

Effective Click Construction of *Bridged*- and *Spiro*-Multicyclic Polymer Topologies with Tailored Cyclic Prepolymers (*kyklo*-Telechelics)

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Abstract: An alkyne–azide addition, i.e., *click*, reaction in conjunction with an *electrostatic self-assembly and covalent fixation* (ESA-CF) process has been demonstrated to effectively construct a variety of unprecedented multicyclic polymer topologies. A series of single cyclic poly(tetrahydrofuran), poly(THF), precursors having an alkyne group (**1a**), an azide group (**1b**), two alkyne groups at the opposite positions (**1c**), and an alkyne group and an azide group at the opposite positions (**1d**) have been prepared by the ESA-CF process. Moreover, a bicyclic 8-shaped precursor having two alkyne groups at the opposite positions (**1e**) was synthesized. The subsequent click reaction of **1a** with linear (**IIa**) and three-armed star (**IIb**) telechelic precursors having azide groups has been performed to construct *bridged*-type two-way (**IIIa**) and three-way (**IIIb**) paddle-shaped polymer topologies, respectively. Likewise, *spiro*-type tandem tricyclic (**IVa**) and tetracyclic (**IVb**) topologies resulted from **1b/1c** and **1b/1e**, respectively. Furthermore, three types of multicyclic topologies that are composed of repeating ring (**Va**), alternating ring/linear (**Vb**), and alternating ring/star (**Vc**) units have been synthesized from **1d**, **1c/IIa**, and **1c/IIb**, respectively.

Introduction

Topologically intriguing polymer architectures have been an enduring synthetic challenge.^{1–4} Notably, the flexible conformational motion of skeletal polymer segments between junctions is relevant to the characteristic features of the topological geometry.¹ Cyclic and multicyclic polymers are particularly unique from the topological viewpoint because of their absence of chain termini in contrast to linear and branched counterparts.⁴

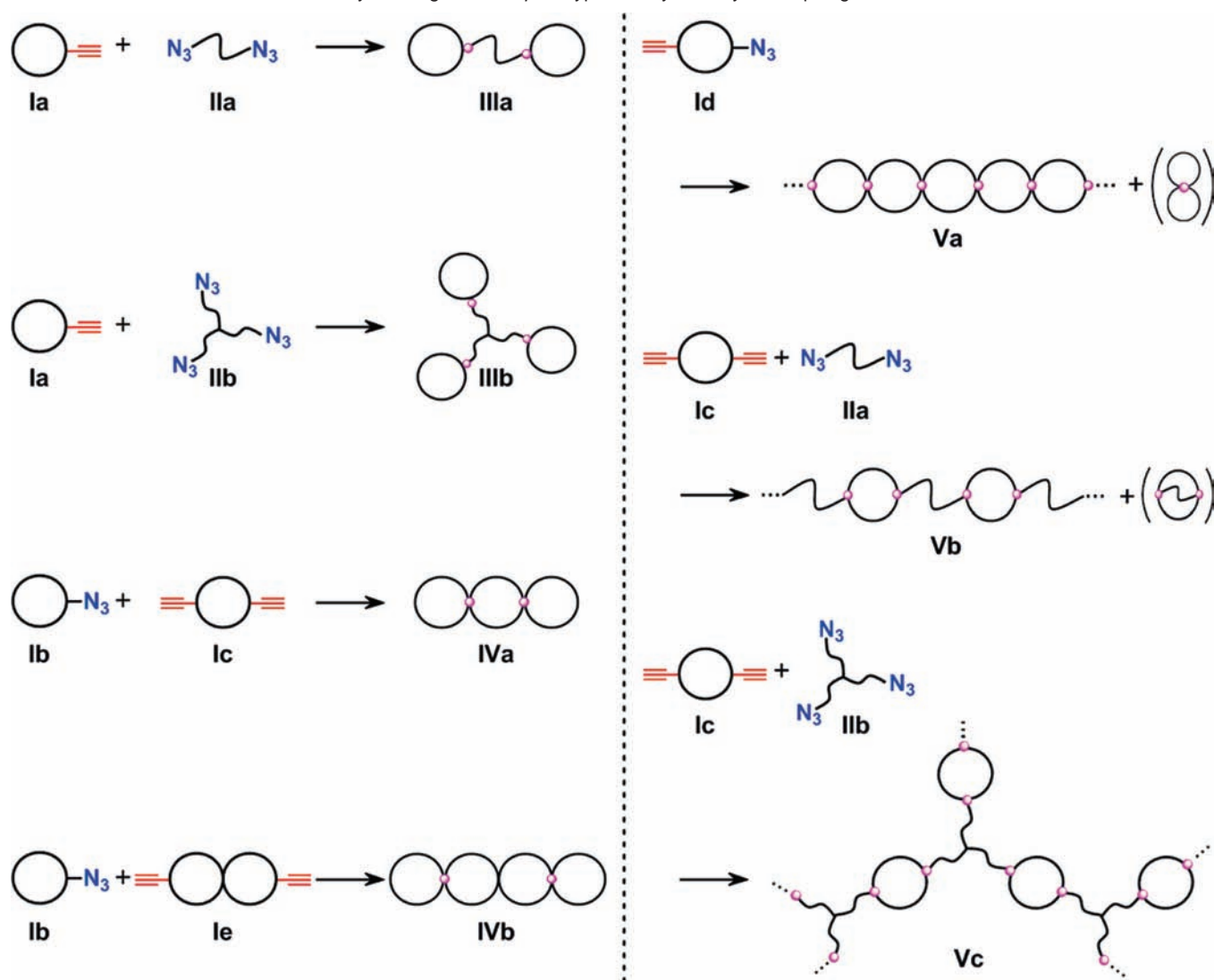
Remarkable progress has been made in the effective and controlled synthesis of *single* cyclic polymers by employing ring-expansion polymerization⁵ and end-to-end prepolymer cyclization processes.⁶ By making use of novel cyclic polymers having prescribed chemical structures, remarkable topology effects have been revealed.⁷ Moreover, cyclic and other topologically unique polymers have been demonstrated to be versatile scaffolds to fabricate nano-objects of unusual shapes, extending the scope of nanoscience and nanotechnologies beyond DNA-based processes.⁸

Multicyclic polymer topologies, divided into *catenated* (mechanically linked) and *bonded* (covalently linked) types based on the connecting mode of the ring units, have also been attractive synthetic targets. As observed in DNA systems, including mitochondrial components⁹ and virus capsids,¹⁰ catenated topologies are inspiring. A number of

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Scheme 1. Click Construction of a Variety of Bridged- and Spiro-Type Multicyclic Polymer Topologies



remarkable achievements have been made in the construction of simple and complex topologies, even Borromean rings.¹¹ Moreover, various innovative methods have been developed for the formation of catenanes comprised of large synthetic polymer ring units.¹²

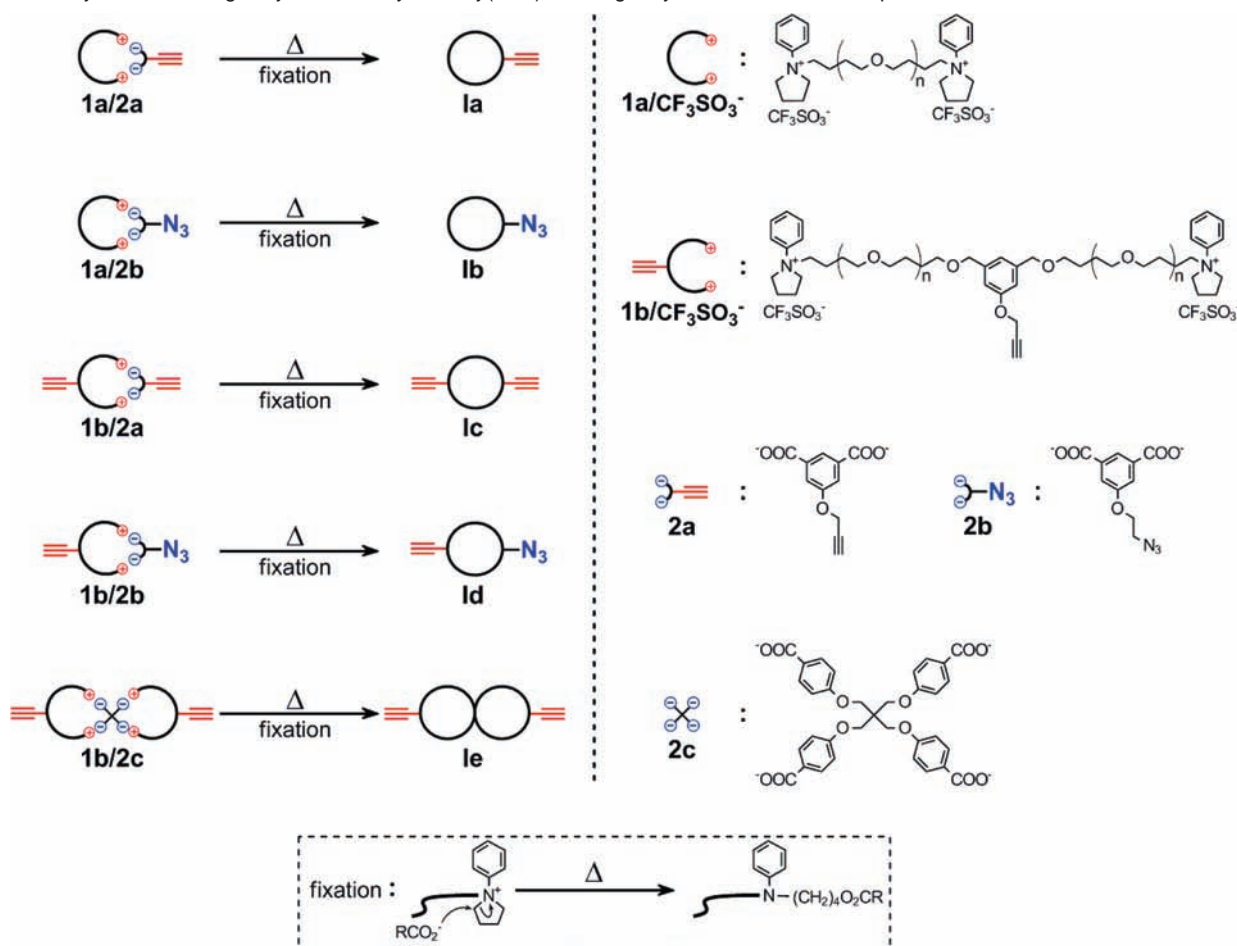
Conversely, in *bonded multicyclic* topologies, there are three subtypes, *fused*, *spiro* and *bridged* structures, according to the covalent linking mode of the ring units.^{1e} By employing an *electrostatic self-assembly and covalent fixation* (ESA-CF) proto-

col¹³ with polymeric self-assemblies comprised of linear and star telechelic precursors having cyclic ammonium salt groups carrying plurifunctional carboxylate counteranions, the three forms of bicyclic constructions, θ (*fused*), 8 (*spiro*), and two-way paddle (*bridged*), as well as a trefoil (*spiro* tricyclic) topology have thus

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Scheme 2. Synthesis of Single Cyclic and Bicyclic Poly(THF)s Having Alkyne and/or Azide Groups via the ESA-CF Process



far been produced.^{13a,14} Moreover, the ESA-CF process can produce *kyklo*-telechelics, cyclic and multicyclic polymers having predetermined functional groups at the designated positions,¹⁵ which have been further utilized to construct complex multicyclic polymer topologies. Thus, a δ -graph (doubly-*fused* tricycle) topol-

ogy has been constructed through the metathesis condensation of an 8-shaped precursor having allyl groups at the opposite positions of the two ring units.¹⁶ Despite elaboration of the methodology, topologically significant constructions such as α -graph (*fused* tricyclic) and K_{3,3} graph (tetracyclic) architectures¹⁷ as well as a variety of *spiro* and *bridged* structures of lower geometrical symmetries have still been elusive, limiting the current scope of synthetic polymer chemistry.

In the present study, we show an effective means to construct a variety of unprecedented multicyclic polymer topologies by taking advantage of an alkyne–azide *cross-coupling*, i.e., click, reaction by employing tailored single cyclic and bicyclic polymer precursors (*kyklo*-telechelics) as large as 300-membered rings obtained by the ESA-CF protocol (Scheme 1). Click chemistry has now been employed to prepare a wide variety of functional polymers as well as block and graft copolymers.^{18,19} Recently, this reaction has also been applied for the synthesis of simple rings and multicyclic

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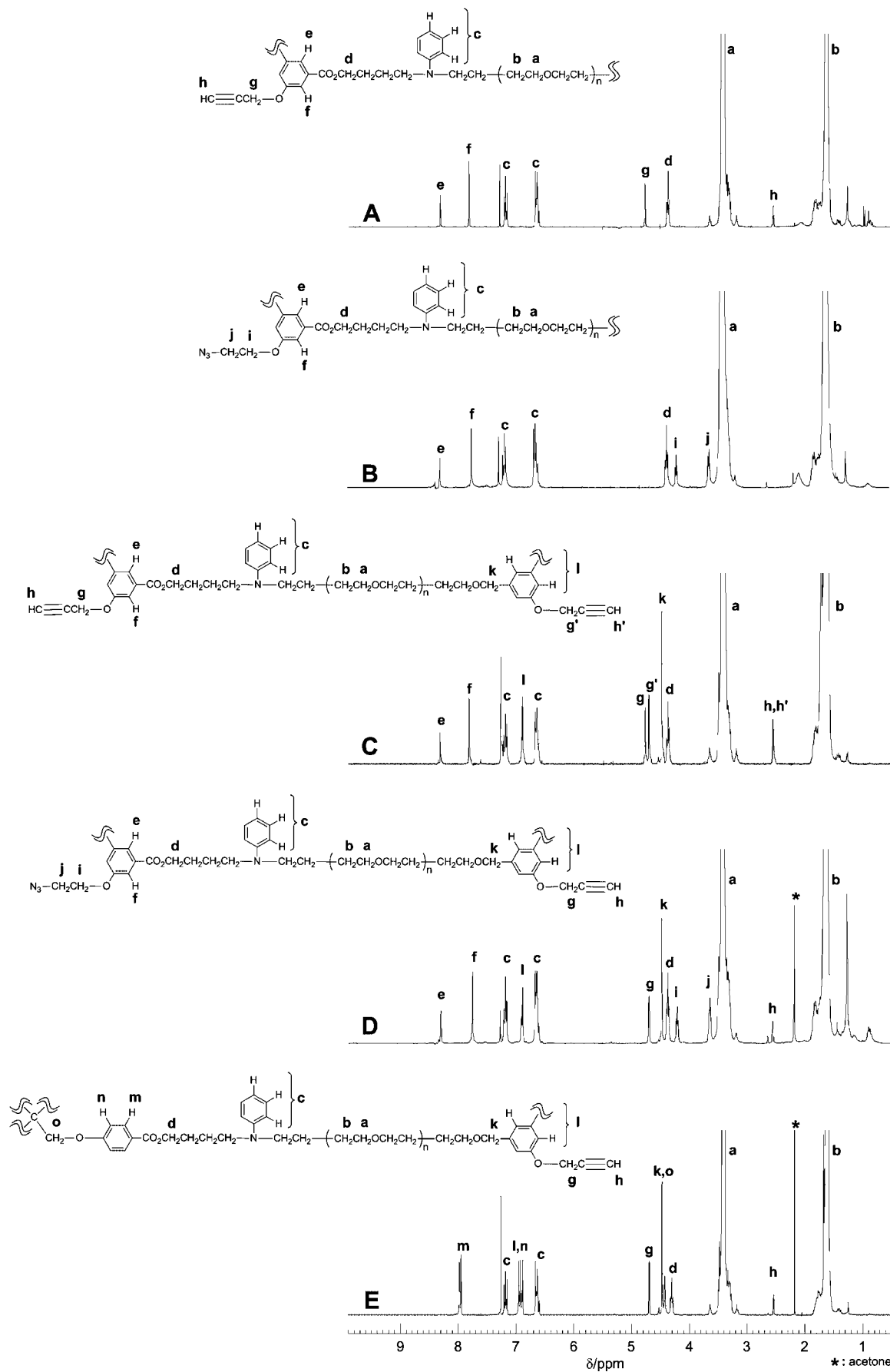
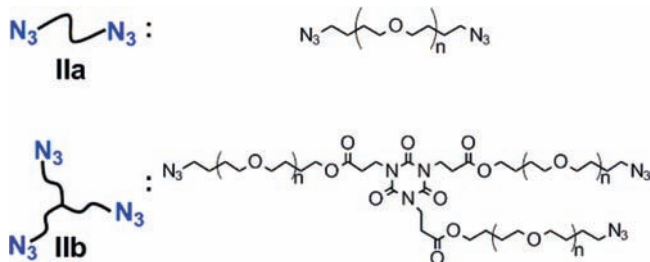


Figure 1. 300 MHz ^1H NMR spectra of single cyclic and bicyclic poly(THF)s. [A] Ia, [B] Ib, [C] Ic, [D] Id, and [E] Ie (CDCl_3 , 40 $^\circ\text{C}$, see Scheme 2 for detailed structures).

Scheme 3. Structures of the Linear and Star Poly(THF)s Having Azide End Groups



polymers²⁰ due to its extremely high efficiency even under high dilution.²¹ It is also notable that the cross-coupling process offers a rational design to selectively combine polymer precursors having different topologies, producing complex constructions of lower geometrical symmetries that are not accessible by one-step processes. In contrast, a metathesis condensation proceeds through the concurrent homo- and cross-coupling of prepolymers, resulting in a mixture of topological isomers.²² Finally, *condensation* cross-coupling processes, such as Pd-mediated Suzuki and Sonogashira

reactions, generally require a base additive, which in turn could cause the chain decomposition of polymer precursors.²³

We have prepared a series of single cyclic and bicyclic poly(THF)s having alkyne and/or azide groups (**Ia–Ie**) as key polymer precursors for the click process. *N*-Phenylpyrrolidinium-terminated telechelic precursors with (**Ib**/CF₃SO₃[−]) and without (**Ia**/CF₃SO₃[−]) an alkyne group at the center position, carrying an alkyne-(**2a**) or azide-functionalized (**2b**) dicarboxylate counteranion, have been employed (Scheme 2). Additionally, linear (**Ia**) and three-armed star (**IIb**) poly(THF)s having azide end groups have been prepared by the end-capping reactions of the respective linear and star living poly(THF)s with tetrabutylammonium azide (Scheme 3). The subsequent click reaction of **Ia/IIa** and **Ia/IIb** selectively afforded, for the first time, poly(THF)s having *bridged*-type two-way (**IIIa**) and three-way (**IIIb**) paddle-shaped topologies, respectively (Scheme 1). Analogously, those having *spiro*-type tandem tricyclic (**IVa**) and tetracyclic (**IVb**) topologies were constructed from **Ib/Ic** and **Ib/Ie**, respectively (Scheme 1). Moreover, three new multicyclic polymers consisting of repeating ring (**Va**), alternat-

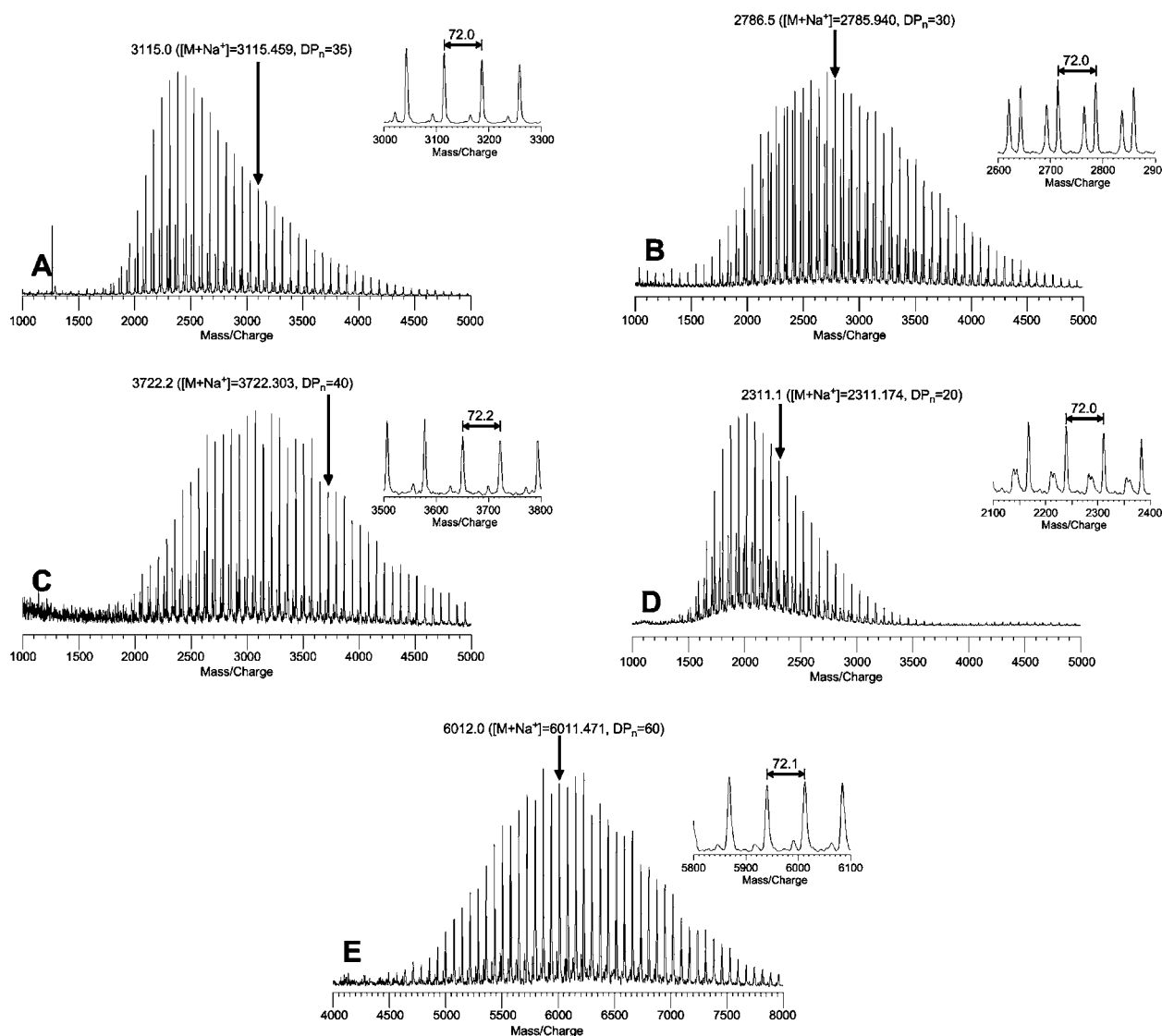


Figure 2. MALDI-TOF mass spectra of single cyclic and bicyclic poly(THF)s. [A] **Ia**, [B] **Ib**, [C] **Ic**, [D] **Id**, and [E] **Ie**. (Linear mode, matrix: dithranol with sodium trifluoroacetate. DP_n denotes the number of monomer units in the product.) The series of side peaks observed in the spectra were assignable as the H⁺ adducts (**Ia–Ie**) and Na⁺ adducts that lost a N₂ molecule from the azide group for **Id**.

Table 1. Mass/Charge Values Calculated for **Ia–Ie**, **IIa**, **IIb**, **IIIa**, **IIIb**, **IVa**, and **IVb** and Those for the Corresponding Peaks Observed in the MALDI-TOF Mass Spectra

sample	formula	calculated mass/charge	observed mass/charge
Ia	$(C_4H_8O) \times 35 + C_{35}H_{40}N_2O_5$ plus Na^+	3115.459	3115.0
Ib	$(C_4H_8O) \times 30 + C_{34}H_{41}N_5O_5$ plus Na^+	2785.940	2786.5
Ic	$(C_4H_8O) \times 40 + C_{50}H_{58}N_2O_8$ plus Na^+	3722.303	3722.2
Id	$(C_4H_8O) \times 20 + C_{49}H_{59}N_5O_8$ plus Na^+	2311.174	2311.1
Ie	$(C_4H_8O) \times 60 + C_{103}H_{112}N_4O_{16}$ plus Na^+	6011.471	6012.0
IIa	$(C_4H_8O) \times 30 + C_4H_8N_6$ plus Na^+	2326.356	2326.3
IIb	$(C_4H_8O) \times 55 + C_{24}H_{36}N_{12}O_9$ plus Na^+	4625.516	4625.2
IIIa	$(C_4H_8O) \times 100 + C_{74}H_{88}N_{10}O_{10}$ plus Na^+	8511.295	8511.8
IIIb	$(C_4H_8O) \times 160 + C_{129}H_{156}N_{18}O_{24}$ plus Na^+	13902.924	13902.5
IVa	$(C_4H_8O) \times 100 + C_{118}H_{140}N_{12}O_{18}$ plus Na^+	9248.203	9248.8
IVb	$(C_4H_8O) \times 120 + C_{171}H_{194}N_{14}O_{26}$ plus Na^+	11537.372	11538.4

ing ring/linear (**Vb**), and alternating ring/star (**Vc**) units were fabricated from **Id**, **Ic/IIa**, and **Ic/IIIb**, respectively (Scheme 1).

Results and Discussion

1. Synthesis of Single Cyclic and Bicyclic Poly(THF) Precursors Having Alkyne and/or Azide Groups. A series of single cyclic poly(tetrahydrofuran), poly(THF), precursors having an alkyne group (**1a**),²⁴ an azide group (**1b**), two alkyne groups at the opposite positions (**1c**), and an alkyne group and an azide group at the opposite positions (**1d**) were prepared by the *electrostatic self-assembly and covalent fixation* (ESA-CF) process using an *N*-phenylpyrrolidinium-terminated poly(THF) precursor (**1a**) and the relevant analogue having an alkyne group

at the center position (**1b**) carrying dicarboxylate counteranions having an alkyne (**2a**) or azide (**2b**) group. Moreover, a bicyclic 8-shaped precursor having two alkyne groups at the opposite positions (**1e**) was also synthesized (Scheme 2).

Therefore, **1a/2a** and **1a/2b** were first prepared through ion-exchange by precipitating the poly(THF) precursor carrying trifluoromethanesulfonate (triflate) counteranions (**1a/CF₃SO₃⁻**, see Figure S1A for the ¹H NMR spectrum in the Supporting Information (SI)) in ice-cooled aqueous solutions containing large excesses of **2a** and **2b**, respectively. The extent of the ion-exchange was determined by ¹H NMR (Figures S1B and S1C in the SI). The ionically linked polymer precursors, **1a/2a** and **1a/2b**, were subjected to heat treatment by refluxing for

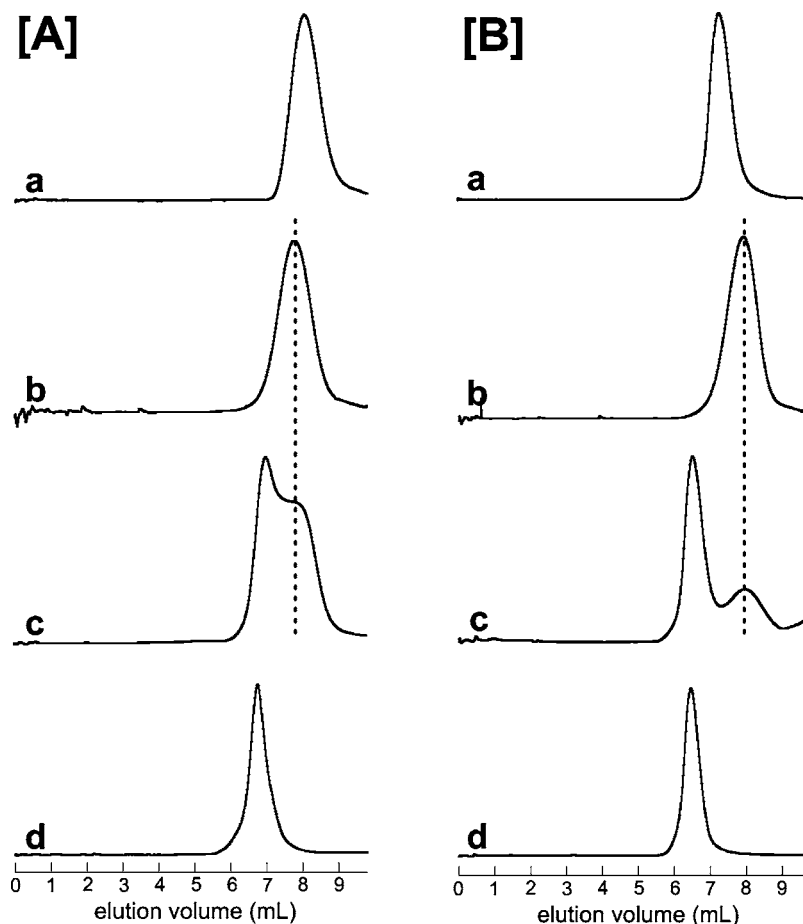


Figure 3. SEC traces of the precursors and products for the construction of *bridged*-type topologies. [A] (a) **1a**, (b) **IIa**, (c) crude **IIIa**, and (d) purified **IIIa**. [B] (a) **Ia**, (b) **IIb**, (c) crude **IIIb**, and (d) purified **IIIb**. (TSK G3000HXL, eluent: THF 1.0 mL/min. **IIIa** and **IIIb** were purified by preparative SEC fractionation.)

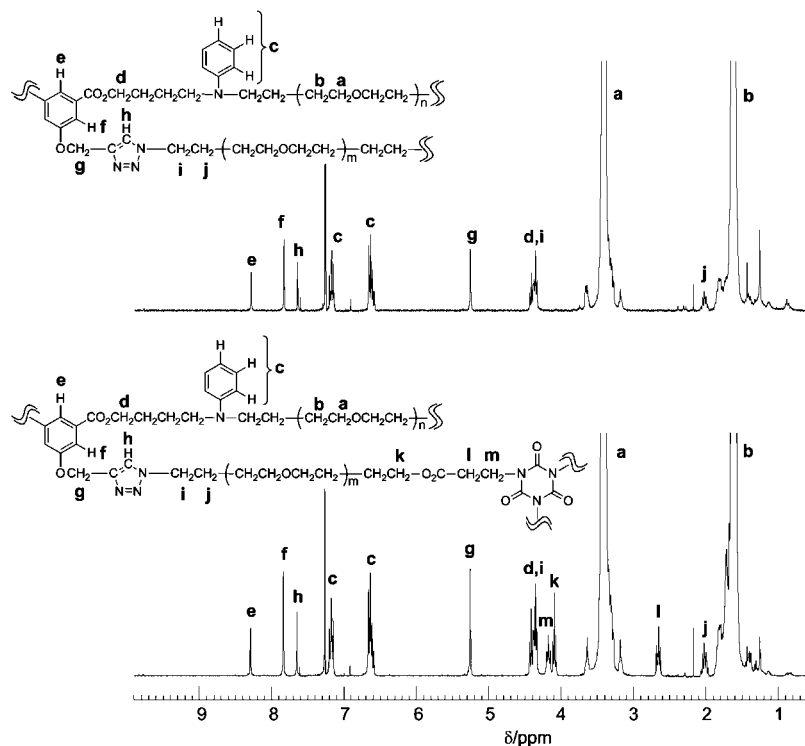


Figure 4. 300 MHz ^1H NMR spectra of (top) **IIIa** and (bottom) **IIIb**. (CDCl_3 , 40 $^\circ\text{C}$. The measurements were carried out after fractionation by preparative SEC.)

Table 2. SEC and ^1H NMR Analyses of the 3D Sizes of the Bridged-Type (**IIIa** and **IIIb**) and Spiro-Type (**IVa** and **IVb**) Multicyclic Polymers

sample	$M_p(\text{SEC})^a$ [kDa]	$M_n(\text{NMR})^b$ [kDa]	$M_p(\text{SEC})/M_n(\text{NMR})$
IIIa	7.8	11	0.68
IIIb	10.7	16	0.68
IVa	8.0	12	0.67
IVb	10.2	15	0.66

^a Peak molecular weight determined by SEC calibrated with linear polystyrene standards. M_p determined as a polystyrene equivalent was converted into that for poly(THF) by a factor of 0.556.³⁰

^b Number-average molecular weight determined by ^1H NMR.

3 h at a concentration of 0.2 g/L to promote ring-opening of the pyrrolidinium salt groups through attack by the dicarboxylate counteranions, leading to the formation of **Ia** and **Ib**, respectively. The completion of the reaction was confirmed by ^1H NMR spectroscopic analysis (Figures 1A and 1B, Figures S1B and S1C in the SI), where the signals for the *N*-phenyl-adjacent methylene groups in **1a** (3.7–4.4 ppm) were replaced with that for the ester-adjacent methylene group, a triplet in **Ia** and **Ib** (4.37 ppm), and the multiplet *N*-phenyl signals in **1a** (7.4–7.6 ppm) were split into two sets in **Ia** and **Ib** (6.6–6.7 and 7.18 ppm). The signals for the ethynyl (2.54 ppm) and propynyl methylene (4.76 ppm) groups in **Ia**, as well as that for the azidomethylene group (3.62 ppm) in **Ib**, were visible.

Likewise, the counterion-exchange of **Ib**/ CF_3SO_3^- (Figure S1D in the SI) prepared through the living polymerization of THF using an alkyne-functionalized initiator gave **Ib/2a** and **Ib/2b** (Figures S1E and S1F in the SI), which were then covalently converted to **Ic** and **Id**, respectively. The ^1H NMR

spectrum of **Ic** showed signals of the two distinctive propynyl groups from the initiator and the counteranion, i.e., the ethynyl protons at 2.53 and 2.54 ppm and the propynyl methylene protons at 4.69 and 4.76 ppm, respectively (Figure 1C). The signals for the ethynyl (2.54 ppm) and azidomethylene (3.63

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- (21) Polymer cyclization by a click chemistry. See: refs 6c–l. The reaction between one unit of an eight-armed star precursor and four units of a bifunctional end-linking reagent reportedly produced a quatrefoil (spiro-tetracyclic) polymer product. If this could happen, the star precursor should react with exactly four end-linking reagents in the course of the reaction. See: Ge, Z.; Wang, D.; Zhou, Y.; Liu, H.; Liu, S. *Macromolecules* **2009**, *42*, 2903–2910.
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- (23) Tezuka, Y.; Komiya, R.; Ido, Y.; Adachi, K. *React. Funct. Polym.* **2007**, *67*, 1233–1242.
- (24) A cyclic poly(THF) having an alkyne group was previously synthesized by the post-functionalization of a ring polymer (ref 23), while in the present study, a dicarboxylate counteranion having an alkyne group (**2a**) was employed for an ESA-CF process to form **Ia**.

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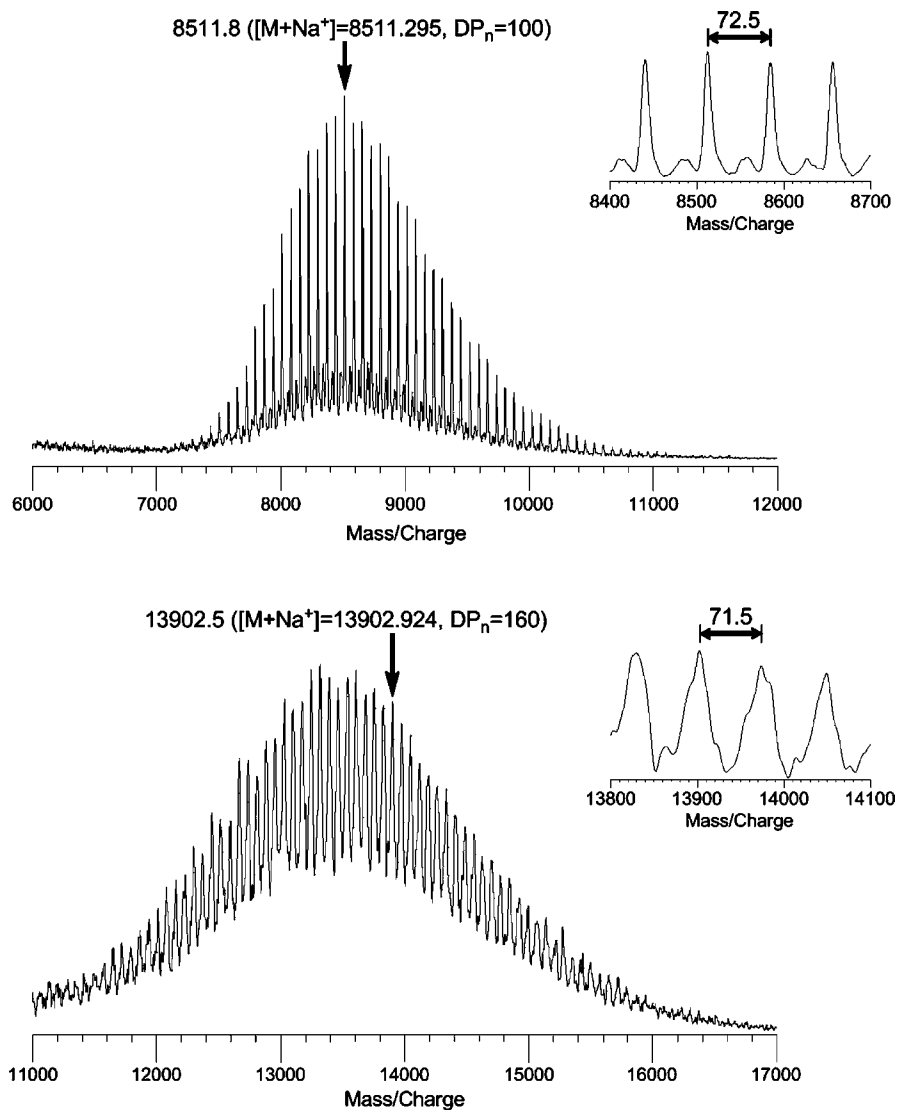


Figure 5. MALDI-TOF mass spectra of (top) **IIIa** and (bottom) **IIIb**. (Linear mode, matrix: dithranol with sodium trifluoroacetate. DP_n denotes the number of monomer units in the product. The measurements were carried out after fractionation by preparative SEC.)

ppm) protons were also visible in **Id** (Figure 1D). Furthermore, 8-shaped bifunctional **Ie** was prepared by the ESA-CF process using a tetracarboxylate counteranion (**2c**) accompanied by 2 equiv of **1b** (**1b/2c**, Figure S1G in the SI).²⁵ The ¹H NMR spectroscopic analysis of **Ie** (Figure 1E) showed the characteristic signals for the propynyl groups at 2.54 and 4.69 ppm, together with those for the tetracarboxylate group.

The MALDI-TOF mass spectra of (**Ia–Ie**) are collected in Figure 2. Uniform series of peaks with an interval of 72 mass units for the repeating THF units were observed, and each peak exactly matched the total molar mass of the initiator fragment, poly(THF) units, and linking group. Thus, in Figure 2A, the peak at $m/z = 3115.0$, which was assumed to be the adduct with Na^+ , corresponds to **Ia** possessing the expected chemical structure with a DP_n of 35; $(\text{C}_4\text{H}_8\text{O}) \times 35 + \text{C}_{35}\text{H}_{40}\text{N}_2\text{O}_5$ plus Na^+ equals 3115.459. Likewise, representative peaks that match the calculated molecular weights were found for **Ib–Ie** (Table 1). Side peaks observed in the series of spectra were assignable

as the H^+ adducts (**Ia–Ie**), and in addition, Na^+ adducts that lost a N_2 molecule from the azide group were noticeable in **Id** (Figure 2).

SEC (Figures S2A, S2B, and S2C in the SI) shows that **Ia–Id** possessed narrow size distributions ($PDI = 1.12–1.26$) and notably smaller hydrodynamic volumes compared to their linear counterparts that were obtained by the reaction of **1a**/ CF_3SO_3^- and **1b**/ CF_3SO_3^- with tetrabutylammonium benzoate. The hydrodynamic volume ratios of **Ia–Id** compared to their corresponding linear counterparts, estimated by the SEC peak molecular weights, were 0.68–0.86, in agreement with those previously reported.^{13a,26} SEC of **Ie** (Figure S2D bottom in the SI) showed a narrow size distribution ($PDI = 1.15$) and apparent molecular weight ($M_p = 5.9$ kDa) significantly higher than that of **1b** after reaction with tetrabutylammonium benzoate ($M_p = 3.7$ kDa) but lower than twice that (2×3.7 kDa = 7.4 kDa). The contraction of the 3D size was estimated to be 0.80, in good agreement with previous studies.²⁵

In addition, linear (**IIa**) and three-armed star (**IIb**) telechelic poly(THF)s having azide end groups were prepared by the end-

(25) The synthesis of 8-shaped polymers by an ESA-CF process has been demonstrated before. See refs 13a and 16, as well as Oike, H.; Hamada, M.; Eguchi, S.; Danda, Y.; Tezuka, Y. *Macromolecules* **2001**, *34*, 2776–2782.

(26) Oike, H.; Mouri, T.; Tezuka, Y. *Macromolecules* **2001**, *34*, 6592–6600.

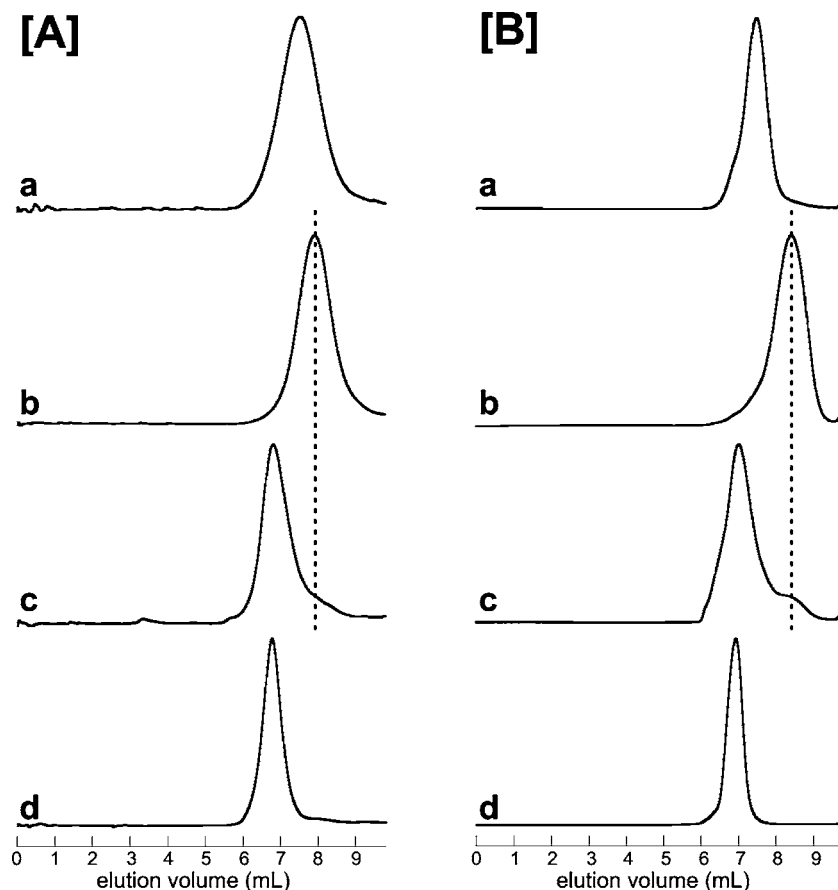


Figure 6. SEC traces of the precursors and products for the construction of *spiro*-type topologies. [A] (a) **Ic**, (b) **Ib**, (c) crude **IVa**, and (d) purified **IVa**. [B] (a) **Ie**, (b) **Ib**, (c) crude **IVb**, and (d) purified **IVb**. (TSK G3000HXL, eluent: THF 1.0 mL/min. **IVa** and **IVb** were purified by preparative SEC fractionation.)

capping reaction of bifunctional and trifunctional living poly-(THF)s, respectively (Scheme 3). The ^1H NMR analyses of the products (Figure S3 in the SI) confirmed a quantitative end-capping reaction. The signal for the azidomethylene groups was visible at 3.30 ppm as a triplet. IR spectroscopic analysis showed the absorption of the azide groups at 2094 cm^{-1} (Figures S4A middle and S4B middle in the SI). MALDI-TOF mass spectra of **IIa** and **IIb** (Figure S5 in the SI) showed uniform series of peaks with an interval of 72 mass units for the repeating THF units, and each peak exactly corresponded to the total molar mass of the main chains and the end groups, along with the initiator fragment in the case of **IIb** (Table 1).

2. Selective Construction of Bridged-Type Two-Way and Three-Way Paddle-Shaped Polymer Topologies by the Click Process. A single cyclic precursor having an alkyne group (**Ia**) was subjected to the click reaction with linear (**IIa**) and three-armed star (**IIb**) telechelic precursors having azide end groups to selectively produce bicyclic (**IIIa**) and tricyclic (**IIIb**) paddle-shaped polymers, respectively (Scheme 1).²⁷ To ensure complete reaction, a slight excess of **Ia** was charged relative to **IIa** and **IIb**. Products **IIIa** and **IIIb** were analyzed by SEC and exhibited a noticeable peak shift toward the higher molecular weight region (Figure 3). The peak molecular weight for **IIIa** ($M_p = 6.7\text{ kDa}$) was nearly equal to the sum of those of the precursors, i.e., two units of **Ia** and one unit of **IIa** ($2 \times 2.5\text{ kDa} + 2.1\text{ kDa} = 7.1\text{ kDa}$). Also, M_p for **IIIb** (11.1 kDa) was close to the total of the corresponding telechelics, three units of **Ia**, and one

unit of **IIb** ($3 \times 2.4\text{ kDa} + 4.6\text{ kDa} = 11.8\text{ kDa}$).²⁸ The yields of **IIIa** and **IIIb** were estimated to be 48% and 57%, respectively, based on the weights and SEC peak area ratios of the crude products. The subsequent isolation of **IIIa** and **IIIb** was performed by means of a preparative SEC fractionation technique (Figures 3A-d and 3B-d).

Furthermore, the extent of the contraction in the 3D sizes of **IIIa** and **IIIb** was estimated by the ratio of the peak molecular weight by SEC to the number-average molecular weight by ^1H NMR ($M_p(\text{SEC})/M_n(\text{NMR})$) after the fractionation (Table 2). The obtained value, 0.68 for both **IIIa** and **IIIb**, was comparable with those of previously reported various multicyclic topologies such as 8-shaped (0.69–0.80),^{13a,25} trefoil-shaped (0.65),^{13a} θ -shaped (0.63),^{13a,29} and δ -graph (0.61)¹⁶ constructions.

By comparing the ^1H NMR spectra of product **IIIa** (Figure 4 top) with precursors **Ia** (Figure 1A) and **IIa** (Figure S3 top in the SI), as well as those of **IIIb** (Figure 4 bottom) with **Ia** (Figure 1A) and **IIb** (Figure S3 bottom in the SI), the selective reaction between the alkyne and azide groups of the prepolymers

(27) A two-way paddle-shaped polymer has been obtained concomitant with a θ -shaped topological isomer. The selective synthesis has not been achieved before. See ref 13a as well as: (a) Tezuka, Y.; Tsuchitani, A.; Oike, H. *Polym. Int.* **2003**, *52*, 1579–1583. (b) Tezuka, Y.; Tsuchitani, A.; Oike, H. *Macromol. Rapid Commun.* **2004**, *25*, 1531–1535.

(28) The molecular weight of **Ia** used for the click reaction with **IIa** is slightly different from that of **Ia** reacted with **IIb**.

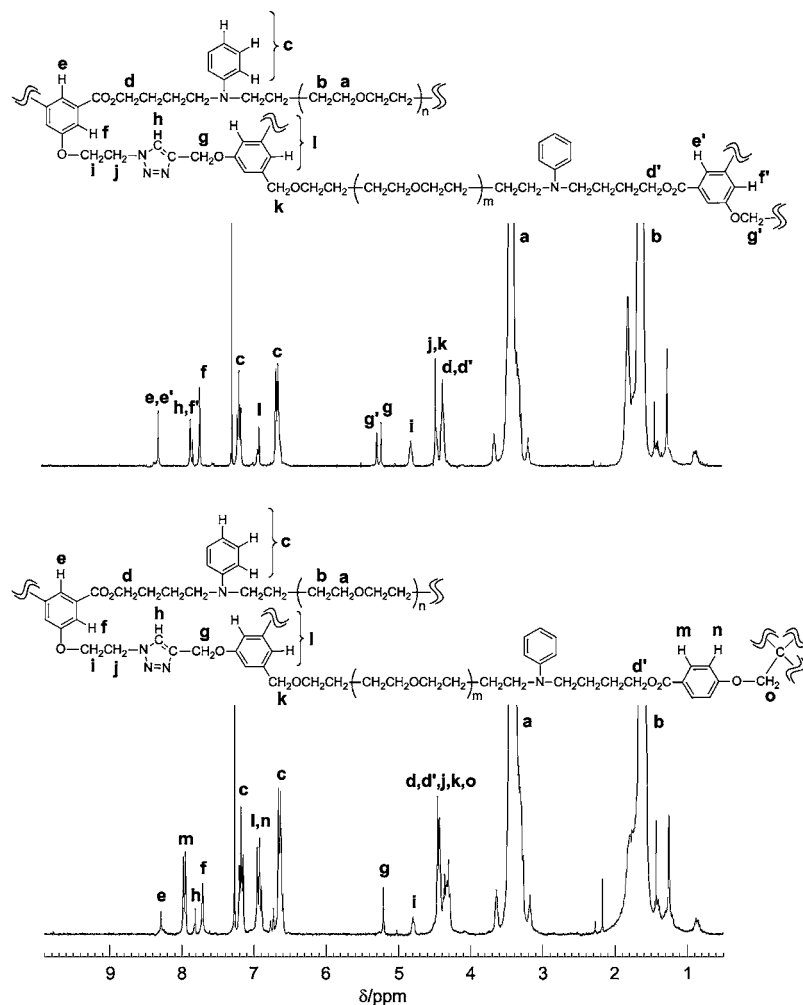


Figure 7. 300 MHz ^1H NMR spectra of (top) **IVa** and (bottom) **IVb**. (CDCl_3 , 40 $^\circ\text{C}$. The measurements were carried out after fractionation by preparative SEC.)

was confirmed. Thus, the signal for the ethynyl proton (2.54 ppm) in **Ia** and that for the azidomethylene protons (3.30 ppm) in **IIa** and **IIb** completely disappeared, and a triazole proton signal emerged at 7.65 ppm in **IIIa** and **IIIb**. Moreover, the signal for the propynyl methylene protons (4.76 ppm) observed in **Ia** was replaced with that for the methylene protons adjacent to the 4-position of the triazole ring (5.26 ppm) in **IIIa** and **IIIb**. The IR absorbance of the azide groups at 2094 cm^{-1} observed in precursors **IIa** and **IIb** was scarcely visible in the products, **IIIa** and **IIIb**, indicating that the reaction proceeded effectively (Figure S4 in the SI). The MALDI-TOF mass spectra of **IIIa** and **IIIb** showed a uniform series of peaks with an interval of 72 mass units corresponding to repeating THF units, and each peak exactly matched the total molar mass of the complementary precursors (Figure 5). Thus, in Figure 5 (top), the peak at $m/z = 8511.8$, which was assumed to be the adduct with Na^+ , corresponds to **IIIa** possessing the expected chemical structure with a DP_n ($n + m$) in the chemical formula in Figure 4) of 100; $(\text{C}_4\text{H}_8\text{O}) \times 100 + \text{C}_{74}\text{H}_{88}\text{N}_{10}\text{O}_{10}$ plus Na^+ equals 8511.295. Furthermore, the sum of twice the molar mass of **Ia** with a DP_n of 35 (Figure 2A, $2 \times (3115.0 - [\text{Na}^+]) = 6184.0$)

and the molar mass of **IIa** with a DP_n of 30 (Figure S5 top in the SI, $(2326.3 - [\text{Na}^+]) = 2303.3$) is 8487.3, in agreement with the molar mass of **IIIa** with a DP_n of 100 ($8511.8 - [\text{Na}^+] = 8488.8$) given above. Analogously, in Figure 5 (bottom), the peak at $m/z = 13\,902.5$, which was also assumed to be the adduct with Na^+ , corresponds to **IIIb** possessing the expected chemical structure with a DP_n ($n + m$) in the chemical formula in Figure 4 bottom) of 160; $(\text{C}_4\text{H}_8\text{O}) \times 160 + \text{C}_{129}\text{H}_{156}\text{N}_{18}\text{O}_{24}$ plus Na^+ equals 13 902.924. The sum of 3-fold the molar mass of **Ia** with a DP_n of 35 (Figure 2A, $3 \times (3115.0 - [\text{Na}^+]) = 9276.0$) and the molar mass of **IIb** with a DP_n of 55 (Figure S5 bottom in the SI, $4625.2 - [\text{Na}^+] = 4602.2$) is 13 878.2, in agreement with the molar mass of **IIIa** with a DP_n of 160 ($13\,902.5 - [\text{Na}^+] = 13\,879.5$) given above. From these results, it was concluded that **IIIa** and **IIIb** had *bridged*-type multicyclic topologies. Of note, the polymer–polymer cross-coupling proceeded under ambient conditions, even at the low concentration of the reactive groups (10^{-3} M).

3. Selective Construction of Spiro-Type Tandem Tricyclic and Tetracyclic Polymer Topologies by the Click Process. A single cyclic precursor having two alkyne groups at the opposite positions (**Ic**) and a bicyclic 8-shaped analogue (**Ie**) were subjected to a click reaction with a single cyclic precursor having an azide group (**Ib**) to selectively produce *spiro*-type tandem tricyclic (**IVa**) and tetracyclic (**IVb**) topologies, respectively

(29) Tezuka, Y.; Tsuchitani, A.; Yoshioka, Y.; Oike, H. *Macromolecules* **2003**, *36*, 65–70.

(30) Burgess, F. J.; Cunliffe, A. V.; Dawkins, J. V.; Richards, D. H. *Polymer* **1977**, *18*, 733–740.

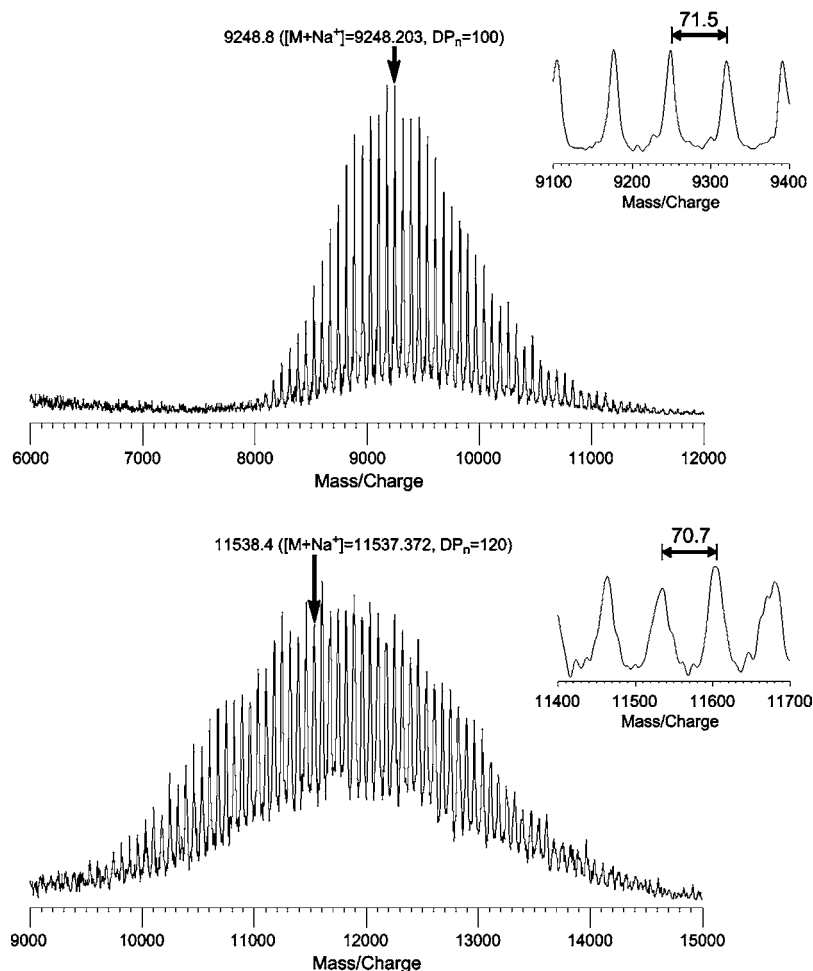


Figure 8. MALDI-TOF mass spectra of (top) **IVa** and (bottom) **IVb**. (Linear mode, matrix: dithranol with sodium trifluoroacetate. DP_n denotes the number of monomer units in the product. The measurements were carried out after fractionation by preparative SEC.)

(Scheme 1). As in the synthesis of the *bridged*-type multicyclic polymers, slightly excess amounts of **Ib** were charged relative to **Ic** and **Ie** to ensure complete cross-coupling.

The progress of the reaction was monitored by means of a SEC technique, where the peak was shifted toward the higher molecular weight region (Figure 6). The observed M_p for **IVa** (7.4 kDa) was almost identical to the sum of those for the precursors; two units of **Ib** and one unit of **Ic** (2×2.1 kDa + 3.1 kDa = 7.3 kDa). On the other hand, the M_p observed for tetracyclic **IVb** (9.2 kDa) was marginally lower (86%) than the individually added M_p values of the prepolymers, two units of **Ib** and one unit of **Ie** (2×2.4 kDa + 5.9 kDa = 10.7 kDa).^{13a,31} The yields of **IVa** and **IVb** were estimated to be 76% and 71%, respectively, based on the weights and SEC peak area ratios of the crude products. The subsequent isolation of **IVa** and **IVb** was performed by means of a preparative SEC fractionation technique (Figures 6A-d and 6B-d).

The $M_p(\text{SEC})/M_n(\text{NMR})$ values were calculated to be 0.67 and 0.66 for fractionated **IVa** and **IVb**, respectively, which were almost identical to those of **IIIa** (0.68) and **IIIb** (0.68) (Table 2).²⁵ This suggests that an increase of the number of ring units in *bridged*- and *spiro*-multicyclic polymer constructions causes comparative contractions in their 3D sizes.

By comparing the ^1H NMR spectra of product **IVa** (Figure 7 top) with precursors **Ic** (Figure 1C) and **Ib** (Figure 1B), as well as those of **IVb** (Figure 7 bottom) with **Ie** (Figure 1E) and **Ib** (Figure 1B), selective reaction between the alkyne and azide groups of the prepolymers was confirmed. Thus, the signals for the ethynyl protons (2.53 and 2.54 ppm in **Ic** and 2.54 ppm in **Ie**) completely disappeared with that of the azidomethylene protons (3.62 ppm) in **Ib**. On the other hand, triazole proton signals emerged at 7.81 ppm in both **IVa** and **IVb**. Moreover, the signals for the propynyl methylene protons (4.69 and 4.76 ppm in **Ic** and 4.69 ppm in **Ie**) were replaced with those for the methylene protons adjacent to the 4-position of the triazole rings (5.24 and 5.26 ppm in **IVa** and 5.21 ppm in **IVb**). The IR absorbance of the azide groups at 2104 cm^{-1} observed in precursor **Ib** was scarcely visible in the products, **IVa** and **IVb** (Figure S6 in the SI), indicating that the reaction proceeded effectively. The MALDI-TOF mass spectra of **IVa** and **IVb** showed uniform series of peaks with an interval of 72 mass units corresponding to the repeating THF units, and each peak exactly matched the total molar mass of the complementary precursors (Figure 8). Thus, in Figure 8 (top), the peak at $m/z = 9248.8$, which was assumed to be the adduct with Na^+ , corresponds to **IVa** possessing the expected chemical structure with a DP_n ($n + m$ in the chemical formula in Figure 7)

(31) The smaller M_p value of crude **IVb** could be due to the peak overlap to excess **Ib**.

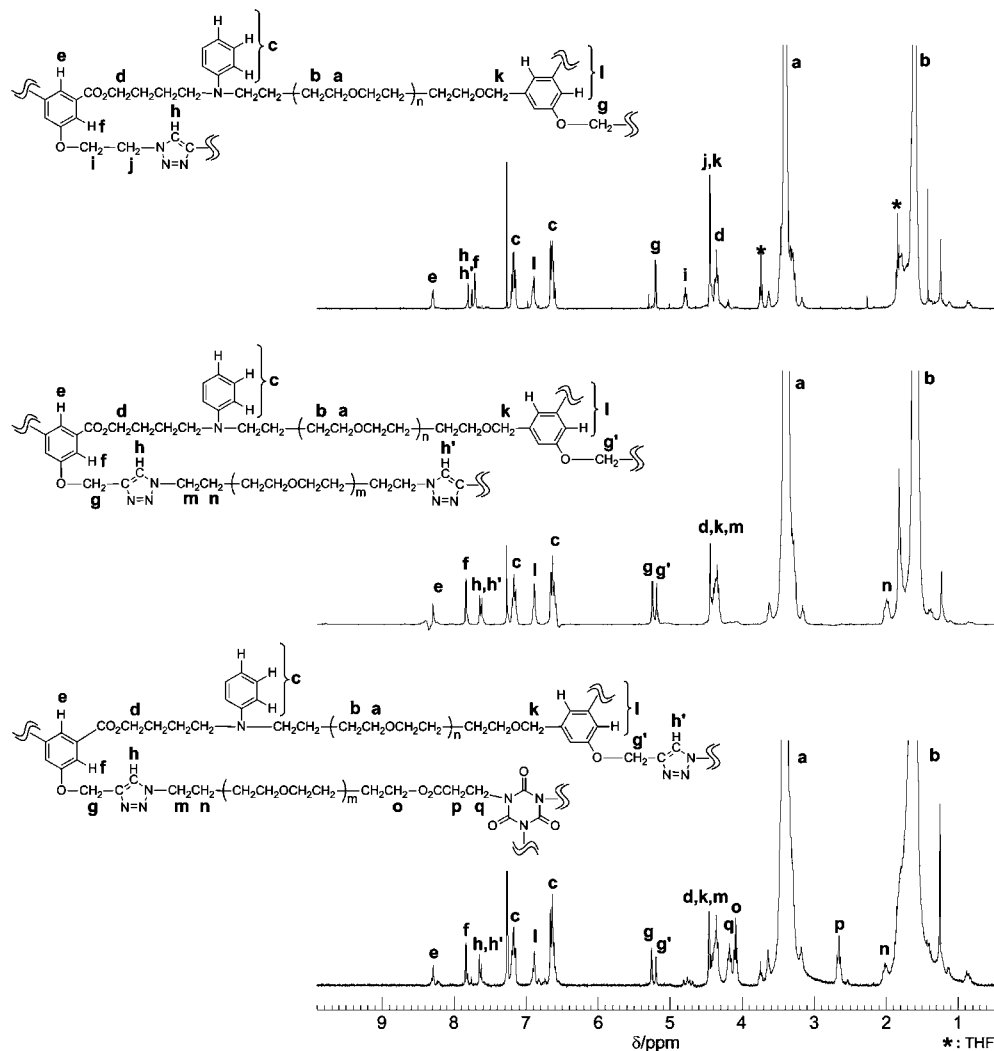


Figure 9. 300 MHz ^1H NMR spectra of (top) **Va**, (middle) **Vb**, and (bottom) **Vc** (CDCl_3 , 40 $^\circ\text{C}$).

of 100; $(\text{C}_4\text{H}_8\text{O}) \times 100 + \text{C}_{118}\text{H}_{140}\text{N}_{12}\text{O}_{18}$ plus Na^+ equals 9248.203. Furthermore, the sum of twice the molar mass of **Ib** with a DP_n of 30 (Figure 2B, $2 \times (2786.5 - [\text{Na}^+]) = 5527.0$) and the molar mass of **Ic** with a DP_n of 40 (Figure 2C, $(3722.2 - [\text{Na}^+]) = 3699.2$) was 9226.2, in agreement with the molar mass of **IVa** with a DP_n of 100 ($9248.8 - [\text{Na}^+] = 9225.8$) given above. Analogously, in Figure 8 (bottom), the peak at $m/z = 11\,538.4$, which was also assumed to be the adduct with Na^+ , corresponds to **IVb** possessing the expected chemical structure with a DP_n ($n + m$ in the chemical formula in Figure 7 bottom) of 120; $(\text{C}_4\text{H}_8\text{O}) \times 120 + \text{C}_{171}\text{H}_{194}\text{N}_{14}\text{O}_{26}$ plus Na^+ equals 11 537.372. The sum of twice the molar mass of **Ib** with a DP_n of 30 ($2 \times (2786.5 - [\text{Na}^+]) = 5527.0$) and the molar mass of **Ic** with a DP_n of 60 (Figure 2E, $(6012.0 - [\text{Na}^+]) = 5989.0$) was 11 516.0, in agreement with the molar mass of **IVb** with DP_n of 120 ($11\,538.4 - [\text{Na}^+] = 11\,515.4$) given above. On the basis of these results, we concluded that **IVa** and **IVb** had *spiro*-type multicyclic topologies.

4. Construction of Multicyclic Polymer Topologies Composed of Repeating Ring, Alternating Ring/Linear and Alternating Ring/Star Units by the Click Process. The click reaction was further applied to the polyaddition of a single cyclic precursor having an alkyne group and an azide

group at the opposite positions (**Id**) to produce a linearly connected *spiro*-type multicyclic polymer (**Va**) (Scheme 1). Moreover, the copolyaddition between a single cyclic precursor having two alkyne groups (**Ic**) and linear (**IIa**) or three-armed star-shaped (**IIb**) precursors having azide end groups was performed to produce multicyclic polymers having alternating ring/linear (**Vb**) or ring/star-branched (**Vc**) polymer units, respectively (Scheme 1). In the case of reaction between bifunctional **Ic** and trifunctional **IIb**, expected to form a network polymer, the conditions were chosen to avoid uncontrolled gelation. Products **Va**, **Vb**, and **Vc**, consisting of various multicyclic polymer units, were obtained in 82%, 67%, and 72% yields, respectively.

The reaction between the alkyne and azide units was confirmed by the ^1H NMR spectra of the products, **Va**, **Vb**, and **Vc** (Figure 9), compared with the precursors, **Id** (Figure 1D), **Ic** (Figure 1C), **IIa**, and **IIb** (Figure S3 in the SI). Thus, the signals for the ethynyl (2.54 ppm), propynyl methylene (4.69 ppm), and azidomethylene (3.63 ppm) groups in **Id** were replaced with those for a triazole proton (7.81 ppm) and the methylene group adjacent to the 4-position of the triazole ring (5.21 ppm) in **Va**. Similarly, the two distinguishable signals each for the ethynyl (2.53 and 2.54 ppm) and propynyl methylene (4.69 and 4.76 ppm) groups in **Ic**,

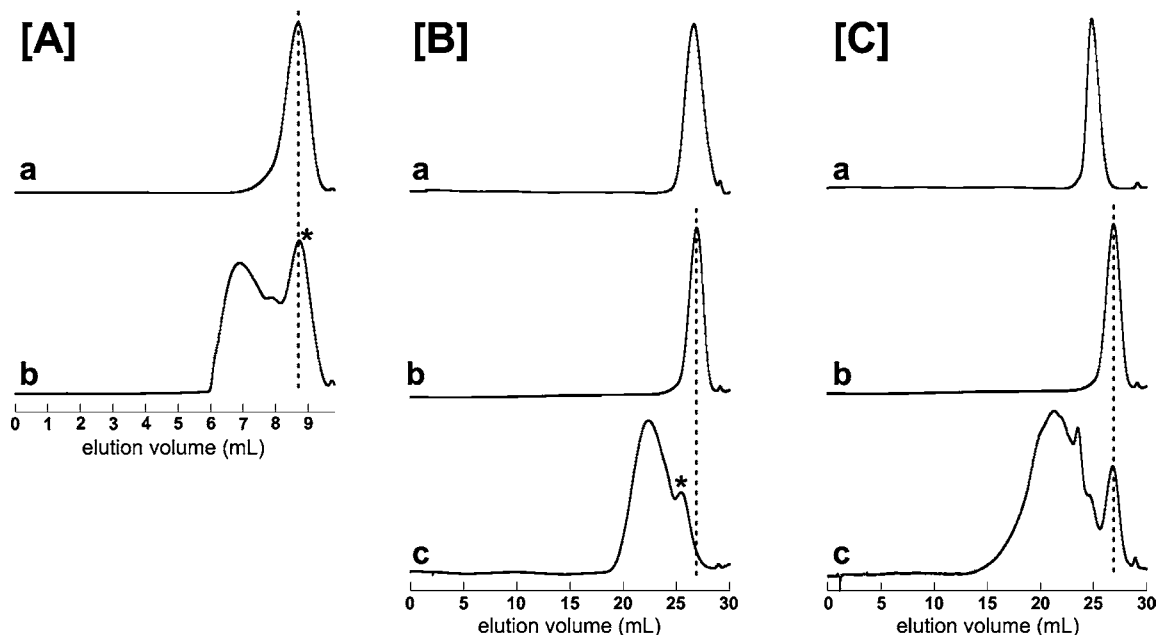


Figure 10. SEC traces of the precursors and products for the construction of multicyclic polymers with repeating ring-containing units. [A] (a) **Id** and (b) **Va**. [B] (a) **IIa**, (b) **Ic**, and (c) **Vb**. [C] (a) **IIb**, (b) **Ic**, and (c) **Vc**. (For [A], TSK G3000HXL, eluent: THF 1.0 mL/min. For [B] and [C], a combination of three columns, TSK G5000HXL, TSK G4000HXL, and TSK G3000HXL, eluent: THF 1.0 mL/min.)

as well as that for the azidomethylene groups (3.30 ppm) in **IIa** and **IIb**, completely disappeared. Instead, the signals for triazole protons (7.62 and 7.65 ppm) and the methylene groups adjacent to the 4-position of the triazole rings (5.20 and 5.26 ppm) emerged in **Vb** and **Vc**. The IR absorbance of the azide groups observed in the precursors (2104 cm^{-1} in **Id** and 2094 cm^{-1} in **IIa** and **IIb**) was scarcely visible in the products, indicating that the reaction proceeded effectively (Figure S7 in the SI).

Finally, SEC showed, upon reaction, notable peak shifts toward the higher molecular weight region with multimodal distributions (Figure 10). The $M_p(\text{SEC})$ of **Va** reached as high as 10.5 kDa, suggesting the formation of a linearly arranged *spiro*-type hexacyclic construction on average. Likewise, the highest $M_p(\text{SEC})$ value observed for **Vb** was 12.8 kDa, presumably multicyclic polymers roughly consisting of four rings connected with three chains in an alternating fashion. On the other hand, the $M_p(\text{SEC})$ of the soluble fraction of **Vc** was 20.1 kDa, corresponding to oligomeric structures consisting of approximately four **Ic** and three **IIb** units.³² In addition, the SEC traces indicated that concurrent intramolecular reactions took place. Thus, an 8-shaped product was formed by the unimolecular reaction of **Id**, and a θ -shaped polymer resulted from the bimolecular reaction of **Ic** and **IIa** (Scheme 1, marked with * in Figure 10).

Conclusions

An alkyne–azide addition, i.e., *click*, reaction in conjunction with an *electrostatic self-assembly and covalent fixation* (ESA-CF) process has been demonstrated as an effective means to combine *kyklo*-telechelics along with linear and branched prepolymers. Accordingly, complex multicyclic polymer topologies such as two- and three-way paddle-shaped

constructions, as well as tandem tricyclic and tetracyclic constructions, were designed and successfully formed. Furthermore, three multicyclic polymers with repeating ring, alternating ring/linear, and alternating ring/star units were produced. This novel synthetic protocol is applicable for the construction of a wide variety of complex polymer topologies including *spiro*- and *bridged*-multicyclic constructions, offering unique opportunities for polymer material designs from the topological point of view. The future developments of *topological polymer chemistry* include combination of the *click* process with an effective homocoupling process such as a metathesis condensation for the construction of *fused* polymer topologies with higher complexities, which are not attainable solely via the present *click* process. This challenge is currently being investigated in our laboratory.

Acknowledgment. This paper is dedicated to Professor Shohei Inoue in honor of his 75th birthday. The authors are grateful to Prof. M. Kakimoto for our access to the NMR apparatus. Financial support from The Mitsubishi Foundation and Tokyo Tech Innovative Research Engineering Award is gratefully acknowledged. T.Y. thanks the KAKENHI (21850013), the Mizuho Foundation for the Promotion of Sciences, The Ogasawara Foundation for the Promotion of Science & Engineering, and the Tokuyama Science Foundation for partial support of this work.

Supporting Information Available: Experimental details for the synthesis of cyclic (**Ia–Id**), bicyclic (**Ie**), linear (**IIa**), and star (**IIb**) polymer precursors, ^1H NMR spectra (**1a/2a**, **1a/2b**, **1b/2a**, **1b/2b**, and **1b/2c**), SEC traces (**Ia–Ie** and the linear counterparts), MALDI-TOF MS spectra (**IIa** and **IIb**), and IR spectra (**Ia–Ie**, **IIa**, **IIb**, **IIIa**, **IIIb**, **IVa**, **IVb**, and **Va–Vc**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA103402C

(32) A gelled material also formed and is expected to be arising from a higher degree of copolyaddition.