Synthesis of Twin-Tail Tadpole-Shaped (Cyclic Polystyrene)-*block*-[Linear Poly (*tert*-butyl acrylate)]$_2$ by Combination of Glaser Coupling Reaction with Living Anionic Polymerization and Atom Transfer Radical Polymerization

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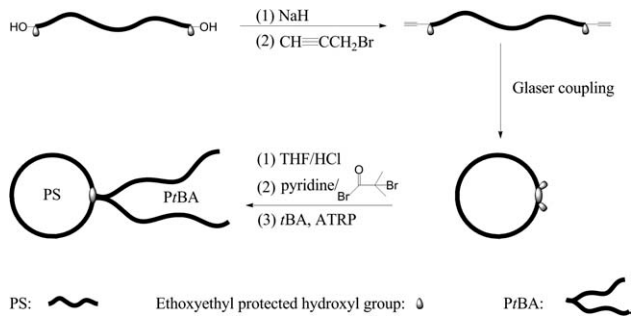
ABSTRACT: The twin-tail tadpole-shaped (cyclic polystyrene)-*block*-[linear poly (*tert*-butyl acrylate)]$_2$ [(*c*-PS)-*b*-(*l*-P*t*BA)$_2$] was synthesized by combination of Glaser coupling reaction with atom transfer radical polymerization (ATRP) and living anionic polymerization (LAP). First, the telechelic PS with an active and an ethoxyethyl-protected hydroxyl groups at both ends was prepared by LAP of St monomers using lithium naphthalenide as initiator and terminated by 1-ethoxyethyl glycidyl ether. And the alkyne groups were introduced onto each PS end by selectively reaction of active hydroxy group with propargyl bromide in NaH/tetrahydrofuran (THF) system. Then, the intramolecular cyclization was carried out by Glaser coupling reaction in pyridine/Cu(I)Br system in air atmosphere. Finally, the macroinitiator of *c*-PS with two bromine groups at the junction point was synthesized via the cleavage of ethoxyethyl group and the subsequent esterification of the deprotected hydroxyl groups with 2-bromoisobutyryl bromide. The copolymer of (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ was obtained by ATRP of *t*BA monomers, and the P*t*BA segment was also hydrolyzed for (cyclic polystyrene)-*block*-(linear polyacrylic acid)$_2$ [(*c*-PS)-*b*-(*l*-PAA)$_2$]. The target copolymers and all intermediates were well characterized by GPC, MALDI-TOF MS, and ^{1}H NMR in detail. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 2444–2451, 2012

KEYWORDS: atom transfer radical polymerization; glaser coupling; living anionic polymerization; polystyrene; poly (*tert*-butyl acrylate); twin-tail tadpole-shaped

INTRODUCTION In the past decades, enduring attentions have been paid to nonlinear copolymers,[1] such as miktoarm star,[2,3] comb-shaped,[4,5] linear-dendritic,[6–8] and cyclic-based copolymers.[9–11] Compared with linear analogues, cyclic polymers show distinctively unique characteristics and physical properties due to their closed ring topology. Therefore, the macrocyclic-based copolymers, including cyclic block,[12] eight-shaped,[13] θ-shaped,[14,15] "Jelly-fish" shaped,[16,17] and tadpole-shaped[18–22] copolymers, have been developed more rapidly.

Among them, the tadpole-shaped copolymer, which consists of a cyclic polymer as head and a linear polymer as tail, is less studied,[18–22] and only a few articles reported their synthesis and characterization. Considering the synthesis of tadpole-shaped linear-cyclic diblock copolymers, three typical strategies have been developed. The first one relies on the intramolecular ring-closure reaction, starting from specially designed linear precursor with two complementary reactive groups located at the chain middle and terminal, respectively.[21,22] The second one uses the intermolecular ring-closure reaction between a functional three-armed star precursor and a complementary reactive reagent.[18,23] The third one uses a cyclic polymer with a functional group to couple with linear polymer chain or to initiate polymerization of the monomer.[24] For example, using the first strategy, Pan and coworkers synthesized (cyclic polystyrene)-*b*-[linear poly (N-isopropylacrylamide)] [(*c*-PS)-*b*-(*l*-PNIPAM)] via intramacromolecular "click" ring-closure reaction of diblock precursor with azido and alkyne groups located at the chain middle and chain terminal, respectively.[22] Using the similar approach, Li and coworkers synthesized amphiphilic linear-cyclic diblock copolymers consisting of PS ring and linear poly(ethylene oxide) (PEO) tail.[25] Relying on the third strategy, Takahito et al. synthesized the tadpole-shaped (*c*-PS)-*b*-(*l*-PS) by the reaction of *c*-PS having an amine in the main chain with carboxylic-terminated *l*-PS.[18] Liu and coworkers synthesized well-defined amphiphilic and thermoresponsive tadpole-shaped linear-cyclic diblock [cyclic poly (N-isopropylacrylamide)]-*b*-(linear Polycaprolactone) [(*c*-PNIPAM)-*b*-(*l*-PCL)]copolymers via ring-opening polymerization (ROP) directly initiating from cyclic precursors.[19]



SCHEME 1 Synthetical illustration of (*c*-PS)-*b*-(*l*-P*t*BA)$_2$.

As for more complex tadpole-shaped copolymer with twin-tail, there are fewer reports.[26] Tezuka's group using "electrostatic self-assembly and covalent fixation" process synthesized a series of tadpole constructions, including twin-tail tadpole-shaped homopolymer [cyclic poly (tetrahydrofuran)-*block*-linear poly (tetrahydrofuran)].[14] However, this synthetical route is based on anionic and cationic polymerizations, rigorous operation conditions are needed, and especially the monomers used are largely limited.

Recently, our group used Glaser coupling reaction between terminal alkyne groups as a new ring-closure technique to synthesize monocyclic PEO and PS successfully.[27] Using this method, telechelic polymer precursors can be prepared through diverse polymerization techniques from difunctional initiators, and alkyne groups could be easily introduced. Moreover, the intramolecular cyclization can be carried out under mild conditions without deoxygenation in high efficiency. Herein, we introduce an active and a protected hydroxyl group onto both PS ends by using 1-ethoxyethyl glycidyl ether (EEGE) as capping agent to living species of PS$^-$Li$^+$. After the modification of active hydroxyl groups into alkyne groups and the subsequent Glaser coupling reaction, there will be two ethoxyethyl-protected hydroxyl groups at the junction point. The protected hydroxyl groups might be recovered and used for ROP of ε-caprolactone[28] and ethylene oxide (EO),[29] or transformed into the dithio group for reversible addition-fragmentation chain transfer polymerization RAFT[30] and the halide group for atom transfer radical polymerization (ATRP)[31,32] or single-electron transfer living radical polymerization (SET-LRP)[33–36] by simple variation of the end groups. In this contribution (Scheme 1), a novel and an universal route is suggested to synthesize the twin-tail tadpole-shaped copolymers with cyclic polystyrene (*c*-PS) as head and linear poly (*tert*-butyl acrylate) or poly (acrylic acid) (PAA) as twin-tail by combination of Glaser coupling reaction with ATRP and living anionic polymerization (LAP) mechanisms.

RESULTS AND DISCUSSION

For the synthesis of twin-tail tadpole-shaped (*c*-PS)-*b*-(*l*-P*t*BA)$_2$, it can be shown as the following steps (Scheme 2): (1) The telechelic polystyrene with a propargyl group and an ethoxyethyl protected hydroxyl group at both ends [(≡/*p*-OH)-PS-(≡/*p*-OH), *p*-OH represented the protected hydroxyl group] was sequentially prepared by LAP of St monomers, termination with EEGE, and then selective propargylation of active hydroxyl groups with propargyl bromide. (2) The intramolecular cyclization of (≡/*p*-OH)-PS-(≡/*p*-OH) was carried out by Glaser coupling reaction in pyridine/Cu(I)Br system in air atmosphere. (3) The macroinitiator with two bromoisobutyryl groups at the junction point [(*c*-PS)-(Br)$_2$] was obtained by hydrolysis of cyclic polystyrene with two ethoxyethyl protected hydroxyl groups at the junction point [(*c*-PS)-(*p*-OH)$_2$] with HCl, then esterification of the recovered (*c*-PS)-(OH)$_2$ with 2-bromoisobutyryl bromide, and finally the ATRP procedure of *t*BA from macroinitiator (*c*-PS)-(Br)$_2$ for target (*c*-PS)-*b*-(*l*-P*t*BA)$_2$.

Synthesis and Characterization of Telechelic Precursors

The telechelic polystyrene with an active hydroxyl group and an ethoxyethyl protected hydroxyl group at both ends [(HO/*p*-OH)-PS-(HO/*p*-OH)] was synthesized by LAP of St monomers initiated from lithium naphthalenide,[27] and EEGE was used as capping agent according to our previous work.[29,37] Figure 1 (Line A) showed the GPC result of (HO/*p*-OH)-PS-(HO/*p*-OH), the monomodal peak and low PDI (1.05) confirmed that the LAP and the capping reaction were successful.

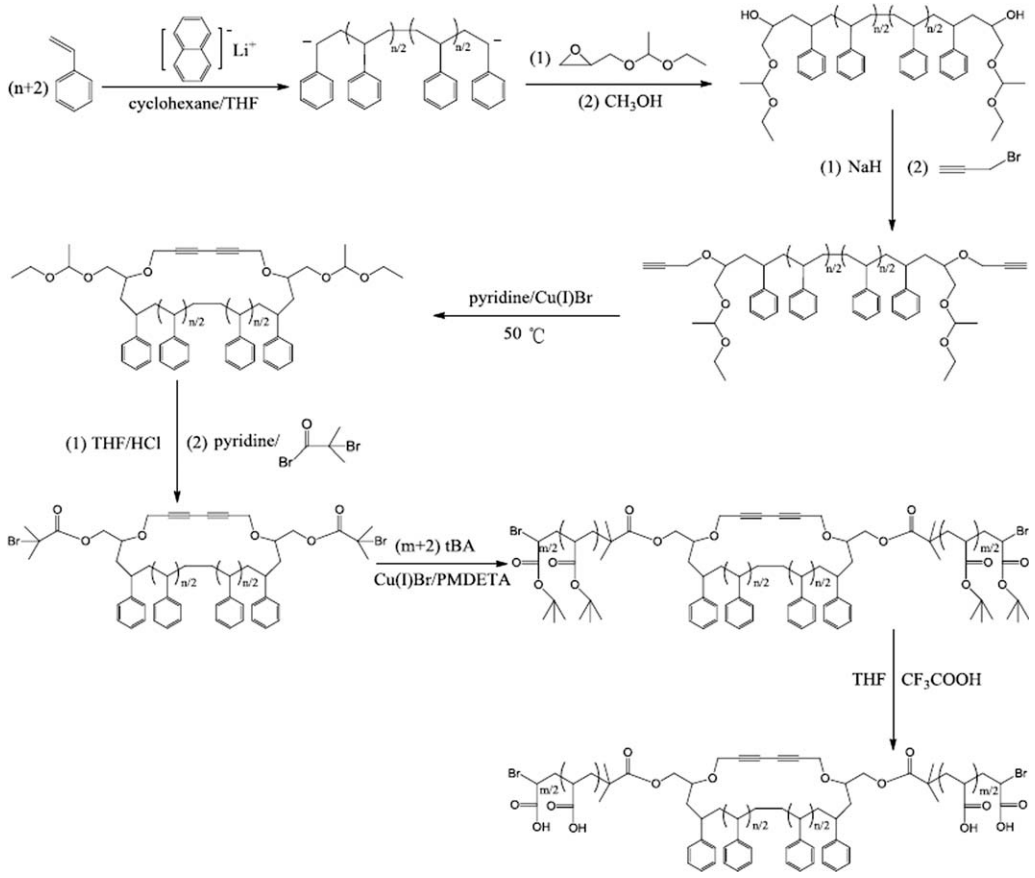
In Figure 2(A), except for the characteristic resonance signals for aromatic protons (—C$_6$***H***$_5$) on PS chain at 6.30–7.30 ppm (a), the ^{1}HNMR spectrum of (HO/*p*-OH)-PS-(HO/*p*-OH) also exhibited the characteristic resonance signals due to ethoxyethyl group proton (—OC**H**(CH$_3$)O—) at 4.50–4.62 ppm (f) and hydroxymethyl group proton (—C**H**(OH)—) at 3.52 ppm (d), which also proved the successful introduction of EEGE onto both polystyrene ends. The functionalization efficiency of end-capping (E.F.$_{\text{End-capping}}$) was calculated according to ^{1}H NMR spectrum and **Formula 1**:

$$\text{E.F.}_{\text{End-capping}} = \frac{A_f}{\frac{A_a}{\frac{M_{n(\text{GPC}),\text{PS}}}{104}\times 5}\times 2}\times 100\% \qquad (1)$$

where the A_a and A_f were the integral area of the aromatic protons (—C$_6$***H***$_5$) on PS chain at 6.30–7.30 ppm (a) and the characteristic ethoxyethyl group proton (—OC**H**(CH$_3$)O—) at 4.50–4.62 ppm (f), respectively. The value of 104 was the molecular weight of St unit. $M_{n(\text{GPC}),\text{PS}}$ was the molecular weight of telechelic (HO/*p*-OH)-PS-(HO/*p*-OH) by GPC measurement. The obtained E. F.$_{\text{End-capping}}$ for series A and series B were 98.0 and 97.0%, respectively.

In the MALDI-TOF MS spectrum for (HO/*p*-OH)-PS-(HO/*p*-OH) [Fig. 3(A)], the molecular mass of each peak was expressed: 104.1 (St) × n + 147.2 (EEGE) × 2 + 107.9 (Ag$^+$), where *n* was the number of St unit. Taking peak 3631.1 *m*/*z* as an example, n was calculated as 31.0, which meant there are 31.0 St units corresponding to this peak. Simultaneously, there were two minor peaks between main peaks, which might be contributed to the byproduct resulted from incomplete end-capping. These byproducts would form multiple segments in the following cyclization procedure and could be removed by fractional precipitation.

The telechelic (≡/*p*-OH)-PS-(≡/*p*-OH) was prepared by an end group transformation reaction of active hydroxyl groups



SCHEME 2 The synthetical procedure for (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ and (*c*-PS)-*b*-(*l*-PAA)$_2$.

on (HO/*p*-OH)-PS-(HO/*p*-OH) with propargyl bromide in the presence of NaH.[38] In Figure 2(B), the ^{1}H NMR spectrum of (≡/*p*-OH)-PS-(≡/*p*-OH) exhibits the characteristic resonance signals due to alkynyl proton and methylene protons of propargyl at 2.29 ppm (k) and 3.85–4.02 ppm (j), respectively. According to ^{1}H NMR spectrum, the E.F.$_{\text{Propargylation}}$ of hydroxyl groups into alkyne groups were obtained by using the **Formula 2**:

$$\text{E.F.}_{\text{Propargylation}} = \frac{\frac{A_j}{2}}{A_f} \times 100\% \quad (2)$$

where A_j was the integral area of methylene group protons (—OC**H**$_2$C≡CH) at 3.85–4.02 ppm (j), A_f was the integral area of ethoxyethyl group proton (—OC**H**(CH$_3$)O—) at 4.50–

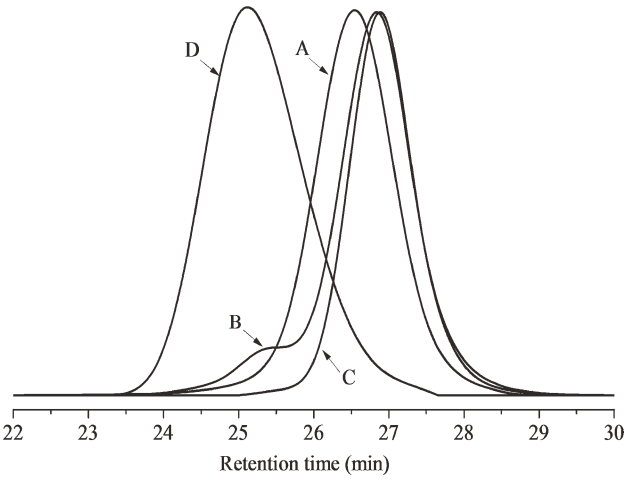


FIGURE 1 GPC profiles of (HO/*p*-OH)-PS-(HO/*p*-OH) (A) (M_n = 3.8 × 10^3 g/mol, PDI = 1.05), (*c*-PS)-(*p*-OH)$_2$ before (B) and after (C) fractional precipitation, and (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ (D) (M_n = 6.9 × 10^3 g/mol, PDI = 1.11).

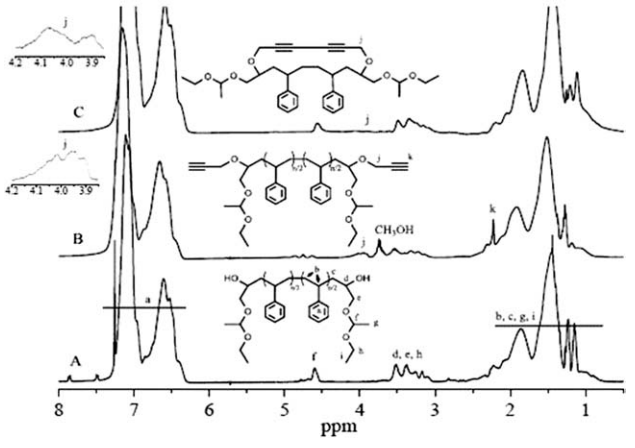


FIGURE 2 ^{1}H NMR (500 MHz) spectra of (HO/*p*-OH)-PS-(HO/*p*-OH) (A), (≡/*p*-OH)-PS-(≡/*p*-OH) (B), and (*c*-PS)-(*p*-OH)$_2$ (C) in CDCl$_3$.

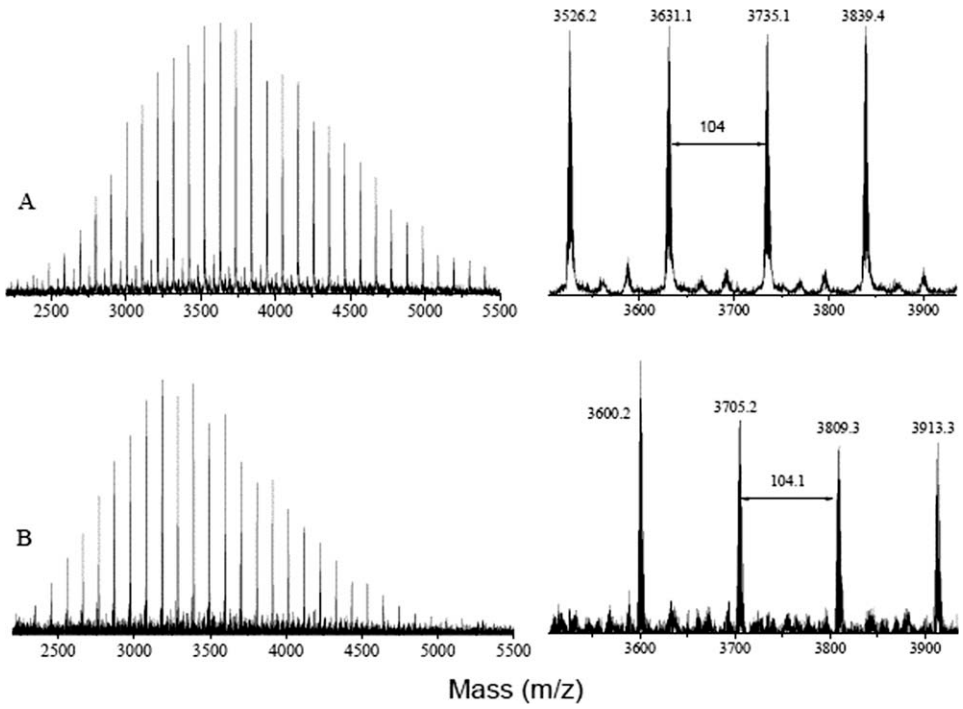


FIGURE 3 The MALDI-TOF MS of (HO/*p*-OH)-PS-(HO/*p*-OH) (A) and (*c*-PS)-(*p*-OH)$_2$ (B).

4.62 ppm (f). The obtained E.F.$_{\text{Propargylation}}$ with high values (99.0% for series A and 98.0% for series B, respectively) confirmed the successful transformation reaction at both PS ends.

Synthesis and Characterization of (*c*-PS)-(*p*-OH)$_2$

The intramolecular cyclization of linear (≡/*p*-OH)-PS-(≡/*p*-OH) was carried out at 50 °C in air atmosphere using Cu(I)Br as catalytic system. Herein, pyridine was used as solvent and ligand simultaneously, the small amount of oxygen dissolved in pyridine was acted as oxidant. In this case, the common ligand as PMDETA was not necessary for the reason that it was difficult to remove during the purification procedure.

By comparing the GPC curves of (*c*-PS)-(*p*-OH)$_2$ (Fig. 1, Line B) with that of (HO/*p*-OH)-PS-(HO/*p*-OH) (Fig. 1, Line A), the noticeable shifting of $M_{\text{n,GPC}}$ may contribute to the different hydrodynamic volume of (*c*-PS)-(*p*-OH)$_2$ from their linear precursors, and the former was smaller than that of the latter due to cyclic structure. The R factors were the ratio of the apparent peak molar mass (M_{p}) corresponding to the signals of (*c*-PS)-(*p*-OH)$_2$ and (HO/*p*-OH)-PS-(HO/*p*-OH) derived from GPC (Table 1), which reflected the difference in the solution dimensions of the two polymer chains with different topological structure. In this work, the *R* values (0.87 and 0.81) agreed with the data (0.76–0.95) reported in refs. [39] and [40]. However, the GPC curve of (*c*-PS)-(*p*-OH)$_2$ showed a shoulder peak corresponding to the linear byproduct by the intermolecular reaction at a lower elution time. In our previous work,[27] it showed that a monomodal GPC profile of cyclic PEO or polystyrene with the cyclization efficiency of almost 100%. Herein, it was presumed that the incomplete end-capping ration of EEGE and propargylation lead to formation of multiple segments, and the method of fractional precipitation was used to remove of intermolecular reaction byproducts. After fractional precipitation, the monomodal GPC profiles with low PDI were obtained (Fig. 1, Line C).

The ^{1}H NMR spectrum of (*c*-PS)-(*p*-OH)$_2$ (Fig. 2C) showed that the resonance signals for alkynyl proton (—C≡C**H**) at 2.29 ppm (k) disappeared after cyclization, which confirmed

TABLE 1 The Data of (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ and Their Precursors

	(HO/*p*-OH)-PS-(HO/*p*-OH)			(*c*-PS)-(*p*-OH)$_2$				(*c*-PS)-*b*-(*l*-P*t*BA)$_2$		
Entry	$M_{\text{n, GPC}}$[a] (g/mol)	$M_{\text{p, GPC}}$[a] (g/mol)	PDI[a]	$M_{\text{n, GPC}}$[a] (g/mol)	$M_{\text{p, GPC}}$[a] (g/mol)	PDI[a]	*R*[b]	$M_{\text{n, GPC}}$[a] (g/mol)	PDI[a]	$M_{\text{n, NMR}}$[c] (g/mol)
A	3800	3990	1.05	3300	3460	1.05	0.87	6900	1.11	10600
B	9200	9860	1.05	8200	8960	1.05	0.91	14500	1.14	30000

[a] Determined by GPC with THF as solvent using PS standards, and M_{p} was the apparent peak molar mass.
[b] R was ratio of the apparent peak molar masses (*M*p) derived from GPC traces of cyclic polystyrene to their linear precursors.
[c] The molecular weight of (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ was calculated according to ^{1}H NMR using **Formula 3**.

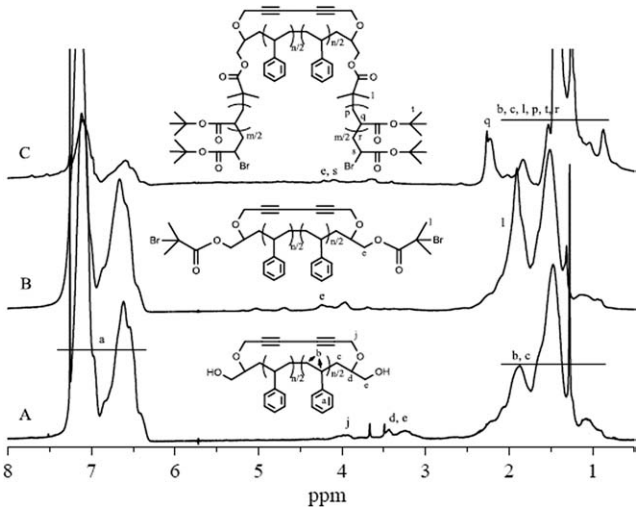


FIGURE 4 ^{1}H NMR (500 MHz) spectra of c-PS-$(OH)_2$ (A), (*c*-PS)-Br_2 (B) and (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ (C) in $CDCl_3$.

the successful synthesis of (*c*-PS)-(*p*-OH)$_2$. Figure 3(B) showed the MALDI-TOF MS spectra of (*c*-PS)-(*p*-OH)$_2$, the molecular mass of each peak for (*c*-PS)-(*p*-OH)$_2$ was expressed: 104.1 (St) × n + 147.2 (EEGE) × 2 + 107.9 (Ag^+) – 1.0 (H) × 2 + 38.1 (—$CH_2C{\equiv}C$—) × 2, where n was the number of St units. Compared with its linear precursor of (HO/*p*-OH)-PS-(HO/*p*-OH), there would be a theoretical shifting of 74.2 *m*/*z* to (*c*-PS)-(*p*-OH)$_2$. Herein, in the top spectrum, the peaks at 3631.1 *m*/*z* corresponded to (HO/*p*-OH)-PS-(HO/*p*-OH) ($n = 31$) and the peaks in the bottom spectrum at 3705.2 *m*/*z* corresponded to (*c*-PS)-(*p*-OH)$_2$ ($n = 31$). Their molecular weights differed by calculated shifting of 74.1 *m*/*z*, which further strongly confirmed the successful cyclization of PS.

Synthesis of Twin-Tail Tadpole-Shaped (*c*-PS)-*b*-(*l*-P*t*BA)$_2$

First, the cyclic polystyrene with two ethoxyethyl-protected hydroxyl groups at the junction point was deprotected in THF with HCl according to the refs. [29] and [37], and the recovered hydroxyl groups were esterified with 2-bromoisobutyryl bromide to form ATRP macroinitiator (*c*-PS)-Br_2 according to our previous work.[41] Then, the tadpole-shaped (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ was obtained by ATRP mechanism.

From the ^{1}H NMR spectrum of (*c*-PS)-$(OH)_2$ [Fig. 4(A)], the complete disappearance of resonance signals for ethoxyethyl proton (—OC**H**(CH_3)O—) at 4.50–4.62 ppm confirmed the successful deprotection of hydroxyl groups on (*c*-PS)-(*p*-OH)$_2$ (100% for E.F.). Compared the ^{1}HNMR spectrum of (*c*-PS)-Br_2 [Fig. 4(B)] with that of (c-PS)-$(OH)_2$ [Fig. 4(A)], the peaks (—C**H**$_2$OCH—) at 3.30–3.43 ppm (e) shifted to 4.03–4.33 ppm, and the noticeably intensified peaks (l) (—C(C**H**$_3)_2$—) at 1.86–1.98 confirmed that the successful proceeding of esterification reaction.

The tadpole-shaped (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ with two P*t*BA homopolymers as tail chains were prepared by ATRP of *t*BA monomers using the (*c*-PS)-Br_2 as macroinitiator, and the length of the P*t*BA chains could be tuned by varying the polymerization time. The GPC trace of (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ (Fig. 1, Line D) displayed a monomodal peak at the lower retention time compared with that of the precursor (HO/*p*-OH)-PS-(HO/*p*-OH), which meant that the bromide groups on the (*c*-PS)-Br_2 successfully initiated the ATRP polymerization of *t*BA (Table 1).

The ^{1}H NMR spectrum of (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ was shown in Figure 4(C), compared with that of (*c*-PS)-Br_2, the new resonance signal at 2.20–2.29 ppm (q) for methine group proton (—CH_2C**H**CO—) and the obviously intensified signal at 1.20–2.29 ppm also confirmed the successful ATRP polymerization of *t*BA. The $M_{n(NMR)}$ of (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ could be calculated from ^{1}H NMR according to **Formula 3**:

$$M_{n(NMR)[(c\text{-}PS)\text{-}b\text{-}(1\text{-}PtBA)_2]} = \frac{A_q}{\frac{A_a}{5} \times 104} \times 128 + M_{n(NMR[(c-PS)-(OH)2])} \quad (3)$$

where A_q was the integral area of the characteristic methine group proton (—CH_2C**H**CO—) at 2.20–2.29 ppm (q) on P*t*BA chain. The $M_{n(NMR)[(c\text{-}PS)\text{-}(OH)2]}$ was the molecular weight of (*c*-PS)-$(OH)_2$ calculated from the ^{1}H NMR spectrum. The others were the same as defined before. The $M_{n(NMR)[(c\text{-}PS)\text{-}b\text{-}(l\text{-}PtBA)2]}$ values obtained by ^{1}H NMR spectrum were larger than the $M_{n(SEC)\ [(c\text{-}PS)\text{-}b\text{-}(l\text{-}PtBA)2]}$ obtained by GPC (Table 1), which might be resulted from the different topological structure of tadpole-shaped (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ from the linear PS standard in GPC measurement.

Finally, the tadpole-shaped (cyclic polystyrene)-*block*-[linear poly (acrylic acid)]$_2$ was synthesized by hydrolysis of (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ using trifluoroacetic acid (TFA) according to ref. 42. The ^{1}H NMR spectrum of obtained (*c*-PS)-*b*-(*l*-PAA)$_2$ showed that the resonance signal at 1.20–2.29 ppm obviously weakened, which confirmed that the amphiphilic tadpole-shaped (*c*-PS)-*b*-(*l*-PAA)$_2$ was also synthesized successfully.

EXPERIMENTAL

Materials

Styrene [St, 99%, Sinopharm Chemical Reagent Co. (SCR)] was washed with 10% NaOH aqueous solution followed by water three times, dried over anhydrous $MgSO_4$, further dried over CaH_2, and distilled under reduced pressure. *Tert*-butyl acrylate (*t*BA, 99%, SCR), cyclohexane (>99%, SCR) and propargyl bromide (>99%, Shanghai Bangcheng Chemical Co.) were dried by CaH_2 for 24 h and distilled before use. Tetrahydrofuran (THF, >99%, SCR) were refluxed and distilled from sodium naphthalenide solution. Copper(I) bromide [Cu(I)Br, 95%, SCR] was stirred overnight in acetic acid, filtered, washed with ethanol and ethyl ether successively, and dried *in vacuo*. *n*-Butyllithium (*n*-Bu^-Li^+) was purchased from Beijing Zhongsheng Huateng Technology Co. EEGE was synthesized from glycidol and ethyl vinyl ether according to the literatures.[29,43] The solution of lithium naphthalenide was synthesized from naphthalene and lithium according to ref. 44, and the concentration was 1.20 mol/L analyzed by titration using hydrochloric acid

(0.1 mol/L). Sodium hydride (NaH, 55%), 2-Bromoisobutyryl bromide (>99%), and *N*,*N*,*N*′,*N*″,*N*‴,-pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Aldrich and used as received. Pyridine (>99%), toluene (99%), TFA, 99%) and other reagents were all purchased from SCR and used as received.

Measurements

Gel permeation chromatographic (GPC) analysis of PS was performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector. One 5-μm LP gel column (500 Å, molecular range 500–2 $\times$ 10^4 g/mol) and two 5-μm LP gel mixed bed column (molecular range 200–3 $\times$ 10^6 g/mol) were calibrated by PS standard samples. The injection volume was 20 μL, and the concentration was 5 mg/mL. ^{1}H NMR spectra were recorded on a DMX 500-MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference for chemical shifts. The matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurement was performed using a Perspective Biosystem Voyager-DESTR MALDI-TOF MS (PEApplied Biosystems, Framingham, MA). For PS samples, a matrix solution of dithranol (20 mg/mL), polymer (10 mg/mL), and cationizing salt of silver trifluoroacetate (10 mg/mL) in THF was mixed in the ratio of matrix: cationizing salt: polymer = 10:4:2, and 0.8 μL of mixed solution was deposited on the sample holder. The spectra were recorded in a reflectron mode, and the mass scale was calibrated externally using PS standards.

Synthesis of Telechelic Polystyrene with an Active Hydroxyl Group and an Ethoxyethyl Protected Hydroxyl Group at Both Ends [(HO/*p*-OH)-PS-(HO/*p*-OH)]

The telechelic (HO/*p*-OH)-PS-(HO/*p*-OH) was obtained by LAP of St monomers initiated by lithium naphthalenide[27] and subsequent end-capping reaction with EEGE in N_2 atmosphere according to our previous work.[29,37] Typically, cyclohexane (90 mL), styrene (10 mL, 87.0 mmol), and THF (5.0 mL) were introduced into a 400-mL dried vacuum ampule successively. In order to remove impurities in the ampule, *n*-Bu^-Li^+ solution was added dropwise until the mixture turned yellowish, and then the calculated lithium naphthalenide solution (4.0 mL, 4.80 mmol) was added rapidly. After the reaction finished, EEGE (5 mL, 34.2 mmol) dissolved in THF (10 mL) was added, and the red solution changed into faint yellow immediately. The solution was stirred for another 15.0 min and terminated with methanol. After removing the solvent, the mixture was diluted with THF and precipitated into an excessive amount of methanol for three times. The precipitate was dried under vacuum at 40 °C for 12.0 h, and the white powder was obtained (yield: 8.15 g, 97%). GPC: M_n = 3.8 $\times$ 10^3 g/mol, PDI = 1.05. MALDI-TOF MS: M_n = 3.8 $\times$ 10^3 g/mol, PDI = 1.05. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 1.13 (CH_3CH_2O—), 1.22 (—CH(CH_3)—),1.26–2.01 (3H, aliphatic main chain —CH_2CH— of PS chain), 3.09–3.43 (CH_3CH_2O—, —CH(OH)CH_2O—), 3.52(—CH(OH)—), 4.50–4.62 (—OCH(CH_3)O—), 6.30–7.30 (5H, aromatic —C_6H_5 of PS chain).

Synthesis of Telechelic Polystyrene with a Propargyl Group and an Ethoxyethyl Protected Hydroxyl Group at Both Ends [(≡/*p*-OH)-PS-(≡/*p*-OH)]

The synthesis of telechelic (≡/*p*-OH)-PS-(≡/*p*-OH) was as follows. Dried (HO/*p*-OH)-PS-(HO/*p*-OH) (3.8 $\times$ 103 g/mol, 3.8 g, 1.0 mmol) and 50 mL THF were added into a 250 mL round bottomed flask, and NaH (0.80 g, 50%, 16.7 mmol) was subsequently added. The solution was allowed to stir at 40 °C for 1.0 h. Then propargyl bromide (2.0 mL, 28.0 mmol) was added dropwise in an ice-water bath, and the solution was stirred at 25 °C for another 8.0 h. After THF was removed by rotary evaporation, the crude products were washed by water, and then purification by precipitation into methanol three times to obtain the yellow powder of functionalized polystyrene. The obtained (≡/*p*-OH)-PS-(≡/*p*-OH) was dried under vacuum at 45 °C for 24.0 h (yield: 3.5 g, 92%). ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 1.13 (CH_3CH_2O—), 1.22 (—CH(CH_3)—),1.26–2.01 (3H, aliphatic main chain —CH_2CH— of PS chain), 2.29 (—C≡CH), 3.09–3.43 (CH_3CH_2O—, —CH(OCH_2—)CH_2O—), 3.52(—CH(OCH_2—)—), 3.85–4.02 (—OCH_2—C≡CH), 4.50–4.62 (—OCH(CH_3)O—), 6.30–7.30 (5H, aromatic —C_6H_5 of PS chain).

Synthesis of Cyclic Polystyrene with two Ethoxyethyl Protected Hydroxyl Groups at the Junction Point [(*c*-PS)-(*p*-OH)$_2$)]

Typically, pyridine (300 mL) and Cu(I)Br (0.86 g, 6.00 mmol) was added into a 1000-mL round-bottomed flask, and the solution was stirred for 1.0 h at 50°C. To a separate flask, (≡/*p*-OH)-PS-(≡/*p*-OH) (3.8 $\times$ 10^3 g/mol, 0.50 g, 0.13 mmol) dissolved in pyridine (500 mL) was added, and this solution was then added to the Cu(I)Br reaction solution via a peristaltic pump at a rate of 10 mL/h (2.7 μmol/h). After another 2.0 h, the reaction solution was concentrated and stirred in mixture solution of methanol and H_2O (1/1 v/v) added with ethylenediaminetetraacetic acid disodium salt (EDTA) to dissolve the copper catalyst residues. Then, the crude product was isolated by filtration and washed by water three times. The obtained (*c*-PS)-(*p*-OH)$_2$ was dried under vacuum for 24.0 h (yield: 0.32 g, 64%). GPC: $M_{n,\ GPC}$ = 3.4 $\times$ 10^3 g/mol, PDI = 1.05. MALDI-TOF MS: M_n = 3.8 $\times$ 10^3 g/mol, PDI = 1.05. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 1.13 (CH_3CH_2O—), 1.22 (—CH(CH_3)—), 1.26–2.01 (3H, aliphatic main chain —CH_2CH— of PS chain), 3.09–3.43 (CH_3CH_2O—, —CH(OCH_2—)CH_2O—), 3.52(—CH(OCH_2)—), 3.85–4.02 (—OCH_2C≡C—C≡C—CH_2O—), 4.50–4.62 (—OCH(CH_3)O—), 6.30–7.30 (5H, aromatic —C_6H_5 of PS chain).

Synthesis of Macroinitiator with Two Bromoisobutyryl Groups at the Junction Point [(*c*-PS)-Br$_2$)]

First, the cyclic polystyrene with two active hydroxyl groups [(*c*-PS)-(OH)$_2$] at the junction point were obtained by the cleavage of ethoxyethyl group on (*c*-PS)-(*p*-OH)$_2$. The (*c*-PS)-(*p*-OH)$_2$ (3.8 $\times$ 10^3 g/mol, 0.32g, 0.08 mmol) were dissolved in 30-mL THF, then 3.0-mL HCl was added. The solution was stirred at room temperature for 3.0 h, then the HCl and THF were removed completely under reduced pressure. The product was precipitated into methanol and dried under vacuum at 45 °C for 24.0 h (yield: 0.3 g, 94%). ^{1}H NMR ($CDCl_3$, δ, ppm,

TMS): 1.26–2.01 (3H, aliphatic main chain —C**H**$_2$C**H**— of PS chain), 3.30–3.43 (—CH(OCH$_2$—)C**H**$_2$OH), 3.52(—C**H**(OCH$_2$)—), 3.85–4.02 (—OC**H**$_2$C≡C—C≡C—C**H**$_2$O—), 6.30–7.30 (5H, aromatic —C$_6$**H**$_5$ of PS chain).

Then, the esterification of the recovered hydroxyl groups on cyclic polystyrene with 2-bromoisobutyryl bromide was carried out in the anhydrous pyridine and the ATRP macroinitiator (*c*-PS)-Br$_2$ was obtained. Typically, (*c*-PS)-(OH)$_2$ (3.8×10^3 g/mol, 0.30 g, 0.08 mmol, 0.16 mmol hydroxyl groups) was dried by azeotropic distillation with toluene and then dissolved in 30 mL of anhydrous pyridine, to which 1.0 mL (8.0 mmol) of 2-bromoisobutyryl bromide was added dropwise at 0 °C in 30 min. After the reaction was allowed to proceed for 48.0 h, a large part of pyridine was evaporated under reduced pressure, and the residue was precipitated into methanol for three times and dried under vacuum at 45 °C for 24.0 h (yield: 0.29 g, 97%). ^{1}H NMR (CDCl$_3$, δ, ppm, TMS): 1.26–2.01 (3H, aliphatic main chain —C**H**$_2$C**H**— of PS chain), 1.86–1.98 (—C(C**H**$_3$)$_2$—), 3.52(—C**H**(OCH$_2$)—), 3.85–4.02 (—OC**H**$_2$C≡C—C≡C—C**H**$_2$O—), 4.03–4.33 (—C**H**$_2$—OCO), 6.30–7.30 (5H, aromatic —C$_6$**H**$_5$ of PS chain).

Synthesis of (Cyclic Polystyrene)-*block*-[Linear Poly (*tert*-butyl acrylate)]$_2$ [(*c*-PS)-*b*-(*l*-PtBA)$_2$]

The tadpole-shaped (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ with two P*t*BA homopolymers as twin-tail was prepared by ATRP of *t*BA monomers using the (*c*-PS)-Br$_2$ as macroinitiator, and the synthesis was as follows. The macroinitiator (*c*-PS)-Br$_2$ (3.8×10^3 g/mol, 0.29 g, 0.08 mmol, 0.16 mmol bromine groups), Cu(I)Br (0.0288 g, 0.20 mmol), PMDETA (0.04 mL, 0.2 mmol), and *t*BA (5.0 mL, 34 mmol) were added into a 100-mL dried ampule. The reaction mixture was degassed by three freeze-pump-thaw cycles and purged with N_2. The ampule was immersed in an oil bath at 90 °C for 6.0 h, and then dipped in liquid nitrogen to stop the polymerization. The products were diluted with THF, passed through a column chromatograph filled with neutral alumina to remove the copper complex, and precipitated into mixture solution of methanol and H_2O (1/1 v/v). Then dried under vacuum at 40 °C for 24.0 h (yield: 0.50 g, conversion = 6.5%). GPC: $M_{n,GPC} = 6.9 \times 10^3$ g/mol; PDI = 1.11. $M_{n,NMR} = 1.09 \times 10^4$ g/mol. ^{1}H NMR (CDCl$_3$, δ, ppm, TMS): 1.07–1.16(—C(C**H**$_3$)$_2$—), 1.26–2.01 (aliphatic main chain —C**H**$_2$C**H**— of PS chain, —C**H**$_2$CH— and — (CO) —OC(C**H**$_3$)$_3$, repeating units of P*t*BA), 2.06–2.40 (—CH$_2$C**H**—, repeating unit of P*t*BA), 3.52 (—C**H**(OCH$_2$) —), 3.85–4.02 (—OC**H**$_2$C≡C—C≡C—C**H**$_2$O—), 4.03–4.33 (—CH(OCH$_2$—)C**H**$_2$O—), 6.30–7.30 (5H, aromatic —C$_6$**H**$_5$ of PS chain).

The hydrolysis of (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ to (*c*-PS)-*b*-(*l*-PAA)$_2$ was described as follows. The tadpole-shaped (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ (0.50 g, containing 1.96 mmol *t*-butyl ester groups) was dissolved in dichloromethane (30 mL), and TFA (0.30 mL, 3.90 mmol) was added dropwise at 0 °C. The solution was stirred at room temperature for 24.0 h. After most of the solvent was removed by evaporation, the tadpole-shaped copolymers (*c*-PS)-*b*-(*l*-PAA)$_2$ was obtained by pouring the concentrated solution into methanol. The resulting precipitate was collected and dried under vacuum at 40 °C for 24.0 h (yield: 0.37 g, 93%). ^{1}H NMR (CDCl$_3$, δ, ppm, TMS): 1.07–1.16(—C(C**H**$_3$)$_2$—), 1.26–2.01 (aliphatic main chain —C**H**$_2$C**H**— of PS chain, —C**H**$_2$CH— repeating units of P*t*BA), 2.06–2.40 (—CH$_2$C**H**—, repeating unit of P*t*BA), 3.52 (—C**H**(OCH$_2$) —), 3.85–4.02 (—OC**H**$_2$C≡C—C≡C—C**H**$_2$O—), 4.03–4.33 (—CH(OCH$_2$—)C**H**$_2$O—), 6.30–7.30 (5H, aromatic —C$_6$**H**$_5$ of PS chain)

CONCLUSION

In this work, well-defined twin-tail tadpole-shaped (*c*-PS)-*b*-(*l*-P*t*BA)$_2$ and (*c*-PS)-*b*-(*l*-PAA)$_2$ were synthesized by combination of Glaser coupling reaction with successive ATRP and LAP mechanisms. The target copolymers and intermediates were well characterized by GPC, MALDI-TOF MS, and ^{1}H NMR in detail. By using this versatile method, the composition and structure of cyclic-based copolymers could be easily designed and tuned.

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