# Polystyrene-*block*-poly(ethylene oxide)-*block*-polystyrene: A New Synthesis Method Using Nitroxide-Mediated Polymerization from Poly(ethylene oxide) Macroinitiators and Characterization of the Architecture Formed

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ABSTRACT: The strategy developed in this report consisted of synthesizing polystyrene (PS) blocks by nitroxide-mediated controlled radical polymerization from poly(ethylene oxide) (PEO) macroinitiators. Difunctional macroinitiators were first prepared in a two-step procedure by reacting PEO ($M_n$ ranging from 1450 to 35000 g/mol) with MONAMS, an alkoxyamine based on *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide, called SG1. A series of polystyrene-*block*-poly(ethylene oxide)-*block*-polystyrene (PS-*b*-PEO-*b*-PS) triblock copolymers was then synthesized with various chain dimensions and PEO block mass fractions from 0.13 to 0.65. Precise insight into the prepared triblock copolymer structure in terms of molecular weight, block length, and polydispersity index was obtained using complementary characterization techniques such as $^1$H NMR spectroscopy and size exclusion chromatography (SEC). These data were completed by two-dimensional chromatography, a combination of liquid chromatography at the critical conditions and SEC, to check purity (homo-PS formation) and composition homogeneity. Well-defined PS-*b*-PEO-*b*-PS triblock copolymers having a large range of chain dimensions ($M_n$ of block copolymers ranging from 5000 to 200000 g/mol) and block lengths ($M_n$ of PS blocks between 2000 and 83000 g/mol) with a low polydispersity index (1.1−1.3) were prepared using this new route.

## 1. Introduction

The amount of interest devoted to block copolymers has grown due to potential exciting applications that exploit self-organization to fabricate high-density data storage media,[1] to lithographically pattern semiconductors with ultrasmall feature sizes,[2] and to prepare ultrafine filters or membranes.[3−5] Copolymers can also be very promising materials because of their amphiphilic properties. Polystyrene-*block*-poly(ethylene oxide)-*block*-polystyrene (PS-*b*-PEO-*b*-PS) is one of these copolymers, combining very different and interesting properties for many industrial applications: polymeric surfactants, compatibilizers in polymer blending, stabilizers,[6,7] and as templates for the preparation of inorganic nanoparticles.[8]

The main advance in block copolymer synthesis in the past decade has been the development of techniques of controlled radical polymerization (CRP). Many methods have been used to produce block copolymers, but living/controlled polymerization is the only way which allows synthesis of block copolymers with well-defined structure. PS-*b*-PEO diblock copolymers with a predictable block molecular weight and narrow polydispersity have been prepared by sequential anionic polymerizations of styrene and ethylene oxide using a variety of initiators containing Na or K counterions.[9−11] Since the C−O−M centers have a lower reactivity than C−M centers, where M is Na or K, ethylene oxide is used as the second monomer. Initiators having Li as the counterion cannot be used because the C−O−Li$^+$ pair is very tight, due to the localization of the negative charge on the oxygen, and insertion of monomers into the O−Li bond is impossible. To overcome the problem of Li$^+$ association, Förster et al.[12] proposed an alternative way which was the use of the strong phosphazine base $t$BuP$_4$ during the synthetic procedure involving initiating moieties having Li as the counterion. The ability of phosphazine to form a complex with Li weakens the strength of O−Li bonding, and insertion of the EO monomer is possible. In this way, well-defined diblock copolymers containing styrene or dienes and ethylene oxide were prepared with narrow molecular weight distributions. Contrary to the PS-*b*-PEO diblock copolymers, the PS-*b*-PEO-*b*-PS triblock copolymer cannot be prepared directly by adding styrene into the anionic living polymerization of ethylene oxide because the alkoxy anion used to polymerize ethylene oxide is not sufficiently basic to initiate the polymerization of styrene.[13] Some controlled radical polymerization methods have been investigated recently. Well-defined PS-*b*-PEO diblock copolymers and poly(methyl methacrylate-*block*-ethylene oxide) (PMMA-*b*-PEO) with controlled block lengths were synthesized using atom transfer radical polymerization (ATRP)[14−16] and nitroxide-mediated polymerization (NMP).[17,18] The PS-*b*-PEO-*b*-PS triblock copolymer has also been synthesized by ATRP,[19,20] but because of the use of metal complexes involving one additional step for their elimination, this method could suffer from limitation in the case of industrial development. There are still relatively few studies that have exploited NMP for the synthesis of amphiphilic triblock copolymers with PEO as the central block compared to the ATRP technique. Indeed, we are aware of only one recent report in which Hornebecq et al.[21] described the synthesis of PEO dialkoxyamine by the addition

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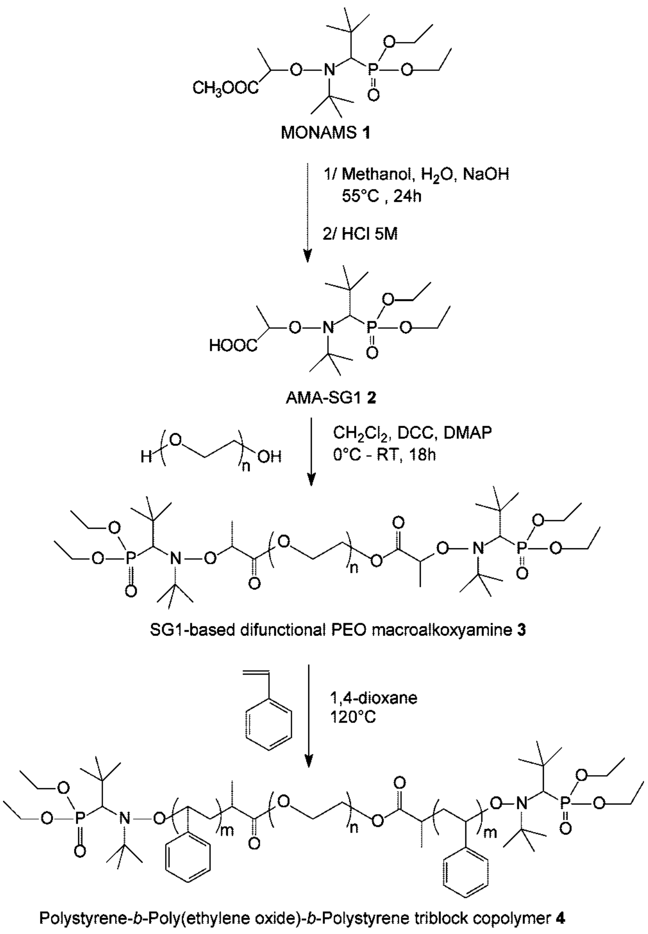
**Scheme 1. Strategy for Polystyrene-*block*-poly(ethylene oxide)-*block*-polystyrene (PS-*b*-PEO-*b*-PS) Triblock Copolymer Synthesis**



of a high-dissociation rate constant alkoxyamine onto PEO diacrylate and the use of this PEO dialkoxyamine as the initiator for the NMP of styrene. A similar preparation of the mono- and difunctional alkoxyamines via intermolecular radical addition onto various activated olefins under mild reaction conditions has also been reported.[22−24]

In this work, we describe the synthesis of PS-*b*-PEO-*b*-PS triblock copolymers using a new method: NMP of styrene with a difunctional PEO macroalkoxyamine. The different steps of the synthesis are described in Scheme 1.

A common strategy for producing block copolymers is the use of a functional terminated polymer as a macroinitiator in a new polymerization reaction. To produce PS-*b*-PEO-*b*-PS copolymers, the first step was based on the synthesis of a difunctional macroinitiator for NMP by coupling a commercial hydroxyl-terminated PEO (synthesized by anionic polymerization) with 2-[*N*-tertiobutyl-*N*-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminooxy]propanoic acid [AMA-SG1 (Scheme 1)]. The SG1-AMA-PEO-AMA-SG1 macroalkoxyamine was then used to initiate the NMP of styrene.

Block copolymers are complex materials that present heterogeneities in several dimensions: molar masses, chemical compositions of the different blocks, presence of residual homopolymer, and differences in architectures. Therefore, a clear and precise characterization of copolymers is difficult to obtain. For example, size exclusion chromatography (SEC) appears not to be efficient enough for determining the molecular weight and polydispersity of copolymers, because two species with different molecular weights and different chemical compositions may have the same hydrodynamic volume. That is why, over the past few years, new techniques have been developed to produce more relevant tools.[25,26] Among them, a very promising one is liquid chromatography under critical conditions (LC-CC).[27−29] Therefore, different techniques, including $^1$H NMR, SEC, and two-dimensional (2D) chromatography, were combined to gain insight into the optimal operating conditions for the preparation of PS-*b*-PEO-*b*-PS triblock copolymers with well-controlled architecture and good composition homogeneity and purity.

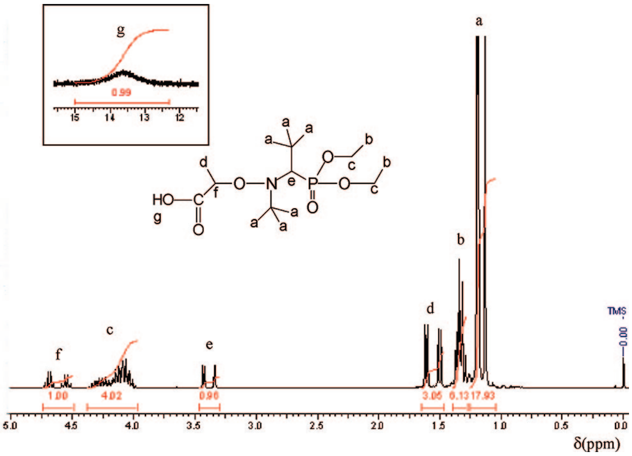


**Figure 1.** $^1$H NMR spectrum (300 MHz) in $CDCl_3$ of the purified 2-[*N*-tertio-butyl-*N*-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propanoic acid alkoxyamine (AMA-SG1). The inset is the same $^1$H NMR spectrum in the region of 12−15 ppm.

## 2. Experimental Section

**2.1. Materials.** All reagents and solvents were used without further purification. 1,4-Dioxane (>99%, ACS reagent), *N*,*N*′-dicyclohexylcarbodiimide (DCC) (99%), 4-dimethylaminopyridine (DMAP) (99%), styrene (99%), and poly(ethylene oxide) (PEO with $M_n$ = 1450, 3350, 10000, and 35000 g/mol, data given by supplier) were all purchased from Sigma-Aldrich Chemical Co. Alkoxyamine **1** [MONAMS (Scheme 1)] was kindly provided by Arkema Co.

**2.2. Synthesis of the Alkoxyamine AMA-SG1 (2).** A two-neck round-bottom flask was charged with 15 g (39 mmol) of MONAMS and 225 mL of methanol. A solution of 2.10 g (52.5 mmol) of NaOH in 150 mL of distilled water was then added. The mixture was heated at 55 °C for 24 h. Then the methanol was evaporated under reduced pressure, and the aqueous phase was washed three times with 60 mL of diethyl ether and acidified until pH 1−2 with an aqueous solution of 5 N HCl. The obtained solution was then extracted twice with 50 mL of dichloromethane. The organic phase was dried over $MgSO_4$, and then the solvent was evaporated under reduced pressure to yield viscous oil which was precipitated by adding pentane. The product was isolated by filtration and dried under reduced pressure, leading to 11.2 g of white powder (77.5% yield). The purified AMA-SG1 alkoxyamine was analyzed by $^1$H NMR spectroscopy, and its spectrum is presented in Figure 1, confirming the efficiency of the hydrolysis of MONAMS into AMA-SG1. $^1$H NMR (300 MHz, $CDCl_3$) of a 50/50 mixture of two diastereoisomeres: $\delta$ 1.23−1.09 (m, 18H, $CH_3$), 1.39−1.27 (m, 6H, $CH_3$), 1.62 and 1.51 (dd, $J_{H-H}$ = 6.98 Hz, 3H, $CH_3$), 3.43 and 3.34 (dd, $J_{H-P}$ = 26.91 Hz, 1H, CH), 4.37−3.97 (m, 4H, $CH_2$), and 4.7 and 4.56 (dq, $J_{H-H}$ = 6.98 Hz, 1H, CH).

**2.3. Synthesis of the Difunctional PEO Macroinitiator SG1-AMA-PEO-AMA-SG1 (3).** The experimental data for synthesis of **3** from PEOs with different molar masses are presented in Table 1. Typically, a two-neck round-bottom flask was charged with 2.60 g of AMA-SG1 (7.08 mmol), 5.13 g of 1450 g/mol PEO (3.54 mmol, 0.5 equiv), 0.42 g of DMAP (3.54 mmol, 0.5 equiv), and 20 mL of anhydrous dichloromethane (DCM). The reaction mixture was cooled to 0 °C in an ice bath and degassed with nitrogen for

**Table 1. Experimental Data Used for the Synthesis of Difunctional SG1-AMA-PEO-AMA-SG1 3 Macroalkoxyamines**

| derivative | PEO $M_n$ (g/mol) | PEO (mmol) | AMA-SG1 (mmol) | DMAP (mmol) | DCC (mmol) | $Vol_{DCM}$ (mL) |
|---|---|---|---|---|---|---|
| **3a** | 1450 | 3.54 | 7.08 | 3.54 | 8.50 | 25 |
| **3b** | 3350 | 3.54 | 7.08 | 3.54 | 8.50 | 43 |
| **3c** | 10000 | 1.77 | 3.54 | 1.77 | 4.25 | 52 |
| **3d** | 35000 | 0.68 | 1.36 | 0.68 | 1.63 | 71 |

10 min. A solution of 1.75 g of DCC (8.50 mmol, 1.2 equiv) in 5 mL of anhydrous dichloromethane was then added dropwise to the mixture at 0 °C under nitrogen. After this addition was complete, the reaction mixture was stirred at room temperature under nitrogen for 20 h. The solution was then filtered to remove the dicyclohexylurea (DCU), and the filtrate was washed three times with 20 mL of a saturated $NaHCO_3$ aqueous solution. The organic phase was dried over $MgSO_4$, and the solution was concentrated under reduced pressure. The residue was then precipitated in cold diethyl ether, filtered, washed with diethyl ether, and dried under vacuum at room temperature in 80−90% yield.

The purity and structure of the synthesized SG1-AMA-PEO-AMA-SG1 compound were determined by $^1H$ NMR and mass spectroscopy. $^1H$ NMR data of compounds **3a**−**d** are summarized in Table 2.

**2.4. Synthesis of the PS-*b*-PEO-*b*-PS Triblock Copolymers (4).** All polymerizations were carried out at 112 or 120 °C under a nitrogen atmosphere (Table 2). Typically, a 100 mL three-neck round-bottom flask was charged with difunctional PEO-macroinitiator **3c** (7.5 g, 0.7 mmol), styrene monomer (8.60 g, 81.8 mmol), and 1,4-dioxane (25 g) (60 wt %) (Table 2, entry 7). The system was fitted with a reflux condenser, and the solution vessel was purged with nitrogen for 30 min to remove all dissolved oxygen. The mixture was immersed in an oil bath at 112 °C for 4 h. Samples were taken periodically for conversion and molar mass analysis using $^1H$ NMR spectroscopy. The crude product was dissolved in dichloromethane and then poured into a large excess of diethyl ether or a mixture of diethyl ether with hexane or ethanol. The choice of nonsolvent for precipitation of the copolymer was made according to the ratio of PS block compared with PEO block. The copolymer was isolated by filtration and then dried under vacuum at room temperature to a constant weight. The conditions and results of other experiments are presented in Tables 3 and 4.

**2.5. Characterization of Compounds 3 and 4.** The synthesized compounds were characterized by various techniques: mass spectroscopy [electrospray and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF)], $^1H$ NMR spectroscopy, size exclusion chromatography, and 2D chromatography.

$^1H$ NMR spectra were recorded at room temperature with a Brüker Advance 300 MHz spectrometer using $CDCl_3$ as the solvent.

MALDI-TOF MS and electrospray ionization mass spectrometry (ESI-MS) were used to analyze samples of **3**. All SG1-AMA-PEO-AMA-SG1 macroalkoxyamines having an expected molar mass of up to approximately 5000 g/mol were analyzed by ESI-MS because it is known that ESI-MS is mainly used for relatively low-molar mass polymers,[30] whereas MALDI-TOF MS was used to analyze the SG1-AMA-PEO-AMA-SG1 sample having molar mass values higher than 5000 g/mol. However, no useful spectra were obtained for sample **3d** (molar mass of ~35000 g/mol).

ESI-MS measurements were carried out on an API III Plus Sciex triple quadrupole spectrometer. Samples were dissolved in methanol at a concentration of 10 mg/mL; 500 $\mu$L of the polymer solution was diluted in 1:1000 volume ratios with a 3 mM solution of ammonium acetate in methanol. The sample solution was then infused into the electrospray interface by a syringe pump at a flow rate of 5 $\mu$L/min.

For the MALDI-TOF experiments, a Brüker Autoflex mass spectrometer was used. The spectrometer was equipped with a nitrogen laser ($\lambda = 337$ nm), a pulse ion extractor, and a reflector. All the spectra were obtained using an accelerating voltage of 20−25 kV and a laser intensity that was 45% greater than the threshold. The polymer solutions were prepared in tetrahydrofuran (THF) at a concentration of 14 mg/mL. The matrix, 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol, 97%, Aldrich), was dissolved in THF at a concentration of 10 mg/mL. A 1 $\mu$L aliquot of the polymer solution was mixed with 100 $\mu$L of the matrix solution and 20 $\mu$L of a sodium iodide solution (10 mg/mL) in THF. A 1 $\mu$L portion of the final solution was deposited onto a sample target plate and allowed to dry in air at room temperature.

The refractive index increments ($dn/dc$) of copolymer **4** solutions in THF with a concentration of up to 5 mg/mL were measured using an Optilab DSP instrument (Wayatt Technology Corp.) at 633 nm. The instrument software generated a graph of the differential refractive indice $\Delta n$ of the sample versus its concentration. The specific refractive index increment $dn/dc$ of each copolymer was obtained from the slope of such a graph.

Size exclusion chromatography was used to determine number- and weight-average molecular weights ($M_n$ and $M_w$, respectively) and polydispersities ($M_w/M_n$, PDI) of copolymer **4**. Two different detection modes were used, and the results were compared. For the first detection mode, SEC was conducted in THF at 30 °C using a Waters 515 isocratic pump equipped with a Waters 2414 refractive index detector, a Waters 2486 UV detector, and a set of Styragel columns (HR4 and HR3, molar mass range of 500−1000000) from Waters. Samples were dissolved in THF at a concentration of 0.5 wt % for several hours before being filtered on 0.2 $\mu$m filters. The flow rate was 1 mL/min. Results were collected and analyzed with Millenium software (Polymer Standards Service). Relative calibration was conducted with standard polystyrene samples (Aldrich). For the second detection mode, SEC was conducted in THF using a Waters 515 HPLC pump and a set of Styragel columns in series (HR4 and HR3, molar mass range of 500−1000000 g/mol). Double detection was ensured with an Optilab DSP interferometric refractometer and a Dawn DSP multiangle laser light scattering (MALLS) photometer ($\lambda = 633$ nm) from Wyatt Technology. Samples were dissolved in THF at 0.2 wt % for several hours before being filtered with 0.2 $\mu$m filters. The flow rate was 0.5 mL/min. Results were collected and analyzed with ASTRA (Wyatt Technology).

The 2D chromatography system used in this study was a combination of LC-CC and SEC. LC-CC was used as the first separation step, followed by SEC. Two chromatography units were connected via one eight-port injection valve. In the first separation step, the PS-*b*-PEO-*b*-PS triblock copolymer was characterized by LC-CC under the critical elution condition of the PS block. The system comprising a Reodyne six-port injection valve with a 20 $\mu$L injection loop, a Waters 515 isocratic pump, a reversed-phase column (Nucleosil C18, 7 $\mu$m particle size, 300 Å pore), and a UV−visible absorption detector (Waters 2487) operated at a wavelength of 258 nm. The mobile phase was a THF/$H_2O$ mixture (86/14, w/w, SDS HPLC grade) at a flow rate of 0.04 mL/min. The injection sample concentration was 0.5 wt % of the copolymer.

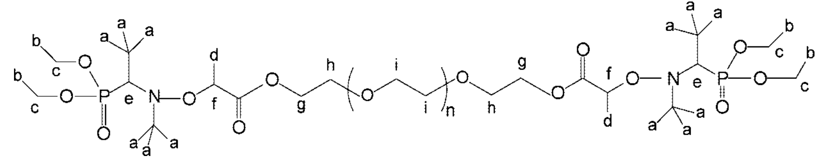
One electrically driven eight-port injection valve (Polymer Standard Service) was used to connect the two chromatography units. In addition, they were connected to two storage loops with volumes of 200 $\mu$L each. The system for the SEC separation step comprised a Waters model 515 HPLC pump, a high-speed column, and a refractive index detector (Waters 2410). The mobile phase was pure THF at a flow rate of 3 mL/min.

Operation of the coupled injection valves was controlled by the software that was used for data collection and processing, which is PSS-GPCUnity-2D-Software (Polymer Standards Service, Mainz, Germany). Molar mass calibration is based on polystyrene standards (Polymer Laboratories).

## 3. Results and Discussion

**3.1. Synthesis of the Difunctional PEO Macroinitiator (3).** The difunctional PEO macroalkoxyamine was prepared by esterification of hydroxyl-terminated PEO polymer with a carboxylic acid-bearing AMA-SG1 alkoxyamine in the presence of DCC to activate the carboxylic group and a catalytic amount of DMAP. Four different difunctional macroalkoxyamines (**3a**−**d**) were synthesized from PEO having $M_n$ values of 1450,

**Table 2. $^1$H NMR Data of Difunctional SG1-AMA-PEO-AMA-SG1 Macroalkoxyamines 3a−d (300 MHz, CDCl$_3$)**



| compound | $^1$H NMR data |
|---|---|
| **3a**, SG1-AMA-PEO$_{1.45k}$-AMA-SG1 | $\delta$ 1.16−1.05 (m, 36H$_a$, CH$_3$), 1.36−1.25 (m, 13H$_b$, CH$_3$), 1.52 and 1.47 (dd, $J_{H-H}$ = 7.79 Hz, 6H$_d$, CH$_3$), 3.32 and 3.23 (ds, $J_{H-P}$ = 25.89 Hz, 2H$_e$, CH), 3.66 (s, 154H$_{i+h}$, CH$_2$), 4.35−3.9 (m, 12H$_{c+g}$, CH$_2$), 4.67 and 4.61 (dq, $J_{H-H}$ = 7.79 Hz, 2H$_f$, CH). |
| **3b**, SG1-AMA-PEO$_{3.35k}$-AMA-SG1 | $\delta$ 1.18−1.07 (m, 34H$_a$, CH$_3$), 1.35−1.28 (m, 12H$_b$, CH$_3$), 1.48 and 1.43 (dd, $J_{H-H}$ = 7.55 Hz, 6H$_d$, CH$_3$), 3.32 and 3.23 (ds, $J_{H-P}$ = 25.46 Hz, 2H$_e$, CH), 3.65 (s, 340H$_{i+h}$, CH$_2$), 4.12−3.88 (m, 12H$_{c+g}$, CH$_2$), 4.69 and 4.62 (dq, $J_{H-H}$ = 7.55 Hz, 2H$_f$, CH). |
| **3c**, SG1-AMA-PEO$_{10k}$-AMA-SG1 | $\delta$ 1.2−1.09 (m, 32H$_a$, CH$_3$), 1.34−1.26 (m, 12H$_b$, CH$_3$), 1.49 and 1.45 (dd, $J_{H-H}$ = 7.17 Hz, 6H$_d$, CH$_3$), 3.20 and 3.29 (ds, $J_{H-P}$ = 25.59 Hz, 2H$_e$, CH), 3.63 (s, 932H$_{i+h}$, CH$_2$), 4.12−3.90 (m, 12H$_{c+g}$, CH$_2$), 4.64 and 4.59 (dq, $J_{H-H}$ = 7.17 Hz, 2H$_f$, CH). |
| **3d**, SG1-AMA-PEO$_{35k}$-AMA-SG1 | $\delta$ 1.25−1.12 (m, 39H$_a$, CH$_3$), 1.25 (m, 12H$_b$, CH$_3$), 1.36 and 1.31 (dd, 6H$_d$, CH$_3$), 3.66 (s, 3518H$_{i+h}$, CH$_2$), 4.25 (m, 12H$_{c+g}$, CH$_2$); H$_e$ and H$_f$ signal intensities were too low compared to the signal intensity of PEO methylene protons to be visualized in the spectrum |

**Table 3. Polymerization Conditions Used for the Preparation of Different Polystyrene-*block*-poly(ethylene oxide)-*block*-polystyrene Triblock Copolymers[a]**

| entry | sample | styrene (mmol) | PEO$_{xK}$ initiator[b] (mmol) | dioxane (g) | target $M_n$[c] (g/mol) | overall time (h) | conversion[d] (%) |
|---|---|---|---|---|---|---|---|
| 1 | **4a** | 4.1 | PEO$_{1.45K}$ (0.090) | 2 | 4700 | 4 | 83 |
| 2 | **4b** | 7.9 | PEO$_{3.35K}$ (0.250) | 5 | 3300 | 15 | 96 |
| 3 | **4c** | 15.9 | PEO$_{3.35K}$ (0.250) | 5 | 6600 | 15 | 94 |
| 4 | **4d** | 23.0 | PEO$_{3.35K}$ (0.250) | 5 | 9600 | 15 | 98 |
| 5 | **4e** | 8.9 | PEO$_{10K}$ (0.090) | 5 | 10300 | 15 | 88 |
| 6 | **4f** | 18.0 | PEO$_{10K}$ (0.090) | 5 | 20800 | 4 | 86 |
| 7 | **4g** | 81.8 | PEO$_{10K}$ (0.710) | 25 | 12000 | 4 | 95 |
| 8 | **4h** | 36.0 | PEO$_{10K}$ (0.090) | 5 | 41600 | 15 | 96 |
| 9 | **4i** | 76.0 | PEO$_{10K}$ (0.090) | 5 | 87800 | 15 | 97 |
| 10 | **4j** | 40.0 | PEO$_{35K}$ (0.028) | 10 | 148600 | 4 | 100 |
| 11 | **4k** | 45.0 | PEO$_{35K}$ (0.028) | 10 | 167000 | 6 | 100 |
| 12 | **4l** | 90.0 | PEO$_{35K}$ (0.028) | 10 | 334300 | 6 | 100 |

[a] All experiments were carried out at 120 °C, except experiment 7 where the polymerization was performed at 112 °C. [b] $x$ is the molar mass of the starting PEO; the value was given by the supplier. [c] Expected PS molar mass at 100% conversion. [d] Determined by $^1$H NMR spectroscopy in CDCl$_3$.

**Table 4. Composition Characterization of the PS-*b*-PEO-*b*-PS Triblock Copolymers**

| | | | experimental $M_n$ of block copolymers | | | | |
|---|---|---|---|---|---|---|---|
| sample | theoretical $M_n$[a] (g/mol) | PEO $M_n$ (g/mol) | $M_n$[b] (g/mol) | $M_n$, DPI[c] (g/mol) | $M_n$, DPI[d] (g/mol) | d$n$/d$c$[e] (mL/g) | PEO weight fraction[f] |
| **4a** | 3900 | 1450 | 5300 | 7400, 1.15 | 3100, 1.04 | 0.307 | 0.276 |
| **4b** | 3200 | 3350 | 6000 | 6000, 1.30 | − | − | 0.563 |
| **4c** | 6200 | 3350 | 7300 | 6800, 1.29 | − | − | 0.469 |
| **4d** | 9400 | 3350 | 14700 | 14100, 1.33 | 9100, 1.16 | 0.319 | 0.227 |
| **4e** | 9100 | 10000 | 15000 | 14800, 1.36 | 16000, 1.10 | 0.111 | 0.667 |
| **4f** | 17900 | 10000 | 17400 | 15800, 1.31 | 19000, 1.09 | 0.131 | 0.575 |
| **4g** | 11400 | 10000 | 22000 | 21900, 1.36 | 26000, 1.11 | 0.161 | 0.455 |
| **4h** | 39900 | 10000 | 30200 | 37500, 1.21 | 35600, 1.08 | 0.188 | 0.333 |
| **4i** | 85200 | 10000 | 74500 | 52500, 1.27 | 53000, 1.19 | 0.227 | 0.135 |
| **4j** | 148600 | 35000 | 87000 | − | 106000, 1.26 | 0.118 | 0.402 |
| **4k** | 167100 | 35000 | 128000 | − | 160000, 1.31 | 0.146 | 0.276 |
| **4l** | 334200 | 35000 | 201000 | 120000, 1.59 | 190000, 1.16 | 0.200 | 0.174 |

[a] Theoretical PS molar mass calculated from the relation target $M_{n,PS}$ × styrene conversion. [b] Determined by $^1$H NMR spectroscopy. [c] Determined by SEC with RI and UV detection. [d] Determined by SEC with RI and MALLS detection. [e] Determined by RI measurements. [f] Calculated from the $M_n$ data determined by NMR.

3350, 10000, and 35000 g/mol, respectively. The purified products **3a−d** were obtained in high yield (80−90%), and their $^1$H NMR characterization agreed well with the expected difunctional PEO macroalkoxyamines (Scheme 1). Indeed, the $^1$H NMR spectrum of **3c** presented in Figure 2 showed that via integration of the $^1$H NMR signal corresponding to the PEO methylene protons (peaks h and i) to a characteristic proton from SG1 (peak e), the expected structure of SG1-AMA-PEO$_{10K}$-AMA-SG1 was confirmed. $^1$H NMR data (list of peaks assignment, multiplicity, and coupling constants) for different difunctional macroalkoxyamines (**3a−d**) are summarized in Table 2.

The effectiveness of the coupling between AMA-SG1 alkoxyamine and PEO is verified by $^1$H NMR spectroscopy; however, the molar masses of the difunctional PEO macroalkoxyamines were determined by ESI-MS or MALDI-TOF MS analysis depending on the starting PEO molar mass. MALDI-TOF and ESI mass spectrometry are soft ionization

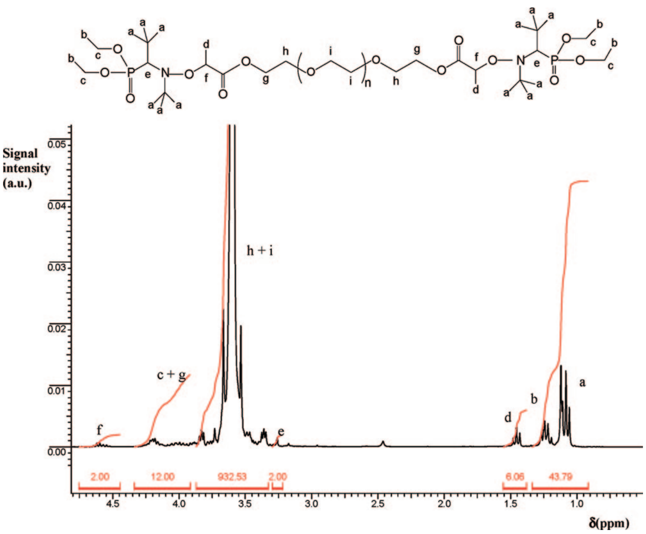


**Figure 2.** $^1$H NMR spectrum (300 MHz) of sample **3c** resulting from the coupling of 2-[*N*-tertio-butyl-*N*-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propanoic acid alkoxyamine (AMA-SG1) with a PEO of 10000 g/mol. The spectrum was recorded in $CDCl_3$.

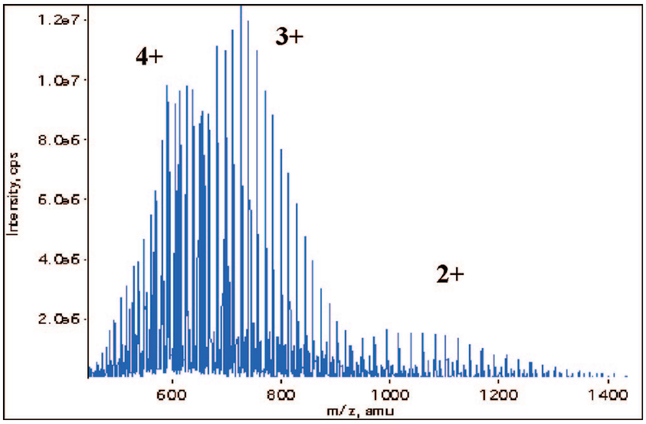


**Figure 3.** Electrospray ionization (ESI) mass spectrum of sample **3a**, resulting from the coupling of 2-[*N*-tertio-butyl-*N*-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propanoic acid alkoxyamine (AMA-SG1) with a PEO of 1450 g/mol. The spectrum was obtained after the addition of ammonium acetate.

techniques that allow the analysis of intact polymer ions with no or little fragmentation.[31] These techniques have been widely used to provide information about the structure of copolymers, e.g., repeat unit and end groups.[14,32−35]

The ESI mass spectrum of **3a** obtained through addition of ammonium acetate is displayed in Figure 3. There are a series of mass spectral peaks in the range of 500−1400 Da which can be divided into four envelopes of doubly, triply, and quadruply charged ions. Two envelopes ranging from *m*/*z* 839 to 1389.9 and from *m*/*z* 981.7 to 1399.9 present the same mass interval between two consecutive peaks ($\Delta m/z = 22$); this means that ions of these envelopes were doubly charged. Similarly, an envelope ranging from *m*/*z* 624.1 to 976.8 with a $\Delta m/z$ of 14.7 includes triply charged ions, and that ranging from *m*/*z* 473.5 to 714.9 with a $\Delta m/z$ of 11 includes quadruply charged ions. Three dominant peak envelopes were distributed to the prevailing polymer, and the minor peak envelope (ranging from *m*/*z* 981.7 to 1399.9) corresponds to the distribution of secondary polymer.

The number of EO units and the molar mass of end groups were calculated in the following way. For a given charge state, the peak corresponding to a mass of *m*/*z* consists of $[M_w(\text{monomer})n + M_w(X) + M_w(Y) + zM_w(\text{cation})]/z$. In this context, *n* is the number of PEO units, X and Y are the end groups, and $M_w$ is the molecular weight of the corresponding species. For an *m*/*z* value found in the mass spectrum, we look for the *n* value in the way that the sum of $[M_w(X) + M_w(Y) + zM_w(\text{cation})]/z$ is positive. Taking into account the molar mass of the expected end groups, we choose the appropriate *n* value among those found. The $M_n$ for the polymer was then calculated as a function of the peak intensity in the mass spectrum using the equation $M_n = (\sum N_i m_i)/(\sum N_i)$, where $N_i$ is the number of chain with mass $m_i$. On the basis of this calculation, we found that the end groups of the major polymer correspond to the AMA-$SG_1$-disubstituted $PEO_{1.45K}$. Depending on the charge state, the $M_n$ values ranged from 2103 (2+) to 2360 (4+) g/mol, giving a mean value of 2220 g/mol in good agreement with the expected structure [$M_n = 2168$ g/mol for SG1-$CH(CH_3)$-COO-$(CH_2CH_2O)_{33}$-OC-$(CH_3)CH$-SG1]. Using the same approach for the minor compound, calculation demonstrates that AMA-SG1 monosubstituted $PEO_{1.45K}$ methyl ether is the most plausible structure. It can be reasonably assumed that the latter compound comes from the starting PEO containing a small amount of the monomethoxy derivative. However, the methoxy group ($\delta$ 3.2−3.3) could not be identified on the $^1$H NMR spectra of **3**, indicating that the final compounds contained only a very small amount of this impurity.

We demonstrated that ions of multiple charge states were formed during ESI of moderately sized PEO which complicate the MS spectrum and affect the signal-to-noise ratio since the signal of each molecule would be distributed over multiple peaks.[36] Indeed, the EIS-MS spectrum of sample **3b** (note given here), the compound resulting from the coupling of AMA-SG1 with $PEO_{3.35K}$, exhibits five distinct envelopes corresponding to three charge states (4+, 5+, and 6+). Examination of the depth of the *m*/*z* values of different ions showed the simultaneous presence of two polymers. Following the same reasoning that we did with sample **3a**, we determined that the major compound, having an average $M_n$ value of 3815 g/mol, can be assigned to the expected difunctional PEO alkoxyamine structure.

The MALDI-TOF spectrum of sample **3c** is shown in Figure 4. Despite its limited resolution, we noted that the mass difference between two consecutive peaks is 44, indicating that the peak envelope represents the molecular weight distribution of the PEO moieties. Each major peak in the mass spectrum corresponds to a polymer species that has *n* OE units (molar weight, $M_w = 44.05$) in addition to end groups [SG1-$CH(CH_3)$-COO and SG1-$CH(CH_3)$-CO, $M_w = 366$ and 350, respectively] and a $Na^+$ ion ($M_w = 23$). On the basis of the experimental spectrum and using the calculation methods detailed above, the number of EO units (*n*) and the nature of end groups can be determined. The obtained *n* value was 217−263 units; it means an average $M_n$ value of 11280 g/mol for the SG1-AMA-$PEO_{10K}$-AMA-SG1 macroalkoxyamine.

**3.2. NMP of Styrene Using the PEO Macroinitiator.** The prepared PEO macroinitiators were used for solution polymerization of styrene in 1,4-dioxane at 112 or 120 °C under an inert atmosphere. The reaction mixture became progressively more viscous and remained homogeneous in appearance throughout the polymerization. The PS-*b*-PEO-*b*-PS copolymers were isolated by precipitation in ethanol after reaction for 4 h at 112 °C (~95% conversion). By varying the monomer to macroinitiator concentration ratio, we synthesized copolymers with a wide range of molecular weights.

To discuss the controlled nature of the polymerization, the conversion of styrene monomer and the experimental molar mass of the PS block were determined by $^1$H NMR of samples taken from the reaction mixture. Following the disappearance

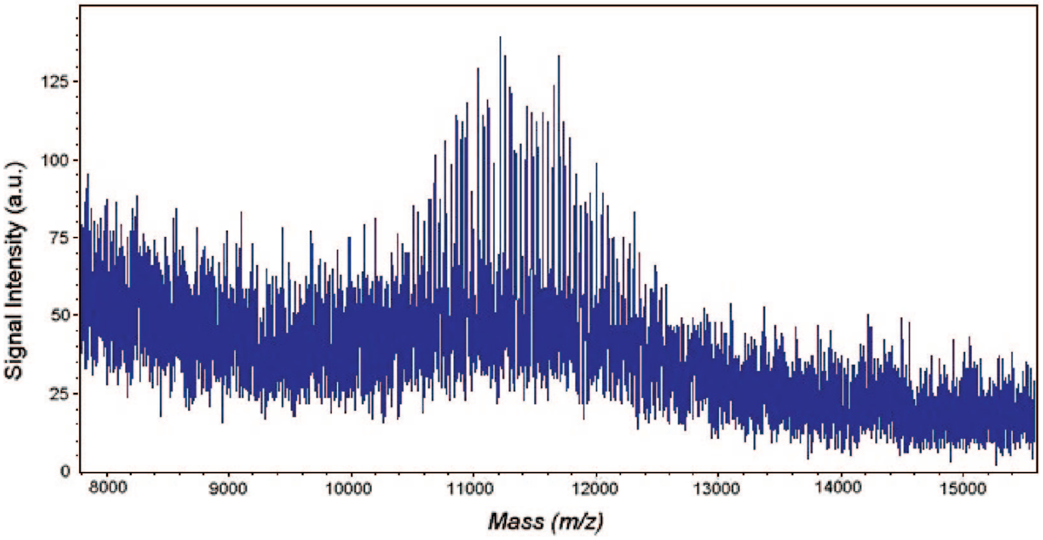


**Figure 4.** Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum of sample **3c**, the compound that results from the coupling of 2-[*N*-tertio-butyl-*N*-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propanoic acid alkoxyamine (AMA-SG1) with a PEO of 10000 g/mol, with dithranol as the matrix.

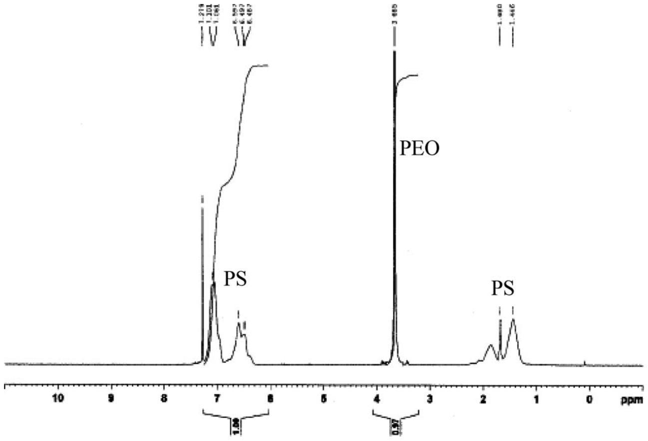


**Figure 5.** $^1$H NMR spectrum (300 MHz) in $CDCl_3$ of the polystyrene-*block*-poly(ethylene oxide)-*block*-polystyrene triblock copolymer **4h**. The sample resulted from the solution polymerization of styrene in 1,4-dioxane at 120 °C using a difunctional PEO macroalkoxyamine of 11280 g/mol as the initiator with an expected PS molar mass of 39900 g/mol.

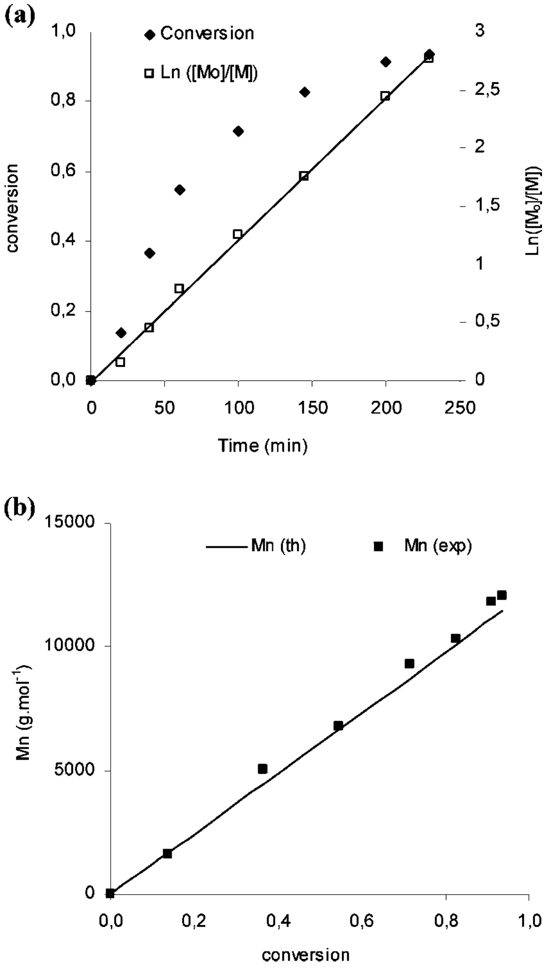


**Figure 6.** NMP of styrene at 112 °C in 1,4-dioxane using the difunctional SG1-AMA-$PEO_{10K}$-AMA-SG1 macroalkoxyamine **3c** as the initiator. (a) Evolution of conversion and ln([$M_o$]/[M]) vs time data. (b) Evolution of $M_n$ with conversion. $M_n$ estimated from the $^1$H NMR spectra of samples collected from the reaction mixture. Experimental conditions: [styrene]/[initiator] = 116; [monomer + initiator] in 1,4-dioxane, 40 wt %.

of the peak of the vinyl protons of the styrene monomer ($\delta$ 5.3 and 5.8) compared to the signal of phenyl protons of styrene and polystyrene ($\delta$ 6.5−7.2) in the reaction mixture, we were able to determine the monomer conversion with good reliability. Given the molar mass of the PEO block, it was easy to deduce that of the PS block formed during polymerization. Thus, the experimental $M_n$ values of the PS block were calculated from the $^1$H NMR spectra (not presented here) of samples collected from the reaction mixture, based on integration of the signal at 1−2.5 ppm due to $CH_2$ and CH protons of PS block (without forgetting to subtract the integration due to the protons of SG1 moieties) to that attributable to ethylene protons of PEO at 3.4 ppm. By the same principle, the $^1$H NMR spectrum of the dry triblock copolymer **4** (Figure 5, spectrum of **4h** recorded in $CDCl_3$) allowed us to determine the $M_n$ of the PS block as well as the copolymer composition. The results are listed in Table 4.

The linearity of the relationship of ln([$M_o$]/[M]) versus reaction time for the polymerization of styrene initiated by difunctional PEO macroalkoxyamine **3c** (Figure 6a) indicates that the number of propagating species remained constant throughout the polymerization. It shows the initiation efficiency of the difunctional PEO macroinitiator which follows first-order

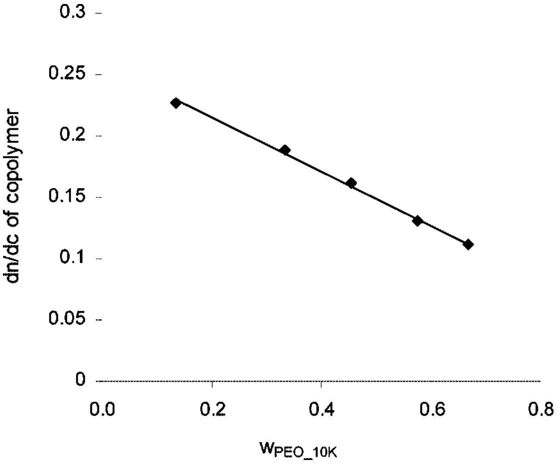


**Figure 7.** d*n*/d*c* variation of PS-*b*-PEO$_{10K}$-*b*-PS triblock copolymers **4e−i** as a function of their PEO weight fractions in tetrahydrofuran at 30 °C.

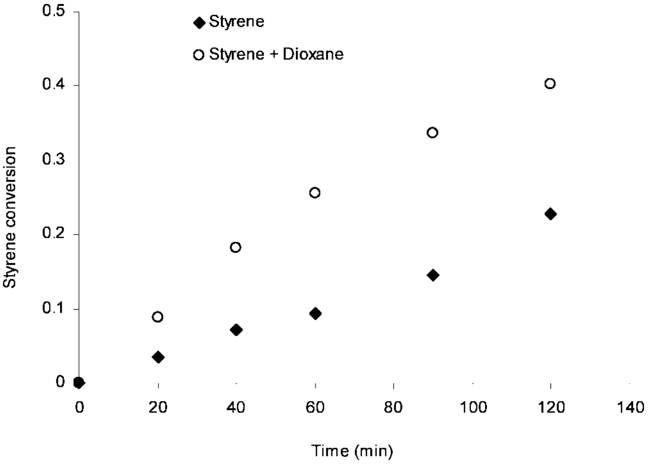


**Figure 8.** Evolution of styrene conversion vs time for the thermal self-polymerization of styrene at 120 °C in 1,4-dioxane [2/1 (w/w) styrene/1,4-dioxane] and in the absence of 1,4-dioxane.

kinetics with respect to the monomer. Control over the growth of polystyrene chains is furthermore evidenced by the linear evolution of the experimental $M_n$ of PS determined by $^1$H NMR with conversion and a good agreement between the experimental $M_n$ and the theoretical values based on conversion (Figure 6b). It implies that the nitroxide-mediated polymerization (NMP) of styrene using difunctional PEO macroalkoxyamines proceeded in a controlled manner.

With the objective of gaining deeper insight into macromolecular characteristics of the obtained block copolymers and confirming the data from $^1$H NMR spectroscopy, two SEC methods were used as complementary analysis techniques: SEC using the relative calibration curve established with polystyrene standards and SEC using MALLS detection. The former SEC method using RI and UV detection gives values of $M_n$ in PS equivalents since the absolute value of $M_n$ cannot be extracted from the universal calibration due to the different Mark−Houwink coefficients ($K$, a) of the two different blocks (PS and PEO). As shown in Table 3, the combination of the three different techniques offers good complementarities and good consistency is observed. The polydispersity indices (PDIs) of the obtained block copolymers have values between 1.04 and 1.31 (MALLS). Combined characterization results led to the conclusion that the synthesized triblock copolymers **4** exhibit a high degree of molecular and compositional homogeneity.

Before their molecular weights were determined by SEC with MALLS detection, it was necessary to measure the specific refractive index increment as a function of the block copolymer concentration (d*n*/d*c*). Interestingly, the availability of triblock copolymer with different compositions allowed us to examine how the specific refractive index increments vary with the relative weight fraction of PEO ($w_{\mathrm{PEO}}$) in the triblocks (Figure 7), where $w_{\mathrm{PEO}}$ was calculated by $^1$H NMR spectroscopy. It was found that the d*n*/d*c* variation of samples **4e−i** consisting of a PEO central block of 10000 g/mol can be fitted by the following equation:

$$dn/dc = 0.2589 - 0.2203 w_{\mathrm{PEO}_{10K}} (\mathrm{mL/g})$$

A linear relationship between d*n*/d*c* and the weight fractions of PEO in this series of triblock copolymers is in agreement with previous observations made with other polymers.[37−39] This equation should be useful in the future for the calculation of d*n*/d*c* values of any PS-*b*-PEO10K-*b*-PS copolymers as well as for the determination of copolymer compositions from d*n*/d*c* analysis at least in the studied range.

**3.3. Purity of the Prepared PS-*b*-PEO-*b*-PS Triblock Copolymer.** The molar masses of the precipitated copolymers presented in Table 3 were not actually in good agreement with the theoretical calculated ones. Agreement between the experimental and thereotical $M_n$ values was observed only when the block copolymers were prepared by using the smallest PEO macroinitiator **3a**, while molar mass values equal to half of the theoretical values based on conversion were obtained for polymerization initiated by **3b−d**.

At this point, we assumed that homopolymerization of styrene initiated by traces of peroxide present in 1,4-dioxane (≤0.005% from the supplier specifications) could take place in the same time as the controlled polymerization initiated by **3**. Styrene is also known to undergo thermal initiation at typical reaction temperatures for stable free radical polymerization.[40] Therefore, the initiation by peroxide resulting from the 1,4-dioxane was checked by a kinetic study of styrene self-polymerization at 120 °C. It must be noted that these operating conditions are those generally used in NMP of styrene. As shown in Figure 8, styrene conversion in 1,4-dioxane [2/1 (w/w) styrene/1,4-dioxane] was 2 times higher than in the absence of 1,4-dioxane. We can conclude from these experiments that a mixture consisting of pure triblock copolymer PS-*b*-PEO-*b*-PS **4** and polystyrene homopolymer should be obtained during styrene polymerization in 1,4-dioxane.

Classical SEC analysis of the crude reaction product of copolymer **4** revealed a chromatogram (not shown here) with only one sharp peak. PS calibration applied to the peak gave an acceptable polydispersity index of 1.2 which is not rigorous because of the relative calibration that was used. In most experiments, due to the small difference in molecular weight between the PS homopolymer and the target PS-*b*-PEO-*b*-PS, their corresponding peaks could not be distinguished from each other. Indeed, the hydrodynamic volumes of these species were too close to one another for SEC to distinguish them. In this context, SEC failed to detect the presence of the PS homopolymer in the mixture. Therefore, we decided to check the purity of the prepared copolymer **4** using LC-CC. Analysis was performed on the crude reaction products, and the results were compared to the data of the precipitated copolymer **4**. To quantify and separate the PS homopolymer from the triblock copolymer, the LC-CC elution condition was set at the critical point of adsorption for PS, meaning that PS homopolymer and PS block of copolymer in the mixture products become “chromatographically invisible” while the PS-PEO-PS block copolymer is expected to behave like a PEO homopolymer having a

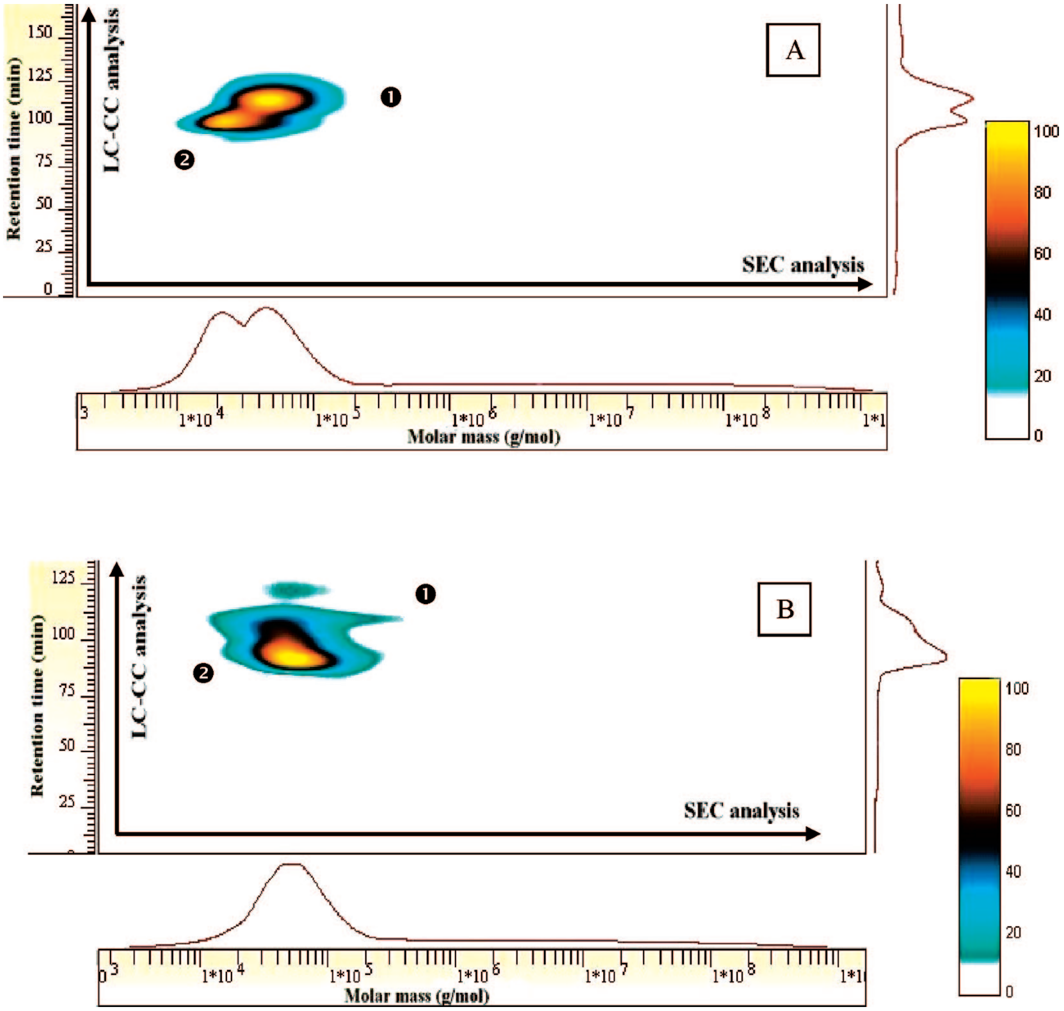


**Figure 9.** Contour plots of the 2D separation of sample **4h** resulting from solution polymerization of styrene in 1,4-dioxane performed at 120 °C using SG1-AMA-PEO$_{10K}$-AMA-SG1 as the initiator (target $M_{n,PS}$ = 41600 g/mol; 96% conversion after 15 h). (A) Crude reaction mixture before the polymer purification step and (B) the corresponding purified copolymer. The first dimension was LC-CC (UV−visible detector), and the second dimension was SEC (differential refractive index detector).

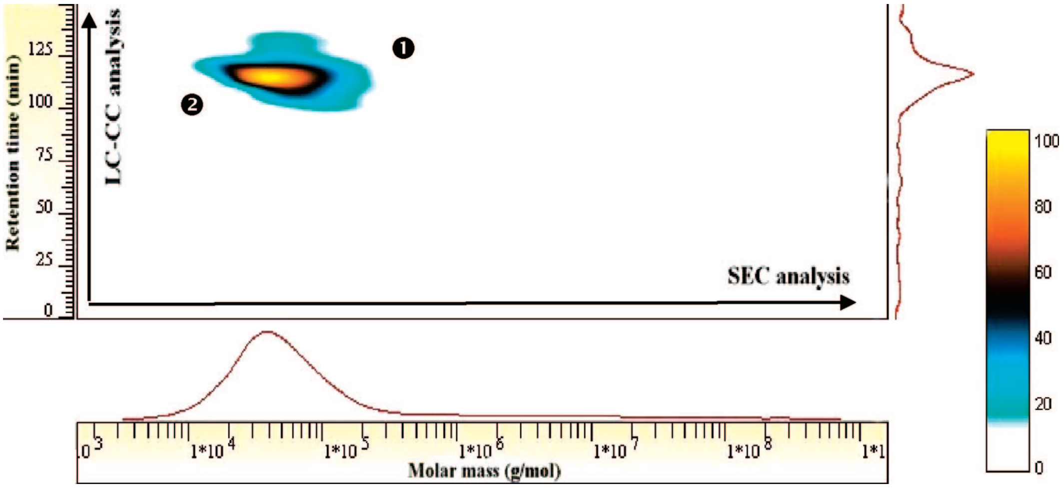


**Figure 10.** Contour plots obtained by 2D chromatography of the reaction mixture resulting from bulk polymerization of styrene performed at 110 °C using SG1-AMA-PEO$_{10K}$-AMA-SG1 as the initiator (target $M_{n,PS}$ = 67000 g/mol; 80% conversion after 15 h before the polymer precipitation step). The first dimension was LC-CC (UV−visible detector), and the second dimension was SEC (differential refractive index detector).

molecular weight equivalent to that of the PEO block. The critical condition of adsorption for PS was determined on silica gel as the stationary phase and with a THF/$H_2O$ mixture as the mobile phase by monitoring the retention volumes of four different PS standards ($M_n$ = 3700, 13700, 29300, and 114100 g/mol). The critical point was found to correspond to an eluent of 86 wt % THF and 14 wt % $H_2O$.

2D chromatography was conducted using LC-CC in the first dimension being connected with SEC in the second dimension as exemplified in Figure 9, where the ordinate axes represent

**Table 5. Component Mass Fractions of Reaction Products from Sample 4h from Experiment 8 (Table 2, entry 8) Determined by 2D Chromatography**

| | sample | component | $M_n$ (g/mol) | $M_w/M_n$ | mass fraction (%) |
|---|---|---|---|---|---|
| **4h**(A) | 1 | PS | 50000 | 1.23 | 55.6 |
| | 2 | PS-PEO-PS | 40000 | 1.31 | 44.4 |
| **4h**(B) | 1 | PS | 50200 | 1.08 | 7.90 |
| | 2 | PS-PEO-PS | 44400 | 1.43 | 92.1 |

the retention time and the chromatogram of the separation in the first dimension while the abscissa indicates the SEC separation of the fraction. The molar mass calibration was carried out using PS standards.

Figure 9 shows the 2D chromatograms observed for sample **4h** (Table 2, entry 8) from the crude reaction mixture (Figure 9A) and for the purified triblock copolymer (Figure 9B). The contour plots clearly indicate that two compounds differing from their chemical composition and molecular mass are present in both samples. The relative fraction of those species is determined from the peak intensities and presented as color codes in the contour plots. The assignment of the fractions is based on the LC-CC separation; with regard to polarity, peak 1 may correspond to a PS homopolymer.

Sample **4h**(A) taken from the reaction mixture before polymer precipitation is then demonstrated to contain a quite high concentration of PS homopolymer (55.6 wt %), confirming the self-polymerization of styrene under the standard NMP conditions, as suggested by the kinetic study described in the legend of Figure 8. In the case of sample **4h**(B), the fraction of PS homopolymer was strongly reduced through the polymer purification step conducted by precipitation in diethyl ether (7.9 wt %). The second peak, assigned to the PS-*b*-PEO-*b*-PS block copolymer, constitutes now the major product. As seen, the obtained block copolymer exhibits a narrow molar mass distribution but also a certain distribution in chemical composition, indicated by the peak broadness in the ordinate direction perhaps due to the presence of diblock copolymers coming from the monofunctional macroinitiator (see section 3.1). A summary of the compositions and molar mass distributions as determined by 2D chromatography analysis for samples **4h**(A) and **4h**(B) is given in Table 5.

Another NMP of styrene using **3c** as the initiator was performed without solvent and at a lower temperature (110 °C) to prevent the formation of PS homopolymer during the polymerization stage. The target molar mass of PS was fixed at 67000 g/mol. After a reaction time of 15 h, the obtained styrene conversion was 80%. The 2D chromatogram of the reaction products before the polymer purification step is presented as contour diagrams in Figure 10. This plot clearly indicates that the quantity of PS homopolymer is strongly reduced to 14.4 wt % versus 55.6 wt % in the former example (Figure 9A). Fraction 2 can be unambiguously assigned to the block copolymer exhibiting a narrow molar mass distribution with an average of ∼44100 g/mol.

From LC-CC measurements, it has been proven that the purification by precipitation permits elimination of the large majority of PS homopolymer. The PS-*b*-PEO-*b*-PS copolymers with well-defined architecture can then be obtained with a purity of >92 wt %.

## 4. Conclusions

The main objective of this work was to develop a new route for preparing A-B-A triblock copolymers using nitroxide-functionalized telechelic PEO. The macroinitiators were prepared by reacting a SG1 derivative with hydroxyl-terminated PEO with various chain lengths. Polymerization of styrene was then initiated in 1,4-dioxane at 112 or 120 °C. The kinetic plots of $\ln([M_o]/[M])$ versus reaction time showed a linear semilogarithmic plot indicating that the polymerization proceeded as a controlled process. The usefulness of this convenient method has been demonstrated in preparing a series of PS-*b*-PEO-*b*-PS compounds having well-defined block architecture. This synthesis strategy appears to be a useful way to prepare a large variety of A-B-A triblock copolymers with a central block consisting of the PEO chain.

A certain discrepancy was, however, noted between the experimental molecular weight of prepared PS-*b*-PEO-*b*-PS and the calculated ones from the theoretical equations derived from the kinetic study. Although the operating conditions were those generally used in controlled radical polymerization, it was shown by a combination of SEC and LC-CC in a two-dimensional setup that traces of peroxide present in 1,4-dioxane can generate a self-homopolymerization of styrene. Removal of coproduced hPS by a precipitation step was proven to afford the PS-*b*-PEO-*b*-PS triblock copolymers in good purity and homogeneity in chain composition.

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