# Synthesis of Poly(2-ethyl-2-oxazoline)-*b*-poly(styrene) Copolymers via a Dual Initiator Route Combining Cationic Ring-Opening Polymerization and Atom Transfer Radical Polymerization

**C. Remzi Becer,**[†,‡,§] **Renzo M. Paulus,**[†,‡,§] **Stephanie Höppener,**[†]
**Richard Hoogenboom,**[†,§] **Charles-André Fustin,**[||] **Jean-François Gohy,**[||] **and**
**Ulrich S. Schubert***[,†,‡,§]

*Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands; Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstrasse 10, 07743 Jena, Germany; Dutch Polymer Institute (DPI), John F. Kennedylaan 2, 5612 AB Eindhoven, The Netherlands; and Unité de Chimie des Matériaux Inorganiques et Organiques (CMAT) and Research Center in Micro- and Nanoscopic Materials and Electronic Devices (CeRMiN), Université catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium*

*Received March 9, 2008; Revised Manuscript Received April 27, 2008*

ABSTRACT: Block copolymers of 2-ethyl-2-oxazoline (EtOx) and styrene were synthesized by a combination of cationic ring-opening polymerization (CROP) and atom transfer radical polymerization (ATRP). Initially, a detailed kinetic investigation for the α-bromoisobutyrylbromide (BrEBBr) initiated CROP of EtOx was performed in acetonitrile at different polymerization temperatures ranging from 100 to 180 °C under microwave irradiation. Poly(2-ethyl-2-oxazoline) (PEtOx) homopolymers with controlled molecular weights and narrow polydispersity indices were synthesized in short reaction times. Polymers with relatively high molar masses and low polydispersity indices ($M_{n,SEC}$ = 48 500 g/mol, PDI = 1.29) could also be obtained. Following the synthesis of a PEtOx macroinitiator ($M_{n,SEC}$ = 3700 g/mol, PDI = 1.09), the ATRP of styrene was performed with CuBr and tris[2-(dimethylamino)ethyl]amine ($Me_6Tren$) as catalytic system. The micellization behavior of the obtained amphiphilic block copolymers was further investigated by dynamic light scattering (DLS) and atomic force microscopy (AFM).

## Introduction

Advanced macromolecular structures constructed by the combination of different monomeric units have attracted great attention because of their enhanced properties for various applications such as, e.g., surface modifiers, coating materials, drug delivery systems, and adhesives.[1] It is now possible to obtain well-defined macromolecules with controlled molecular weight, polydispersity index, architecture, and terminal functionalities by employing controlled/"living" polymerization methods. These polymerizations may proceed by anionic,[2] cationic,[3] group transfer,[4] metathesis,[5] Ziegler−Natta,[6] or various radical mechanisms.[7–10]

Recently, Yagci et al. have reviewed the mechanistic transformations of controlled/"living" polymerization techniques which provide a facile route to the synthesis of block copolymers that cannot be performed by a single polymerization method.[11] Moreover, Du Prez et al. discussed the combination of different polymerization techniques using dual initiators to synthesize block copolymers which do not require any intermediate transformation and protection steps.[12] A dual initiator, or more general a heterofunctional initiator, contains at least two initiation sites with selective and independent initiating groups for the concurrent polymerization mechanisms. Matyjaszewski et al. have examined a general method for the transformation of "living" carbocationic polymerizations into "living" radical polymerizations without any modification of the initiating sites, and they presented a successful synthesis of AB-type block copolymers of tetrahydrofuran (THF) and styrene (St) or methyl (meth)acrylate, respectively.[13] Voit et al. employed a "grafting from" method for the synthesis of complex macromolecular structures consisting of *N*-isopropylacrylamide and 2-alkyl-2-oxazolines and investigated their lower critical solution temperature behavior.[14] These reports are only a few examples that demonstrate the importance of exploiting and improving the combination of different polymerization techniques in order to obtain well-defined block copolymers combining the properties of both monomer sequences.[15–20]

Recently, we reported the cationic ring-opening polymerization (CROP) of 2-ethyl-2-oxazoline (EtOx) using commercially available acetyl halides as initiators.[21] The apparent rate of polymerization for the CROP of EtOx initiated by acetyl bromine was found to be slightly higher than the rate obtained with methyl *p*-toluenesulfonate (MeTs) as initiator in acetonitrile (AN). Moreover, the rate of polymerization was found to be lower for acetyl chloride and faster for acetyl iodide in comparison to MeTs.[22]

Here we report a detailed kinetic investigation of the α-bromoisobutyrylbromide (BrEBBr)-initiated CROP of EtOx and the direct use of the obtained polymers as macroinitiators for the atom transfer radical polymerization (ATRP) of St without the need of postpolymerization modifications for transforming the mechanism from ionic to radical. Moreover, the possibility of synthesizing relatively high molecular weight PEtOx homopolymers using BrEBBr as initiator are demonstrated for the first time to the best of our knowledge. In addition, the micelle formation of the obtained amphiphilic block copolymers was investigated.

## Experimental Section

**Materials.** 2-Ethyl-2-oxazoline (EtOx) (≥99%, Aldrich) was distilled over barium oxide and stored under argon. Styrene (St) (≥99%, Aldrich) and anisole (Biosolve Ltd.) were passed through neutral alumina oxide column prior to use. CuBr (99.999%, Aldrich) was purified as described in the literature.[23] Acetonitrile (AN)

---

* Corresponding author. E-mail: ulrich.schubert@uni-jena.de.
[†] Eindhoven University of Technology.
[‡] Friedrich-Schiller-University Jena.
[§] Dutch Polymer Institute.
[||] Université catholique de Louvain.

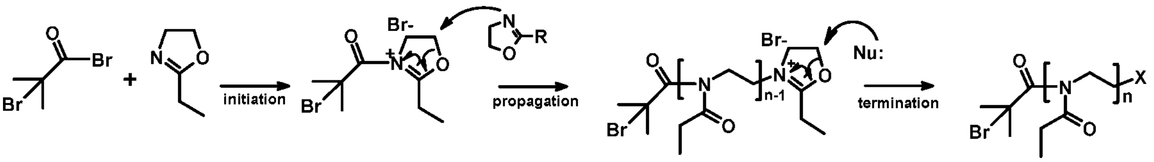
10.1021/ma800527h CCC: $40.75

**Table 1. Conversion and Molecular Weight Data of Relatively High Molecular Weight PEtOx Homopolymers**

| sample | M/I[a] | react time [min] | conv[b] [%] | $M_{n,theo}$[b] [g/mol] | $M_{n,SEC}$[c] [g/mol] | PDI |
|---|---|---|---|---|---|---|
| M1 | 100 | 8 | 43 | 4 500 | 7 350 | 1.12 |
| M2 | 200 | 16 | 46 | 9 350 | 12 800 | 1.13 |
| M3 | 400 | 42 | 65 | 26 000 | 27 000 | 1.15 |
| M4 | 1000 | 104 | 84 | 83 500 | 38 700 | 1.25 |
| M5 | 2000 | 208 | 100 | 198 500 | 48 500 | 1.29 |

[a] Initial monomer to initiator ratios. [b] Monomer conversions were determined by measuring GC. [c] Theoretical molecular weights were calculated by this formula ($M_{n,theo} = 230 + (([EtOx]/[BrEBBr]) \times \text{monomer conversion} \times 99.13)$).

**Scheme 1. Schematic Representation of the Cationic Ring-Opening Polymerization of EtOx Initiated by BrEBBr (X = Br or OH)[a]**



[a] Nu = nucleophile, in the current work water is used to quench the polymerizations.

(Biosolve Ltd.) was dried over molecular sieves (3 Å). α-Bromoisobutyrylbromide (BrEBBr) (98%, Aldrich) was used as received. Tris[2-(dimethylamino)ethyl]amine ($Me_6Tren$) was synthesized according to a synthetic procedure described in the literature.[24]

**Equipment and Analysis.** GC measurements were performed on a Interscience Trace GC used with a Trace column RTX-5 and a PAL autosampler. $^1H$ NMR spectroscopy was recorded on a Varian Mercury 400 MHz NMR in deuterated methylene chloride. The chemical shifts were calibrated with respect to tetramethylsilane (TMS). Size exclusion chromatography (SEC) was measured on a Shimadzu system equipped with a SCL-10A system controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10A UV detector, and both a PSS Gram30 and a PSS Gram1000 column in series. *N,N*-Dimethylacetamide with 5 mmol of LiCl was used as eluent at 1 mL/min flow rate, and the column oven was set to 60 °C. For the kinetic investigation of the BrEBBr-initiated EtOx polymerization, SEC measurements were performed on a Shimadzu system equipped with a SCL-A10 system controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10A UV-detector at 254 nm, and a PLgel 5 $\mu$m Mixed-D column at 50 °C utilizing a chloroform:triethylamine:2-propanol (94:4:2) mixture as eluent at a flow rate of 1 mL/min. The molecular weight and the molecular weight distribution of the prepared polymers were calculated using poly(styrene) standards in both SEC systems. MALDI measurements were performed on a Voyager-DE PRO Biospectrometry Workstation (Applied Biosystems, Foster City, CA) time-of-flight mass spectrometer in linear mode. The spectra were obtained in the positive ion mode. Ionization was performed with a 337 nm pulsed nitrogen laser. The sample was prepared with a multiple-layer spotting technique utilizing *t*-2-(3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) as matrix and NaI as salt, as described in the literature.[25] Cationic ring-opening polymerizations were performed using the Emrys Liberator monomode microwave synthesizer (Biotage) under temperature control utilizing an IR temperature sensor. Dynamic light scattering (DLS) experiments were performed on a Malvern CGS-3 equipped with a He−Ne laser (633 nm). The measurements have been performed at an angle of 90° and at a temperature of 25 °C. The results were analyzed by the CONTIN method which is based on an inverse-Laplace transformation of the data, which gives access to a size distribution histogram for the analyzed micellar solutions. AFM images of the micelles were obtained using a Digital Instruments Nanoscope IV scanning force microscope in tapping mode using NCL type cantilevers (Si, 48 N/m, 330 kHz, Nanosensors). The samples were prepared by spin-coating a dilute solution of micelles on a silicon wafer. The micelles were prepared by first dissolving the copolymer in DMF at a concentration of 1 g/L. In a next step, a water volume equal to half the DMF volume was added under stirring by steps of 50 $\mu$L, followed by the addition of the same water volume in one shot. Afterward, the solution was dialyzed against water to remove the DMF. The final concentration was about 0.3 g/L.

**Synthesis.** *Typical CROP of EtOx for a Kinetic Investigation.* A stock solution was prepared with EtOx (10 mL, 9.9 mmol), AN (15 mL), and BrEBBr (12 $\mu$L, $9.9 \times 10^{-2}$ mmol) for a total volume of 25 mL. The monomer to initiator ratio was 100 to 1, and the monomer concentration was 4 M. From this stock solution, 1 mL aliquots were transferred into several microwave vials. Subsequently, 25 of these vials were heated with different predefined reaction times and temperatures (five vials for each investigated temperature). All reactions were terminated by the automated addition of 100 $\mu$L water using the liquid handling system of the microwave synthesizer. Samples were taken from the microwave reactors and diluted (100 $\mu$L of crude sample + 1000 $\mu$L of chloroform) for GC analysis, and AN was used as internal standard to calculate the monomer conversions. A second sample from the reactors was withdrawn and diluted (100 $\mu$L of crude sample + 1000 $\mu$L of chloroform:triethylamine:2-propanol (94:4:2) mixture) for GPC analysis.

*Upscaling of the PEtOx Macroinitiator Synthesis.* EtOx (8 mL, 7.92 mmol), AN (12 mL), and BrEBBr (384 $\mu$L, 1.98 mmol) were added to a microwave vial, which has an inner volume of 22 mL. It was reacted in the microwave synthesizer at 140 °C for 500 s, and a few drops of water were added to terminate the polymerization. The polymer solution was then diluted by adding chloroform, and the polymer was precipitated into cold diethyl ether. The white precipitate was filtered, washed with cold diethyl ether, and stored at 25 °C in a vacuum oven.

*ATRP of St Initiated by PEtOx Macroinitiators.* 0.067 g (0.467 mmol) of CuBr and 124 $\mu$L (0.467 mmol) of $Me_6Tren$ were added to a 25 mL Schlenk flask and stirred under argon. Predegassed anisole (10 mL) and 10.7 mL of St (93.4 mmol) were added into the flask. After bubbling with argon and stirring for at least 30 min, 1.73 g (0.467 mmol) of PEtOx macroinitiator dissolved in 10 mL of anisole, which was degassed in another flask, were added to the Schlenk flask via a degassed syringe. An initial sample was taken, and the Schlenk flask was placed into the oil bath preheated to 70 °C and reacted for 7 h. At certain time intervals, aliquots (~2 mL) were withdrawn and quenched with air. These samples were analyzed by GC and GPC to determine the monomer conversion and molecular weight data, respectively.

## Results and Discussion

**Kinetic Investigation for the PEtOx Macroinitiator Synthesis.** The reaction mechanism for the BrEBBr-initiated cationic ring-opening polymerization of 2-ethyl-2-oxazolines is outlined in Scheme 1. The strong electrophilic character of the acid bromide initiates the reaction and results in the formation of a cationic oxazolinium ring. Propagation occurs by the attack of next monomer to this cationic ring. Although both ionic and

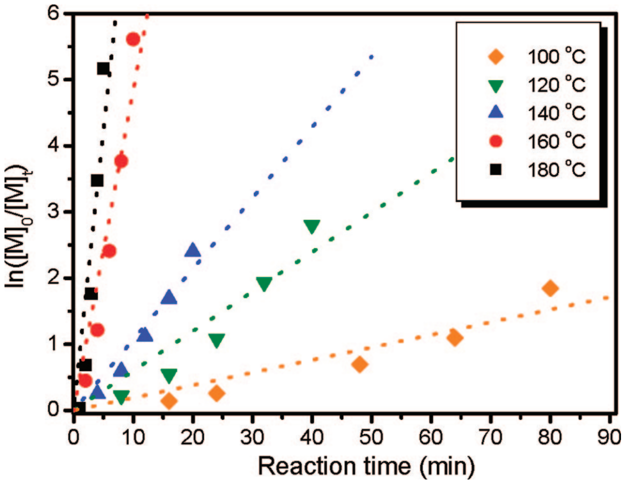


**Figure 1.** Semilogarithmic plot for CROP of EtOx initiated by BrEBBr at different polymerization temperatures.

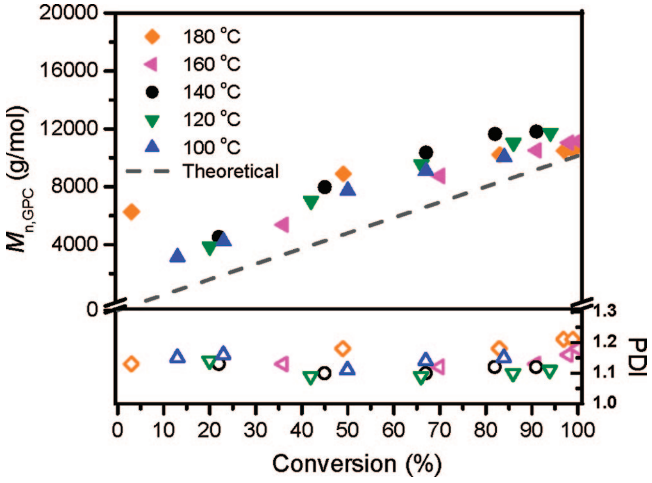


**Figure 2.** Molecular weight and polydispersity indices of PEtOx plotted against monomer conversions.

covalent species can be present during the polymerization of 2-oxazolines with bromide counterions, the polymerization proceeds almost exclusively via the present cationic species.[26,27] When all the monomer is consumed, a second oxazoline-based monomer can be added to synthesize block copolymers or a nucleophile (i.e., water) can be added to terminate the polymerization reaction. The end group of the chain (depicted as X in Scheme 1) can be either a covalently bonded bromine or a hydroxyl group, if water is added after the polymerization. The common initiators used in CROP of oxazolines are benzyl halides, tosylate, or triflate derivatives. Functional end groups can be introduced into the polymer chains by utilizing functionalized initiators, which requires additional synthesis and purification steps, or by employing postpolymerization modifications. Preferably, a commercially available functional initiator is used for simplicity. Here we report the use of commercially available BrEBBr as a new heterofunctional initiator for the CROP of EtOx followed by the ATRP of St in order to synthesize amphiphilic diblock copolymers by combination of two polymerization mechanisms without the need to perform postpolymerization modifications.

In order to gain more insights in the BrEBBr-initiated CROP of EtOx, a kinetic study was performed under microwave irradiation in AN as solvent. Polymerization temperatures and times were selected according to the results obtained for the acetyl bromide-initiated CROP of EtOx.[21] The resulting semilogarithmic first-order kinetic plot is depicted in Figure 1. Slow initiations and relatively fast propagations are observed at low polymerization temperatures (100 and 120 °C) as indicated by the two slopes in the kinetic plot. The apparent rate constants of the polymerizations were found to be $7.92 \times 10^{-3}$, $24.9 \times 10^{-3}$, $44.6 \times 10^{-3}$, $202 \times 10^{-3}$, and $351 \times 10^{-3}$ L mol$^{-1}$ s$^{-1}$ at 100, 120, 140, 160, and 180 °C, respectively. The apparent rate constants are in the same range as those observed for acetyl bromide-initiated polymerizations.[21] The molecular weights of the obtained polymers were measured by SEC and calculated according to poly(styrene) standards. It is shown in Figure 2 that the obtained molecular weights are slightly above the theoretical line and the polydispersity indices are below 1.25 at all investigated temperatures. These plots indicate a living polymerization mechanism with relatively low polydispersity indices even at full monomer conversions. The possibility of initiation by tertiary bromide was tested by using ethyl-2-bromoisobutyrate (EBB) as an initiator. A solution of EtOx in AN was reacted in the microwave for 2 h at 140 °C and characterized with GC, GPC, and $^1$H NMR. There was no polymer found, and no conversion of the monomer was detected by using EBB as an initiator for the CROP of EtOx, demonstrating that only the acid bromide group of BrEBBr initiates the EtOx polymerization. A representative MALDI-TOF mass spectrometry spectrum of a BrEBBr-initiated EtOx homopolymer is displayed in Figure 3. The main distribution, separated by the mass of one monomer unit, could be fitted to the poly(2-ethyl-2-oxazoline) with one iodine end group and one hydroxy end group. The presence of iodine instead of bromine on the PS terminus can be explained by an exchange reaction with sodium iodide, which was used as a salt for the MALDI analysis. The hydroxy end group of the polymer at the PEtOx end is formed since an excess amount of water is added to the polymerization mixture after microwave heating to stop the polymerization. There are two other relatively small distributions visible in the MALDI-TOF MS spectrum, and they correspond to polymers with bromide end groups instead of iodine and/or hydroxy.[21]

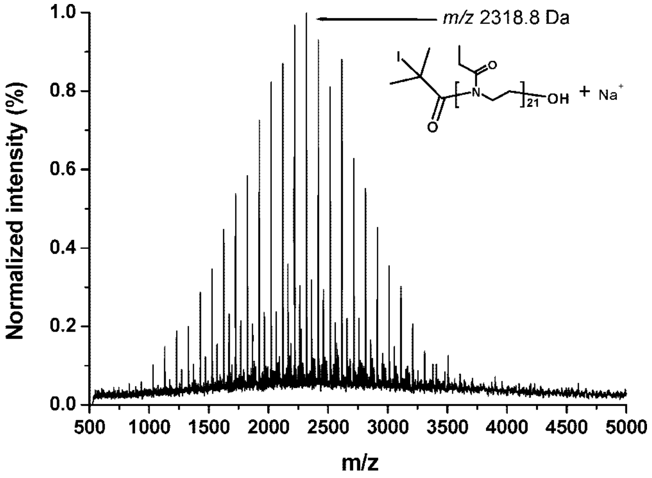


**Figure 3.** MALDI-TOF MS spectrum of BrEBBr-initiated CROP of EtOx. NaI was used as a salt in the DCTB matrix.

According to the results obtained from the semilogarithmic kinetic plot, the activation energy of the BrEBBr initiated CROP of EtOx was calculated from the corresponding Arrhenius plot, which is shown in Figure 4. The value obtained is 67.9 ± 5.6 kJ/mol at the temperature range of 100−180 °C, which is comparable to the previously reported values of 69.3[21] and 68.7 kJ/mol[28] using acetyl bromide and benzyl bromide as initiators for the EtOx polymerization, respectively.

During the kinetic investigation, we could also overcome the challenge of synthesizing well-defined PEtOx homopolymers with

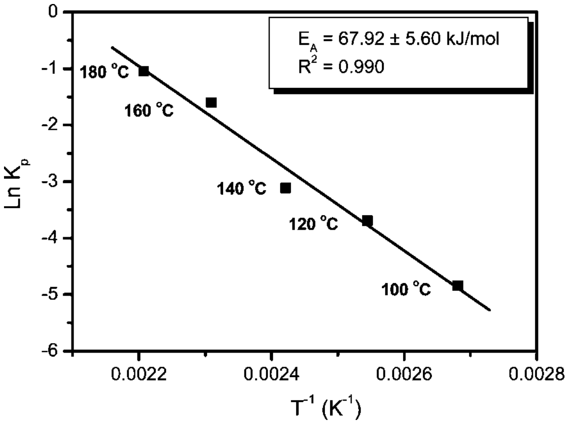


**Figure 4.** Arrhenius plot of BrEBBr-initiated CROP of EtOx in AN.

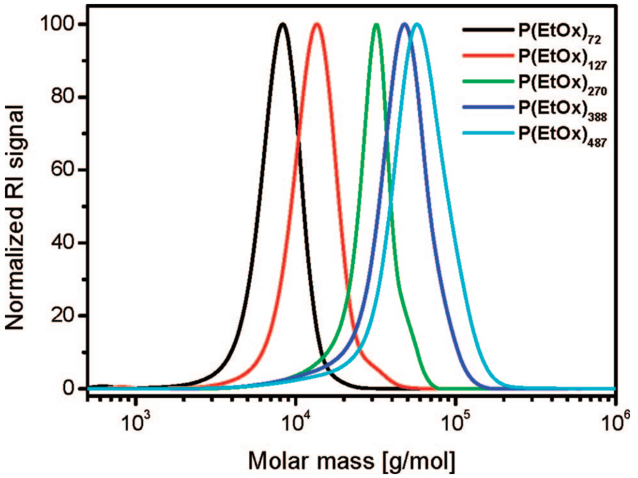


**Figure 5.** SEC traces of PEtOx homopolymers.

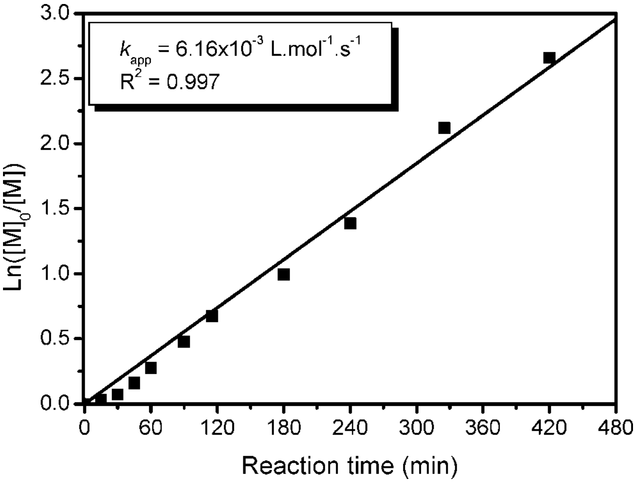


**Figure 6.** Semilogarithmic kinetic plot of ATRP of St initiated by PEtOx.

relatively high molecular weights and low polydispersity indices. Different monomer to initiator ratios (100, 200, 400, 1000, and 2000) were used for the polymerization, and reasonably well-defined homopolymers of PEtOx were obtained with molecular weights up to 48 500 g/mol and polydispersity indices remaining below 1.3. Corresponding SEC traces of the synthesized PEtOx homopolymers are shown in Figure 5 (the results are summarized in Table 1). Polydispersity indices and deviation from theoretical molecular weights increase when the monomer to initiator ratio exceeds 1000. The number-average molecular weights listed in Table 1 are relative values that were calculated according to the PS standards. Besides, a possible reason for this observation might be the occurrence of chain transfer reactions, which are more pronounced at higher monomer conversions.

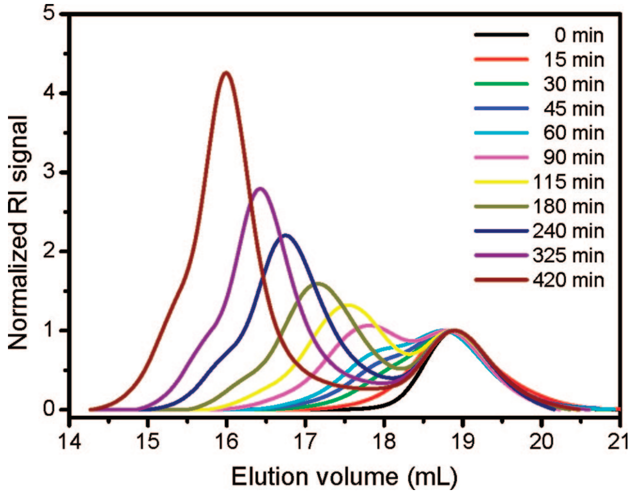


**Figure 7.** SEC traces of the samples withdrawn from the block copolymerization of St via ATRP.

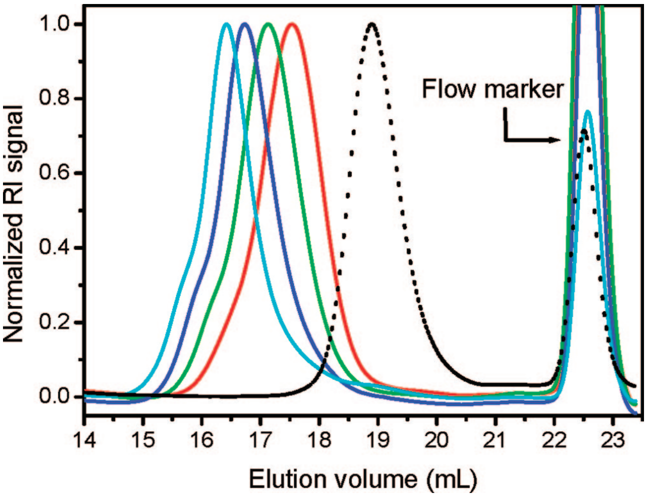


**Figure 8.** SEC traces of PEtOx-*b*-PS copolymers after precipitation; left to right: P9, P8, P7, P6 and P0.

**Table 2. Conversion and Molecular Weight Data of PEtOx-*b*-PS Prior to Purification**

| sample | react time [min] | conv[a] [%] | $M_{n,theo}$[b] [g/mol] | $M_{p,SEC}$[c] [g/mol] |
|---|---|---|---|---|
| P0 | 0 | | 3 700 | 4 150 |
| P1 | 15 | 3 | 4 320 | 4 150 |
| P2 | 30 | 7 | 5 150 | 4 300 |
| P3 | 45 | 15 | 6 820 | 6 600 |
| P4 | 60 | 24 | 8 700 | 7 600 |
| P5 | 90 | 38 | 11 610 | 8 700 |
| P6 | 115 | 49 | 13 910 | 10 600 |
| P7 | 180 | 63 | 16 820 | 14 400 |
| P8 | 240 | 75 | 19 320 | 19 500 |
| P9 | 325 | 88 | 22 030 | 25 000 |
| P10 | 420 | 93 | 23 070 | 35 400 |

[a] Monomer conversions were determined by measuring GC. [b] Theoretical molecular weights were calculated by this formula ($M_{n,theo} = 3700 + (([St]/[PEtOx]) \times \text{monomer conversion} \times 104.15)$). [c] Peak maximum of the block copolymers in the corresponding SEC traces.

**Block Copolymerization of EtOx and Styrene.** According to the knowledge obtained from the kinetic investigation, a PEtOx macroinitiator was synthesized in a large scale (6.11 g) by using the BrEBBr heterofunctional initiator. The molar mass

**Scheme 2. Atom Transfer Radical Polymerization of St Initiated by a PEtOx Macroinitiator**

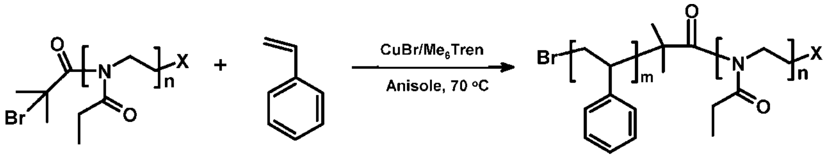


**Table 3. Characterization Data of PEtOx-*b*-PS after Purification**

| sample | $M_{n,SEC}$[a] (g/mol) | PDI | $DP_{EtOx,SEC}$[b] | $DP_{S,NMR}$[c] | $M_{n,NMR}$[d] (g/mol) | $R_h$ (nm) | $D_c$ (nm) |
|---|---|---|---|---|---|---|---|
| P0 | 3 700 | 1.09 | 35 | | | | |
| P6 | 10 200 | 1.20 | 35 | 97 | 13 800 | 141 | 19 |
| P7 | 13 100 | 1.24 | 35 | 124 | 16 600 | 93 | 22 |
| P8 | 16 500 | 1.27 | 35 | 136 | 17 900 | 77 | 24 |
| P9 | 22 200 | 1.23 | 35 | 168 | 21 200 | 114 | 28 |
| P10 | 35 200 | 1.21 | 35 | 224 | 27 000 | 84 | 35 |

[a] Number-average molecular weight of PEtOx-*b*-PS calculated by measuring SEC. [b] Degree of polymerization for the PEtOx block calculated by optimized SEC. [c] Degree of polymerization for the second block of PEtOx-*b*-PS calculated from $^1$H NMR measurements. [d] Molecular weights of the block copolymers calculated by the combination of SEC and $^1$H NMR results. The hydrodynamic radius ($R_h$) is determined by a CONTIN analysis of the DLS data. The diameter of the core ($D_c$) is determined by measuring the height of the micelles from AFM images.

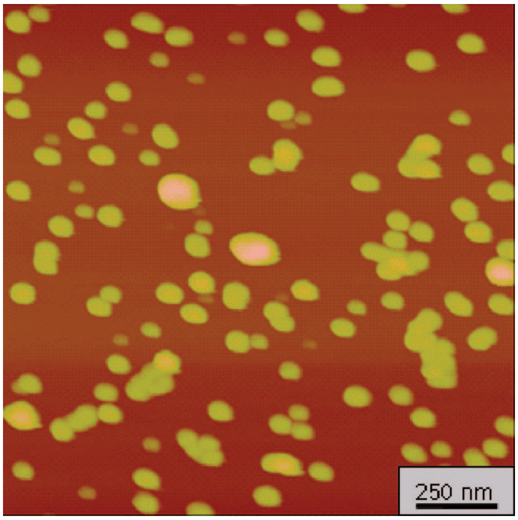


**Figure 9.** AFM height image recorded on micelles, obtained from copolymer P7, deposited on a silicon substrate.

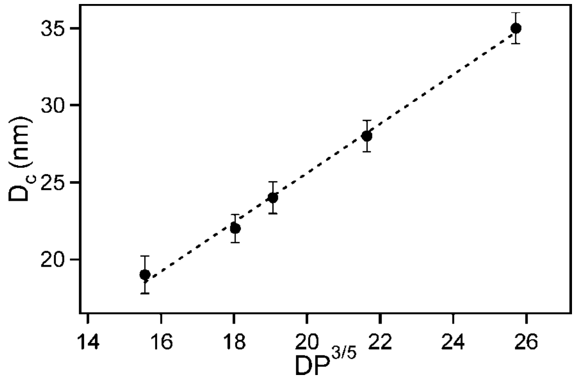


**Figure 10.** Relationship between the measured (AFM) core size of the micelles and the 3/5th power of the degree of polymerization of the PS block. The dotted line represents a linear regression performed on those data.

of the PEtOx macroinitiator was measured by SEC ($M_{n,SEC}$ = 3700 g/mol, $M_w/M_n$ = 1.09), and the monomer conversion (~100%) was determined by $^1$H NMR spectroscopy.

The above-mentioned PEtOx was subsequently used as a macroinitiator for the ATRP of St in order to obtain well-defined PEtOx-*b*-PS diblock copolymers. Various ligands, i.e., *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), 2,2-bipyridyl (BPy), and *N*-(*n*-hexyl)-2-pyridylmethanimine (NHPMI),[29,30] were tested for the ATRP of St in the presence of CuBr metal salt. However, none of these ligands provided a good initiation for the ATRP of St. Therefore, a more active ligand, $Me_6Tren$, was selected, and in this case it was possible to initiate the ATRP of St. The overall reaction scheme of ATRP of St initiated by PEtOx is shown in Scheme 2.

The polymerization was performed in anisole at 70 °C for 7 h. A linear relationship was observed in the semilogarithmic kinetic plot which indicates a controlled growth of the second block (Figure 6). The apparent rate of polymerization was calculated from this plot as $6.16 \times 10^{-3}$ L mol$^{-1}$ s$^{-1}$. The aliquots were withdrawn from the polymerization mixture in a relatively large scale (ca. 2 mL) in order to be able to purify and further characterize the copolymers. In this way, it was possible to synthesize a set of amphihilic block copolymers with a constant length of the first PEtOx block and increasing length of the second PS block. The samples taken at different time intervals were characterized by SEC. A shift of the peak to lower elution volumes is clearly visible in Figure 7, evidencing the chain extension. On the other hand, it was observed that some amount of unreacted macroinitiator remained in the polymerization mixture. The possible explanation for this could be the presence of chain transfer initiated EtOx chains without ATRP initiator functionality. The conversion and molecular weight data of the samples measured directly from the polymerization solutions are summarized in Table 2. Monomer conversions were measured with GC, and anisole was used as an internal standard. In the SEC measurements, the peak maxima of the block copolymers were listed for a better comparison. It was observed that the peak maxima of the SEC traces for the samples taken at different reaction times were shifting to the high molecular weight region, and this is a strong indication for the controlled polymerization of St.

The block copolymers were purified by a simple precipitation into a selective nonsolvent. Methanol is a nonsolvent for PS, whereas it is a good solvent for PEtOx. As such, precipitation of the polymerization samples into methanol yielded pure PEtOx-*b*-PS (Figure 8). The molecular weight data and polydispersity indices of those purified diblock copolymers are listed in Table 3. The average degree of polymerization (DP) for the styrene block and the corresponding experimental molecular weights were calculated from $^1$H NMR measurements.

**Micellization Study of the Block Copolymers.** The micellization behavior of the different amphiphilic copolymers has been studied in water. Because of the rather short PEtOx block, the copolymers are not directly soluble in water. They have thus been first dissolved in a nonselective solvent, i.e. DMF, and water has been added to trigger the micellization. In a last step, DMF was removed by dialysis against water (see Experimental Section for more details). The obtained micelles have been characterized by DLS and AFM. For all copolymers, a CONTIN analysis of the DLS data revealed a single, relatively broad, population. The DLS data did not show any significant dependence on dilution, in agreement with the formation of "frozen" micelles.[31] The hydrodynamic radii, summarized in Table 3, seem large considering the molecular weight of the copolymers. Moreover, there is no visible correlation between the measured $R_h$ and the composition of the copolymers. Since all copolymers have the same hydrophilic block length and a hydrophobic block length increasing from P6 to P10, a corresponding increase of $R_h$ was expected, according to the usual trend observed for block copolymer micelles.[31] This lack of correlation could be due to the formation of aggregates of micelles. Even if the CONTIN histograms only show a single population, this peak accounts in fact for unresolved isolated micelles and small clusters of micelles.[32] This behavior is a common feature for micellar objects presenting only a steric stabilization from water-soluble coronal blocks, such as poly(ethylene oxide)[32,33] or PEtOx.[34,35] Moreover, the copolymers used in this study have a rather short hydrophilic block, providing thus a poor stabilization of the micelles. To help clarify the situation and to possibly observe isolated objects, the micelles have been deposited onto silicon substrates by spin-coating and were subsequently characterized in the dry state by AFM. A typical height image recorded on such a sample is shown in Figure 9. Isolated micelles but also small clusters are clearly seen, confirming their tendency to aggregate. To avoid tip convolution effects, the height of the micelles have been measured. This height can be assimilated to the diameter of the micellar core since the coronal block is short and collapsed in the dried state. The results are reported in Table 3. Here, a clear correlation between the copolymer compositions is observed; the diameter of the core increased progressively with the length of the PS block. For classical hairy micelles the size of the core should scale linearly with the 3/5th power of the degree of polymerization of the insoluble block.[36] Such a plot has been constructed (see Figure 10), and the linear relationship is clearly evidenced. This shows that despite the tendency to form aggregates, well-defined, isolated micelles following the classical scaling laws can be obtained.

## Conclusions

We demonstrated the use of a commercially available heterofunctional initiator for the CROP of EtOx followed by the ATRP of St. A detailed kinetic study was first conducted for BrEBBr in a microwave synthesizer at different polymerization temperatures. The propagation rate constant of the CROP of EtOx and the activation energy of the polymerization were calculated according to the results obtained in this kinetic investigation. Additionally, we presented the controlled synthesis of PEtOx homopolymers with relatively high molecular weights and polydispersity indices below 1.3 by using this initiator.

PEtOx-*b*-PS copolymers with different PS chain length were synthesized by ATRP from the PEtOx macroinitiator prepared earlier. Those diblock copolymers were obtained with controlled molecular weights and relatively narrow polydispersity indices.

Micellization in water of these amphihilic block copolymers was investigated by DLS and AFM measurements. The results clearly showed a correlation between the length of the PS block and the diameter of the core of the micelles. Moreover, preliminary AFM measurements on annealed thin films for the phase separation behavior of the synthesized block copolymers exhibited the formation of different morphologies which will be the topic of a forthcoming manuscript.

**Acknowledgment.** This work forms part of the research program of the Dutch Polymer Institute (DPI), project number 502. C.A.F. is Research Associate of the FRS-FNRS. J.F.G. and C.A.F. thank the "Politique Scientifique Fédérale" for financial support in the frame of the "Interuniversity Attraction Poles Programme (PAI VI/27): Functional Supramolecular Systems".

## References and Notes

(1) Riess, G.; Hurtrez, G.; Bahadur, P. In Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1985; Vol. *2*, p 324.

(2) Szwarc, M. *Nature (London)* **1956**, *178*, 1168.

(3) Matyjaszewski, K. *Cationic Polymerizations, Mechanisms, Synthesis, and Applications*; Marcel Dekker: New York, 1996.

(4) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnhem, W. B.; Rajan-Babn, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.

(5) Novak, B. M.; Risse, W.; Grubbs, R. H. *Adv. Polym. Sci.* **1992**, *102*, 47.

(6) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664.

(7) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.

(8) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.

(9) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.

(10) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.

(11) Yagci, Y.; Tasdelen, M. A. *Prog. Polym. Sci.* **2006**, *31*, 1133.

(12) Bernaerts, K. V.; Du Prez, F. E. *Prog. Polym. Sci.* **2006**, *31*, 671.

(13) Kajiwara, A.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 3489.

(14) Rueda, J.; Zschoche, S.; Komber, H.; Schmaljohann, D.; Voit, B. *Macromolecules* **2005**, *38*, 7330.

(15) Cianga, I.; Hepuzer, Y.; Serhatli, E.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2199.

(16) Xu, S. Q.; Zhao, H. Y.; Tang, T.; Huang, B. T. *Chin. J. Polym. Sci.* **1999**, *17*, 145.

(17) Christova, D.; Velichkova, R.; Goethals, E. J. *Macromol. Rapid Commun.* **1997**, *18*, 1067.

(18) Erdogan, T.; Bernaerts, K. V.; Van Renterghem, L. M.; Du Prez, F. E.; Goethals, E. J. *Des. Monomers Polym.* **2005**, *8*, 705.

(19) Christova, D.; Velichkova, R.; Goethals, E. J.; Du Prez, F. E. *Polymer* **2002**, *43*, 4585.

(20) Bernaerts, K. V.; Schacht, E. H.; Goethals, E. J.; Du Prez, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3206.

(21) Paulus, R. M.; Becer, C. R.; Hoogenboom, R.; Schubert, U. S. *Macromol. Chem. Phys.* **2008**, *209*, 794.

(22) Hoogenboom, R.; Fijten, M. W. M.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1830.

(23) Arehart, S. V.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2221.

(24) Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 8629.

(25) Meier, M. A. R.; Schubert, U. S. *Rapid Commun. Mass Spectrom.* **2003**, *17*, 713.

(26) Dworak, A. *Macromol. Chem. Phys.* **1998**, *199*, 1843.

(27) Hoogenboom, R.; Paulus, R. M.; Fijten, M. W. M.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1487.

(28) Hoogenboom, R.; Fijten, M. W. M.; Brandli, C.; Schroer, J.; Schubert, U. S. *Macromol. Rapid Commun.* **2003**, *24*, 98.

(29) Zhang, H.; Schubert, U. S. *Chem. Commun.* **2004**, 858.

(30) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190.

(31) Gohy, J.-F. *Adv. Polym. Sci.* **2005**, *190*, 65.

(32) Regev, O.; Gohy, J.-F.; Lohmeijer, B. G. G.; Varshney, S. K.; Hubert, D. H. W.; Frederik, P.; Schubert, U. S. *Colloid Polym. Sci.* **2004**, *282*, 407.

(33) Jada, A.; Hurtrez, G.; Siffert, B.; Riess, R. *Macromol. Chem. Phys.* **1996**, *197*, 3697.

(34) Hoogenboom, R.; Wiesbrock, F.; Huang, H.; Leenen, M. A. M.; Thijs, H. M. L.; van Nispen, S. F. G. M.; van der Loop, M.; Fustin, C.-A.; Jonas, A. M.; Gohy, J.-F.; Schubert, U. S. *Macromolecules* **2006**, *39*, 4719.

(35) Hoogenboom, R.; Wiesbrock, F.; Leenen, M. A. M.; Thijs, H. M. L.; Huang, H.; Fustin, C.-A.; Guillet, P.; Gohy, J.-F.; Schubert, U. S. *Macromolecules* **2007**, *40*, 2837.

(36) Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: Oxford, UK, 1998.

MA800527H