Synthesis of Amphiphilic Tadpole-Shaped Copolymers by Combination of Glaser Coupling with Living Anionic Polymerization and Ring-Opening Polymerization

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ABSTRACT: The tadpole-shaped copolymers polystyrene (PS)-*b*-[cyclic poly(ethylene oxide) (PEO)] [PS-*b*-(*c*-PEO)] contained linear tail chains of PS and cyclic head chains of PEO were synthesized by combination of Glaser coupling with living anionic polymerization (LAP) and ring-opening polymerization (ROP). First, the functionalized polystyrene-glycerol (PS-Gly) with two active hydroxyl groups at ω end was synthesized by LAP of St and the subsequent capping with 1-ethoxyethyl glycidyl ether and then deprotection of protected hydroxyl group in acid condition. Then, using PS-Gly as macroinitiator, the ROP of EO was performed using diphenylmethylpotassium as cocatalyst for AB$_2$ star-shaped copolymers PS-*b*-(PEO-OH)$_2$, and the alkyne group was introduced onto PEO arm end for PS-*b*-(PEO-Alkyne)$_2$. Finally, the intramolecular cyclization was performed by Glaser coupling reaction in pyridine/Cu(I)Br/*N,N,N′,N″,N″*-

pentamethyldiethylenetriamine system under room temperature, and tadpole-shaped PS-*b*-(*c*-PEO) was formed. The target copolymers and their intermediates were well characterized by size-exclusion chromatography, proton nuclear magnetic resonance spectroscopy, and fourier transform infrared spectroscopy in details. The thermal properties was also determined and compared to investigate the influence of architecture on properties. The results showed that tadpole-shaped copolymers had lower T_m, T_c, and X_c than that of their precursors of AB$_2$ star-shaped copolymers. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 2227–2235, 2012

KEYWORDS: anionic polymerization; Glaser coupling; poly(ethylene oxide) (PEO); poly(styrene); ring-opening polymerization (ROP); tadpole-shaped copolymers

INTRODUCTION The relationship between structures and properties of copolymers was always an important topic for polymer chemists and physicists. Due to the development of various polymerization mechanisms[1–5] and coupling techniques,[6–8] a library of copolymers emerged, such as comb-shaped,[9] hyperbranched,[10] dendritic,[11] star-shaped,[5] cycle-based (including single cycle, eight-shaped, tadpole-shaped, theta-shaped, etc.)[12] copolymers. The typical tadpole-shaped copolymer was constructed by a linear tail and a cyclic head chain, which was also the simplest topological structure composed by linear and cyclic subchains. This kind of tadpole-shaped copolymer might be used as the model copolymer for theoretical research such as the microdomain morphologies in bulk and self-assembly behavior in solution, as well as be endowed with some special properties and applications.

For example, via the living anionic/cationic polymerization, Beinat et al.[13] synthesized polystyrene (PS)-*b*-[cyclic poly (chloroethyl vinyl ether) (PCEVE)] [PS-*b*-(*c*-PCEVE)] by intramolecular cyclization between the cationized α-acetal group

at PCEVE end and γ-styrenyl group at junction point of diblock copolymer precursor, Oike et al.[14(a)] synthesized poly (tetrahydrofuran)(PTHF)-*b*-(*c*-PTHF) by cyclization through an "electrostatic self-assembly and covalent fixation" process, Kubo et al.[15] synthesized PS-*b*-(*c*-PS) by cyclization between α-carboxyl, ω-amino on PS end and the subsequent coupling between amino group on cyclic PS and carboxyl group on linear PS end. Via the reversible addition-fragmentation chain transfer polymerization, Shi et al.[16] synthesized poly(*N*-isopropylacrylamide) (PNIPAM)-*b*-(*c*-PS) by cyclization between α-alkyne group at PS end and γ-azide group at junction point (click chemistry). Via the atom transfer radical polymerization and ring-opening polymerization (ROP), Li and coworkers[17] synthesized poly(ethylene oxide)-*b*-(*c*-PS) by cyclization between α-azide group at PS end and γ-alkyne group at junction point. As an expanded work, the tadpole-shaped copolymers of [poly(ʟ-lactide)(PLLA)]$_2$-*b*-[cyclic-poly(ε-caprolactone) (PCL)] [(PLLA)$_2$-*b*-(*c*-PCL)] with two linear tails was synthesized by combination of ROP and photo-crosslinking method,[18] and (PNIPAM)$_2$-*b*-(*c*-PEO) with two
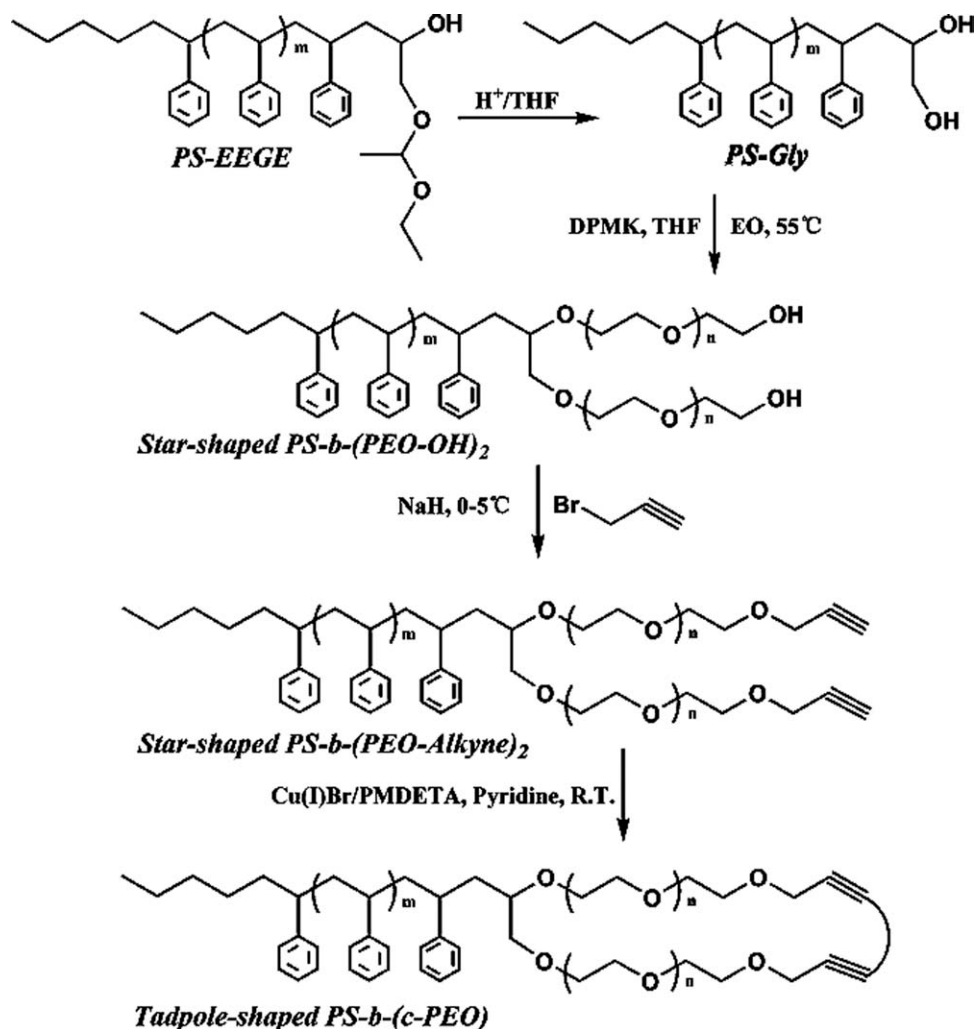
SCHEME 1 The synthetical procedure of tadpole-shaped PS-b-(c-PEO) and its precursor of AB$_2$ star-shaped PS-b-(PEO-OH)$_2$, PS-b-(PEO-Alkyne)$_2$.

linear tails was also synthesized by combination of single-electron transfer living radical polymerization with click chemistry.[19] However, the researches in properties of tadpole-shaped copolymers were still limited because of the rarely synthesized model copolymers, which was again dominantly limited by the cyclization method.

Summarizing from the literature, the techniques adopted for cyclization could be classified into ring-closure and ring-expansion techniques, and the former technique involved cyclization of the linear polymer precursor with heterodifunctional or homodifunctional groups. The key requirements of ring-closure technique involved: (a) the modification procedure of functionalities was easily realized, (b) the cyclization technology should show the high efficiency (no linear byproduct occurred and no further purification procedure involved), and (c) the cyclization could be conducted under mild conditions (such as the usage of solvent with low boiling point, operation under room temperature, without serious deoxygenization procedure, etc.). For example, the widely used click chemistry between alkyne and azide

groups could only meet the requirement of conduction (b) because that the alkyne and azide groups should be selectively or deliberately modified onto each end of precursors, and the click reaction was usually proceeded under elevated temperature and in solvent with high boiling point (such as dimethyl formamide (DMF)).[16,17,19] Thus, screening an efficient and universal cyclization method was still a very valuable work. Very recently, the Glaser coupling reaction between alkyne groups with high efficiency had been widely used in organic[20] and polymer chemistry.[21] By using this method, we had successfully synthesized A$_2$B$_2$ star-shaped copolymers[22] and cyclic PS or PEO polymers,[23] the Glaser coupling reaction could meet all the above (a), (b), and (c) requirement of conditions simultaneously.

The block copolymers contained PEO and PS subchains had been modeled for various researches on morphology,[24] crystalline,[25] and self-assembly behavior.[26] Interestingly, Li and coworkers[17] synthesized tadpole-shaped PEO-b-(c-PS) and compared its properties with the linear counterparts. In this presentation, by combination of multiple polymerization
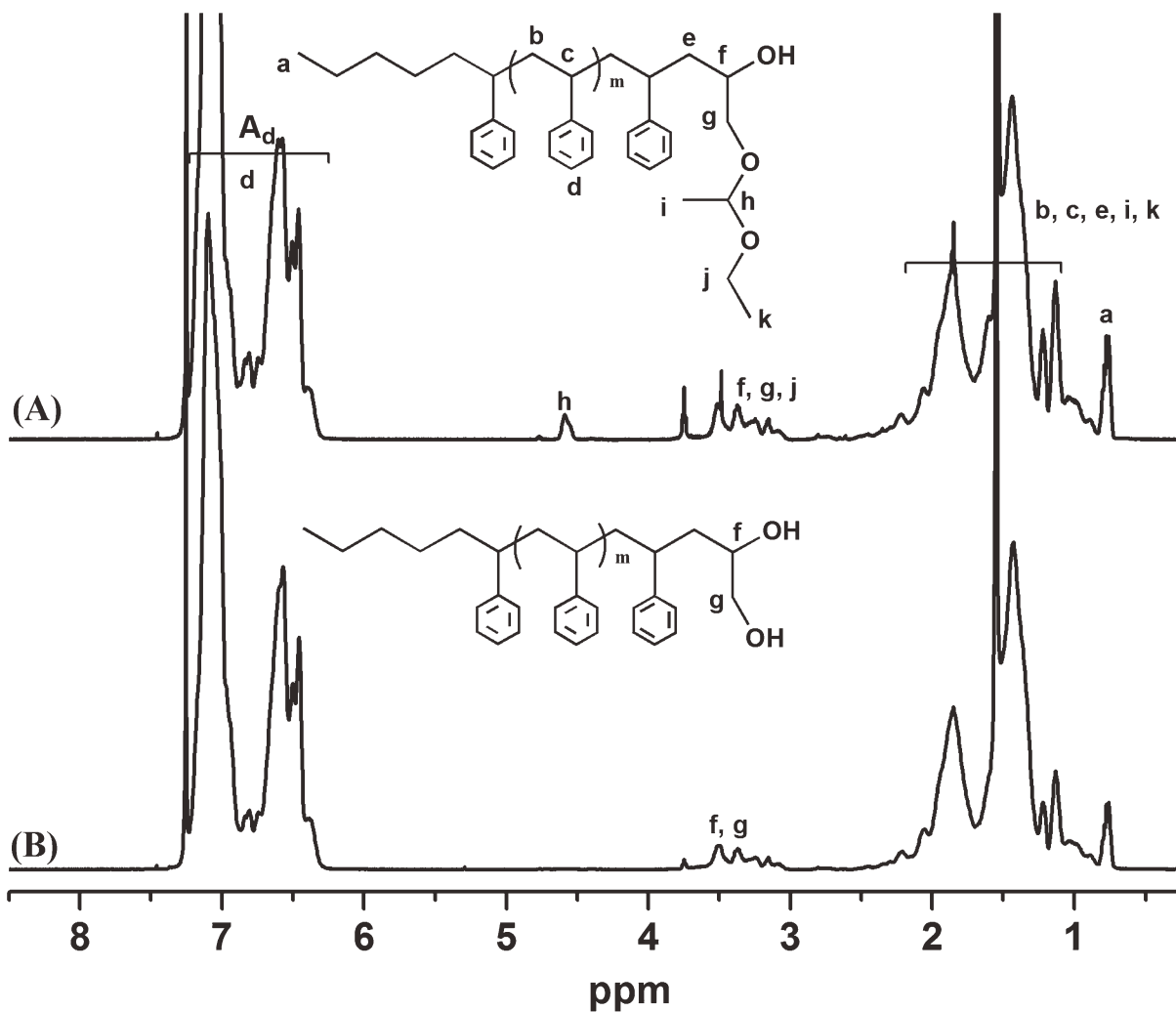
FIGURE 1 The ^{1}H NMR spectra of PS-EEGE(A) and PS-Gly (B) (in CDCl$_3$).

mechanisms with Glaser coupling, we designed and synthesized another kind of novel tadpole-shaped PS-b-(c-PEO), which had the inversed structure with that of Li and coworkers.[17] The thermal properties of amphiphilic tadpole-shaped copolymers was preliminarily investigated and compared with that of their precursors of AB$_2$ star-shaped copolymers.

RESULTS AND DISCUSSION

Synthesis and Characterization of AB$_2$ Star-shaped PS-b-(PEO-OH)$_2$ and PS-b-(PEO-Alkyne)$_2$ Precursors

According to our previous work,[27] the functionalized precursors PS-(1-ethoxyethyl glycidyl ether) (PS-EEGE) with an active and a protected hydroxyl group at ω-end were synthesized by capping poly(styryl)lithium(PS$^-$Li$^+$) with EEGE, and then PS-Gly with two active hydroxyl groups at ω-end was obtained by hydrolysis of ethoxyethyl group under acid conditions. Subsequently, PS-Gly was used as macroinitiator for precursor of AB$_2$ star-shaped PS-b-(PEO-OH)$_2$ by ROP of EO monomer, and AB$_2$ star-shaped PS-b-(PEO-Alkyne)$_2$ was

obtained by modification with propargyl bromide in NaH/THF system at 0–5 °C (Scheme 1).

The ^{1}H NMR spectra of functionalized PS-EEGE and PS-Gly were shown in Figure 1. Besides the resonance signals at 0.80 ppm attributed to α-methyl group protons (—CH_3) and the signals at 6.30–7.30 ppm attributed to aromatic protons (—C$_6H_5$) on PS chain, the appearance of signals for methine group proton (—OCH(CH$_3$)O—) at 4.65–4.76 ppm and protons (—CH(OH)CH_2O—, CH$_3$CH_2O—) at 3.05–3.63 ppm in Figure 1(A) proved the addition of EEGE to PS chain end. The functionalization efficiency of EEGE reached 96.3%, and the unfunctionalized PS could be removed by thin layer chromatography using toluene/THF as eluent according to our previous work.[28] After hydrolysis of protected ethoxyethyl group, the characteristic resonance signal for methine group proton (—OCH(CH$_3$)O—) at 4.65–4.76 ppm disappeared completely (100%) in spectrum for PS-Gly [Fig. 1(B)], which confirmed the successful synthesis of macroinitiator PS-Gly.

Using the obtained PS-Gly as macroinitiator and diphenylmethylpotassium (DPMK) as deprotonated agent (Scheme 1),
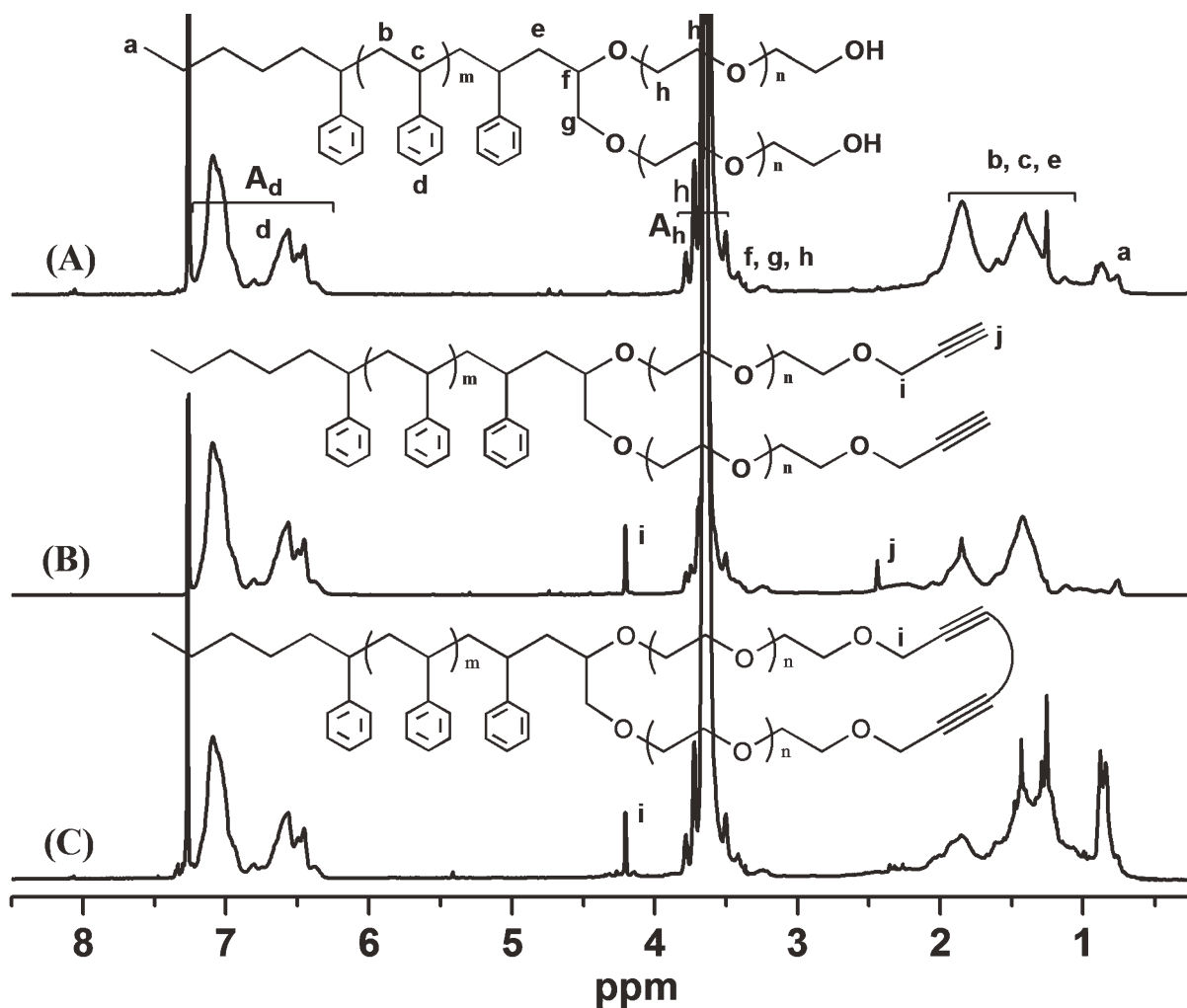
FIGURE 2 The ^{1}H NMR spectra of PS-*b*-(PEO-OH)$_2$ (A), PS-*b*-(PEO-Alkyne)$_2$ (B), and PS-*b*-(c-PEO) (C) (in CDCl$_3$).

the ROP of EO proceeded in THF smoothly for AB$_2$ star-shaped PS-*b*-(PEO-OH)$_2$. Figure 2(A) showed the ^{1}H NMR spectrum of AB$_2$ star-shaped PS-b-(PEO-OH)$_2$ copolymers, besides the resonance signals at 6.30–7.30 ppm for aromatic protons (—C$_6$**H**$_5$) on PS block, the appearance of resonance signals at 3.53–3.70 ppm for methylene group protons (—C**H**$_2$C**H**$_2$O) on PEO block confirmed the successful polymerization of EO. The molecular weight of PS-*b*-(PEO-OH)$_2$ ($M_{n,NMR,[PS-b-(PEO-OH)2]}$) was determined according to the already known $M_{n,SEC,PS}$ and $M_{n,NMR,PS}$ of PS-EEGE using Formula (1) (Fig. 2):

$$M_{n,NMR,[PS-b-(PEO-OH)2]} = \frac{5 \times A_h \times M_{n,SEC,PS}}{4 \times 104 \times A_d} \times 44 + [M_{n,NMR,PS} - 72] \quad (1)$$

Here, A_h and A_d were the integral area of the peak at 3.53–3.70 ppm for methylene group protons (—C**H**$_2$C**H**$_2$O) on PEO block and at 6.30–7.30 ppm for aromatic protons (—C$_6$**H**$_5$) on PS block, respectively. The value of 44 was the molecular weight of EO monomer unit, and the value of 72 was the mass of deprotected ethoxyethyl group.

In the presence of NaH, alkyne group was introduced onto PEO arm-end by reacting PS-*b*-(PEO-OH)$_2$ with propargyl bromide. Figure 2(B) showed ^{1}H NMR spectrum of PS-*b*-(PEO-Alkyne)$_2$, the characteristic resonance signal for methylene group protons (—OC**H**$_2$C≡CH) at 4.20 ppm and for methine group proton (—CH$_2$C≡C**H**) at 2.44 ppm were all detected and discriminated clearly. The efficiency of propargylation could be determined by using the Formula 2:

$$\text{E.F.} = \frac{\frac{A_i/4}{A_d/5}}{M_{n,NMR,PS}/104} \times 100\% \quad (2)$$

where A_i was the integral area of the peak at 4.20 ppm for methylene group protons (—OC**H**$_2$C≡CH), and others were the same as defined before. The obtained E.F. for PS-*b*-(PEO-Alkyne)$_2$(I) PS-*b*-(PEO-Alkyne)$_2$(II) were 99.5% and 99.7%, respectively. Comparing with the size-exclusion chromatography (SEC) of PS-EEGE, a monomodal peak and low polydispersity indice (PDI) shifted to the shorter retention time corresponded to PS-*b*-(PEO-Alkyne)$_2$ (Fig. 3, Table 1) again confirmed the successful synthesis of AB$_2$ star-shaped precursors.
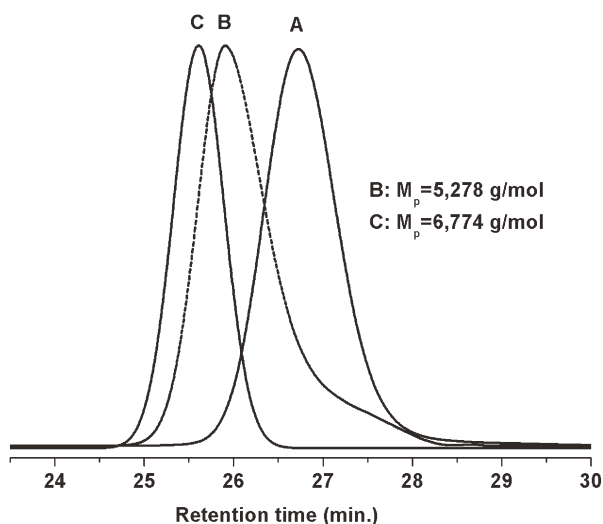
FIGURE 3 The SEC curves of PS-EEGE(A) (M_n = 3,800 g mol^{-1}, PDI = 1.04), PS-b-(PEO-Alkyne)$_2$ (C) (M_n = 6,300 g mol^{-1}, PDI = 1.05) and PS-b-(c-PEO)(B) (M_n = 5,100 g mol^{-1}, PDI = 1.10).

Synthesis and Characterization of Tadpole-shaped PS-b-(c-PEO) Copolymers

In the pyridine/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA)/Cu(I)Br system, the Glaser coupling between alkyne and alkyne groups at PEO arm-end proceeded at room temperature. By comparing the curves of Figure 3(B,C), it was found that the SEC curve of tadpole-shaped copolymer shift to longer elution time, that was, the hydrodynamic volume of tadpole-shaped products was noticeably smaller than that of their star-shaped precursors. The unimodal SEC curves of tadpole-shaped copolymers indicated that the cyclization process was complete and rather successful. The R ratio (0.78 and 0.68) between the apparent peak molar mass (M_p) corresponding to the signals of tadpole-shaped and star-shaped copolymer was derived from SEC (Table 1), which reflected the difference in solution dimension of two topological copolymer chains. From ^{1}H NMR spectrum [Fig. 2(C)], the resonance signal for methine proton (—CH$_2$C≡CH) at 2.44 ppm disappeared completely and also confirmed the successful formation of tadpole-shaped PS-b-(c-PEO) copolymers with the efficiency of almost 100%.

Furthermore, the tadpole-shaped copolymers and their precursors were also traced by Fourier Transform Infrared (FTIR) spectroscopy (Fig. 4). In all three spectra, a multipeak at 1605, 1493, and 1442 cm^{-1} (benzene bend vibration) and a strong band at 2992–2756 cm^{-1} for the methylene group (—CH$_2$CH—) attributed to PS were detected, as well as the strong band at 1115 cm^{-1} was attributed to the ether linkage (—C—O—C—) on PEO chains. Clearly, the stretch absorption at 3248 cm^{-1} for alkyne group (—C≡CH) was detected in Figure 4(B) after the modification with propargyl bromide, and this characteristic signal was again disappeared in Figure 4(C) once the 1,3-dinyes group formed after Glaser coupling reaction. These results were consistent well with the copolymer structure defined above and further confirmed the successful synthesis of tadpole-shaped copolymer.

Thermal Properties of Star-shaped PS-b-(PEO-OH)$_2$ and Tadpole-shaped PS-b-(c-PEO)

The melting and crystallization behaviors of copolymers were investigated by differential scanning calorimetry (DSC) as shown in Figure 5 and Table 2. The crystallization temperature (T_c) was obtained from the cooling run, and the melting temperature (T_m) and the degree of crystallinity (X_c) were obtained from the second heating run. Clearly, only a single melting and a crystallization peak assigned to PEO blocks were observed. Values of the enthalpy of fusion ($\Delta_{fus}H$) were obtained from peak areas, and T_m or T_c were obtained from positions of peak maxima (Table 2).

The results showed that T_c, T_m, and X_c of tadpole-shaped PS-b-(c-PEO) copolymers were lower than that of star-shaped PS-b-(PEO-OH)$_2$ copolymers, which might be derived from their structural difference of copolymers with the same compositions. To represent this difference, the entropy of fusion were calculated from $\Delta_{fus}S = \Delta_{fus}H/T_m$, and the yielded values for PS-b-(c-PEO) were lower than that for PS-b-(PEO-OH)$_2$. As was expected, the linear and cyclic PEO segment are similarly conformationally restricted in the crystalline state, but the stem of a cyclic PEO was more restricted in the melt state, and the tadpole-shaped PS-b-(c-PEO) copolymers would give the lower parameters of T_c, T_m, and X_c. This similar phenomenon was also reported by others for linear PEO homopolymer and the corresponding cyclic derivative.[30]
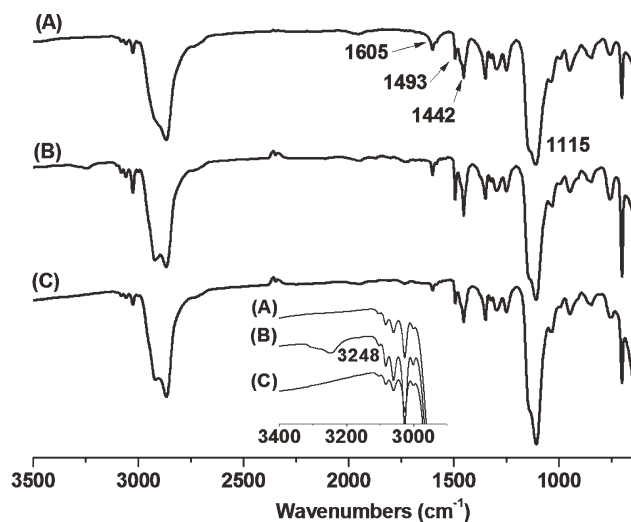
TABLE 1 The Data of Tadpole-Shaped PS-b-(c-PEO) and its Precursor of Star-Shaped PS-b-(PEO-Alkyne)$_2$

	Star-shaped PS-b-(PEO-Alkyne)$_2$				Tadpole-shaped PS-b-(c-PEO)			
Entry	$M_{n,SEC}$[a] (g mol^{-1})	$M_{p,SEC}$[a] (g mol^{-1})	PDI[a]	$M_{n,NMR}$[b] (g mol^{-1})	$M_{n,SEC}$[a] (g mol^{-1})	$M_{p,SEC}$[a] (g mol^{-1})	PDI[a]	R[c]
I	6,300	6,774	1.05	6,900	5,100	5,278	1.10	0.78
II	12,300	15,873	1.07	16,500	9,200	10,756	1.12	0.68

[a] Determined by SEC with THF as solvent using PS standards.
[b] The molecular weights of star-shaped copolymers were calculated according to ^{1}H NMR using Formula: $M_{n,NMR,[PS-b-(PEO-Alkyne)2]} = M_{n,NMR,[PS-b-(PEO-OH)2]} + 38 \times 2$, where the value of 38 was the mass difference between a propargyl group and a proton.

[c] The R was ratio of the apparent peak molar masses (M_p) derived from SEC curves of tadpole-shaped copolymers to their precursors of star-shaped copolymers.
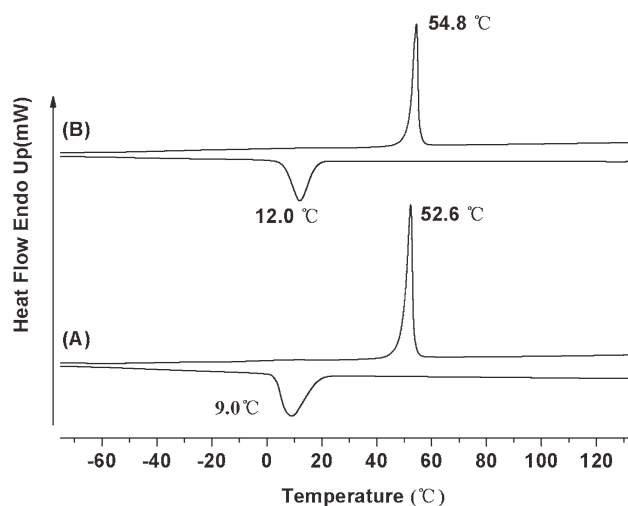
FIGURE 4 FTIR spectra of PS-*b*-(PEO-OH)$_2$ (A), PS-*b*-(PEO-Alkyne)$_2$ (B), and PS-*b*-(c-PEO) (C).

FIGURE 5 DSC curves of PS-*b*-(c-PEO) (A) and PS-*b*-(PEO-OH)$_2$ (B) in cooling run and the second heating run.

On the other hand, we also found that the parameters of T_c, T_m, and X_c decreased with the length decrease of PEO segment from Entry II to Entry I, which should be attributed mainly to the crystalline imperfection of the short chain length and lower content of PEO segments in copolymers (Table 2). Using a linear PEO homopolymer and the corresponding cyclic derivatives (Entry III, the detailed synthetic procedure was accorded to our previous work[23]) as comparison, the highest X_c were obtained for the PEO homopolymer, which further confirmed the interference of PS segment on crystallization behavior of PEO segment.

EXPERIMENTAL

Materials
The styrene (St, Aldrich, 98%) monomer was washed with 10% NaOH aqueous solution followed by water three times successively, dried over CaH$_2$, and distilled under reduced pressure. The ethylene oxide (EO) monomer and toluene, propargyl bromide (>99%) were dried by CaH$_2$ and then distilled, stored at −20 °C before use. Tetrahydrofuran [THF, Sinopharm Chemical Reagent Co. (SCR), 99%] were refluxed

over sodium wire, then distilled from sodium naphthalenide solution. Copper(I) bromide (Cu(I)Br, 95%) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried *in vacuo*. PMDETA (Aldrich) was used as received. All other regents and solvents were purchased from SCR and used as received except for declaration.

DPMK solution was prepared according to the literature,[31] and the concentration was 0.75 mol L^{-1}. EEGE was synthesized from glycidol and ethyl vinyl ether according to Fitton et al.[32] and distilled under reduced pressure (b.p. 152–154 °C), and the purity exceeded 99.7 GC%.[33] *n*-Butyllithium (*n*-BuLi) was prepared from butyl chloride and lithium metal according to the literature[34] and analyzed by the double-titration method[35] with the concentration of 1.45 mol L^{-1}.

Measurements
SEC was performed in THF at 35 °C with an elution rate of 1.0 mL min^{-1} on an Agilent1100 with a G1310A pump, a G1362A refractive index detector and a G1314A variable wavelength detector, and the polystyrene was used as standard samples. ^{1}H NMR spectra were obtained at a DMX500

TABLE 2 The Thermal Properties of Tadpole-Shaped PS-*b*-(c-PEO) and Star-Shaped PS-*b*-(PEO-OH)$_2$

	Star-shaped PS-*b*-(PEO-OH)$_2$					Tadpole-shaped PS-*b*-(c-PEO)				
Entry	T_c (°C)[a]	T_m (°C)[b]	$\Delta_{fus}H$ (J g^{-1})[c]	$\Delta_{fus}S$ [J (K g)$^{-1}$][d]	X_c (%)[e]	T_c (°C)[a]	T_m (°C)[b]	$\Delta_{fus}H$ (J g^{-1})[c]	$\Delta_{fus}S$ [J (K g)$^{-1}$][d]	X_c (%)[e]
I	8.9	48.8	99.4	0.3087	46.5	5.5	46.3	76.6	0.2398	35.8
II	12.0	54.8	125.1	0.3815	58.5	9.0	52.6	88.6	0.2720	41.5
III[f]	35.9	55.9	155.8	0.4735	72.9	17.2	48.5	121.8	0.3787	57.0

[a] T_c denote the crystallization temperatures of PEO segments in the second cooling run.
[b] T_m were the melting points of PEO segments in the second heating run.
[c] $\Delta_{fus}H$ denote the fusion enthalpies of PEO segments in the second heating run.

[d] $\Delta_{fus}S = \Delta_{fus}H/T_m$.
[e] $X_c = \Delta_{fus}H/\Delta_{fus}H^o$, where $\Delta_{fus}H^o$ is 213.7 J g^{-1} accorded to ref. 29.
[f] Entry III was a comparison of linear PEO homopolymer ($M_{n,SEC}$ = 4,800 g mol^{-1}, PDI = 1.06) and the corresponding cyclic derivative($M_{n,SEC}$ = 3,800 g mol^{-1}, PDI = 1.08).

MHz spectrometer with tetramethylsilane as the internal standard and $CDCl_3$ as the solvent. FTIR spectra were recorded on NEXUS 470 FTIR instrument, the polymer samples were dissolved in dry THF and then cast onto a NaCl disk to form the film by the evaporation of the solvent under infrared lamp. DSC was performed on a DSC Q2000 thermal analysis system (Shimadzu, Japan). Samples were first heated from -80 to 150 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere, followed by cooling to -80 °C at -10 °C min^{-1} after stopping at 150 °C for 3 min, and finally heating to 150 °C at 10 °C min^{-1} after stopping at -80 °C for 3 min.

Synthesis of Macroinitiator of Functionalized Polystyrene-glycerol (PS-Gly) with two Hydroxyl Groups at ω-End

The functionalized PS-EEGE was synthesized by anionic polymerization of St according to our previous work under the nitrogen (N_2) atmosphere,[28] where the gas-tight rubber tube was used to seal the reactor, and the syringe was used to introduce the reagents. Typically, the St (15 mL), cyclohexane, (140 mL), and THF (4 mL) were charged into a 500 mL dried ampoule under nitrogen atmosphere, then the n-Bu$^-$Li$^+$ solution (2.41 mL, 3.50 mmol) was injected by a syringe under magnetic stirring. The reaction was kept at room temperature for 3 h, then the mixture of EEGE (3.0 mL, 20.55 mmol) and THF (6 mL) was added promptly and the system was stirred for another 3 h before the termination by methanol. After the solvent was evaporated, the product was purified by dissolution/precipitation twice with THF/methanol and the obtained white powder of functionalized PS-EEGE was dried under vacuum at 45 °C for 12 h with a constant weight (13.50 g, 99.0% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.80 (m, $CH_3(CH_2)_3$—), 1.13–2.01 (m, CH_3CH_2O—, $CH_3(CH_2)_3$—, aliphatic main chain —CH_2CH— of PS chain), 3.05–3.63 (m, CH_3CH_2O—, —$CH(OH)CH_2O$—, integral area 5.03), 4.65–4.76 (m, —$OCHO$—, integral area 1.00), 6.30–7.30 (m, 5H, aromatic —C_6H_5 of PS chain, integral area 179.71). $M_{n,SEC}$ = 3800 g mol^{-1}, PDI = 1.04, $M_{n,NMR}$ = 3900 g mol^{-1}.

The macroinitiator of functionalized polystyrene-glycerol (PS-Gly) with two hydroxyl groups at ω-end was synthesized by hydrolysis of ethoxyethyl group on PS-EEGE. Typically, 10.00 g PS-EEGE was dissolved in 150 mL THF, then 13 mL HCl (37%) was added and stirred for 2 h at room temperature. The PS-Gly was obtained by removing the formed salts and precipitation in methanol twice, and dried under high vacuum at 45 °C for 12 h till to a constant weight (9.62 g, 96.2% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 3.02–3.61 (m, —$CH(CH_2OH)OH$, integral area 3.00), 6.30–7.30 (m, 5H, aromatic —C_6H_5 of PS chain, integral area 178.84).

Synthesis of AB$_2$ Star-shaped Polystyrene-b-[Poly(ethylene oxide)-hydroxy]$_2$ [PS-b-(PEO-OH)$_2$] with a Hydroxyl Group at Each PEO Arm-end and Polystyrene-b-[Poly(ethylene oxide)-Alkyne]$_2$ [PS-b-(PEO-Alkyne)$_2$] with an Alkyne Group at Each PEO Arm-end

Typically, the dried PS-Gly (4.52 g) was dissolved in 130 mL THF and charged into a 250 mL dried ampoule, and the

needed DPMK solution (3.17 mL, 2.38 mmol) was added dropwise by a syringe under magnetic stirring. Then, the ampoule was placed into an ice bath and the cold EO (4.39 mL, 3.82 g) was added quickly, and the solution was heated to 55 °C and stirred for 72 h. The solution was terminated by acid methanol, and the solvent was evaporated, subsequently, the copolymers of PS-b-(PEO-OH)$_2$ were precipitated into cold petroleum ether (30–60 °C) slowly and dried under vacuum at 45 °C for 12 h till to a constant weight (7.99 g, 95.8% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.80 (m, $CH_3(CH_2)_3$—), 1.13–2.01 (m, $CH_3(CH_2)_3$—, aliphatic main chain —CH_2CH— of PS chain), 3.05–3.70 (m, —$CH(O$—)CH_2O—, —CH_2CH_2O— of PEO block, integral area 145.98), 6.30–7.30 (m, 5H, aromatic —C_6H_5 of PS chain, integral area 100.00).

For the preparation of copolymer PS-b-(PEO-Alkyne)$_2$, dried PS-b-(PEO-OH)$_2$ (4.01 g) was added into a 150 mL round-bottomed flask. The polymer was dissolved in THF (80 mL), and then NaH (0.1392 g, 5.8 mmol) was added. The solution was allowed to stir at 40 °C for 1.0 h, and then the propargyl bromide (0.45 mL, 5.8 mmol) was added dropwise at 0–5 °C. The solution was stirred at 25 °C for 24 h, and the pH of the solution was adjusted to 7.0 by addition of 0.1 mol L^{-1} hydrochloric solution. After THF was removed by rotary evaporation, the products were extracted with CH_2Cl_2 (100 mL $\times$ 2), and then the organic layer was dried over $MgSO_4$ before purification by precipitation into anhydrous ethyl ether three times, and dried under vacuum at 45 °C for 12 h till to a constant weight (3.42 g, 85.3% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 2.44 (—$CH_2C\equiv CH$, integral area 1.11), 3.05–3.70 (m, —$CH(O$—)CH_2O—, —CH_2CH_2O— of PEO block, integral area 147.21), 4.20 (—$CH_2C\equiv CH$, integral area 2.21), 6.30–7.30 (m, 5H, aromatic —C_6H_5 of PS chain, integral area 100.00). $M_{n,SEC}$ = 6300 g mol^{-1}, PDI = 1.05, $M_{n,NMR}$ = 6900 g mol^{-1}. FTIR: 1605, 1493, 1442, and 1115 cm^{-1}, 3248 (—$C\equiv CH$) cm^{-1}.

Synthesis of Tadpole-shaped Polystyrene-b-[cyclic-Poly(ethylene oxide)] PS-b-(c-PEO) by Glaser Coupling Reaction

Typically, into a 1000 mL round bottomed flask was added pyridine (300 mL), Cu(I)Br (0.3502 g, 2.81 mmol), PMDETA (0.52 mL, 2.81 mmol) and the solution was stirred for 2.0 h. To a separate flask, PS-b-(PEO-Alkyne)$_2$ (0.2000 g, 0.058 mmol alkyne groups) was dissolved in pyridine (200 mL), and this solution was then added into the Cu(I)Br/PMDETA system via a peristaltic pump at a rate of 4.17 mL h^{-1}. After another 12 h, pyridine was removed by reduced pressure distillation. The crude product was purified by passing through a neutral alumina column using CH_2Cl_2 as eluent to remove the copper catalyst residues. After concentration, the product was decentralized in H_2O and purified by an ultrafiltration membrane to remove low-molecular weight impurities. The pure products were recovered by precipitation into cold petroleum ether and dried under vacuum at 45 °C for 12 h till to a constant weight (0.1452 g, 72.6% yield). ^{1}H NMR ($CDCl_3$) δ ppm: 0.80 (m, $CH_3(CH_2)_3$—), 1.13–2.01 (m, $CH_3(CH_2)_3$—, aliphatic main chain —CH_2CH— of PS chain), 3.05–3.70 (m, —$CH(O$—)CH_2O—, —CH_2CH_2O— of PEO block,

integral area 146.86), 4.20 ($-CH_2C\equiv C-$, integral area 2.20), 6.30–7.30 (m, 5H, aromatic $-C_6H_5$ of PS chain, integral area 100.00). $M_{n,SEC} = 5100$ g mol^{-1}, PDI = 1.10.

CONCLUSIONS

The tadpole-shaped PS-b-(c-PEO) contained a linear tail chain of PS and a cyclic head chain of PEO were synthesized by combination of Glaser coupling with living anionic polymerization and ROP. The cyclization procedure was rather efficient and successful under mild conditions such as pyridine/Cu(I)Br/PMDETA system. By comparing tadpole-shaped PS-b-(c-PEO) with its precursors of star-shaped PS-b-(PEO-OH)$_2$ copolymers, the thermal properties were determined to investigate the influence of architecture on properties. The results showed that tadpole-shaped copolymers had lower T_m, T_c, and X_c than that of star-shaped copolymers, respectively, and these phenomenon could be attributed to the higher steric effect and restricted conformation in melt state.

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