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Intermolecular radical addition of alkoxyamines onto olefins: An easy access to advanced macromolecular architectures precursors

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Abstract

Novel ''second generation'' alkoxyamines, derived from *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (so-called SG1) as initiators for nitroxide-mediated polymerization (NMP) were synthesized by intermolecular radical 1,2-addition (IRA) of a high dissociation rate constant alkoxyamine (BlocBuilder®, also called MAMA-SG1) onto various activated olefins, such as *n*-butyl acrylate, acrylic acid, dimethylacrylamide, 2-hydroxyethylacrylate and styrene. The potential of this radical addition was further applied to the synthesis of multifunctional alkoxyamines as precursors for complex macromolecular architectures, namely 3- and 4-arm star polymers. For this, tri- and tetra-acrylates were synthesized by reaction of acryloyl chloride with the 1,1,1-tris(hydroxymethyl)ethane and pentaerythritol, respectively, in the presence of triethylamine. The addition of MAMA-SG1 onto these olefins led to the tri- and tetra-functional SG1-based alkoxyamines which were further used to prepare polystyrene stars of controlled molecular weights and polydispersity values not exceeding 2. The individual arms were recovered by hydrolysis of the ester groups of the star core originating from the alkoxyamine initiator under basic conditions. The decreasing molecular weight determined by GPC during hydrolysis demonstrated the star architecture of the polymers.

Keywords: Intermolecular radical addition; Nitroxide-mediated polymerization; Star polymers

1. Introduction

Since the original works of Rizzardo et al. [1] and Georges et al. [2] who could control the radical polymerization of styrene in the presence of 2,2,6,6-tetramethylpiperidinoxyl nitroxide (TEMPO), much efforts have been devoted to the development of the so-called nitroxide-mediated polymerization (NMP), with a view to achieve polymers of well-defined molecular weights and architectures with controlled properties. The *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (so-called SG1) nitroxide-based alkoxyamines reported earlier by our group [3,4] represented major advances in this field, by allowing the polymerization control of a large variety of monomers. This could lead to the design and obtention of novel block copolymers that were not accessible with the TEMPO nitroxide [5]. However, the potential offered by the SG1 has been up to now poorly exploited for the synthesis of more complex macromolecular architectures, such as star polymers, star ABC (miktoarm) copolymers and star-like copolymers. Only Gnanou et al. [6] reported the obtention of 3-arm star polymers from a tri-alkoxyamine initiator derived from SG1. Its synthesis consisted in the esterification of 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione with 2-bromopropionyl bromide, followed by reaction of the obtained tri-brominated compound with SG1 in the presence of CuBr and 2,2′-bipyridine.

We recently reported novel tertiary SG1-based alkoxyamines, particularly alkoxyamine **1** (BlocBuilder®) [7] (Scheme 1), whose particular reactivity is of high interest. Indeed, due

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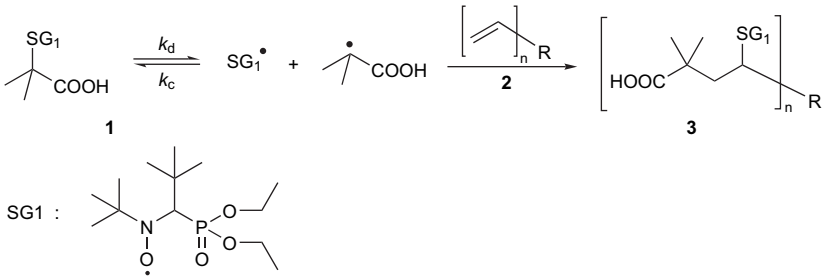


Scheme 1. Intermolecular radical addition of tertiary alkoxyamine Blocbuilder® (**1**) onto an activated olefin (**2**) leading to the alkoxyamine adducts **3**.

to their low cleavage temperature, they can participate in clean intermolecular radical 1,2-addition (IRA) onto various activated olefins in mild condition reactions [8]. As represented in Scheme 1, new functionalized alkoxyamines can thus be achieved, with the R-functionality corresponding to the olefin substituent. Moreover, the use of multi-olefins ($n > 2$) in this process leads to multi-alkoxyamines that can be used as NMP initiators to obtain *n*-arm star polymers by the core-first approach. Few works were reported on the use of alkoxyamines for radical additions. Studer et al. [9] described the intermolecular radical addition of TEMPO-derived alkoxyamines onto olefins. Leroi et al. used SG1-based alkoxyamines to perform radical additions/cyclizations on bis-olefins [10] and indolinones/indolines [11] and Nicolas et al. [12] reported the synthesis of a water-soluble SG1-dialkoxyamine by this way, but up to now very little work has been reported on intermolecular radical 1,2-addition of SG1-derived alkoxyamines onto activated olefins.

We aimed at showing here the versatility of our approach by describing the synthesis of a large range of novel alkoxyamine models by the IRA of the alkoxyamine **1** onto various activated olefins such as *n*-butyl acrylate, acrylic acid, dimethylacrylamide, 2-hydroxyethylacrylate and styrene as well as tri- and tetra-acrylates for the obtention of star polymers.

2. Experimental

2.1. Materials

Alkoxyamine **1** (Blocbuilder®) was kindly provided by Arkema (France). *n*-Butyl acrylate, acrylic acid, dimethylacrylamide, 2-hydroxyethylacrylate, styrene, 1,1,1-tris(hydroxymethyl)ethane, pentaerythritol and acryloyl chloride were purchased from Aldrich. All reactants and solvents were used as-received.

2.2. Analytical techniques

^{1}H, ^{13}C, ^{31}P NMR spectra were obtained on a Bruker Advance 300 spectrometer in $CDCl_3$ or DMSO-d_6. Electrospray ionization mass spectroscopy (ESI-MS) was performed on a Sciex API III Plus mass spectrometer, triple quadrupole. Number-average molecular mass, and weight average molecular mass were determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump equipped with three ''Styragel'' columns HR 3 (4.6 mm × 300 mm, separation between 500 and 30 000 g mol^{-1}), HR 4 (4.6 mm × 300 mm, separation between 5000 and 600 000 g mol^{-1}), and HR 5 (4.6 mm × 300 mm, separation between 2000 and 4×10^6 g mol^{-1}) and two detectors: UV/visible (Waters 486) and RI (Waters 2414). THF was the mobile phase, with a flow rate of 1 mL min^{-1}. Calibration was based on polystyrene standards.

2.3. Synthesis of multi-acrylates

2.3.1. 1,1,1-Tris(hydroxymethyl)ethane tri-acrylate (*M6*)

1,1,1-Tris(hydroxymethyl)ethane (5 g, 41.6 mmol) was finely dispersed in THF (100 mL) with triethylamine (18 mL, 129 mmol, 1.03 eq. per OH function) in an ice bath. Acryloyl chloride (15.2 mL, 187.3 mmol, 1.5 eq. per OH function) was added dropwise into the mixture under nitrogen atmosphere. The mixture was stirred at room temperature for 20 h. After evaporation of THF and remaining acryloyl chloride, water was added to the residue, followed by two extractions with diethyl ether. The combined organic phases were washed with HCl (5 wt%), water and $NaHCO_3$ (5 wt%). After drying on magnesium sulfate, filtration and removal of the solvent, the oily product was dried under vacuum pump, to remove the traces of acrylic acid. Yield: 50%. ^{1}H NMR (ppm, DMSO-d_6): 6.35 (dd, 3H), 6.19 (dd, 3H), 5.98 (dd, 3H), 4.12 (s, 6H), 1.03 (s, 3H). ESI-MS: $C_{17}H_{18}O_6$, $M = 282.3$ g mol^{-1}; *m/z* $[M + H]^+ = 283$; $[M + NH_4]^+ = 300$; $[M + Na]^+ = 305$.

2.3.2. Pentaerythritol tetra-acrylate (*M7*)

M7 has been prepared by following the procedure described above. Yield: 48%. ^{1}H NMR (ppm, CCl_3): 6.40 (dd, 3H), 6.12 (dd, 4H), 5.90 (dd, 4H), 4.29 (s, 4H). ESI-MS: $C_{17}H_{20}NO_8$, $M = 352.34$ g mol^{-1}; *m/z* $[M + H]^+ = 353$; $[M + NH_4]^+ = 370$; $[M + Na]^+ = 375$, $[M + K]^+ = 321$.

2.4. General procedure for intermolecular radical addition (IRA) onto olefins

A solution of alkoxyamine **1** (3 g, 7.87 mmol, 1 M) and the olefin (7.87 mmol, 1 M) in *tert*-butanol (*t*-BuOH) was introduced in a Schlenk tube equipped with a rotaflo, deoxygenated by nitrogen bubbling and heated at 100 °C for 1 h under stirring. The reaction mixture was then concentrated under reduced pressure. **A1**, **A5**, **A6** and **A7**: the alkoxyamines were precipitated in pentane. **A2**, **A3**, and **A4**: the yellowish oil was dissolved in diethyl ether and extracted with sodium hydroxide solution (5 wt%). The aqueous phase was then

acidified with concentrated aqueous hydrochloride until pH 1, and then extracted with dichloromethane. After drying on magnesium sulfate, filtration and evaporation of dichloromethane, the alkoxyamine was obtained as a white powder.

*2.4.1. 2,2-Dimethyl-4-[N-tertio-butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]-4-butoxycarbonyl butanoic acid (**A1**)*

Yield: 63%. ^{1}H NMR (ppm, $CDCl_3$): major diastereomer: 10.00 (b, 1H), 4.54–4.49 (m, 1H), 4.27–3.90 (m, 6H), 3.29 (d, $J = 24$ Hz, 1H), 2.58–2.52 (m, 1H), 2.24–2.16 (m, 1H), 1.64–1.57 (m, 2H), 1.43–1.46 (m, 2H), 1.32–1.23 (m, 6H), 1.22 (s, 6H), 1.16 (s, 9H), 1.08 (s, 9 H), 0.93 (t, $J = 9$ Hz, 3H); ^{13}C NMR (ppm, $CDCl_3$): major diastereomer: 181.53 (C), 172.70 (C), 83.48 (CH), 69.50 (d, $J = 139.6$ Hz, CH), 64.19 (CH_2), 62.00 (d, $J = 6.04$ Hz, CH_2), 61.49 (C), 58.88 (d, $J = 7.55$ Hz, CH_2), 40.91 (CH_2), 40.04 (C), 35.47 (d, $J = 5.28$ Hz, C), 30.11 (CH_2), 29.61 (d, $J = 5.28$ Hz, CH_3), 27.79 (CH_3), 22.94 (CH_3), 19.00 (CH_2), 16.24 (d, $J = 6.79$ Hz, CH_3), 16.02 (d, $J = 6.79$ Hz, CH_3), 13.51 (CH_3). ^{31}P NMR (ppm, $CDCl_3$): major diastereomer: 24.48 (80%); minor diastereomer: 24.27 (20%). ESI-MS: $C_{24}H_{48}NO_8P$, $M = 509.31$ g mol^{-1}; *m/z* $[M + H]^+ = 510$; $[M + NH_4]^+ = 527$; $[M + Na]^+ = 532$; $[M + K]^+ = 548$.

*2.4.2. 2,2-Dimethyl-4-[N-tertiobutyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]-4-phenyl butanoic acid (**A5**)*

Yield: 59%. ^{1}H NMR (ppm, $CDCl_3$): major diastereomer: 7.28–7.13 (m, 5H), 4.85 (dd, $J = 2.3$ Hz, J = 11.7 Hz, 1H), 4.41–3.91 (m, 4H), 3.34 (d, $J = 26.8$ Hz, 1H), 2.88 (dd, $J = 2.8$ Hz, $J = 13.6$ Hz, 1H), 2.26 (dd, $J = 12.8$ Hz, $J = 13.0$ Hz, 1H), 1.31 (dt, $J = 1.7$ Hz, $J = 6.9$ Hz, 6H), 1.24 (s, 9H), 1.06 (d, $J = 7.7$ Hz, 1H), 0.80 (s, 9H); minor diastereomer: 7.28–7.13 (m, 5H), 5.17 (dd, $J = 2.3$ Hz, $J = 11.7$ Hz, 1H), 4.41–3.91 (m, 4H), 3.38 (d, $J = 26.62$ Hz, 1H), 2.77 (dd, $J = 2.8$ Hz, $J = 13.6$ Hz, 1H), 2.20 (dd, $J = 12.8$ Hz, $J = 13.0$ Hz, 1H), 1.31–1.21 (m, 12H), 1.24 (s, 9H), 0.80 (s, 9H). ^{31}P NMR (ppm, $CDCl_3$): major diastereomer: 25.20 (54%); minor diastereomer: 24.03 (46%). ESI-MS: $C_{25}H_{44}NO_6P$, $M = 485.59$ g mol^{-1}; *m/z*: $[M + H]^+ = 486$; $[M + NH_4]^+ = 503$; $[M + Na]^+ = 508$.

*2.4.3. 2,2-Dimethyl-4-[N-tertiobutyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]-pentanedioic acid (**A2**)*

Yield: 80%. ^{1}H NMR (ppm, $CDCl_3$): 4.60–4.45 (m, 2H, diastereomer 1 + diastereomer 2), 4.49–3.90 (m, 8H, dia 1 + dia 2), 3.42 (d, 1H, $J = 28.33$ Hz, dia 2), 3.29 (d, 1H, $J = 24.49$ Hz, dia 1), 2.58 (dd, 1H, $J = 3.59$ Hz, $J = 14.17$ Hz, dia 1), 2.36 (dd, 1H, $J = 13$ Hz, $J = 13$ Hz, dia 1), 2.27 (dd, 1H, $J = 11.7$ Hz, $J = 11.7$ Hz, dia 2), 2.11 (dd, 1H, $J = 3.78$ Hz, $J = 13.59$ Hz, dia 2), 1.40–1.28 (m, 24H, dia 1 + dia 2), 1.18 (s, 9H, dia 2), 1.17 (s, 9H, dia 1), 1.16 (s, 9H, dia 1), 1.15 (s, 9H, dia 2).

^{31}P RMN (ppm, $CDCl_3$): major diastereomer: 24.88 (65%); minor diastereomer: 27.12 (35%). ESI-MS: $C_{20}H_{40}NO_8P$, $M = 453.51$ g mol^{-1}; *m/z* $[M + H]^+ = 454$; $[M + NH_4]^+ = 471$; $[M + Na]^+ = 476$.

*2.4.4. 2,2-Dimethyl-4-(dimethylcarbamoyl)-4-[N-tertio-butyl-N-(1-diethoxyphosphoryl-2,2-di-methylpropyl)aminoxy]-butanoic acid (**A3**)*

Yield: 69%. ^{1}H NMR (ppm, $CDCl_3$): 5.02 (dd, $J = 2.27$ Hz, $J = 11.52$ Hz, 1H, dia 2), 4.92 (dd, $J = 3$ Hz, $J = 12$ Hz, 1H, dia 1), 4.27–3.80 (m, 8H, dia 1 + dia 2), 3.35 (d, $J = 25.88$ Hz, 1H, dia 2), 3.29 (d, $J = 25.9$ Hz, 1H, dia 1), 3.27 (s, 3H, dia 2), 3.20 (s, 3H, dia 1), 2.85 (s, 3H, dia 2), 2.87 (s, 3H, dia 1), 2.66 (dd, $J = 3$ Hz, $J = 13.59$ Hz, 1H, dia 1), 2.55 (dd, $J = 3$ Hz, $J = 15$ Hz, 1H, dia 2), 2.31 (dd, $J = 12.28$ Hz, 12.40 Hz, 1H, dia 2), 2.24 (dd, $J = 12.47$ Hz, $J = 12.50$ Hz, 1H, dia 1), 1.35–1.22 (m, 24 H, dia 1 + dia 2), 1.21 (s, 9H, dia 1), 1.17 (s, 9H, dia 2), 1.15 (s, 9H, dia 1), 1.08 (s, 9H, dia 1). ^{31}P NMR (ppm, $CDCl_3$): major diastereomer: 24.68 (71%); minor diastereomer: 24.47 (29%). ESI-MS: $C_{27}H_{54}N_3O_8P$, $M = 580.58$ g mol^{-1}; *m/z* $[M + H]^+ = 481$; $[M + NH_4]^+ = 498$; $[M + Na]^+ = 503$; $[M + K]^+ = 519$.

*2.4.5. 2,2-Dimethyl-4-[N-tertiobutyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]-4-(2-hydroxyethyl)-carbonyl butanoic acid (**A4**)*

Yield: 85%. ^{1}H NMR (ppm, $CDCl_3$): 4.57 (dd, 1H, $J = 3.21$ Hz, $J = 11.89$ Hz, dia 1), 4.45 (dd, 1H, $J = 4.16$ Hz, $J = 11.71$ Hz, dia 2), 4.33–3.73 (m, 16H, dia 1 + dia 2), 3.36 (d, 1H, $J = 27.01$ Hz, dia 2), 3.35 (d, 1H, $J = 25.87$ Hz, dia 1), 2.52 (dd, 1H, $J = 3.21$ Hz, $J = 13.98$ Hz, dia 1), 2.25 (dd, 1H, $J = 12.84$ Hz, $J = 12.78$ Hz, dia 1), 2.16 (dd, 1H, $J = 3.97$ Hz, $J = 13.60$ Hz, dia 2), 2.11 (dd, 1H, $J = 13.04$ Hz, $J = 13.04$ Hz, dia 2), 1.34–1.22 (m, 24 H, dia 1 + dia 2), 1.18 (s, 9H, dia 2), 1.16 (s, 9H, dia 1), 1.10 (s, 9H, dia 2), 1.08 (s, 9H, dia 2). ^{31}P NMR (ppm, $CDCl_3$): major diastereomer: 24.51 (61%); minor diastereomer: 23.88 (37%). ESI-MS: $C_{22}H_{44}NO_9P$, $M = 497.56$ g mol^{-1}; *m/z* $[M + H]^+ = 498$; $[M + NH_4]^+ = 515$; $[M + Na]^+ = 520$; $[M + K]^+ = 536$.

*2.4.6. Tri-alkoxyamine **A6***

Yield: 35%. ^{1}H NMR (ppm, $CDCl_3$): 0.5–1.4 (93H), 2.0–2.6 (6H), 3.1–3.4 (3H), 3.8–4.3 (18H), 4.3–4.6 (3H), 8.4–9.4 (3H). ^{31}P NMR (ppm, $CDCl_3$): 24.42 (s). ESI-MS: $C_{65}H_{126}N_3O_{24}P_3$, $M = 1425.8$ g mol^{-1}; *m/z* $[M + NH_4]^+ = 1443.9$; $[M + Na]^+ = 1448.8$, $[M + 2NH_4]^{2+} = 731.1$, dialkoxyamine: $[M + NH_4]^+ = 1062.7$.

*2.4.7. Tetra-alkoxyamine **A7***

Yield: 33%. ^{1}H NMR (ppm, $CDCl_3$): 0.5–1.4 (120H), 2.0–2.6 (8H), 3.1–3.4 (4H), 3.8–4.3 (24H), 4.3–4.6 (4H), 8.4–9.4 (4H). ^{31}P NMR (ppm, $CDCl_3$): 24.38 (s). ESI-MS: $C_{85}H_{164}N_4O_{32}P_4$, $M = 1877.0$ g mol^{-1}; *m/z* $[M + 2NH_4]^{2+} = 956.9$; tri-alkox. $[M + 2NH_4]^{2+} = 757.8$; di-alkox.: $[M + 2NH_4]^{2+} = 558.7$.

2.5. Synthesis and hydrolysis of star polystyrenes by NMP

Five milliliters of styrene and **A6** (or **A7**) alkoxyamine were introduced in a 25 mL two-necked round-bottom flask, fitted with septum, condenser, and degassed for 20 min by nitrogen bubbling. The mixture was then heated to 120 °C

(30 min ramp temperature: 20–120 °C) under N_2 and vigorous magnetic stirring. Samples were withdrawn at predefined times for determination of the conversion (^{1}H NMR) and the number-average molecular weight and polydispersity (GPC). The final polymer mixture was dissolved in a minimum THF and precipitated in cold methanol.

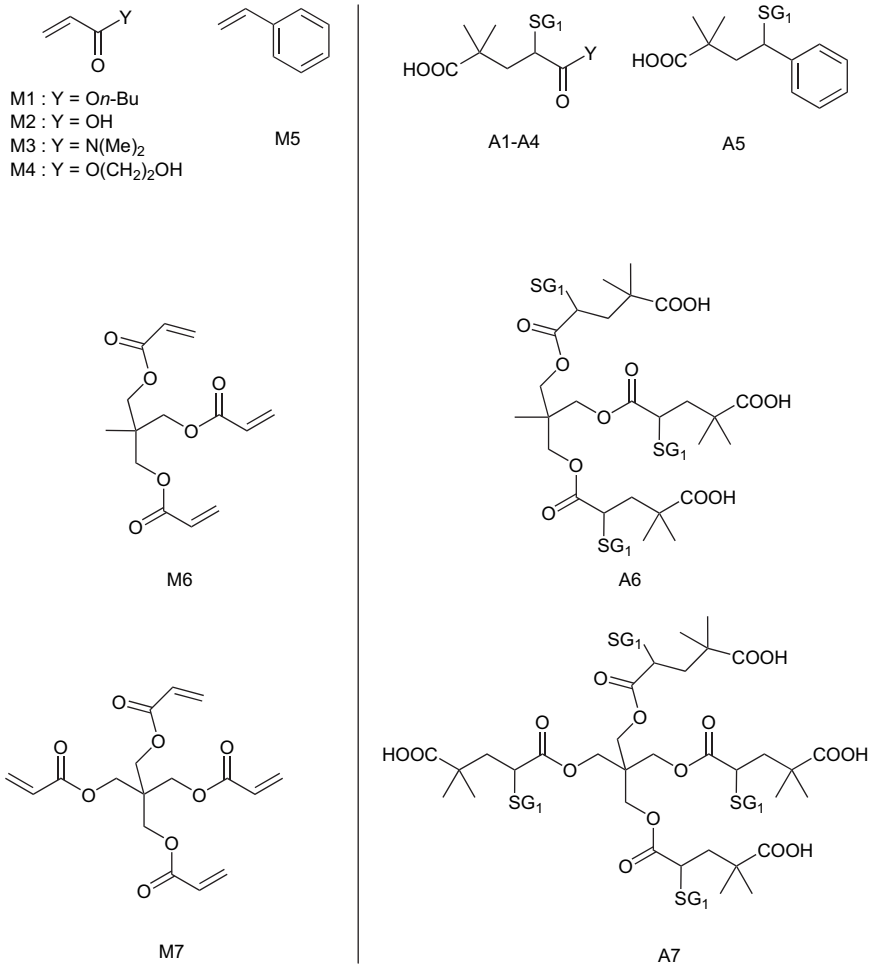
Hydrolysis of the ester groups present in the star core was performed at 70 °C in THF:water (90:10) with at minimum 25 eq. sodium hydroxide per ester function. Samples were withdrawn at defined times during the hydrolysis, dried and analyzed by GPC.

3. Results and discussion

3.1. Synthesis of alkoxyamines by IRA

To demonstrate the feasibility and versatility of the IRA, we have investigated the series of olefins shown in Scheme 2. The initiating alkoxyamine was a SG1-based alkoxyamine, developed by Arkema and so-called Blocbuilder® or MAMA-SG1 (**1**). The success of the reaction relies on the higher k_d value and C–ON bond dissociation energy (BDE) of the compound **1** compared to that of the alkoxyamine **3** resulting from the addition on the olefin double bond, which bears a less stabilized and bulky secondary radical as the alkyl part (Scheme 1) [13]. If the reaction temperature is carefully chosen, only the cleavage of the alkoxyamine **1** occurs, and therefore high yield of the 1,2 adduct is expected.

The reaction conditions have been optimized for *n*-butyl acrylate. It appeared that the best results (with regards to purity and yield) were obtained by performing the reaction in a Schlenk tube in deoxygenated *tert*-butanol at 100 °C for 1 h, at 1 mol L^{-1} in alkoxyamine with 1 eq. of olefin per nitroxide. These conditions are very convenient experimentally, and were applied to the synthesis of the alkoxyamines **A1**–**A5** (Scheme 2). For all the reactions the conversion in monomer was determined by ^{1}H NMR on the crude mixture obtained at the end of the reaction. The conversions were above 90% for all the monomers investigated, indicating the efficiency of the reaction. The adducts arising from *n*-butyl acrylate (**A1**) and styrene (**A5**) were isolated by precipitation in pentane with a good yield (63% and 59%, respectively). The adducts **A2**, **A3** and **A4** were purified easily by extraction from acidified aqueous solution with dichloromethane, and the yields were quite good as well (80%, 69%, and 85%, respectively). It has to be pointed out that depending on the olefin nature the isolated alkoxyamines are obtained in different diastereomer ratios. This result can be explained by different



Scheme 2. Structure of the different olefins used (**M1**–**M7**) and corresponding alkoxyamines obtained by intermolecular radical addition (**A1**–**A7**).

recombination rate constants of the SG1 nitroxide with the 1,2-radical adduct [14].

The intermolecular radical addition thus appears as versatile and straightforward method to prepare novel alkoxyamines, by choosing the appropriate starting olefin. For example, the alkoxyamines **A2** and **A4** obtained from acrylic acid and 2-hydroxyethylacrylate are of a particular interest, with their di-COOH and OH/COOH di-functional structure, respectively: the polymer obtained by NMP with this kind of alkoxyamine as initiator can be involved, through its di-functional α-chain end, in polycondensation reactions to lead to grafted copolymer architectures.

In order to further exploit the versatility of the intermolecular addition we investigated multi-acrylates as the starting olefins for the obtention of multi-alkoxyamines to achieve star-like macromolecular architectures. For this purpose, the 1,1,1-tris(hydroxymethyl)ethane tri-acrylate **M6** and pentaerythritol tetra-acrylate **M7** were prepared by reaction of acryloyl chloride (1.5 eq. with respect to OH functions) with 1,1,1-tris(hydroxymethyl)ethane and pentaerythritol, respectively, in the presence of triethylamine. The products were isolated with good purity by simple Et_2O extraction and washings with 5 wt% aqueous HCl, water and 5 wt% $NaHCO_3$ successively. The eventually remaining traces of acrylic acid were removed under vacuum. The intermolecular radical addition of the alkoxyamine **1** onto the obtained multi-acrylates was performed under similar conditions than that performed onto the above mentioned olefins, except that THF was used as a solvent (poor tetra-acrylate solubility in *t*-BuOH) and a slight excess of **1** (1.3 eq. per double bond) was introduced in reaction, with regards to steric hindrance considerations. The adducts were purified by precipitation in pentane, similarly to **A1**. Concerning the reaction of **1** with the tri-acrylate **M6**, the ESI-MS analysis revealed the presence of the expected tri-alkoxyamine **A6** but also the dialkoxyamine containing one remaining unreacted double bond. Residual vinyl peaks were indeed observed by ^{1}H NMR and quantification of the side product was performed using the peak integrals of vinyl protons and those relative to SG1 (N–C*H*–P). The molar fraction of the desired tri-alkoxyamine was thus estimated as 85%. Same analysis was performed on the product obtained from pentaerythritol tetra-acrylate, revealing the minor presence of di- and tri-SG1 adducts, besides the expected tetra-alkoxyamine. ^{1}H NMR analysis using vinyl protons and SG1 peak integrals showed a molar fraction of the tetra-alkoxyamine of 79%. These results are in good accordance with those reported by Nicolas et al. [12] who obtained dialkoxyamines from tri(ethylene glycol)diacrylate from **1** with a molar fraction of 92% (8% mono-alkoxyamine). They are consistent with the fact that an increasing steric hindrance on the olefins decreases the efficiency of the intermolecular 1,2-addition.

3.2. Star polymer synthesis

The tri- and tetra-alkoxyamines **A6** and **A7** were used as initiators to perform NMP of styrene to achieve 3- and 4-arm star polymer architectures (Scheme 3). Fig. 1(a) and (b) shows the curves relative to $\ln[M_0]/[M]$ versus time and M_n (and Ip) versus conversion for the polymerization of styrene with tri-alkoxyamine **A6** as initiator. Whatever the targeted molecular weight, the kinetics was of first order with respect to monomer and the molecular weights increased linearly with the conversion (and were close to the expected ones),

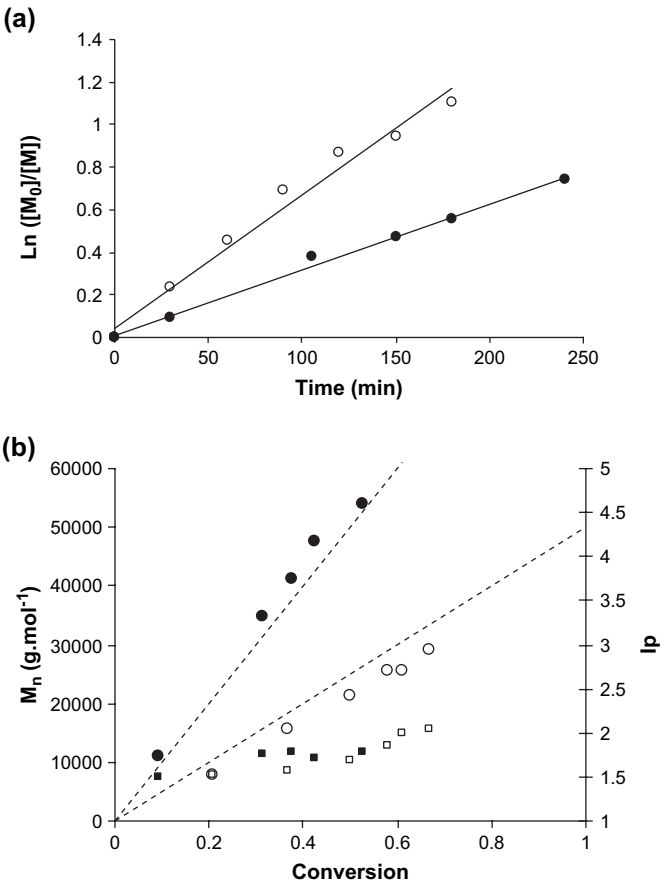
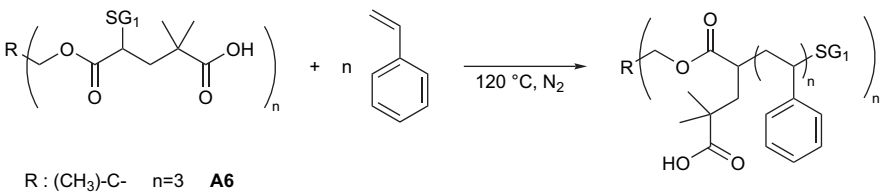


Fig. 1. Nitroxide-mediated polymerization of styrene with the tri-alkoxyamine **A6** as initiator: (a) ln ($[M_0]/[M]$) versus time and (b) M_n (rounds) and Ip (squares) versus conversion; (○, □) targeted M_n of 50 000 g mol^{-1} (●, ■) targeted M_n of 100 000 g mol^{-1} (theoretical line in dots).



R : (CH_3)-C- n=3 **A6**
R : C- n=4 **A7**

Scheme 3. Synthesis of star polystyrene from the multi-alkoxyamines by NMP.

showing that the polymerization was well controlled. The polydispersity increased with conversion from Ip = 1.4–2. Nevertheless, the GPC chromatographic peaks remained well symmetric whatever the conversion (Fig. 2(a)). This increase in polydispersity can be explained by (i) the few amount of di-substituted alkoxyamine side product whose alkyl fragments can initiate chains (linear) and (ii) the star–star coupling due to the termination reactions which are never totally negligible. Similar results were obtained for the polymerization of styrene from the tetra-alkoxyamine **A7** initiator (targeted M_n: 50 000 g mol^{-1}), with a better polydispersity ranging from 1.4 to 1.7 (from 10 to 50% conversion). Nevertheless, GPC traces presented a slight shoulder towards low molecular weights (Fig. 2(b)), probably due to the initiation by the alkyl fragment of the di- and tri-alkoxyamine minor side products, thus leading to a less homogeneous star polymer than for the 3-arm one.

To check the star architecture of the polymers, the esters of the core were cleaved (at 70 °C in THF:water 90:10 mixture, >25 eq. of NaOH per ester function) to recover the individual linear polymer chains. The decrease in polymer molecular weight determined by GPC as a function of hydrolysis time is showed in Fig. 3 for a 4-arm star polystyrene of 19 000 g mol^{-1} (Ip = 1.57). The polymer molecular weight at the end of the hydrolysis was of 6200 g mol^{-1}, which was a bit more than that expected for a rigorously 4-arms star polystyrene. It has to be pointed out here that star polymers present a lower hydrodynamic volume than a linear polymer with the same molecular weight. This implies that the real number-average molecular weight of the star polymer tested is higher than 19 000 g mol^{-1} determined by GPC, whereas the final M_n after hydrolysis corresponds rigorously to that obtained by GPC (linear chains at the end of the hydrolysis). Assuming a monodisperse 4-arm star polystyrene, the real molecular weight can be estimated using the relation $M_{n\ star} = M_{n\ linear}\ (g'_{[\eta]})^{-1/(1+\alpha)}$, where $g'_{[\eta]}$ is the ratio between the intrinsic viscosities of a star polymer and a linear

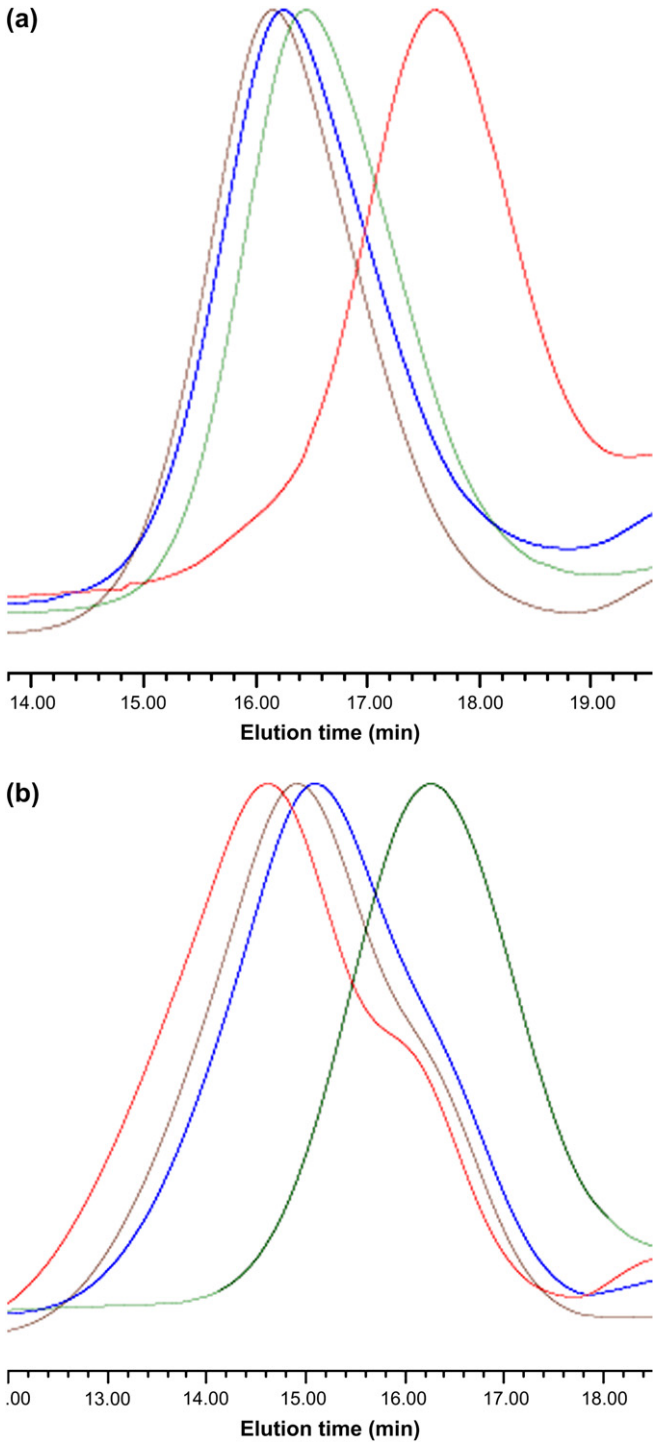


Fig. 2. GPC chromatograms of the polystyrene stars as a function of conversion (targeted M_n of 50 000 g mol^{-1}): (a) 3-arm star: conversions of 0.09, 0.31, 0.42, 0.52 from right to left side and (b) 4-arm star: 0.15, 0.27, 0.40, 0.45 from right to left side.

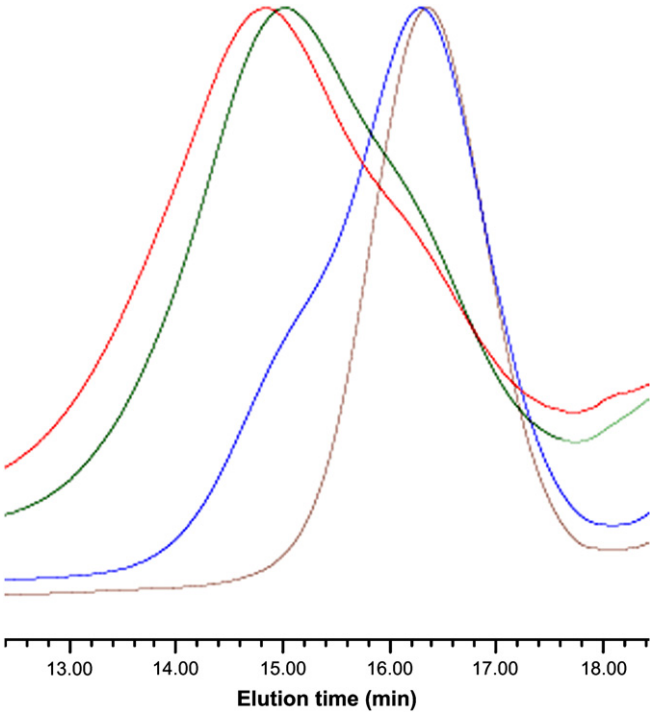


Fig. 3. GPC chromatograms obtained during hydrolysis of the ester groups of the star core for 4-arm star polystyrene. From left to right: $t = 0$, 1.5 h, 25 h, 7 days.

polymer of the same molecular weight, equal to 0.72 for a 4-arm polystyrene (with $\alpha = 0.725$) [15]. It comes a real molecular weight of 23 000 g mol^{-1}, and the decrease observed in molecular weight upon hydrolysis down to 6200 g mol^{-1} becomes fully consistent with a 4-arm star architecture. Nevertheless, we have to precise here that the obtained 4-star polystyrene is not rigorously monodisperse, due to star–star coupling and minor presence of 3-arm and ''2-arm'' (linear) star polymers arising from the di- and tri-alkoxyamine side products, as mentioned above. The hydrolysis on the 3-arm polystyrene stars gave typically the same results with a molecular weight decreasing factor closer to 2 than to 3, for the reasons invoked previously. Finally, whatever the targeted molecular weight and the star arm number, the linear polystyrene chains obtained after hydrolysis presented a very low polydispersity (Ip ~ 1.2, Fig. 3, right peak), indicating that every branch of the star was obtained in the controlled manner. The intermolecular radical addition of alkoxyamine onto double bond compounds appears thus to be a promising method for preparing easily novel precursors for star macromolecular architectures with well-defined molecular weights and acceptable polydispersity. Furthermore, the functional COOH groups available on the tri- and tetra-alkoxyamines **A6** and **A7** (Scheme 2) open the door for further coupling capacities to design star ''alternate'' copolymers.

4. Conclusion

We showed here the potential of the intermolecular 1,2 radical addition of the tertiary SG1-derived alkoxyamine Blocbuilder® onto olefins of interest for the synthesis of novel alkoxyamines as precursors of functional/complex macromolecular architectures by nitroxide-mediated polymerization. The feasibility and easy handling of the synthesis was demonstrated on common monomers, as acrylates, styrene and dimethylacrylamide. The methodology was then applied to the preparation of multi-alkoxyamines by intermolecular addition of the Blocbuilder® onto multi-acrylates, for the synthesis of star polymers. NMP of the styrene in the presence of the tri- and tetra-alkoxyamines led to 3- and 4-arm stars with controlled molecular weights and polydispersity index not exceeding 2. Further studies on polymerization of other monomers and obtention of star-like block copolymers, as well as on their physico-chemical properties are under progress.

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