ATRP−RCM Synthesis of Cyclic Diblock Copolymers

Kaoru Adachi,[†] Satoshi Honda, Shotaro Hayashi, and Yasuyuki Tezuka*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT: A versatile synthetic means for cyclic diblock copolymers has been developed by the combination of atom transfer radical polymerization (ATRP) and ring-closing metathesis (RCM) techniques. Thus, first, an A−B type allyl-telechelic diblock copolymer comprised of two different acrylate ester segments, i.e., poly(methyl acrylate)-*b*-poly(*n*-butyl acrylate), poly(MA)-*b*-poly(BA), was prepared via the ATRP of MA, followed by the addition of the second monomer, BA, with allyl bromide as an initiator and with allyltributylstannane as an end-capping reagent, respectively. Alternatively, an A−B−A type allyl-telechelic triblock copolymer comprised of poly(BA) and poly(ethylene oxide), poly(EO), segments was prepared via the ATRP of BA using a poly(EO) macroinitiator having 2-bromoisobutyryl end groups, followed by the end-capping reaction with allyltributylstannane. The subsequent RCM of the allyl-telechelic block copolymers under dilution in the presence of Grubbs catalyst could afford the corresponding A−B type cyclic diblock copolymers.

Introduction

Block copolymers have widely been recognized as a potentially important soft material due to their self-assembled structures constructed by the combination of polymer segments having different and incompatible chemical compositions.[1] They could form micelles and vesicles in solution[2] and such unique morphologies, as lamellar, cylinder, sphere, and even more complex structures, in bulk nanometer scale.[3] Moreover, extensive studies have been undertaken by employing star, H-shaped, and other branched block copolymers to reveal distinctive static and dynamic properties dictated by their nonlinear polymer topologies.[4]

Cyclic block copolymers are also unique by their absence of free chain ends and are theoretically anticipated[5] and indeed experimentally confirmed as distinctive against their linear or branched counterpart, in their structures as well as their dynamics.[6−10] These cyclic block copolymers were typically obtained through a bimolecular end-to-end cyclization process using a telechelic A−B−A triblock copolymer, such as poly(dimethylsiloxane)-*b*-polystyrene-*b*-poly(dimethylsiloxane),[6] poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide),[7] and polystyrene-*b*-polybutadiene (or polyisoprene)-*b*-polystyrene, as precursors.[8,9] Recent efforts to achieve the practical synthesis of cyclic block copolymers of prescribed combination of two specific segments include an unimolecular cyclization process with an asymmetrically telechelic A−B diblock copolymer.[11,12] Thus, a cyclic polystyrene-*b*-polyisoprene copolymer has been synthesized by a unimolecular end-to-end ring closure of an allyl-telechelic, i.e., α-isopropylidine-ω-diethylacetal block copolymer precursor.[11] A cyclic poly(methyl acrylate)-*b*-polystyrene copolymer has also been synthesized through the "click" process using α-alkyn-ω-azide block copolymer precursor obtained by the atom transfer radical polymerization (ATRP).[12] Alternatively, a ring expansion polymerization process has been applied to prepare cyclic poly(methyl acrylate)-*b*-poly(*N*-isopropylacrylamide) copolymer by using a cyclic RAFT initiator.[13]

It is also notable that a number of intriguing synthetic processes have recently been developed for the preparation of cyclic polymers either by the end-linking of polymer precursors[14] or by the ring-expansion polymerization technique.[15] We have also reported an effective polymer cyclization process by making use of allyl-telechelic precursors, readily obtainable either through a living cationic ring-opening polymerization of THF[16] or through an atom transfer radical polymerization (ATRP) of acrylates.[17] They were subsequently subjected to a ring-closing metathesis (RCM) reaction (ATRP−RCM process) to give cyclic polymers in high yields.[16,17] Moreover, a dicyclic 8-shaped polymer was synthesized through the double metathesis reaction of a 4-armed star telechelics having allyl groups obtainable by making use of the ATRP technique.[18]

As an extension of the preceding studies, we report here on the effective synthesis of cyclic diblock copolymers based on the ATRP−RCM process using either A−B or A−B−A type allyl-telechelic block copolymer precursors, obtained via the ATRP technique, recognized as a versatile means to produce a variety of block copolymers[19] (Scheme 1).

Experimental Section

Materials. Methyl acrylate (99%, Aldrich) was distilled before use. *n*-Butyl acrylate (99%, Nacalai Tesque) was distilled under reduced pressure. Allyl bromide (97%, Aldrich) was used after distillation. Dichloromethane (99%, Kanto Chemical) was distilled from CaH_2. Poly(ethylene glycol), poly(EO), ($M_n = 2000$, Aldrich), 2-bromoisobutyryl bromide (98%, Aldrich), triethylamine (99%, Kanto Chemical), Cu(I)Br (99%, Nacalai Tesque), 2,2′-bipyridyl (99%, Nacalai Tesque), 4,4′-dinonyl-2,2′-dipyridyl (97%, Aldrich), allyltributhyltin (97%, Aldrich), Grubbs catalyst first generation (ruthenium(II) dichloride phenylmethylene bis(tricyclohexylphosphine) [$RuCl_2(PCy_3)_2(=CHPh)$], Aldrich), alumina (Wako Chemical, aluminum oxide, activated, 300 mesh), and other chemicals were used as received.

Synthesis of Allyl-Telechelic Poly(MA). An allyl-telechelic poly(MA) was synthesized by the ATRP of methyl acrylate, MA, with allyl bromide as an initiator and subsequent end-capping reaction with allyltributylstannane. As a typical example, into a flask were placed Cu(I)Br (22 mg, 0.15 mmol), 2,2′-bipyridyl (60 mg, 0.38 mmol), MA (1.1 g, 13 mmol), and allyl bromide (20 mg, 0.17 mmol), and the mixture was degassed by a freeze−pump−thaw technique three times. Subsequently, the flask was sealed under vacuum and placed in an oil bath to proceed the reaction with stirring at 90 °C for 2 h. The reaction was then quenched by cooling, and allyltributylstannane (1.6 g, 4.8 mmol) in benzene (1.0 mL) was added to heat again at 90 °C to stand overnight. The polymer product was recovered and purified through column chromatography

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* Corresponding author. E-mail: ytezuka@o.cc.titech.ac.jp.

[†] Current address: Department of Chemistry and Materials Technology, Kyoto Institute of Technology.

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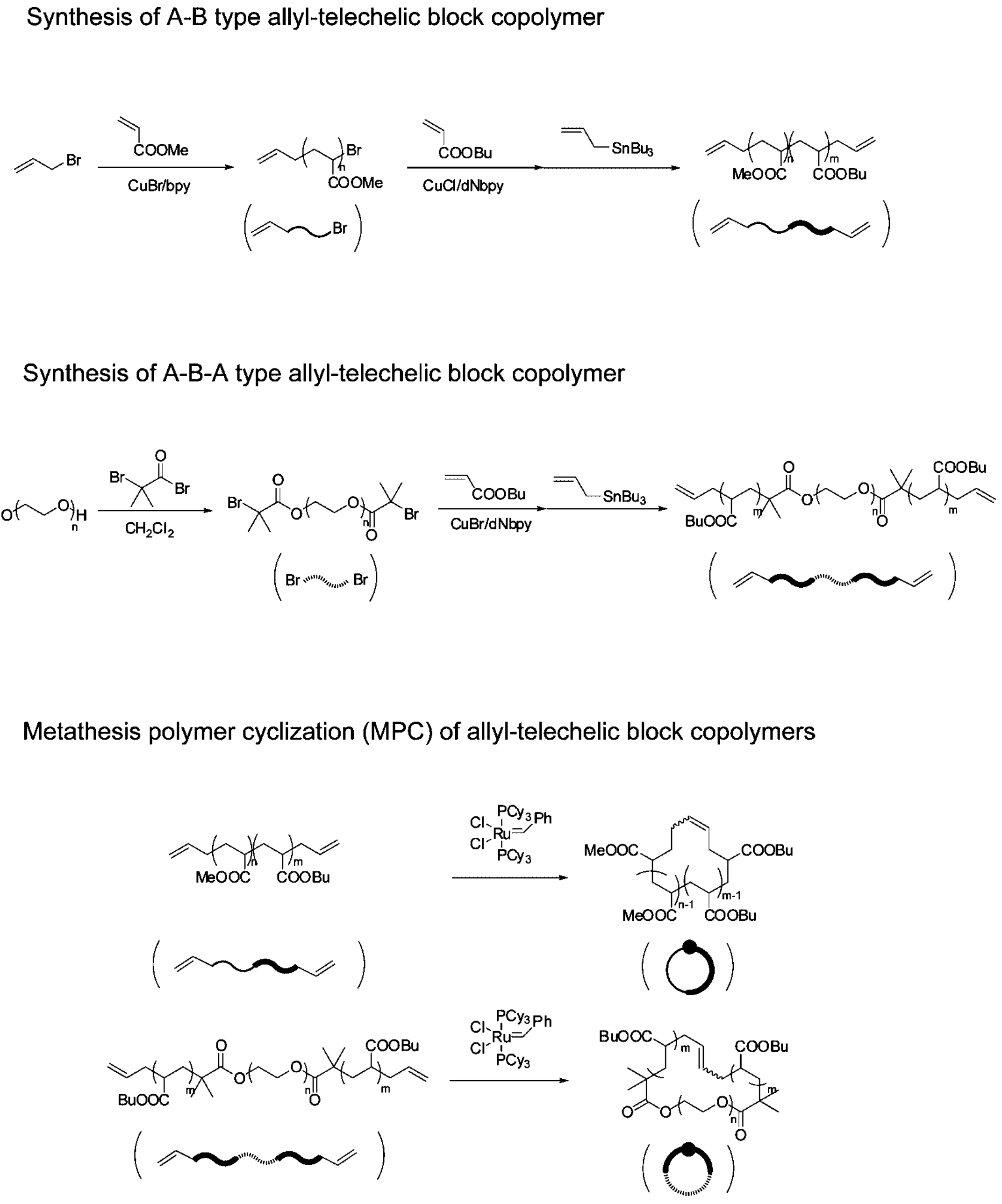
Scheme 1. Atom Transfer Radical Polymerization (ATRP) Synthesis of A−B and A−B−A Type Allyl-Telechelic Block Copolymers and Ring-Closing Metathesis (RCM) Synthesis of A−B Type Cyclic Diblock Copolymers



with alumina, followed by the precipitation into hexane. Yield: 421 mg (38%), M_p (the peak molecular weight by SEC calibrated by polystyrene standards) = 3300, PDI = 1.48. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22−2.15 (m, $-CH_2CHCO-$), 2.15−2.55 (m, $-CH_2CHCO-$), 3.47−3.84 (m, $-OCH_3$), 5.04 (m, 4H, $-CH_2CH{=}CH_2$), 5.67 (m, 2H, $-CH_2CH{=}CH_2$).

Synthesis of A−B Type Allyl-Telechelic Block Copolymer, Poly(MA)-*b*-Poly(BA). First, a poly(MA) precursor having an allyl and a bromoalkyl end groups was prepared by the ATRP as described above, and the polymer product was recovered before the addition of allyltributylstannane. An A−B type allyl-telechelic block copolymer was then prepared by the ATRP with the subsequent addition of *n*-butyl acrylate, BA. Thus, into a flask were placed poly(MA) precursor (200 mg, 0.05 mmol), BA (360 mg, 2.8 mmol), Cu(I)Cl (10 mg, 0.1 mmol), and 4,4′-dinonyl-2,2′-bipyridyl (80 mg, 0.2 mmol), and the mixture was degassed by a freeze−pump−thaw technique three times. Subsequently, the flask was sealed under vacuum and placed in an oil bath to proceed the reaction with stirring at 90 °C for 6 h. The reaction was then quenched by cooling, and allyltributylstannane (1.6 g, 4.8 mmol) in benzene (0.5 mL) was added to heat again at 90 °C to stand overnight. The polymer product was recovered and purified through the column chromatography with alumina, followed by the precipitation into hexane. Yield: 200 mg (36%), M_p (the peak molecular weight by SEC calibrated by polystyrene standards) = 9700, PDI = 1.34. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88−1.05 (m, $-CH_2CH_3$), 1.22−2.15 (m, $-CH_2CHCO-$, $-OCHH_2CH_2CH_2CH_3$), 2.15−2.55 (m, $-CH_2CHCO$), 3.47−3.84 (m, $-OCH_3$), 3.90−4.38 (m, $-COOCH_2CH_2-$), 5.04 (t, 9.8 Hz, 4H, $-CH_2CH{=}CH_2$), 5.67 (m, 2H, $-CH_2CH{=}CH_2$).

Synthesis of A−B−A Type Allyl-Telechelic Block Copolymer, Poly(BA)-*b*-Poly(EO)-*b*-Poly(BA). First, a poly(EO) macroinitiator having 2-bromoisobutyryl groups was prepared by the following procedure. Into an anhydrous CH_2Cl_2 solution (50 mL) containing poly(EO) having hydroxyl end groups (M_n: 2000, 10 g, 5.0 mmol) and triethylamine (1.20 g, 12 mmol) cooled in an ice bath, 2-bromoisobutyryl bromide (3.0 g, 13 mmol) in anhydrous CH_2Cl_2 solution (30 mL) was added dropwise under dry nitrogen over 2 h. The solution was then allowed to warm to room temperature to proceed the reaction with stirring for 24 h. The reaction solution was then filtered and was poured into water (100 mL), and the aqueous phase was extracted by three portions of CH_2Cl_2 (100 mL). The crude product was recovered by evaporating the solvent and was purified by the precipitation of the 10 mL of CH_2Cl_2 solution into diethyl ether to give poly(EO) having 2-bromoisobutyryl groups. Yield: 4.8 g (41%), M_p (the peak molecular weight by SEC calibrated by polystyrene standards) = 2000, PDI = 1.35. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.94 (s, 12H, $-CBr(CH_3)_2$), 3.65−3.76 (m, $-OCH_2-$, $-CO_2CH_2CH_2$), 4.33 (t, 4.8 Hz, 4H, $-CO_2CH_2-$).

An allyl-telechelic A−B−A type block copolymer, poly(BA)-*b*-poly(EO)-*b*-poly(BA), was subsequently prepared by the ATRP using the obtained poly(EO) macroinitiator described above. Thus, into a flask were placed poly(EO) macroinitiator (200 mg, 0.087 mmol), BA (867 mg, 6.8 mmol), 4,4′-dinonyl-2,2′-dipyridyl (dNbpy) (78 mg, 0.19 mmol), and Cu(I)Br (10 mg, 0.07 mmol), and the mixture was degassed by a freeze−pump−thaw technique three times. The reaction was allowed to proceed under stirring at 90 °C for 3 h. Thereupon allyltributylstannane (150 mg, 0.45 mmol) was added to continue the reaction further under stirring at 90 °C for 8 h. The polymer product was recovered through the column chromatography with alumina and was purified by the precipitation into methanol. Yield: 948 mg (89%), M_p (the peak molecular weight by SEC calibrated by polystyrene standards) = 7800, PDI = 1.16. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88−1.05 (m, $-CH_2CH_3$), 1.28−1.92 (m, $-C(CH_3)_2-$, $-CH_2CHCO-$, $-CH_2CH_2CH_3$), 2.11−2.60 (m, $-CH_2CHCO-$), 3.54−3.83 (m, $-OCH_2-$), 3.90−4.16 (m, $-CH_2CHCO_2CH_2-$, $-CH_2OCO-$), 4.17 (m, 4H, $-CO_2CH_2-$), 5.04 (m, 4H, $-CH_2CH{=}CH_2$), 5.67 (m, 2H, $-CH_2CH{=}CH_2$).

Metathesis Polymer Cyclization of A−B Type Allyl-Telechelic Block Copolymer, Poly(MA)-*b*-Poly(BA). An allyl-telechelic A−B type block copolymer (50 mg) was dissolved in CH_2Cl_2 (100 mL) by stirring at ambient temperature for 10 min. A weighed amount of Grubbs catalyst first generation (15 mg) was then added, and the reaction was allowed to proceed under refluxed for 8 h and after further addition of Grubbs catalyst (5 mg) for 19 h. The polymer product was recovered by evaporating the solvent and was purified by the column chromatography with alumina. Yield: 48 mg (96%), M_p (the peak molecular weight by SEC calibrated by polystyrene standards) = 8900, PDI = 1.42. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88−1.05 (m, $-CH_2CH_3$), 1.28−1.92 (m, $-C(CH_3)-$, $-CH_2CHCO-$, $-CH_2CH_2CH_3$), 2.11−2.60 (m, $-CH_2CHCO$), 3.90−4.38 (m, $-CH_2CHCO_2CH_2-$, $-CH_2OCO-$), 5.32 (m, $-CH{=}CH-$).

The metathesis polymer cyclization of allyl-telechelic poly(MA) was also performed in a similar procedure, and the polymer product was recovered by the precipitation into hexane (yield: 73%).

Metathesis Polymer Cyclization of Allyl-Telechelic A−B−A Type Block Copolymer, Poly(BA)-*b*-Poly(EO)-*b*-Poly(BA). Allyl-telechelic A−B−A type block copolymer (100 mg) was dissolved in CH_2Cl_2 (0.5 L) by stirring for 0.5 h. Thereupon, a weighed amount of Grubbs catalyst first generation (30 mg) was added, and the reaction was allowed to proceed under reflux for 48 h. The polymer product was recovered by evaporating the solvent and was purified through the column chromatography with alumina followed by the precipitation into metanol. Yield: 37 mg (37%), M_p (the peak molecular weight by SEC calibrated by polystyrene standards) = 6700, PDI = 1.09. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88−1.05 (m, $-CH_2CH_3$), 1.28−1.92 (m, $-C(CH_3)_2-$, $-CH_2CHCO-$, $-CH_2CH_2CH_3$), 2.11−2.60 (m, $-CH_2CHCO-$), 3.54−3.83 (m, $-OCH_2-$), 3.90−4.38 (m, $-CH_2CHCO_2CH-$, $-CH_2OCO-$), 5.31 (m, $-CH{=}CH-$).

Measurements. ^{1}H NMR spectra (300 MHz) were recorded on a JEOL JNM-AL300 apparatus in $CDCl_3$. The proton chemical shifts (ppm) were referenced to the signal of tetramethylsilane. Size exclusion chromatography (SEC) measurements were performed either using a Shodex GPC101 equipped with a refractive index detector model Shodex RI-71S or a Tosoh model DP-8020 equipped with a refractive index detector model RI 8020. A column of either Shodex LF-804 (300 mm × 8.0 mm i.d., 6 μm average particle size) or TSK G3000HXL (300 mm × 7.8 mm i.d., 5 μm average particle size) was employed with tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min. The molecular weights of the products were calibrated by polystyrene standards. Matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF MASS) spectra were taken on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser (λ = 337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by a linear-positive ion mode. The sample polymer solution (1 g/L) was prepared in THF. The matrix, 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol, Aldrich), and sodium trifluoroacetate (Aldrich) were dissolved in THF (10 and 1 g/L, respectively). The polymer solution (50 μL) was then mixed with 50 μL of the matrix solution. A 1 μL portion of the final solution was deposited onto a sample target plate and allowed to dry in air at room temperature. Mass values were calibrated by the three-point method with insulin plus H^+ at 5734.62, insulin β plus H^+ at 3497.96, and α-cyano-4-hydroxycinnamic acid dimer plus H^+ at 379.35.

Results and Discussion

1. Synthesis of Allyl-Telechelic Block Copolymers. *1.1. A−B Type Allyl-Telechelic Block Copolymer, Poly(MA)-b-Poly(BA).* We have performed the ATRP of methyl acrylate (MA) using allyl bromide as an initiator in the presence of Cu(I)Br and 2,2′-bipyridyl, based on the procedure reported by Matyjaszewski.[20] The subsequent end-capping reaction with allyltributylstannane was conducted to cause the allylation of terminal bromoalkyl groups either directly or after the block copolymerization of the second monomer, *n*-butyl acrylate (BA), in the presence of Cu(I)Cl and 4,4′-dinonyl-2,2′-dipyridyl (dNbpy) (Scheme 1). ^{1}H NMR of both products obtained after the end-capping reaction, i.e., a telechelic poly(MA) (S-Figure 1 (top), in Supporting Information) and an allyl-telechelic poly(MA)-*b*-poly(BA) (Figure 1, top), showed the signals attributed to terminal allyl groups at 5.04 and 5.67 ppm, respectively. The signal of methyne proton adjacent to the bromine atom at 4.23 ppm was completely eliminated after the allylation.[17,18,21]

The obtained allyl-telechlelic poly(MA) was then subjected to MALDI-TOF MS analysis (Figure 2, top).[22] The spectrum showed uniform series of peaks with the peak interval of 86 mass units, which coincided with the molecular weight of MA monomer. Each peak corresponds exactly to the molecular mass summing up the linear poly(MA) having allyl end groups. As an example, the peak (assumed to be the adduct with Na^+) at 2688.1 corresponds to the product with the DP_n of 30, $(C_4H_6O_2) \times 30 + C_6H_{10}$, plus Na^+ as 2687.85. Thus, the presence of allyl groups on opposite ends of the polymer was confirmed for both the initiator fragment and the end-capping reaction.

SEC traces of the poly(MA) precursor having a bromoalkyl end group and the subsequent A−B type allyl-telechelic block copolymer, poly(MA)-*b*-poly(BA), were compared (Figure 3, top and middle) to show the shift of the unimodal profile of the former (M_p of 5400 (polystyrene standard) and PDI of 1.40) toward the higher molecular weight region with retaining unimodal peak profile (M_p of 9700 (polystyrene standard) and PDI of 1.34). This is indicative of the quantitative conversion of the poly(MA) precursor to initiate the ATRP of the second monomer, BA.

1.2. A−B−A Type Allyl-Telechelic Block Copolymer, Poly(BA)-b-Poly(EO)-b-Poly(BA). An A−B−A type allyl-telechelic block copolymer precursor, i.e., poly(BA)-*b*-poly(EO)-*b*-poly(BA), was also prepared through the ATRP of BA using a bifunctional poly(EO) macroinitiator, followed by the end-capping reaction with allyltributylstannane in situ (Scheme 1). The poly(EO) macroinitiator was prepared by the esterification

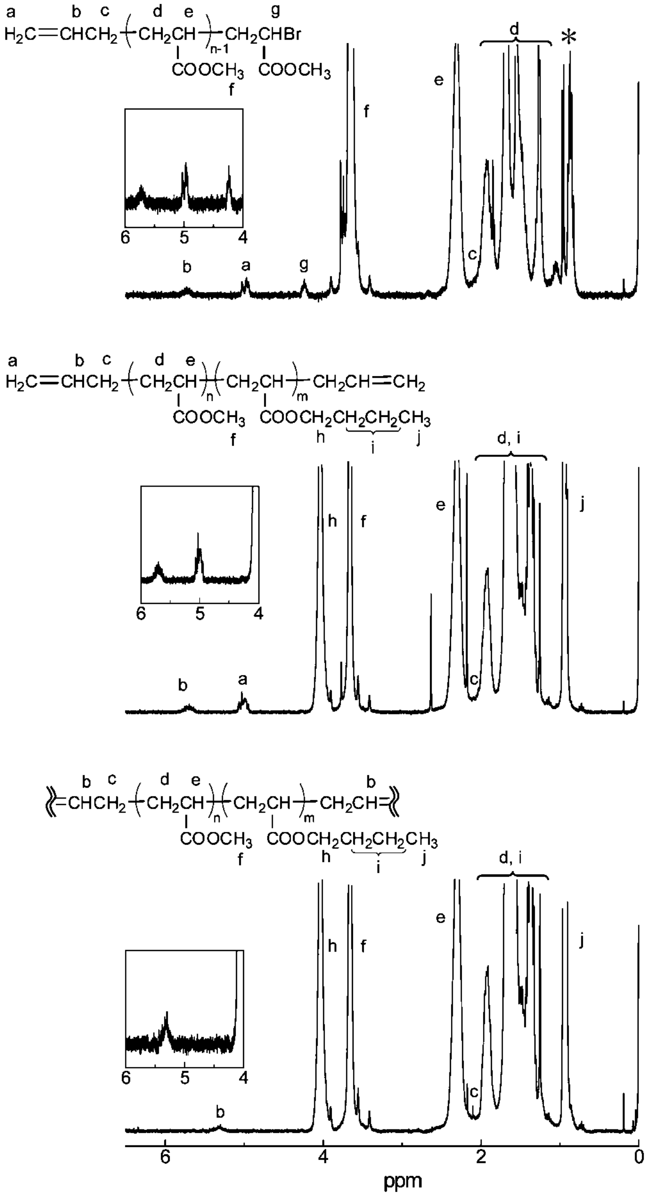


Figure 1. 300 MHz ^{1}H NMR spectra of α-allyl-ω-bromopoly(methyl acrylate, MA) precursor (top), allyl-telechelic poly(MA)-*b*-poly(butyl acrylate, BA) block copolymer (middle), and poly(MA)-*b*-poly(BA) cyclic block copolymer obtained by the ring-closing metathesis (RCM) reaction (bottom) ($CDCl_3$, 40 °C; the signal with * is due to the residual solvent, hexane).

of hydoroxy-telechelic poly(EO) (M_n = 2000) with 2-bromoisobutyryl bromide. The block copolymerization of the second monomer, *n*-butyl acrylate (BA), was conducted in the presence of Cu(I)Br and a 2,2′-bipyridyl derivative, dNbpy, and the subsequent end-capping reaction was performed with allyltributylstannane to cause the allylation of terminal bromoalkyl groups[23] (Scheme 1).

The ^{1}H NMR spectrum of the block copolymer product (Figure 4, middle) showed the signals attributed to the terminal allyl groups at 5.04 and 5.67 ppm, in addition to the overflowed main-chain methylene signals from poly(EO) segment at 3.7 ppm and the large signal due to the ester methylene protons in BA units at around 4.1 ppm. The effective initiation/end-capping (allylation) processes were confirmed by that the shift of the signal attributed to methyne proton adjacent to bromine atom from 4.34 to 4.17 ppm and the subsequent elimination after the allylation as observed in Figure 4 (top).

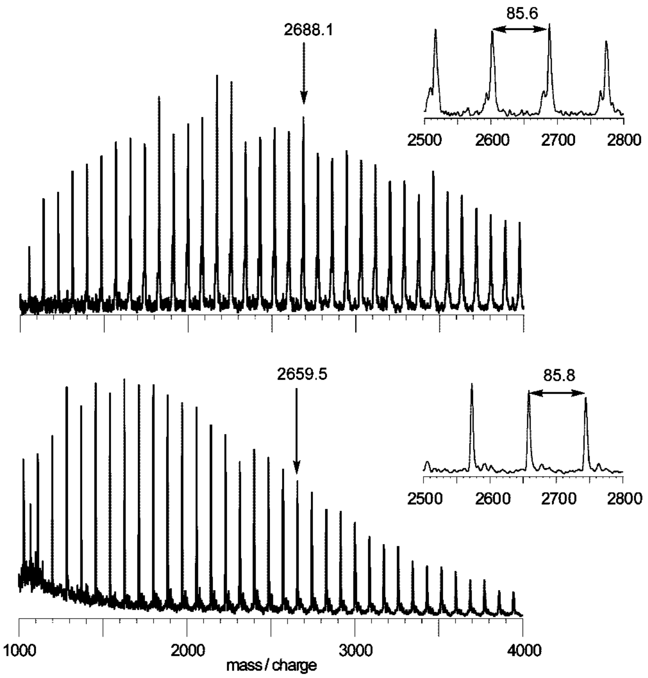


Figure 2. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of allyl-telechelic poly(methyl acrylate, MA) precursor (top) and the cyclic poly(MA) obtained by the ring-closing metathesis (RCM) reaction (bottom) (linear mode, matrix: dithranol with sodium trifluoroacetate).

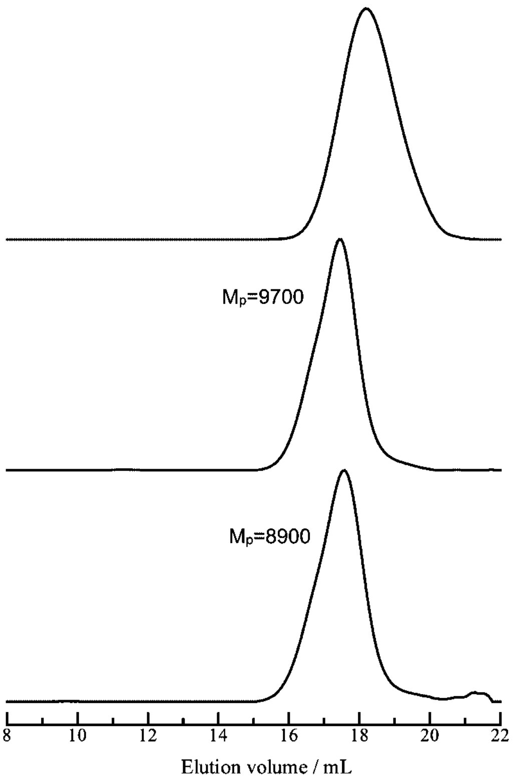


Figure 3. Size exclusion chromatography (SEC) traces of α-allyl-ω-bromopoly(methyl acrylate, MA) precursor (top), allyl-telechelic poly(MA)-*b*-poly(butyl acrylate, BA) block copolymer (middle), and poly(MA)-*b*-poly(BA) cyclic block copolymer obtained by the ring-closing metathesis (RCM) reaction (bottom) (Shodex LF-804, eluent: tetrahydrofuran (THF) 1.0 mL/min).

SEC traces of the poly(EO) precursor having 2-bromoisobutyryl end groups and the subsequent block copolymer, poly(BA)-*b*-poly(EO)-*b*-poly(BA), were compared (Figure 5, top and

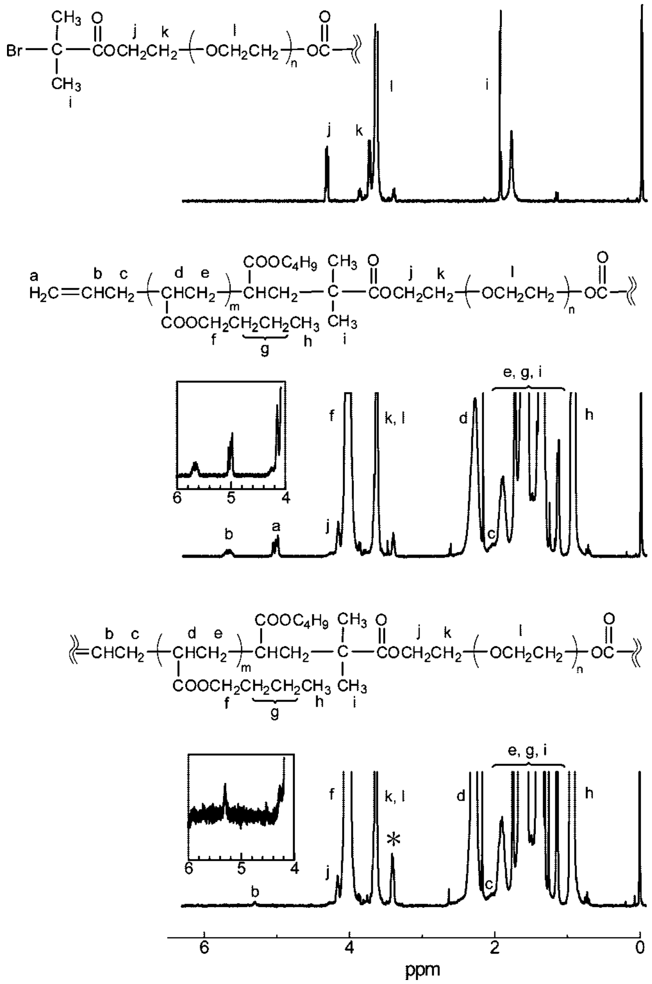


Figure 4. 300 MHz ^{1}H NMR spectra of α,ω-bromobutyrylpoly(ethylene oxide, EO) precursor (top), allyl-telechelic poly(butyl acrylate, BA)-*b*-poly(EO)-*b*-poly(BA) block copolymer (middle), and poly(BA)-*b*-poly(EO) cyclic block copolymer obtained by the ring-closing metathesis (RCM) reaction (bottom) ($CDCl_3$, 40 °C; the signal with * is due to unassignable side products).

middle) to show the shift of the unimodal profile of the former (M_p of 2000 and PDI of 1.35) toward the higher molecular weight region with retaining unimodal peak profile (M_p of 7800 (polystyrene standard) and PDI of 1.16). It is again indicative of the quantitative conversion of the 2-bromoisobutyryl end groups in the poly(EO) precursor to initiate the ATRP of the second monomer, BA.

2. Synthesis of Cyclic Diblock Copolymers. As a model reaction of the metathesis polymer cyclization (MPC) of the A−B and A−B−A type allyl-telechelic block copolymers, we have first conducted the MPC of the allyl-telechelic poly(MA) precursor in CH_2Cl_2 in the presence of Grubbs catalyst first generation under high dilution (0.2−0.5 g/L) by refluxing for up to 48 h. The reaction was monitored by ^{1}H NMR (S-Figure 1 (bottom) in Supporting Information) and by MALDI-TOF MS (Figure 2, bottom) analysis. ^{1}H NMR showed that the signals assigned to the terminal allyl groups were replaced by those attributed to the inner olefinic group at 5.32 ppm (both of trans and cis).[24] The MALDI-TOF mass spectrum of the cyclization product showed the uniform series of peaks with the peak interval of 86 mass units. Each peak corresponds exactly to the molecular mass summing up the cyclic poly(MA) having one inner olefinic group (Figure 2, bottom). As an example, the peak (assumed to be the adduct with Na^+) at 2659.5 corresponds to the product with the DP_n of 30, $(C_4H_6O_2) \times 30 + C_4H_6$, plus Na^+ as 2659.80. The molecular weight difference of the linear telechelics and obtained product was observed to be 28.6, corresponding to the molecular mass of eliminated ethylene unit of 28 by ring-closing metathesis reaction. It is also notable that the peaks assignable to either the unreacted linear precursor or the higher molecular weight byproducts, such as dimer and trimer, were not visible. Therefore, selective and effective polymer cyclization was confirmed to occur in the applied MPC process.

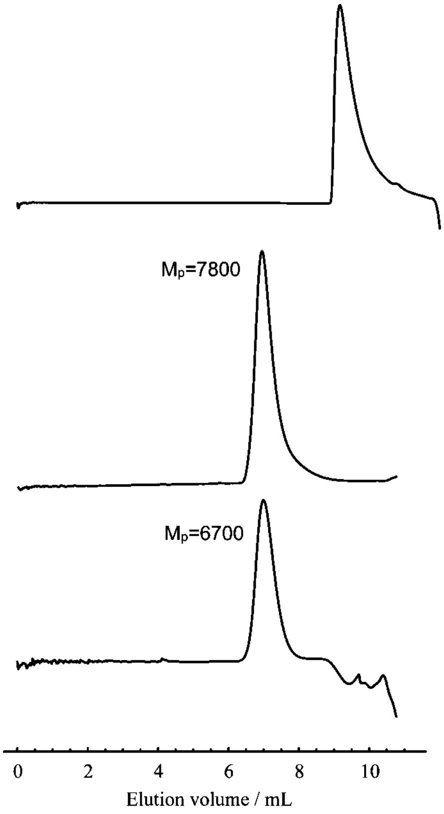


Figure 5. Size exclusion chromatography (SEC) traces of α,ω-bromobutyrylpoly(ethylene oxide, EO) precursor (top), allyl-telechelic poly(butyl acrylate, BA)-*b*-poly(EO)-*b*-poly(BA) block copolymer (middle), and poly(BA)-*b*-poly(EO) cyclic block copolymer obtained by the ring-closing metathesis (RCM) reaction (TSK G3000HXL, eluent: tetrahydrofuran (THF) 1.0 mL/min).

On the basis of the model reaction above, A−B and A−B−A type allyl-telechelic block copolymers was subjected to the MPC process under the relevant dilution (0.5 g/L) in the presence of Grubbs catalyst. ^{1}H NMR spectra of the products from block copolymer precursors (Figure 1, bottom, and Figure 4, bottom) showed the signals attributed to the inner olefinic group at 5.32/5.31 ppm (both trans and cis), totally replacing those due to the terminal allyl groups visible before the reaction.

SEC (Figure 3, bottom, and Figure 5, bottom) showed a unimodal peak in the absence of noticeable shoulder traces at the higher MW region, indicating the exclusive intramolecular reaction under the applied dilution. SEC also showed that the apparent molecular weights of the cyclic block copolymers were measured to be 8900 and 6700, respectively corresponding to 8% and 14% reduction in their 3D size by comparing with the starting allyl-telechelic linear precursors. The smaller 3D size, i.e., the hydrodynamic volume, against their linear precursors is consistent with the formation of the cyclic polymer products.

Conclusions

The ATRP−RCM process using A–B and A–B–A type allyl-telechelic block copolymer precursors has been confirmed as an effective means for the synthesis of cyclic block copolymers.

Thus, linear block copolymer precursors were conveniently obtained by the block copolymerization of two comonomers through the ATRP (A–B type block copolymer) with an allyl-functionalized (macro)initiator and by the ATRP with a bromoisobutyryl-telechelic polymer precursor (A−B−A type block copolymer), followed by the end-capping reaction with allyltributylstannane. The subsequent metathesis polymer cyclization (MPC) in the presence of Grubbs catalyst proceeded effectively to give cyclic diblock copolymers. Since the ATRP is applicable for the production of various types of block copolymers, this method will be applied for the preparation of complex block copolymers with the combination of not only different segments but also different topologies. These challenges are currently in progress in our laboratory.

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Supporting Information Available: Figure showing the ^{1}H NMR spectra of the allyl-telechelic poly(MA) and the cyclization product. This material is available free of charge via Internet at http://pubs.acs.org.

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