

ATRP–RCM polymer cyclization: synthesis of amphiphilic cyclic polystyrene-*b*-poly(ethylene oxide) copolymers

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A novel amphiphilic block copolymer, *i.e.*, cyclic polystyrene-*b*-poly(ethylene oxide) (cyclic PS-*b*-PEO **2**), was synthesized through atom-transfer radical polymerization (ATRP), followed by ring-closing metathesis (RCM). Thus, a bromobenzyl-terminated PS-*b*-PEO-*b*-PS (**6**) was first prepared by ATRP of styrene using a PEO macroinitiator having 2-bromoisobutyryl groups (**5**). The subsequent end-group conversion into allyl groups was performed quantitatively with allyltrimethylsilane (ATMS) in the presence of TiCl₄. The allyl-telechelic triblock copolymer PS-*b*-PEO-*b*-PS (**7**) thus obtained was subjected to metathesis polymer cyclization with a Grubbs' 2nd generation catalyst to produce amphiphilic cyclic PS-*b*-PEO (**2**).

1. Introduction

Cyclic polymers are gaining growing interest since they are distinctive from their linear and branched counterparts by the absence of chain ends, and their unique properties often rely on their particular topologies.^{1–3} Moreover, cyclic block copolymers constructed by the combination of incompatible segments may provide novel properties and functions by their self-assemblies causing the “amplification” of the *topology effect*.

The synthesis of a cyclic block copolymer is carried out, as for a cyclic homopolymer, either by end-to-end ring closure or by ring-expansion polymerization.⁴ The former process involves a bimolecular, *homo*-unimolecular or *hetero*-unimolecular reaction. The bimolecular process is apparently not practical due to the kinetic suppression in the second-order reaction particularly under dilution, which is a prerequisite to avoid concurrent intermolecular reactions. On the other hand, a handful of examples of *homo*- and *hetero*-unimolecular processes with telechelics having identical or complementary reactive groups have demonstrated the production of cyclic block copolymers. The *hetero*-unimolecular process has first been applied to synthesize cyclic polystyrene-*b*-polyisoprene (PS-*b*-PI) through the intramolecular acetalization in dilution.⁵ More versatile polymer cyclization by alkyne–azide click chemistry has subsequently been introduced to form cyclic poly(methyl acrylate)-*b*-polystyrene⁶ and PS-*b*-PI.⁷ The *click* polymer cyclization was further applied to produce complex cyclic block copolymers having 8-shaped⁸ and θ -shaped⁹ topologies, as well as to give a unimeric macrocyclic structure from a micelle.¹⁰

The alternative *homo*-unimolecular process is considered practically more viable because symmetric telechelic precursors are readily accessible in comparison with the relevant *hetero*-telechelics. Thus, PS-*b*-PI-*b*-PS triblock telechelics with 1,1-diphenylethylene end groups were prepared and subjected to polymer cyclization through radical coupling by the addition of potassium naphthalide.¹¹ More recently an alkyne coupling reaction (Glaser coupling) was introduced to form a cyclic PS-*b*-PEO copolymer.¹²

We have developed an effective *homo*-unimolecular process by the ring-closing metathesis (RCM) of a symmetric telechelics having olefinic groups, which is conveniently obtainable through the direct end-capping reaction of a variety of living polymers.¹³ In conjunction with ATRP, the quantitative conversion of the bromo termini into allyl groups on poly(acrylate)s was achieved by a reaction with allyltributylstannane (Keck allylation).¹⁴ The allyl-telechelics were then subjected to RCM under dilution to produce effectively cyclic diblock copolymers, including an amphiphilic poly(butyl acrylate)-*b*-PEO.

Remarkably, a micelle formed from the obtained cyclic amphiphile exhibits a significantly enhanced thermal stability in comparison with the one from the linear counterpart.¹⁵ This finding is regarded as the first example of an amplified *topology effect* by a synthetic cyclic polymer upon self-assembly.¹⁶

In order to promote further studies on the subject, the ATRP–RCM polymer cyclization process must be tuned to provide a variety of cyclic block copolymers having the programmed combination of segment components with narrow PDIs. In particular, amphiphilic block copolymers comprised of polystyrene components are of importance since self-assembled structures by linear PS-*b*-PEO copolymers have extensively been studied to show the formation of micelles to vesicles and further complex aggregates.^{17,18} Therefore, relevant cyclic PS-*b*-PEO counterparts could provide unique opportunities to reveal novel

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topology effects upon self-assembly. However, our preliminary attempts by Keck allylation for the quantitative conversion of the bromobenzyl end groups of ATRP-based polystyrene into allyl groups were unsuccessful contrary to the case with bromoester end groups. Thus in this report, we show an alternative allylation process for the ATRP-based polystyrene precursor and the subsequent effective synthesis of cyclic PS-*b*-PEO copolymers.^{13,14,19}

It is noteworthy also that ring-expansion polymerization is now becoming an alternative attractive approach to synthesize cyclic block copolymers, in which the dilution in the cyclization process can be avoided. Various cyclic esters, typically ϵ -caprolactone and β -butyrolactone, are known to undergo ring-expansion polymerization by a cyclic tin initiator.²⁰ Now the incorporated initiator fragment can be removed to maintain the stable cyclic polymer structure by introducing short UV-cross-linkable segments during the ring-expansion polymerization.²¹ More recently, an *N*-heterocyclic carbene initiator was applied to construct cyclic gradient copolymers from cyclic esters.²² In addition, a RAFT process using a cyclic chain transfer agent was reported to form a cyclic block copolymer comprised of poly(methyl acrylate) and poly(*N*-isopropyl acrylamide) segments.²³ Moreover, various ring-containing block copolymers having tadpole-, sun- and 8-shaped structures as well as a heterocatenane have also been subjects of recent research efforts.^{24–28}

2. Experimental

2.1 Reagents and materials

Styrene (99%, Nacalai Tesque, Inc.) was purified by passing it through an alumina column. CH₂Cl₂ (99%, Kanto Chemical Co., Inc.) was distilled from CaH₂ before use. A PEO macroinitiator having 2-bromoisobutyryl end groups (**5**, M_n (NMR) = 2300) was prepared by esterification of hydroxy-terminated PEO (M_n = 2000, Aldrich) with 2-bromoisobutyryl bromide (98%, Aldrich) and triethylamine (99%, Kanto Chemical Co., Inc.) according to the previously reported procedure.^{14,19} CuBr (99%, Nacalai Tesque, Inc.), 2,2'-bipyridyl (bpy) (99.5%, Nacalai Tesque, Inc.), benzal bromide (97%, Aldrich), allyltrimethylsilane (ATMS, 98%, Aldrich), TiCl₄ (99%, Nacalai Tesque, Inc.), methanol (Godo Co., Inc.), *n*-hexane (Godo Co., Inc.), Grubbs' 1st and 2nd generation catalysts (Aldrich), ethyl vinyl ether (99%, Aldrich) and activated alumina (300 mesh, Wako Pore Chemical Industries, Ltd.) were used as received.

2.2 Synthesis of bromobenzyl-terminated PS (**3**)

Benzal bromide (0.17 mL, 1.0 mmol), styrene (11.5 mL, 0.10 mol), bpy (468 mg, 3.0 mmol), and CuBr (143 mg, 1.0 mmol) were put in a test tube. The mixture was degassed by freeze-pump-thaw cycles, and the test tube was sealed under vacuum. The resulting suspension was stirred at 110 °C for 6 h. The reaction was quenched by cooling in liquid nitrogen. After allowing to warm to room temperature, the reaction mixture was filtered through a plug of alumina. The eluent was concentrated and poured into methanol to precipitate, allowing isolation of **3** as white solid (3.36 g). M_p (SEC) = 8000, PDI = 1.22. ¹H NMR: δ (ppm) 1.05–2.62 (m, -CH₂CH(Ph)-), 4.31–4.61 (m, -CH(Ph)-Br), 6.25–7.45 (m, -CH₂CH(C₆H₅)-).

2.3 Synthesis of allyl-telechelic PS (**4**)

TiCl₄ (1.0 mL, 9.1 mmol) and ATMS (1.0 mL, 6.3 mmol) were added to a CH₂Cl₂ solution (5.0 mL) of **3** (700 mg, 0.10 mmol), and the mixture was stirred at 0 °C for 20 min. The reaction was quenched by addition of methanol, and the resulting solution was concentrated and poured into methanol to precipitate, allowing isolation of **4** as white solid (540 mg) in 77% yield. M_p (SEC) = 8800, PDI = 1.19. ¹H NMR: δ (ppm) 1.05–2.55 (m, -CH₂CH(Ph)-), 4.71–4.92 (m, -CH₂CH=CH₂), 5.48 (br s, -CH₂CH=CH₂), 6.21–7.42 (m, -CH₂CH(C₆H₅)-).

2.4 Synthesis of cyclic PS (**1**)^{13,14,19}

A Grubbs' 1st generation catalyst (8.2 mg, 10 μ mol) was added to a CH₂Cl₂ solution (90 mL) of **4** (45.0 mg, 5.0 μ mol), and the resulting solution was refluxed for 24 h. Another portion of a Grubbs' 1st generation catalyst (8.2 mg, 10 μ mol) was added, and the mixture was further refluxed for 24 h. Ethyl vinyl ether was added, and the mixture was stirred at room temperature for 1 h. The solution was concentrated and poured into methanol to precipitate, allowing isolation of **1** as white solid (25.4 mg) in 56% yield. M_p (SEC) = 7500, PDI = 1.28. ¹H NMR: δ (ppm) 0.79–2.42 (m, -CH₂CH(Ph)-), 4.70–4.98 (m, -CH=CH-), 6.25–7.46 (m, -CH₂CH(C₆H₅)-).

2.5 Synthesis of bromobenzyl-terminated PS-*b*-PEO-*b*-PS (**6**)

PEO macroinitiator **5** (1.00 g, 0.44 mmol), styrene (11.5 mL, 100 mol), bpy (469 mg, 3.0 mmol), and CuBr (143 mg, 1.0 mmol) were put in a test tube. The mixture was degassed by freeze-pump-thaw cycles, and the test tube was sealed under vacuum. The resulting suspension was stirred at 110 °C for 2.5 h. The reaction was quenched by cooling in liquid nitrogen. After allowing to warm to room temperature, the reaction mixture was diluted with THF and filtered through a plug of alumina. The eluent was concentrated and poured into methanol to precipitate, allowing isolation of **6** as colorless solid (1.91 g). M_n (NMR) = 4500–2400–4500 for PS-PEO-PS, M_p = 12 100, PDI = 1.21. ¹H NMR: δ (ppm) 0.78–1.10 (m, CH₃), 1.10–2.58 (m, -CH₂CH(Ph)-, -CH₂CH(Ph)-), 3.31–3.94 (m, -OCH₂-), 4.31–4.58 (m, -CH(Ph)-Br), 6.28–7.39 (m, -CH₂CH(C₆H₅)-).

2.6 Synthesis of allyl-telechelic PS-*b*-PEO-*b*-PS (**7**)

TiCl₄ (1.0 mL, 9.1 mmol) and ATMS (1.0 mL, 6.3 mmol) were added to a CH₂Cl₂ solution (5.0 mL) of **6** (1.80 g, 0.15 mmol), and the mixture was stirred at 0 °C for 20 min. The reaction was quenched by addition of methanol, and the resulting solution was concentrated and poured into methanol to precipitate, allowing isolation of **7** as colorless solid (1.45 g) in 81% yield. M_n (NMR) = 4800–2300–4800 for PS-PEO-PS, M_p = 11 500, PDI = 1.25. ¹H NMR: δ (ppm) 0.79–1.08 (m, CH₃), 1.08–2.58 (m, -CH₂CH(Ph)-, -CH₂CH(Ph)-), 3.29–3.95 (m, -OCH₂-), 4.72–4.96 (m, -CH₂CH=CH₂), 5.45 (br s, -CH₂CH=CH₂), 6.30–7.38 (m, -CH₂CH(C₆H₅)-).

2.7 Synthesis of amphiphilic cyclic PS-*b*-PEO (**2**)^{13,14,19}

A Grubbs' 2nd generation catalyst (17 mg, 20 μ mol) was added to a CH₂Cl₂ solution (240 mL) of **7** (120 mg, 10 μ mol), and the

resulting solution was refluxed for 24 h. Another portion of a Grubbs' 2nd generation catalyst (17 mg, 20 μ mol) was added, and the mixture was further refluxed for 24 h. Ethyl vinyl ether was added, and the reaction mixture was stirred at room temperature for 1 h. The solution was concentrated and poured into methanol to precipitate, allowing isolation of **2** as colorless solid (39.8 mg) in 33% yield. M_n (NMR) = 7900–1800 for PS-PEO, M_p = 10 700, PDI = 1.20. ^1H NMR: δ (ppm) 0.80–1.09 (m, CH_3), 1.09–2.56 (m, $-\text{CH}_2\text{CH}(\text{Ph})-$, $-\text{CH}_2\text{CH}(\text{Ph})-$), 3.29–3.99 (m, $-\text{OCH}_2-$), 4.69–4.95 (m, $-\text{CH}=\text{CH}$), 6.29–7.42 (m, $-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)-$).

2.8 Measurements

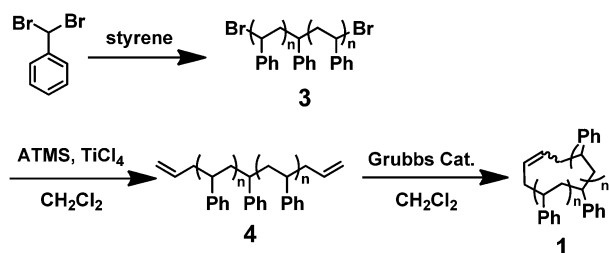
^1H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer operating at 300 MHz using CDCl_3 as a solvent. Proton chemical shifts were reported relative to the signal of tetramethylsilane. SEC measurements were performed on a Tosoh model CCPS equipped with a refractive index detector model RI 8020 and a TSK G3000HXL column equilibrated at 40 $^\circ\text{C}$. THF was used as an eluent at a flow rate of 1.0 mL min^{-1} . Linear PS standards were used for calibration, and the peak molecular weight (M_p) of polymer samples was reported as a linear PS equivalent. MALDI-TOF mass spectra were recorded on a Shimadzu AXIMA Performance mass spectrometer equipped with a nitrogen laser ($\lambda = 337 \text{ nm}$). The spectrometer was operated at an accelerating potential of 20 kV in a linear positive ion mode with pulsed ion extraction. THF solutions of a polymer sample (1.0 mg mL^{-1}), dithranol (10 mg mL^{-1}) and silver trifluoroacetate (2.0 mg mL^{-1}) were mixed (50/50/50 in $\mu\text{L}/\mu\text{L}/\mu\text{L}$), and a 1 μL portion of the mixture was deposited onto a sample target plate. Mass values were calibrated by the three-point method using insulin plus H^+ at 5734.62, insulin β plus H^+ at 3497.96 and α -cyanohydroxycinnamic acid dimer plus H^+ at 379.35.

3. Results and discussion

3.1 Synthesis of cyclic PS (1)

In order to establish an optimized synthetic protocol for a cyclic PS-*b*-PEO copolymer, we first examined the ATRP-RCM polymer cyclization of a PS homopolymer as shown in Scheme 1. In this connection, Quirk and coworkers recently reported the preparation of cyclic PS homopolymers through the combination of anionic polymerization and RCM.²⁹

Thus, bromobenzyl-terminated PS **3** was prepared by ATRP of styrene initiated by benzal bromide in the presence of bpy and CuBr .^{30,31} Signals from the methyne protons adjacent to the



Scheme 1 Synthesis of cyclic PS **1**.

bromine atoms were visible at 4.31–4.61 ppm as a multiplet (Fig. 1, top). M_p (SEC) was determined to be 8000 with a PDI of 1.22 (Fig. 2, top).

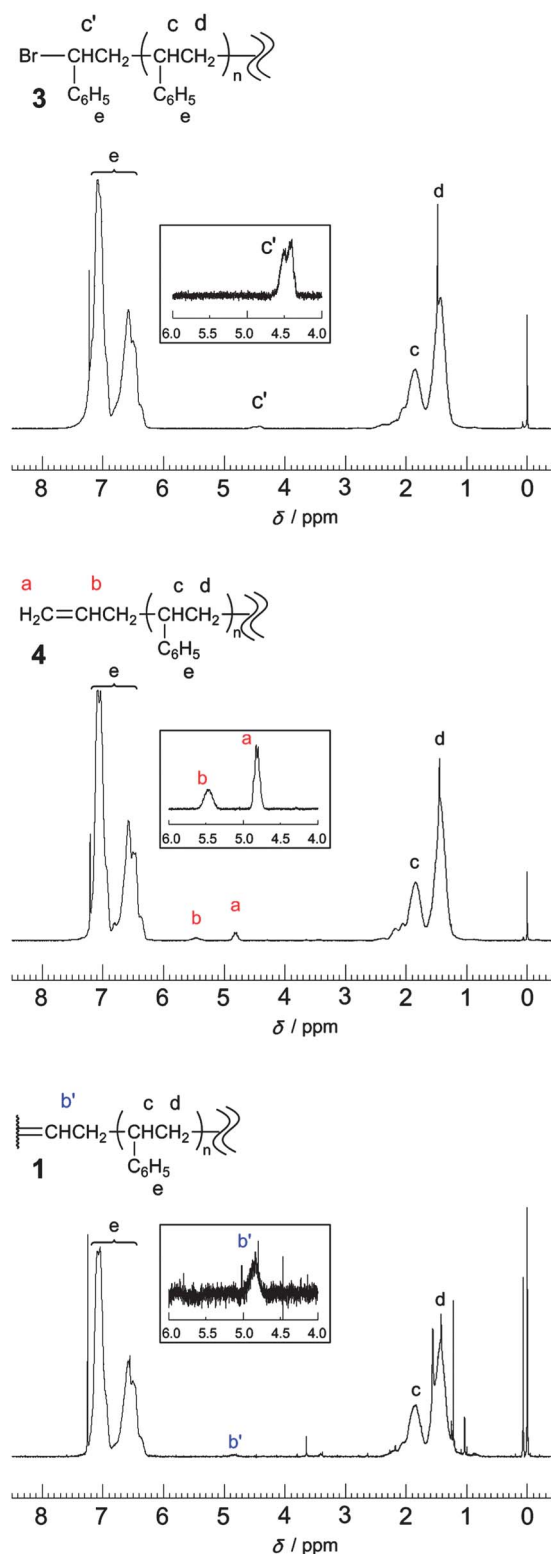


Fig. 1 ^1H NMR spectra of bromobenzyl-terminated PS **3**, allyl-telechelic PS **4** and cyclic PS **1**.

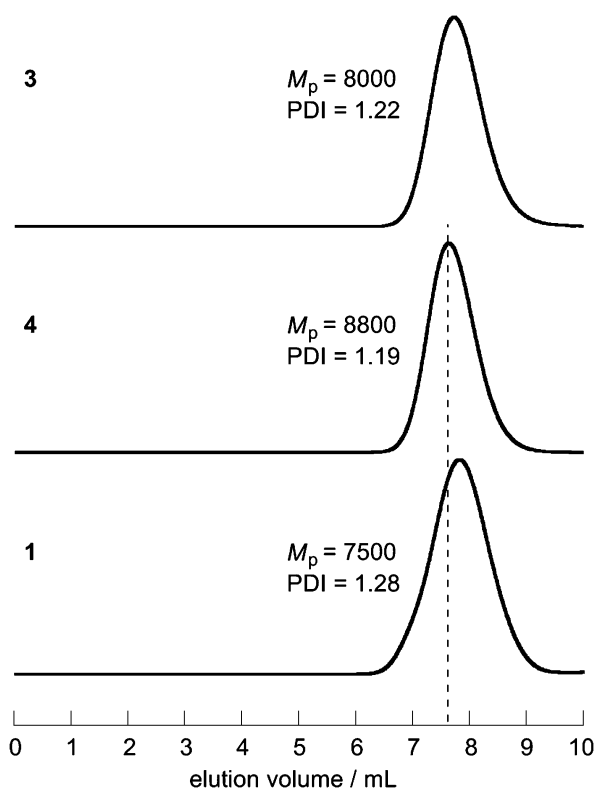


Fig. 2 SEC profiles of bromobenzyl-terminated PS **3**, allyl-telechelic PS **4** and cyclic PS **1**.

In order to convert the bromobenzyl end groups of **3**, we initially attempted Keck allylation with allyltributyltin as reported in the preceding poly(acrylate)s.^{14,19} The reaction, however, was sluggish with the concurrent formation of unidentifiable side products. We have subsequently found that an alternative allylation reaction with a large excess of ATMS in the presence of TiCl_4 proceeded effectively.^{32,33} The NMR spectrum of **3** showed that signals from the methyne protons adjacent to the bromine atoms completely disappeared after the allylation, and those of the terminal olefin groups appeared at 4.71–4.92 and 5.48 ppm (Fig. 1, middle).³⁴

Obtained allyl-telechelic PS **4** was then subjected to intramolecular RCM in the presence of a Grubbs' 1st generation catalyst (2 equiv. in twice) by refluxing for 48 h in dilution (0.50 g L^{-1}). The completion of the reaction was indicated by the emergence of signals at 4.70–4.98 ppm from the internal olefin group in place of those at the termini (Fig. 1, bottom).³⁴

The SEC profiles of telechelic **4** and RCM product **1** are shown in Fig. 2, middle and bottom, respectively. M_p (SEC), corresponding to the hydrodynamic volume of a polymer in solution, of product **1** (7500) was smaller than that of prepolymer **4** (8800). This also supports the formation of a cyclic product, which has a smaller hydrodynamic volume than the linear counterpart of the relevant chain length.^{35–37} Moreover, the SEC peak remained unimodal after the cyclization, indicating the absence of intermolecular chain-extension to form dimeric or higher oligomeric products.

The MALDI-TOF mass spectra of **4** and **1** showed uniform series of peaks with an interval of 104 mass units, which is the

molecular weight of a styrene unit, and each peak exactly matched to the total molar mass of the repeating units and linking structure (Fig. 3 and Table 1). For example, the observed peak at 4341.51, which is assumed to be an adduct with Ag^+ , corresponds to **4** possessing the expected chemical structure with a DP_n of 40; $(\text{C}_6\text{H}_5) \times 40 + \text{C}_5\text{H}_8$ plus Ag^+ equals to 4342.07 based on the average isotope distribution. A series of peaks corresponding to an Ag^+ adduct was also found for **1**. Thus, the peak at 4314.38 was from the product with a DP_n of 40; $(\text{C}_6\text{H}_5) \times 40 + \text{C}_3\text{H}_4$ plus Ag^+ equals to 4314.02 based on the average isotope distribution. Since cyclic **1** was produced from allyl-telechelic **4** by the elimination of an ethylene molecule, their molecular weights should differ by 28 mass units. This was confirmed by the mass spectral data ($4341.51 - 4314.38 = 27.13$, Table 1, $\text{DP}_n = 40$), coupled with the NMR and SEC results, to substantiate the formation of cyclic PS **1**.

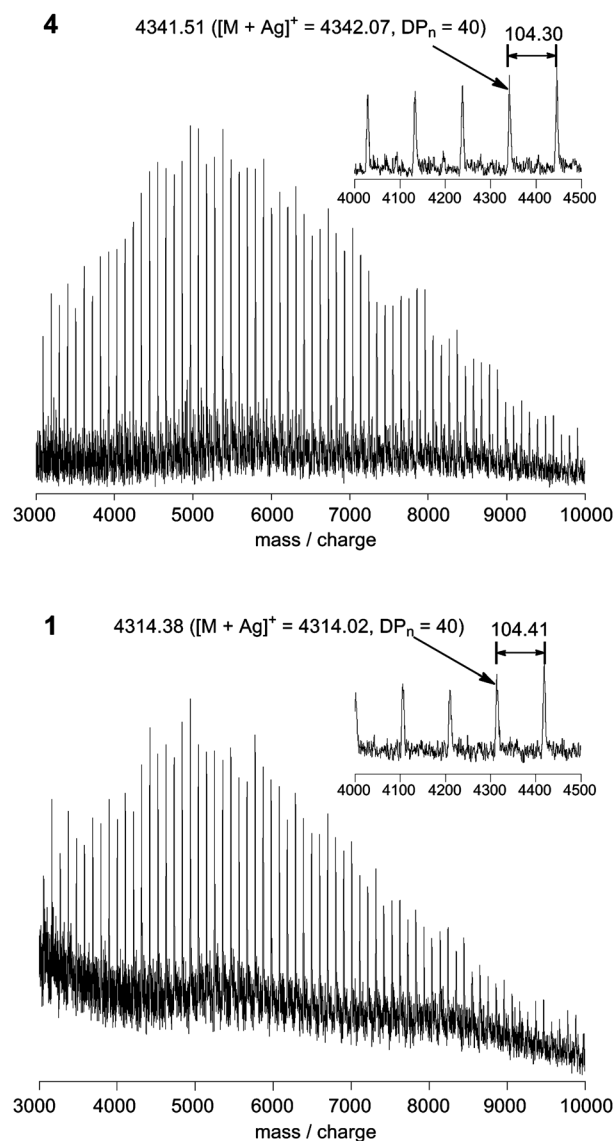


Fig. 3 MALDI-TOF mass spectra of (top) allyl-telechelic PS **4** and (bottom) cyclic PS **1**.

Table 1 Calculated and observed m/z values of allyl-telechelic linear PS **4** and cyclic PS **1** for a range of 4000–5000. The calculated values are on the basis of the average isotope distribution

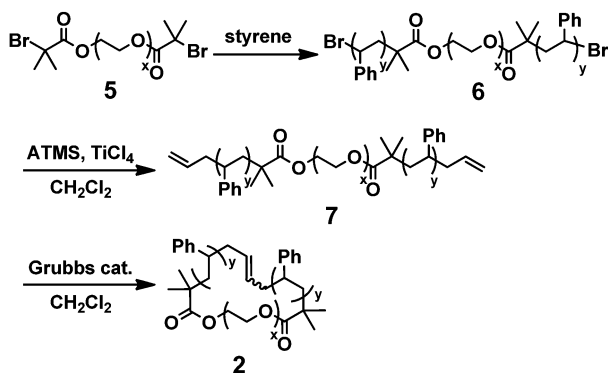
DP_n	Linear 4		Cyclic 1		Linear 4 – cyclic 1
	Calculated	Observed	Calculated	Observed	Observed
37	4029.62	4028.67	4001.56	4001.53	27.14
38	4133.77	4133.02	4105.71	4105.70	27.32
39	4237.92	4237.55	4209.87	4210.23	27.32
40	4342.07	4341.51	4314.02	4314.38	27.13
41	4446.22	4445.92	4418.17	4418.68	27.24
42	4550.38	4549.96	4522.32	4522.85	27.11
43	4654.53	4654.15	4626.47	4627.17	26.98
44	4758.68	4758.36	4730.63	4730.92	27.44
45	4862.83	4862.19	4834.78	4835.44	26.75
46	4966.98	4966.03	4938.93	4939.37	26.66

3.2 Synthesis of amphiphilic cyclic PS-*b*-PEO (**2**)

Based on the results for the PS homopolymer described in the preceding section, the ATRP–RCM process was applied to relevant ABA-type triblock copolymers. Thus, PS-*b*-PEO-*b*-PS having bromobenzyl end groups **6** was prepared by ATRP of styrene initiated using the PEO macroinitiator having 2-bromoisobutyryl groups **5** under an analogous reaction conditions (Scheme 2). By referencing to the signal of the dimethyl groups adjacent to the ester linkage, the M_n (NMR) of the PS segments was determined to be 4500×2 (Fig. 4, top).³⁸

The bromobenzyl end groups of **6** were converted into allyl functionalities by treatment with ATMS as in the step from **3** to **4**. The resulting allyl-telechelic triblock copolymer (PS-*b*-PEO-*b*-PS) **7** was subsequently subjected to RCM in dilution (0.50 g L^{-1}). Notably, the reaction with a Grubbs' 1st generation catalyst, used in the synthesis of cyclic PS **1**, was observed prohibitively slow. Fortunately, an alternative Grubbs' 2nd generation catalyst, known to be more stable and reactive, was found effective to complete the RCM reaction to give cyclic PS-*b*-PEO copolymer **2**.

The ^1H NMR spectra showed that the signals from the methyne protons adjacent to the bromine atoms at 4.31–4.58 ppm in **6** completely disappeared after the allylation, and those due to the terminal olefin groups appeared at 4.72–4.96 and 5.45 ppm in **7** (Fig. 4, top and middle).³⁴ Moreover, upon RCM,



Scheme 2 Synthesis of amphiphilic cyclic PS-*b*-PEO copolymer **2**.

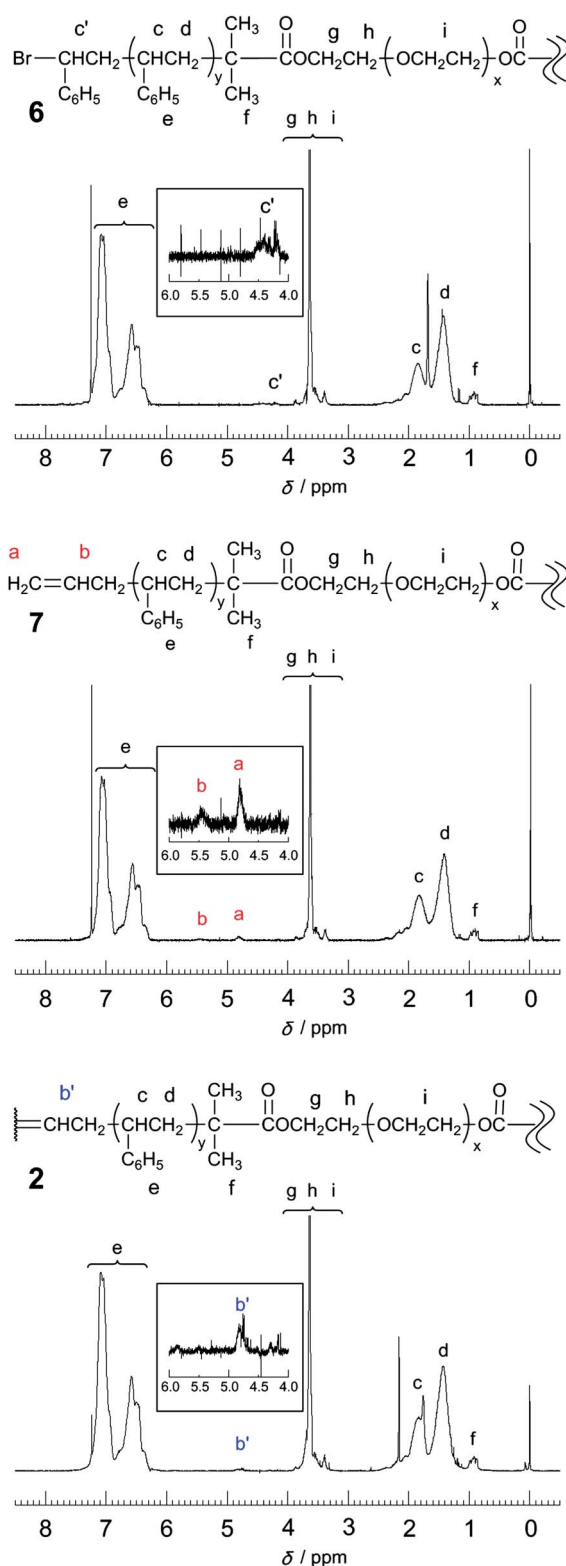


Fig. 4 ^1H NMR spectra of bromobenzyl-terminated PS-*b*-PEO-*b*-PS **6**, allyl-telechelic PS-*b*-PEO-*b*-PS **7** and cyclic PS-*b*-PEO **2**.

signals from the internal olefin group appeared at 4.69–4.95 ppm in place of the terminal allyl groups (Fig. 4, bottom).³⁴ M_n (NMR) for PS-*b*-PEO-*b*-PS **7** and PS-*b*-PEO **2** was determined to be 4800–2300–4800 and 7900–1800, respectively.

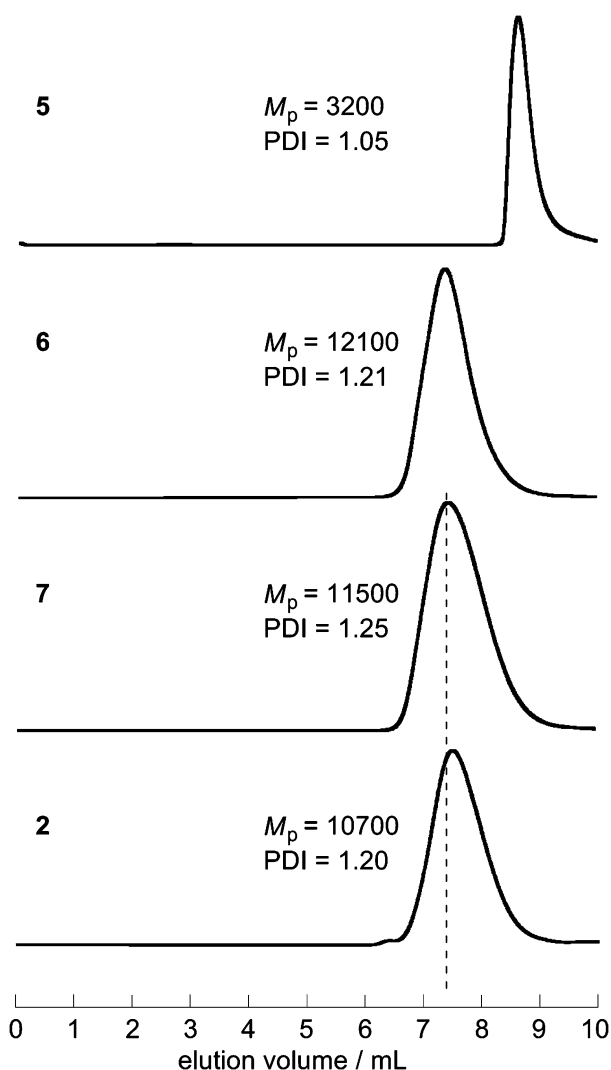


Fig. 5 SEC profiles of macroinitiator **5**, 2-bromobenzyl-terminated PS-*b*-PEO-*b*-PS **6**, allyl-telechelic PS-*b*-PEO-*b*-PS **7** and cyclic PS-*b*-PEO **2**.

The progress of the block copolymerization, allylation, and subsequent cyclization was further confirmed by the SEC analysis of a series of the intermediates and final product, **5**, **6**, **7** and **2**, as shown in Fig. 5. The block copolymerization from **5** to form **6** resulted in a large increase in M_p (SEC) from 3200 to 12 100. The subsequent end group conversion of **6** to give **7** did not cause any significant change in the elution profile, indicating that the PEO segment was intact during the allylation using ATMS. Finally, the RCM of linear precursor **7** into cyclic **2** caused a decrease in M_p (SEC) from 11 500 to 10 700 in accord with the reduction in the hydrodynamic volume by polymer cyclization.^{35–37} Based on these results, along with the full characterization of cyclic homo-PS **1**, the formation of amphiphilic cyclic PS-*b*-PEO **2** was substantiated.

4. Conclusions

We demonstrated the effective construction of cyclic PS homopolymer **1** and amphiphilic cyclic PS-*b*-PEO copolymer **2** by sequential ATRP, allylation with ATMS, and RCM. The synthetic

methodology of a cyclic block copolymer structure is now extended to those containing PS block segments and will be further applicable for various (co)polymers that can be prepared by ATRP.^{14,19} This will certainly contribute to the development of topology-based polymer materials design through their self-assembly.

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