Articles

Designing 8-Shaped Polymer Topology by Metathesis Condensation with Cyclic Poly(THF) Precursors Having Allyl Groups

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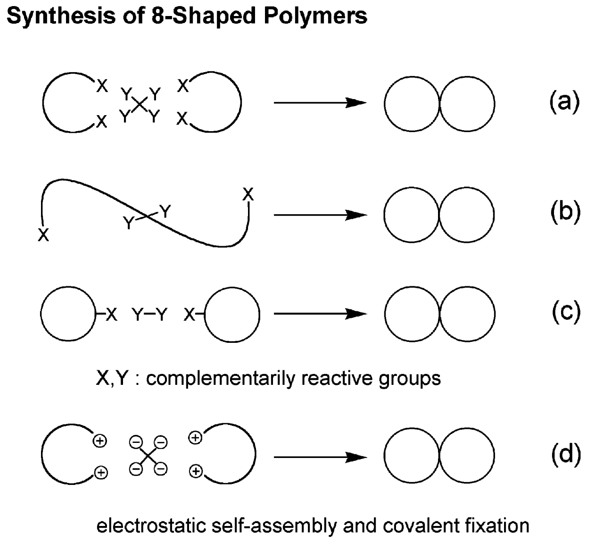
ABSTRACT: A metathesis condensation process was applied for the synthesis of double cyclic, 8-shaped poly(THF)s. Thus, first, a cyclic poly(THF) having an allyl group, **1**, was subjected to the intermolecular metathesis condensation. The bimolecular condensation reaction was found to proceed in the presence of a Grubbs catalyst, while with noticeable concurrent reactions. Alternatively, a twin-tailed tadpole, i.e., "a ring with two branches" structure, poly(THF) having tail-end allyl groups, **2**, and a *kyklo*-telechelic poly(THF) having two allyl groups at opposite positions, **3**, were prepared for the intramolecular metathesis condensation. The unimolecular reactions proceeded effectively even under dilution of the polymer concentration at 0.2 g/L to produce the corresponding 8-shaped poly(THF)s. These products were unequivocally characterized by means of ^{1}H NMR, SEC, and MALDI−TOF MASS techniques.

Introduction

Macromolecules comprising single and multiple cyclic polymer units have gained a growing interest due to their unique properties unlike linear and branched counterparts.[1−6] Among three double cyclic polymer topologies, i.e., an 8-shaped, a θ-shaped, and a manacle-shaped constructions,[6−12] the 8-shaped polymer has repeatedly been a synthetic challenge (Scheme 1).[9−12] Thus, first, two units of bifunctionally living polymers were subjected to the reaction with an equimolar amount of a tetrafunctional coupling reagent under high dilution (Scheme 1a).[9,10] An alternative unimolecular double cyclization process was devised by Deffieux et al. (Scheme 1b),[11] and a cyclic polymer precursor having a reactive group was prepared by Kubo et al. for the intermolecular coupling reaction with a complementarily reactive bifunctional reagent under equimolar conditions (Scheme 1c).[12]

Scheme 1



We have also reported an efficient 8-shaped polymer synthesis by an "electrostatic self-assembly and covalent fixation" process.[13−16] A novel telechelic precursor having moderately strained cyclic ammonium salt groups carrying a tetrafunctional carboxylate counteranion was prepared and subjected to the covalent conversion through the ring-opening reaction under appropriate dilution (Scheme 1d). Thus, 8-shaped poly(THF)[15] and polystyrene[16] were obtained in good yields.

The "electrostatic self-assembly and covalent fixation" process could also afford cyclic polymer precursors having functional groups at the designated location of the ring polymer structure (*kyklo*-telechelics).[17] In the present study, we performed novel syntheses of 8-shaped polymers through the metathesis condensation of cyclic polymer precursors having allyl groups in the presence of a Grubbs catalyst (Scheme 2). The metathesis condensation process, or the ring-closing metathesis (RCM), has been recognized as a versatile means to give a variety of macrocyclic compounds,[18,19] and we have recently developed an efficient metathesis polymer cyclization with a linear poly(THF) precursor having allyl terminal groups.[20] Thus, first, a cyclic polymer precursor having an allyl group[17] was subjected to an *intermolecular* metathesis condensation (Scheme 2A). Second, two types of cyclic polymer precursors, namely a twin-tailed tadpole, i.e., "a ring with two branches" structure, poly(THF) having tail-end allyl groups,[21] and a *kyklo*-telechelic poly(THF) having two allyl groups at

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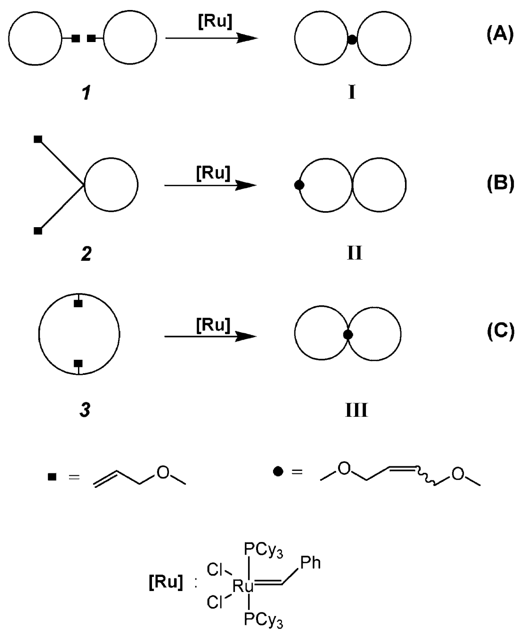
Scheme 2

8-Shaped Polymers by Metathesis Condensation



opposite positions,[17] were applied for an *intramolecular* metathesis condensation (Scheme 2B,C).

Experimental Section

Materials. A cyclic poly(THF) having an allyl group (MW of 4500 and PDI of 1.23), **1**, and a twin-tailed tadpole poly(THF) having tail-end allyl groups (MW of 8100 and PDI of 1.06), **2**, were prepared by the method described previously.[17,21] A *kyklo*-telechelic poly(THF) having two allyl groups (MW of 6400 and PDI of 1.20), **3**, was synthesized from a center-functional poly(THF) having an allyl group together with the terminal *N*-phenylpyrrolidinium salt groups.[22] Thus, the ion-exchange reaction was performed with sodium 5-allyloxyisophthalate, followed by the covalent conversion reaction under dilution (0.2 g/L) by the similar procedure detailed before.[17] The product, **3**, was isolated in 52% yield. The structures of **1**, **2**, and **3** are shown in Figures 1, 3, and 6, respectively. A Grubbs catalyst, ruthenium(II) dichloride phenylmethylene bis(tricyclohexylphosphine) $[RuCl_2(PCy_3)_2({=}CHPh)]$, was purchased from Strem Chemicals Co., Ltd., and used without further purification. Dichloromethane (99%, Kanto Chemical Co., Ltd.,) was distilled over CaH_2. Other reagents were used as received otherwise noted.

Intermolecuar Metathesis Condensation of a Cyclic Poly(THF) Having an Allyl Group, 1. A cyclic poly(THF) having an allyl group, **1** (76 mg, 1.8×10^{-2} mmol), and a Grubbs catalyst (5.6 mg, 6.9×10^{-3} mmol) were dissolved in 5 mL of dichloromethane. The solution was heated to reflux for 48 h. After solvent was removed by evaporation, the product was subjected to the preparative TLC with silica gel (Merck, silicagel PF_{254}). The eluent was *n*-hexane/acetone (65/35 in vol/vol). The recovered yield was 45 mg. A portion of the product (36 mg) was further purified by means of a preparative SEC fractionation technique. A stabilizer for the SEC eluent, i.e., 2,6-di-*tert*-butyl-4-methylphenol, was removed by the precipitation of the product into acetone cooled at −78 °C. The yield was 10 mg.

I: NMR ($CDCl_3$): δ 1.50−1.80 (m, CH_2CH_2O), 3.25−3.50 (m, CH_2CH_2O), 4.35 (t, 4H, $J = 6.3$ Hz, CO_2CH_2), 4.64 (m, 1.5H, $=CHCH_2O-$, cis isomer), 4.75 (m, 0.5H, $=CHCH_2O$, trans isomer), 5.96 (m, $=CHCH_2O$, trans isomer),[23] 6.11 (m, $=CHCH_2O$, cis isomer),[23] 6.62 (m, 6H, Ar−*H* ortho and para to N), 7.16 (m, 4H, Ar−*H* meta to N), 7.75 (m, 2H, Ar−*H* ortho to OCH_2), 8.26 (m, 1H, Ar−*H* para to OCH_2).

Intramolecular Metathesis Condensation of a Twin-Tailed Tadpole Poly(THF) Having Tail-End Allyl Groups, 2. As a typical example, a twin-tailed tadpole poly(THF) having tail-end allyl groups, **2** (24 mg, 2.9×10^{-3} mmol), and a Grubbs catalyst (3.6 mg, 4.4×10^{-3} mmol) were dissolved in 120 mL of dichloromethane. The solution was heated to reflux for 48 h. After solvent was removed by evaporation, the product was subjected to the preparative TLC with silica gel. The eluent was *n*-hexane/acetone/triethylamine (63/32/5 in vol/vol/vol). The recovered yield was 11 mg.

II: NMR ($CDCl_3$): δ 1.50−1.80 (m, CH_2CH_2O), 2.41−2.43 (m, 12H, NCH_2), 3.25−3.50 (m, CH_2CH_2O), 3.95 (d, 3H, $J =$ 3.1 Hz, $=CHCH_2O$, cis isomer), 4.02 (d, 1H, $J = 4.5$ Hz, $=CHCH_2O$, trans isomer), 4.35 (t, 4H, $J = 6.3$ Hz, CO_2CH_2), 5.69 (m, 0.5 H, $=CHCH_2O$, trans isomer), 5.79 (m, 1.5H, $=CHCH_2O$, cis isomer), 8.08 (m, 4H, Ar−*H*).

Intramolecular Metathesis Condensation of a *kyklo*-Telechelic Poly(THF) Having Two Allyl Groups, 3. As a typical example, a *kyklo*-telechelic poly(THF) having two allyl groups, **3** (46 mg, 7.2×10^{-3} mmol), and the Grubbs catalyst (9.0 mg, 1.1×10^{-2} mmol) were dissolved in 250 mL of dichloromethane. The solution was heated to reflux for 48 h. After solvent was removed by evaporation, the product was subjected to the preparative TLC with silica gel. The eluent was *n*-hexane/acetone (65/35 in vol/vol). The recovered yield was 30 mg.

III: NMR ($CDCl_3$): δ 1.50−1.80 (m, CH_2CH_2O), 3.25−3.50 (m, CH_2CH_2O), 4.35 (t, 4H, $J = 6.3$ Hz, CO_2CH_2), 4.45 (s, 4H, $ArCH_2O$), 4.58 (m, 1.5H, $=CHCH_2OAr$ meta to CH_2O, cis isomer), 4.62 (m, 1.5H, $=CHCH_2OAr$ meta to CO_2CH_2, cis isomer), 4.69 (m, 0.5H, $=CHCH_2OAr$ meta to CH_2O, trans isomer), 4.75 (m, 0.5H, $=CHCH_2OAr$ meta to CO_2CH_2, trans isomer), 5.94 (m, $=CHCH_2O$, trans isomer),[23] 6.09 (m, $=CHCH_2O$, cis isomer),[23] 6.62 (m, 6H, Ar−*H* ortho and para to N), 6.82 (m, 3H, Ar−*H* ortho to CH_2O), 7.14 (m, 4H, Ar−*H* meta to N), 7.74 (m, 2H, Ar−*H* ortho to CO_2CH_2, ortho to $=CHCH_2O$), 8.27 (m, 1H, Ar−*H* ortho to CO_2CH_2, para to $=CHCH_2O$).

Measurements. SEC measurements were performed using a Tosoh model CCPS equipped with a refractive index detector model RI 8020, a UV detector model UV 8020 at 254 nm, and a conductivity detector model CM 8010. A column of either a TSK G3000HXL or a TSK G4000HXL (both 300 mm × 7.8 mm i.d., 5 μm average particle size) was employed with THF as an eluent at a flow rate of 1.0 mL/min at 40 °C. In a typical procedure, 40 μL of sample solution (sample concentration of 0.5 wt %) was injected. SEC fractionation was carried out using a JAI model LC-908W CCPS apparatus with a refractive index detector model RI-5 and with a column set of JAIGEL-2H-AF (300 mm × 20 mm i.d., exclusion molecular weight of 5K for polystyrene) and JAIGEL-3H-AF (300 mm × 20 mm i.d., exclusion molecular weight of 70K for polystyrene). The sample solution (3 mL containing 36 mg of the crude product from **1**) was injected and recycled before fractionation. The eluent was THF at a flow rate of 3.5 mL/min. ^1H NMR spectra were recorded with a JEOL JNM-AL300 apparatus in $CDCl_3$ at 40 °C. The proton chemical shifts (ppm) were referenced from a signal of tetramethylsilane. MALDI−TOF MASS spectra were taken on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser ($\lambda = 337$ 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), was 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 two-point method with insulin β plus H^+ at 3497.96 and α-cyanohydroxycinnamic acid dimer plus H^+ at 379.35.

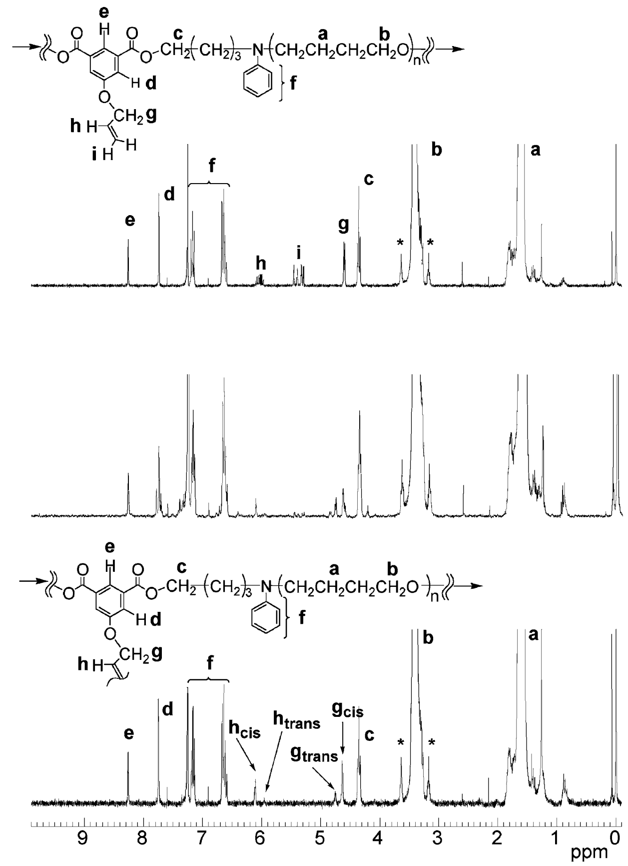


Figure 1. The 300 MHz ^{1}H NMR spectra of a cyclic poly(THF) having an allyl group (**1**, top) and the metathesis condensation product before (middle) and after (bottom) the SEC fractionation (CDCl$_3$, 40 °C; * = satellite signal).

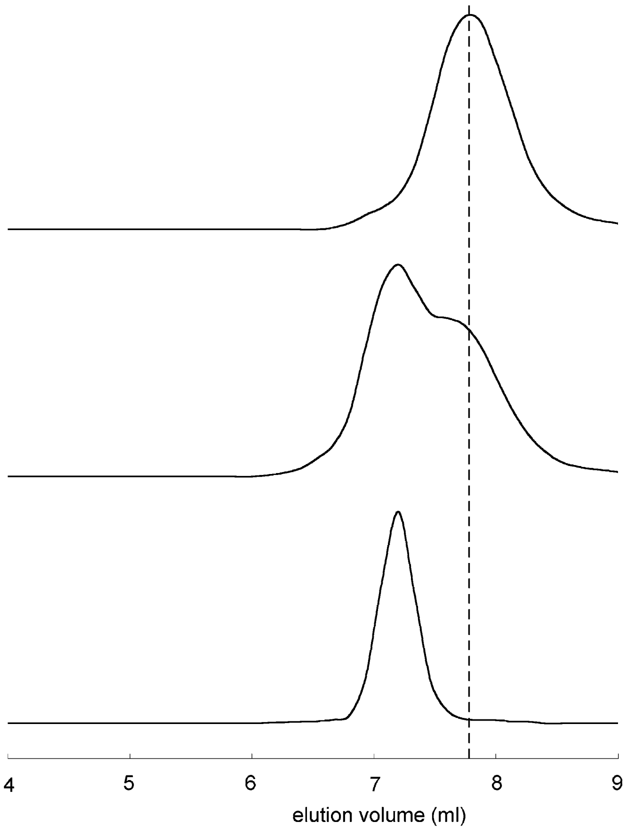


Figure 2. SEC traces (RI) of a cyclic poly(THF) having an allyl group (**1**, top) and the metathesis condensation product before (middle) and after (bottom) the preparative SEC fractionation (TSK G3000HXL, eluent: THF, 1 mL/min).

Results and Discussion

Intermolecular Metathesis Condensation of a Cyclic Poly(THF) Having an Allyl Group, 1. A cyclic poly(THF) having an allyl group, **1**,[17] was subjected to the metathesis condensation in the presence of a Grubbs catalyst to produce an 8-shaped polymer (Scheme 2A). The reaction was conducted at various catalyst concentrations, and the quantitative conversion of allyl groups in **1** was observed in 48 h at the catalyst concentration of 10^{-3} M, comparable to the concentration of allyl groups. The ^{1}H NMR spectra of the precursor, **1**, and the product (Figure 1, top and middle, respectively) show that the signals due to terminal vinyl protons at 5.36 and 6.01 ppm in **1** were completely removed after the reaction, and instead those due to inner alkene protons appeared at 5.96 and 6.11 ppm. At the same time, however, noticeable concurrent reactions were indicated by the unassigned peaks at 4.4–4.9 ppm and by the inconsistent signal intensity ratio between the inner alkene groups and the aminoester groups at the polymer ring unit. Moreover, SEC of the product (Figure 2) showed a profile consisting not only of a major fraction corresponding to the 8-shaped product at the higher molecular weight region but also of a minor fraction at the lower molecular weight comparable to that of the precursor, **1**, and this shoulder fraction accompanies an intense UV absorption in contrast with **1**. In this bimolecular process, the reaction obeys the second-order kinetics involving two allyl groups located in separate polymer molecules. Therefore, the increased polymer substrate concentration with the relatively high dose of the catalyst was required to achieve the quantitative conversion of allyl groups of **1**. Such reaction conditions, in turn, caused noticeable concurrent reactions.[24]

SEC fractionation was subsequently performed to isolate the 8-shaped product, **I**. The recovered product (27.9% yield) showed the narrow molecular weight distribution (Figure 2, bottom). The quantitative ^{1}H NMR analysis of the product (Figure 1, bottom) confirmed the expected structure of the 8-shaped poly(THF) product, **I**.[23]

Intramolecular Metathesis Condensation of a Twin-Tailed Tadpole Poly(THF) Having Tail-End Allyl Groups, 2. A twin-tailed tadpole poly(THF) precursor having tail-end allyl groups, **2**, prepared previously,[21] was then subjected to the intramolecular metathesis condensation under various dilutions at the polymer concentration of 0.2–5.0 g/L (Scheme 2B). The catalyst was charged in a slightly excess molar quantity to allyl groups, but as low as ca. 10^{-5} M. As in the relevant metathesis polymer cyclization with a linear poly(THF) precursor having allyl groups,[20] the intramolecular metathesis condensation of **2** was found to proceed effectively even under such dilution. Thus, the 8-shaped product, **II**, was obtained in dilution at 0.2 g/L and was recovered after the purification by preparative TLC (45.0% yield). The ^{1}H NMR spectra of the product **II** together with the precursor **2** (Figure 3) show that the signals due to the tail-end vinyl protons in **2** at 5.22 and 5.91 ppm were replaced nearly quantitatively by those due to inner alkene protons (cis and trans signals at 5.79 and 5.69 ppm, respectively). This indicates that the catalytic activity of the Grubbs catalyst is scarcely

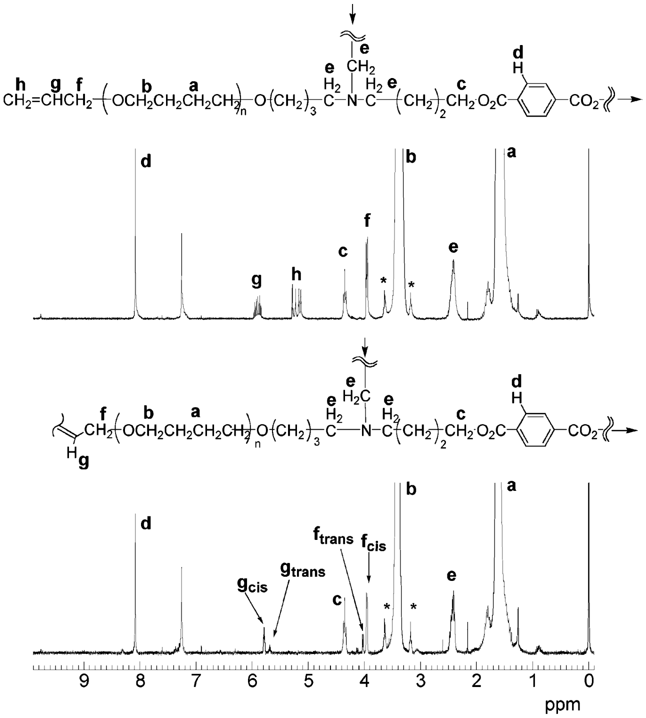


Figure 3. The 300 MHz ^{1}H NMR spectra of a twin-tailed tadpole poly(THF) having tail-end allyl groups (**2**, top) and the metathesis condensation product (bottom) ($CDCl_3$, 40 °C; * = satellite signal).

affected by the presence of aminoester groups located along the backbone polymer segment.

The metathesis condensation products obtained at various precursor concentrations were also compared by SEC (Figure 4). The SEC peak profile became narrower along with dilution by eliminating the shoulder fraction at the higher molecular weight region observed in the products at higher precursor concentrations. Finally, the 8-shaped product, **II**, obtained in an almost pure form at 0.2 g/L, showed a narrow size distribution and a marginally smaller hydrodynamic volume than the precursor, **2**.

The 8-shaped poly(THF), **II**, and the twin-tailed tadpole precursor, **2**, were further examined by MALDI–TOF MASS spectroscopy (Figure 5). The product, **II**, showed a uniform series of peaks corresponding to poly(THF) (peak interval of 72 mass units); each peak corresponds exactly to the molar mass summing up the linking structure produced by the metathesis condensation reaction of allyl end groups in **2**. As an example, the peak (assumed to be the adduct with H^+) at 6357.0 corresponds to the product with the DP_n of 80, (C_4H_8O) × 80 + $C_{32}H_{50}N_2O_6$, plus H^+ as 6356.404. The twin-tailed tadpole polymer precursor, **2**, also showed a major series of the peaks corresponding to the H^+ adduct. Thus, the peak (assumed to be the adduct with H^+) at 6328.2 corresponds to the product with the DP_n of 80, (C_4H_8O) × 80 + $C_{34}H_{54}N_2O_6$, plus H^+ as 6328.350. A minor series of peaks observed in both spectra correspond to their Na^+ adducts. Since the 8-shaped poly(THF) products, **II**, are produced from the precursor, **2**, by the elimination of an ethylene molecule, their molecular weights differ by 28 mass units. This was confirmed by the two TOF–MASS spectra shown in Figure 5. The peak distribution of the precursor **2** was observed to shift marginally toward the lower molecular weight by comparing with that of the 8-shaped product. This is presumably due to the different ionization efficiency for the precursor and the product of the same DP_n.

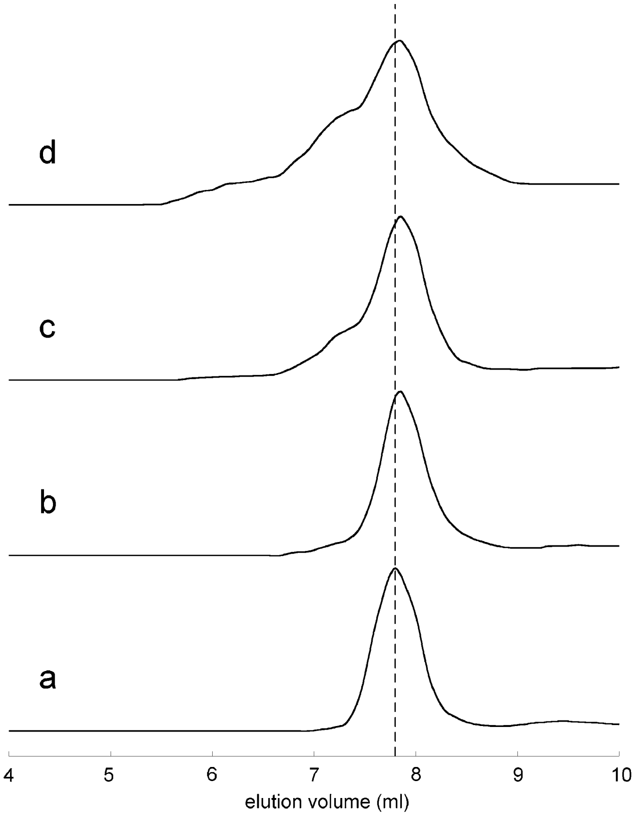


Figure 4. SEC traces (RI) of a twin-tailed tadpole poly(THF) having two tail-end allyl groups (**2**, a) and the quantitatively recovered product after the metathesis condensation (b–d). Concentration of the **2** in methylene chloride: (b) 0.2 g/L, (c) 1.0 g/L, and (d) 5.0 g/L (TSK G4000HXL, eluent: THF, 1 mL/min).

Intramolecular Metathesis Condensation of a *kyklo*-Telechelic Poly(THF) Having Two Allyl Groups, 3. A *kyklo*-telechelic poly(THF) having two allyl groups, **3**, was prepared by a similar procedure detailed before.[17] The subsequent metathesis condensation was performed in dichloromethane under reflux in dilution at the precursor concentration of 0.2–5.0 g/L. As in the case of the reaction with **2**, the catalyst was charged in a slightly excess molar quantity to allyl groups in the cyclic polymer precursor. An efficient metathesis condensation was again confirmed in this intramolecular reaction. It is remarkable that the intramolecular reaction with **3** proceeded more selectively in comparison with the intermolecular process with **1** having the relevant allyl group.[25] Thus, the 8-shaped product, **III**, was obtained at 0.2 g/L and was recovered after the purification by preparative TLC (65.5% yield).

The ^{1}H NMR spectra of the product **III** together with the precursor **3** (Figure 6) show that a pair of signals due to the two sets of terminal vinyl protons in the precursor **3** at 5.36 and 6.01 ppm and at 5.33 and 6.04 ppm, respectively, were totally removed after the reaction, and those due to inner alkene protons (cis and trans signals at 6.09 and 5.94 ppm, respectively) appeared instead. The quantitative ^{1}H NMR analysis of the product confirmed the expected structure of the 8-shaped poly(THF) product, **III**.[23]

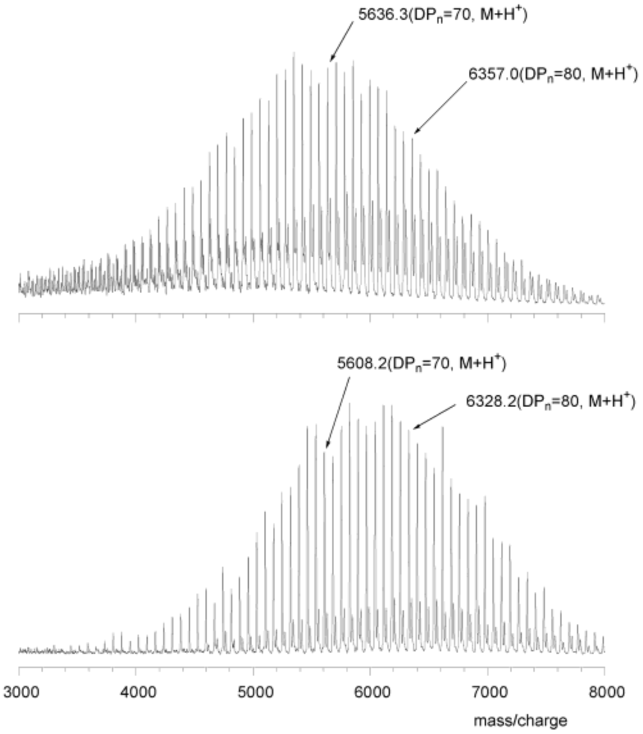


Figure 5. MALDI−TOF MASS spectra of (bottom) an 8-shaped poly(THF), **II**, and of (top) a twin-tailed tadpole poly(THF) having tail-end allyl groups, **2** (linear mode, matrix: dithranol with sodium trifluoroacetate).

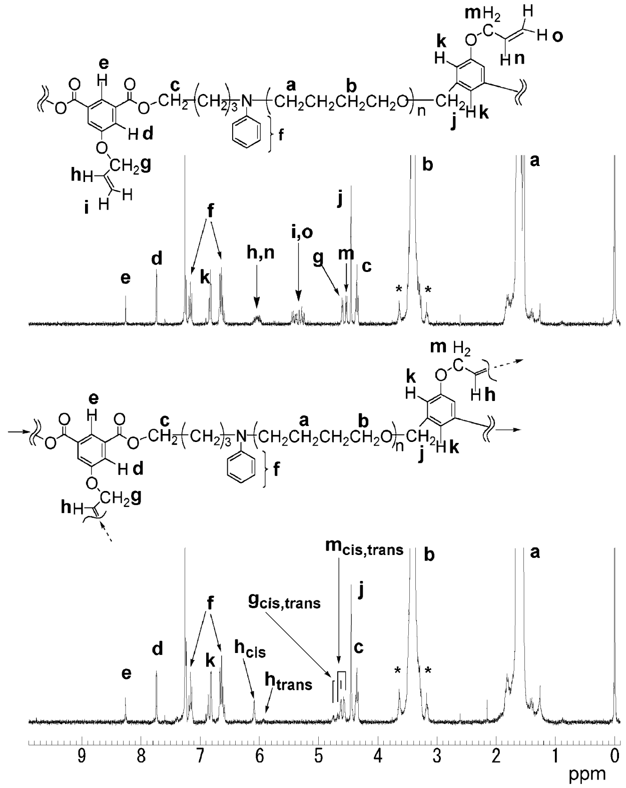


Figure 6. The 300 MHz ^{1}H NMR spectra of a *kyklo*-telechelic poly(THF) having two allyl groups (**3**, top) and the metathesis condensation product (bottom) (CDCl$_3$, 40 °C; * = satellite signal).

The SEC of the products obtained at various dilutions (Figure 7) shows that the intramolecular process dominated with dilution toward 0.2 g/L, and the 8-shaped product **III** with a nearly symmetrical profile as in the precursor **3** was eventually obtained. The hydrodynamic volume of the product, **III**, was marginally smaller than that of **3**. This accords with the effective intramolecular cyclization by the present metathesis condensation process.

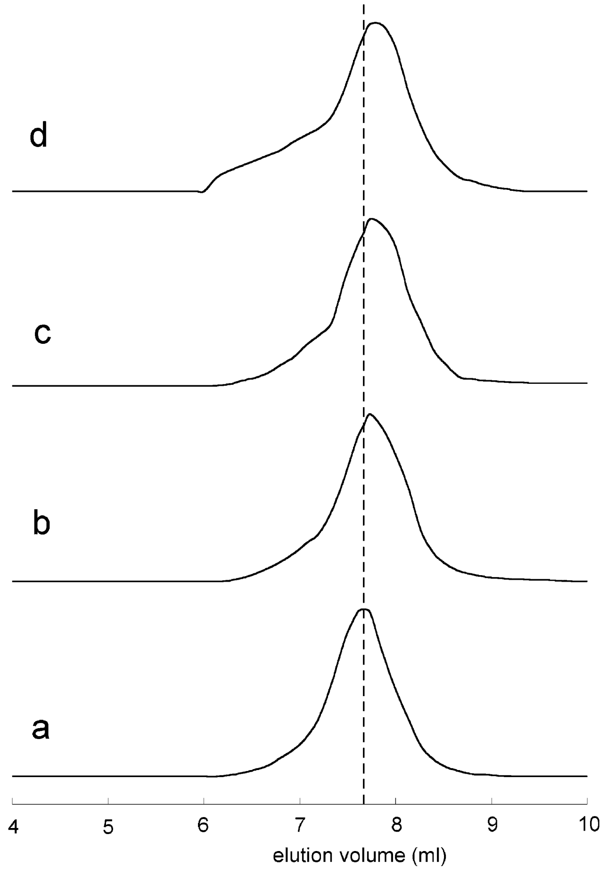


Figure 7. SEC traces (RI) of a *kyklo*-telechelic poly(THF) having two allyl groups (**3**, a) and the quantitatively recovered product after the metathesis condensation (b−d). Concentration of the **3** in methylene chloride: (b) 0.2 g/L, (c) 1.0 g/L, and (d) 5.0 g/L (TSK G3000HXL, eluent: THF, 1 mL/min).

The 8-shaped poly(THF), **III**, and the precursor, **3**, were further examined by MALDI−TOF MASS spectroscopy (Figure 8). The product, **III**, showed a uniform series of peaks corresponding to poly(THF) (peak interval of 72 mass units); each peak corresponds exactly to the molar mass summing up the linking structure produced by the metathesis condensation reaction of pendant allyl groups in **3**. As an example, the peak (assumed to be the adduct with Na$^+$) at 4996.9 corresponds to the product with the DP$_n$ of 60, (C_4H_8O) × 60 + $C_{40}H_{42}N_2O_6$, plus Na$^+$ as 4996.211. The *kyklo*-telechelic polymer precursor, **3**, also showed a major series of the peaks corresponding to the Na$^+$ adduct. Thus, the peak (assumed to be the adduct with Na$^+$) at 5024.8 corresponds to the product with the DP$_n$ of 60, (C_4H_8O) × 60 + $C_{42}H_{46}N_2O_6$, plus Na$^+$ as 5024.265. A minor series of peaks were observed in the spectrum for the product, **III**, corresponds to the H$^+$ adduct. Since the 8-shaped poly(THF) products are produced from the precursor, **3**, by the elimination of an ethylene molecule, their molecular weights differ by 28 mass units. This was again confirmed by the two TOF−MASS spectra shown in Figure 8.

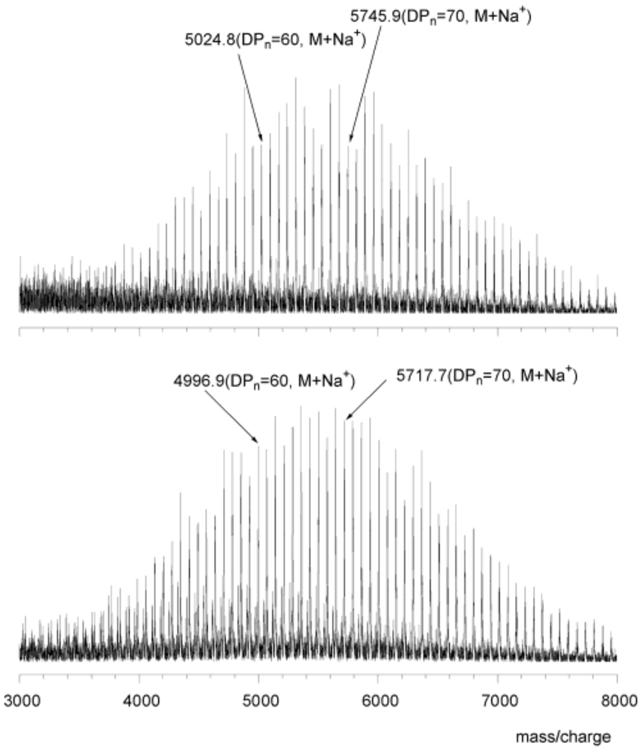


Figure 8. MALDI−TOF MASS spectra of (bottom) an 8-shaped poly(THF), **III**, and of (top) a *kyklo*-telechelic poly(THF) having two allyl groups, **3** (linear mode, matrix: dithranol with sodium trifluoroacetate).

Conclusions

Double cyclic, 8-shaped poly(THF)s were synthesized through intermolecular and intramolecular metathesis condensation of cyclic polymer precursors having allyl groups. While the intermolecular metathesis condensation with a cyclic polymer precursor having an allyl group, **1**, accompanied noticeable concurrent reactions, alternative intramolecular processes by either a twin-tailed tadpole poly(THF) having tail-end allyl groups, **2**, or a *kyklo*-telechelic poly(THF) having two allyl groups at opposite positions, **3**, were found to proceed effectively. The 8-shaped poly(THF)s were thus obtained in pure forms with appreciable yields. Further applications of metathesis condensation process by making use of cyclic and multicyclic polymer precursors obtainable by the “electrostatic self-assembly and covalent fixation process” are now in progress to construct novel multicyclic polymer topologies.

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(23) The apparent signal intensity of inner alkene protons, in particular those located in the vicinity of the junction point of the 8-shaped structure, was noticeably reduced (ca. 70−80% of the expected values) presumably due to their rapid T_2 relaxation. Therefore, the metathesis selectivity was estimated by comparing the intensity of the neighboring allyl protons with that of the aminoester protons in the cyclic polymer unit. The complete conversion of the pendant vinyl groups in the precursors **1** and **3** was also confirmed, and the chemical shifts of allyl protons in the precursors and in the products are marginally distinguished each other. Also, in the ^{13}C NMR of the obtained 8-shaped polymers, signals of the linking groups within the main chain segments were strongly suppressed due to their rapid T_2 relaxation.

(24) The isomerization of allyl ethers to the internal vinyl ether could take place under high dose of a Grubbs catalyst, and this could lead to the deactivation of the catalyst. See: Maynard, H. D.; Grubbs, R. H. *Macromolecules* **1999**, *32*, 6917−6924.

(25) During the intramolecular metathesis condensation, one of the two allyl groups in the precursor polymer reacts with a Grubbs catalyst to form an intermediate Ru−carbene complex, followed by the unimolecular reaction with another allyl group. This first-order process could be favored in comparison with the second-order intermolecular reaction, thus avoiding from concurrent side reactions like a self-decomposition of the Ru−carbene species.

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