Preparation of Tadpole-Shaped Amphiphilic Cyclic PS-*b*-linear PEO via ATRP and Click Chemistry

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ABSTRACT: Amphiphilic tadpole-shaped copolymers consisting of a polystyrene (PS) ring and a poly(ethylene oxide) (PEO) tail were synthesized via atom transfer radical polymerization (ATRP) and click chemistry. First, PEO with a propargyl group and an ATRP initiating group was prepared via click chemistry and esterification. Then, a diblock copolymer, PEO-*b*-PS, which contained a propargyl group at the junction point and an azide group at the PS chain end, was prepared via ATRP of styrene, followed by transformation of the PS bromo end to an azide group. Finally, cyclization of the PS segment via click chemistry in dilute solution led to the formation of cyclic PS-*b*-linear PEO (*c*-PS-*b*-PEO). Because both the chain length of PEO and the ring size of cyclic PS can be easily tuned, a series of *c*-PS-*b*-PEOs was prepared. All of the polymers were characterized with gel permeation chromatography, NMR spectroscopy, FTIR, and matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF MS). *c*-PS-*b*-PEOs showed smaller hydrodynamic volumes compared with their linear precursors. Self-assembly of one *c*-PS-*b*-PEO sample and its linear precursor in water was preliminarily investigated by transmission electron microscopy. We found that vesicles were the main morphologies for both polymers, but they were different in size; those from *c*-PS-*b*-PEO were much larger.

Introduction

During the past few years, growing interest has been directed to the synthesis and properties of nonlinear copolymers, including miktoarm star, linear-dendritic, and macrocyclic-based copolymers.[1−3] Compared with the corresponding linear analogs, the cyclic polymers exhibit distinct properties, such as different glass-transition temperatures, lower hydrodynamic volume, and reduced viscosity.[2] Therefore, the macrocyclic-based homopolymers and copolymers, including cyclic block copolymers and sun-shaped, tadpole-shaped, eight-shaped, and θ-shaped polymers, have continued to attract more attention in the past decade.[4−16] However, the properties of the macrocyclic-based copolymers, except for those of the cyclic block copolymers,[17] have not been well studied experimentally because of the limited availability of such polymers. Therefore, synthesis of well-defined new cyclic polymers is still very important.

The formation of a macrocycle is the key step in the synthesis of macrocyclic-based polymers. Monomer insertion[6,12,14,18,19] and cyclization of linear precursors are two well-known approaches[20−23] to preparing well-defined cyclic polymers with narrow molecular weight distributions. The first approach is mainly applied to synthesize cyclic polyester and cyclic polyethylene. If a well-defined linear precursor with both α and ω ends is easily accessed, then the second approach can be used for many types of macrocycles with high efficiency. Anionic polymerization coupled to other reactions, such as nucleophilic substitution, metathesis reaction, and amidification, is among the most widely used strategy for preparing these polymers. Limited monomer types and rigorous conditions for the preparation of polymer precursors are the main disadvantages of this synthetic method. Recent development in the controlled radical polymerization (CRP), such as atom transfer radical polymerization (ATRP)[24] and the reversible addition−fragmentation chain transfer polymerization,[25] has made it possible to prepare many kinds of well-defined linear precursors with α,ω ends. Combined with the click chemistry, a copper-catalyzed 1,3-dipolar cycloadditon reaction,[26] CRP has been used to prepare many new macrocyclic polymers.[13,16,27,28]

The simplest example of tadpole-shaped polymer is composed of one macrocycle connected to one linear polymer chain. If the chemical composition of the macrocycle is different from that of the linear chain, then the tadpole-shaped polymer is considered to be a block copolymer. Although much effort has been devoted to the synthesis of sun-shaped and tadpole-shaped amphiphilic copolymers with more than one tail,[11,15] the availability of the simplest amphiphilic tadpole-shaped block copolymers is still very limited. Beinat et al. synthesized cyclic poly(chloroethyl vinyl ether)-*b*-linear polystyrene (PS) by cyclization of PCEVE segment via intramolecular coupling of the block copolymer precursor.[4] Very recently, Shi et al. synthesized cyclic PS-*b*-linear poly(*N*-isopropylacrylamide) by combination of click chemistry and RAFT polymerization.[13]

Poly(ethylene oxide)-*b*-PS (PEO-*b*-PS) is a block copolymer with known amphiphilic property and immiscibility of the two blocks. The phase morphology,[29] crystalline,[30] and self-assembly of PEO-*b*-PS in solution or air/water interfaces[31−33] have been well studied. Therefore, it is of interest to synthesize cyclic PS-*b*-linear PEO (*c*-PS-*b*-PEO) and compare its properties with those of the linear counterparts.

In this work, we report the synthesis of a new tadpole-shaped amphiphilic block copolymer consisting of one PS ring and one PEO tail. The synthetic strategy is based on two click reactions and one ATRP, as shown in Scheme 1. Both the chain length of the PS ring and the PEO tail of the tadpole block copolymer can be tuned. The preliminary self-assembly of the *c*-PS-*b*-PEO in water is presented.

Experimental Section

Materials. Poly(ethylene glycol) monomethyl ether ($M_n = 2000$ and 5000, Fluka), propargyl alcohol (98.0%, Shenyang Chemical Works), α-bromoisobutyrate bromide (98%, Aldrich), CuBr (99.999%, Aldrich), $CuBr_2$ (99%, Aldrich), *N*,*N*,*N*′,*N*″,*N*″-pentamethyl diethylenetriamine (PMDETA, 99%, Aldrich), and NaN_3 (98.0%, Zhejiang Dongyangkaiming Chemicals Company) were

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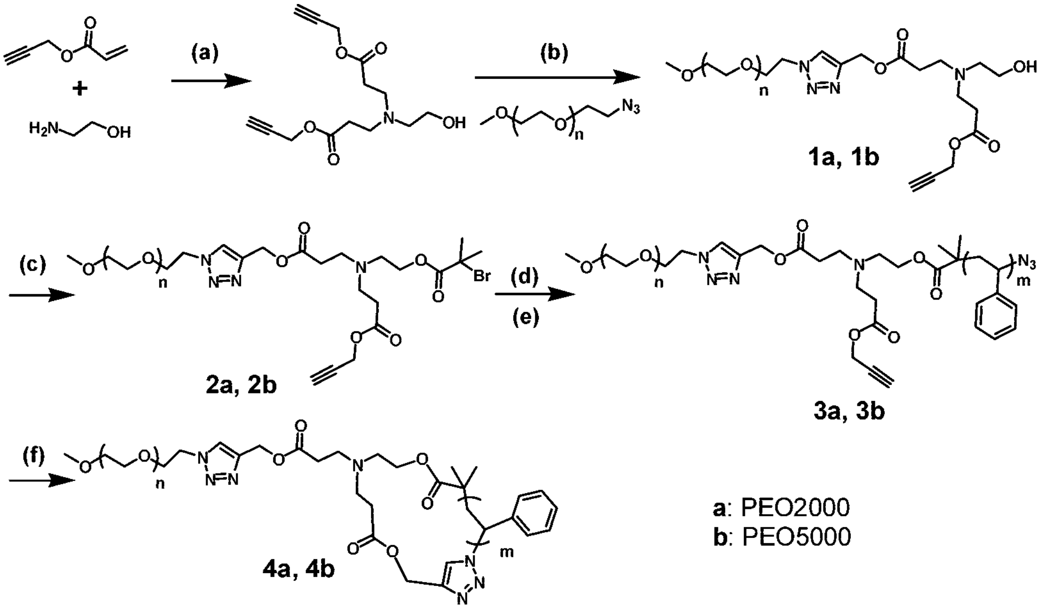
Scheme 1. Synthesis of Cyclic Polystyrene-*b*-linear Poly(ethylene oxide) (*c*-PS-*b*-PEO)[a]



[a] (a) *tert*-Butanol/THF, r.t.; (b) CuBr/PMDETA, dichloromethane, r.t.; (c) 2-bromoisobutyrate bromide, triethylamine, dichloromethane; (d) styrene, CuBr/PMDETA, 80 °C; (e) NaN_3, DMF; (f) CuBr/PMDETA, DMF. THF: tetrahydrofuran; PMDETA: *N*,*N*,*N*′,*N*″,*N*″-pentamethyl diethylenetriamine; DMF: *N*,*N*-dimethylformamide.

used as received. 2-Aminoethanol (98%, Beijing Yili Chemicals Company) was distilled under vacuum. Triethylamine (99%, Shantou Xilong Chemical Factory) was dried with KOH and distilled just before use. Styrene (98%, Beijing Chemicals Company) was washed with 2 M NaOH, dried with $CaCl_2$, and distilled over CaH_2 under vacuum. Cyclohexanone (99.5%, Beijing Chemicals Company) was distilled over CaH_2. *N*,*N*-Dimethylformamide (DMF, 99.5%, Beijing Chemicals Company) was dried with $MgSO_4$ and distilled under vacuum. Dichloromethane (99.5%, Beijing Tongguang Chemicals Company), chloroform (99%, Beijing Tongguang Chemicals Company), and tetrahydrofuran (THF, 99.9%, Beijing Chemicals Company) were refluxed individually in the presence of CaH_2, followed by distillation. α-Methoxy-ω-azide-poly(ethylene glycol) (PEO2000-N_3 and PEO5000-N_3) and acryloyl chloride were synthesized according to literature methods.[34,35] Propargyl acrylate was synthesized from propargyl alcohol and acryloyl chloride according to literature method.[36]

Characterization. Gel permeation chromatography (GPC) was carried out in THF (flow rate: 1 mL/min) at 35 °C with a Waters 1525 binary HPLC pump equipped with a Waters 2414 refractive index detector and three Waters Styragel HR columns (1×10^4, 1×10^3, and 500 Å pore sizes). Monodisperse PS standards were used for calibration. ^1H NMR (400 or 300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker-400 spectrometer and Varian-300 spectrometer in $CDCl_3$ with tetramethylsilane as the internal reference for chemical shifts. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. α-Cyano-4-hydroxycinnamic acid was used as the matrix. Mass spectra were acquired in linear mode at an acceleration voltage of +19 kV. FT-IR spectra were recorded as KBr pellets using a Bruker VECTOR 22 FT-IR spectrometer. Preparative GPC was performed with a LC-9201 recycling preparative HPLC (Japan Analytical Industry) equipped with a JAIGEL-2.5H column (600 × 200 mm^2). Chloroform was the eluent at a flow rate of 3.5 mL/min.

Synthesis of *N*,*N*-Bis(2-propargyloxycarbonyl ethyl)-2-hydroxylethyl amine (BPHA). Propargyl acrylate (27 g, 0.25 mol) was dissolved in a mixture of THF (34 mL) and *tert*-butanol (38 mL). 2-Aminoethanol (5 g, 0.08 mol) was then added to the mixture. The mixture was stirred for 24 h at room temperature. Solvent was removed by a rotary evaporator. The product was purified by silica gel chromatography (ethyl acetate/petroleum ether v/v = 1/6) to produce a pale-yellow oil in 91% yield. ^1H NMR (300 MHz, $CDCl_3$, δ): 4.71 (d, 4H, $HC{\equiv}CCH_2$), 3.61 (t, 2H, CH_2CH_2OH), 3.3−3.1 (broad, 1H, CH_2CH_2OH), 2.83 (t, 4H, NCH_2CH_2CO), 2.61 (t, 2H, NCH_2CH_2OH), 2.53 (t, 4H, NCH_2CH_2CO), 2.52 (t, 2H, $HC{\equiv}C$). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 171.65 (CH_2CO), 77.50 ($HC{\equiv}C$), 74.99 ($HC{\equiv}C$), 58.94 (CH_2CH_2OH), 55.91 ($HC{\equiv}CCH_2$), 52.00 ($COCH_2CH_2$), 48.98 (NCH_2CH_2OH), 32.42 ($COCH_2CH_2$).

Synthesis of 1. Take the synthesis of **1a** as an example. PEO2000-N_3 (3.4 g, 1.7 mmol), BPHA (4.8 g, 17 mmol), PMDETA (700 μL, 3.5 mmol), and dichloromethane (85 mL) were added to an ampule and subjected to three freeze−pump−thaw cycles. CuBr (0.50 g, 3.5 mmol) was added when the mixture was frozen. The ampule underwent another freeze−pump−thaw cycle and was sealed under vacuum. The reaction was carried out for 4 h at room temperature. Then, copper catalyst was removed with a neutral Al_2O_3 column. The product (3.5 g) was obtained in 90% yield by precipitation from ethyl ether/petroleum ether (v/v 1/1). $M_{n,GPC} = 3430$, $M_w/M_n = 1.03$.

Polymer **1b** was synthesized in a similar way, except that PEO5000-N_3 was used as the starting material. Yield: 95%, $M_{n,GPC} = 6600$, $M_w/M_n = 1.05$.

Synthesis of 2. Take the synthesis of **2a** as an example. Polymer **1a** (3.5 g, 1.1 mmol) and triethylamine (0.20 g, 2.0 mmol) were dissolved in dichloromethane (30 mL). 2-Bromoisobutyrate bromide (2.0 mL, 16 mmol) in dichloromethane (10 mL) was added dropwise to the mixture at 0 °C. The mixture was stirred overnight at room temperature. The precipitated salt was filtered, and the solvent was removed by evaporation. The crude product was dissolved in THF, and the solution was passed through a neutral Al_2O_3 column. The polymer (3.3 g) was obtained in 88% yield by precipitation from ethyl ether/petroleum ether (v/v 1/1). $M_{n,GPC} = 3450$, $M_w/M_n = 1.03$.

Polymer **2b** was synthesized in a similar way with **1b** as the starting material. Yield: 79% $M_{n,GPC} = 6580$, $M_w/M_n = 1.04$.

Synthesis of 3. Take the synthesis of **3a-2** as an example. First, ATRP of St with **2a** as the initiator was conducted. Following the procedure for the synthesis of **1a**, polymer **2a** (0.30 g, 0.13 mmol), $CuBr_2$ (1.3 mg, 5.8 μmol), styrene (1.30 g, 0.0130 mol), PMDETA (13.5 μL, 0.0680 mmol), cyclohexanone (0.74 mL), and CuBr (9.0

mg, 0.063 mmol) were sealed in an ampule. After being stirred for 10 min at room temperature to allow the formation of catalyst complex, the ampule was placed in an oil bath preheated to 80 °C; the polymerization was carried out for 9 h at this temperature. Copper catalyst was removed with a neutral Al_2O_3 column. The polymer (0.80 g) was obtained in 50% yield after precipitation from petroleum ether. Then, the bromine end group of this polymer was transformed to an azide group by reaction with NaN_3. The above polymer was dissolved in 6.0 mL of DMF, and NaN_3 (0.16 g, 2.5 mmol) was added. The solution was stirred for 12 h at room temperature. Inorganic salts were removed by passing the reaction solution through an Al_2O_3 column. After the removal of DMF using a rotary evaporator, the polymer was recovered by precipitation into petroleum ether. Yield: 88%. $M_{n,GPC} = 10\,140$, $M_w/M_n = 1.07$.

3a-1. ATRP, [styrene]$_0$/[**2a**]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[PMDETA]$_0$ = 100/1/0.5/0.05/0.55, solvent: cyclohexanone, [styrene]$_0$ = 4.8 M, 80 °C, 4 h, yield: 36%. Substitution reaction, 0.98 g of polymer, 0.27 g NaN_3, 10 mL of DMF, 12 h. Product: 0.90 g (yield: 92%), $M_{n,GPC} = 5870$, $M_w/M_n = 1.05$.

3a-3. ATRP, [styrene]$_0$/[**2a**]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 200/1/1/1, solvent: cyclohexanone, [styrene]$_0$ = 4.8 M, 80 °C, 11 h, yield: 49%. Substitution reaction, 1.43 g of polymer, 0.16 g NaN_3, 6 mL of DMF, 12 h. Product: 1.30 g (yield: 91%), $M_{n,GPC} = 18\,070$, $M_w/M_n = 1.07$.

3b-1. ATRP, [styrene]$_0$/[**2b**]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[PMDETA]$_0$ = 200/1/0.5/0.05/0.55, solvent: cyclohexanone, [styrene]$_0$ = 4.8 M, 80 °C, 5.5 h, yield: 38%. Substitution reaction, 0.92 g of polymer, 0.12 g NaN_3, 6 mL of DMF, 20 h. Product: 0.80 g (yield: 87%), $M_{n,GPC} = 10\,630$, $M_w/M_n = 1.06$.

3b-2. ATRP, [styrene]$_0$/[**2b**]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[PMDETA]$_0$ =300/1/0.75/0.075/0.82, solvent: cyclohexanone, [styrene]$_0$ = 4.8 M, 80 °C, 11.5 h, yield: 49%. Substitution reaction, 1.65 g of polymer, 0.12 g NaN_3, 6 mL of DMF, 20 h. Product: 1.59 g (yield: 96%), $M_{n,GPC} = 17\,480$, $M_w/M_n = 1.08$.

Synthesis of 4. Take the synthesis of **4a-2** as an example. PMDETA (150 μL, 0.70 mmol), CuBr (0.10 g, 0.70 mmol), and DMF (50 mL) were used to form a catalyst complex solution. The catalyst solution was degassed and thermostated at 80 °C. A solution of **3a-2** (0.40 g, 0.044 mmol) in DMF (40 mL) was degassed with three freeze−pump−thaw cycles, and it was then added to the catalyst solution via a syringe four times (10 mL solution portion) at a time interval of 6 h. After the last addition, the reaction was carried out for 8 h. DMF was removed by a rotary evaporator, and copper catalyst was removed by a neutral Al_2O_3 column. The polymer was precipitated from petroleum ether and dried under vacuum. The cyclization product was purified with preparative GPC. Yield: 72%. $M_{n,GPC} = 8280$, $M_w/M_n = 1.05$.

Synthesis of other tadpole copolymers was similar to that of **4a-2**. PMDETA (450 μL, 2.1 mmol), CuBr (0.30 g, 2.1 mmol), and DMF (100 mL) were used to form a catalyst complex solution.

4a-1. Diblock copolymer **3a-1** (0.70 g, 0.12 mmol) in 70 mL of DMF, 80 °C, seven times (10 mL each), time interval: 4 h. The product was purified with preparative GPC. Yield: 75%, $M_{n,GPC} = 5050$, $M_w/M_n = 1.04$.

4a-3. Diblock copolymer **3a-3** (0.70 g, 0.038 mmol) in 70 mL of DMF, 80 °C, seven times (10 mL each), time interval: 4 h. The product was purified with preparative GPC. Yield: 61%, $M_{n,GPC} = 14\,720$, $M_w/M_n = 1.07$.

4b-1. Diblock copolymer **3b-1** (0.40 g, 0.034 mmol) in 40 mL of DMF, 100 °C, four times (10 mL each), time interval: 8 h. The product was purified with preparative GPC. Yield: 65%, $M_{n,GPC} = 9180$, $M_w/M_n = 1.06$.

4b-2. Diblock copolymer **3b-2** (0.60 g, 0.028 mmol) in 60 mL of DMF, 100 °C, six times (10 mL each), time interval: 8 h. The product was purified with preparative GPC. Yield: 45%, $M_{n,GPC} = 15\,420$, $M_w/M_n = 1.09$.

Self-Assembly of the Tadpole-Shaped Copolymers in Water. Copolymer (10 mg, **3a-2** or **4a-2**) was dissolved in 10 mL of THF, and the solution was stirred at 35 °C for 5 h. Polymer solution (1.0 mg/mL, 2.0 mL) was taken out, and double-distilled water was added to the solution at a rate of 0.3 vol %/min under stirring. In total, 10 mL of water was added. Most of the THF was then evaporated out on an evaporator for 10 h until blue tint became prominent. Residual THF was evaporated under reduced pressure. The final concentration of the aggregate suspension was 0.2 mg/mL. A droplet of the sample solution was placed on a 400 mesh copper grid covered with Formvar membrane. Most of the liquid was removed by blotting with a filter paper after 30 min. The sample was then negatively stained with 2 μL of uranyl acetate solution (2% aqueous solution) for 30 s. The grid was air dried before observation was conducted on a JEOL JEM-100CXII at an acceleration voltage of 100 kV.

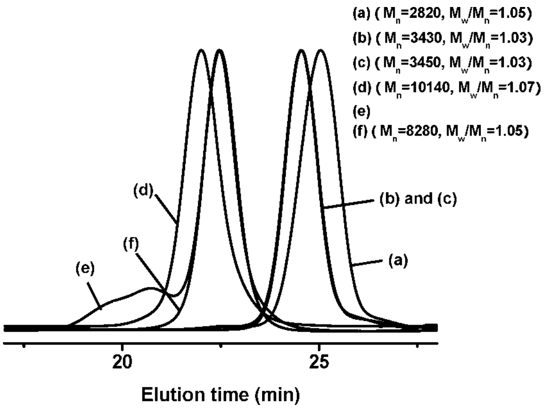


Figure 1. GPC traces of (a) PEO2000-N_3, (b) **1a**, (c) **2a**, (d) **3a-2**, (e) crude **4a-2**, and (f) **4a-2**. GPC: gel permeation chromatography; PEO: poly(ethylene oxide).

Results and Discussion

There are three main strategies for preparing tadpole-shaped block polymers: one is by direct chemical coupling of a functionalized macrocycle and a linear polymer chain; the second is by polymerization with a ring polymer as initiator; and the third is by intramolecular cyclization of a linear diblock polymer precursor. In the third method, tadpole-shaped copolymers can be obtained along with their linear analogs so that the differences between the two can be easily compared. As shown in Scheme 1, our method for preparing *c*-PS-*b*-PEO is by cyclization of a linear diblock copolymer, PEO-*b*-PS, which contains a propargyl group at the junction point of the two blocks and an azide group at the PS chain end. First, PEO containing a propargyl group and a 2-bromoisobutyrate group at the same chain end was synthesized via click chemistry and esterification. Then, linear PEO-*b*-PS precursor was synthesized via ATRP of styrene, followed by azidation of the formed bromo ends in PS chain with sodium azide. Finally, *c*-PS-*b*-PEO was prepared by intramolecular click chemistry under dilute conditions. Changing DP$_n$ values of azide-terminated PEO and the ATRP conditions of styrene can easily tune the block lengths of the copolymers.

Synthesis of 1a and 1b. We synthesized BPHA via Michael addition[37] between 2-aminoethanol and excess of propargyl acrylate. The propargyl group did not react with amino group under the present conditions, and pure BPHA was obtained in high yield. Reaction of PEO-N_3 with an excess of BPHA by click chemistry was straightforward. After reaction, the purification of polymers by precipitation recovered the desired polymer in high yield. Characterizations of the polymers were done by GPC, ^{1}H NMR spectroscopy, FT-IR, and MALDI-TOF MS. For example, the GPC trace of **1a** is unimodal and symmetrical. It was shifted toward shorter elution time as compared with that of PEO2000-N_3, while keeping the polydispersity index unchanged (Figure 1a,b). As shown in the IR spectrum of **1a** (Figure 2), the strong absorption characteristic of the azide groups at 2110 cm^{-1} disappeared completely, and absorption

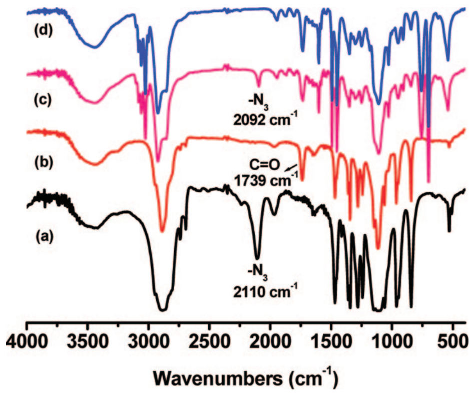


Figure 2. IR spectra of (a) PEO2000-N_3, (b) **1a**, (c) **3a-2**, and (d) **4a-2**. PEO: poly(ethylene oxide).

typical of ester groups at 1739 cm^{-1} appeared, demonstrating that click chemistry between PEO2000-N_3 and BPHA was quite efficient. Figure 3 is the ^1H NMR spectrum of **1a**. Resonance peaks f, d, and e (integration ratio is 2/2/1), which are assigned to protons related to the formation of triazole, were clearly observed. Resonance peaks g and a are protons typical of propargyl methylene groups and methyl end groups of PEO, respectively. The integration ratio of resonance peaks g, f, and a is 2/2/3, suggesting the desired structure integrity of **1a**. MALDI-TOF MS of **1a** was also measured and shown in Figure 4. Two series of repeating peaks can be clearly seen, both of which have an interval of 44, corresponding to the molecular weight of ethylene oxide unit. The molecular formula of **1a** is $C_{(17+2n)}H_{(26+4n)}N_4O_{(6+n)}$. Take $n = 44$ (for PEO2000): **1a** plus Na^+ sums to 2342.729, and **1a** plus K^+ sums to 2358.837. They correspond exactly to the measured values of 2342.5 and 2358.5. All of these results confirmed that only one PEO2000-N_3 reacted with one BPHA to form **1a**.

Synthesis of **1b** was similar to that of **1a**. NMR and IR results (not shown) revealed efficient click reaction between PEO5000-N_3 and BPHA.

Synthesis of Heterofunctional ATRP Initiators (2a and 2b). Synthesis of **2** was quite simple through the esterification reaction between hydroxyl groups in **1** and 2-bromoisobutyrate bromide. The reaction was quite efficient, and the purification was very easy. GPC trace of **2a** (Figure 1c) was the same as that of **1a**. The ^1H NMR spectrum of **2a** is shown in Figure 5a. The integration ratio of resonance peaks l, m, and f is 2/6/2, suggesting that all hydroxyl groups were converted to the corresponding esters. Synthesis and characterization of **2b** was similar to that of **2a**.

Synthesis of PS-*b*-PEO Diblock Copolymer Precursors (3). Propargyl 2-bromoisobutyrate was reported to initiate the ATRP of styrene.[27,38] Because of the low ratio of initiator/monomer and relative stable benzyl radical, no transfer reaction of benzyl radicals to propargyl groups would occur. In this regard, **2** can be an effective macroinitiator for the ATRP of styrene. Chain lengths of PS could be easily controlled by varying the feed molar ratio of monomer/initiator and the polymerization time. A high degree of bromo-end functionality and low polydispersity of PS are necessary for the following substitution reactions. Therefore, we added persistent radicals ($CuBr_2$) and stopped the polymerization at a relatively lower monomer conversion. Detailed polymerization conditions were described in the Experimental Section. We did not characterize these polymers but directly used them for the next step. The bromo-end groups in the PS chain were easily transformed to azides by a nucleophilic substitution reaction with NaN_3 at room temperature.[27,38,39] Again, high efficiency and easy purification resulted in the high yield of PEO-*b*-PS precursors with a propargyl group at the junction point of the two blocks and an azide group at the PS chain end. Block copolymers with different chain length of either PEO or PS were obtained, and the characterization results are summarized in Table 1.

We take **3a-2** as an example to demonstrate the characterization. Figure 1d is the GPC trace of **3a-2**. It is a symmetric unimodal curve, completely shifted toward shorter elution time as compared with **2a**. The polydispersity index is 1.07. The IR spectrum shown in Figure 2c reveals the presence of an azide group in the copolymer (2092 cm^{-1}). Figure 5b is the ^1H NMR spectrum of **3a-2**. Resonance peaks b, n, o, and p are protons typical of PEO and PS segments. The characteristic peak of the methine proton next to the terminal azido group should appear at ~3.9 ppm, and peak l should move to ~3.7 ppm,[36] but they could not be clearly seen because of the overlap with peaks c and b. Chemical shifts of resonance peaks e, f, g, d, and a did not change relative to macroinitiator **2a**, and the integration ratio was 1/2/2/2/3, suggesting that one propargyl group is at the junction point of PEO-*b*-PS. The number-average DP_n of PS segment can be determined from the integration ratio of the resonance peaks p and b. It is 65 for **3a-2,** and the number-average molecular weight of **3a-2** can thus be calculated to be 9160. To confirm the structure integrity of **3a-2** further, we measured the MALDI-TOF MS of **3a-2** (Figure 6). The average molecular weight was 8960, which is in good agreement with the M_n estimated by the NMR spectrum. No contamination of **2a** ($M_n = 3450$) can be seen. Therefore, diblock copolymer precursor, **3a-2**, consisting of PEO ($DP_n = 44$) and PS ($DP_n = 65$) was successfully synthesized.

Characterization of other diblock copolymers is compiled in the Supporting Information and Table 1.

Synthesis of Tadpole-Shaped Copolymers (4). The cyclization reaction of α,ω-end-functionalized polymer precursors is usually carried out in highly dilute solution to suppress intermolecular reaction. Click chemistry was applied to cyclization in very dilute solution; pure cyclic polymers were obtained when the polymer precursors were continuously added to the catalyst solution.[13,27] However, the final amount of the product was very small in these systems. In our case, to obtain a relatively large amount of final polymer samples, step addition of polymer precursors was employed to the cyclization of PS at a relatively higher concentration. Click reactions of **3a** and **3b** were carried out at 80 and 100 °C respectively. We took **4a-2** to be an example to illustrate the cyclization procedure. The click reaction, monitored by IR measurement, is quantitative, as revealed from the complete disappearance of azide vibration (data not shown). However, the GPC trace of the crude product (Figure 1e) indicated coexistence of the intermolecular coupling product (peak at shorter retention time) and the intramolecular coupling product (peak at longer retention time); the weight percentage of the cyclic product was estimated to be ~80% of the total product.

Purification of cyclic polymer from the linear polymer impurity can be done by fractional precipitation,[21] selective reaction with ion-exchange resin,[22] preparative GPC,[40] and liquid adsorption chromatography under critical conditions (LACCC).[41] Fractional precipitation and LACCC may not be easy for copolymers because the critical condition is difficult to find. In the case that the linear precursor was absent, the product consisted of only tadpole copolymer and the intermolecular coupling impurity that had at least double molecular weight of the tadpole-shaped copolymer. The elution trace of the impurity in **4a-2** was distinguishable from that of the tadpole-shaped copolymer, which made it possible to remove the impurity with preparative GPC. We therefore purified all of the tadpole copolymers with preparative GPC;

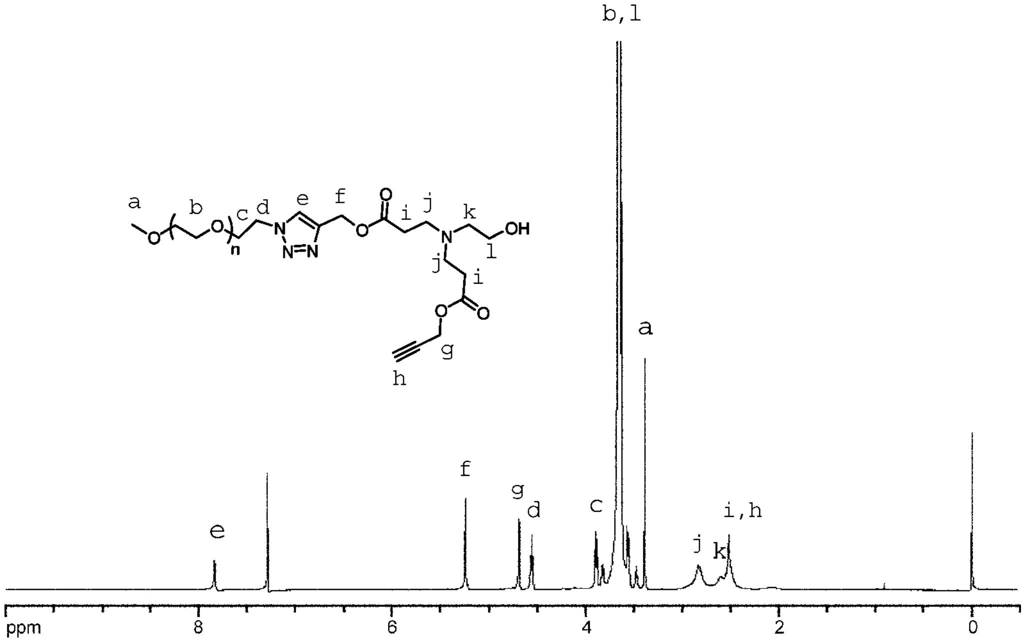


Figure 3. ^{1}H NMR spectrum of **1a** in $CDCl_3$.

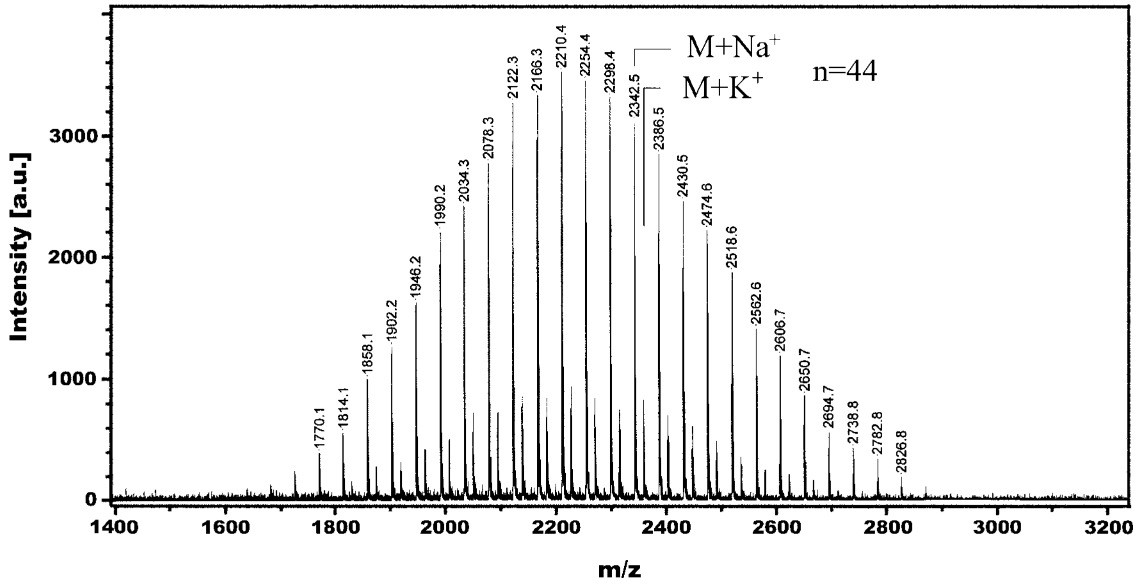


Figure 4. MALDI-TOF mass spectrum of **1a**: ($M = C_{(17+2n)}H_{(26+4n)}N_4O_{(6+n)}$). Matrix: α-cyano-4-hydroxycinnamic acid; cation source: Na^+ and K^+ in glassware, solvents and reagents. MALDI-TOF: matrix-assisted laser desorption ionization time-of-flight.

the yield of purified tadpole copolymers is >60% for **4a** with a shorter PEO chain and >45% for **4b** with a longer PEO chain.

Purified **4a-2** was characterized by GPC, MALDI-TOF, NMR, and IR. The GPC trace of **4a-2** (Figure 1f) was unimodal and symmetrical with narrow molecular weight distribution, but **4a-2** had a longer retention time than **3a-2**, suggesting the existence of a cyclic structure. Figure 2d is the IR spectrum of **4a-2**; it was the same as that of **3a-2**, except for the disappearance of the peak at 2092 cm^{-1}, typical absorption of azide groups. Figure 5c is the ^{1}H NMR spectrum of **4a-2**; signals of propargyl methylene protons (peak g) moved from 4.65 ppm to ~5.07 ppm after cyclization, but signals from the newly formed triazole protons (peak h) overlapped with the first triazole protons (peak e). DP$_n$ of cyclic PS segment was determined from the integration ratio of resonance peaks p and b in the ^{1}H NMR spectrum, which is 68 for **4a-2**, a little higher than that in **3a-2**. Therefore, the real number-average molecular weigh of **4a-2** was calculated to be 9500. As can be seen in the MALDI-TOF MS of **4a-2** (Figure 6), the average molecular weight was 9280, which is in agreement with the M_n estimated by NMR spectrum. For other tadpole-shaped copolymers, the GPC traces, NMR, and IR spectra are shown together with those of the linear precursors in the Supporting Information. DP$_n$ values of PS in other tadpole-shaped copolymers were calculated as for **4a-2** and collected in Table 1. For copolymers with longer PS chains, the polymer yields were low, and the calculated DP$_n$ of cyclic PS was larger than those of the precursors; we attributed this to purification by precipitation and preparative GPC.

It is expected that the hydrodynamic volume of a cyclic polymer is lower than the linear one with the same molecular weight. This feature can be described using $\langle G_c \rangle$ ($= M_{p,c}/M_{p,l}$), where $M_{p,c}$ and $M_{p,l}$ are peak values of the molecular weight of the cyclic polymer and linear precursor by GPC. For example, $\langle G_c \rangle$ of cyclic PS was experimentally found to be 0.78. $\langle G \rangle$

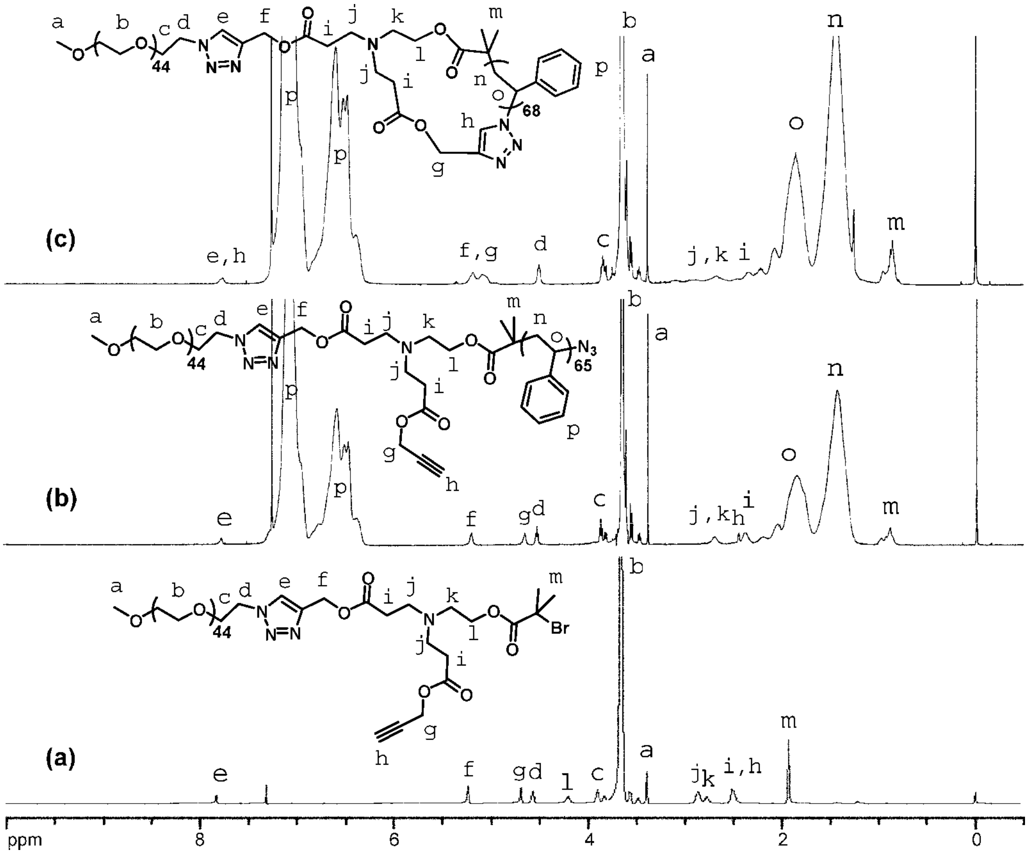


Figure 5. ^{1}H NMR spectra of (a) **2a**, (b) **3a-2**, and (c) **4a-2** in CDCl$_3$.

Table 1. Number-Average Molecular Weight (M_n) and Polydispersity Index (PDI = M_w/M_n) Data of Linear Diblock Copolymers (3) and Tadpole-Shaped Copolymers (4) as Calculated by Gel Permeation Chromatography (GPC) and ^{1}H NMR Spectroscopy

polymer[a]	yield (%)	M_p[b]	M_n[b]	PDI[b]	$<G_{exptl}>$[c]	$<G_{calcd}>$[d]	M_n[e]	DP_{PS}[e]
3a-1	33	6250	5870	1.05			6040	35
4a-1	75	5260	5050	1.04	0.84	0.91	6140	36
3a-2	44	10 750	10 140	1.07			9160	65
4a-2	72	8700	8280	1.05	0.81	0.86	9470	68
3a-3	45	19 900	18 070	1.07			18 310	153
4a-3	61	14 860	14 720	1.07	0.75	0.83	19 770	167
3b-1	33	11 720	10 630	1.06			11 640	60
4b-1	65	10 180	9180	1.06	0.87	0.92	12 470	68
3b-2	47	19 830	17 480	1.08			21 730	157
4b-2	45	16 590	15 420	1.09	0.84	0.87	23 600	175

[a] **3a-1** to **3a-3** were prepared with **2a** as the macroinitiator and **3b-1** and **3b-2** were prepared with **2b** as the macroinitiator. [b] Determined from GPC. [c] $<G_{exptl}> = M_{p,c}/M_{p,l}$ [d] $<G_{calcd}> = (<G_{c,PS}>)(F_{PS}) + (<G_{l,PEO}>)(F_{PEO})$, $<G_{c,PS}> = 0.78$, $<G_{l,PEO}> = 1$, $F_{PS} = DP_{PS}/(DP_{PS} + DP_{PEO})$, $F_{PEO} = DP_{PEO}/(DP_{PS} + DP_{PEO})$. [e] Determined from ^{1}H NMR.

of *c*-PS-*b*-PEO can roughly be estimated by the following equation[4,13]

$$<G_{calcd}> = <G_{c,PS}>(F_{PS}) + <G_{l,PEO}>\ (F_{PEO})$$

where $<G_{calcd}>$ stands for calculated $<G>$; $<G_{c,PS}>$ is $<G_c>$ of cyclic PS; $<G_{l,PEO}> = 1$; $F_{PS} = DP_{PS}/(DP_{PS} + DP_{PEO})$; and $F_{PEO} = DP_{PEO}/(DP_{PS} + DP_{PEO})$. The $<G_{cal}>$ values of tadpole-shaped copolymers were calculated and are listed in Table 1; these data suggested that tadpole-shaped copolymers have the expected compact structure. The experimental values are lower than the calculated ones, which may imply that the calculation based on such a simple addition of cyclic and linear structures is not so reliable. The GPC, NMR, and IR results of tadpole-shaped copolymers, together with those of the linear precursors, demonstrated that tadpole-shaped copolymers consisting of a PS ring and a PEO tail were synthesized.

Self-Assembly of Tadpole-Shaped Copolymers (3a-2 and 4a-2) in Water. Amphiphilic diblock copolymers can form polymer micelles in water with hydrophilic segments solvated in the coronal shell and hydrophobic segments packed in the core.[31] Self-assembly of PEO-*b*-PS in solution has been reported in the literature.[32,42] Depending on the copolymer chain length, concentration, and preparation methods, many types of morphology have been observed. PEO-*b*-PS with long PEO chain and short PS chain (F_{EO}, mole fraction of EO units, >0.8) could directly dissolve in water and form spherical micelles with PS as the core and PEO as the corona.[42] Eisenberg and coworkers[32] systematically studied the aggregation of PEO-*b*-PS with shorter PEO chain ($F_{EO} < 0.5$) in water by continuous water addition method. The polymer was originally dissolved in a common solvent (for example THF or DMF); water was then added slowly to induce the aggregation of PS chains and the transformation of the morphologies; finally, a large amount of water was added to stabilize the formed morphologies. The DP_n of PS was usually >100, and multiple morphologies with vesicles and rods were observed. We prepared an aggregate solution of **3a-2** and **4a-2** in water in a way similar to that reported by Eisenberg. Vesicles with diameters ranging from 50 to 100 nm and a wall thickness of 15 nm were observed for **3a-2** (Figure 7a). Micelles with diameters of ~30 nm coexisted with vesicles. In the case of **4a-2**, vesicles were the only morphologies (Figure 7b), but their size distributions were quite broad. Large vesicles (diameters ~300 nm) coexisted with small vesicles (diameters about 60−100 nm), with the former morphologies being predominant. We further characterized the aggregates by

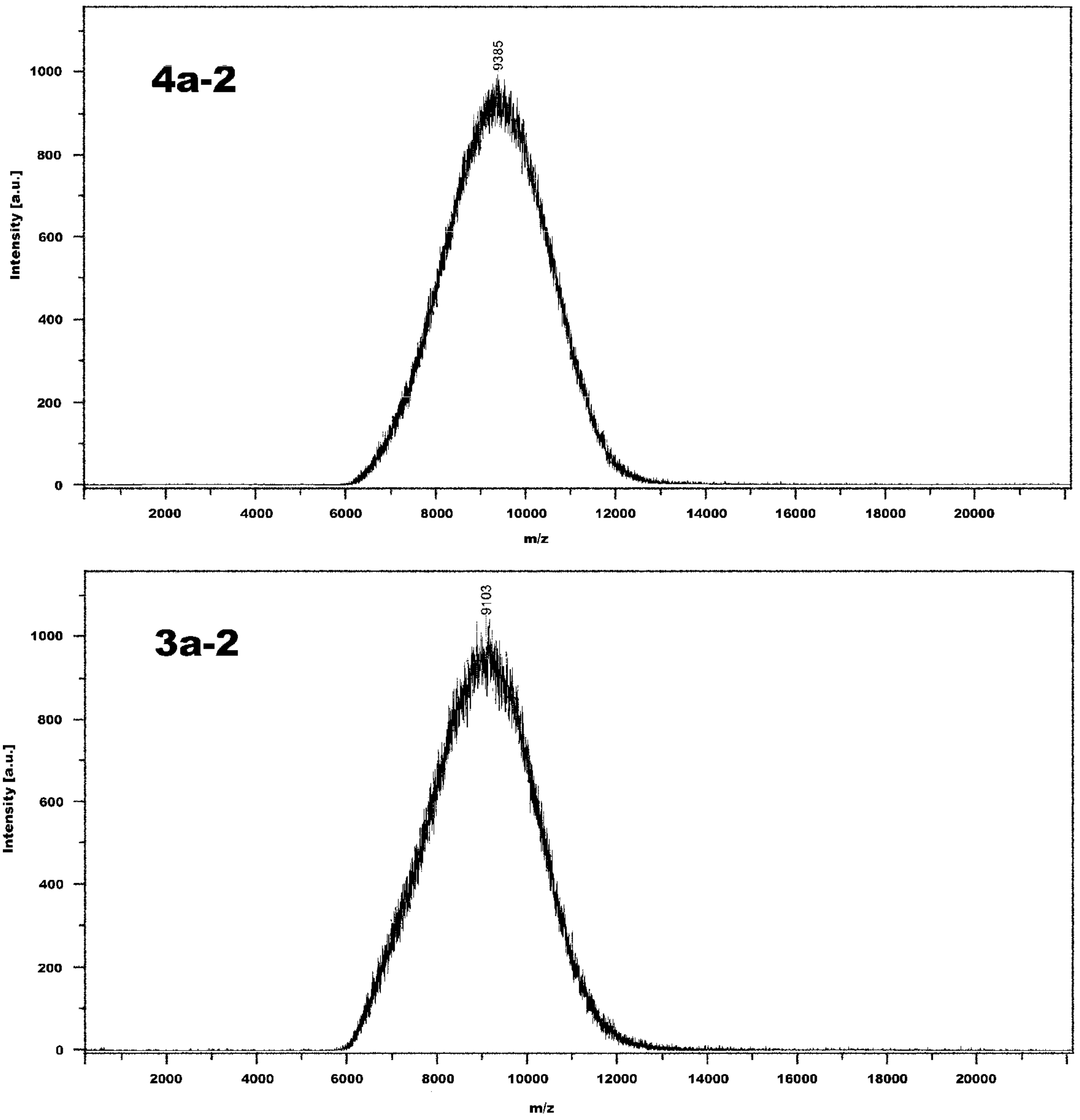


Figure 6. MALDI-TOF mass spectra of **3a-2** (M_n = 8960, M_w/M_n = 1.017) and **4a-2** (M_n = 9280, M_w/M_n = 1.015). Matrix: α-cyano-4-hydroxycinnamic acid; cation source: Na^+ and K^+ in glassware, solvents and reagents. MALDI-TOF: matrix-assisted laser desorption ionization time-of-flight.

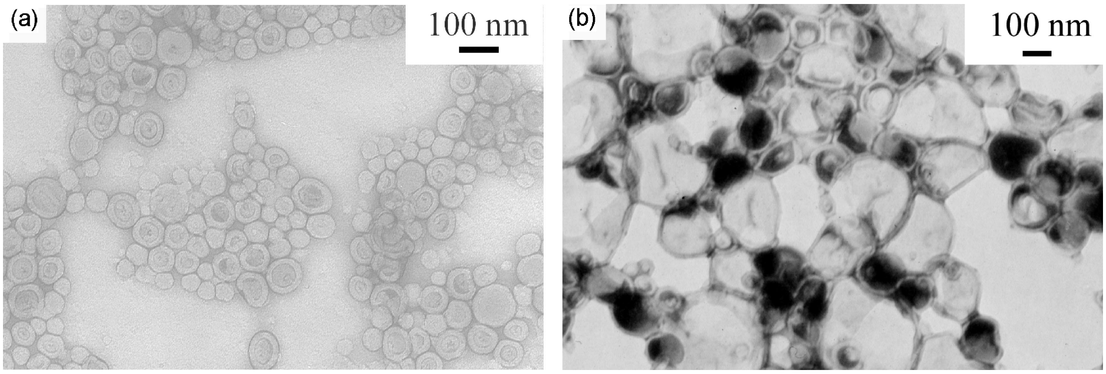


Figure 7. TEM graphs of aggregate of (a) **3a-2** and (b) **4a-2** in water at a concentration of 0.2 mg/mL. TEM: transmission electron microscopy.

dynamic laser light scattering methods; the results revealed that for **3a-2**, the average diameter of the aggregates was 70 nm, whereas that of **4a-2** was 160 nm (Supporting Information). The difference in morphology and size of the aggregates may reasonably be attributed to the cyclic PS structure, which may restrict chain stretching of PS during self-assembly. We are now systematically studying the different aggregating behavior of linear block copolymer **3** and tadpole-shaped copolymer **4.**

Conclusions

A series of tadpole-shaped copolymers consisting of cyclic PS and a linear PEO tail were synthesized by the combination of two click reactions and one ATRP. The first click chemistry used in the synthesis of ATRP macroinitiators made it easy to change the chain lengths and composition (if other azide-terminated polymers were used instead of PEO-N_3) of the tail. Linear diblock precursors with controlled molecular weights and low polydispersity indexes were prepared by ATRP, which runs under mild conditions and is tolerant of functional groups. The second click chemistry lead to a high conversion of functional groups when it was used in the cyclization of linear precursors. The cyclization conditions are needed to be optimized to reduce the intermolecular coupling reaction. This method provides the possibility of changing the size and composition of the tadpole-shaped copolymers. Our preliminary study on the self-assembly of these new polymers revealed that polymer topology did affect both the morphologies and the sizes of the aggregates; further detailed study should be necessary and is currently undergoing in our laboratory.

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Supporting Information Available: Gel permeation chromatography (GPC) traces of **3a-1**, **4a-1**, **3a-3**, **4a-3**, **3b**, and **4b**. ^{1}H NMR spectra of **3a-1**, **4a-1**, **3a-3**, and **4a-3**. IR spectra of **3a-1**, **4a-1**, **3a-3**, **4a-3**, **3b**, and **4b**. DLS characterization of the self-assembly of **3a-2** and **4a-2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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