Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 5251–5257

polymer

www.elsevier.com/locate/polymer

Synthesis of poly(ethylene oxide)-*block*-poly(methyl methacrylate)-*block*-polystyrene triblock copolymers by two-step atom transfer radical polymerization

Xiaoyi Sun[a], Hailiang Zhang[a,b,*], Xiaohua Huang[a], Xiayu Wang[a], Qi-Feng Zhou[c]

[a]*Institute of Polymer Science, Xiangtan University, Xiangtan 411105, Hunan Province, China*
[b]*Key Laboratory for Advanced Materials and Rheological Properties of Ministry of Education, Xiangtan University, Xiangtan 411105, Hunan Province, China*
[c]*Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*

Received 29 December 2004; received in revised form 9 April 2005; accepted 26 April 2005

Abstract

The synthesis of ABC triblock copolymer poly(ethylene oxide)-*block*-poly(methyl methacrylate)-*block*-polystyrene (PEO-*b*-PMMA-*b*-PS) via atom transfer radical polymerization (ATRP) is reported. First, a PEO–Br macroinitiator was synthesized by esterification of PEO with 2-bromoisobutyryl bromide, which was subsequently used in the preparation of halo-terminated poly(ethylene oxide)-*block*-poly(methyl methacrylate) (PEO-*b*-PMMA) diblock copolymers under ATRP conditions. Then PEO-*b*-PMMA-*b*-PS triblock copolymer was synthesized by ATRP of styrene using PEO-*b*-PMMA as a macroinitiator. The structures and molecular characteristics of the PEO-*b*-PMMA-*b*-PS triblock copolymers were studied by FT-IR, GPC and ^{1}H NMR.

Keywords: Atom transfer radical polymerization; Block copolymer; Poly(ethylene oxide)

1. Introduction

Within the past 30 years, experimental procedures have been established for the synthesis of well-defined linear ABC triblock copolymers. These well-defined structures have elicited fascination not only for theoreticians modeling phase behavior [1–3] but also in the physical realm for studying morphological transitions [4–6]. Many unique morphologies and interesting microdomain structures have been observed and reported in such ABC materials [7–12].

In comparison with diblock copolymers, linear ABC triblock copolymers have more independent parameters on their phase behavior, thus displaying a variety of different morphologies [13]. The investigations show that the morphology of the ternary system is influenced not only by the overall molecular weight, the mole fraction of each of the block, and temperature but also by the sequence of the blocks [14,15], chemical modification of one block [8], and the solvent [16].

Traditionally, block copolymers are synthesized by the sequential living polymerizations of different monomers in the same polymerization system [17,18] or by coupling reaction of the preformed functional polymers [19]. To prepare well-defined triblock copolymers with narrow molecular weight distribution, living anionic polymerization is usually used [20–22], but the monomers used in the anionic polymerization are limited. The recent development of controlled/‘living’ radical polymerizations, especially atom transfer radical polymerization (ATRP), has opened a new route to synthesize polymers with well-defined structures [23–32]. ATRP has been well studied because it is not only fit for a variety of monomers [24–26], but also one of most effective methods to prepare precise block copolymers by the sequential polymerization of different monomers [27–30]. Matyjaszewski and coworkers have demonstrated the ability of ATRP to prepare multiblock copolymers [33–35]. ABC triblock copolymers of poly (tBA-*b*-styrene-*b*-methyl acrylate) [34,35] and ABCBA multiblock copolymer of poly(4-vinylpyridine-*b*-MMA-*b*-tBA-*b*-MMA-*b*-4-vinylpyridine) [35] were reported.

---

* Corresponding author. Tel.: +86 732 8293717; fax: +86 732 8293264.
E-mail address: hailiangzhang@xtu.edu.cn (H. Zhang).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.04.058

Wooley et al. [36] prepared an ABC triblock copolymer of poly(tBA-*b*-methyl acrylate-*b*-styrene) using ATRP methods. Pan et al. [37] synthesized poly(LLA-*b*-St-*b*-MMA) triblock copolymers by combination of ATRP and ROP. Recently, Dhamodharan et al. [38] reported the synthesis of ABC triblock copolymers of poly(styrene-*b*-tBA-*b*-MMA) and CBABC multiblock copolymer of poly(MMA-*b*-tBA-*b*-styrene-*b*-tBA-*b*-MMA) by ATRP.

Here, we design a novel ABC triblock copolymer consisting of crystallizable PEO, amorphous PMMA and PS blocks as A, B and C components, respectively. The aim of the research is to investigate the compatibility among three different components and the crystallization behavior of PEO in this ternary system. To our knowledge, such a ternary system has hardly been explored. In this paper we describe the synthesis of PEO-*b*-PMMA-*b*-PS triblock copolymers by the ATRP route. The structures and molecular characteristics of the PEO-*b*-PMMA-*b*-PS triblock copolymers were studied by FT-IR, GPC and ^{1}H NMR. The compatibility and the potential morphological behavior of this ABC ternary system are under our investigation.

2. Experimental

2.1. Materials

2-Bromoisobutyryl bromide (98%, Alfa) was freshly distilled at room temperature under vacuum. Triethylamine (TEA) was refluxed with *p*-toluenesulfonyl chloride and then 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% $NaHCO_3$ and with water again, and finally distilled from CaH_2. PEO ($M_n = 5000$, Alfa) was dried by azeotropic distillation with toluene before use. Traces of residual toluene were removed under vacuum. Chlorobenzene (99%, Acros) was washed with concentrated sulphuric acid to remove thiophenes, followed by washed twice with water, once with 5% sodium carbonate solution, and again with water before dried with anhydrous calcium chloride and distilled. CuCl was prepared from $CuCl_2 \cdot 2H_2O$, then stirred in glacial acetic acid and washed with methanol, and finally dried in vacuum. Methyl methacrylate (MMA) and styrene (St) were passed through a column with activated Al_2O_3 (120–160 mesh) to remove the inhibitor, respectively, stored over CaH_2, and then vacuum distilled before polymerization. All other reagents (*p*-toluenesulfonyl chloride (*p*-TSCl), tetrahydrofuran (THF), 2,2′-bipyridine (bpy), ether, ethanol, toluene) were purchased from commercial sources and used as received without purification.

2.2. Preparation of PEO–Br macroinitiator

A 0.915 g (7.5 mmol) sample of DMAP in 20 ml of dry methylene dichloride was mixed with 0.505 g (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, 2.875 g (12.5 mmol) of 2-bromoisobutyryl bromide in 20 ml of CH_2Cl_2 was added. To the formed yellow dispersion was added 25 g (5 mmol) of PEO 5000 in 100 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 PEO–Br 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 diethyl ether, and dried in vacuum.

2.3. Preparation of PEO-b-PMMA diblock copolymer by ATRP

PEO-*b*-PMMA diblock copolymers were synthesized by solution polymerization in chlorobenzene. In a typical run, a glass tube was filled with 0.25 g (0.05 mmol) of PEO–Br macroinitiator, 0.50 g (5 mmol) of MMA, 0.0050 g (0.05 mmol) of CuCl, 0.0234 g (0.15 mmol) of bpy and 1.125 g of chlorobenzene. After degassed with three freeze-pump-thaw cycles, the tube was sealed under vacuum and then immersed in a thermostated oil bath at 50 °C. At a certain time, the tube was withdrawn and cooled to room temperature. The reaction mixture was diluted with THF. After passing the solution through a column with activated Al_2O_3 to remove the catalyst, and precipitating into ether, PEO-*b*-PMMA diblock copolymer was obtained and dried in a vacuum oven overnight at room temperature.

2.4. Preparation of PEO-b-PMMA-b-PS triblock copolymer by ATRP

PEO-*b*-PMMA-*b*-PS triblock copolymers were synthesized by bulk polymerization. In a typical run, a glass tube was filled with 0.216 g (0.02 mmol) of PEO-*b*-PMMA (a), 0.416 g (4 mmol) of styrene, 0.0020 g (0.02 mmol) of CuCl, 0.0094 g (0.06 mmol) of bpy. After degassed with three freeze-pump-thaw cycles, the tube was sealed under vacuum and then immersed in a thermostated oil bath at 110 °C. At a certain time, the tube was withdrawn and cooled to room temperature. The reaction mixture was diluted with THF. After passing the solution through a column with activated Al_2O_3 to remove the catalyst, and precipitating into ether, PEO-*b*-PMMA-*b*-PS triblock copolymer was obtained and dried in a vacuum oven overnight at room temperature.

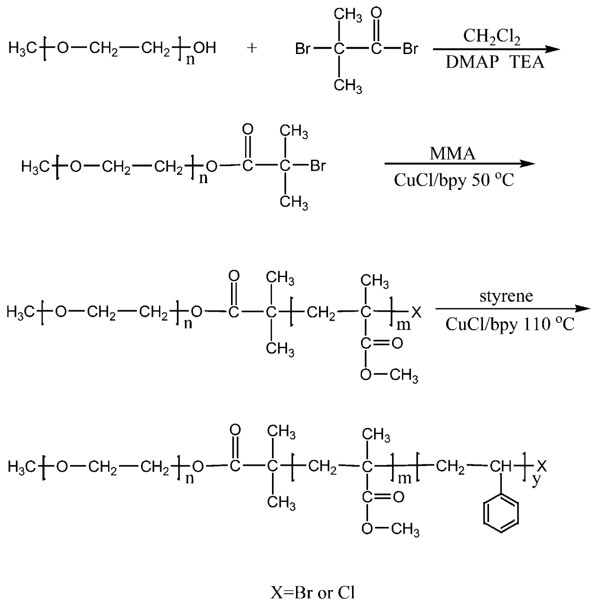
2.5. Characterization

The yield of the polymerization was determined gravimetrically. FT-IR spectra of PEO–Br macroinitiator and related block copolymers were recorded on a Perkin–Elmer Spectrum One Fourier Transform Infrared Spectrometer using the KBr pellet technique. The number average molecular weights M_n and polydispersity M_w/M_n were measured with a Waters 1515 gel permeation chromatograph equipped with three Styragel columns (10^3, 10^4 and 10^5 Å) using THF as an eluent (1.0 ml/min) at 30 °C. The column system was calibrated by a set of monodisperse polystyrene standards. ^{1}H NMR spectra were obtained at 25 °C on a Bruker AV400 NMR spectrometer (400 MHz) using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal reference.

3. Results and discussion

The synthetic procedures of PEO–Br macroinitiator, PEO-*b*-PMMA diblock copolymer and PEO-*b*-PMMA-*b*-PS triblock copolymer are presented in Scheme 1.

First, a bromo telechelic PEO macroinitiator (PEO–Br) was synthesized by reacting PEO with 2-bromoisobutyryl bromide according to the literature [39]. The chemical structure of the resulting PEO–Br macroinitiator was characterized by a 400 MHz ^{1}H NMR spectroscopy (Fig. 1). The complete substitution of the hydroxyl group of PEO in $CDCl_3$ around 2.45 ppm disappeared after the esterification and two new signals have appeared at 4.33 and 1.94 ppm due to the substituted PEO. The peak area ratio of *a*, *b* and *d* is 6:2:3, which also confirmed the complete esterification. Thus the obtained PEO–Br macroinitiator is functionalized with ω-α-bromoisobutyryl group. By comparison of the integral ratio of signals (a) and (c), molecular weight of PEO–Br was estimated to be 5500 g/mol.



Scheme 1. Synthetic route of PEO-*b*-PMMA-*b*-PS triblock copolymer.

The PEO-*b*-PMMA diblock copolymer was then prepared by using PEO–Br as initiator. CuBr/bpy and CuCl/bpy were used, respectively, to catalyze atom transfer radical polymerization of MMA with PEO–Br macroinitiator in this work. The reaction was carried out in chlorobenzene solution at 50 °C. The molar ratio of MMA, PEO–Br, CuBr or CuCl, bpy was 100:1:1:3.

Fig. 2(a) shows a typical GPC curve of the PEO-*b*-PMMA diblock copolymers synthesized by using PEO–Br as an initiator and CuBr/bpy complex as a catalyst under ATRP condition. As observed, the resulting block copolymer displayed bimodal elution peak with a still remaining unreacted PEO–Br part. It implied that the PEO–Br/CuBr initiation/catalyst system gave essentially uncontrolled polymerization, which was attributed to its inefficient initiation.

Matyjaszewski et al. [40,41] reported utilizing halide exchange to improve control of ATRP. They found that the mixed halogen system R-Br/CuCl would give faster initiation, slower propagation, and therefore better control of molecular weight and polydispersity. To avoid the above inefficient initiation phenomenon, we are preferable to carry out the reaction using a PEO–Br/CuCl mixed halogen system.

Fig. 2(b) shows a typical GPC curve of the PEO-*b*-PMMA diblock copolymers synthesized by using PEO–Br as an initiator and CuCl/bpy complex as a catalyst. The resulting copolymer displayed narrow and unimodal elution peak, and moreover there is no tail on the low molecular weight, i.e., no remaining PEO–Br macroinitiator even at low MMA conversion. The results agree with Matyjaszewski et al.'s finding [40,41] and confirm that halide exchange could improve control of ATRP.

As a result of utilizing halide exchange technique [41], the obtained PEO-*b*-PMMA diblock copolymers were end capped with Cl or Br group. The PEO-*b*-PMMA-*b*-PS triblock copolymers were subsequently prepared by ATRP of styrene using PEO-*b*-PMMA-X (X = Cl or Br) as initiator and CuCl/bpy as catalyst. Two PEO-*b*-PMMA diblock copolymers ($M_{n,NMR}$ 10,800 or 8000 g/mol) were used as macroinitiator in this work to initiate ATRP of St. The molar ratio of St, PEO-*b*-PMMA-X, CuCl and bpy was 200:1:1:3. The reaction condition was similar to the preparation of diblock copolymer, except the reaction was carried out in bulk and the temperature was raised to 110 °C.

Fig. 3 reveals the representative FT-IR spectra of PEO, PEO–Br and the related di- and triblock copolymers. The ether stretch occurs at 1109 cm^{-1} for the copolymers and PEO precursor. After acetylation reaction, a carbonyl stretch occurs at 1734 cm^{-1} correspondingly in the spectrum of PEO–Br macroinitiator (Fig. 3(b)). The spectra of the di- and triblock copolymers (Fig. 3(c) and (d)) also exhibit 1734 cm^{-1} absorption peak, assigned to the

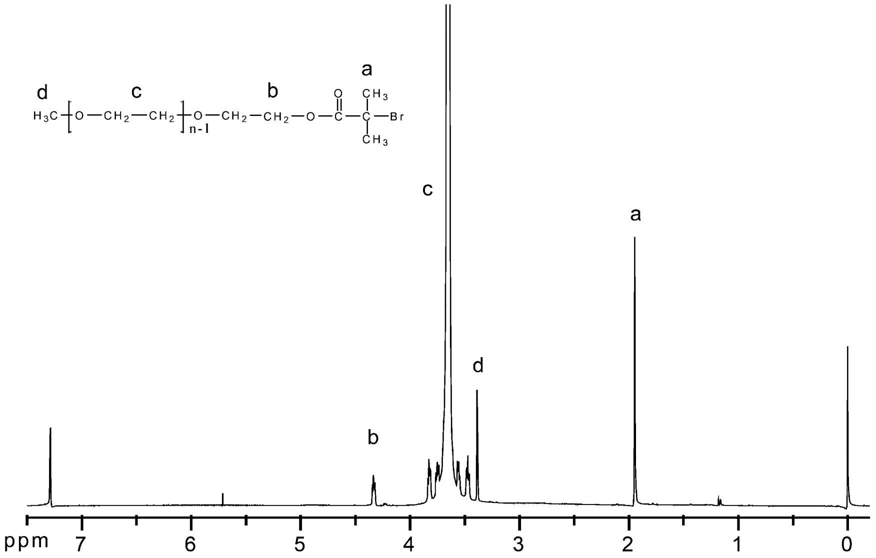


Fig. 1. ^1H NMR spectrum of PEO–Br macroinitiator.

carbonyl absorption of PMMA block, which is much stronger than that of PEO–Br macroinitiator. All of the characteristic absorptions for PEO and PMMA segments appear in Fig. 3(c) and (d). A new absorption band between 3100 and 3000 cm^{-1} and two new peaks at 1602 and 700 cm^{-1} in Fig. 3(d), illustrate the presence of PS block in triblock copolymer. The intensity of peak at 1493 and 1453 cm^{-1} increased also owe to the PS block. The bands at 963 and 843 cm^{-1} are the characteristic of the crystalline phase of PEO [42]. The two peaks appear in the spectra of the copolymers, and their intensities are associated with the content of PEO block and its crystallinity.

GPC analysis was performed to determine the molecular weights and molecular weight distributions of the triblock copolymers. GPC chromatographs of all triblock copolymers showed unimodal peaks. Fig. 4 presents the GPC curves of PEO-*b*-PMMA (a) and its related triblock copolymers (1, 2, 3, 4). After the chain extension reaction, the molecular weight increased from 15,100 to 31,100 g/mol. The polydispersity of the copolymer is a little higher than the macroinitiator, but is still lower than the theoretical value of 1.5 for the controlled/'living' free radical polymerization. This is also the case for other four triblock copolymers (5, 6, 7, 8).

The chemical structure of PEO-*b*-PMMA diblock copolymer and PEO-*b*-PMMA-*b*-PS triblock copolymer was confirmed by ^1H NMR spectroscopy, which was also used to determine the composition of the copolymers. Fig. 5(a) shows the ^1H NMR spectrum of a PEO-*b*-PMMA diblock copolymer ($M_{n,GPC}=15{,}100$ g/mol, $M_w/M_n=1.10$). The signals (e, f and g) at 0.8–1.2, 1.7–2.0, 3.60 ppm are ascribed to the repeated MMA unit. Characteristic resonance of –CH_2–CH_2– bond (signal (c)) in PEO units is also present in the ^1H NMR spectrum of the diblock copolymer.

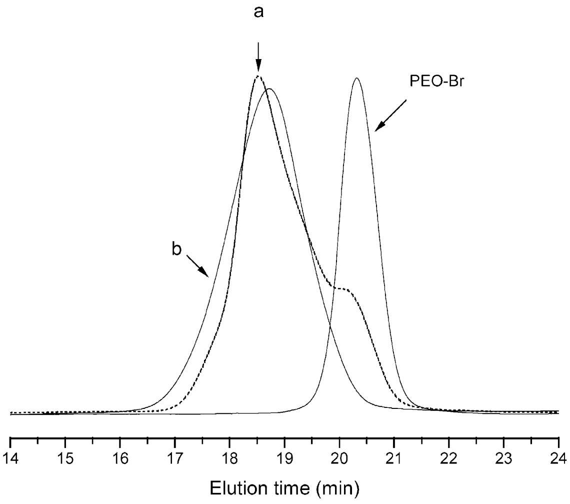


Fig. 2. GPC traces of PEO–Br and PEO-*b*-PMMA diblock copolymers ((a) catalyzed by CuBr/bpy; (b) catalyzed by CuCl/bpy).

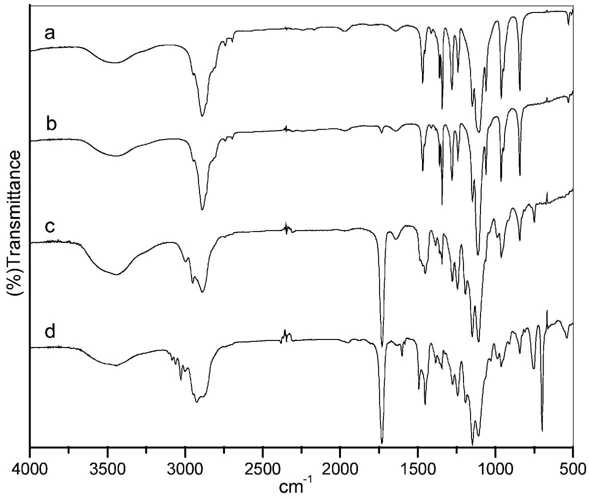


Fig. 3. FT-IR spectra of (a) PEO, (b) PEO–Br, (c) PEO-*b*-PMMA-a and (d) PEO-*b*-PMMA-*b*-PS-3.

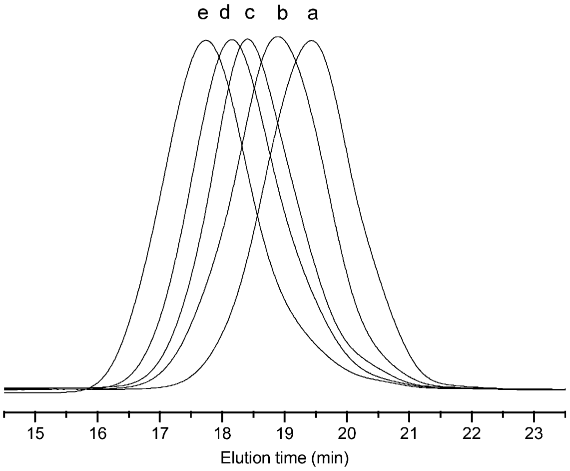


Fig. 4. GPC traces of (a) PEO-*b*-PMMA-a, (b) PEO-*b*-PMMA-*b*-PS-1, (c) PEO-*b*-PMMA-*b*-PS-2, (d) PEO-*b*-PMMA-*b*-PS-3 and (e) PEO-*b*-PMMA-*b*-PS-4.

These data illustrate the presence of both PEO and MMA blocks in the polymer chain. The composition of the diblock copolymers was determined by means of ^{1}H NMR spectroscopy from the integral ratio of the signals originated from the PMMA block at 0.85 ppm, 1.02 ppm, 1.21 ppm (signal (e), 3H, CH_3) and from the PEO–Br and MMA region (3.4–3.8 ppm) (signal (c), 4H, $-CH_2-CH_2-$, signal (g), 3H, $O-CH_3$) according to the following equation:

$$f_{\mathrm{MMA}} = \frac{(I_e \times 100/3)}{[I_e \times 100/3 + (I_{c+g} - I_e) \times 44/4]}$$

Where I_e and I_{c+g} are the integral of the signals originated from the PMMA block at 0.8–1.2 ppm and the PMMA and PEO block at 3.4–3.8 ppm; 100 and 44 are the molar masses of MMA and $-CH_2-CH_2-O$ repeat unit in PEO segment respectively. Calculated from f_{MMA} and M_n estimated by NMR analysis of PEO–Br, we can obtain the number average molecular weights of the corresponding PEO-*b*-PMMA diblock copolymers, which are shown in Table 1.

The typical ^{1}H NMR spectrum of PEO-*b*-PMMA-*b*-PS triblock copolymer was given in Fig. 5(b). Two new signals have appeared at 1.24–1.63 and 6.29–7.22 ppm, respectively due to the characteristic resonance of $-CH_2-$ bond (signal (i)) and benzene ring (signal (h)) in PS units. The ^{1}H NMR spectrum also provides strong evidence for the presence of both PEO and PMMA segments in the polymer chain.

The absolute molecular weight of PEO-*b*-PMMA-*b*-PS triblock copolymer can be calculated by means of ^{1}H NMR spectroscopy from the integral ratio of the signals originated from the PEO, PMMA and PS blocks according to the following equation:

$$f_{\mathrm{St}} = \frac{(I_h \times 104/5)}{[I_h \times 104/5 + (I_e \times 100/3)/f_{\mathrm{MMA}}]}$$

Where I_e and I_h are the integral of the signals originated from the PMMA block at 0.8–1.2 ppm and the PS block at 6.29–7.22 ppm, respectively; 104 and 100 are the molar masses of St and MMA, and f_{MMA} is the mass fraction of MMA in the corresponding PEO-*b*-PMMA diblock copolymer. Calculated from f_{St} and M_n estimated by NMR analysis of the related PEO-*b*-PMMA diblock copolymer, we can obtain the number average molecular weight of the corresponding PEO-*b*-PMMA-*b*-PS triblock copolymers.

Table 1 presents the molecular weights, molecular weight distributions, and compositions (block lengths and PEO contents in weight) of all triblock copolymers synthesized in this work. All copolymers showed relatively narrow molecular weight distributions. Two series of triblock copolymers were synthesized using PEO-*b*-PMMA of M_n 10,800 or 8000. The PS block length ranges

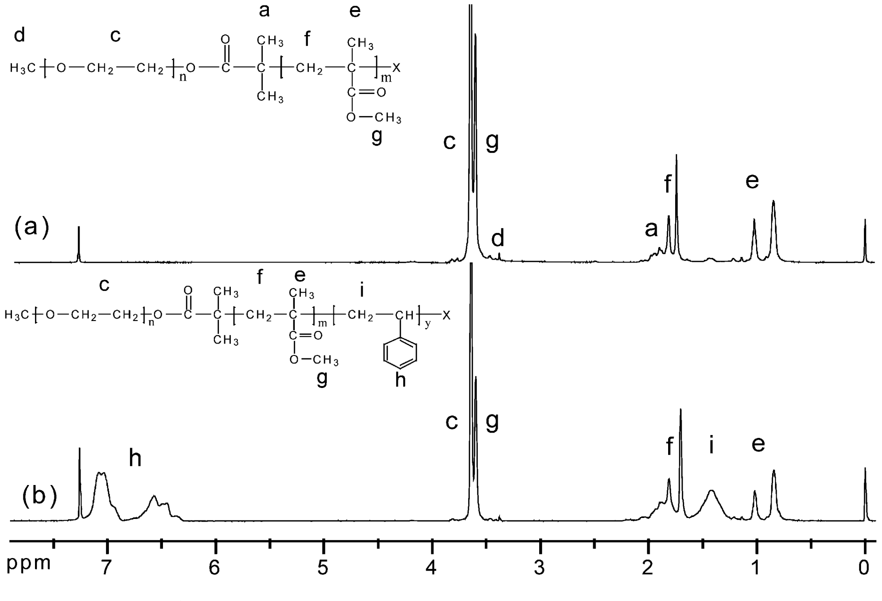


Fig. 5. ^{1}H NMR spectra of (a) PEO-*b*-PMMA and (b) PEO-*b*-PMMA-*b*-PS.

Table 1
GPC and NMR data of PEO-*b*-PMMA-*b*-PS triblock copolymers and its precursors

Samples	Macro-initiator	Yield[a] (%)	$M_{n,GPC}$[b] ($\times10^{-4}$)	M_w/M_n (GPC)	$M_{n,NMR}$[c] ($\times10^{-4}$)	f_{MMA}[d] (NMR)	f_{St}[d] (NMR)	f_{PEO}[d] (NMR)
PEO			0.89	1.02	0.53			
PEO–Br			0.98	1.02	0.55			
PEO-*b*-PMMA-a		67.7	1.51	1.10	1.08	49		51
PEO-*b*-PMMA-*b*-PS-1	a	40.1	1.81	1.13	1.34	40	19	41
PEO-*b*-PMMA-*b*-PS-2	a	44.5	2.20	1.10	1.44	37	25	38
PEO-*b*-PMMA-*b*-PS-3	a	53.8	2.48	1.13	1.77	30	39	31
PEO-*b*-PMMA-*b*-PS-4	a	65.7	3.11	1.17	2.12	25	49	26
PEO-*b*-PMMA-b		49.5	1.17	1.09	0.80	31		69
PEO-*b*-PMMA-*b*-PS-5	b	28.0	1.21	1.11	0.85	29	6	65
PEO-*b*-PMMA-*b*-PS-6	b	40.2	1.59	1.12	1.21	21	34	45
PEO-*b*-PMMA-*b*-PS-7	b	54.5	2.56	1.17	1.60	16	50	34
PEO-*b*-PMMA-*b*-PS-8	b	63.2	2.97	1.19	1.86	13	57	30

[a] Yield was calculated according to equation: Yield(%) $= W_p/(W_i + W_m) \times 100\%$, where W_p, W_i and W_m are the weight of the block copolymer produced, the initial weights of the related macroinitiator and monomer, respectively.

[b] The measured M_n of the PEO-*b*-PMMA-*b*-PS triblock copolymer by GPC.

[c] M_n estimated by NMR analysis of PEO-*b*-PMMA-*b*-PS.

[d] Weight fraction of PMMA, PS and PEO in the copolymer determined by ^{1}H NMR spectroscopy, respectively.

from a few hundred to more than 10,000, corresponding to 6–57 wt% in the copolymers. It must be mentioned that M_n's measured by GPC of the copolymers are much higher than the actual one, which is ascribed to the difference in hydrodynamic properties of copolymer and PS, the later was used as the standard in GPC measurements.

4. Conclusions

ABC triblock copolymers PEO-*b*-PMMA-*b*-PS with different molecular weights were successfully synthesized by atom transfer radical polymerization method in two steps. FT-IR, ^{1}H NMR and GPC measurements confirmed the block architecture of the copolymers. Two series of triblock copolymers with PMMA block lengths of M_n 5300 or 2500 were synthesized. The PS block length ranges from a few hundred to more than 10,000 in the triblock copolymers, corresponding to 6–57% in weight. All of the triblock copolymers synthesized in this work have relatively narrow molecular weight distributions and unimodal peaks in the GPC chromatographs.

Acknowledgements

The authors thank the National Nature Science Foundation of China (20374042), the Specialized Research Fund for the Doctoral Program of Higher Education (20040530002) and Scientific Research Fund of Hunan Provincial Education Department (02B007) for financial support of this work.

References

[1] Zheng W, Wang ZG. Macromolecules 1995;28:7215.
[2] Abetz V, Stadler R, Leibler L. Polym Bull 1996;37:135.
[3] Phan S, Fredrickson GH. Macromolecules 1998;31:59.
[4] Breiner U, Krappe U, Stadler R. Macromol Rapid Commun 1996;17:567.
[5] Elbs H, Fukunaga K, Stadler R, Sauer G, Magerle R, Krausch G. Macromolecules 1999;32:1204.
[6] Shefelbine TA, Vigild ME, Matsen MW, Hajduk DA, Hillmyer MA, Cussler EL, et al. J Am Chem Soc 1999;121:8457.
[7] Auschra C, Stadler R. Macromolecules 1993;26:2171.
[8] Breiner U, Krappe U, Thomas EL, Stadler R. Macromolecules 1998;31:135.
[9] Hueckstaedt H, Goldacker T, Goepfert A, Abetz V. Macromolecules 2000;33:3757.
[10] Brinkmann S, Stadler R, Thomas EL. Macromolecules 1998;31:6566.
[11] Balsamo V, Collins S, Hamley IW. Polymer 2002;43:4207.
[12] Krappe U, Stadler R, Voigt-Martin I. Macromolecules 1995;28:4558.
[13] Bates FS, Fredrickson GH. Phys Today 1999;52:32.
[14] Mogi Y, Nomura M, Kotsuji H, Ohnishi K, Matsushita Y, Noda I. Macromolecules 1994;27:6755.
[15] Hückstädt H, Göpfert A, Abetz V. Polymer 2000;41:9089.
[16] Matsushita Y, Yamada K, Hattori T, Fujimoto T, Sawada Y, Nasagawa M, et al. Macromolecules 1983;16:10.
[17] He T, Zou YF, Pan CY. J Polym Sci, Part A: Polym Chem 2002;40:3367.
[18] Tian D, Dubois Ph, Jerome R. Macromolecules 1997;30:1947.
[19] Fradet A. In: Aggarwal SL, Russo S, editors. Comprehensive polymer science. London: Pergamon; 1996. p. 133 (second supp.).
[20] Auschra C, Stadler R. Polym Bull 1993;30:257.
[21] Lescanec RL, Fetters FJ, Thomas EL. Macromolecules 1998;31:1680.
[22] Goldacker T, Abetz V, Stadler R, Erukhimorich I, Leibler L. Nature 1999;398:137.
[23] Patten TE, Xia J, Abernathy T, Matyjaszewski K. Science 1996;272:866.
[24] Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614.
[25] Wang JS, Matyjaszewski K. Macromolecules 1995;28:7901.
[26] Patten TE, Matyjaszewski K. Adv Mater 1998;10:901.
[27] Kotani Y, Kamigaito M, Sawamoto M. Macromolecules 2000;33:2819.

[28] Matyjaszewski K, Shipp DA, McMurtry GP, Gaynor SG, Pakula T. J Polym Sci, Part A: Polym Chem 2000;38:2023.

[29] Kagawa Y, Minami H, Okubo M, Zhou J. Polymer 2005;46:1045.

[30] Kurjata J, Chojnowski J, Yeoh CT, Rossi NAA, Holder SJ. Polymer 2004;45:6111.

[31] Huang CF, Kuo SW, Lee HF, Chang FC. Polymer 2005;46:1561.

[32] Burguière C, Chassenieux C, Charleux B. Polymer 2003;44:509.

[33] Matyjaszewski K, Acar MH, Beers KL, Coca S, Davis KA, Gaynor SG, et al. Polym Prepr (Am Chem Soc, Div Polym Chem) 1999;40:966.

[34] Davis KA, Matyjaszewski K. Macromolecules 2000;33:4039.

[35] Davis KA, Matyjaszewski K. Macromolecules 2001;34:2101.

[36] Ma Q, Wooley KL. J Polym Sci, Part A: Polym Chem 2000;38:4805.

[37] Tao L, Luan B, Pan CY. Polymer 2003;44:1013.

[38] Ramakrishnan A, Dhamodharan R. Macromolecules 2003;36:1039.

[39] Jankova K, Chen XY, Kops J, Batsberg W. Macromolecules 1998;31:538.

[40] Matyjaszewski K, Wang JL, Grimaud T, Shipp DA. Macromolecules 1998;31:1527.

[41] Matyjaszewski K, Shipp DA, Wang JL, Grimaud T, Patten TE. Macromolecules 1998;31:6836.

[42] Bailey FE, Koleske JV. Poly(ethylene oxide). New York: Academic Press; 1976.