

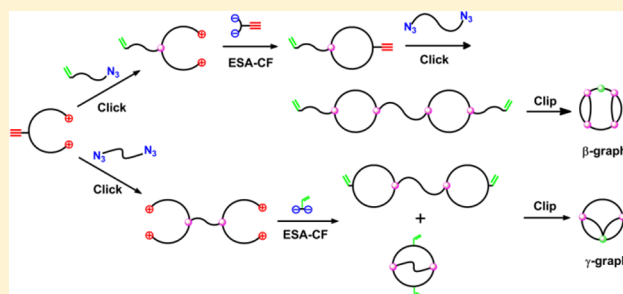
Folding Construction of Doubly Fused Tricyclic, β - and γ -Graph Polymer Topologies with *kyklo*-Telechelic Precursors Obtained through an Orthogonal Click/ESA-CF Protocol

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S Supporting Information

ABSTRACT: An alkyne–azide addition (click) reaction of a linear poly(tetrahydrofuran), poly(THF), precursor having an alkyne group at the center position and cyclic ammonium salt end groups has been applied with the complementary linear poly(THF) precursors having an azide group at single or both chain ends to produce asymmetric star- and H-shaped poly(THF) precursors having cyclic ammonium salt end groups. The subsequent electrostatic self-assembly and covalent fixation (ESA-CF) process after introducing dicarboxylate counteranions having an additional alkene or alkyne group could afford the designated *kyklo*-telechelic precursors, having either a tadpole form containing an alkyne group at the top-head and an alkene group at the tail-end positions or an isomeric manacle/theta form containing two alkene groups at the orthogonal positions. The further click coupling of the former with a linear telechelic precursor having azide groups followed by the metathesis folding (clip) process could produce effectively a doubly fused tricyclic polymer having β -graph topology. Moreover, the convergent folding by the clip reaction of the latter manacle/theta isomeric precursors could produce exclusively another doubly fused tricyclic polymer having γ -graph topology.



INTRODUCTION

Cyclic and multicyclic polymer architectures are unique by the absence of chain termini, in contrast to linear and branched counterparts, and remain fascinating and challenging synthetic targets.^{1–5} A remarkable progress has now been achieved to produce a wide variety of single cyclic polymers based on newly developed end-to-end prepolymer linking processes as well as on an alternative ring-expansion polymerization.^{6–8} And by making use of newly obtained cyclic polymers having diverse chemical compositions, unprecedented topology effects by cyclic polymers have now been unequivocally demonstrated.^{1,9}

In contrast, a class of *multicyclic* polymer topologies consisting of the three subclasses of *fused*, *spiro*, and *bridged* forms have still been an ongoing synthetic challenge.^{1,10} We have thus developed an *electrostatic self-assembly and covalent fixation* (ESA-CF) protocol,^{1,11} in which linear and star telechelic precursors having cyclic ammonium salt groups carrying plurifunctional carboxylate counteranions were employed to form polymeric self-assemblies as key intermediates. The three forms of dicyclic constructions, i.e., θ (*fused*), 8 (*spiro*), and manacle (*bridged*), as well as a spiro-tricyclic, trefoil construction have been effectively produced through the covalent conversion of the corresponding electrostatic polymer self-assemblies.¹¹ Moreover, a variety of *spiro*- and *bridged*-type multicyclic polymer topologies have been constructed through an alkyne–azide click reaction by employing tailored single cyclic and multicyclic polymer

precursors having functional groups at the prescribed positions (*kyklo*-telechelics) obtainable also by the ESA-CF protocol.¹²

A group of *fused*-multicyclic polymer topologies, in contrast to their *spiro*- and *bridged*-counterparts, are considered particularly intriguing in the context of not only topological geometry but also by their biofunctional relevance. Notably, a set of cyclic peptides, *cyclotides*, having *fused*-multicyclic structures formed through the covalent folding by the intramolecular S–S linkage with cysteine residues, have shown extraordinary stability and bioactivity ascribed to their unique folded forms.¹³ Accordingly, the effective and programmed polymer folding by synthetic polymers into designated multicyclic forms has now become an attractive challenge.¹⁴ Thus, we have reported the construction of a doubly *fused* tricycle, δ -graph topology through the metathesis clip folding of an 8-shaped precursor having alkene groups at the opposite positions of the two ring units, obtainable by the ESA-CF protocol.¹⁵ Furthermore, a γ -graph (doubly *fused* tricyclic) and an unfolded tetrahedron-graph (triply *fused* tetracyclic) polymers have recently been constructed through tandem click and clip reactions in conjunction with the ESA-CF process.¹⁶ However, a variety of topologically significant polymers, having an α -graph (doubly *fused* tricyclic) and a $K_{3,3}$ graph¹⁷ (triply *fused* tetracyclic) as well as a prism graph

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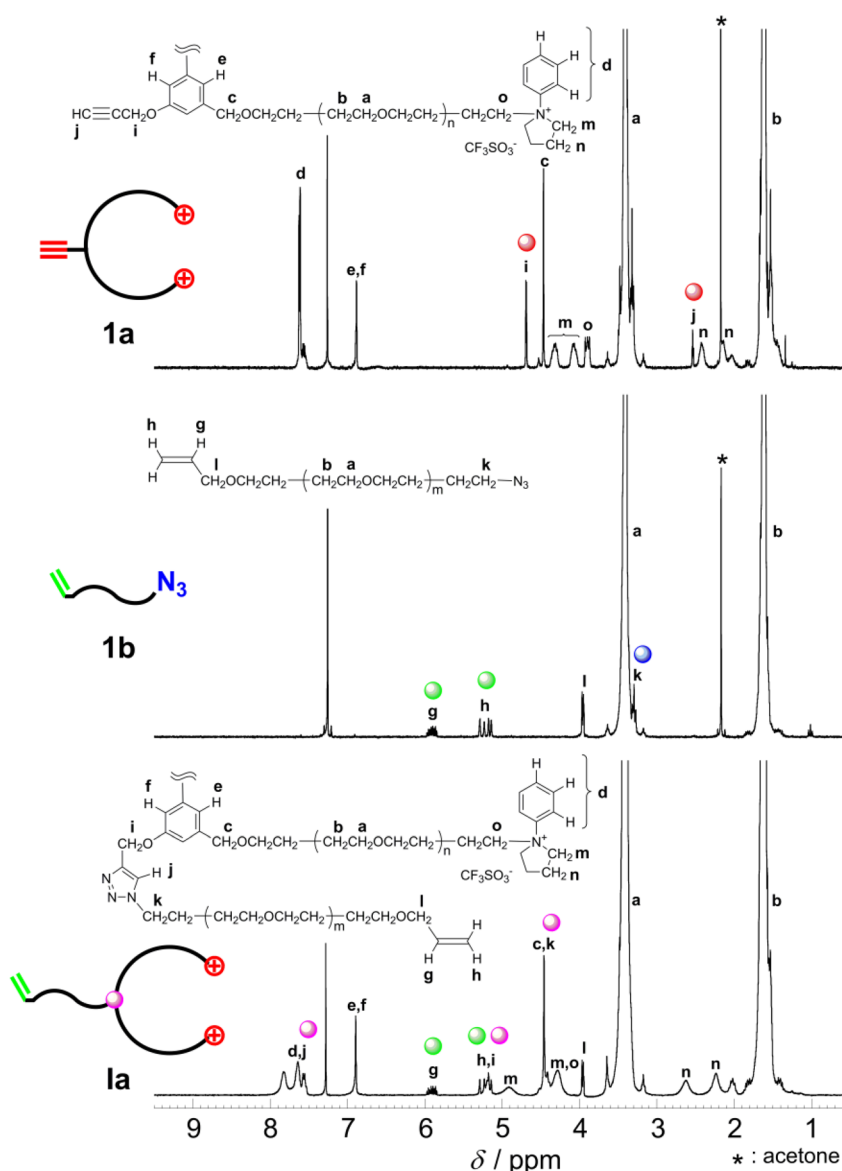


Figure 1. ^1H NMR (300 MHz) spectra of (top) a poly(THF) having an alkyne group at the center position and *N*-phenylpyrrolidinium salt end groups (**1a**), (middle) a poly(THF) having an azide and an alkyne group (**1b**), and (bottom) a star poly(THF) having two cyclic ammonium salts and one alkene end groups (**1a**) (CDCl_3 , 40°C).

produce exclusively another doubly fused tricyclic polymers having γ -graph topology.

RESULTS AND DISCUSSION

Click Synthesis of Star- and H-Shaped Telechelic Poly(THF)s Having *N*-Phenylpyrrolidinium Salt Groups.

An electrostatic self-assembly and covalent fixation (ESA-CF) process has extensively been employed to construct a variety of complex polymer topologies.^{1,8} A variety of linear telechelic precursors having a modestly strained cyclic ammonium, i.e., *N*-phenylpyrrolidinium, salt group at single or both chain ends, as well as star-telechelic precursors uniformly functionalized at all chain ends, have so far been applied for the ESA-CF process.⁸ In this study, we have introduced an asymmetric three-armed star precursor having two cyclic ammonium and one alkene end groups, as well as an H-shaped precursors having four cyclic ammonium salt groups, by making use of a designated polymer

precursor having an alkyne group at the center position and having *N*-phenylpyrrolidinium salt end groups, **1a** (Scheme 1).

The alkyne–azide addition (click) reaction of **1a** ($M_n(\text{NMR}) = 3800$) was then carried out with a linear poly(THF) precursor having an azide and an alkene group, **1b** ($M_n(\text{NMR}) = 1800$), which was prepared through a living polymerization of THF by using an alkene-functionalized initiator and an azide anion end-capper. The click reaction was conducted in the presence of CuSO_4 and sodium ascorbate as a catalyst and THF/water as reaction medium to retain cyclic ammonium salt groups in **1a** intact during the reaction. To ensure the complete reaction, a slight excess of **1b** was charged relative to **1a**. After the purification by column chromatography with silica gel, a star polymer product having two *N*-phenylpyrrolidinium salts and one alkene end group, **1a**, was recovered in 74% yield.

Furthermore, an H-shaped poly(THF) having *N*-phenylpyrrolidinium salt end groups, **1b**, was prepared by the click reaction of **1a** ($M_n(\text{NMR}) = 4700$), with a linear precursor having azide end groups, **1c** ($M_n(\text{NMR}) = 1900$) (Scheme 1).

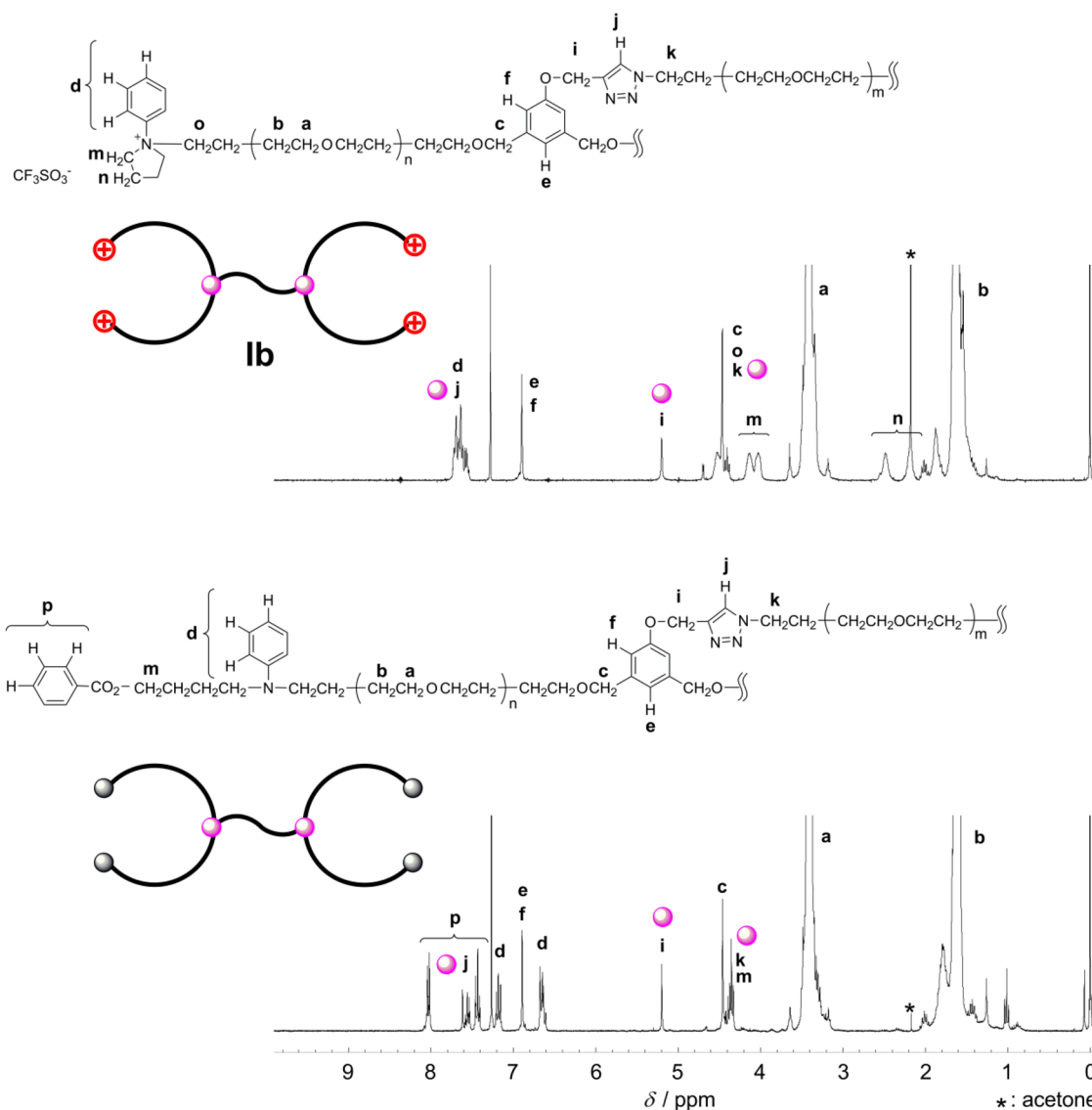


Figure 2. ^1H NMR (300 MHz) spectra of (top) an H-shaped poly(THF) having *N*-phenylpyrrolidinium salt end groups (**Ib**) and (bottom) the covalent conversion product by the ring-opening reaction with a benzoate anion (CDCl_3 , 40 $^\circ\text{C}$).

In this process, a slightly excess of **1a** was charged relative to the bifunctional **1c** in order to complete the reaction. The product **Ib** was isolated after the continuous extraction of an excess amount of **1a** and the copper catalyst residue. As an alternative process to prepare an H-shaped telechelic precursor, we also employed a linear poly(THF) precursor having two sets of triflate ester groups at both chain ends. However, the initiation reaction could not proceed simultaneously from all the four initiating groups to give the four living propagating segments.

By comparing the ^1H NMR spectra of the click products, **1a** and **Ib**, with the prepolymers, **1a**, **1b**, and **1c** (Figures 1 and 2, respectively), the selective addition reactions of the alkyne group in **1a** with the azide groups of either prepolymer, **1b** or **1c**, was confirmed. Thus, the signals for the ethynyl proton (2.54 ppm) and for the propynyl methylene protons (4.76 ppm) in **1a** were replaced by the signal assignable for the methylene protons on the triazole ring unit emerged at 5.20 ppm both in **1a** (though with peak broadening) and in **Ib**. Also by IR, the azide absorption at 2094 cm^{-1} observed in precursors **1b** and **1c** became scarcely visible in the products,

1a and **Ib**, indicating that the click reaction proceeded effectively (Figure S1).

The *N*-phenylpyrrolidinium salt groups of **1a** and **Ib** were then subjected to the ring-opening reaction with a benzoate anion, in order to substantiate their chemical structures unequivocally by means of the MALDI-TOF mass and SEC techniques together with the NMR analysis. The ^1H NMR spectra of the covalently converted products from **1a** and from **Ib** (Figure S2 and Figure 2 (bottom), respectively) commonly showed the signal of the ester methylene protons at 4.25 ppm both for **1a** and **Ib**, in addition to the signals of the *N*-phenyl protons at around 6.6 and 7.2 ppm, replacing the signal of *N*-phenyl protons on the pyrrolidinium group at around 7.7 ppm visible before the reaction.

The MALDI-TOF mass spectra of the covalently converted products both from **1a** and from **Ib** showed a uniform series of peaks with an interval of 72 mass units corresponding to the repeating THF unit, and each peak exactly matched the total molar mass of the poly(THF) produced from the complementary precursors (Figures S3 and S4 for the ring-opening derivatives from **1a** and from **Ib**, respectively). Thus, in Figures

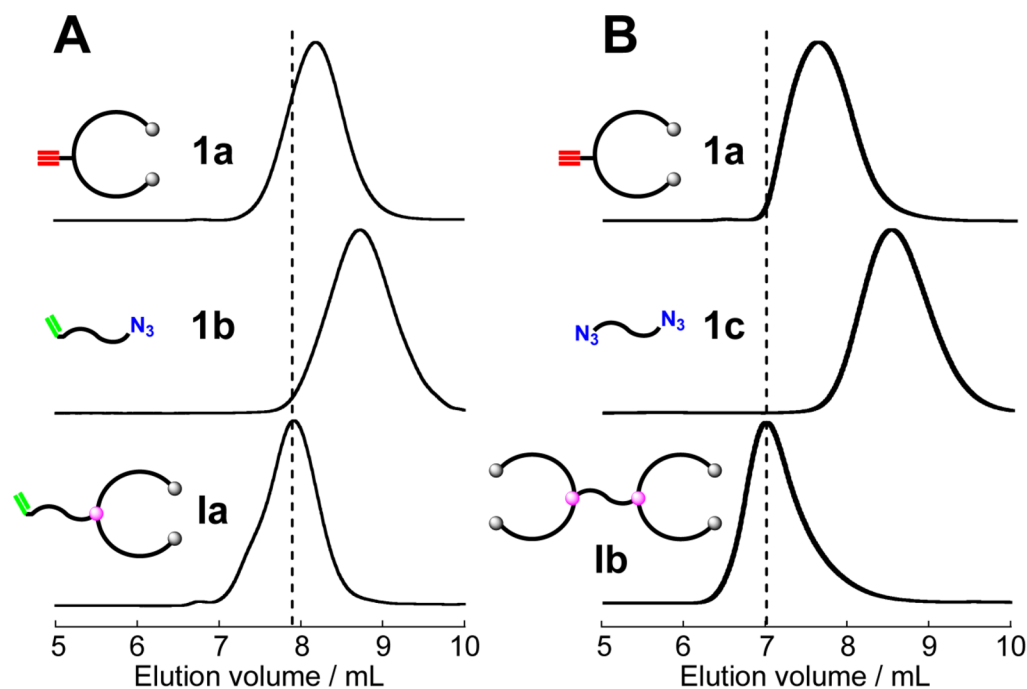


Figure 3. SEC traces of [A] (top) a poly(THF) having an alkyne group at the center position and *N*-phenylpyrrolidinium salt end groups (**1a**), (middle) a poly(THF) having an azide and an alkyne group (**1b**), and (bottom) a star poly(THF) having two cyclic ammonium salts and one alkene end group (**Ia**), and [B] (top) a poly(THF) having an alkyne group at the center position and *N*-phenylpyrrolidinium salt end groups (**1a**), (middle) a poly(THF) having azide groups (**1c**), and (bottom) an H-shaped poly(THF) having *N*-phenylpyrrolidinium salt end groups (**Ib**). (Measured after the covalent conversion of *N*-phenylpyrrolidinium salt end groups of **1a**, **Ia**, and **Ib** by the ring-opening reaction with a benzoate anion, THF was used as eluent at the flow rate of 1.0 mL/min, with TSK G4000HXL as a column.)

S3 and S4, the peak at $m/z = 4623.0$ and at $m/z = 6240.0$, both of which were assumed to be the adducts with Na^+ , correspond to the ring-opening products from **Ia** and from **Ib** possessing the expected chemical structures with a DP_n ($n + m$ in the chemical formula in Figure S2) of 50; $(\text{C}_4\text{H}_8\text{O}) \times 50 + \text{C}_{98}\text{H}_{108}\text{N}_{10}\text{O}_{11}$ plus Na^+ equals 4622.641, and with a DP_n ($n + m$ in the chemical formula in Figure 2 (bottom)) of 60; $(\text{C}_4\text{H}_8\text{O}) \times 60 + \text{C}_{114}\text{H}_{140}\text{N}_{10}\text{O}_{15}$ plus Na^+ equals 6239.857, respectively.

Moreover, the SEC comparison of the covalent converted products of star- and H-shaped structures, **Ia** and **Ib**, with the precursors, **1a** (also measured after the ring-opening of the pyrrolidinium salt groups by benzoate anions) and **1b**, and with **Ia** and **1c**, respectively, showed a noticeable peak shift toward the higher molecular weight region (Figure 3, A and B, respectively). Thus, the peak molecular weight for the covalent conversion derivative from **Ia** ($M_p = 4800$) was noticeably higher than those of the precursors, i.e., **1a** ($M_p = 3700$) and **1b** ($M_p = 1700$), respectively. Similarly, the peak molecular weight for the covalent derivative from **Ib** ($M_p = 10\,300$) was noticeably higher than those of the precursors, i.e., **1a** ($M_p = 5600$) and **1c** ($M_p = 2400$), respectively.

Construction of β -Graph Polymer Topology. The star-telechelic precursor, **Ia**, having two cyclic ammonium and one alkene end group, was then subjected to the ESA-CF process after introducing a dicarboxylate counteranion having an additional alkyne group, **2a** (Scheme 1). The ion-exchange reaction was conducted by the simple precipitation of **Ia** carrying triflate counteranions into an aqueous solution containing excess of **2a** as a sodium salt form. The ^1H NMR spectrum of the ion-exchange product, **Ia/2a** (Figure 4, top), showed the signal of an ethynyl proton in the carboxylate counteranion, **2a** at 2.47 ppm, and the nearly quantitative

conversion of 96% was confirmed. A solution of the obtained ionic self-assembly, **Ia/2a**, was then refluxed under dilution (0.2 g/L) in THF for 3 h to proceed the covalent conversion by the nucleophilic ring opening of the pyrrolidinium salt groups by carboxylate anions. The tadpole polymer, **II**, having an alkyne group at the top-head position and an alkene group at the tail-end position, was then isolated after the purification with the column chromatography on silica gel in 80% yield.

The ^1H NMR comparison of **Ia/2a** with **II** (Figure 4, the top two spectra) indicated that the broad signals of the methylene protons at around 4.0 ppm for the pyrrolidinium ring unit were removed along with the covalent conversion reaction, and the triplet signal of the ester methylene protons at 4.37 ppm became visible. In addition, the signal of the *N*-phenyl protons on the pyrrolidinium unit observed at 7.4–8.0 ppm for **Ia/2a** was shifted to the split two-set signals at 6.5–6.8 and 7.2 ppm for **II** after the reaction. The signals of ethynyl (2.53 ppm) and of vinyl methyn ($-\text{CH}=$, around 5.9 ppm) protons remained visible in **II**.

The MALDI-TOF mass of **II** (Figure S5) showed the peak at $m/z = 4598.2$, corresponding to the expected chemical structure **II** (assumed to be the adduct with Na^+) with a DP_n ($n + m$ in the chemical formula in Figure 4) of 50; $(\text{C}_4\text{H}_8\text{O}) \times 50 + \text{C}_{98}\text{H}_{108}\text{N}_{10}\text{O}_{11}$ plus Na^+ equals 4598.576. The SEC showed that the apparent peak MW ($M_p = 4300$) of **II** (Figure 5, top) was lower than the starting star precursor (**Ia**, $M_p = 4800$, Figure 3A, bottom) to confirm the 3D size reduction upon the polymer cyclization.

The tadpole precursor, **II**, was then subjected to the further click reaction with a linear precursor having azide end groups, **1c** ($M_n(\text{NMR}) = 1900$) (Scheme 1). Thus, a twice molar amount of **II** was charged relative to **1c** in the presence of CuSO_4 and sodium ascorbate as a catalyst in a THF/water

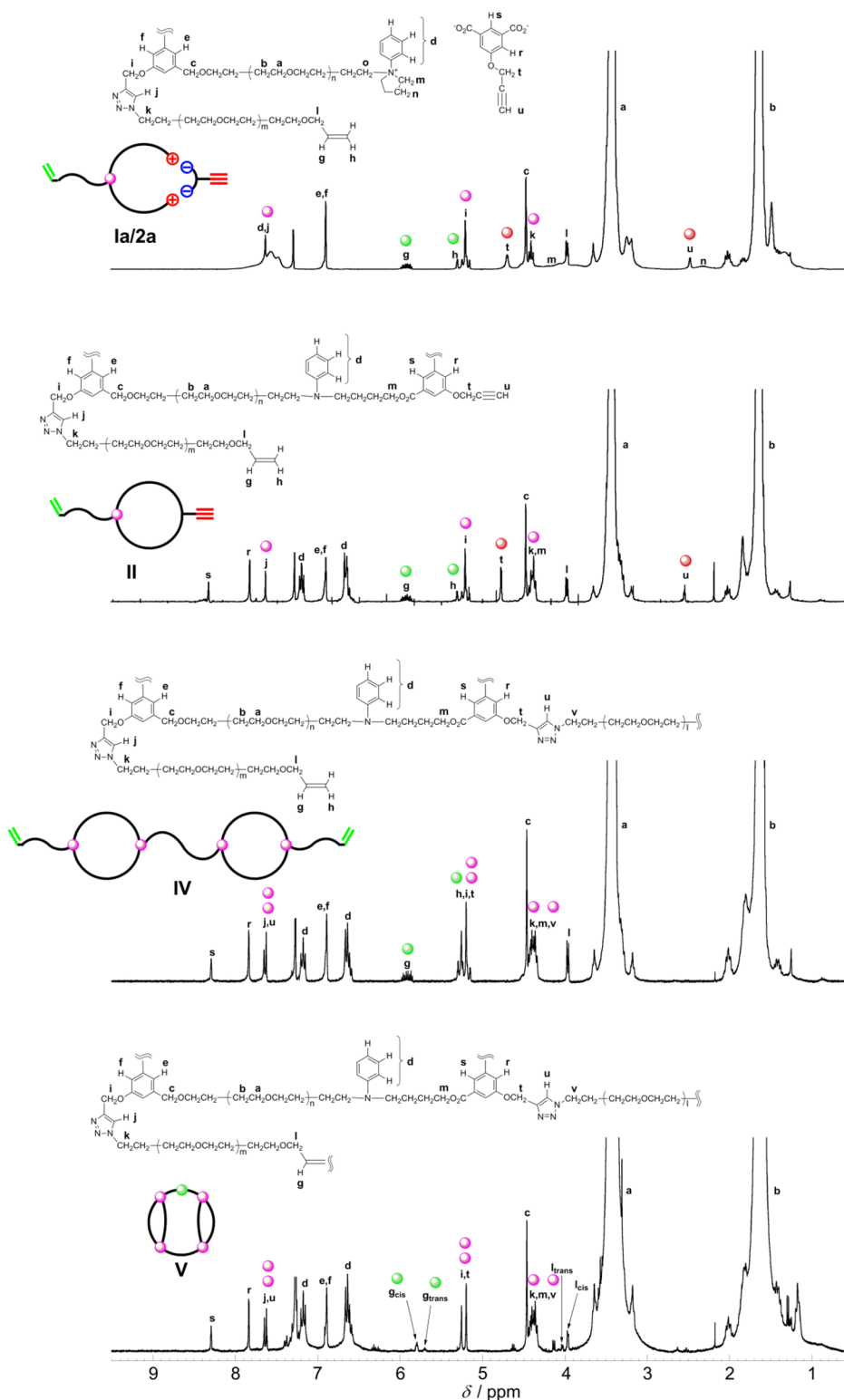


Figure 4. ^1H NMR (300 MHz) spectra of a star telechelic precursor after introducing a dicarboxylate counteranion having an alkyne group (Ia/2a), a tadpole poly(THF) having an alkyne group at the top-head position and an alkene group at the tail-end position (II), a double-tadpole poly(THF) having two outward branches with alkene chain ends (IV), and a doubly fused tricyclic, β -graph, poly(THF) (V) (CDCl_3 , 40 $^\circ\text{C}$).

mixture to proceed the reaction under homogeneous condition. The obtained dicyclic product, IV, comprised of two tadpole units linked by a linear linker segment at their head positions, contains allyloxy groups at the end of two outward branch segments. The product IV was first recovered as a crude product through the column chromatography with silica gel and

was finally isolated by means of the preparative SEC fractionation technique in 32% yield (Figure 5).

The ^1H NMR spectrum of IV (Figure 4) showed the new singlet signal of the triazole proton at 7.65 ppm, by replacing the signal of the ethynyl proton at 2.53 ppm observed in II, to confirm the selective click combination of the two units of

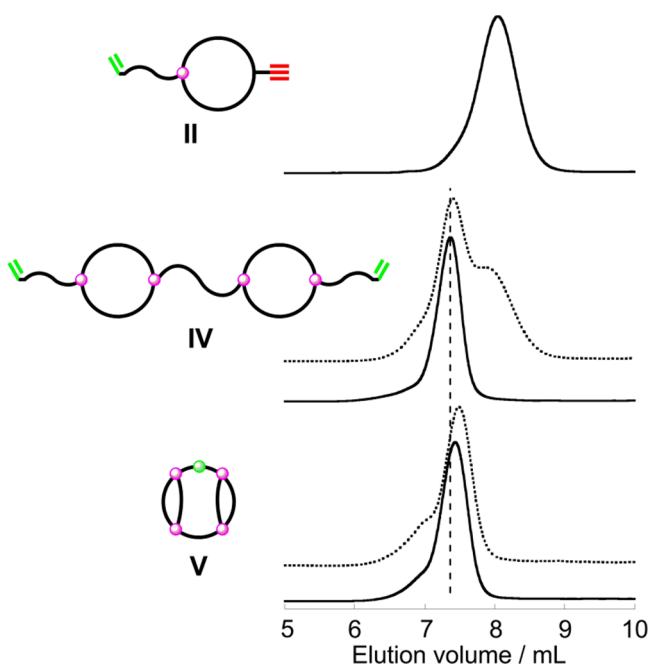


Figure 5. SEC traces of (top) a tadpole poly(THF) having an alkyne group at the top-head position and an alkene group at the tail-end position, **II**, (middle) a double-tadpole poly(THF) having two outward branches with alkene chain ends, **IV**, and (bottom) a doubly fused tricyclic, β -graph, poly(THF), **V**. Broken lines and solid lines show those obtained before and after SEC fractionation, respectively. (THF was used as eluent at the flow rate of 1.0 mL/min, with TSK G4000HXL as a column.)

alkyne-functionalized tadpole, **II**, with one unit of the linear precursor having azide end groups, **1c**.

The MALDI-TOF mass spectrum of **IV** in Figure 6 (top) showed uniform series of peaks with an interval of 72 mass units due to the repeating THF unit, and each peak exactly matched the total molar mass of the obtained poly(THF) having the chemical structures in **IV**. Thus, the peak at $m/z = 11264.0$, which was assumed to be the adduct with Na^+ , corresponds to **IV** possessing the expected chemical structure with a DP_n ($n + m + l$ in the chemical formula in Figure 4) of 130; $(\text{C}_4\text{H}_8\text{O}) \times 130 + \text{C}_{118}\text{H}_{150}\text{N}_{11}\text{O}_9$ plus Na^+ equals 11 263.500. The SEC (Figure 5) showed that the apparent peak MW of the purified **IV** ($M_p = 9900$) was notably higher than each of the starting precursors, **II** ($M_p = 4300$) and **1c** ($M_p = 2400$), to confirm the effective polymer linking reaction.

Finally, the double-tadpole polymer precursor, **IV**, having allyloxy groups at the outward tail-end positions, was subjected to the metathesis condensation (clip) reaction to produce a doubly fused tricyclic, β -graph, poly(THF), **V** (Scheme 1). The reaction was conducted under dilution (0.2 g/L) in CH_2Cl_2 in the presence of a Grubbs first generation catalyst.^{15,16} The reaction was allowed to continue for 96 h by the repeated addition of the catalyst. The product **V** was first recovered after the treatment with the column chromatography with alumina and with silica gel and finally isolated in 33% yield upon the subsequent preparative SEC fractionation to remove the higher molecular weight byproducts formed through the intermolecular condensation.

The ^1H NMR spectrum of **V** (Figure 4, bottom) showed the signals of the inner alkenyl methyn ($-\text{CH}=\text{}$) protons at 5.70 (trans) and at 5.80 (cis) ppm and of the oxymethylene protons adjacent to the inner alkenyl group at 3.96 ppm (cis) and at

4.03 ppm (trans), respectively, by replacing the signals of the chain-end allyloxy protons observed at around 5.9 and 4.0 ppm for **IV**. The cis/trans ratio was around 4/1 as reported before.¹⁹ Other signals remained unchanged to support that the selective metathesis condensation proceeded to completion.

The MALDI-TOF mass spectrum of **V** (Figure 6, bottom) showed uniform series of peaks with an interval of 72 mass units due to the repeating THF unit, and each peak exactly matched the total molar mass of the obtained poly(THF) units having all sets of the initiator and the linking group. Thus, the peak at $m/z = 11235.2$, which was assumed to be the adduct with Na^+ , corresponds to **V** possessing the expected chemical structure with a DP_n ($n + m + l$ in the chemical formula in Figure 4) of 130; $(\text{C}_4\text{H}_8\text{O}) \times 130 + \text{C}_{116}\text{H}_{146}\text{N}_{11}\text{O}_9$ plus Na^+ equals 11235.446. The mass difference of 28 in **IV** and **V** confirmed the metathesis reaction by the elimination of an ethylene molecule from the former to produce the latter selectively. The SEC (Figure 5) showed that the apparent peak MW (M_p) of **V** (8900) was noticeably reduced from that of the starting **IV** (9900), consistent with the intramolecular condensation to yield **V**.

Convergent Construction of γ -Graph Polymer Topology. The H-shaped poly(THF) precursor having cyclic ammonium salt groups, **Ib**, was also subjected to the ESA-CF process after the introduction of two units of a dicarboxylate counteranion having an allyloxy group, **2b**. The ion-exchange reaction was conducted through the precipitation of **Ib**, carrying triflate counteranions, into an ice-cooled aqueous solution containing a large excesses of **2b** in a sodium salt form. By this process, the polymeric topological isomers comprised of manacle-shaped and θ -shaped poly(THF)s having allyloxy groups at the orthogonal positions, **IIIa,b**, could be produced (Scheme 1). The effective ion-exchange reaction as high as 90% conversion was confirmed by the ^1H NMR analysis of the ionically linked product, **Ib/2b** (Figure S6). The ionic self-assembly product, **Ib/2b**, was then subjected to the heat treatment by refluxing under dilution (0.2 g/L) in THF with a small portion of methanol (24:1 by vol:vol) for 24 h. The ring-opening reaction of the pyrrolidinium salt groups by the dicarboxylate counteranions in **2b**, leading to the formation of the dicyclic isomer products, **IIIa,b**.

The ^1H NMR analysis of **IIIa,b** (Figure 7) showed the triplet signal of the ester methylene protons became visible at 4.36 ppm together with those of the methylene protons on the triazole unit at 5.37 ppm, while the signal of the methylene protons in the pyrrolidinium ring unit at around 3.8–4.2 ppm observed for **Ib/2b** disappeared (Figure S6). The signal of the *N*-phenyl protons on the pyrrolidinium group observed at 7.4–7.8 ppm for **Ib/2b** were shifted to the two sets of signals at 6.6–6.7 and 7.2 ppm for **IIIa,b** after the reaction. The signals of the allyloxy protons at 4.60 and 5.29–5.44 ppm remained visible for **IIIa,b**.

The MALDI-TOF mass spectrum of **IIIa,b** (Figure 8, top) showed uniform series of peaks with an interval of 72 mass units due to the repeating THF unit, and each peak exactly matched the total molar mass of the obtained poly(THF) having the chemical structures of **IIIa,b**. Thus, the peak at $m/z = 5906.2$, which was assumed to be the adduct with Na^+ , corresponds to the expected chemical structure of **IIIa,b** possessing a DP_n ($n + m$ in the chemical formula in Figure 7) of 60; $(\text{C}_4\text{H}_8\text{O}) \times 60 + \text{C}_{92}\text{H}_{104}\text{N}_{10}\text{O}_{13}$ plus Na^+ equals 5907.329.

The SEC analysis of the product **IIIa,b** together with the H-shaped precursor (measured after the ring-opening of the

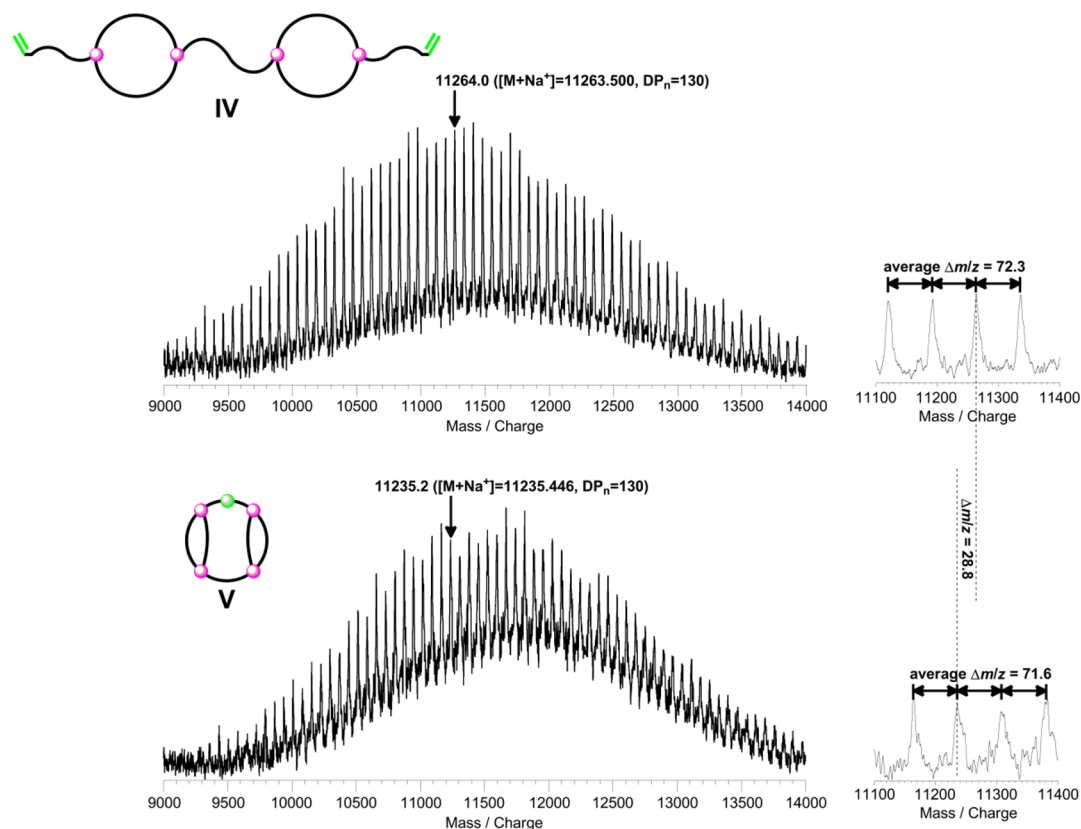


Figure 6. MALDI-TOF mass spectra of (top), a double-tadpole poly(THF) having two outward branches with alkene chain ends (IV) and (bottom) a doubly fused tricyclic, β -graph, polymer product (V) (linear mode, matrix: dithranol with sodium trifluoroacetate; DP_n denotes the number of monomer units in the products).

pyrrolidinium salt groups by benzoates) is shown in Figure 9. Despite the presence of two constitutional isomer components in **IIIa,b**, having presumably different 3D sizes each other, the unimodal size distribution ($PDI = 1.27$) was observed because the hydrodynamic volumes of the two isomers are expected to be similar.^{11,20} Nevertheless, the apparent peak MW ($M_p = 8400$) of **IIIa,b**, corresponding to its hydrodynamic volume, was marginally smaller than that of the H-shaped counterpart, **Ib** ($M_p = 10\,300$, also measured after the covalent conversion of the pyrrolidinium groups). The reduction of the hydrodynamic volume of **IIIa,b** compared to that of the H-shaped precursor, **Ib**, is consistent with the 3D size reduction expected upon the polymer cyclization.

Finally, the dicyclic manacle/theta polymer product having two allyl groups at the orthogonal positions, **IIIa,b**, was subjected to the convergent folding reaction through the clip reaction to exclusively produce a doubly fused tricyclic, γ -graph, polymer product, **VI**. The construction of the γ -graph polymer topology was recently achieved through an alternative tandem click/ESA-CF protocol by using a manacle-shaped precursor having two allyl groups at the opposite positions.¹² The clip folding reaction was conducted under dilution (0.1 g/L) in toluene for 48 h in the presence of a Hoveyda–Grubbs second generation catalyst, which was observed more effective than a Grubbs first generation catalyst. The product **VI** was recovered after the treatment with the column chromatography with alumina and with silica gel in 25% yield.

The 1H NMR of the product **VI** (Figure 7) showed the signals of the inner alkenyl methyn protons at 5.98 ppm (trans) and 6.11 ppm (cis), together with the oxymethylene protons

adjacent to the inner alkenyl group at 4.66 ppm (cis) and 4.76 ppm (trans), respectively, by removing those of the allyloxy protons visible at 4.60 and 5.29–5.44 ppm for the precursor, **IIIa,b**. The cis/trans ratio was estimated as 2/1 in this clip reaction involving the allyloxy phenyl group and employing the Hoveyda–Grubbs second generation catalyst. The cis/trans selectivity was thus noticeably different from the observed ratio of 4/1 in the previous β -graph polymer synthesis, involving the allyloxy alkyl group and employing a Grubbs first generation catalyst. Other signals remained intact to confirm the selective metathesis condensation to proceed.

The MALDI-TOF mass spectrum of **VI**, prepared separately using the precursor **1a** having the lower molecular weight, (Figure 8, bottom), showed uniform series of peaks with the interval of 72 mass units due to the repeating THF unit, and each peak exactly matched the total molar mass of the obtained poly(THF) having all sets of the initiator and the linking group. Thus, the peak at $m/z = 5878.6$, which was assumed to be the adduct with Na^+ , corresponds to **VI** possessing the expected chemical structure with a DP_n ($n + m$ in the chemical formula in Figure 7) of 60; $(C_4H_8O) \times 60 + C_{90}H_{100}N_{10}O_{13}$ plus Na^+ equals 5879.275. The mass difference of 28 between **IIIa,b** and **VI** again confirmed the effective metathesis reaction by the elimination of an ethylene molecule.

The SEC showed the unimodal size distribution ($PDI = 1.14$) for the clip folding product **VI** (Figures 9), and the apparent peak MW ($M_p = 7400$) was noticeably reduced from that of the precursor, **IIIa,b** ($M_p = 8400$), which is again consistent with the 3D size reduction associated with the polymer cyclization during the formation of **VI**.

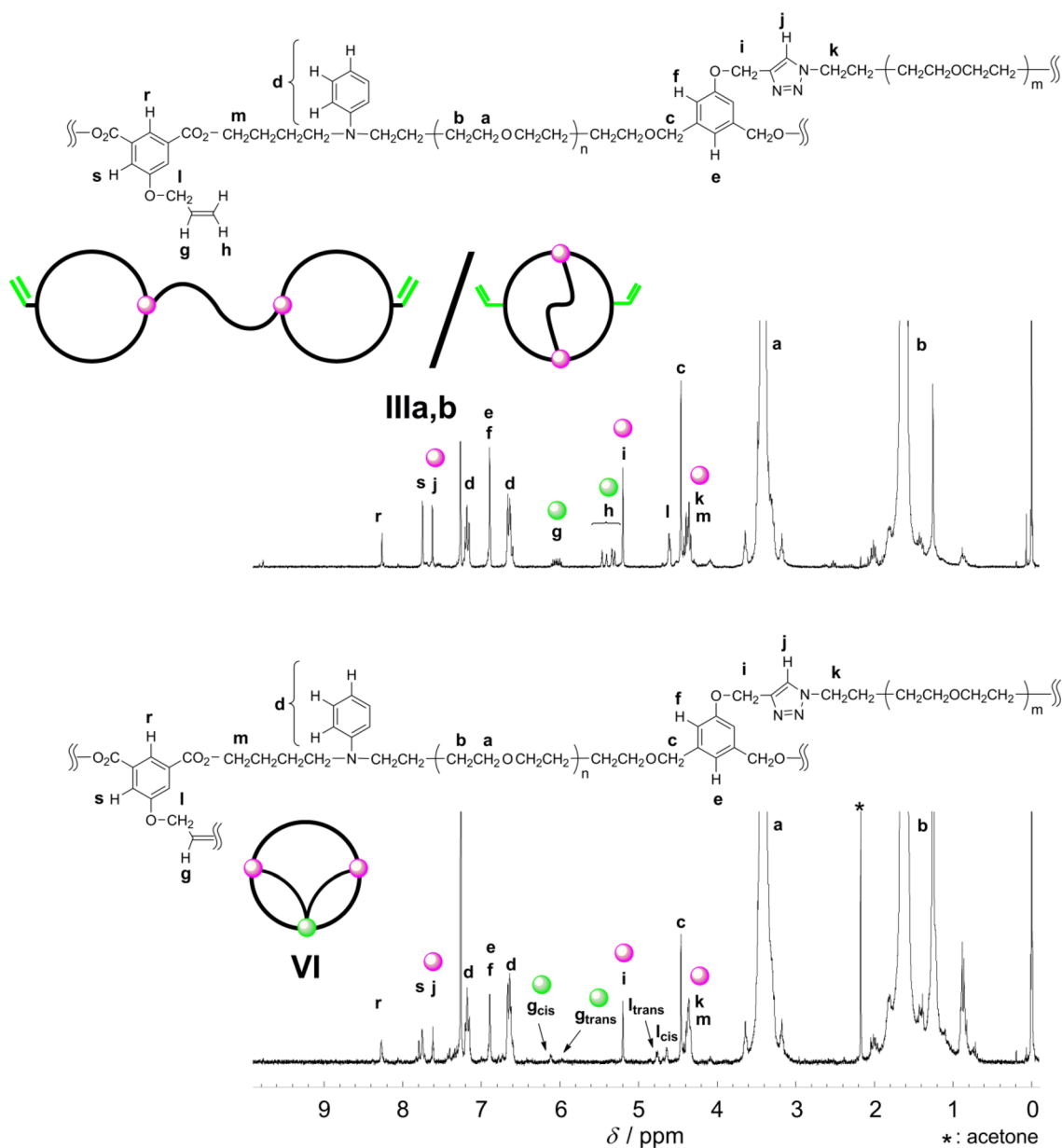


Figure 7. ^1H NMR (300 MHz) spectra of (top) a topological isomer mixture of manacle- and θ -shaped poly(THF)s having allyloxy groups at the orthogonal positions (**IIIa,b**) and (bottom) a doubly fused tricyclic, γ -graph, polymer product (**VI**) (CDCl_3 , 40 °C).

CONCLUSION

We have demonstrated herein the construction of doubly fused tricyclic, β - and γ -graph polymer topologies. The key polymer precursors, an asymmetric three-armed star and an H-shaped telechelic polymer precursor having cyclic ammonium salt groups at the prescribed chain ends, were obtained through the click reaction using a polymer precursor having cyclic ammonium salt end groups and having an additional alkyne group at the center position. The click reaction with complementary precursors having azide end groups was conducted to give the star-shaped and the H-shaped telechelic polymer precursor keeping cyclic ammonium salt groups intact during the reaction. The subsequent ESA-CF process with designated dicarboxylate counteranions having additional alkene or alkyne group could afford the *kyklo*-telechelic precursors, having either a tadpole form having an alkene and an alkyne group at the top-head and the tail-end positions, and

a manacle/theta isomeric mixture having two alkene groups at the opposite positions, respectively. The further click coupling of the former with a linear telechelic precursor having azide groups, followed by the clip folding process could produce, for the first time, a doubly fused tricyclic polymers having β -graph topology. Moreover, the convergent clip folding of the latter isomeric mixture precursors could produce a sole form of a doubly fused tricyclic polymers having γ -graph topology. This work demonstrates an orthogonal click/ESA-CF protocol as a versatile synthetic means to construct complex polymer topologies to extend the current frontier of synthetic polymer chemistry.

EXPERIMENTAL SECTION

Materials. A linear poly(tetrahydrofuran), poly(THF), having *N*-phenylpyrrolidinium salt end groups and an alkyne group at the center position (**1a**, $M_n(\text{NMR}) = 3800$, $M_p(\text{SEC}) = 3700$, and PDI = 1.24, $M_n(\text{NMR}) = 4700$, $M_p(\text{SEC}) = 5600$, and PDI = 1.17, and $M_n(\text{NMR})$

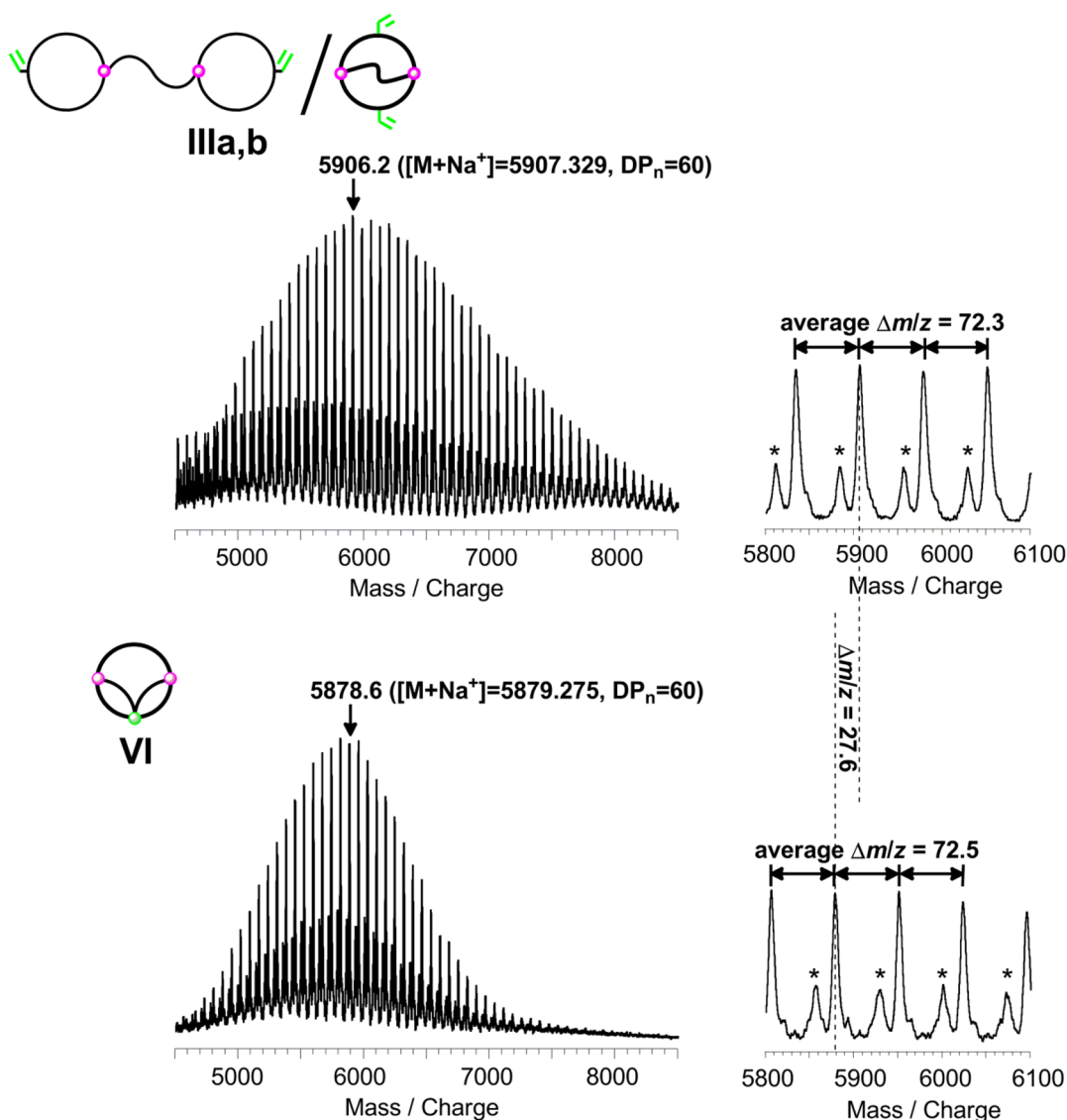


Figure 8. MALDI-TOF mass spectra of (top) a topological isomer mixture of manacle- and θ -shaped poly(THF)s having allyloxy groups at the orthogonal positions (**IIIa,b**) and (bottom) a doubly fused tricyclic, γ -graph, polymer product (**VI**) (linear mode, matrix: dithranol with sodium trifluoroacetate; DP_n denotes the number of monomer units in the products). The peaks with an asterisk are assigned to the proton adducts.

= 2700, $M_p(\text{SEC}) = 2100$, and $PDI = 1.30$), a linear poly(THF) having an azide and an alkene end groups (**1b**, $M_n(\text{NMR}) = 1800$, $M_p(\text{SEC}) = 1700$, and $PDI = 1.27$), and a linear poly(THF) having azide end groups (**1c**, $M_n(\text{NMR}) = 1900$, $M_p(\text{SEC}) = 2400$, and $PDI = 1.17$) as well as disodium 5-propargyloxyisophthalate (**2a**) and disodium 5-allyloxyisophthalate (**2b**) were prepared according to the method reported previously.¹² The peak molecular weight (M_p) of **1a** was measured by SEC after the ring-opening reaction of the *N*-phenylpyrrolidinium salt end groups with benzoate anions. *N*-Phenylpyrrolidine was prepared as reported before.²¹

THF (Godo Co., Inc.) was distilled over Na wire. CH_2Cl_2 was distilled over CaH_2 . Trifluoromethanesulfonic anhydride (triflic anhydride) (98%, Nacalai Tesque, Inc.) was distilled from P_2O_5 just before use, and 2,6-di-*tert*-butylpyridine (DTBP, 97%, Aldrich) was distilled prior to use. Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (99.5+%, Wako Pure Chemical Industries, Ltd.), sodium ascorbate (98.0+%, Wako Pure Chemical Industries, Ltd.), a Grubbs first generation catalyst (Aldrich), a Hoveyda–Grubbs second generation catalyst (Aldrich), and ethyl vinyl ether (99%, Aldrich) were used as received. For flash chromatography, Wakosil C-300 (Wako Pure Chemical Industries, Ltd.) was used.

Synthesis of a Three-Armed Star Poly(THF) Having Two *N*-Phenylpyrrolidinium Salt Groups and One Alkene End Group (1a**).** A THF (2 mL) solution containing the weighed amount of **1a**/ CF_3SO_3^- (92 mg, 24 μmol) and **1b** (48 mg, 27 μmol) was placed in a sample vial, and N_2 gas was bubbled under stirring. Thereupon, an aqueous solution (0.5 mL) containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (91 mg, 0.37 mmol) and sodium ascorbate (141 mg, 0.71 mmol) was added dropwise to proceed the reaction stirred for 5 h. To the reaction mixture, CH_2Cl_2 was added to treat with aqueous NH_4Cl solutions four times and with deionized water twice. The organic phase was separated and dried with anhydrous Na_2SO_4 . After concentrated under reduced pressure, the residual product was subjected to silica gel column chromatography. After, washing with $\text{CHCl}_3/\text{acetone}$ (2/1 v/v), the eluted fraction with $\text{CHCl}_3/\text{methanol}$ (2/1 vol/vol) was collected to isolate the product **1a** (103 mg, $M_n(\text{NMR}) = 5600$, $M_p(\text{SEC}) = 4800$, and $PDI = 1.21$). ^1H NMR of **1a** (CDCl_3) δ : 1.44–1.79 (b, $\text{CH}_2\text{CH}_2\text{O}$), 2.11–2.45 (b, 4H, *endo*- NCH_2CH_2), 2.45–2.83 (b, 4H, *exo*- NCH_2CH_2), 3.23–3.61 (b, $\text{CH}_2\text{CH}_2\text{O}$), 3.96 (d, 2H, $J = 5.5$ Hz, $\text{OCH}_2\text{CH}=\text{CH}_2$), 4.12–4.38 (b, 8H, NCH_2CH_2 , *endo*- NCH_2), 4.38–4.59 (b, 2H, CH_2CH_2 -triazole), 4.47 (s, 4H, ArCH_2O), 4.72–5.09 (b, 4H, *exo*- NCH_2), 5.09–5.37 (m, 4H, $\text{OCH}_2\text{CH}=\text{CH}_2$, ArOCH_2 -triazole), 5.83–6.00 (m, 1H,

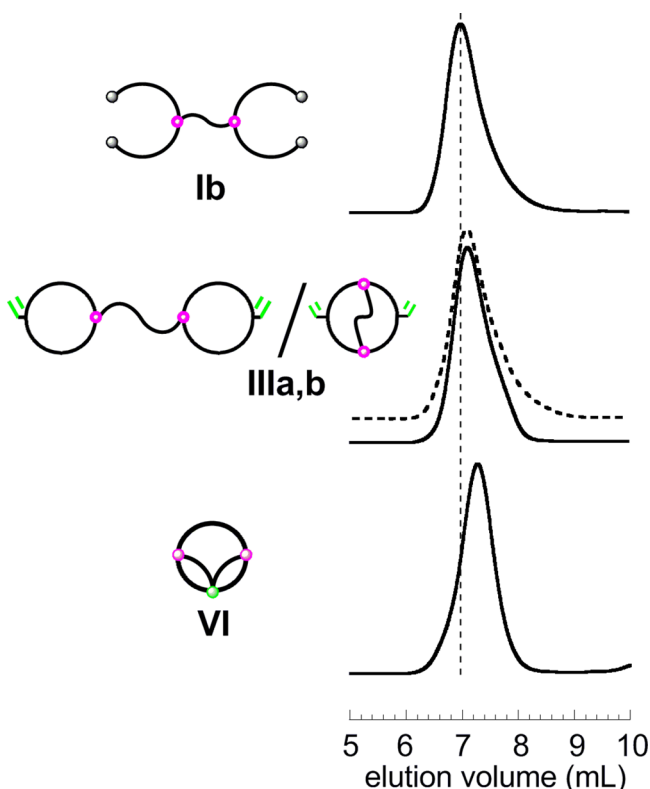


Figure 9. SEC traces of (top) an H-shaped poly(THF) having *N*-phenylpyrrolidinium salt end groups (**Ib**, measured after the covalent conversion of *N*-phenylpyrrolidinium salt end groups by the ring-opening reaction with a benzoate anion), (middle) a topological isomer mixture of manacle-shaped and θ -shaped poly(THF)s having allyloxy groups at the orthogonal positions (**IIIa,b**), and (bottom) a doubly fused tricyclic, γ -graph, polymer product (**VI**). Broken lines and solid lines show those obtained before and after SEC fractionation, respectively. (THF was used as eluent at the flow rate of 1.0 mL/min, with TSK G4000HXL as a column.)

OCH₂CH=CH₂), 6.90 (s, 3H, Ar-*H* ortho and para to OCH₂-triazole), 7.47–8.04 (m, 11H, NAr-*H*, triazole-*H*).

Synthesis of an H-Shaped Poly(THF) Having *N*-Phenylpyrrolidinium Salt End Groups (Ib**).** A THF/water (9.6/2.4 in mL/mL) solution containing the weighed amount of **Ia**/CF₃SO₃[−] (494 mg, 105 μ mol) and **Ic** (95 mg, 50 μ mol) was placed in a sample vial, and N₂ gas was bubbled under stirring for 0.5 h. Thereupon, CuSO₄·5H₂O (187 mg, 0.75 μ mol) and sodium ascorbate (297 mg, 1.50 μ mol) were added to proceed the reaction under stirring at ambient temperature for 3 h. To the reaction mixture, CH₂Cl₂ was added to filtrate the precipitates. After the evaporation of the solvents, the residual product was subjected to the continuous extraction by methanol for 2 days to remove the remaining **Ia** charged in excess and the copper catalyst residue, to isolate the product, **Ib** (460 mg, *M_n*(NMR) = 12 500, *M_p*(SEC) = 10 300, and PDI = 1.24). ¹H NMR of **Ib** (CDCl₃) δ : 1.56–1.77 (b, CH₂CH₂O), 2.05–2.24 (b, 8H, *endo*-NCH₂CH₂), 2.33–2.48 (b, 8H, *exo*-NCH₂CH₂), 3.34–3.54 (b, CH₂CH₂O), 3.88–4.17 (b, 16H, *endo*-,*exo*-NCH₂CH₂), 4.40 (t, 4H, *J* = 7.1 Hz, triazole-CH₂CH₂), 4.46 (s, 8H, ArCH₂O), 5.20 (d, 4H, *J* = 5.9 Hz, ArOCH₂-triazole), 6.89 (s, 6H, Ar-*H* ortho and para to OCH₂-triazole), 7.49–7.69 (m, 22H, NAr-*H*, triazole-*H*).

Synthesis of a Tadpole Poly(THF) Having an Alkyne Group at the Top-Head Position and an Alkene Group at the Tail-End Position (II**).** Into a vigorously stirred aqueous solution (40 mL) containing **2a** (38 mg) kept at 0 °C, an acetone solution (1.5 mL) containing **Ia** (74 mg, 13 μ mol) was added dropwise. The precipitate formed was collected by filtration to give the product **Ia/2a** (65 mg) in 96% ion-exchange yield. ¹H NMR of **Ia/2a** (CDCl₃) δ : 1.53–1.79 (b,

CH₂CH₂O), 2.02–2.27 (b, 8H, *endo*-NCH₂CH₂), 2.33–2.52 (b, 8H, *exo*-NCH₂CH₂), 2.47 (s, 1H, ArOCH₂C≡CH), 3.29–3.60 (b, CH₂CH₂O), 3.75–4.19 (b, 16H, *endo*-,*exo*-NCH₂CH₂), 3.96 (d, 2H, *J* = 5.5 Hz, OCH₂CH=CH₂), 4.40 (t, 2H, *J* = 7.2 Hz, CH₂CH₂-triazole), 4.46 (s, 4H, ArCH₂O), 4.70 (m, 2H, ArOCH₂C≡CH), 5.12–5.35 (m, 4H, OCH₂CH=CH₂, ArOCH₂-triazole), 5.83–6.01 (m, 1H, OCH₂CH=CH₂), 6.89 (s, 3H, Ar-*H* ortho and para to OCH₂-triazole), 7.36–8.03 (b, 11H, NAr-*H*, triazole-*H*).

A THF solution (325 mL) of **Ia/2a** (65 mg), corresponding 0.2 g/L, was prepared by stirring for 30 min and was refluxed for 3 h. The solvent was then removed by evaporation. The residual product was first subjected to a plug of silica gel with *n*-hexane/acetone (2/1 vol/vol), followed by the reprecipitation into an ice-cooled water to isolate the product **II** as colorless oil (52 mg, *M_n*(NMR) = 5300, *M_p*(SEC) = 4300, and PDI = 1.18). ¹H NMR of **II** (CDCl₃) δ : 1.48–1.78 (b, CH₂CH₂O), 2.53 (t, 1H, *J* = 2.2 Hz, ArOCH₂C≡CH), 3.23–3.61 (b, CH₂CH₂O), 3.96 (d, 2H, *J* = 5.5 Hz, OCH₂CH=CH₂), 4.37 (t, 4H, ArCO₂CH₂), 4.40 (t, 2H, CH₂CH₂-triazole), 4.46 (s, 4H, ArCH₂O), 4.76 (d, 2H, *J* = 2.2 Hz, ArOCH₂C≡CH), 5.13–5.37 (m, 4H, OCH₂CH=CH₂, ArOCH₂-triazole), 5.82–6.01 (m, 1H, OCH₂CH=CH₂), 6.53–6.75 (m, 6H, Ar-*H* ortho and para to N), 6.89 (s, 3H, Ar-*H* ortho and para to OCH₂-triazole), 7.12–7.25 (m, 4H, Ar-*H* meta to N), 7.62 (s, 1H, triazole-*H*), 7.82 (d, 2H, *J* = 1.3 Hz, Ar-*H* ortho to OCH₂C≡CH), 8.32 (s, 1H, Ar-*H* para to OCH₂C≡CH).

Synthesis of a Double Tadpole Poly(THF) Having Allyloxy End Groups at the Two Outward Branch Segments **IV.** A THF solution (2 mL) containing **Ic** (9.3 mg, 4.9 μ mol) and **II** (51.5 mg, 9.7 μ mol) was placed in a sample vial, and N₂ gas was bubbled through the solution. Thereupon, an aqueous solution (0.5 mL) containing CuSO₄·H₂O (18.4 mg, 74 μ mol) and sodium ascorbate (30.1 mg, 0.15 mmol) was added to result in a black precipitate. After adding water to dissolve the precipitate, the reaction was allowed to proceed under stirring for 24 h. To the reaction mixture, CH₂Cl₂ was added to treat with aqueous NH₄Cl solutions four times and with deionized water once. The organic phase was separated and dried with anhydrous Na₂SO₄. After concentrated under reduced pressure, the residual product was subjected to silica gel column chromatography with acetone. The obtained crude product was fractionated by preparative SEC to isolate the product **IV** as pale red oil (19.4 mg, *M_n*(NMR) = 15 000, *M_p*(SEC) = 9900, PDI = 1.12). ¹H NMR of **IV** (CDCl₃) δ : 1.48–1.95 (b, CH₂CH₂O), 3.23–3.61 (b, CH₂CH₂O), 3.96 (d, 4H, *J* = 5.5 Hz, OCH₂CH=CH₂), 4.29–4.45 (m, 16H, ArCO₂CH₂, CH₂CH₂-triazole), 4.46 (s, 8H, ArCH₂O), 5.11–5.36 (m, 12H, OCH₂CH=CH₂, ArOCH₂-triazole), 5.83–6.00 (m, 2H, OCH₂CH=CH₂), 6.55–6.76 (m, 12H, Ar-*H* ortho and para to N), 6.89 (s, 6H, Ar-*H* ortho and para to OCH₂-triazole), 7.12–7.24 (m, 8H, Ar-*H* meta to N), 7.63 (s, 2H, CH₂ArOCH₂-triazole-*H*), 7.65 (s, 2H, O₂CArOCH₂-triazole-*H*), 7.84 (s, 4H, O₂CAr-*H* ortho to OCH₂-triazole), 8.29 (s, 2H, O₂CAr-*H* para to OCH₂-triazole).

Synthesis of Poly(THF)s Comprised of Manacle-Shaped and θ -Shaped Isomers Having Allyloxy Groups at the Orthogonal Positions (IIIa,b**).** Into a vigorously stirring aqueous solution (100 mL) containing **2b** (260 mg) kept in an ice-cooled bath (<5 °C), a THF solution (2 mL) containing **Ib** (244 mg, 20 μ mol) was added dropwise. The precipitate formed was collected by filtration and dried in vacuo for 1 h to give the product **Ib/2b** (198 mg) in 90% ion-exchange yield. ¹H NMR of **Ib/2b** (CDCl₃) δ : 1.55–1.77 (b, CH₂CH₂O), 2.02–2.27 (b, 8H, *endo*-NCH₂CH₂), 2.33–2.52 (b, 8H, *exo*-NCH₂CH₂), 3.34–3.54 (b, CH₂CH₂O), 3.75–4.19 (b, 16H, *endo*-,*exo*-NCH₂CH₂), 4.40 (t, 4H, *J* = 7.1 Hz, triazole-CH₂CH₂), 4.46 (s, 8H, ArCH₂O), 4.58 (d, 4H, *J* = 6.0 Hz, OCH₂CH=CH₂), 5.20 (d, 4H, *J* = 5.9 Hz, ArOCH₂-triazole), 5.29–5.44 (m, 4H, OCH₂CH=CH₂), 5.98–6.11 (m, 2H, OCH₂CH=CH₂), 6.89 (s, 6H, Ar-*H* ortho and para to OCH₂-triazole), 7.41–7.80 (m, 26H, NAr-*H*, CO₂ArOCH₂-triazole-*H*, Ar-*H* ortho to OCH₂CH=CH₂), 8.43 (d, 2H, *J* = 8.81 Hz, Ar-*H* para to OCH₂CH=CH₂).

A THF/methanol (576/24 in mL/mL) solution of **Ib/2b** (120 mg), corresponding to 0.20 g/L, was prepared by stirring for 30 min and was heated to reflux for 24 h. The solvent was then removed by evaporation. The residual product was first subjected to a plug of silica

gel with hexane/acetone (1/1 in vol/vol), followed by the fractionated with a preparative SEC apparatus (Japan Analytical Industry Co., Ltd. LC-908 equipped with two columns, JAIGEL-3H and JAIGEL-2H, and THF as an eluent at 3.5 mL/min) to give **IIIa,b** (54 mg, M_n (NMR) = 13 000, M_p (SEC) = 8400, PDI = 1.16). ^1H NMR of **IIIa,b** (CDCl_3) δ : 1.49–1.73 (m, $\text{CH}_2\text{CH}_2\text{O}$), 3.23–3.55 (m, $\text{CH}_2\text{CH}_2\text{O}$), 4.36 (t, 8H, J = 6.4 Hz, ArCO_2CH_2), 4.40 (t, 4H, J = 7.1 Hz, triazole- CH_2CH_2), 4.46 (s, 8H, ArCH_2O), 4.60 (d, J = 6.0 Hz, 4H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.20 (d, 4H, J = 5.9 Hz, ArOCH_2 -triazole), 5.29–5.44 (m, 4H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.98–6.11 (m, 2H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 6.60–6.66 (m, 12H, Ar- H ortho and para to N), 6.89 (s, 6H, Ar- H ortho and para to OCH_2 -triazole), 7.19 (t, J = 9.8 Hz, 8H, Ar- H meta to N), 7.62 (s, 2H, $\text{CO}_2\text{ArOCH}_2$ -triazole- H), 7.74 (s, 4H, Ar- H para to $\text{OCH}_2\text{CH}=\text{CH}_2$), 8.26 (d, 2H, Ar- H para to $\text{OCH}_2\text{CH}=\text{CH}_2$).

Synthesis of a Doubly Fused Tricyclic, β -Graph, Poly(THF) (V). To a CH_2Cl_2 (95 mL) solution containing **IV** (18.3 mg, 1.4 μmol) in a flame-dried 200 mL flask, the weighed amount of a Grubbs first generation catalyst (1.2 mg, 1.5 μmol) was added. The reaction was allowed to proceed under reflux by adding repeatedly the Grubbs first generation catalyst (1.2 mg, 1.5 μmol) three times at the interval of every 24 h. Thereafter, ethyl vinyl ether (0.5 mL) was added to the reaction mixture to continue stirring for further 2 h. After the solvent was removed under reduced pressure, the residual product was subjected to silica gel column chromatography. After washing with CH_2Cl_2 and with ethyl acetate, the eluted fraction with acetone was collected. The recovered product was further subjected to alumina column chromatography with acetone and once again to silica gel column chromatography to remove the catalyst residues. The obtained crude product (10.8 mg) was finally fractionated by preparative SEC to give the product **V** (6.0 mg, M_n (NMR) = 15 000, M_p (SEC) = 8900, PDI = 1.12). ^1H NMR of **V** (CDCl_3) δ : 1.32–1.94 (b, $\text{CH}_2\text{CH}_2\text{O}$), 3.21–3.61 (b, $\text{CH}_2\text{CH}_2\text{O}$), 3.96 (m, 1.6H, $\text{OCH}_2\text{CH}=\text{CH}$, cis isomer), 4.03 (m, 0.4H, $\text{OCH}_2\text{CH}=\text{CH}$, trans isomer), 4.25–4.45 (m, 1.6H, ArCO_2CH_2 , CH_2CH_2 -triazole), 4.46 (s, 8H, ArCH_2O), 5.20 (s, 4H, $\text{CH}_2\text{ArOCH}_2$ -triazole), 5.26 (s, 4H, $\text{O}_2\text{CArOCH}_2$ -triazole), 5.70 (m, 0.4H, $\text{OCH}_2\text{CH}=\text{CH}$, trans isomer), 5.80 (m, 1.6H, $\text{OCH}_2\text{CH}=\text{CH}$, cis isomer), 6.45–6.80 (m, 12H, Ar- H ortho and para to N), 6.89 (s, 6H, Ar- H ortho and para to OCH_2 -triazole), 7.08–7.24 (m, 8H, Ar- H meta to N), 7.62 (s, 2H, $\text{CH}_2\text{ArOCH}_2$ -triazole- H), 7.65 (s, 2H, $\text{O}_2\text{CArOCH}_2$ -triazole- H), 7.84 (s, 4H, O_2CArH ortho to OCH_2 -triazole), 8.29 (s, 2H, O_2CArH para to OCH_2 -triazole).

Synthesis of a Doubly Fused Tricyclic, γ -Graph, Poly(THF) (VI). To a toluene (200 mL) solution containing **IIIa,b** (20 mg, 1.6 μmol) in a flame-dried flask, the weighed amount of a Hoveyda–Grubbs second generation catalyst (4.0 mg, 6.4 μmol) was added to proceed the reaction under reflux for 48 h. Thereafter, ethyl vinyl ether (10 mL, 104 mmol) was added to the reaction mixture at ambient temperature to continue stirring for further 12 h. After the solvent was removed under reduced pressure, the residual product was subjected to silica gel column chromatography with hexane/acetone (1/1 in vol/vol) and to alumina column chromatography with CHCl_3 to remove the catalyst residue to give the product **VI** (5 mg, M_n (NMR) = 12 600, M_p (SEC) = 7400, PDI = 1.14). ^1H NMR of **VI** (CDCl_3) δ : 1.46–1.79 (b, $\text{CH}_2\text{CH}_2\text{O}$), 3.23–3.55 (b, $\text{CH}_2\text{CH}_2\text{O}$), 4.29–4.47 (m, 12H, ArCO_2CH_2 , triazole- CH_2CH_2), 4.46 (s, 8H, ArCH_2O), 4.66 (m, 2.7H, $\text{OCH}_2\text{CH}=\text{CH}$, cis isomer), 4.76 (m, 1.3H, $\text{OCH}_2\text{CH}=\text{CH}$, trans isomer), 5.20 (d, 4H, J = 5.9 Hz, ArOCH_2 -triazole), 5.98 (m, 0.7H, $\text{OCH}_2\text{CH}=\text{CH}$, trans isomer), 6.11 (m, 1.3H, $\text{OCH}_2\text{CH}=\text{CH}$, cis isomer), 6.60–6.66 (m, 12H, Ar- H ortho and para to N), 6.89 (s, 6H, Ar- H ortho and para to OCH_2 -triazole), 7.19 (t, J = 9.8 Hz, 8H, Ar- H meta to N), 7.62 (s, 2H, $\text{CO}_2\text{ArOCH}_2$ -triazole- H), 7.74 (s, 4H, Ar- H ortho to $\text{OCH}_2\text{CH}=\text{CH}$), 8.26 (d, 2H, Ar- H para to $\text{OCH}_2\text{CH}=\text{CH}$).

Measurements. ^1H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer operating at 300 MHz with CDCl_3 as a solvent. SEC measurements were performed at 40 $^\circ\text{C}$ on a Tosoh model CCPS equipped with a TSK G4000HXL as a column and with a refractive index detector model RI 8020. THF was used as an eluent at a flow rate of 1.0 mL/min. Linear polystyrene standards were used for

calibration, and the M_p (SEC) values were reported as poly(THF) equivalents. MALDI-TOF mass spectra were recorded on a Shimadzu AXIMA Performance spectrometer equipped with a nitrogen laser (λ = 337 nm). The spectrometer was operated at an accelerating potential of 20 kV in a linear positive ion mode with pulsed ion extraction. A THF solution (10 μL , 10 mg/mL) of a polymer sample, a THF solution (100 μL , 20 mg/mL) of dithranol, and a THF solution (100 μL , 10 mg/mL) of sodium trifluoroacetate were mixed, and a portion of the mixture was deposited onto a sample target plate. Mass values were calibrated by the three-point method using peaks from α -cyanohydroxycinnamic acid dimer plus H^+ at m/z = 379.35, insulin β plus H^+ at m/z = 3497.96, and insulin plus H^+ at m/z = 5734.62.

■ ASSOCIATED CONTENT

Supporting Information

IR of **1a**, **1c**, and **1b**, ^1H NMR of **1a** and **1b/2b**, and MALDI-TOF mass spectra of **1a**, **1b**, and **II** measured after the covalent conversion of *N*-phenylpyrrolidinium salt end groups by the ring-opening reaction with a benzoate anion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(18) The doubly *fused* tricyclic, β -graph and γ -graph polymer topologies constructed in this study are expressed as $\text{III}_6(0,4)[0^a-0^a-0^b-0^b]$ and as $\text{III}_5(0,3)[0^{a,b}-0^a-0^b]$, respectively, according to the systematic notation (ref 10).

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