Synthesis, Characterization, and Thermal Behavior of H-Shaped Copolymers Prepared by Atom Transfer Radical Polymerization

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ABSTRACT: The H-shaped copolymers $(PSt)_2PEG(PSt)_2$, which are constructed by attaching two polystyrene branches to both ends of poly(ethylene glycol), were synthesized by atom transfer radical polymerization (ATRP). The synthetic strategy involves the synthesis of 2,2-bis(methylene α-bromopropionate) propionyl chloride, the preparation of 2,2-bis(methylene α-bromopropionate) propionyl terminated poly(ethylene glycol) (BMBP−PEG−BMBP), and then ATRP of styrene at 110 °C using BMBP−PEG−BMBP/CuBr/2,2′-bipyridine as the initiating system. The structure of the H-shaped copolymers was confirmed by NMR spectroscopy and GPC measurements. The thermal behavior of the H-shaped copolymers was investigated by differential scanning calorimeter. The high molecular weight poly(ethylene glycol) in the H-shaped copolymers shows higher crystalline ability, and the degree of crystallinity, X_c, decreases with the decrease of PEG weight fraction in the copolymers.

Introduction

H-shaped polymers can be considered as two sidearms attached to the each end of one polymer chain or the connection of two polymeric A blocks in the two AB_2 miktoarm star polymers through a covalent bond (Figure 1, parts a and b). The connection of two B blocks in two AB_2 stars affords π-shaped copolymers (Figure 1c). Because of their special structure, they show unique morphologies[1] and very interesting rheological properties of entangled polymer melts and solutions.[2−5] Therefore, the syntheses of H-shaped copolymers have become attractive research projects, and several H- and π-shaped copolymers have been prepared in recent years.[6−10] The synthetic strategies of these copolymers are based on anionic polymerization, and there are two general synthetic routes. One is anionic polymerization together with chlorosilane as coupling agent.[1,6−9] Another method is repeating the reactions of living anionic polymer chain with aromatic diolefin or polymer capped with aromatic olefin.[10] Due to the limited numbers of vinyl monomers applied in the living anionic polymerization, until now, H-shaped polymers were prepared from only a few kinds of polymers, such as polystyrene (PSt), polyisoprene (PI) and polybutadiene (PBD). In addition, after each reaction of living polymer chain with linking agents, troublesome purification for removing contaminants from the crude products is necessary, because the coupling reactions cannot go to completion and side reactions may occur.[8] Therefore, finding a new, convenient, and more versatile synthetic strategy is challenging.

In the research program on star-shaped copolymers, we synthesized a series of star-shaped polymers by controlled radical polymerization using multifunctional initiators[11−13] or by the combination of controlled radical and ring-opening polymerizations.[14] In the latter case, the synthetic strategy is based on a heterofunctional macroinitiator bearing two chemically different functional groups that are able to initiate independently two different kinds of polymerizations. Thus, we try to extend the synthetic strategies to prepare H-shaped copolymers. Compared to anionic polymerization, the controlled radical polymerizations are more versatile in monomers, and they are easier to operate. Poly(ethylene glycol) (PEG) is a water-soluble and crystallizable polymer, which leads to very interesting solution and solid-state behaviors.[15−17] Therefore, block and star polymers containing the PEG block have been extensively studied,[18−21] and they demonstrated unique morphologies and properties.[22−24] In this paper, we report for the first time the synthesis of the H-shaped copolymer $(PSt)_2PEG(PSt)_2$ by atom transfer radical polymerization (ATRP) using multifunctional macroinitiator, and the thermal behaviors were also investigated by differential scanning calorimeter (DSC) methods.

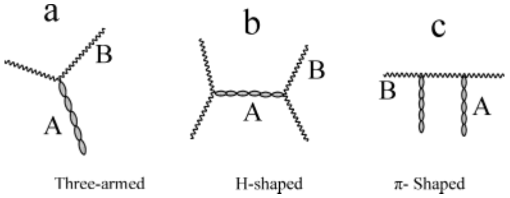

Figure 1. Molecular architectures of three-armed polymers (a), H-shaped polymers (b), and π-shaped polymers (c).

Experiment Section

Materials. 2,2-Bis(hydroxymethyl)propionic acid (BHPA, The First Shanghai Chemical Reagent Factory, 98%) was dried at 50°C before use. 2,2′-Bipyridine (bpy, Aldrich, 99%) was purified by recrystallization from *n*-hexane.[25] Chloroform was washed with oil of vitriol (15% v/v) three times and then with distilled water until neutralization. After being dried over anhydrous $CaCl_2$, CH_3Cl was distilled. Thionyl chloride (The First Shanghai Chemical Reagent Factory, >99%) was distilled before use. Triethylamine was dried with potassium hydroxide, refluxed with *p*-toluenesulfonyl chloride, and then distilled. Styrene (The First Shanghai Chemical Reagent Factory, 99%) was distilled under reduced pressure, and stored in a refrigerator. Poly(ethylene glycol) (PEG, $M_{n,PEG} = 8500$ g/mol, $M_w/M_n = 1.02$ and $M_{n,PEG} = 27\,000$ g/mol, $M_w/M_n = 1.03$) was freed of water by azeotropic distillation using benzene. 2-Bromopropionic acid (99%, analytical grade), CuBr (analytical

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Table 1. Conditions and Results of ATRP of St Using BMBP−PEG−BMBP as Initiator and CuBr/Bpy as Catalyst and Ligand[a]

no.	sample	St (g)	time (h)	convn[b] (%)	$M_{\mathrm{n,th}}$[c]	$M_{\mathrm{n,NMR}}$[d]	$M_{\mathrm{n,GPC}}$	M_w/M_n
	$(\mathrm{BMBP})_2\mathrm{PEG1}$					9300		1.02
1	$(\mathrm{PEG1})(\mathrm{PSt1})_4$	4.0	2	14	18 900	19 300	18 300	1.03
2	$(\mathrm{PEG1})(\mathrm{PSt2})_4$	4.0	7	53	45 300	46 100	41 400	1.06
3	$(\mathrm{PEG1})(\mathrm{PSt3})_4$	6.0	10	42	52 100	53 300	46 700	1.07
	PSt3[e]						12 500	1.11
	$(\mathrm{BMBP})_2\mathrm{PEG2}$					27 800		1.02
4	$(\mathrm{PEG2})(\mathrm{PSt1})_4$	2.0	10	35	65 800	66 200	33 100	1.09
5	$(\mathrm{PEG2})(\mathrm{PSt2})_4$	3.5	10	31	86 600	87 800	55 400	1.10
6	$(\mathrm{PEG2})(\mathrm{PSt3})_4$	4.0	11	48	93 000	95 800	60 900	1.09

[a] St was polymerized in THF at 110 °C with the molar ratio in feed: BMBP−PEG-BMBP/CuBr/bpy = 1/4/12. The weight BMBP−PEG-BMBP is 0.5 g, and the volume of THF is 1.5 mL. The molecular weights of PEG1 and PEG2 are 8500 and 27 000, respectively. [b] Conversion was calculated on the basis of the gravimetric method. [c] The number-average molecular weight of H-shaped copolymers, $M_{\mathrm{n,th}} = ([\mathrm{M}]_0/[\mathrm{I}]_0) \times \mathrm{convn} \times 104 + M_{\mathrm{n,PEG}}$, where $[\mathrm{M}]_0$ and $[\mathrm{I}]_0$ are initial molar concentrations of St and macroinitiator, 104 and $M_{\mathrm{n,PEG}}$ are molecular weights of St and BMBP−PEG−BMBP. [d] Calculated according to eq 1. [e] PSt3 was obtained by the hydrolysis of $(\mathrm{PEG1})(\mathrm{PSt3})_4$ (see Experiment).

grade) and other chemicals were purchased from the First Shanghai Chemical Reagent Factory, and they were used without further purification.

Synthesis of 2,2-Bis(methyl-α-bromopropionate) Propionyl Chloride (BBPC) (1). α-Bromopropionyl chloride (85 g, 0.50 mol), 2,2-bis(hydroxymethyl)propionic acid (30 g, 0.22 mol), and chloroform (150 mL) were added into a 500 mL flask equipped with a magnetic stirring bar and a condenser connected to an anhydrous $\mathrm{CaCl_2}$ tube for protection from moisture in the air. After the mixture was refluxed for 16 h, the chloroform and the excess α-bromopropionyl chloride were removed by distillation under reduced pressure. Thionyl chloride (20 mL, 0.27 mol) was added to the flask, and the mixture was heated to reflux and kept at reflux temperature for 5 h. Then the thionyl chloride was distilled off under reduced pressure. The crude product was distilled under reduced pressure two times, and the product, 2,2-bis(methyl α-bromopropionate) propionyl chloride (85.1 g, 90% yield) was collected at 150 °C/0.1Pa. Anal. Calcd for $\mathrm{C_{11}H_{15}Br_2ClO_5}$: C, 31.26; H, 3.55. Found: C, 31.52; H, 3.66. ^{1}H NMR δ (ppm): 1.45 [S, 3H, CH_3C], 1.80−1.83 [D, 6H, CH_3CHBr], 4.33−4.52 [6H, CH(Br), and CH_2O], ^{13}C NMR δ (ppm): 174.7 (C-Cl); 169.2 (COO); 65.8, 65.7 65.6 (CH$_2$O); 56.1 (C-CCl); 39.3 (CBr); 21.4 (CH$_3$−CBr); 17.8 (CH$_3$−C)

Synthesis of PEG Capped with Two 2,2-Bis(methyl-α-bromopropionate) Propionate Groups (2). A typical procedure for preparation of PEG capped with two 2,2-bis(methyl α-bromopropionate) propionate groups (BMBP−PEG−BMBP) was as follows. Water-free PEG1 ($M_{\mathrm{n,PEG}}$ = 8500 g/mol, 15 g, 1.8 mmol), benzene (60 mL), and freshly distilled triethylamine (1.8 g, 18 mmol) were added into a 150 mL two-necked flask with a magnetic stirring bar. After the flask was cooled to 0 °C, compound **1** (7.4 g, 18 mmol) was added dropwise over 2 h. The reaction mixture was warmed to room temperature and stirred for an additional 2 h, followed by refluxing overnight. After $\mathrm{Et_3NH^+Cl^-}$ was filtered off, product **2** was precipitated into diethyl ether and collected by vacuum filtration. After redissolving the solid in $\mathrm{CH_2Cl_2}$, the precipitation cycle was repeated two more times. The solid product was dried in a vacuum oven at 40 °C for 24 h to obtain the macroinitiator, BMBP−PEG−BMBP (79% yield). ^{1}H NMR δ (ppm): 1.45 [CH_3C]; 1.80−1.83 [CH_3CHBr]; 3.61 [−OCH_2CH_2O−]; 4.33−4.52 [CH(Br), and COOCH_2].

Synthesis of H-Shaped Block Copolymer 3 ($\mathbf{PSt_2PEGPSt_2}$). The synthesis of H-shaped block copolymers was as follows. The macroinitiator, BMBP−PEG−BMBP (0.5 g, 0.054 mmol, $M_{\mathrm{n,NMR}}$ = 9300), CuBr (0.031 g, 0.21 mmol), bpy (0.10 g, 0.65 mmol), St (4 g, 38.5 mmol), and THF (1.5 mL) were successively added into a glass tube. The mixture in the tube was degassed by three freeze−vacuum−thaw cycles. The tube was sealed under vacuum and then immersed into an oil bath thermostated at 110 °C. After the reaction was carried out for 7 h, the tube was rapidly cooled to room temperature by ice water. The polymer solution in THF was passed through a short column of neutral alumina to remove the metal salt. By addition of the polymer solution into an excess of petroleum ether (30−60 °C), the H-shaped copolymer was precipitated and collected by vacuum filtration. The H-shaped copolymer was obtained in 53% yield after being dried at 40 °C in the vacuum oven for 24 h. $M_{\mathrm{n,NMR}}$ = 46 100, M_w/M_n = 1.06. ^{1}H NMR δ (ppm): 6.30−7.32 [aromatic protons]; 3.61 [−OCH_2CH_2O−]; 1.29−2.12 [methylene and methine protons].

Hydrolysis of the H-Shaped Block Copolymers. The H-shaped block copolymer (2 g, sample 3 in Table 1) was dissolved in THF (10 mL) in a 100 mL round-bottomed flask fitted with a refluxing condenser. Into the polymer solution was added a sodium hydroxide solution in water (10 mL, 1 N (aqueous)), and the mixture was refluxed for 24 h. The residue, which was obtained after the volatiles in the reaction mixture were removed under reduced pressure, was extracted with $\mathrm{CH_2Cl_2}$ three times. The extracts were combined and followed through a short column of neutral alumina to remove the salt. After $\mathrm{CH_2Cl_2}$ was evaporated under reduced pressure, the residue was dissolved in cyclohexane, and then filtered to remove the undissolved solid. By adding the filtrate into an excess of petroleum ether (30−60 °C), the hydrolyzed product precipitated was collected by filtration and then dried at 40 °C in a vacuum oven for 24 h to afford the product (PSt) (1.43 g, 71.5% yield). $M_{\mathrm{n,GPC}}$ = 12 500, M_w/M_n = 1.11. ^{1}H NMR δ (ppm): 6.30−7.32 [aromatic protons]; 1.29−2.21 [methylene and methine protons]. The undissolved solid obtained by filtration was dissolved in water, and then filtered. After evaporation of water in the filtrate under reduced pressure, PEG (14% yield) was obtained for NMR measurement. $M_{\mathrm{n,NMR}}$ = 8500, M_w/M_n = 1.02. ^{1}H NMR δ (ppm): 3.61 [−OCH_2CH_2O−].

Characterization. ^{1}H NMR spectra were recorded on a Bruker DMX-300 nuclear magnetic resonance (NMR) instrument with $\mathrm{CDCl_3}$ as solvent and tetramethylsilane (TMS) as internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Vector-22 FT-IR instrument. The molecular weight and molecular weight distribution of the polymers were measured using a Waters 150C gel permeation chromatography (GPC) equipped with microstyragel columns (10^3, 10^4, and 10^5 Å) and Waters RI detector at 30°C. Molecular weights were calibrated against low polydispersity polystyrene standards. THF was used as eluent at a flow rate of 1.0 mL/min. Differential scanning calorimeter (DSC) was performed on a Mettler-Toledo DSC-8210 instrument at heating and cooling rates of 10 °C/min. Indium and benzoic acid were used as temperature calibration standards. T_gs were determined as the midpoint of the transition process, and the exothermic and the endothermic maximum temperatures were taken as the crystallization temperature (T_c) and the melting temperature (T_m), respectively. The heat of fusion ($\Delta H_c^{\mathrm{PEG}}$) was determined based on the integration of exothermic peak and the sample weight.

Results and Discussion

Synthesis of Macroinitiator PEG Capped with Two BMBP Groups (BMBP—PEG—BMBP) (2).

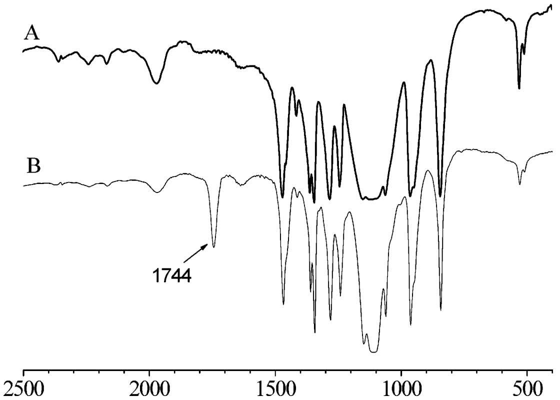
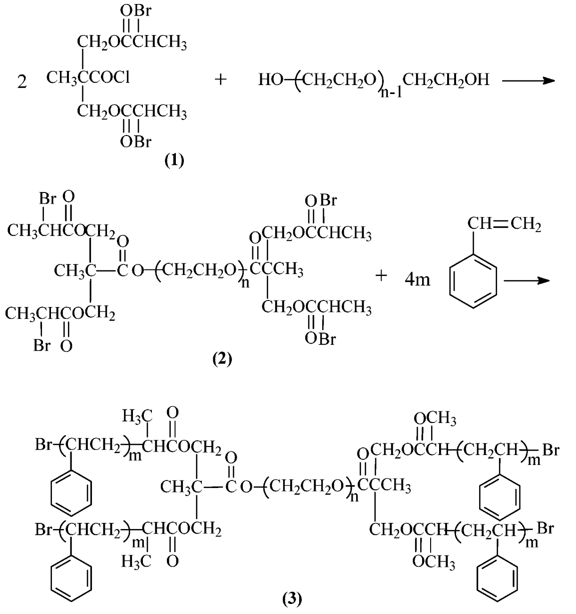


Figure 2. FTIR spectra of PEG with molecular weight 27 800 before (A) and after reaction with BBPC (B).

Scheme 1



H-shaped block copolymers were synthesized according to Scheme 1. The esterification reaction between 2,2-bis(hydroxylmethyl) propionic acid (BHPA) and PEG produced complicated products, probably due to the self-condensation reaction of BHPA. Therefore, BHPA was first reacted with an excess of 2-bromopropionyl chloride, and subsequently reacted with thionyl chloride to afford BBPC in higher yield (~90%). To ensure the complete reaction of the PEG hydroxyl groups with BBPC, an excess of BBPC was used, which can be easily removed by precipitation into diethyl ether. The formation of macroinitiators, BMBP−PEG−BMBP, can be confirmed by their FT-IR spectra. Figure 2 shows FT-IR spectra of PEG before and after reaction with BBPC. When comparing with FT-IR spectrum of the starting PEG in Figure 2A, we could find a characteristic carbonyl-stretching band of ester at $\nu = 1744$ cm^{-1} in Figure 2B, which must be the result from the esterification reaction of PEG with BBPC. Other evidence for the formation of BMBP−PEG−BMBP is their ^{1}H NMR spectra. A typical ^{1}H NMR spectrum is shown in Figure 3B. In comparison with ^{1}H NMR spectrum of PEG shown in Figure 3A, Figure 3B shows new resonances at $\delta = 4.33-4.52$ (a), 1.80−1.83 (d), and 1.45 ppm (c), which are ascribed to the BMBP group. The appearance of a resonance at $\delta = 4.25-4.33$ (a′) is due to ester methylene groups at the ends of PEG that were formed from the esterification reaction of BBPC with PEG. Therefore, we can infer that all hydroxyl groups in PEG were completely transformed to the ester groups from the integration ratio = 8:3 of resonances (a + a′) to c in Figure 3B.

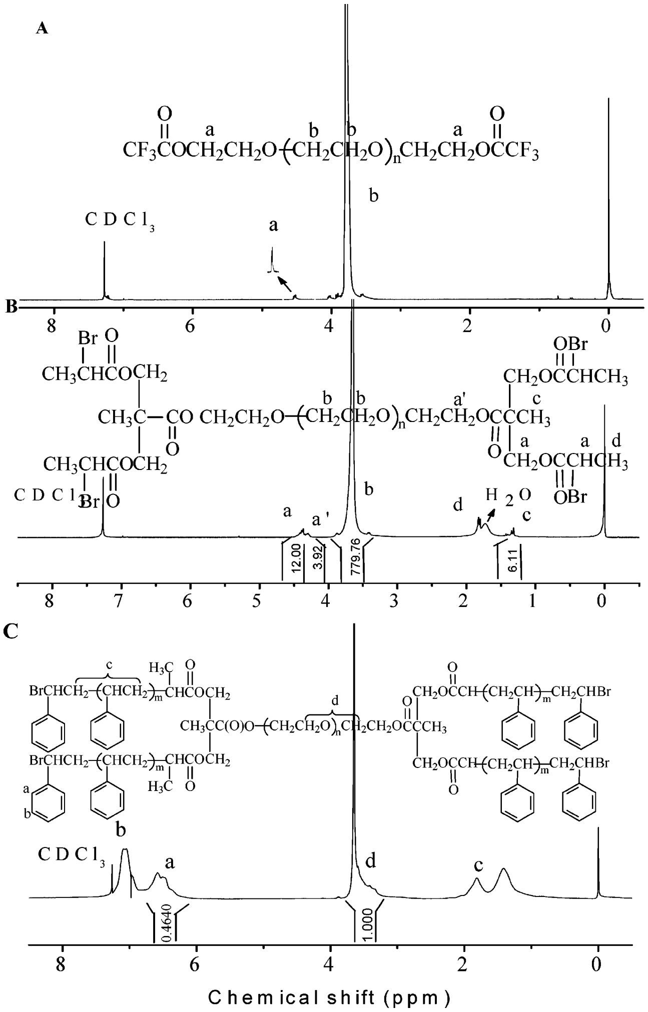


Figure 3. ^{1}H NMR spectra of PEG1 ($M_{n,PEG} = 8500$) treated with trifluoroacetic anhydride (A); macroinitiator PEG1-(BMBP)$_2$ with $M_{n,PEG} = 9300$ (B) and PEG1(PSt3)$_4$ $M_{n,PEG}$ = 46 700 (no.3 in Table 1) (C).

Synthesis of H-Shaped Block Copolymer 3 ((PSt)$_2$PEG(PSt)$_2$). Although PEG can form a complex with copper ion, it did not affect the polymerization of vinyl monomers.[26] Thus, BMBP−PEG−BMBP was used as multifunctional macroinitiator in the ATRP of St with CuBr/bpy as catalyst system. Table 1 details the polymerization conditions and the results. GPC measurements were used to follow the polymerization. Parts A−C of Figure 4 show the GPC traces of H-shaped copolymers obtained at different polymerization times. We could see that the GPC curves are successively shifted to higher molecular weight positions with the progress of polymerization. Another method to increase the molecular weight of PSt branches is the increase of the initial molar ratio of monomer to macroinitiator as shown in Figure 4D. All GPC curves in Figure 4 are single and symmetrical, indicating that the pure H-shaped copolymers were obtained. If the H-shaped copolymers contain four and three branches and/or two branches formed due to the intramolecular irreversible termination reactions and/or the inefficient initiation during the polymerization, the GPC curves should have

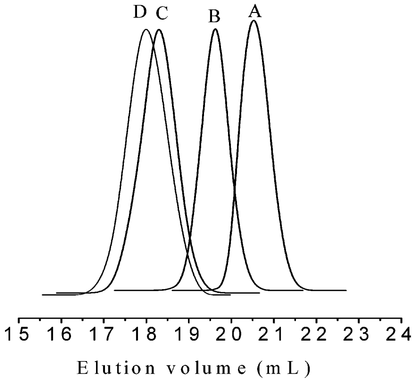


Figure 4. GPC traces: macroinitiator $(BMBP)_2PEG1$ in Table 1 (A); $PEG1(PSt1)_4$ obtained from 2 h polymerization with the feed weight ratio St/ BMBP−PEG−BMBP = 4/0.5 ($M_{n,GPC}$ = 18 300, M_w/M_n = 1.03; no. 1 in Table 1) (B); $PEG1(PSt2)_4$ obtained from 7 h polymerization with the feed weight ratio St/BMBP−PEG−BMBP = 4/0.5 ($M_{n,GPC}$ = 41 400, M_w/M_n = 1.06; no. 2 in Table 1) (C); $PEG1(PSt3)_4$ obtained from 10 h polymerization with the feed weight ratio St/ BMBP−PEG−BMBP = 6/0.5 ($M_{n,GPC}$ = 46 700, M_w/M_n = 1.07; no. 3 in Table 1) (D).

a tail at lower molecular weight position at least. To further confirm this conclusion, their ^{1}H NMR spectra were measured. Figure 3C represents a typical ^{1}H NMR spectrum of the H-shaped copolymer (no. 1 in Table 1). Except characteristic methylene protons signal of PEG at δ = 3.61 (d), the aromatic protons signals at δ = 6.30−6.80 (a), 6.80−7.32 ppm (b), and methylene and methine protons signals of PSt backbone at δ = 2.12−1.29 (c) demonstrate that the macroinitiator initiated the polymerization of St to form H-shaped copolymers. On the basis of the^{1}H NMR data, the number-average molecular weight, $M_{n,NMR}$, can be calculated according to eq 1.

$$M_{n,NMR} = [(I_a/2)/(I_d/4)](N_{PEG}\text{-}1) \times 104 + M_{n,PEG} \quad (1)$$

where N_{PEG} is the degree of polymerization of PEG, which was calculated based on the NMR spectrum; I_a and I_d are the integral values of the signals at δ = 6.30−6.80 (a) and 3.61 ppm (d), respectively; 104 and $M_{n,PEG}$ are the molecular weights of St and BMBP−PEG−BMBP, respectively. The calculated results are listed in Table 1, and we find that $M_{n,NMR}$ agrees well with the theoretical number-average molecular weight, $M_{n,th}$, which indicates that the pure H-shaped copolymer was obtained and the molecular weight can be controlled by the initial molar ratio of St to macroinitiator and conversion.

Hydrolysis of the H-Shaped Block Copolymer $(PSt)_2PEG(PSt)_2$. Since the H-shaped copolymers studied are constructed by connection of four PSt blocks and one PEG segment via ester linkages (Scheme 1), they are easier to hydrolyze in alkaline solution, forming PSt and PEG. To determine whether all four initiating sites in each macroinitiator molecule initiated ATRP of St and whether the intramolecular irreversible termination reactions occurred during the polymerization, the H-shaped copolymers obtained were hydrolyzed by refluxing a mixture of the copolymer and sodium hydroxide in THF and water. The two polymers were easily isolated from the hydrolyzed products using the procedure described in the Experimental Section, and then they were analyzed by GPC and ^{1}H NMR. Figure 5 shows typical GPC curves of the H-shaped copolymer (no. 3 in Table 1) and the two polymers isolated from the hydrolyzed products. Those two polymers at lower molecular weight positions should be PSt and PEG respectively according to the structure shown in Scheme 1. For confirming the structures of hydrolyzed products, Figure 6 details their ^{1}H NMR spectra. The typical resonances for PSt appear at δ = 6.30−7.32 (Figure 6A), and that for PEG, the methylene resonance at δ = 3.61 is observed (Figure 6B). The molecular weight of PSt obtained was measured, and is listed in Table 1. The value is close to $^1/_4$ of the molecular weight of PSt branches in the H-shaped copolymer before hydrolysis (no. 3 and PSt3 in Table 1). This suggests that the initiation efficiency for all four sites in the macroinitiator molecule was high, and that the pure H-shaped copolymers can easily be obtained and purified. The narrow polydispersity index of the hydrolyzed product, PSt, and a single, symmetrical GPC curve as shown in Figure 5B demonstrate that each initiating site in one macroinitiator molecule has almost the same possibility to propagate. Thus, we can conclude that the chain length of PSt blocks can be controlled by the feed molar ratio of St to macroinitiator and conversion.

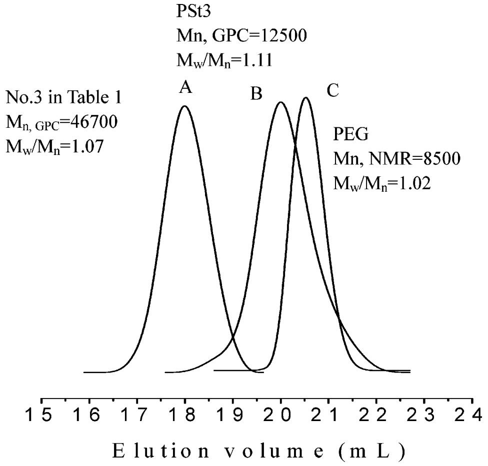


Figure 5. GPC curves: the H-shaped copolymer $PEG1(PSt3)_4$ with $M_{n,GPC}$ = 46 700 and M_w/M_n = 1.07 (no. 3 in Table 1) (A); the PSt block obtained from the hydrolysis of no. 3 in Table 1 (B); poly(ethylene glycol) isolated from the hydrolyzed product (C).

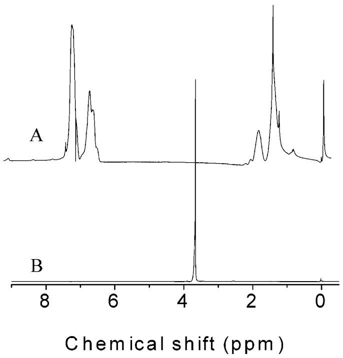


Figure 6. ^{1}H NMR spectra of PSt (A) and PEO (B) obtained from the hydrolysis of H-shaped copolymer $PEG1(PSt3)_4$ (no. 3 in Table 1).

Thermal Behavior of H-Shaped Copolymers. Phase segregation of the block copolymers, PSt-*b*-poly(ethylene oxide) (PSt-*b*-PEO), occurs due to immiscibility between PSt and PEO.[22] The PEO is a crystalline polymer, its crystallization and melting behaviors were

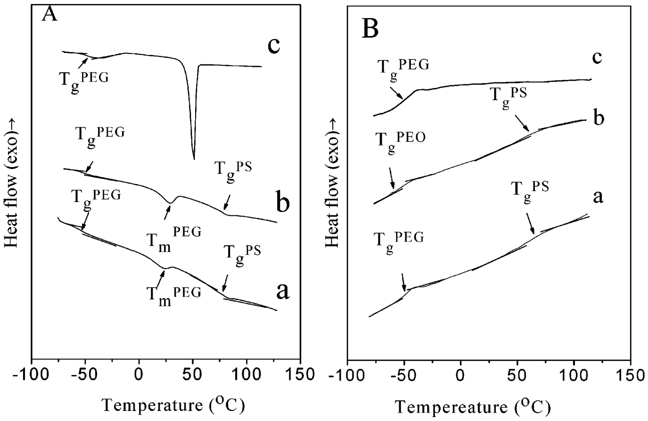


Figure 7. DSC heating (A) and successive cooling scans (B) of the H-shaped copolymers, nos. 3 (a), 2 (b), and 1 (c) in Table 1.

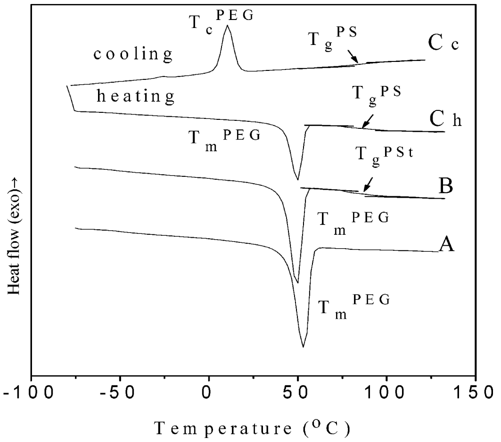


Figure 8. DSC cooling (C_c) and successive heating scans (A, B, C_h) of H-shaped copolymers: (A) no. 4 ($M_{n,PEG(NMR)} = 27\,000$, $M_{n,PSt(NMR)} = 38\,400$, $M_w/M_n = 1.09$); (B) no. 5 ($M_{n,PEG(NMR)} = 27\,000$, $M_{n,PSt(NMR)} = 60\,000$, $M_w/M_n = 1.10$); (C) no. 6 ($M_{n,PEG(NMR)} = 27\,000$, $M_{n,PSt(NMR)} = 68\,000$, $M_w/M_n = 1.09$) in Table 1 at heating and cooling rates of 10 °C/min.

studied in detail by Kovacs and co-workers.[27-29] Thus, we studied the phase separation behaviors of the H-shaped copolymers obtained by DSC method since they contain PSt and PEG blocks. The DSC curves of two series of H-shaped copolymers with the molecular weights of PEG, $M_{n,PEG} = 8500$ and 27 000, were measured, and they are shown in Figures 7 and 8. The molecular weight and molecular weight distribution data of the copolymers used in the DSC investigation are listed in Table 1. Parts A and B of Figure 7 show the heating and cooling DSC traces of the first series of samples (nos. 1−3 in Table 1), respectively. On the heating curves in Figure 7A, there are three phase transition temperatures: the glass transition temperature (T_g^{PEG}) of PEG at around −51 to −55 °C, the crystalline melting temperature (T_m^{PEG}) of PEG at 22 to 49 °C, and the T_g^{PS} of PSt at around 77 °C. All the DSC data are listed in Table 2, and we find that with an increase of the PSt fraction in the H-shaped copolymers, the T_m^{PEG}s decreased from 49.5 (c) to 26.6 (b) and to 22.0 °C (a), and the T_g^{PEG}s also decreased from −51.2 (c) to −54.2 (b) and to −55.2 °C (a) (Figure 7A). When the weight fractions of PSt in the copolymers were 83.8% and 81.2% respectively, their T_g^{PS}s were 77.8 and 77.3 °C. But the T_g^{PSt} of the copolymer containing 54.1 wt % of PSt was not detected, probably because the molecular weight of each PSt block ($M_{n,NMR} = 2500$) is too low, and phase separation is difficult under the DSC conditions. On the cooling curves in Figure 7B, parts B-a and B-b, T_g^{PEG} and T_g^{PS} are observed, but no exothermic crystallization peak (T_c^{PEG}) for PEG was detected, probably because the molecular weight of the PEG was too low ($M_{n,PEG} = 8500$) to achieve equilibrium phase separation to form the crystallized domains. Increasing the molecular weight of PEG should help it to crystallize, so the thermal phase transition behaviors of the H-shaped copolymers containing the higher molecular weight of PEG ($M_{n,PEG} = 27\,000$) were studied.

Table 2. DSC Data of H-Shaped Copolymer S_2PEGS_2 at a Heating Rate of 10 °C/min

no.	sample	f_{PEG} (%)	ΔH_c^{PEG} (J/g)	X_c^{PEG} (%)	T_m^{PEG} (°C)	T_g^{PEG} (°C)[a]	T_g^{PSt} (°C)[a]
1	$(PEG1)(PSt1)_4$	0.459			49.5	−51.2	
2	$(PEG1)(PSt2)_4$	0.188			26.6	−54.2	77.3
3	$(PEG1)(PSt3)_4$	0.162			22.0	−55.2	77.8
4	$(PEG2)(PSt4)_4$	0.412	−41.98	49.7	52.2		77.8
5	$(PEG2)(PSt5)_4$	0.313	−26.14	41.0	49. 2		76.0
6	$(PEG2)(PSt6)_4$	0.284	−22.49	38.6	49.5		75.2

[a] T_g^{PEG} and T_g^{PSt} were measured on the heating process.

Figure 8 shows the heating DSC traces (A, B, Ch) of the second series of H-shaped copolymers, No 4−6, and the cooling DSC trace (Cc) of no. 6 in Table 1. All the DSC data are listed in Table 2. Different from samples nos. 1−3, the sample nos. 4−6 were prepared from macroinitiator with $M_{n,NMR} = 27\,800$. All the heating curves in Figure 8 show strong endothermic T_m^{PEG} peaks. Upon cooling, an exothermic T_c^{PEG} peak occurred at 9.8−10.5 °C, which demonstrates that the PEG domains formed from the phase segregation are crystalline. The difference between these results and those observed in Figure 7B is ascribed to the ability of the higher molecular weight PEG segment to crystallize. The degree of crystallinity, X_c can be calculated according to eq 2.

$$X_c = \Delta H_c/(f_{PEG} \times \Delta H_f^0) \qquad (2)$$

where $\Delta H_f^0 = 205$ J/g, which is the heat of fusion of 100% crystalline PEG;[29] f_{PEG} is the weight fraction of PEG in the copolymer, which can be calculated based on ^{1}H NMR data. The calculated X_c values are listed in Table 2. As we discussed, no exothermic crystallization peak of sample nos. 1−3 with $M_{n,PEG} = 8500$ was detected, and thus their X_c values could not be estimated. For sample nos. 4−6 with $M_{n,PEG} = 27\,000$, the X_c values decrease slowly from 49.7% to 41.0%, to 38.6% with the decrease of PEG weight fraction in the H-shaped copolymers (Table 2).

An H-shaped copolymer, $(PSt)_2$−polyisoprene−$(PSt)_2$ with a volume fraction of 0.36 of the PSt blocks, yielded a lamellar morphology, and when the composition of copolymer was varied, their morphologies were altered.[1] Whether this PSt−PEG H-shaped copolymer system has it too is under investigation.

Conclusion

The H-shaped copolymers with PEG backbone and four PSt branches, $(PSt)_2PEG(PSt)_2$ were successfully prepared by ATRP using multifunctional macroinitiator BMBP−PEG−BMBP and CuBr/bpy as catalyst system. To ensure complete reaction of the PEG hydroxyl groups with BBPC, an excess of BBPC in the reaction is necessary. The structure of the reaction product, BMBP−

PEG−BMBP was confirmed by its ^{1}H NMR data. Because of the living nature of the ATRP of St, the four PSt branches of the H-shaped copolymers have similar molecular weights, which was verified by analyzing the GPC and ^{1}H NMR data of the hydrolyzed product, PSt. The H-shaped copolymers with lower molecular weight ($M_{n,PEG}$ = 8500) PEG show endothermic T_m^{PEG} peak on heating DSC curves, but no exothermic T_c^{PEG} on cooling DSC curves. For the H-shaped polymers made from higher molecular weight ($M_{n,PEG}$ = 27 000) PEG, both T_m^{PEG} on heating and T_c^{PEG} on cooling curves were observed due to the ability of the higher molecular weight PEG segment to crystallize. The degree of crystallinity of PEG increases with the increase of its weight fraction, f_{PEG} in the copolymers.

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