

Preparation of Amphiphilic Ternary Block Copolymers with PEO as the Middle Block and the Effect of PEO Position on the Glass Transition Temperature (T_g) of Copolymers

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ABSTRACT: The copolymer of polystyrene-*block*-poly(ethylene oxide)-*block*-poly (*tert*-butyl acrylate) (PS-*b*-PEO-*b*-PtBA) was prepared, the synthesis process involved ring-opening polymerization (ROP), nitroxide-mediated polymerization (NMP), and atom transfer radical polymerization (ATRP), and 4-hydroxyl-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTEMPO) was used as parent compound. The PEO precursors with α -hydroxyl- ω -2,2,6,6-tetramethylpiperidinyl-1-oxy end groups (TEMPO-PEO-OH) were first obtained by ROP of EO using HTEMPO and diphenylmethylpotassium (DPMK) as the coinitiator. The TEMPO at one end of PEO chain mediated the polymerization of St using benzoyl peroxide as initiator. The resultant PS-*b*-PEO-OH reacted further with 2-bromoisobutryl bromide and then initiated the polymerization of *t*BA in the presence of CuBr and PMDETA by ATRP. The ternary block copolymers PS-*b*-PEO-*b*-PtBA and intermediates were characterized by gel permeation chromatography, Fourier transform infrared, and nuclear magnetic resonance spectroscopy in detail. Differential scanning calorimetry measurements confirmed that the PS-*b*-PEO-*b*-PtBA with PEO as middle block can weaken the interaction between PS and PtBA blocks, the glass transition temperature (T_g) for two blocks were approximate to their corresponding homopolymers comparing with the PEO-*b*-PS-*b*-PtBA with PEO as the first block. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 2624–2631, 2008

Keywords: atom transfer radical polymerization (ATRP); block copolymers; nitroxide-mediated polymerization; poly(ethylene oxide); ring-opening polymerization

INTRODUCTION

In the past decades, several controlled polymerization methods including reverse addition-fragmentation chain transfer (RAFT) polymerization,¹ nitroxide-mediated polymerization (NMP),² and

atom transfer radical polymerization (ATRP)³ have been developed, which provide some convenient routes for polymer scientists to synthesize copolymers with well-defined structures, such as block,⁴ graft,⁵ star-shaped,⁶ hyperbranched,⁷ and macrocyclic⁸ copolymers.

Among the copolymers with complicated structures, ternary block copolymers occupied an important position, because their special properties resulted from more independent parameters influencing the phase behavior⁹ and

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morphologies, so that the special attention is paid on them because of their potential applications in many fields, such as self-assembly,¹⁰ biomaterials,¹¹ compatibilizers for polymer blends,¹² and so on.

As it is well known, poly(ethylene oxide) (PEO) is one of the most widely used segment in the preparation of ABC amphiphilic triblock copolymers,^{13–17} since it shows some outstanding properties as biocompatibility, crystallizability, and well dissolubility in water and most organic solvents. Traditionally, most of ternary block copolymers containing the PEO segment were synthesized by a sequential two-step approach involved in two polymerization methods, such as sequential two steps anionic polymerization and ATRP,¹⁸ anionic polymerization and sequential two steps ATRP,¹⁹ and anionic polymerization and sequential two steps RAFT.²⁰ Furthermore, in the most part of the existing linear ABC triblock copolymers,^{21,22} the PEO segment was always located in the end block, and only a few articles reported the synthesis of ternary block copolymers with PEO as the middle block,^{23–25} but in these cases at least two sequential anionic polymerizations were demanded, so only limited monomers could be used. In the sequential anionic polymerization of a set of monomers (A, B, C) it should meet the order of the pK_a (A) > pK_a (B) > pK_a (C),²⁴ (pK_a is the corresponding conjugate acids of the monomers), but there were few examples which satisfied this condition. In the preparation of ABC triblock copolymers, it was found that the variation of arrangement sequence of ABC triblock copolymers may exert the influence on the physicochemical properties and self-assembly morphologies, so it aroused our interests to explore the causes.

In this article, by means of small molecule 4-hydroxyl-2,2,6,6-tetramethylpiperidiny-1-oxyl (HTEMPO), the TEMPO-PEO-OH with different functional end groups was synthesized first, and then it was used as precursors to prepare ternary block copolymers with PEO as the middle block. Our work provided a facile route to prepare the ABC triblock copolymers with PEO as middle block. Preliminary investigation confirmed that PS-*b*-PEO-*b*-PtBA with PEO as middle block could weaken the interaction between PS and PtBA blocks, the T_g for them were approximate to the corresponding homopolymers comparing with the PEO-*b*-PS-*b*-PtBA with PEO as the first block.

EXPERIMENTAL

Materials

HTEMPO was synthesized according to the literature,²⁶ and the purity was 98.7% determined by gas chromatographic-mass spectrometric (GC-MS) analysis. Ethylene oxide (EO) was purchased from Sinopharm Chemical Reagent (SCR), dried by calcium hydride for 1 week and then distilled, stored at -20 °C before use. Benzoyl peroxide (BPO; SCR) was recrystallized from ethanol. Tetrahydrofuran (THF, SCR, 99%) and pyridine (SCR, 99.5%) were refluxed over sodium wire and distilled. Dimethyl sulfoxide (DMSO, SCR, 98%), *N,N*-dimethylformamide (DMF, SCR, 98%), and *tert*-butyl acrylate (*t*BA, Aldrich, 98%) were dried over CaH_2 and distilled under reduced pressure. Styrene (St, SCR, >99.5%) was washed with 10% NaOH aqueous solution and water successively, then dried over anhydrous $MgSO_4$, further dried over CaH_2 and distilled under reduced pressure. CuBr (98%, Acros) was purified by stirring overnight in acetic acid and filtered, then washed with ethanol and diethyl ether successively, and finally dried under vacuum. 2-Bromoisobutyryl bromide (98%) and *N,N',N'',N''',N''''*-pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Aldrich and used as received. Other reagents (SCR) were purified by common procedures. Diphenylmethyl potassium (DPMK) was prepared as in the literature,²⁷ and the concentration was 0.65 M.

Measurement

The number average molecular weight (M_n) and polydispersity index (M_w/M_n) of polymers were measured by gel permeation chromatography (GPC). For the TEMPO-PEO, GPC was performed in 0.1 M $NaNO_3$ aqueous solution at 40 °C with an elution rate of 0.5 mL/min on an Agilent 1100 assembled by a G1310A pump, a G1362A refractive index detector, and a G1315A diode-array detector, and PEO standard were used for calibration. GPC traces of the other copolymers were performed in tetrahydrofuran (THF) at 35 °C with an elution rate of 1.0 mL/min on an Agilent 1100 assembled by a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector, and polystyrene standards were used for calibration. Gas chromatographic-mass spectrometric (GC/MS) analysis for HTEMPO was carried out by using

a Finnigan Voyager system with mass selective detection operating in electronic ionization (EI). A silica capillary column was 30 m \times 0.25 mm (I.D.) with 0.25- μ m film thickness (DB-5 Restek). The GC/MS parameters were as follows: ion source temperature 200 °C, carrier gas helium, column flow 1 mL/min; temperature program from 100 to 200 °C at 15 °C/min, splitless injection at 250 °C; ionization was achieved at 70 eV. ^1H NMR spectra were obtained by a DMX 500 MHz spectrometer using tetramethylsilane (TMS) as the internal standard and CDCl_3 , CD_3OD as the solvent. Fourier transform infrared (FTIR) spectra were recorded on Magna 550 FTIR instrument, the polymer samples were dissolved in dry dichloromethane or methanol and then cast film onto a NaCl tablet. The differential scanning calorimetry (DSC) analysis was carried out with a PerkinElmer Pyris 1 DSC instrument under a nitrogen flow (10 mL/min), all the samples were first heated from -70 to 140 °C at 10 °C/min, then cooled to -70 °C at 10 °C/min, and scanned two times to erase the thermal history. An ultrafiltration separator was purchased from the Shanghai Institute of Nuclear Research (Chinese Academy of Sciences), the cutoff molecular weight of the poly(ether sulfone) film was 50,000 (calibrated with a global protein).

Synthesis of Prepolymers TEMPO-PEO-OH

In a reaction kettle, 1.52 g HTEMPO (8.8 mmol) dried by azeotropic distillation with dry toluene was dissolved in 40 mL THF and 40 mL DMSO under dry nitrogen atmosphere, and the required amount of DPMK solution was added. Afterward, 40 mL EO (35.2 g, 0.8 mol) was introduced, and the vessel was heated to 60 °C under stirring for 72 h. The reaction was terminated by addition of a few drops of acidified methanol. The crude product was purified by dissolution/precipitation thrice with chloroform/ethyl ether, and the pink powder was obtained.

^1H NMR (CD_3OD , in the presence of calculated amount of ammonium formate and palladium-on-carbon, δ , ppm): 1.15–1.18 (s, 12H, $-\text{CH}_3$ of TEMPO group), 1.45 and 1.95 (d, 4H, $-\text{CH}_2-$ of TEMPO group), 3.36–3.75 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$ of PEO chain).

Synthesis of Diblock Copolymers PS-*b*-PEO-OH

An ampoule containing solution of styrene (14 mL, 0.10 mol), refined DMF 10 mL, BPO (0.186 g,

0.77 mmol), and TEMPO-PEO (A) (3 g, 1 mmol, containing 1 mmol TEMPO groups) was degassed by three freeze-pump-thaw cycles and sealed. The vessel was immersed in preheated oil bath at 90 °C for 3 h and then heated to 120 °C under nitrogen atmosphere. After a given time interval, the resulting polymer was precipitated in cold petroleum ether (30 – 60 °C), filtered and dried under vacuum.

^1H NMR (CDCl_3 , δ , ppm): 0.80–2.20 (m, $-\text{CH}_3$, $-\text{CH}_2-$ of TEMPO group and $-\text{CH}_2\text{CH}-$ of PS main chain), 3.36–3.80 (m, $-\text{CH}_2\text{CH}_2\text{O}-$ of PEO), 6.30–7.20 (m, the phenyl of PS main chain), 7.40, 7.50, 7.90 (the residual phenyl group of the initiator BPO).

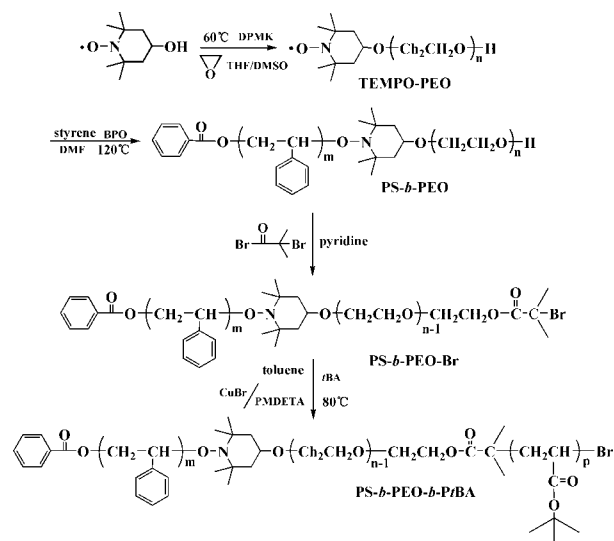
Synthesis of Macroinitiator PS-*b*-PEO-Br

The diblock copolymers PS-*b*-PEO (A) 12 g (0.8 mmol) dried by azeotropic distillation with dry toluene was dissolved in 60 mL of anhydrous pyridine, 1 mL (8 mmol) of 2-bromoisobutyryl bromide was added dropwise at 0 °C. The mixture was stirred for 3 h at 0 °C, followed by stirring at room temperature for 24 h. Pyridine was removed by azeotropic distillation with dry toluene. The crude product dissolved in ethanol was purified by an ultrafiltration membrane to remove low-molecular weight impurities. Then ethanol was removed from the product by distillation, the reddish remains of PS-*b*-PEO-Br were dried in vacuum at 50 °C.

^1H NMR (CDCl_3 , δ , ppm): 0.80–2.20 (m, $-\text{CH}_3$, $-\text{CH}_2-$ of TEMPO group and $-\text{CH}_2\text{CH}-$ of PS main chain), 1.94 (s, Br- $\text{C}(\text{CH}_3)_2-\text{COO}-\text{CH}_2-$), 3.36–3.80 (m, $-\text{CH}_2\text{CH}_2\text{O}-$ of PEO), 4.33 (m, Br- $\text{C}(\text{CH}_3)_2-\text{COO}-\text{CH}_2-$), 6.30–7.20 (m, the phenyl of PS main chain), 7.40, 7.50, 7.90 (the residual phenyl group of the initiator BPO).

Synthesis of Ternary Block Copolymers PS-*b*-PEO-*b*-PtBA

In a typical ATRP process, 3 g (0.2 mmol) macroinitiator PS-*b*-PEO-Br (A) was dissolved in 10-mL anhydrous toluene in a 100-mL ampoule. Then 5-mL of *t*BA, 28.8 mg (0.2 mmol) of CuBr, and 0.04 mL (0.2 mmol) of PMDETA were added into the solution. The system was degassed by three freeze-pump-thaw cycles, and then the ampoule was sealed and immersed in an oil bath at 80 °C. After a certain time interval, the ampoule was dipped into liquid nitrogen to stop



Scheme 1. The synthesis process of PS-*b*-PEO-*b*-PtBA triblock copolymers.

the polymerization. The solution was diluted with THF and passed through the neutral alumina column to remove the copper salt. The products were purified by dissolution/precipitation twice with THF/petroleum ether and dried at 50 °C in vacuum for 24 h.

^1H NMR(CDCl_3 , δ , ppm): 0.80–2.20 (m, $-\text{CH}_3$, $-\text{CH}_2-$ of TEMPO group, $-\text{CH}_2\text{CH}-$ and $(\text{CH}_3)_3\text{COOC}-$ of *t*BA and $-\text{CH}_2\text{CH}-$ of PS main chain), 1.94 (s, $\text{Br}-\text{C}(\text{CH}_3)_2-\text{COO}-\text{CH}_2-$), 2.22 (s, 1H, $-\text{CH}_2\text{CH}-$ of PtBA), 3.36–3.80 (m, $-\text{CH}_2\text{CH}_2\text{O}-$ of PEO), 4.33 (m, $\text{Br}-\text{C}(\text{CH}_3)_2-\text{COO}-\text{CH}_2-$), 6.30–7.20 (m, the phenyl of PS main chain), 7.40, 7.50, 7.90 (the residual phenyl group of the initiator BPO).

Synthesis of Ternary Block Copolymers PEO-*b*-PS-*b*-PtBA

The used PEO-*b*-PS-*b*-PtBA sample was prepared by combination of “Click Chemistry” with atom transfer nitroxide radical chemistry, and the molecular weight for each block is PEO₃₁₀₀-*b*-PS₇₃₀₀-*b*-PtBA₅₃₀₀.²⁸

RESULTS AND DISCUSSION

In this presentation, a stable nitroxide radical TEMPO group was introduced to one end of PEO chain which was performed by anionic

polymerization using HTEMPO as parent compound, the resultant TEMPO-PEO-OH prepolymer served as macromolecular initiator to mediate the polymerization of St by NMP and the polymerization of *t*BA by ATRP. The whole process is outlined in Scheme 1.

Synthesis of Prepolymers TEMPO-PEO-OH

To achieve the PEO with TEMPO and hydroxyl groups at both ends, a small molecule HTEMPO mixed with DPMK was used as coinitiator to polymerize the EO through ROP. Two approaches had been tried to perform this polymerization. First, the $\text{TEMPO}^-\text{Na}^+$ was prepared by the reaction of HTEMPO with metal sodium under nitrogen atmosphere,^{29,30} but the reaction efficiency was low. To overcome this disadvantage, DPMK was used as an activating agent to partially transform the hydroxyl group of HTEMPO into an alcoholate to initiate the ROP of EO,³¹ and a mixed solvent of DMSO/THF (v/v: 1:1) was used to substitute the pure THF for increasing the solubility of alcoholates. Figure 1 shows the GPC traces of TEMPO-PEO prepared by HTEMPO and DPMK system, the resulting polymers showed a unimodal trace with a narrow polydispersity index of less than 1.15, and all the polymerization data are listed in Table 1. Figure 2(A) shows a typical ^1H NMR spectrum of prepolymer TEMPO-PEO, which was measured in the presence of calculated amount of ammonium formate and palladium-on-carbon because of the paramagnetism of nitroxide radicals. The resonances for the methylene protons

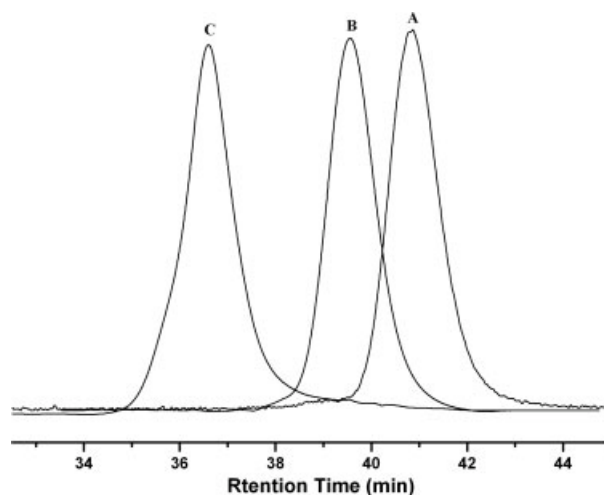


Figure 1. GPC traces of prepolymer TEMPO-PEO (A: $M_n = 3.1 \times 10^3$; B: $M_n = 3.5 \times 10^3$; C: $M_n = 5.6 \times 10^3$).

Table 1. Polymerization Data of TEMPO-PEO Prepolymers and Diblock Copolymers PS-*b*-PEO

Example	TEMPO-PEO		PS- <i>b</i> -PEO		PS- <i>b</i> -PEO-Br
	$M_n (\times 10^3)^a$	M_w/M_n^a	$M_n (\times 10^3)^b$	M_w/M_n^b	E.F. ^b
A	3.1	1.07	15.2	1.27	99.1
B	3.5	1.10	7.4	1.09	98.7
C	5.6	1.13	18.3	1.24	99.0

^a Determined by GPC calibrated against PEO standards.

^b Determined by ¹H NMR.

of PEO repeating units were observed in the region 3.36–3.80 ppm, the signals at 1.15 and 1.18 ppm were attributed to the methyl of HTEMPO, and the resonances for the methylene protons of HTEMPO were at 1.45 and 1.95 ppm.

Synthesis of Diblock Copolymers PS-*b*-PEO-OH

The NMP of styrene was conducted using BPO as initiator in the presence of TEMPO-PEO-OH at 120 °C. Figure 3 shows the GPC traces of crude and purified products of diblock copolymers PS-*b*-PEO, respectively, and a small peak at long retention time (low-molecular weight region) before purification can be observed. It may be arisen by the lower diffusing rate of TEMPO-PEO-OH than the small molecule TEMPO leading to the decrease of its trapping efficiency for propagating PS radicals. Thus small quantity of PS radicals were not captured, the PS homopolymer and some remained TEMPO-PEO-OH were observed (Fig. 3, dotted curve). Many other groups also reported this

phenomenon.²⁹ The PS homopolymer could be removed from the products by washing with cold cyclohexane, and TEMPO-PEO-OH could be removed by ultrafiltration separation. The disappearance of small peak in Figure 3 (dash line) supported the successful purification.

Figure 2(B) shows the ¹H NMR spectrum of diblock copolymer PS-*b*-PEO. Besides, the resonances for the methylene protons of PEO repeating units in the region 3.36–3.80 ppm, the resonances of the phenyl groups at 6.30–7.20 ppm for PS, and separate resonances at 7.40, 7.50, 7.90 ppm for the residual phenyl group from the initiator BPO were observed, which was attached on the ends of PS chains and quite different from chemical shift of phenyl rings on PS chains. As it is well known, the PS-*b*-PEO block copolymers may form the micelle in THF,³² so the molecular weight of PS-*b*-PEO derived from GPC might be inaccurate. To obtain the reliable molecular weight of PS-*b*-PEO, the M_n of diblock copolymers was calculated by the following eq 1 from ¹H NMR:

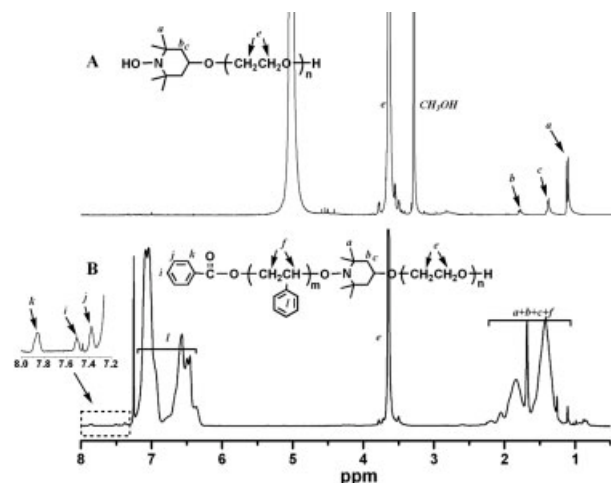


Figure 2. ¹H NMR spectrum of (A) TEMPO-PEO (CD₃OD) and (B) PS-*b*-PEO (CDCl₃).

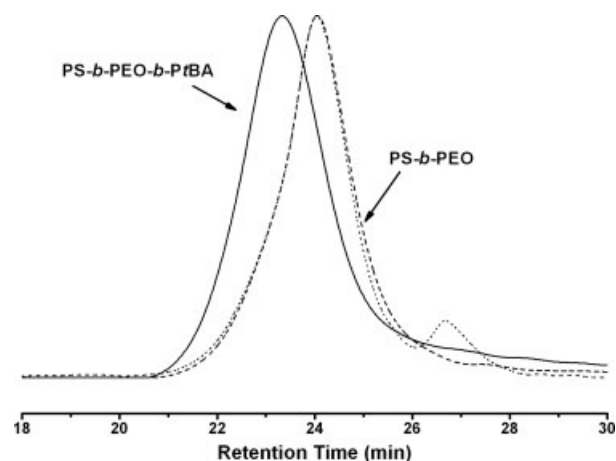


Figure 3. The GPC traces of PS-*b*-PEO and PS-*b*-PEO-*b*-PtBA (dot and dash line represent the PS-*b*-PEO before and after purification, respectively).

$$M_{n\text{PS-}b\text{-PEO}} = \frac{4A_I}{5A_e} \times \frac{M_{n(\text{PEO})}}{44} \times 104 + M_{n(\text{PEO})} \quad (1)$$

where A_I and A_e represent the integral area of phenyl protons on the PS main chains and all protons of the PEO main chain, respectively. $M_{n(\text{PEO})}$ is the M_n of the TEMPO-PEO, 44 and 104 is the molecular weight (M_w) of EO and St, respectively. All the data are listed in Table 1.

Esterification of PS-*b*-PEO with 2-Bromoisobutyryl Bromide

To guarantee high efficiency of the reaction of the hydroxyl at the end of diblock copolymers PS-*b*-PEO with 2-bromoisobutyryl bromide, a 10-fold molar excess of 2-bromoisobutyryl bromide was used. The resulting products were characterized by ^1H NMR as shown in Figure 4(A). The appearance of signal at 4.33 ppm (h) for the methylene closed to the ester bond gave an evidence that the reaction took place successfully. The reaction efficiency can be calculated by eq 2, and the data are listed in Table 1.

$$E.F. = \frac{A_h}{A_k} \times 100\% \quad (2)$$

where A_h and A_k are the integral area of methylene protons H_h closed to the ester bond and

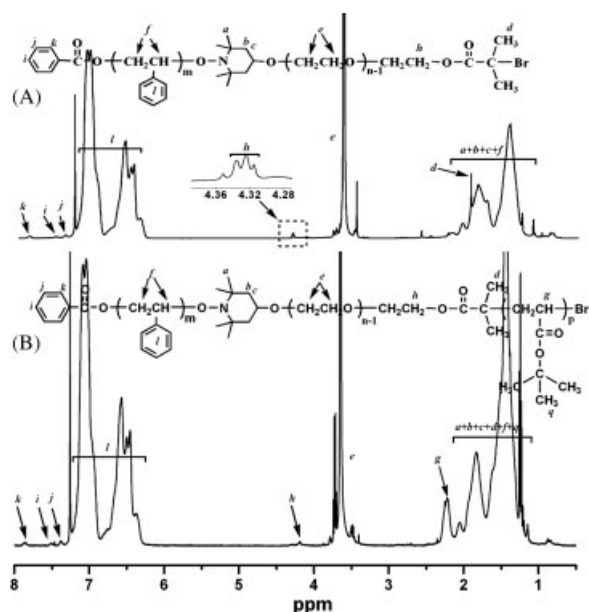


Figure 4. ^1H NMR spectra (CDCl_3) of (A) PEO-*b*-PS-Br and (B) PS-*b*-PEO-*b*-PtBA.

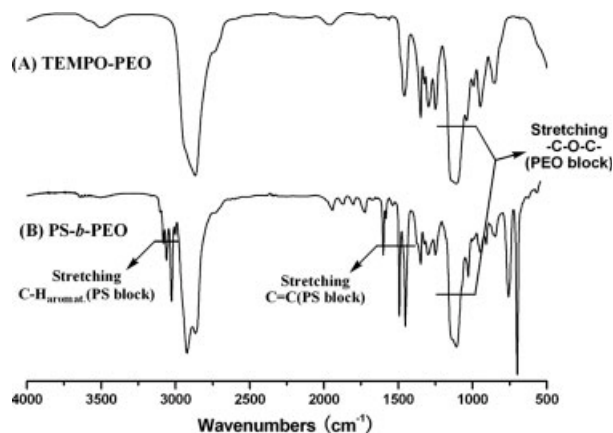


Figure 5. IR spectra of (A) TEMPO-PEO and (B) PS-*b*-PEO.

the protons H_k of residual phenyl group from the initiator BPO at the PS chain end, respectively. The efficiency was near to 100%.

Figure 5 shows the FTIR spectra of TEMPO-PEO-OH and PS-*b*-PEO-OH. In Figure 5(B), besides the peak at 1115 cm^{-1} for C—O—C stretching for PEO repeating units, the typical absorption peaks of PS block at $1450\text{--}1600\text{ cm}^{-1}$ for C=C_{aromat} stretching and at $3020\text{--}3100\text{ cm}^{-1}$ for C—H_{aromat} stretching were observed. In Figure 6(A), the conspicuous signal at 1735 cm^{-1} for the ester bond supported the success of esterification.

Preparation of ABC Triblock Copolymers PS-*b*-PEO-*b*-PtBA

The polymerization of *t*BA was carried out by a classic method of ATRP using PS-*b*-PEO-Br as initiator in the presence of CuBr/PMDETA. Figure 3 shows the GPC trace of final products, a

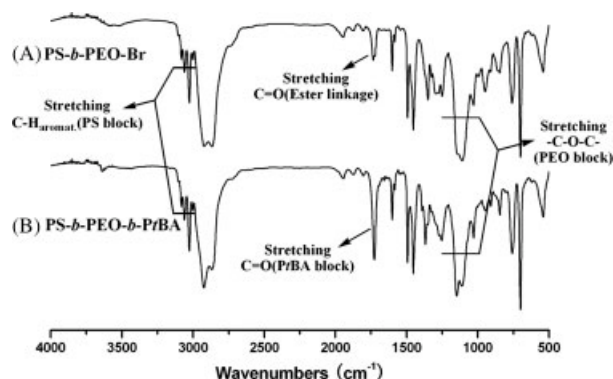


Figure 6. IR spectra of (A) PS-*b*-PEO-Br and (B) PS-*b*-PEO-*b*-PtBA.

Table 2. Polymerization Data of Triblock Copolymers PS-*b*-PEO-*b*-PtBA

Example	PS- <i>b</i> -PEO	PS- <i>b</i> -PEO- <i>b</i> -PtBA				
		$M_n (\times 10^3)^b$	M_w/M_n^a	wt % PEO ^b	wt % PS ^b	wt % PtBA ^b
A1	A	20.5	1.29	15.1	59.0	25.9
A1	A	22.0	1.30	14.1	55.0	30.9
B1	B	10.6	1.22	33.0	36.8	30.2
C1	C	21.8	1.40	25.7	58.2	16.1
C1	C	21.0	1.38	26.7	60.2	13.1

^a Determined by GPC calibrated against PS standards.

^b Number average molecular weight and weight percentage (wt %) were determined by ¹H NMR.

unimodal symmetric peak confirmed the ATRP of *t*BA was successful and no uninitiated PS-*b*-PEO-Br was remained. ¹H NMR spectrum for triblock copolymers PS-*b*-PEO-*b*-PtBA was shown in Figure 4(B). The new peaks at 2.22 ppm for the methine protons of PtBA and 1.50 ppm for methyl protons of PtBA could be observed, besides the characteristic signals of EO units at 3.36–3.70 ppm and St units at 6.30–7.30 ppm. To obtain the reliable M_n of triblock copolymers, the following eq 3 from ¹H NMR was used. The data are listed in Table 2.

$$M_{n(\text{triblock})} = \frac{4A_g}{A_e} \times \frac{M_{n(\text{PEO})}}{44} \times 128 + M_{n(\text{PS-}b\text{-PEO})} \quad (3)$$

where A_g and A_e represent the integral area of methine protons on the main chain of PtBA and all protons of the PEO main chain, respectively. $M_{n(\text{PEO})}$ is the M_n of the TEMPO-PEO. 44 and 128 is the M_w of EO and *t*BA. $M_{n(\text{PS-}b\text{-PEO})}$ is the M_n of diblock copolymers PS-*b*-PEO calculated by eq 1. Figure 6(B) shows the IR spectrum of triblock copolymer PS-*b*-PEO-*b*-PtBA, besides the characteristic peaks of PS and PEO, the signal at 1735 cm⁻¹ for ester bonds was strengthened obviously comparing with the spectrum of PS-*b*-PEO-Br [Fig. 6 (A)].

Effect of PEO Block Position on the T_g of PS-*b*-PEO-*b*-PtBA and PEO-*b*-PS-*b*-PtBA

The glass transition temperatures (T_g) of PS-*b*-PEO-*b*-PtBA (A1) and PEO-*b*-PS-*b*-PtBA were determined by DSC at a heating rate of 10 °C/min under a nitrogen atmosphere. Considering the same thermal history of the prepared samples, the results of the second heating run were discussed. As Figure 7 shows that T_g of PEO

segment for both triblock copolymers was nearly the same and observed at -51 to -52 °C, however, the T_g for PS and PtBA blocks were quite different. For PEO-*b*-PS-*b*-PtBA, the T_g of PtBA was 38 and 70 °C for PS as Figure 7(A) shows, but for PS-*b*-PEO-*b*-PtBA, the T_g was 34 °C for PtBA and 89 °C for PS. Obviously, the PEO position can exert great effect on the interaction between blocks. When the PEO block located in the middle of triblock copolymers, the blocks of PS and PtBA was separated and the interaction between them was weakened, the movement of chain segments for both of them was more free and approximate to their corresponding homopolymers. When the PEO block was located at the end of the triblock copolymer, the interaction between PS and PtBA was strengthened, and the difference of T_g s between them was shortened, and T_g of PtBA was enhanced and PS was lowered. The PEO block position in triblock

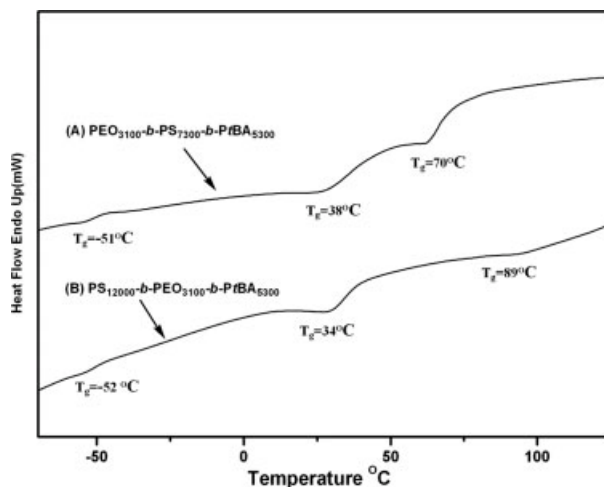


Figure 7. DSC thermograms of (A) PEO₃₁₀₀-*b*-PS₇₃₀₀-*b*-PtBA₅₃₀₀ and (B) PS_{12,000}-*b*-PEO₃₁₀₀-*b*-PtBA₅₃₀₀.

copolymers may affect their self-assembly morphologies, and the concerned investigation is undergoing.

CONCLUSIONS

A simple and universal route for preparation of PS-*b*-PEO-*b*-PtBA with PEO as the middle block was suggested by the combination of NMP and ATRP using PEO with α -hydroxyl- ω -2,2,6,6-tetramethylpiperidinyl-1-oxy end groups (TEMPO-PEO-OH) as precursors. ^1H NMR, FTIR, and GPC data demonstrated that the polymerization were under control and successful. DSC measurements confirmed that the PS-*b*-PEO-*b*-PtBA with PEO as middle block can weaken the interaction between PS and PtBA blocks, the T_g for these two blocks were approximate to the corresponding homopolymers comparing with the PEO-*b*-PS-*b*-PtBA with PEO as the first block.

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REFERENCES AND NOTES

- Chiefari, J.; Chong, Y. K. B.; 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, 5559–5562.
- Hawker, C. J. *J Am Chem Soc* 1994, 116, 11185–11186.
- Matyjaszewski, K.; Xia, J. H. *Chem Rev* 2001, 101, 2921–2990.
- Jia, Z. F.; Liu, C.; Huang, J. L. *Polymer* 2006, 47, 7615–7620.
- Vidovic, E.; Klee, D.; Hocker, H. *J Polym Sci Part A: Polym Chem* 2007, 45, 4536–4544.
- Wang, G. W.; Huang, J. L. *Macromol Rapid Commun* 2007, 28, 298–304.
- Vanjinathan, M.; Shanavas, A.; Raghavan, A.; Nasar, A. S. *J Polym Sci Part A: Polym Chem* 2007, 45, 3877–3893.
- Jia, Z. F.; Fu, Q.; Huang, J. L. *Macromolecules* 2006, 39, 5190–5193.
- Tyler, C. A.; Qin, J.; Bates, F. S.; Morse, D. C. *Macromolecules* 2007, 40, 4654–4668.
- Zhu, J.; Jiang, W. *Macromolecules* 2005, 38, 9315–9323.
- Deng, M. X.; Wang, R.; Rong, G. Z.; Sun, J. R.; Zhang, X. F.; Chen, X. S.; Jing, X. *Biomaterials* 2004, 25, 3553–3558.
- Auschra, C.; Stadler, R. *Macromolecules* 1993, 26, 6364–6377.
- Bailey, T. S.; Pham, H. D.; Bates, F. S. *Macromolecules* 2001, 34, 6994–7008.
- Duxin, N.; Liu, F. T.; Vali, H.; Eisenberg, A. *J Am Chem Soc* 2005, 127, 10063–10069.
- Bang, J.; Kim, S. H.; Drockenmuller, E.; Misner, M. J.; Russell, T. P.; Hawker, C. J. *J Am Chem Soc* 2006, 128, 7622–7629.
- Zhang, H. L.; Sun, X. Y.; Wang, X. Y.; Zhou, Q. F. *Macromol Rapid Commun* 2005, 26, 407–411.
- Niu, H. J.; Zhang, L. W.; Gao, M. Y.; Chen, Y. M. *Langmuir* 2005, 21, 4205–4210.
- Mahajan, S.; Cho, B.; Allgaier, J.; Fetters, L. J.; Coates, G. W.; Wiesner, U. *Macromol Rapid Commun* 2004, 25, 1889–1894.
- Liu, S. Y.; Weaver, J. V. M.; Tang, Y. Q.; Billingham, N. C.; Armes, S. P. *Macromolecules* 2002, 35, 6121–6131.
- Sun, X. Y.; Zhang, H. L.; Huang, X. H.; Wang, X. Y.; Zhou, Q. F. *Polymer* 2005, 46, 5251–5257.
- Jiang, X. Z.; Luo, S. Z.; Armes, S. P.; Shi, W. F.; Liu, S. Y. *Macromolecules* 2006, 39, 5987–5994.
- Cai, Y. L.; Armes, S. P. *Macromolecules* 2004, 37, 7116–7122.
- Vivas, M.; Contreras, J.; López-Carrasquero, F.; Lorenzo, A. T.; Arnal, M. L.; Balsamo, V.; Müller, A. J.; Laredo, E.; Schmalz, H.; Abetz, V. *Macromol Symp* 2006, 239, 58–67.
- Grubbs, R. B. *Macromol Chem Phys* 2005, 206, 625–627.
- Müller, A. J.; Arnal, M. L.; López-Carrasquero, F. *Macromol Symp* 2002, 183, 199–204.
- Kurosaki, T.; Lee, K. W.; Okawara, M. *J Polym Sci Part A: Polym Chem* 1972, 12, 3295–3310.
- Francis, R.; Taton, D.; Logan, J. L.; Masse, P.; Gnanou, Y.; Duran, R. S. *Macromolecules* 2003, 36, 8253–8259.
- Lin, W.; Fu, Q.; Zhang, Y.; Huang, J., unpublished work.
- Lu, G. Q.; Jia, Z. F.; Yi, W.; Huang, J. L. *J Polym Sci Part A: Polym Chem* 2002, 40, 4404–4409.
- Hua, F. J.; Yang, Y. L. *Polymer* 2001, 42, 1361–1368.
- Lambert, O.; Dumas, P.; Hurtrez, G.; Riess, G. *Macromol Rapid Commun* 1997, 18, 343–351.
- Angot, S.; Taton, D.; Gnanou, Y. *Macromolecules* 2000, 33, 5418–5426.