Macromolecules **1998,** *31,* 538−541

Synthesis of Amphiphilic PS-*b*-PEG-*b*-PS by Atom Transfer Radical Polymerization

Katja Jankova, Xianyi Chen, Jorgen Kops,* and Walther Batsberg[†]

Department of Chemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark

Received July 10, 1997
Revised Manuscript Received November 12, 1997

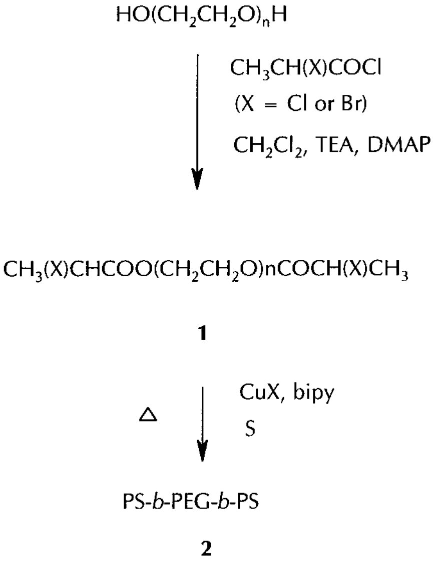
Introduction. Amphiphilic block copolymers are of considerable interest for various applications in which the combination of hydrophilic and hydrophobic properties of these materials may be utilized, e.g. as emulsifiers, dispersion stabilizers, and compatibilizers. In particular block copolymers composed of poly(ethylene glycol) (PEG)/poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) have been extensively studied and the micellar phase structures investigated.[1,2]

PEG may be combined with other polymers into block or graft copolymers and we previously synthesized a block copolymer having polyisobutylene as the hydrophobic middle block and PEG as the outer hydrophilic blocks by coupling of the segments into a triblock structure.[3] The corresponding amphiphilic block copolymers with polystyrene (PS) as the hydrophobic middle block have been synthesized by anionic polymerization whereby living difunctional PS was extended by polymerization of ethylene oxide to the triblock structure.[4] The synthesis of block copolymers with controlled block lengths requires efficient controlled/“living” polymerization. The diblock copolymers PS-*b*-PEG have also been prepared by anionic polymerization using a monofunctional initiator.[5−7] These block copolymers have been investigated as polymeric stabilizers in emulsion polymerization.[8] The phase behaviour in bulk as well as in aqueous solutions have been studied,[9] and recently interesting observations regarding novel morphologies of aggregates of the PS-*b*-PEG diblock copolymers have been reported.[10,11]

The PS-*b*-PEG-*b*-PS triblock copolymers can not be prepared by anionic polymerization as in case of the polymer with PS as the middle block; however, such triblock copolymers have previously been prepared by coupling of PS and PEG preformed segments.[5] In addition, PS-*b*-PEG-*b*-PS has been obtained by using peroxide terminated PEG to initiate free radical polymerization of styrene;[12] however, simultaneous formation of homo PS occurred, and separation of this from the triblock copolymer was not attempted.

Recent developments in free radical polymerization have made it possible to control such polymerizations and obtain polymers with predetermined molecular weights and narrow molecular weight distributions.[13−18] Two major types of systems have been investigated, that is the nitroxide mediated radical polymerization (NMRP) in which the polymerization is controlled by reversible termination between the propagating free radical and a stable nitroxyl radical most often TEMPO[13,14] and atom transfer radical polymerization (ATRP) where a transition metal compound acts as a carrier of a halogen atom in a reversible redox process.[17,18] Recently a PS-*b*-PEG diblock copolymer was synthesized in our laboratory using the NMRP route.[19] In this case the synthesis was carried out from a tosylated monomethoxy PEG derivatized by reaction with 2,2,6,6-tetramethyl-1-(2-hydroxy-1-phenylethoxy)piperidine. This macroinitiator with an end-positioned nitroxide group (TEMPO), when heated in the presence of styrene yielded the diblock copolymer. However, the polymerization was accompanied by homo PS formation.

Scheme 1



In this paper we describe how well-defined triblock copolymers PS-*b*-PEG-*b*-PS may be synthesized by the ATRP route. The synthesis is outlined in Scheme 1 and first a difunctional hydrophilic 2-bromo (or chloro) propionate PEG macroinitiator (**1**) is synthesized, which is subsequently used in the preparation of triblock copolymers PS-*b*-PEG-*b*-PS (**2**) by being heated with styrene in bulk and solution under ATRP conditions.

Experimental Section. Materials. 2-Bromopropionyl chloride (BPC, Technical Grade) and 2-chloropropionyl chloride (CPC, 97%), both from Aldrich, were freshly distilled by room temperature under vacuum. Triethylamine (TEA) was refluxed with *p*-toluenesulfonyl chloride and distilled. The resulting amine free TEA was stored over CaH_2. Before use it was refluxed and distilled again. 4-(Dimethylamino)pyridine (DMAP) was recrystallized from toluene. Methylene dichloride (CH_2Cl_2) was shaken with portions of concentrated H_2SO_4 until the acid layer remained colorless, then washed with water, aqueous 5% Na_2HCO_3 and with water again, and finally distilled from CaH_2. CuBr was purified according to a published procedure.[17] PEG 2000 (Aldrich) was dried by azeotropic distillation with toluene before use. Traces of residual toluene was removed under vacuum. Styrene (Riedel-de Haen) was passed through a column with activated Al_2O_3 (Aldrich, neutral, Brockman I, Standard Grade, ca. 150 mesh, 58 Å) to remove the inhibitor, stored over CaH_2, and then vacuum distilled before polymerization. All other reagents (CuCl, 2,2′-bipyridine (bipy), hexane, xylene, ether, ethanol, dioxane, toluene, cyclohexane) were

---

[†] Risø National Laboratories, Department of Condensed Matter Physics and Chemistry, DK-4000 Roskilde, Denmark.

S0024-9297(97)01018-8 CCC: $15.00

purchased from commercial sources and used after the usual drying and/or distillation without further pretreatment unless otherwise indicated.

Preparation of PEG Macroinitiators. A 0.92 g (7.5 mmol) sample of DMAP in 10 mL of dry methylene chloride was mixed with 0.7 mL (5.0 mmol) of TEA. The solution was transferred into a 250 mL three-neck round-bottom flask equipped with condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer. After cooling to 0 °C, 1.2 mL (12.5 mmol) of CPC or 1.3 mL (12.5 mmol) of BPC in 10 mL of CH_2Cl_2 was added. To the formed yellow dispersion was added 5.00 g (2.5 mmol) of PEG 2000 in 50 mL of dry CH_2Cl_2 dropwise during 1 h under dry nitrogen; subsequently the temperature was allowed to rise to room temperature. The reaction was continued under stirring for 18 h. The solution was filtered, half of the solvent was evaporated, and the PEG macroinitiator was precipitated in cold diethyl ether. After dissolution in absolute ethanol, the solution was stored overnight to recrystallize the product. The macroinitiator was filtered, washed with cold ether, and dried in vacuum.

Polymerizations. 1. ATRP of Styrene Using the PEG Macroinitiators. PS-*b*-PEG-*b*-PS triblock copolymers were synthesized by either bulk or solution polymerization. Thus, in a typical bulk polymerization, a glass tube was charged with 0.50 g (0.25 mmol) of PEG dichloro- or dibromomacroinitiator, 0.050 g (0.50 mmol) of CuCl or 0.072 g (0.50 mmol) of CuBr and 0.234 g (1.50 mmol) of bipy. 5 mL (43.61 mmol) of styrene were added, and the system was degassed three times and then heated at 110 °C (in the case of Br−PEG−Br macroinitiator and CuBr/bipy) or at 130 °C (in the case of Cl−PEG−Cl/CuCl/bipy) under nitrogen for 20 h. In case of solution polymerization the amount of monomer was 1 mL (8.72 mmol), which was diluted with 5 mL of xylene. All other conditions (amounts of Cl−PEG−Cl or Br−PEG−Br, CuCl/bipy or CuBr/bipy, temperatures, and duration of the polymerizations) were otherwise kept the same as above. The crude products were dissolved in dichloromethane, filtered, and precipitated in a large excess of hexanes. The polymers were dried in vacuum at room temperature and the yields determined gravimetrically.

2. Purification of Triblock Copolymers. The separation of the triblock copolymers from possible homo PS and PEG macroinitiator was carried out partly according to the procedure previously described.[19] Thus, the crude product was extracted with cyclohexane at room temperature three times for 3 days, for possible removal of PS. The residue was purified (after drying and weighing) by extraction twice with distilled water at room temperature in order to remove possible unreacted PEG macroinitiator. The purified product was dried in vacuum and weighed.

Measurements. The structure of reactants, macroinitiators, and block copolymers was characterized by ^{1}H NMR, using a Bruker 250 or 500 MHz spectrometer and DMSO-d_6, CD_2Cl_2 or $CDCl_3$ as solvents. The block copolymer composition was determined by either the M_n or the ratio of the NMR signal intensity of the phenyl peak region (6.4−7.3 ppm) to that of the PEG region (3.4−3.8 ppm). Initiator efficiency was calculated based either on the M_n taking the yield of the polymer into consideration or on the amount of the extracted Cl−PEG−Cl (Br−PEG−Br) macroinitiators. The number-average (M_n) and weight-average (M_w) molecular weights of the PEG 2000 and macroinitiators were determinated by GPC, using a Waters 200 gel permeation chromatograph equipped with four Ultrastyragel columns (1 × 10^6, 2 × 10^4, and 1 × 10^3 Å pore size). M_n and M_w of the macroinitiators were also determined along with the values for the resulting PS-*b*-PEG-*b*-PS triblock copolymers on a Viskotek Co. instrument with Nucleosil modified columns: 500, 100, and 50 Å. Measurements on both chromatographs were performed in THF solvent at room temperature with a 1 mL/min flow and calibrations based on polystyrene standards.

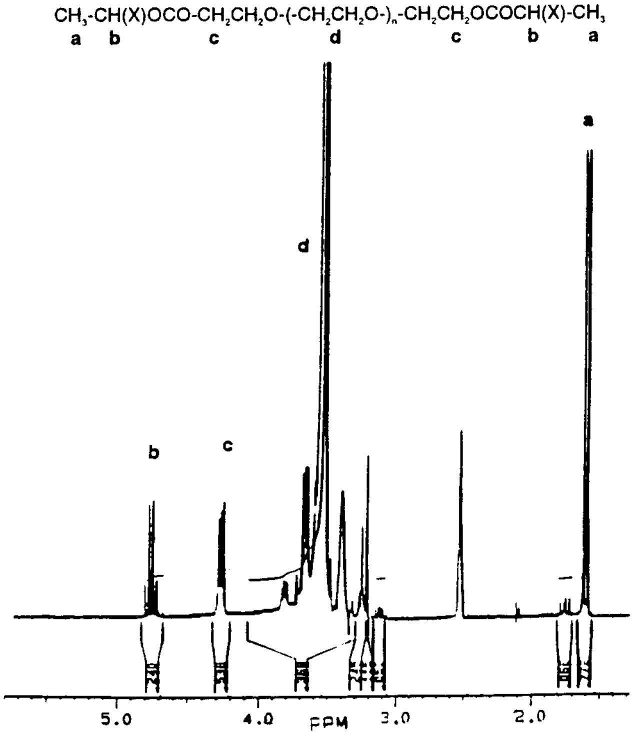


Figure 1. ^{1}H NMR spectrum of macroinitiator **1** in DMSO-d_6.

Results and Discussion. In the first step of the synthesis of PS-*b*-PEG-*b*-PS triblock copolymers (Scheme 1) telechelic macroinitiators are prepared by reacting PEG with acid chlorides. In order to avoid cleavage of the polymer chains as found in case of other derivatizations of PEG[20] the reaction was carried out at 0 °C in CH_2Cl_2 in the presence of TEA and DMAP. The conditions are similar to those used for preparation of PEG−tosylates or −succinates[3,21] and carried out as given under the Experimental Section for the present purpose. The complete substitution of the hydroxyl groups was proved by ^{1}H NMR spectroscopy. The OH signal of PEG[22,23] in DMSO-d_6 around 4.56 ppm had disappeared after the esterification and a new signal appeared at 4.24 ppm, due to the substituted PEG (Figure 1). Quantitative ester substitution was tested by adding to the solution of 2-bromopropionate telechelic PEG in the NMR tube a small amount of the starting PEG, whereupon the signal at 4.56 ppm reappeared. By GPC analysis it was found that the synthesis of the Cl−PEG−Cl and Br−PEG−Br macroinitiators involved no molecular weight reduction since narrow symmetrical signals were observed at essentially the same position as the starting PEG. The data are given in Table 1.

Table 1. Molecular Weight Characteristics of PEG 2000 and Macroinitiators Thereof

		GPC results	
polymer	M_n^{theor}	M_n	M_w/M_n
PEG 2000	2000	1920	1.13
Cl−PEG−Cl	2180	2120	1.11
Br−PEG−Br	2270	2150	1.11

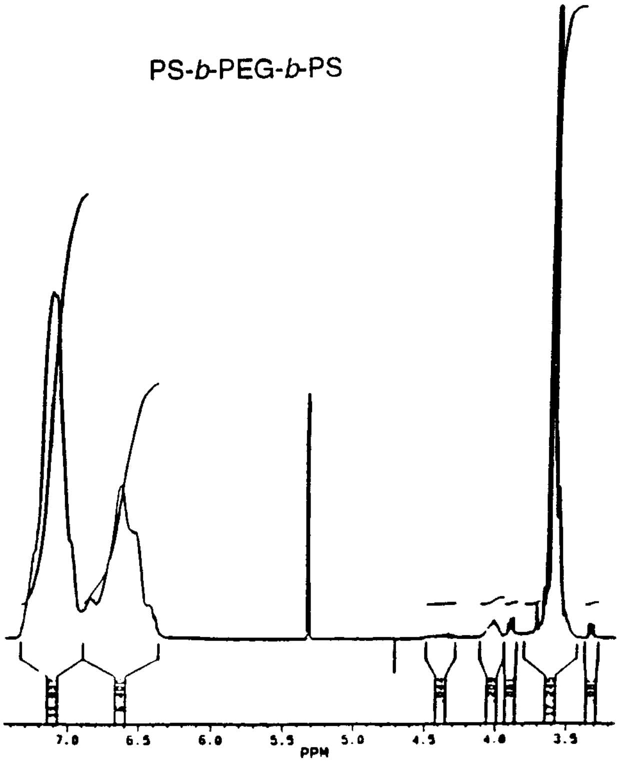


Figure 2. ^{1}H NMR spectrum of triblockcopolymer **2** in CD_2Cl_2.

Before the actual synthesis of PS-*b*-PEG-*b*-PS model experiments had been carried out with ethyl 2-bromo (or chloro) propionic esters (EBP and ECP) to help establish the reaction conditions required for the ATRP of styrene, and also to determine the efficiency of an ester initiator in this type of polymerization. In the case of bulk polymerization with EBP at 110 °C a 88% conversion was obtained after 16 h and $M_n = 8700$ corresponding to 81% initiation efficiency based on a theoretical $M_n = 10\,800$. In solution with ECB at 130 °C a 57% yield was obtained after 20 h and $M_n = 3\,500$ corresponding to 83% initiation efficiency based on a theoretical $M_n = 2\,900$.

The telechelic Cl−PEG−Cl and Br−PEG−Br macroinitiators were used to initiate ATRP of styrene in bulk and in solution for formation of PS-*b*-PEG-*b*-PS. The product purification was carried out by extraction (as described under the Experimental Section) with cyclohexane (for PS) and water (for PEG macroinitiators). For the different triblock copolymers various amounts were extracted, as seen in Table 2; however, GPC analysis of the cyclohexane extracts showed no change in the elution traces from the original triblock copolymer products indicating partial solubility of the triblocks with relatively high PS contents in this solvent. The NMR spectra confirmed this; nevertheless, a slightly higher PS content was found, and it was calculated that the PS homopolymer contents in the triblocks were below 3% and 9% in the total polymers prepared by solution and bulk copolymerization respectively (Table 2). The amounts of the water extractables are small and the high initiation efficiencies of the PEG macroinitiators calculated on this basis are given in Table 2. Both macroinitiators resulted in 54% conversion of the styrene in bulk, whereas the solution polymerization with Cl−PEG−Cl led to 67% and with Br−PEG−Br to 48% yield, respectively. However, these latter yields appear to be too high compared to the bulk preparations, and also the PS contents determined by NMR appear to be too high. This may be due to residual *p*-xylene, which is difficult to separate effectively from the low molecular weight polymers.

Figure 2 shows the ^{1}H NMR spectrum of PS-*b*-PEG-*b*-PS by bulk polymerization initiated by the Cl−PEG−Cl macroinitiator. Integration of the aromatic and aliphatic peak regions gave 91 and 87% PS contents which are close to the theoretical values of 83 and 84% (for Cl−PEG−Cl and Br−PEG−Br, respectively). According to the ^{1}H NMR data for triblocks obtained by solution polymerization by the same macroinitiators, the PS content of the samples was 67−57%, in good agreement with the calculated values.

GPC curves of the Cl−PEG−Cl macroinitiator and the resulting triblock copolymers obtained in bulk and solution are presented in Figure 3. The GPC curves indicate that PS-*b*-PEG-*b*-PS block copolymers are formed in both cases, since the entire elution curves are shifted linearly toward higher molecular weights. This indicates the involvement of essentially all PEG macroinitiator chains in initiating the ATRP of styrene. Also, the triblocks obtained have narrow M_w/M_n values—below 1.3 and 1.4 for Cl−PEG−Cl and Br−PEG−Br respectively, which further indicates a high efficiency of the macroinitiators and a low degree of uncontrolled polymerizations generated by side reaction particularly thermal polymerization.

Conclusions. It has been demonstrated that 2-chloro (or bromo) propionate telechelic PEG macroinitiators are efficient in ATRP of styrene. New PS-*b*-PEG-*b*-PS triblock copolymers with controlled structures have been synthesized and characterized, which have not been obtained previously by direct polymerization from a macroinitiator. Such macroinitiators may be prepared from other hydroxyl-terminated polymers, and various types of monomers may be polymerized.

Table 2. Characteristics of the PS-*b*-PEG-*b*-PS Triblock Copolymers

								PS content in PS-*b*-PEG-*b*-PS (%)		
macroinitiator	polymerization	yield (%)	$M_n \times 10^{-3}$	M_w/M_n	i_{eff}[a] (%)	cyclohexane extract (%)	homo PS	theor	NMR	GPC
Cl−PEG−Cl	bulk	54	19.7	1.29	98	26	9	83	91	90
Cl−PEG−Cl	solution	67	4.7	1.28	88	30	3	58	67	58
Br−PEG−Br	bulk	54	13.3	1.36	90	7	2	84	87	85
Br−PEG−Br	solution	48	3.4	1.42	84	19	3	48	55	41

[a] Based on the amounts of nonextractable macroinitiator.

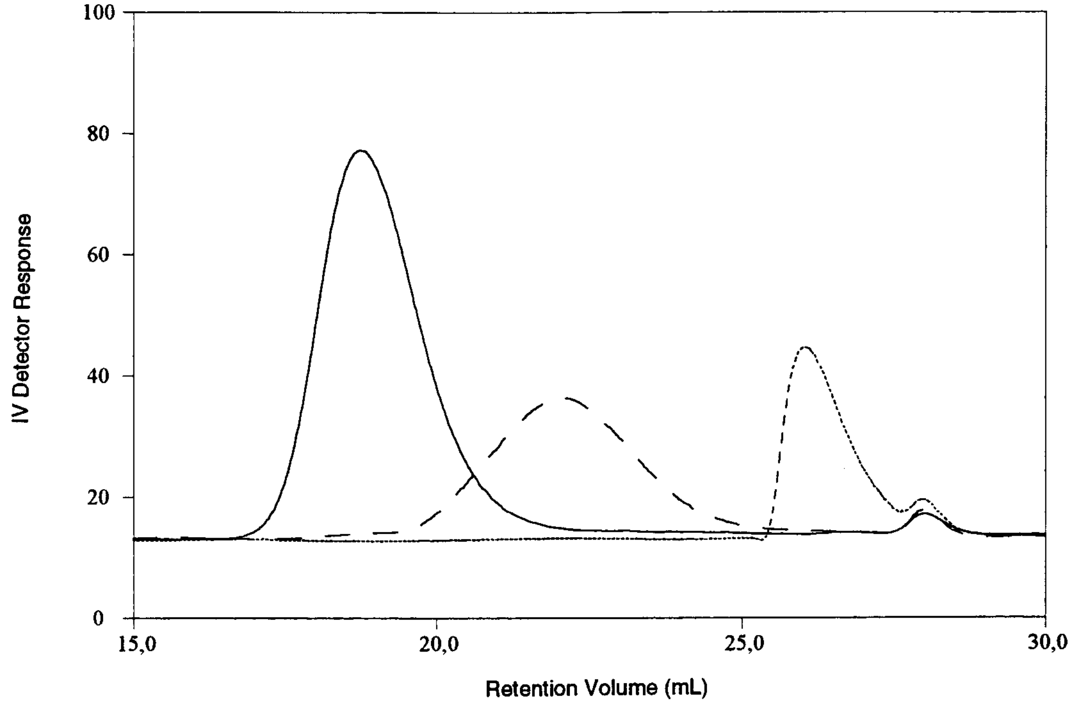


Figure 3. GPC traces of macroinitiator **1** (- -) and its related triblockcopolymers **2** prepared in xylene (— —) and in bulk (—), respectively.

Acknowledgment. This study was supported by the Danish Materials Technology Program MUP2 and was carried out within the framework of the Danish Polymer Centre.

References and Notes

(1) Mortensen, K. *J. Phys: Condens. Matter* **1996**, *8*, A103.
(2) Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. *Macromolecules* **1994**, *27*, 2414.
(3) Gao, B.; Kops, J. *Polym. Bull.* **1995**, *34*, 279.
(4) Richards, D. H.; Szwarc, M. *Trans Faraday Soc.* **1959**, *55*, 1644.
(5) Finaz, G.; Rempp, P.; Parrod J. *Bull. Soc. Chim. Fr.* **1962**, 262.
(6) O'Malley, J. J.; Marchessault, R. H. *Macromol. Synth.* **1972**, *4*, 35.
(7) Quirk, R. P.; Kim, J.; Tkausch, C.; Chun, M. *Polym. Int.* **1996**, *39*, 3.
(8) Jialanella, G. L.; Firer, E. M., Piirma I. *J. Polym. Sci.: Polym. Chem.* **1992**, *30*, 1025.
(9) Mortensen, K.; Brown, W.; Almdahl, K.; Alami, E.; Jada, J. *Langmuir* **1997**, In Press.
(10) Yu, K.; Eisenberg, A. *Macromolecules* **1996**, *29*, 6359.
(11) Yu, K.; Zhang, L.; Eisenberg, A. *Langmuir* **1996**, *12*, 5980.
(12) Uyanik, N.; Baysal, B. M. *J. Appl. Polym. Sci.* **1990**, *41*, 1981.
(13) Georges, M. K.; Vergin, P. R. N.; Kazmaier, P. M.; Hamer, G. K.; *Macromolecules* **1993**, *26*, 2987.
(14) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 1185.
(15) Wayland, B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.
(16) Yoshida, E.; Ishizone, T.; Hirao, A.; Nakahama, S.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 3119.
(17) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(18) Kata, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(19) Chen, X.; Gao, B.; Kops, J. *Polymer* **1998**, *39*, 911.
(20) Harris, J. M. *J. M. S. - Rev. Macromol. Chem. Phys.* **1985**, *C25*, 325.
(21) Zalipski, S.; Gilon, C.; Zilkha. *Eur. Polym. J.* **1983**, *19*, 1177.
(22) Dust, J. M.; Fang, Z-H.; Harris, J. M. *Macromolecules* **1990**, *23*, 3742.
(23) Jankova, K.; Kops, J. *J. Appl. Polym. Sci.* **1994**, *54*, 1027.

MA9710186