CH_2Cl_2 was added. The organic layer was separated, and then the aqueous layer was extracted with CH_2Cl_2 (200 mL). The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated. The residue obtained was then treated with a mixture of MeOH (100 mL), ammonia solution (20% solution in water, 3 mL), and $Cu(OAc)_2$ (130 mg, 0.71 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 eluting with pure pentane gradually increasing to 5:95 ethyl acetate/pentane to afford 2.5 g (72% yield) of **2**, as an orange oil that crystallized at temperature below −25°C.

MS (CI, CH_4): *m/z* (%) 246 (M, 100) 190 (M-56, 86); HRMS (CI, CH_4) Calcd for $C_{16}H_{24}NO$ (M^+): 246.1858; found: 246.1860. Anal. Calcd for $C_{16}H_{24}NO$: C, 78.04; H, 9.75; N, 5.69. Found: C, 77.51; H, 9.50; N, 5.21.

Synthesis of 2,2,5-Trimethyl-3-(1′-(phenyl)-ethoxy)-4-p-vinylphenyl-3-azahexane (3)

To a Schlenk flask, (1-bromoethyl)-benzene (3.66 g, 19.7 mmol), the functionalized 2,2,5-trimethyl-4-phenyl-3-

azahexane-3-nitroxide (TIPNO) **2** (4.7 g, 19.1 mmol), and 32 mL of toluene were added. To a second Schlenk flask, copper powder (1.929 g, 30.3 mmol), copper(I) bromide (301.6 mg, 2.1 mmol), 32 mL of toluene, and PMDETA (0.8 mL, 3.8 mmol) were added. The two reaction solutions were deoxygenated by bubbling nitrogen for 15 min. The nitroxide solution was then added to the solution of copper derivatives under nitrogen atmosphere, and the resulting solution was further stirred at room temperature under inert atmosphere. 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 pure alkoxyamine **3** was obtained as a clear oil (1.72 g, 25.6% yield).

^{1}H NMR (300 MHz, $CDCl_3$, two diastereoisomers, δ): 7.38–7.14 (m, 18H), 6.65 (dd, 1H, J = 17.3 Hz and 10.9 Hz, —C**H**=CH_2), 6.60 (dd, 1H, J = 17.3 Hz and 10.9 Hz, —C**H**=CH_2), 5.68 (d, 1H, J = 17.3 Hz and 0.8 Hz, 1H, —CH=C$\mathbf{H_2}$ *trans*), 5.62 (d, 1H, J = 17.3 Hz and 0.8 Hz, 1H, —CH=C$\mathbf{H_2}$ *trans*), 5.13 (d, 1H, J = 10.9 Hz and 0.8 Hz, 1H, —CH=C$\mathbf{H_2}$ *cis*), 5.10 (d, 1H, J = 10.9 Hz and 0.8 Hz, 1H, —CH=C$\mathbf{H_2}$ *cis*), 4.83 (q + q, 2H, C**H**—O), 3.34 (d, 1H, J = 10.6 Hz, C**H**—N), 3.22 (d, 1H, J = 10.8 Hz, C**H**—N), 2.25 (two m, 2H, CH—*i*Pr), 1.56 (d, 3H, J = 6.6 Hz, C$\mathbf{H_3}$—CH—O), 1.47 (d, 3H, J = 6.6 Hz, C$\mathbf{H_3}$—CH—O), 1.23 (d, 3H, J = 6.4 Hz, C$\mathbf{H_3}$—*i*Pr), 0.98 (s, 9H, *t*Bu), 0.84 (d, 3H, J = 6.3 Hz, C$\mathbf{H_3}$—*i*Pr), 0.71 (s, 9H, *t*Bu), 0.48 (d, 3H, J = 6.6 Hz, C$\mathbf{H_3}$—*i*Pr), and 0.15 (d, 3H, J = 6.6 Hz, C$\mathbf{H_3}$—*i*Pr). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 145.91, 145.13, 142.63, 142.43 (aromatic), 137.10 (—**C**H=CH_2), 135.75, 135.59, 131.29, 131.24, 128.27, 128.26, 127.20, 127.09, 126.85, 126.36, 126.36, 125.50, 125.32 (aromatic), 113.08, 112.94 (—CH=$\mathbf{C}H_2$), 83.69, 83.03 (CH—O), 72.08, 71.99 (CH—N), 60.74, 60.61 (*t*Bu—N), 32.19, 31.79 (CH—*i*Pr), 28.66, 28.47 (*t*Bu), 24.91, 23.34, 22.33, 22.16, 21.35, 21.24 ppm (CH_3). Anal. Calcd for $C_{24}H_{33}NO$: C, 82.05; H, 9.40; N, 3.98. Found: C, 81.49; H, 9.56; N, 3.63. Found: C, 81.34; H, 9.58.

Synthesis of Linear Polyalkoxyamines

The styryl TIPNO-based nitroxide **2** (1.82 g, 12.2 mmol) was dissolved in 8 mL of isopropyl alcohol in an open flask. The solution was vigorously stirred, and finely ground Mn(salen)Cl catalyst (724 mg, 2 mmol) was added, followed by $NaBH_4$ (737 mg, 19.5 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 petroleum ether gradually increasing first to pure ethyl acetate and second to 90:10 ethyl acetate/MeOH. Six fractions, **9a** (eluent: 100:0 petroleum ether/ethyl acetate, m = 658 mg, M_n = 1300 g mol^{-1}, M_w/M_n = 2.2), **9b** (eluent: 100:00 petroleum ether/ethyl acetate, m = 119 mg, M_n = 2200 g mol^{-1}, M_w/M_n = 1.25), **9c** (eluent: 90:10 petroleum ether/ethyl acetate, m = 139 mg, M_n = 1230 g mol^{-1}, M_w/M_n = 3.65), **9d** (eluent: 70:30 until 50:50 petroleum ether/ethyl acetate, m = 204 mg, M_n = 4750 g mol^{-1}, M_w/M_n = 1.15), **9e** (eluent: 25:75 until 0:100 petroleum ether/ethyl acetate, m = 226 mg, M_n = 3200 g mol^{-1}, M_w/M_n = 1.2), and **9f** (eluent: 100:0 ethyl acetate/MeOH, m = 366 mg, M_n = 1900 g mol^{-1}, M_w/M_n = 2.55), were separated to give oligomeric polyalkoxyamines.

Analysis of 9d

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.75–7 (m, H aromatic), 4.83 (s, 2H, C**H**—O), 3.33 (s, 1H, C**H**—N), 3.22 (s, 1H, C**H**—N), 2.25 (s, 2H, C**H**—*i*Pr), 1.55 (s, 3H, C$\mathbf{H_3}$—CH—O), 1.45 (d, 3H, C$\mathbf{H_3}$—CH—O), 1.24 (s, 3H, C$\mathbf{H_3}$—*i*Pr), 0.98 (s, 9H, *t*Bu), 0.63 (s, 3H, C$\mathbf{H_3}$—*i*Pr), 0.44 (s, 9H, *t*Bu), 0.25 (s, 3H, C$\mathbf{H_3}$—*i*Pr), and 0.0 (s, 3H, C$\mathbf{H_3}$—*i*Pr). Anal. Calcd for $C_{16}H_{25}NO$: C, 77.73; H, 10.12; N, 5.66. Found: C, 76.20; H, 10.04; N, 5.61.

General Procedure for Styrene Polymerization: Preparation of Branched Polystyrene

A mixture of alkoxyamine **3** (191.6 mg, 0.545 mmol) and styrene (17.78 g, 171 mmol) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 120°C for 7 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 = 39,800 g mol^{-1}, M_w/M_n = 1.9, conversion = 63.7%) by quenching the reaction in an ice bath. Polystyrene was precipitated with MeOH.

General Procedure for Cleavage of the C—ON Bond of the Branched Polystyrene

The procedure has been adjusted until after post-treatment the molecular weight of the polymer is constant. A typical procedure is given as follows: a mixture of polymer sample (50 mg), 2-methyl-5-*tert*-butylthiophenol (20 μL, 0.132 mmol), and chlorobenzene (1 mL) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 125°C for 7 h. The solution was evaporated to dryness under reduced pressure, and the crude polystyrene was directly analyzed by SEC.

General Procedure for Acrylate Polymerization: Preparation of Branched Poly(*n*-butyl acrylate)

A mixture of the alkoxyamine **3** (203 mg, 0.578 mmol), the corresponding nitroxide **2** (7.1 mg, 0.028 mmol), and *n*BA (19.38 g, 151.4 mmol) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 125°C for 24 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 = 54,000 g mol^{-1}, M_w/M_n = 3.5, conversion = 60%) by immersing the reaction flask in an ice bath.

General Procedure for Cleavage of the C—ON Bond of the Branched Poly(*n*-butyl acrylate)

The procedure has been adjusted until after post-treatment the molecular weight of the polymer is constant. A typical

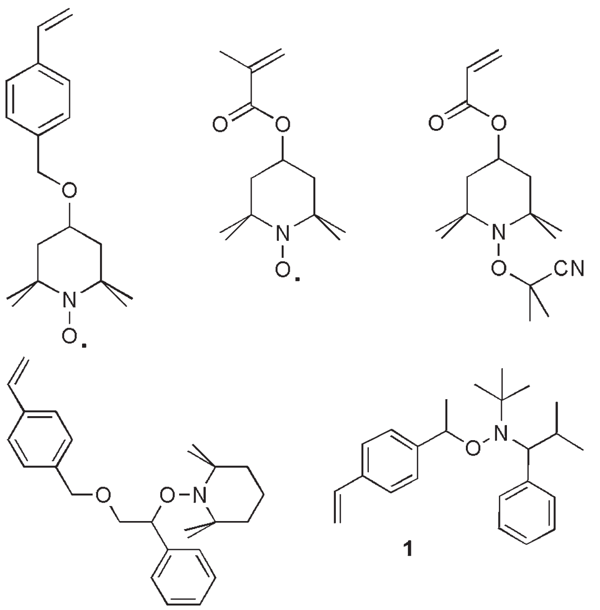


FIGURE 1 Examples of polymerizable nitroxides and alkoxyamine inimers to synthesize hyperbranched architectures.

procedure is given as follows: a mixture of the polymer sample (50 mg), 2-methyl-5-*tert*-butylthiophenol (20 μL, 0.132 mmol), and chlorobenzene (1 mL) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 125°C for 7 h. The solution was evaporated to dryness under reduced pressure, and the crude poly(*n*-butyl acrylate) was directly analyzed by SEC.

General Procedure for Styrene Polymerization: Preparation of Multiblock Polystyrene

A mixture of the alkoxyamine **9a** (100 mg, $n = 0.405$ mmol alkoxyamine equivalents) and styrene (12.57 g, 121 mmol) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 115°C for 6 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 ($M_n = 110{,}000$ g mol^{-1}, $M_w/M_n = 2.11$, conversion $= 51.7\%$) by quenching the reaction in an ice bath. Polystyrene was precipitated with MeOH.

General Procedure for Cleavage of the C—ON Bond of the Multiblock Polystyrene

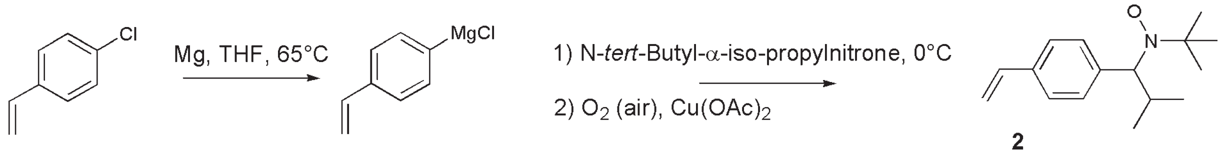
The procedure has been adjusted until after post-treatment the molecular weight of the polymer is constant. A typical procedure is given as follows: a mixture of the polymer sample (40 mg), 2-methyl-5-*tert*-butylthiophenol (20 μL, 0.132 mmol), and chlorobenzene (2 mL) was degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 125°C for 3 h. The solution was evaporated to dryness under reduced pressure, and the crude polystyrene was directly analyzed by SEC.

DISCUSSION

Synthesis of Branched Polymers

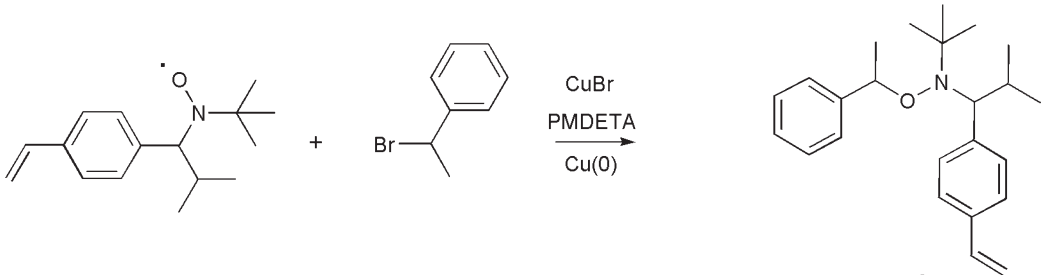
Synthesis of the Inimer

Several nitroxides[47–50] and alkoxyamine inimers[24,51–58] (Fig. 1) were dedicated to the synthesis of branched polymers by NMRP. Most of them are based on 2,2,6,6-tetramethylpiperidine-*N*-oxyl (Tempo) nitroxide. Recently, we have described the inimer **1**[25] (Fig. 1) containing the TIPNO and the styryl radical fragment. Inimer **1** has efficiently controlled the synthesis of branched polystyrene and branched poly (*n*-butyl acrylate). Here, we report the synthesis of the styryl TIPNO-based nitroxide **2** (Scheme 1) and its corresponding inimer **3** (Scheme 2) incorporating the 1-phenylethyl moiety. Its synthesis is straightforward as reaction of styryl magnesium chloride with *N*-*tert*-butyl-α-*iso*-propylnitrone followed by a copper-catalyzed oxidation reaction by air gives **2** in overall good yield of 72%. The inimer **3** was obtained in 25.6%



2

SCHEME 1 Synthesis of the polymerizable TIPNO-based nitroxide **2**.



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SCHEME 2 Synthesis of the alkoxyamine inimer **3**.

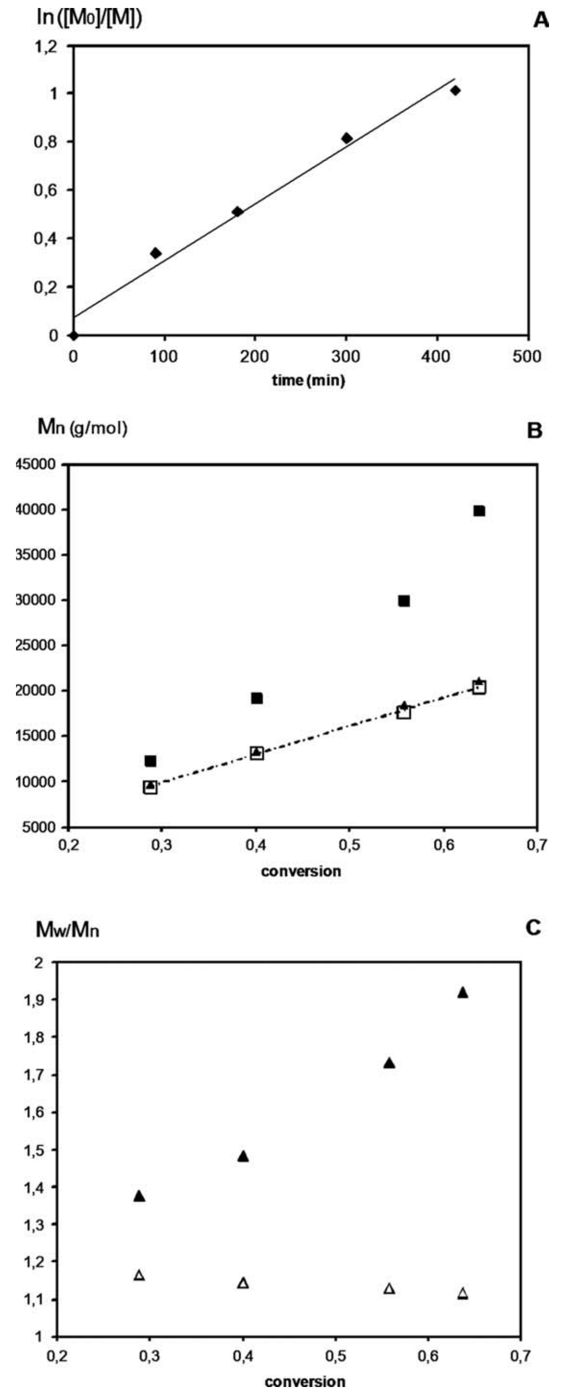


FIGURE 2 A Kinetic plot for bulk polymerization of styrene at 120°C with the inimer **3**. **B**: Plot of the experimental molar masses of the polystyrene architecture before (M_n; ■) and after (M_n; □) thiol treatment versus conversion for bulk polymerization of styrene at 120°C with the inimer **3**. Plot of the theoretical molar masses [M_n(th); ▲ versus conversion supposing the vinyl group of **3** unreactive at all stages of the polymerization. **C**: Plot of dispersity of the polystyrene architecture before (M_w/M_n; ▲) and after (M_w/M_n; △) thiol treatment versus conversion for bulk polymerization of styrene at 120°C with the inimer **3**. Experimental conditions: [Styrene]/[**3**] = 313; bulk; T = 120°C.

yield by nitroxide radical coupling[59] reaction between 1-phenylethyl bromide and **2**.

Synthesis of Branched Polystyrene

We have observed that the inimer **1**[25] efficiently initiates and controls the bulk polymerization of styrene to yield branched polystyrene. Furthermore, the branching was starting at a conversion of around 30%.

To compare inimer **3** with inimer **1**, the bulk polymerization of styrene initiated by the inimer **3** was investigated at 120°C under bulk conditions, using a ratio of 313 between styrene and **3**.

A linear relationship between $\ln([M]_0/[M])$ versus time was observed [Fig. 2(A)] from the beginning until the end of the experiment of polymerization, indicating that no detectable termination occurred in this system. Moreover, the molecular weight [Fig. 2(B)] and the dispersity [Fig. 2(C)] increase with conversion. The polystyrene (M_n = 39,800 g mol^{-1}; M_w/M_n = 1.9) was obtained after 7 h with a conversion of 63.7%. Its SEC traces (Fig. 3) have indicated a multimodal molecular weight distribution that could be explained by the presence of two polystyrene architectures at least, one is a linear polystyrene macroinimer and the second is a branched polystyrene where each branch point is an alkoxyamine function. To check this hypothesis, the polystyrene samples were treated with 2-methyl-5-*tert*-butylthiophenol at 125°C in chlorobenzene during 7 h in order to cleave alkoxyamine functions and the post-treating crude polystyrenes were analyzed by SEC. Indeed, under these conditions, the **C—ON** bond of any alkoxyamine function undergoes an irreversible[60] homolytic cleavage as its releasing radical fragment very quickly removes[61] hydrogen atom from thiol.

After the treatment with thiol, the molecular weight M_n (Fig. 4) and the dispersity (Fig. 4) of the polystyrene architecture decrease. For example, the polystyrene sample obtained after 7 h of polymerization has given a linear monodisperse polystyrene (M_n = 20,400 g mol^{-1}; M_w/M_n = 1.11). Moreover, M_n increases linearly with conversion [Fig. 2(B)], and the dispersity [Fig. 2(C)] is around 1.1–1.2 at all stages of the polymerization that are the typical features of a controlled radical polymerization. As Yang coworkers,[47] we accounted

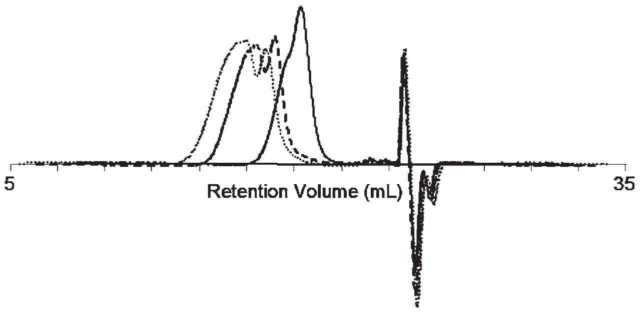


FIGURE 3 SEC traces of alkoxyamine-functionalized polystyrene architecture for 28.7% (black unbroken line), 55.7% (black broken line), and 63.7% (black dotted line) of conversion. Experimental conditions: [Styrene]/[**3**] = 313; bulk; T = 120°C.

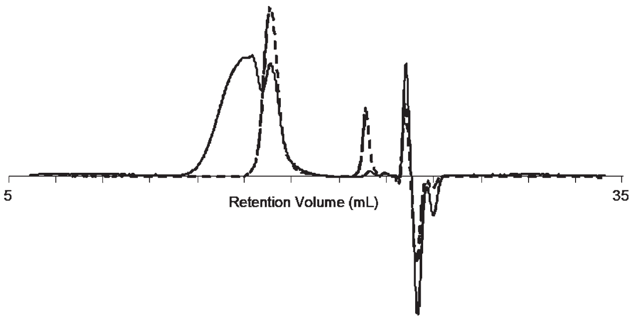


FIGURE 4 SEC traces of polystyrene architecture for 63.7% of conversion before (unbroken lines) and after (dotted lines) thiol treatment. Experimental conditions: [Styrene]/[**3**] = 313; bulk; T = 120°C.

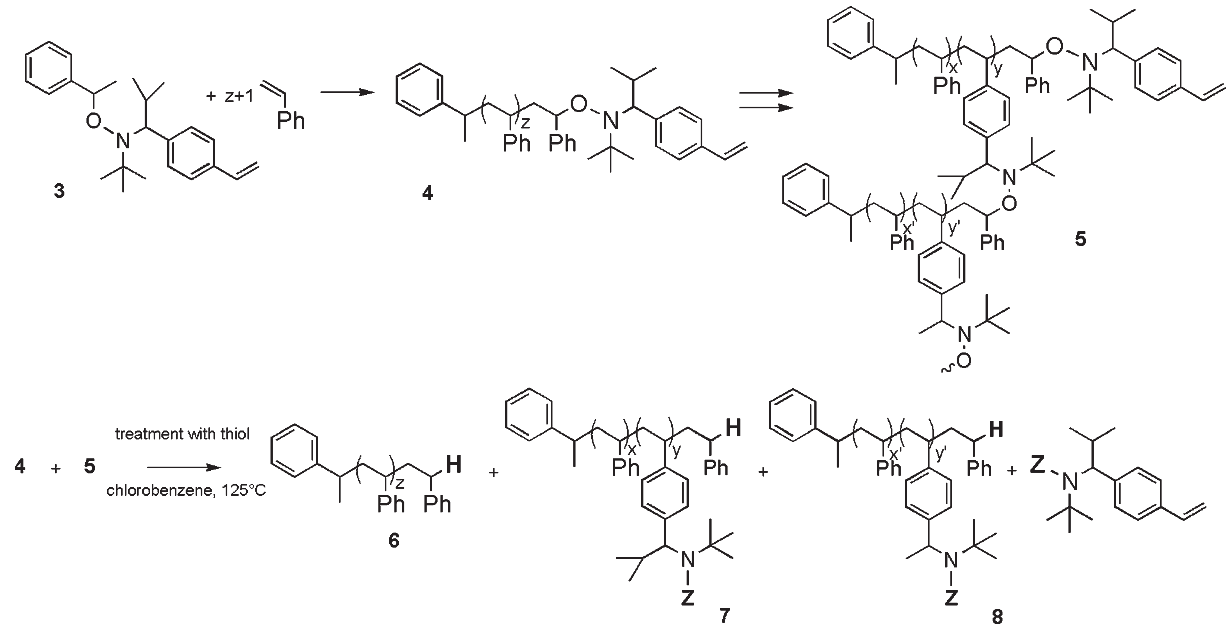
for these results by the presence of branched polystyrene. At low conversion, the inimer **3** is transformed into the linear monodisperse polystyrene macroinimer **4** (Scheme 3). As the conversion increases, branching occurs more and more by random copolymerization of styrene and **4** affording a mixture of **4** (narrow peak in Fig. 3) and the branched polystyrene **5** (Scheme 3), displaying a broad peak at higher molecular weight that is growing (Fig. 3) to the detriment of the one of **4**. As for the inimer **1**,[25] the branching starts at a conversion of around 30%. After thiol treatment, the architectures **4** and **5** have yielded the mixture of linear polystyrenes **6**, **7**, and **8** (**Z** = H, OH, or sulfoxide function[62]; Scheme 3) contaminated by molecular byproducts. The investigation of the breaking of alkoxyamine function reveals that the branches of **5** and the macroinimer **4** have nearly the same molecular weight M_n [Fig. 2(B)] during the whole polymerization, as it is attested by the narrow dispersity of the mixture composed of **6**, **7**, and **8**. Moreover, M_n is in good agreement with the theoretical molecular weight M_n(th) calculated assuming that the vinyl group of the inimer **3** does not react. It comes from these latter results that the alkoxyamine functions of **5** located at the chain end of a branch or incorporated in it display similar reactivity.

To conclude, the polymerization of styrene is controlled as until the end of the experiment of polymerization, the molecular weight of the macroinimer **4** is growing linearly with conversion and its dispersity is narrow. Meanwhile, the random copolymerization of styrene with one fraction of **4** takes place to yield a branched polystyrene with controlled length of branch.

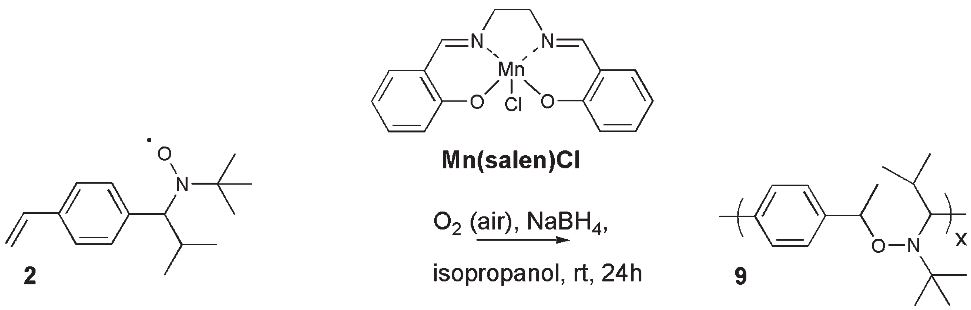
Synthesis of Branched Poly(*n*-butyl acrylate)

As TIPNO is an efficient nitroxide[45] for the controlled and living polymerization of *n*BA, **3** was also tested as initiator/regulator of the bulk polymerization of *n*BA to obtain branched poly-(*n*-butyl acrylate). The experiment was carried out at 125°C using a molar ratio [*n*BA]/[**3**] of 261, with 5% of free nitroxide **2** that was added to control the propagation rate of the polymerization. The poly(*n*-butyl acrylate) with $M_n = 54{,}000$ g mol^{-1} and a dispersity of 3.5 was obtained after 24 h (conversion 60%). The apparent molecular weight [see Supporting Information Fig. S1(B)] and the dispersity [see Supporting Information Fig. S1(C)] increase with the conversion. Starting from a value of 1.5 (conversion: 20%), M_w/M_n reaches a final value of 3.5 (conversion: 60%). The molecular weight distribution is broad, exhibiting unimodal SEC profiles. A linear relationship between $\ln([M]_0/[M])$ versus time was again observed, indicating that no detectable termination occurred in this system [See supporting information: Fig. S1(A)].

As in the case of styrene, the polymer was submitted to the treatment with thiol under the same conditions. Supporting Information Figure S2 presents the GPC traces of one



SCHEME 3 Synthesis of the macroinimer **4** and the branched polystyrene **5** by NMRP with the alkoxyamine inimer **3**.



SCHEME 4 Synthesis of the oligomeric polyalkoxyamines **9** by manganese self-coupling of polymerizable TIPNO-based nitroxide **2**.

polymer sample before and after this treatment. As for styrene, the decrease of molecular weight and the narrower dispersity (M_w/M_n around 1.2–1.3) is consistent with the presence of a branched poly(*n*-butyl acrylate) architecture. Moreover, the synthesis of the branch is controlled as its molecular weight [Supporting Information Fig. S1(B)] is growing linearly with conversion and its dispersity is low [Supporting Information Fig. S1(C)]. As an example, the architecture obtained with a conversion of 60% was converted into the linear monodisperse poly(*n*-butyl acrylate) ($M_n = 22{,}000$ g mol^{-1}; $M_{th} = 20{,}400$ g mol^{-1}; $M_w/M_n = 1.3$).

It is again reasonable to assume that the molecular inimer **3** has yielded monodisperse acrylate macroinimers. Then, the starting copolymerization of these macroinimers and *n*BA affords branched poly(*n*-butyl acrylate) architectures and provides a good control over the length of the branch and its dispersity. As for the inimer **1**,[25] the branching starts at a conversion of around 19%.

To conclude, for styrene and *n*BA, as the inimer **1**, inimer **3** initiates and also polymerizes to give a macromolecular architecture whose broad dispersity is the outcome of its branched character. The synthesis of branches, accompanied by narrow dispersity, is controlled as their molecular weight is a linear function of conversion that demonstrates the high chain-end fidelity of the nitroxide **2** and nitroxides incorporated in the branch points.

Synthesis of Multiblock Polymers

Synthesis of Linear Polyalkoxyamines

The incorporation of alkoxyamine units in simple macromolecular architectures enables to prepare through nitroxide exchange reactions more sophisticated architectures such as star polymers,[63,64] polymer hybrids,[65,66] macrocycles,[67] and polymer brushes[68] and to control crystal assembly.[69] In the same manner, linear polymers containing several alkoxyamine functions have appeared as versatile polyinitiators[43] to synthesize multiblock copolymers. They were obtained by nitroxide radical self-coupling,[42] from TEMPO-based diol by polycondensation[70] with adipolyl chloride, or by polyaddition[44] with diisocyanate.

A general method of synthesis of alkoxyamine is the radical coupling of functionalized styrene substrates and nitroxide using manganese-based epoxidation catalysts[46,71] such as Mn(Salen)Cl (Scheme 4). This prompted us to investigate the self-coupling of the styryl TIPNO-based nitroxide **2**.

The reaction with, as previously described, a high loading[46,71] of manganese catalyst to favor the formation of alkoxyamines has been carried out in isopropanol at room temperature for 1 day. Compound **2** has completely disappeared and has polymerized to afford a mixture of linear oligomeric polymers **9** (Scheme 4) with a TIPNO-based alkoxyamine function as repeating unit according to ^{1}H NMR analysis (see Supporting Information Fig. S3). High conversion (95%) was reached. By careful chromatography on silica, six oligomeric and more and more polar polyalkoxyamines were successfully separated and characterized by SEC. The results are given in Table 1. Compound **9a** displays a broad dispersity; however, it was possible to obtain well-defined polyalkoxyamines like **9d** (Fig. 5).

The ^{1}H NMR spectrum of **9d** (Supporting Information Fig. S3) reminds the one of a molecular TIPNO-based[45] alkoxyamine, but with broad peaks, that supports the synthesis of a polymer chain through the formation of a **C—ON** bond by self-coupling of **2**. Indeed, it clearly indicates the absence of vinylic protons and displays a broad singlet at 4.83 ppm, attributed to the proton of the H—C—ON fragment and at 2.25 ppm attributed to the methyne proton of the isopropyl group of **9d**. Furthermore, the diastereotopic methyls of the CH_3—CH—ON fragment (^{1}H singlet signals at 1.55 and 1.45 ppm), of the isopropyl substituent (^{1}H singlet signals at 1.24, 0.63, 0.25, and 0 ppm), and of the *tert*-butyl group (^{1}H singlet signals at 0.98 and 0.44 ppm) appear in the ^{1}H NMR spectrum of **9d**. Under the conditions of the formation of alkoxyamines, side reactions such as epoxidation[46,71] of the styrenic group or ring opening of the prepared epoxide by nucleophilic attack might also contribute to the total

TABLE 1 Average molecular weights and dispersity of synthesized polyalkoxyamines

	9a	9b	9c	9d	9e	9f
M_n[a] (g mol^{-1})	1,300	2,200	1,230	4,750	3,200	1,900
M_w/M_n[a]	2.2	1.25	3.65	1.15	1.12	2.55

[a] Apparent values for the polyalkoxyamines from SEC analysis using linear polystyrene standard calibrations.

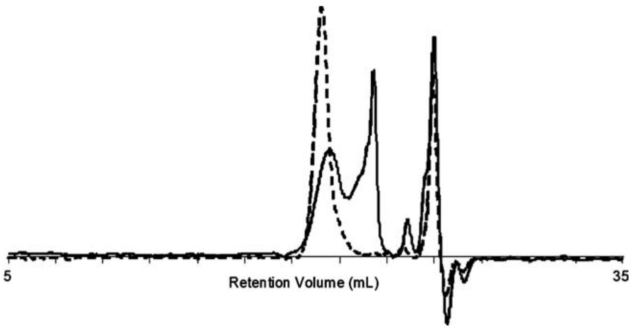


FIGURE 5 SEC traces of oligomeric polyalkoxyamines **9a** (black unbroken line) and **9d** (black broken line).

consumption of the vinyl group of polyalkoxyamine **9d**. Therefore, polyalkoxyamines with identical average degree of polymerization can be synthesized, but with different chain extremities displaying various polarity. As a result, these polyalkoxyamines are separated by chromatography on silica and may display similar molecular weights.

Two polyalkoxyamines **9a** ($M_n = 1300$ g mol^{-1} and $M_w/M_n = 2.2$) and **9d** ($M_n = 4750$ g mol^{-1} and $M_w/M_n = 1.15$) were tested as polyinitiators in NMRP to prepare multiblock polystyrenes.

Synthesis of Multiblock Polystyrenes

The effectiveness of the polyalkoxyamines **9a** displaying a broad molecular weight distributions and the monodisperse **9d** for the living free radical polymerization of styrene was probed at 115°C in bulk under the same conditions. The polystyrene architecture **10** (Fig. 6) with a broad dispersity was obtained.

The treatment of **10** (Scheme 5) with 2-methyl-5-*tert*-butylthiophenol has given the polystyrene architecture **11**. Compound **11** displays narrower dispersity than **10**, accompanied by a decrease of the experimental molecular weight (Fig. 6), that confirms the synthesis of the multiblock polystyrene **10** (Scheme 5) in which the link between consecutive polystyrene blocks is an alkoxyamine function: **11** (**Z** = H, OH, or sulfoxide function[62]; Scheme 5) is a mixture of all the polystyrene blocks formed during the styrene insertion in **9a** or **9d**. The narrow molecular weight distribution [Fig. 7(C)] of **11** demonstrates that all the polystyrene blocks have mostly the same length.

With **9a**, a linear relationship between $\ln([M]_0/[M])$ versus time was observed [Fig. 7(A)]. The molecular weight M_n(**10**, **9a**) of the multiblock polystyrene **10** first increases linearly with conversion and then is nearly constant independently of the monomer's consumption [Fig. 7(B)]. M_w/M_n decreases with conversion [Fig. 7(C)], and its value is between 2 and 2.8.

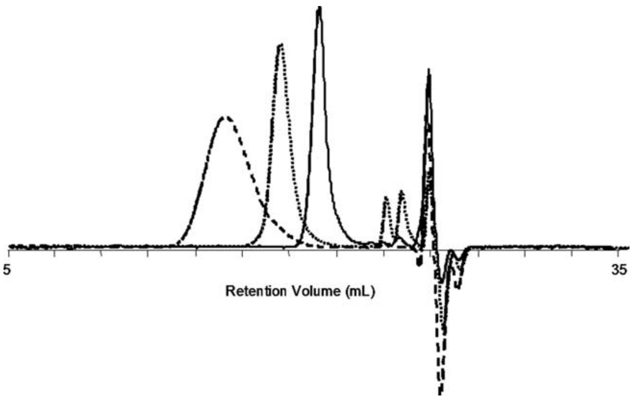


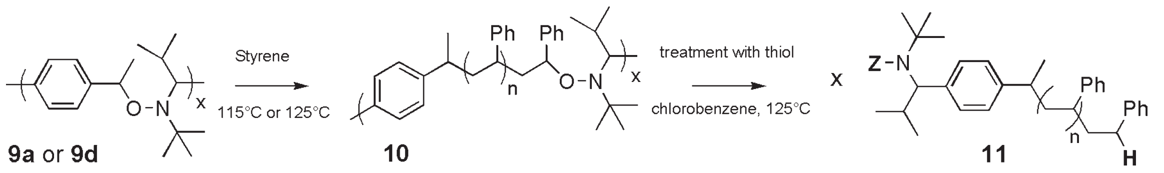
FIGURE 6 SEC traces of oligomeric polyalkoxyamines **9d** (black unbroken line) and polystyrene architecture **10** before (black broken line) and after (black dotted line) thiol treatment.

A rather acceptable control [Fig. 7(B, C)] was achieved for the growing of the polystyrene blocks: starting from a value of 1.6 (conversion: 2.5%), M_w/M_n reaches a final value of 1.37 (conversion: 51.7%) and M_n(**11**, **9a**) is a linear function of the conversion.

Using a ratio of 300 between the number of styrene monomers and the number of alkoxyamine function in **9a**, the multiblock polystyrene **10** ($M_n = 102{,}500$ g mol^{-1}; $M_w/M_n = 2.05$) and the mixture **11** of polystyrene blocks ($M_n = 25{,}300$ g mol^{-1}; $M_w/M_n = 1.37$) were obtained after 6 h with a conversion of 51.7%.

Finally, the ratio between M_n(**10**, **9a**) and M_n(**11**, **9a**) [Fig. 8(A)] is between 3.3 and 4.4. In other words, the multiblock polystyrene **10** contains 3–4 blocks on average.

The seminal works of Otsuka et al.[43] and Hawker et al.[72] can explain the evolution of M_n(**10**, **9a**) with the conversion. Indeed, Hawker et al.[72] have proved that the growing macroalkoxyamines based on different TEMPO during polymerization of styrene exchange their molecular nitroxides to give macroalkoxyamines that stem from radical cross-coupling reactions. Interestingly, Otsuka et al.[70] have demonstrated that this exchange also takes place when several alkoxyamine functions are incorporated in the main chain of a linear polymer. Monodisperse polyalkoxyamines containing TEMPO-based alkoxyamines undergo thermal reorganiza-



SCHEME 5 Synthesis of the multiblock polystyrene **10** and their polystyrene blocks **11** after thiol treatment (**Z** = H, OH, or sulfoxide function[62]).

tion[70] (exchange of TEMPO-end-capped polymers) on heating to afford polyalkoxyamines with lower molecular weight and broader dispersity. Moreover, a mixture of two monodisperse distinct polyalkoxyamines[66] with two different molecular weights M_1 and M_2 on heating gives hybrid polyalkoxyamines displaying broad dispersity and a molecular weight between M_1 and M_2.

In the same manner, for styrene and **9a**, at all stages of the polymerization, the mediating nitroxides that are TIPNO-end-capped polystyrenes with various lengths (Scheme 5) are exchanged between the growing polystyrene chains, which induces a broadening of the dispersity and a decrease of molecular weight and function of time for the multiblock polystyrene **10**.

During all the polymerization, M_n(**11**, **9a**) is a linear function of conversion. As a result, as in the study reported by Otsuka and coworkers,[44] the molecular weight M_n(**10**, **9a**) of the

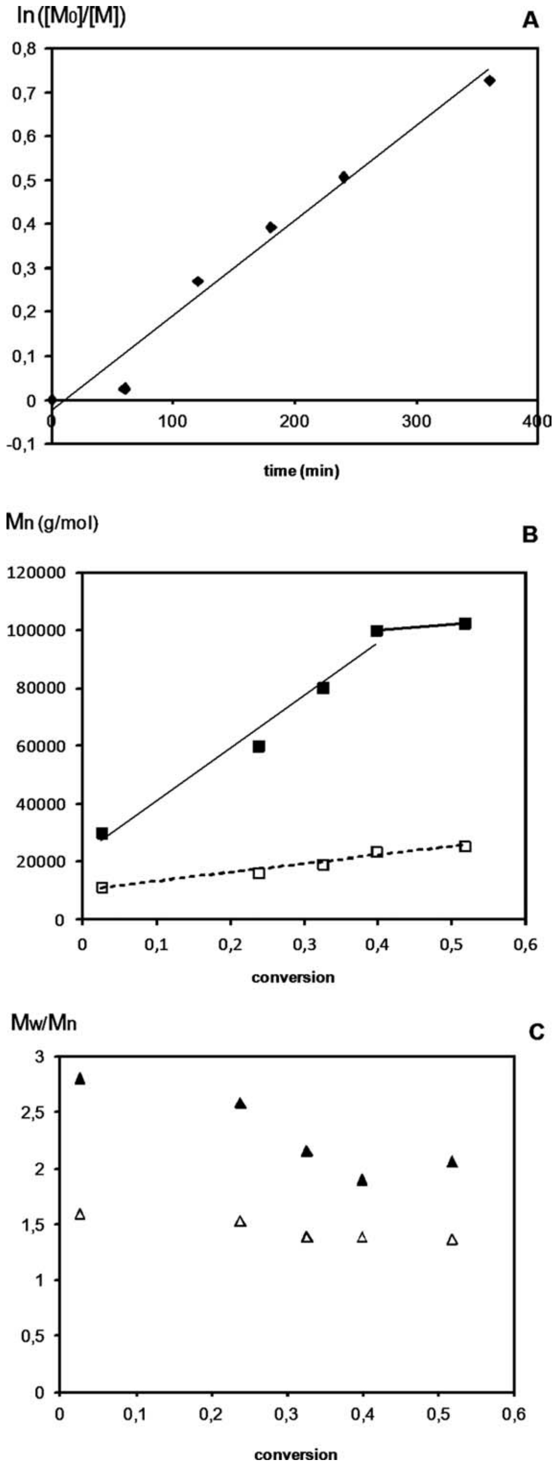


FIGURE 7 **A**: Kinetic plot for bulk polymerization of styrene at 115°C with the polyalkoxyamine **9a**. **B**: Plot of the experimental molar masses of the polystyrene architecture before (M_n; ■) and after (M_n; □) thiol treatment versus conversion for bulk polymerization of styrene at 115°C with the polyalkoxyamine **9a**. **C**: Plot of dispersity of the polystyrene architecture before (M_w/M_n; ▲) and after (M_w/M_n; △) thiol treatment versus conversion for bulk polymerization of styrene at 115°C with the polyalkoxyamine **9a**. Experimental conditions: $n_{\text{styrene}}/n_{\text{number of alkoxyamine function in } \mathbf{9a}} = 300$; bulk; $T = 115°C$.

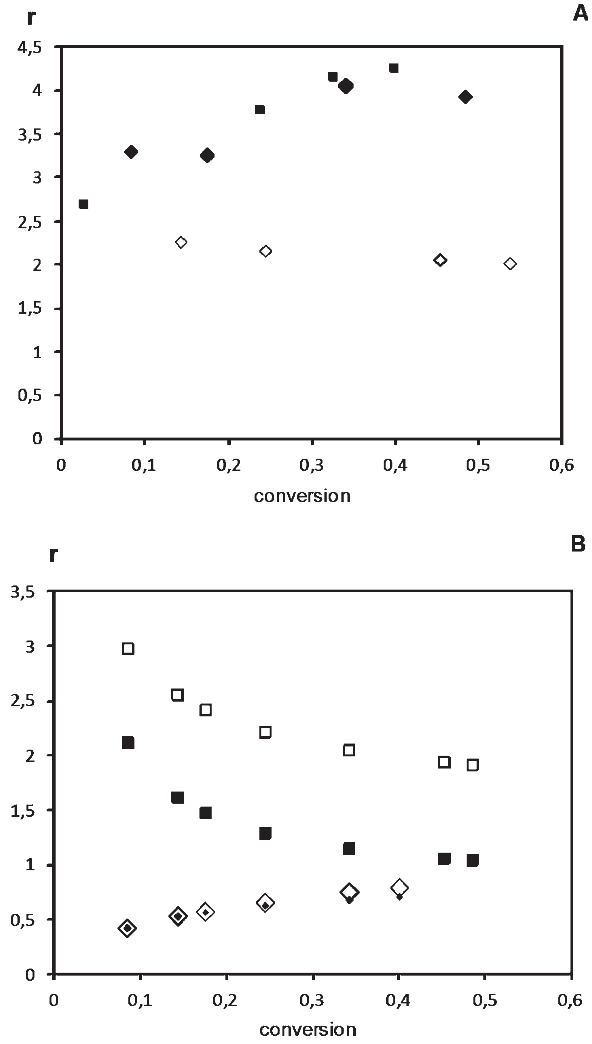


FIGURE 8 **A**: plot of $r = M_n$(multiblock)/M_n(block) at 115°C (black symbol) for **9a** (■) and **9d** (◆) and at 125°C (red symbol) for **9d** (◇). **B**: Plot of $r = M_n$(multiblock, 125°C)/M_n(multiblock, 115°C) (■), M_n(block, 125°C)/M_n(block, 115°C) (□) for **9d** and plot of M_n(multiblock, **9d**)/M_n(multiblock, **9a**) (◆), M_n(block, **9d**)/M_n(block, **9a**) (◇) at 115°C.

multiblock polystyrene **10** also increases linearly until 40% of conversion. From this conversion, M_n(**10**, **9a**) remains constant despite a further increase of conversion. The decrease of M_n(**10**, **9a**) induced by the exchange reaction of the mediating nitroxides offsets its increase by monomer consumption at such extent that M_n(**10**, **9a**) is constant even if the conversion continues to increase. Furthermore, the starting broad molecular weight distribution ($M_w/M_n = 2.8$) of the multiblock polystyrene **10** could be the result of the relatively high dispersity ($M_w/M_n = 1.6$) of **11** and the high dispersity ($M_w/M_n = 2.2$) of the polyinitiator **9a**. In addition, as the M_w/M_n of **11** decreases, M_w/M_n of the multiblock **10** also decreases.

To improve *a priori* the control over the M_n and M_w/M_n of the multiblock polystyrenes **10** and to increase the number of blocks, the monodisperse and higher molecular weight polyinitiator **9d** was tested at 115°C.

For **9d**, the logarithmic conversion has also exhibited a linear relationship with time [Fig. 9(A)]. Compound **9d** also provides a good control over M_n(**10**, **9d**), as Figure 9(B) shows a linear increase of M_n(**10**, **9d**) with conversion during the whole polymerization. With **9d**, M_n(**10**, **9d**) does not stagnate. Unlike **9d**, the intrinsic broad molecular weight distribution of **9a** anticipates the broadening generated by the nitroxide exchange. Thus, M_n(**10**, **9d**) becomes constant at lower conversion with **9a** than with **9d**.

Moreover, M_w/M_n of **10** decreases with conversion and its values lie between 1.7 and 2.8. Compounds **9a** and **9d** give similar values for M_w/M_n, except at conversion above 50% [Fig. 9(C)]. Even if **9d** is well defined, its impact on the dispersity of the multiblock polystyrene **10** is negligible.

Furthermore, the controls with **9a** and **9d** over the synthesis of the polystyrene blocks are nearly of the same level except for the dispersity. The insertion of styrene in **9d** is controlled [Fig. 9(B)] as M_n(**11**, **9d**) increases linearly with conversion and M_w/M_n decreases with conversion. M_w/M_n remains lower with **9d** than with **9a** [Fig. 9(C)]: starting from a value of 1.45 (conversion: 8.5%), M_w/M_n reaches a final value of 1.2 (conversion: 48.5%).

Compound **9d** has given the multiblock polystyrene **10** with $M_n = 82{,}000$ g mol^{-1} and $M_w/M_n = 1.73$ and the mixture **11** of polystyrene blocks with $M_n = 20{,}900$ g mol^{-1} and $M_w/M_n = 1.2$ at a conversion of 48.5% after 6 h of polymerization. The livingness is also established as a shift (Fig. 6) toward higher molecular weight is observed for both multiblock and block polystyrenes, and no traces of unreacted polyinitiator **9d** was detected by SEC. Furthermore, the ratio between M_n(**10**, **9d**) and M_n(**11**, **9d**) is between 3.3 and 4 [Fig. 8(A)]. Finally, remarkably enough M_n(**10**, **9d**)/M_n(**10**, **9a**) is nearly equal to M_n(**11**, **9d**)/M_n(**11**, **9a**) [Fig. 8(B)] and lies between 0.4 and 0.8.

Even if **9d** has a much higher molecular weight than **9a**, the multiblock **10** synthesized with **9d** contains again 3–4 blocks on average and surprisingly M_n(**10**, **9d**) $\leq$ M_n(**10**, **9a**). Therefore, the molecular weight of the polyinitiator has a

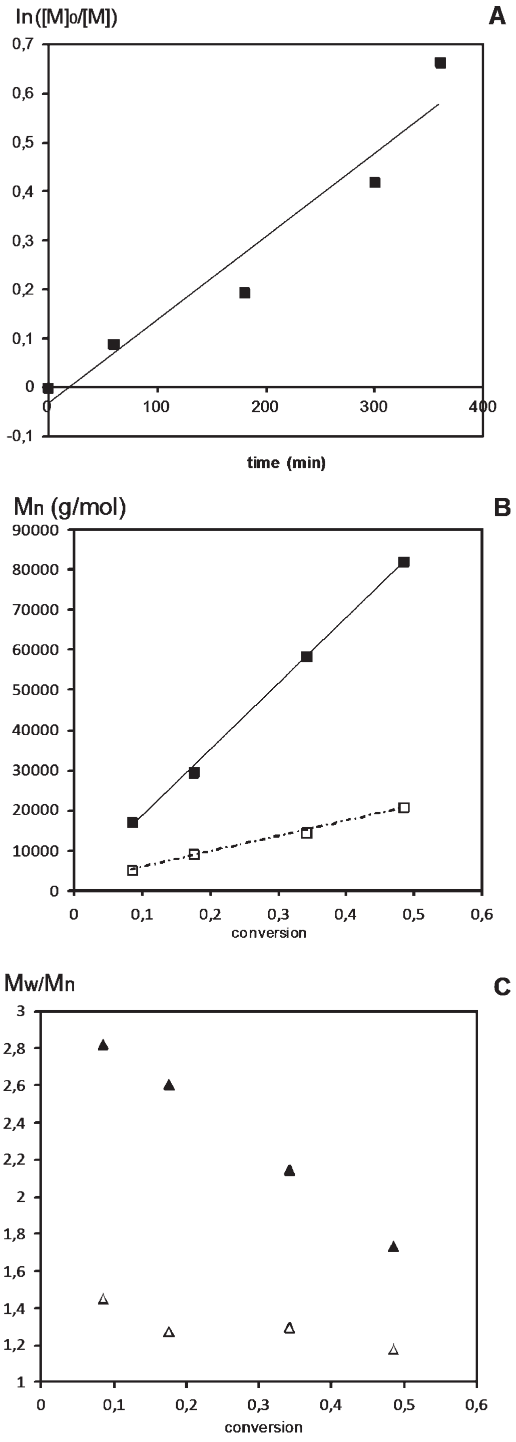


FIGURE 9 A: Kinetic plot for bulk polymerization of styrene at 115°C with the polyalkoxyamine **9d**. **B**: Plot of the experimental molar masses of the polystyrene architecture before (M_n; ■) and after (M_n; □) thiol treatment versus conversion for bulk polymerization of styrene at 115°C with the polyalkoxyamine **9d**. **C**: Plot of dispersity of the polystyrene architecture before (M_w/M_n; ▲) and after (M_w/M_n; △) thiol treatment versus conversion for bulk polymerization of styrene at 115°C with the polyalkoxyamine **9d**. Experimental conditions: $n_{\text{styrene}}/n_{\text{number of alkoxyamine function in } \mathbf{9d}} = 300$; bulk; $T = 115$°C.

weak influence on the number of polystyrene blocks in **10**. Moreover, as Otsuka et al.,[70] we can reasonably assume that the exchange of the mediating nitroxides controls the number of blocks and the molecular weight of the multiblock polystyrene **10**.

To check this hypothesis, the polymerization with **9d** has been repeated at 125°C to favor the exchange reaction of nitroxide and by doubling the starting quantity of styrene.

A kinetic of first order and as expected an increase of the rate of polymerization induced by the increase in the temperature were observed [see Supporting Information Fig. S4(A)]. The increase of temperature also induces lower dispersity [Fig. 8(C)] for the multiblock **10** (M_w/M_n around 1.7–1.9). At low conversion, M_w/M_n is around 2.8 at 115°C, and for nearly the same conversion at 125°C, it decreases to 1.7–1.9, which is the typical value obtained at 115°C but for higher conversion.

As at 115°C, the insertion of styrene in **9d** is controlled [see Supporting Information Fig. S4(B)] at 125°C. The quality of the control is good as remarkably enough, except at low conversion, M_n(**11**, 125°C)/M_n(**11**, 115°C) is around 2 [Fig. 8(B)], which is the starting ratio $n_{\mathrm{Sty},125°\mathrm{C}}/n_{\mathrm{Sty},115°\mathrm{C}}$. In contrast, M_n(**10**, 125°C)/M_n(**10**, 115°C) is around 1 except at low conversion [Fig. 8(B)]. As with **9a** at 115°C, for **9d** at 125°C, M_n(**10**, **9d**) increases linearly with conversion until reaching a constant value of 90,000 g mol^{-1} from 53% of conversion [Supporting Information Fig. S4(B)]. The rate of exchange reaction of nitroxide was increased by the increase in the temperature so that M_n(**10**, **9d**) reaches a value independent of the conversion.

Finally, the ratio between M_n(**10**, **9d**) and M_n(**11**, **9d**) is between 1.8 and 2.3 [Fig. 8(A)]. The multiblock **10** synthesized with **9d** at 125°C contains two blocks on average. When the temperature is increased, the number of polystyrene blocks in **7** decreases, which confirms the hypothesis of Otsuka and Takahara.

To conclude, it was possible to synthesize multiblock polystyrenes from the linear polyalkoxyamines **9a** and **9d**. The number of polystyrene blocks is mostly independent of the molecular weight of **9a** and **9d** and is a function of the temperature. A good control was achieved over the molecular weight and the dispersity of the polystyrene blocks. The molecular weight of the multiblock polystyrene first increases linearly with the conversion and then is constant with it. All these results are consistent with the explanation proposed by Otsuka and Takahara, namely, the exchange reaction of the mediating TIPNO-end-capped polystyrenes during the polymerization.

CONCLUSIONS

A TIPNO-based nitroxide containing a styryl substituent was easily obtained in good yield. Its alkoxyamine including the α-methyl benzyl radical moiety efficiently initiates and controls the polymerization of styrene and *n*BA to give first well-defined macromonomers that at higher conversion undergo copolymerization with the monomer to yield branched polymers with alkoxyamine unit at branch point. The synthesis of the branches was controlled in terms of molecular weight and dispersity. Furthermore, the self-coupling of this polymerizable nitroxide by manganese coupling has yielded a mixture of oligomers including TIPNO-based alkoxyamine as repeating unit. These oligomeric polyalkoxyamines were partially separated by chromatography on silica and have inserted styrene to give multiblock polystyrenes. The insertion of styrene was controlled as all polystyrene blocks display nearly the same length increasing linearly with conversion. The dispersity of the multiblock decreases with conversion and its value lies between 1.7 and 2.8. Its molecular weight is first a linear function of the conversion before reaching a constant value despite further consumption of styrene. The number of blocks on which the molecular weight of the initiating polyalkoxyamines has nearly no impact depends on the temperature. These latter results can be explained by the fact that on heating the multiblock polystyrene, chains grow and meanwhile exchange their mediating macromolecular TIPNO-based nitroxides of different lengths. This nitroxide is currently under further investigation to get new architectures.

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