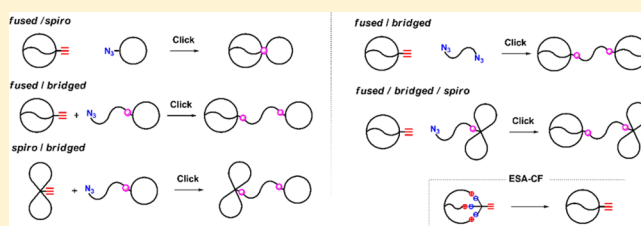


Construction of Hybrid-Multicyclic Polymer Topologies Composed of Dicyclic Structure Units by Means of An ESA-CF/Click-Linking Protocol[‡]Yoichiro Tomikawa, Takuya Yamamoto,[†] and Yasuyuki Tezuka*

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S Supporting Information

ABSTRACT: A series of tri- and tetracyclic polymer topologies, composed of an elementary dicyclic unit of either *theta*-, *eight*- or *manacle*-forms, have been constructed by means of an ESA-CF (electrostatic self-assembly and covalent fixation) protocol in conjunction with an alkyne–azide click linking technique. Thus, a *theta*-shaped poly(THF) precursor having an alkyne group at the junction position (Ic) has newly been prepared by an ESA-CF process using an assembly (Ib/2d), composed of a star poly(THF) having *N*-phenylpyrrolidinium salt groups carrying a counteranion of a trifunctional carboxylate having an alkyne group. In addition, monocyclic polymer precursors having an azide group (IIa) as well as linear-cyclic (tadpole) (IIb) and linear-dicyclic (twin-head tadpole) (IIc) polymer precursors, both having an azide group at the tail-end position, have been prepared through the tandem click reaction of the respective monocyclic and dicyclic (*eight*-form) precursors having an alkyne group (Ia and Ib, respectively) with a linear asymmetric telechelic poly(THF) having an azide and an hydroxyl groups (Id), followed by the esterification with 4-azidobenzoic acid. A variety of hybrid-tricyclic polymer topologies (IIIa, IIIb, and IIIc) composed of a dicyclic (*theta*- or *eight*-shaped) and a monocyclic (simple ring or tadpole-shaped) units, and moreover, an unprecedented hybrid-tetracyclic topology composed of all three elementary dicyclic units of *theta*-, *eight*- and *manacle*-forms (IVb), in addition to a double-*theta* topology (IVa) have been constructed through the effective click-linking of complementarily reactive *kyklo*-telechelic precursors.



■ INTRODUCTION

The precision designing of *monocyclic* polymer structures has now been accomplished through newly developed synthetic protocol, including end-linking reactions of polymer precursors,^{1–4} and alternative ring-expansion polymerizations.^{5–10} Thereupon, unprecedented topology effects by monocyclic polymers arisen from the elimination of their chain termini have now been revealed in comparison with their linear and branched counterparts.^{11–13}

Notably, moreover, a variety of *multicyclic* polymer architectures have now emerged as an attractive challenge in the frontier of synthetic polymer chemistry.^{11,14–17} From a geometry viewpoint, *multicyclic* polymer topologies are expressed by graph construction of three elementary *fused*-, *spiro*- or *bridged*-subclasses, and these correspond to *theta*-, *eight*- and *manacle*-forms, respectively, in the dicyclic category.^{11,18} (Scheme 1) We have so far demonstrated that an *electrostatic self-assembly and covalent fixation* (ESA-CF) protocol is a versatile means to produce each of three forms of *dicyclic* constructions.^{11,19} Besides, a series of tricyclic and further multicyclic polymer homologues in each *fused*-, *spiro*- or *bridged*-topologies have subsequently been constructed by making use of the ESA-CF technique in conjunction with an alkyne–azide addition, i.e., *click*, and an olefin metathesis,

i.e., *clip*, reaction.¹¹ Those include, in particular, *fused*-tricyclic (β -, γ - and δ -graphs), *fused*-tetracyclic (unfolded tetrahedron-graph, $K_{3,3}$ graph) and even *fused*-pentacyclic (Shippo-form) topologies,^{20–24} as well as *spiro*-multicyclic up to seven rings (trefoil- and quatrefoil forms, tandemly linked triple and quadruple ring-forms, etc.).^{25–29} and *bridged*-multicyclic counterparts (three- and four-way paddle-forms, etc.).^{25,26}

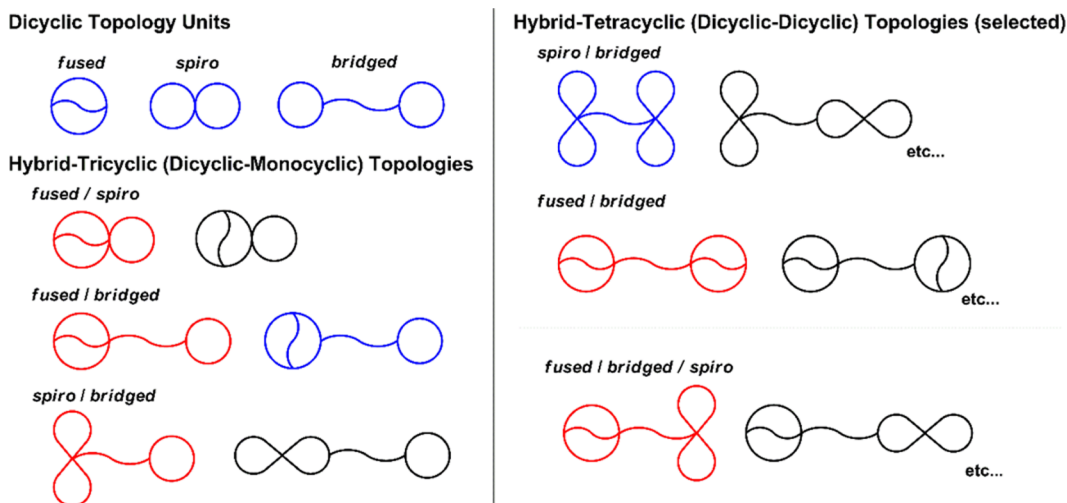
On the other hand, another class of *hybrid-multicyclic* polymer topologies, composed of either elementary units of *fused*-, *spiro*-, and *bridged*-forms (Scheme 1) has scarcely been constructed.³⁰ The effective construction of such low-symmetry, complex structures inevitably demands the tailored designing of monocyclic and multicyclic polymer precursors (*kyklo*-telechelics) having suitably reactive groups at the prescribed positions.³¹ In addition, highly effective polymer linking processes should be introduced to address adversarial kinetic effects by sterically demanding polymer reagents with the low concentration of reactive groups.

We report herein a systematic synthesis of a class of *hybrid-multicyclic* polymers, composed of an elementary dicyclic unit of

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Scheme 1. Three Elementary Dicyclic Topology Units and Hybrid Tricyclic and Tetracyclic Topologies Therefrom^a

^aThose in blue are previously reported, and those in red are constructed in this work.

either *theta*-, *eight*-, or *manacle*-forms, by taking advantage of a *click* polymer-linking protocol in conjunction with the ESA-CF process, which affords a variety of *kyklo*-telechelic polymer precursors having an alkyne or an azide group at the designated positions. (Schemes 1 and 2) The alkyne–azide *click* polymer linking process was observed as an exceptionally powerful means even with di- and tricyclic, core-clickable *kyklo*-telechelics having an alkyne group deliberately introduced at the sterically crowded, core junction position having four and six emanating polymer segments.³⁰ Unprecedented *spiro/bridged* hybrid, tetracyclic and hexacyclic polymer topologies, i.e., a double-*eight* and a double-*trefoil* forms, have subsequently been constructed effectively.³⁰

In the present study, we have introduced a *theta*-shaped poly(THF) precursor having an alkyne group at the junction position (Ic) as a key *kyklo*-telechelic precursor, newly prepared by an ESA-CF process using an assembly (1b/2d), composed of a star poly(THF) having *N*-phenylpyrrolidinium salt groups carrying a counteranion of a trifunctional carboxylate having an alkyne group. In addition, a monocyclic polymer precursors having an azide group (IIa) as well as a linear-cyclic (tadpole) (IIb) and a linear-dicyclic (twin-head tadpole) (IIc) polymer precursors, both having an azide group at the tail-end position, have been prepared through the tandem *click* reaction of the respective mono- and dicyclic *eight*-shaped precursors having an alkyne group (Ia and Ib, respectively) with a linear asymmetric telechelic poly(THF) having azide and hydroxyl groups (1d), followed by the esterification with 4-azidobenzoic acid. A variety of hybrid-tricyclic polymer topologies (IIIa, IIIb and IIIc) composed of a dicyclic (*theta*- or *eight*-shaped) and a monocyclic (simple ring or tadpole-shaped) units, and moreover, an unprecedented hybrid-tetracyclic topology combined with all three elementary dicyclic units of *theta*-, *eight*-, and *manacle*-forms (IVb), in addition to a double-*theta* topology (IVa) have been constructed through effective *click*-linking of complementarily reactive *kyklo*-telechelic precursors. (Scheme 2)

RESULTS AND DISCUSSION

1. Preparation of Monocyclic and Dicyclic Polymer Precursors (*kyklo*-Telechelics) Having an Alkyne or an Azide group. 1.1. *kyklo*-Telechelics Having an Alkyne Group

at the Designated Position. Three types of *kyklo*-telechelics having an alkyne group have been employed in this study, namely a *monocyclic* poly(THF) having an alkyne group (Ia),³¹ a *dicyclic eight*-shaped poly(THF) having an alkyne group (Ib),³⁰ and a newly prepared, *dicyclic, theta*-shaped poly(THF) having an alkyne group at the junction position (Ic). (Scheme 2) An ESA-CF process has been applied for the synthesis of Ic with an assembly (1b/2d) consisting of a star telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups (1b) carrying a counteranion of a tricarboxylate having an alkyne group (2d), (Scheme 2). The assembly 1b/2d was formed through the simple precipitation of the precursor 1b/triflate into aqueous solution containing an excess amount of 2d as a sodium salt form. The ion-exchange reaction proceeded effectively with the ion-exchange yield of 74%. The covalent conversion reaction of the ion pair, 1b/2d, took place through the nucleophilic ring-opening reaction of pyrrolidinium salt group in 1b by carboxylate anions in 2d. Under appropriate dilution (0.1 g/L), the electrostatic assembly 1b/2d tends to dissociate into a uniform ionic pair consisting of one units of trifunctional 1b and one unit of trifunctional 2d, where the cations and anions balance the charges. The subsequent covalent conversion of 1b/2d was completed under reflux in THF (with a small amount of methanol to keep the reaction homogeneous) for 12 h, to give a product Ic in 14% yield after the silica-gel treatment, to remove the side products having ionic species. SEC of the obtained Ic in comparison with the star polymer precursor (Figure S2) showed the notable constriction of the hydrodynamic volume to accord with the formation of a *fused* dicyclic product.

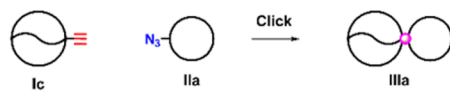
The ¹H NMR spectra of the isolated product Ic together with the ionic polymer self-assembly (1b/2d) (Figure 1) confirm the covalent conversion by the ring-opening of *N*-phenylpyrrolidinium salt groups by the carboxylate counteranion. Thus, the *N*-phenyl proton signals (g, h, and i) at 7.49–7.71 ppm shifted to those at 6.59–6.70 and 7.19 ppm along with the covalent conversion. Besides, the pyrrolidinium ring proton signal (j) at around 4 ppm was replaced by the ester methylene proton signal (j) newly appeared at 4.39 ppm. The propargyloxy methine (HC≡) proton signals (p) at 2.14 ppm were visible throughout the covalent conversion process.

The MALDI-TOF mass spectrum of the product Ic (Figure 2) showed a uniform series of peaks with an interval

Scheme 2. Construction of Hybrid-Tricyclic and Hybrid-Tetracyclic Polymer Topologies with Complementary Reactive *kyklo*-Telechelic Precursors Having an Alkyne or an Azide Group at the Prescribed Position

Hybrid-Tricyclic Topologies

fused / spiro



fused / bridged



spiro / bridged



Hybrid-Tetracyclic Topologies

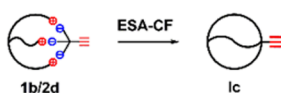
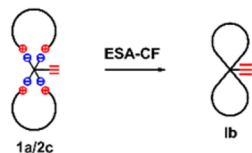
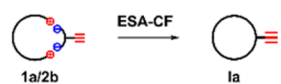
fused / bridged



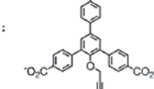
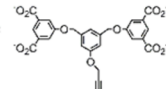
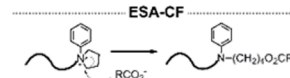
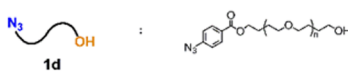
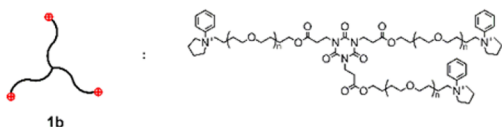
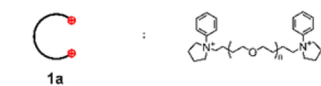
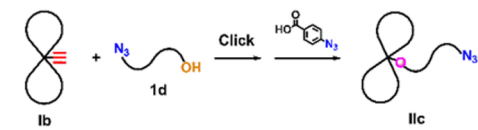
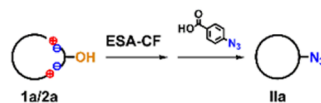
fused / bridged / spiro



Kyklo-telechelics having an alkyne group



Kyklo-telechelics having an azide group



of 72 mass units corresponding to repeating THF monomer units, and each peak exactly matched the total molar mass of the expected poly(THF) product having an alkyne group at the core position. Thus, the peak at $m/z = 5071.1$, which is assumed to be the adduct with Na^+ , corresponds to **Ic** possessing the expected chemical structure with a DP_n of 50; $(\text{C}_4\text{H}_8\text{O}) \times 50 + \text{C}_{84}\text{H}_{92}\text{N}_6\text{O}_{16}$ plus Na^+ equals 5070.04.

1.2. *kyklo*-Telechelics Having an Azide Group at the Designated Position. Three types of *kyklo*-telechelic poly(THF)s

having an azide group at the designated position have also been prepared for the subsequent alkyne–azide *click* polymer-linking reaction. Thus, first, a monocyclic poly(THF) having an azide group (**IIa**) was prepared through the esterification of a monocyclic poly(THF) precursor having an hydroxyl group, obtainable by the ESA-CF process with the self-assembly (**1a/2a**), reported before.³¹ (Scheme 2) The obtained product having an azide group (**IIa**) was unequivocally characterized by means of the ^1H NMR (Figure S3, top) and MALDI–TOF

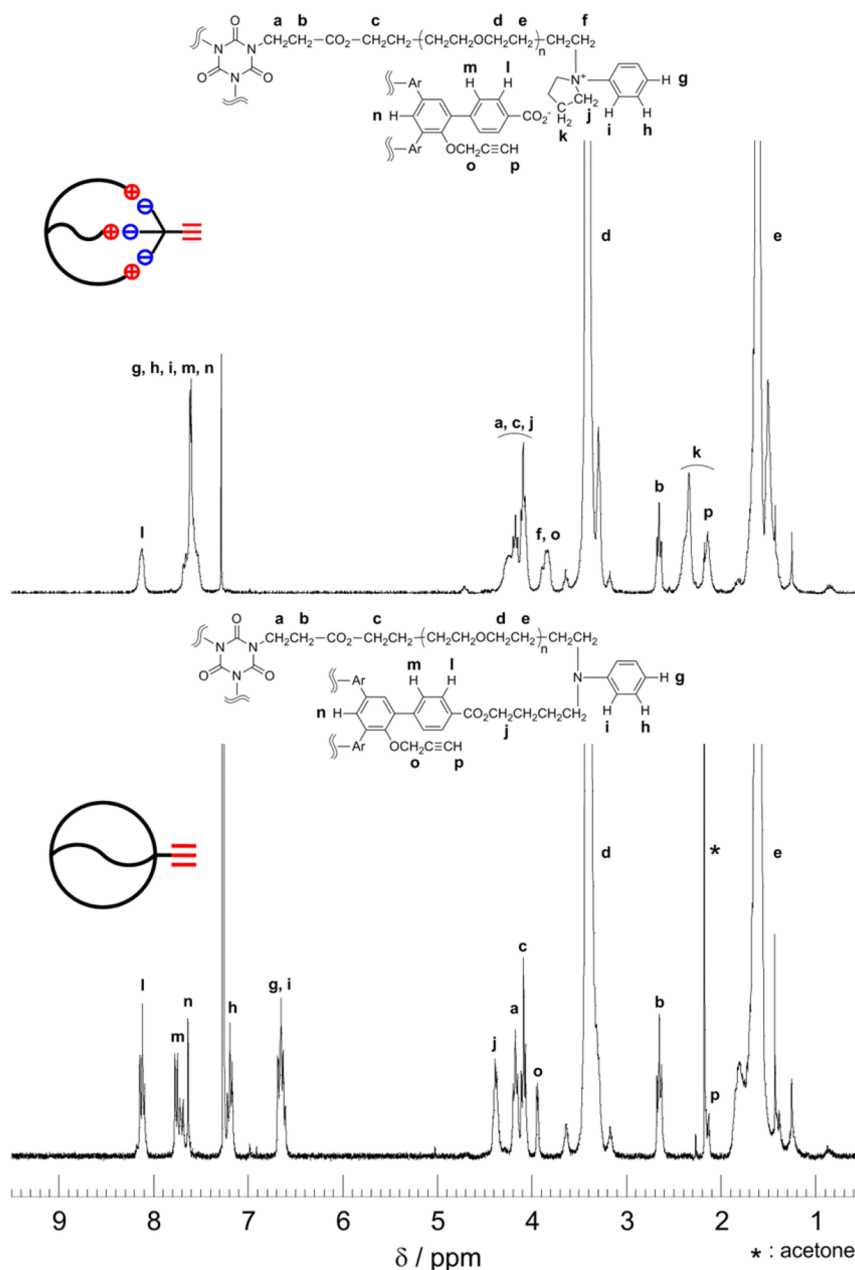


Figure 1. 300 MHz ^1H NMR spectra of (top) an electrostatic self-assembly consisting of one units of a star-telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups and one unit of a tricarboxylate counteranion carrying an additional alkyne group (**1b/2d**) and (bottom) an *theta*-shaped poly(THF) having an alkyne group at the core position (**1c**). (CDCl_3 , 40 $^\circ\text{C}$).

mass spectroscopy (Figure S3, bottom), together with the precursor having a hydroxyl group.

Moreover, two additional *kyklo*-telechelics having an azide group, i.e., a linear-cyclic (tadpole) (**IIb**) and a linear-dicyclic (twin-head tadpole) (**IIc**) polymer precursors both having an azide group at the tail-end position (Scheme 2), have been prepared through the tandem *click* reaction of the respective monocyclic and dicyclic precursors having an alkyne group (**Ia** and **Ib**, respectively) with a linear asymmetric telechelic poly(THF) having an azide and an hydroxyl groups (**1d**, See Supporting Information for the preparation details as well as ^1H NMR (Figure S1, top) and MALDI–TOF mass (Figure S1, bottom)). (Scheme 2) The *click* polymer-linking reaction between **Ia** (or **Ib**) and **1d** was conducted in the presence of Cu(I)Br and 2,2'-bipyridine as a catalyst in THF solution.

The crude products were subjected to the preparative SEC technique to remove the remaining unreacted precursors (Figure 3, dotted lines). The isolated products having a hydroxyl group at the tail-end position were then esterified with 4-azidobenzoic acid in the presence of EDAC and DMAP in THF solution. The products **IIb** and **IIc** were finally recovered after the silica-gel treatment with the overall yields of 23% and 31%, respectively.

The *click* polymer-linking reactions between **Ia** (or **Ib**) and **1d**, as well as the subsequent esterification by 4-azidobenzoic acid were conveniently monitored by means of the SEC technique. Thus, SEC (Figures 3-A and 3-B) showed that the both products **IIb** and **IIc** retained narrow size distribution ($\text{PDI} = 1.07$ and 1.05 , respectively), to confirm the absence of any concurrent degradation during the *click* polymer-linking

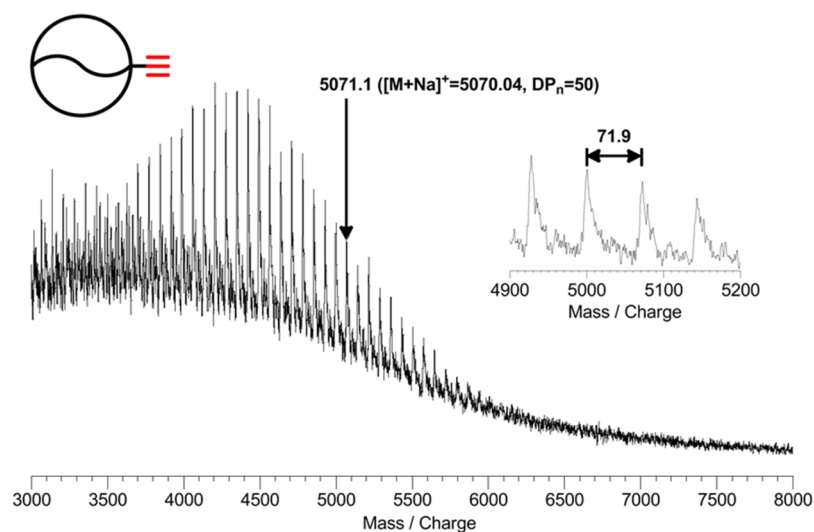


Figure 2. A MALDI–TOF mass spectrum of a *theta*-shaped poly(THF) having an alkyne group at the core position (**Ic**). (Linear mode, matrix: dithranol with sodium trifluoroacetate. DP_n denotes the number of monomer units in the product.)

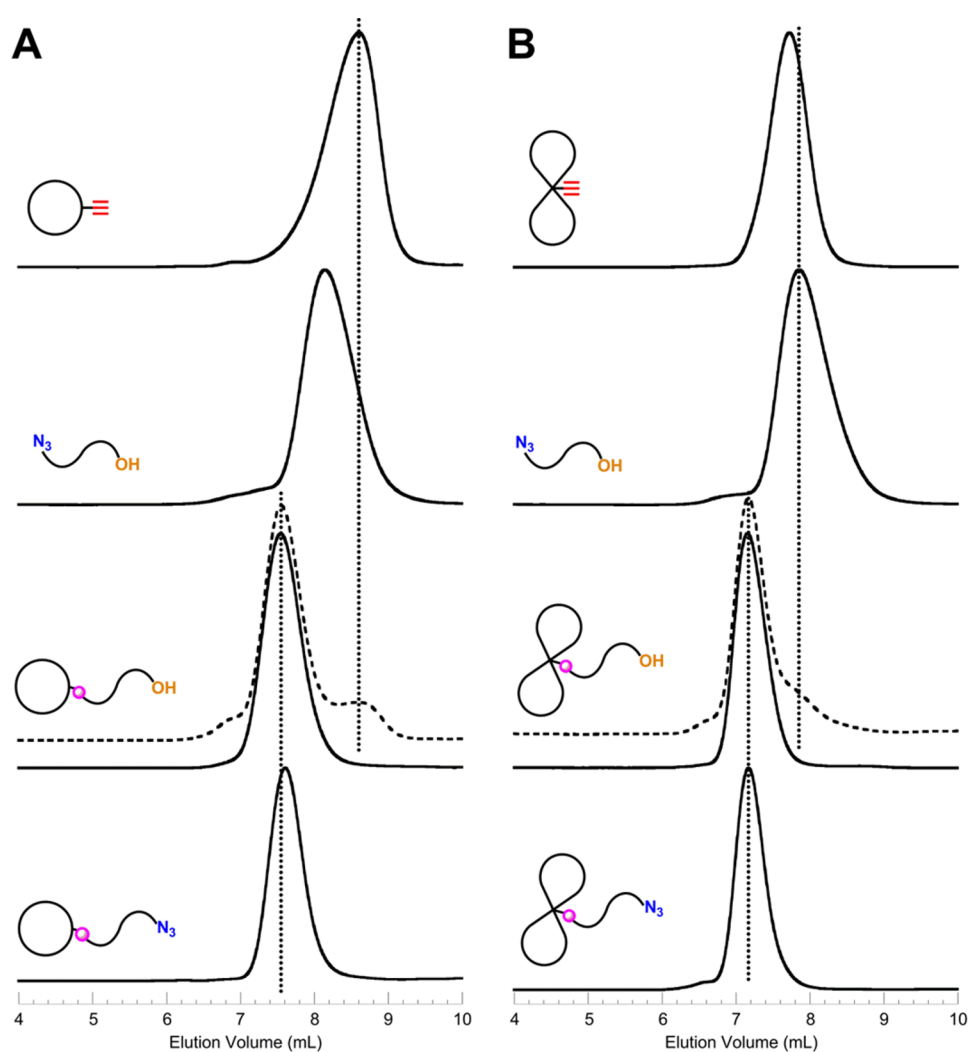


Figure 3. SEC traces of (A, from top to bottom) **Ia**, **1d**, the click-linking product of **Ia** and **1d**, and **IIb**, and (B, from top to bottom) **Ib**, **1d**, the click-linking product of **Ib** and **1d**, and **IIc**. Broken lines and solid lines show those obtained before and after SEC fractionation, respectively. THF as an eluent, 1.0 mL/min.

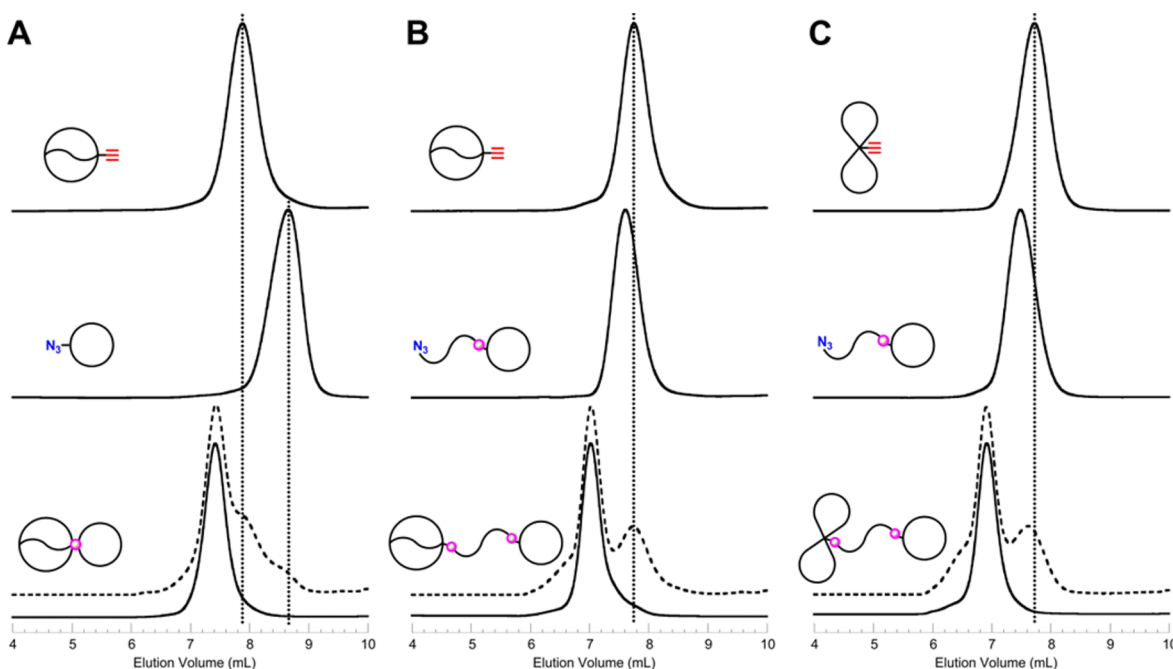


Figure 4. SEC traces of (A) (top) **IIa**, (middle) **Ic**, and (bottom) the click-linking product **IIIa**, (B) (top) **IIb**, (middle) **Ic**, and (bottom) the click-linking product **IIIb**, and (C) (top) **IIb**, (middle) **Ib**, and (bottom) the click-linking product **IIIc**. Broken lines and solid lines (traces in bottom) show those obtained before and after SEC fractionation, respectively (THF as an eluent, 1.0 mL/min).

reactions and the subsequent esterification. SEC showed also that the peak molecular weights, $M_p(\text{SEC})$ s, of **IIb** (4.6 kDa) and of **IIc** (8.4 kDa) were close to the sum of those of the precursors, **Ia** ($M_p(\text{SEC}) = 1.8$ kDa) and **Id** ($M_p(\text{SEC}) = 2.8$ kDa), as well as **Ib** ($M_p(\text{SEC}) = 4.2$ kDa) and **Id** ($M_p(\text{SEC}) = 3.9$ kDa), respectively, to confirm the effective *click* linking reaction to proceed.

The ^1H NMR spectra showed that the 4-azidobenzoate signals at 7.07 and 8.04 ppm became visible for both **IIb** and **IIc** after the esterification. (Figures S4 and S7, respectively) The MALDI-TOF mass measurements were applied for a series of the products having an azide group (**IIb** and **IIc**) for further characterization. The observed peaks were reasonably assigned by taking into account for the elimination of N_2 from the azide group in these products under the measurement conditions. (Figures S5 and S8, respectively) Moreover, IR analysis of a series of the products indicated the each reaction steps by the presence/absence of the absorption at 2123 cm^{-1} due to the azide group. (Figures S6 and S9)

2. Construction of Hybrid-Multicyclic Polymer Topologies Composed of Dicyclic Structure Units. **2.1. Hybrid-Tricyclic Polymer Topologies Composed of a Monocyclic and a Dicyclic Structure Units.** A series of hybrid-tricyclic, i.e., fused-spiro, fused-bridged, and spiro-bridged, polymer topologies have been constructed by the *click* polymer-linking reaction of complementary *kyklo*-telechelic precursors having a monocyclic and a dicyclic structure units. Thus, a *theta*- or an *eight*-shaped dicyclic poly(THF)s having an alkyne group, **Ic** and **Ib**, were combined with a poly(THF) precursor having an azide group, either a monocyclic poly(THF) having an azide group (**IIa**), a linear-cyclic (tadpole) (**IIb**) or a linear-dicyclic (twin-head tadpole) polymer precursor (**IIc**) both having an azide group at the tail-end position. A *click* polymer-linking reaction was conducted by mixing the complementary pair of the *kyklo*-telechelic precursors having an alkyne or an azide group in

THF in the presence of Cu(I)Br and 2,2'-bipyridine as a catalyst for 24 h. The progress of the reaction was monitored by SEC (Figure 4, parts A, B, and C), where the distinct peak-shift toward the higher molecular weight region was commonly observed. And the peak molecular weights, $M_p(\text{SEC})$, of the products, **IIIa** (5.7 kDa), **IIIb** (8.5 kDa) and **IIIc** (9.4 kDa) were commonly close to the sum of those of the precursors, **IIa** ($M_p(\text{SEC}) = 2.0$ kDa) and **Ic** ($M_p(\text{SEC}) = 3.5$ kDa) for **IIIa**, **IIb** ($M_p(\text{SEC}) = 4.6$ kDa) and **Ic** ($M_p(\text{SEC}) = 4.0$ kDa) for **IIIb**, and **IIb** ($M_p(\text{SEC}) = 4.6$ kDa) and **Ib** ($M_p(\text{SEC}) = 4.3$ kDa) for **IIIc**, respectively. The products **IIIa**, **IIIb**, and **IIIc** were isolated after the preparative SEC technique to remove the remaining unreacted precursors (Figure 4, solid lines, PDI = 1.06 for **IIIa**, PDI = 1.08 for **IIIb**, and PDI = 1.07 for **IIIc**, respectively), followed by the silica-gel treatments. The isolated yields of **IIIa**, **IIIb** and **IIIc** were 29%, 40% and 32%, respectively.

The ^1H NMR inspection of the products **IIIa**, **IIIb**, and **IIIc** (Figure S, top, middle and bottom, respectively) confirmed that the effective *click* polymer-linking reaction between the respective complementary reactive precursors. Thus, the 4-azidobenzoate signals at 7.07 and 8.04 ppm visible for both **IIa** and **IIb** (Figure S3, top and S4, bottom, respectively) as well as the propargyloxy methine ($\text{HC}\equiv\text{C}-$) and methylene ($\equiv\text{C}-\text{CH}_2\text{O}-$) proton signals (**p** and **o**, respectively) at 2.14 and 3.95 ppm (Figure 1, bottom) visible for **Ic** were replaced by *endo*-triazole methine and *exo*-triazole methylene signals (**o** and **p**, respectively) at 7.08 and 4.56 ppm for **IIIa**, 7.01 and 4.54 ppm for **IIIb**, and 8.15–8.24 and 5.32–5.38 ppm for **IIIc**, respectively. Besides, the IR inspection of the products, **IIIa**, **IIIb**, and **IIIc**, showed that the azide absorption for the precursors at 2123 cm^{-1} for **IIc**, **IIb**, and **IIc** were totally eliminated to support quantitative *click* reaction to proceed (Figures S10, S11 and S12).

The MALDI-TOF mass measurements of the tricyclic products, **IIIa**, **IIIb**, and **IIIc** (Figure 6, top, middle, and bottom,

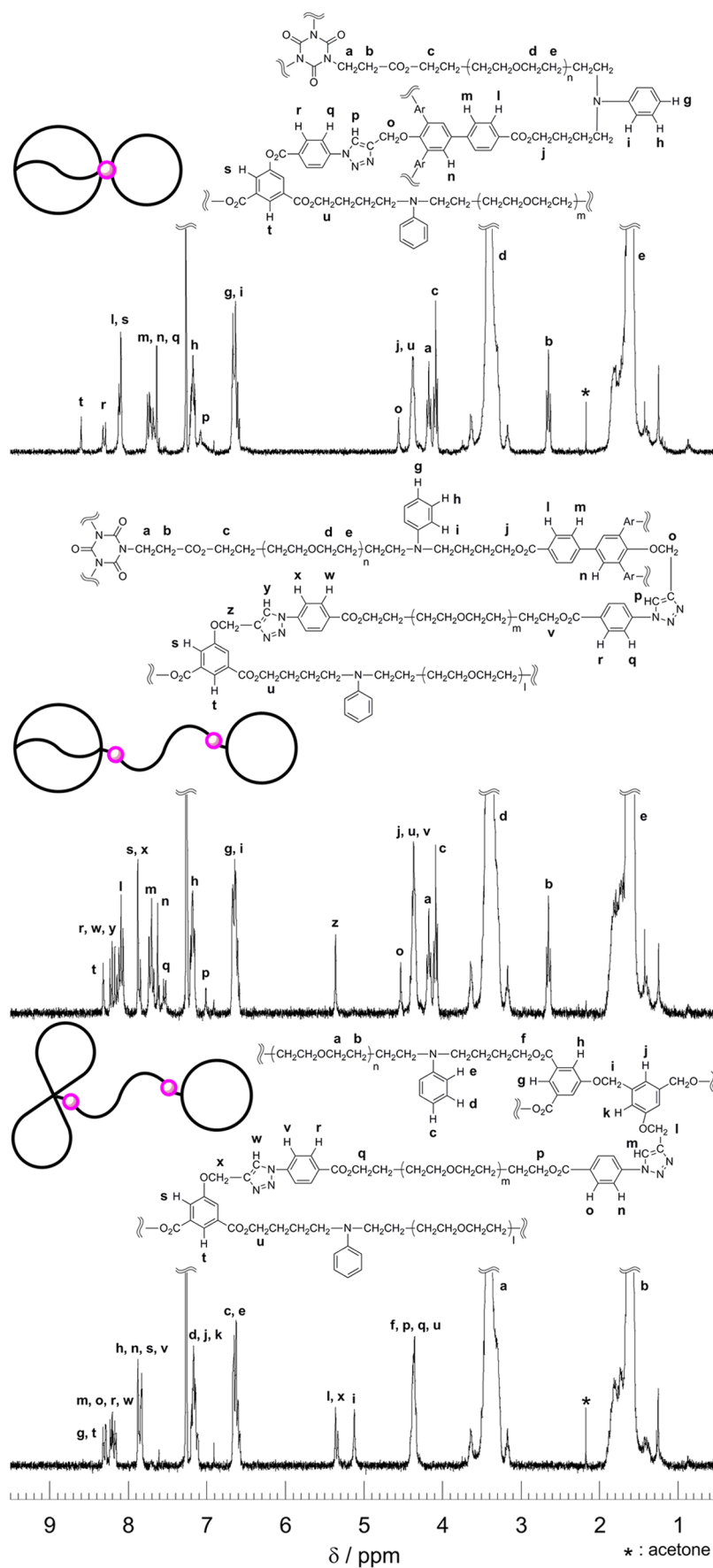


Figure 5. 300 MHz ^1H NMR spectra of (top) a *fused-spiro* hybrid tricyclic poly(THF) (IIIa) (middle) a *fused-bridged* hybrid tricyclic poly(THF) (IIIb) and (bottom) a *spiro-bridged* hybrid tricyclic poly(THF) (IIIc). (CDCl_3 , 40°C).

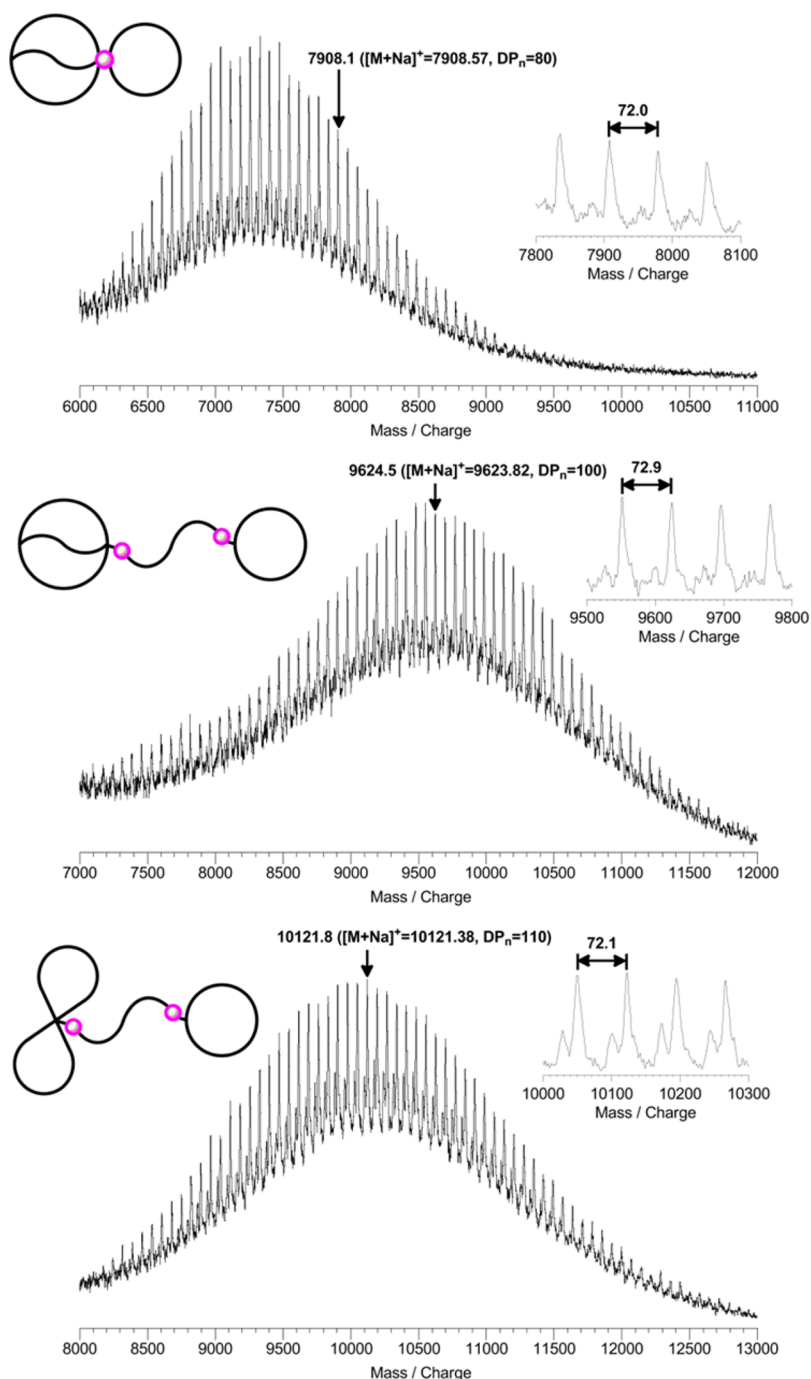


Figure 6. MALDI–TOF mass spectra of (top) a *fused-spiro* hybrid tricyclic poly(THF) (**IIIa**) (middle) a *fused-bridged* hybrid tricyclic poly(THF) (**IIIb**) and (bottom) a *spiro-bridged* hybrid tricyclic poly(THF) (**IIIc**). (Linear mode, matrix: dithranol with sodium trifluoroacetate. DP_n denotes the number of monomer units in the product.)

respectively) were conducted to show commonly a uniform series of peaks with an interval of 72 mass units corresponding to repeating THF monomer units, and each peak exactly matched the total molar mass of the poly(THF) products having the respective linking groups of **IIIa**, **IIIb**, and **IIIc**. Thus, for **IIIa**, the peak at $m/z = 7908.1$, which is assumed to be the adduct with Na^+ , corresponds to **IIIa** possessing the expected chemical structure with a DP_n of 80; $(C_4H_8O) \times 80 + C_{123}H_{133}N_{11}O_{22}$ plus Na^+ equals 7908.57. For **IIIb**, the peak at $m/z = 9624.5$, which is assumed to be the adduct with Na^+ , corresponds to **IIIb** possessing the expected chemical

structure with a DP_n of 100; $(C_4H_8O) \times 100 + C_{137}H_{148}N_{14}O_{25}$ plus Na^+ equals 9623.82. Finally, for **IIIc**, the peak at $m/z = 10121.8$, which is assumed to be the adduct with Na^+ , corresponds to **IIIc** possessing the expected chemical structure with a DP_n of 110; $(C_4H_8O) \times 110 + C_{128}H_{140}N_{12}O_{20}$ plus Na^+ equals 10121.38. Moreover, the sum of the mass of the precursors coincides with those of the products. As an example, the peak mass of **IIIb** (9624.5 as Na^+ adduct, Figure 6) coincides with the sum of **Ia** (5071.1 as Na^+ adduct, Figure 2) and **Ib** (4577.9 as Na^+ adduct, Figure S5) within experimental error.

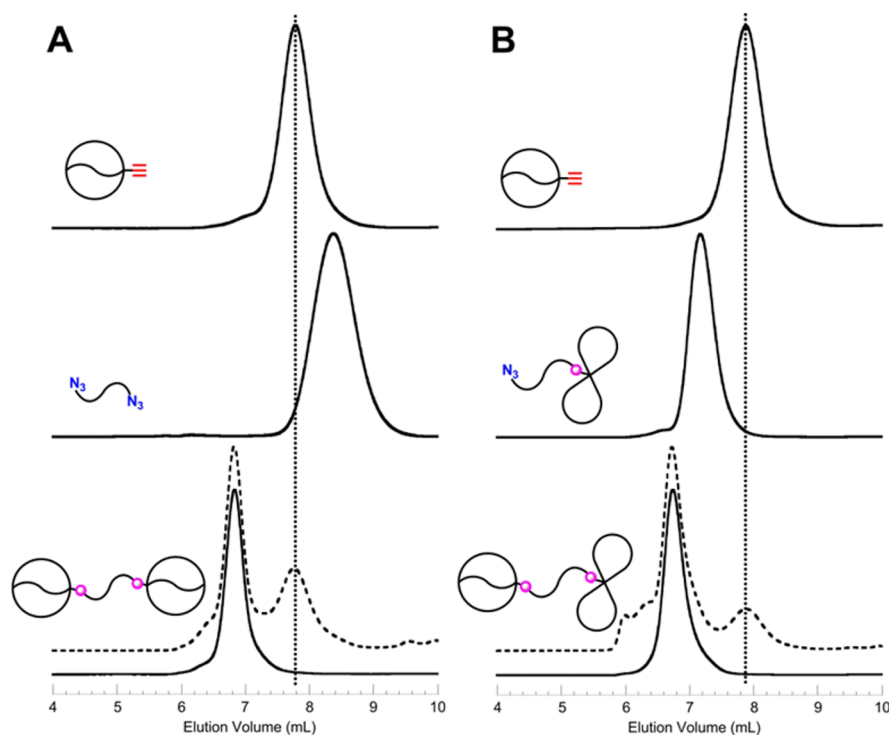


Figure 7. SEC traces of (A) (top) **1c**, (middle) **1c**, and (bottom) the click-linking product **IVa**, and (B) (top) **1c**, (middle) **1c**, (bottom) the click-linking product **IVb**. Broken lines and solid lines (traces in bottom) show those obtained before and after SEC fractionation, respectively. (THF as an eluent, 1.0 mL/min.).

2.2. A Hybrid-Tetracyclic Polymer Topology Composed of Three Elementary Dicyclic Structure Units. Finally, an unprecedented hybrid-tetracyclic topology composed of three elementary dicyclic units of *theta*-, *eight*-, and *manacle*-forms (**IVb**), in addition to a double-*theta* topology (**IVa**), has been constructed through the *click* polymer-linking reactions of complementarily reactive *kyklo*-telechelic precursors. (Scheme 2) Thus, the *click* polymer-linking of two units of a *theta*-shaped dicyclic poly(THF) having an alkyne group, **1c**, with a linear poly(THF) precursors having azide end groups (**1c**) was carried out to produce **IVa**. On the other hand, a complementary pair of *kyklo*-telechelic precursors having an alkyne and an azide group (**1c** and **1c**, respectively) were combined to give the product, **IVb**.

These *click* polymer-linking reactions were again conducted by mixing the complementary pair of the *kyklo*-telechelic precursors with Cu(I)Br and 2,2'-bipyridine as a catalyst in a THF solution for 64 h (for **IVa**) and for 36 h (for **IVb**), respectively. The progress of the reaction was monitored by SEC (Figure 7, parts A and B), where the distinct peak-shift toward the higher molecular weight region was commonly confirmed. And the peak molecular weights, $M_p(\text{SEC})$ s, of the products, **IVa** (10.3 kDa) and **IVb** (11.2 kDa) were close to the corresponding sum of twice of the precursors, **1c** ($M_p(\text{SEC}) = 4.0$ kDa) and **1c** ($M_p(\text{SEC}) = 2.3$ kDa), and those of the precursors, **1c** ($M_p(\text{SEC}) = 3.5$ kDa) and **1c** ($M_p(\text{SEC}) = 8.4$ kDa), respectively. The hybrid-tetracyclic polymer products **IVa** and **IVb** were finally isolated in 24% and in 27% yield, respectively, after the fractionation by means of a preparative SEC technique (Figure 7, bottom, solid lines, PDI = 1.05 for both **IVa** and **IVb**).

The ^1H NMR spectra of the products **IVa** and **IVb** (Figure 8, top and bottom, respectively) confirmed again that the *click* polymer-linking between the respective complementary

precursor pairs. Thus, the propargyloxy methine ($\text{HC}\equiv\text{C}-$) and methylene($\equiv\text{C}-\text{CH}_2\text{O}-$) proton signals (**p** and **o**, respectively) at 2.14 and 3.95 ppm (Figure 1, bottom) visible for **1c** were replaced by *endo*-triazole methine and *exo*-triazole methylene signals (**o** and **p**, respectively) at 7.70 and 4.35–4.47 ppm for **IVa**, and 7.02 and 4.54 ppm for **IVb**, respectively. Besides, IR inspection of the products, **IVa** and **IVb**, showed that the azide absorption for the precursors at 2095 (**1c**) and 2123 (**1c**) cm^{-1} were totally eliminated to support quantitative *click* reaction to proceed (Figures S13 and S14).

The MALDI-TOF mass spectra of the products, **IVa** and **IVb**, having the number-average molecular weight of as high as over 12 kDa, showed the resolved peaks of high resolutions (Figure 9, top and bottom, respectively). Thus, a uniform series of peaks with an interval of 72 mass units was observed corresponding to the repeating THF monomer units. For **IVa**, the peak at $m/z = 12420.0$, which was assumed to be the adduct with Na^+ , corresponds to **IVa** possessing the expected chemical structure with a DP_n of 130; $(\text{C}_4\text{H}_8\text{O}) \times 130 + \text{C}_{172}\text{H}_{192}\text{N}_{18}\text{O}_{32}$ plus Na^+ equals 12420.46. And, the observed mass value of **IVa** having DP_n of 130, thus two unit of **1c** having DP_n of 50 (Figure 2) and one unit of **1c** having DP_n of 30 (the observed peak at $m/z = 2326.3$, corresponding to the Na^+ adduct of 2326.37), coincided with the sum of the peak mass values of twice of **1c** and **1c**. Also for **IVb**, the peak at $m/z = 13156.4$, which was assumed to be the adduct with Na^+ , corresponds to **IVb** possessing the expected chemical structure with a DP_n of 140; $(\text{C}_4\text{H}_8\text{O}) \times 140 + \text{C}_{177}\text{H}_{192}\text{N}_{16}\text{O}_{31}$ plus Na^+ equals 13157.02. And again, the observed mass value of **IVb** having DP_n of 140, thus one unit of **1c** having DP_n of 50 (the observed peak at $m/z = 5071.1$, corresponding to the Na^+ adduct, Figure 2) and one unit of **1c** having DP_n of 90 (the observed peak at $m/z = 8110.8$, corresponding to the Na^+

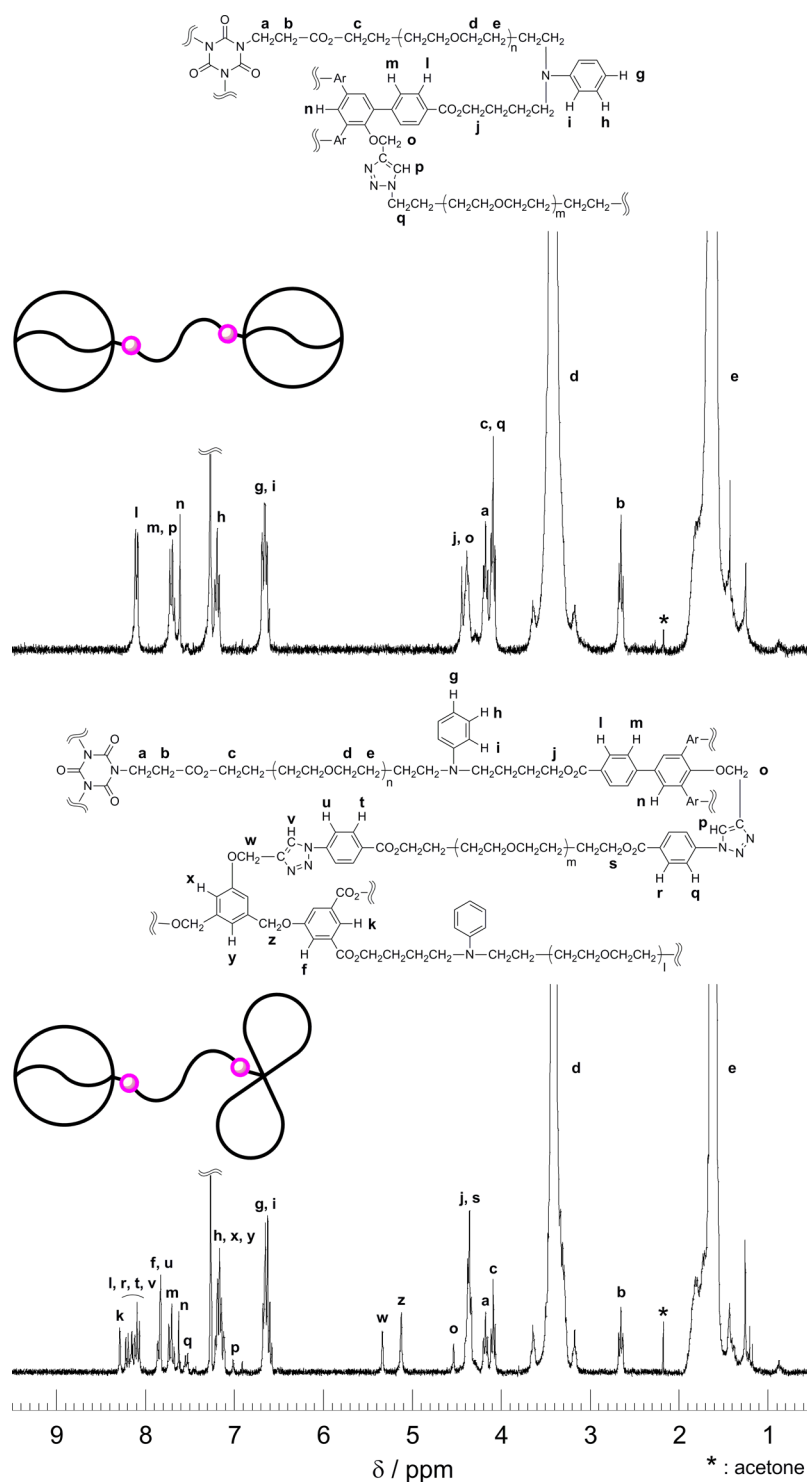


Figure 8. 300 MHz ¹H NMR spectra of (top) a *fused-bridged* (double-*theta* form) hybrid tetracyclic poly(THF) (IVa) and (bottom) a *fused-bridged*-*spiro* hybrid tetracyclic poly(THF) (IVb) (CDCl₃, 40 °C).

adduct of 8110.52, Figure S8, bottom), coincided with the sum of the peak mass values of Ic and Iic.

CONCLUSIONS

We have constructed a variety of tricyclic polymer topologies having a mixture of a dicyclic (*theta*- or *eight*-shaped) and a simple ring unit (IIIa, IIIb, and IIIc), and moreover, unprecedented tetracyclic topologies including double-*theta* (IVa) and another composed of three elemental dicyclic units

of *theta*-, *eight*- and *manacle*-forms (IVb), through effective *click*-linking of complementarily reactive *kyklo*-telechelic pre-cursors which are obtainable by means of the ESA-CF protocol. These products were then fully characterized by means of ¹H NMR, MALDI-TOF mass, FT-IR, and SEC techniques. The achievements described here together with future challenges will promise to push forward the current frontier of the *topological polymer chemistry*, and eventually to realize a conceptually novel polymer material design principle by

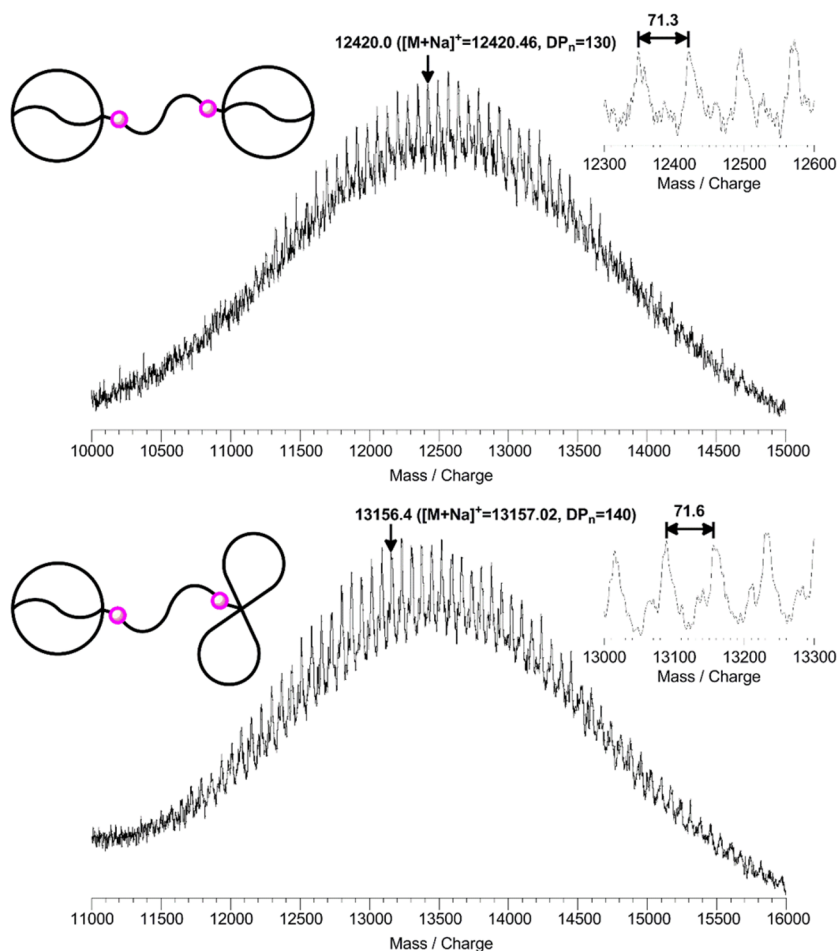


Figure 9. MALDI–TOF mass spectra of (top) a *fused-bridged* hybrid (double-*theta* form) tetracyclic poly(THF) (**IVa**) and (bottom) a *fused-bridged-spiro* hybrid tetracyclic poly(THF) (**IVb**). (Linear mode, matrix: dithranol (for **IVa**) and DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) (for **IVb**) with sodium trifluoroacetate. DP_n denotes the number of monomer units in the product.)

tuning their basic polymer properties based on their nonlinear topologies

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b00637.

Experimental section and ^1H NMR of **1d**, **IIa**, **IIb**, and **IIc** and the relevant precursors, MALDI–TOF mass of **1d**, **IIa**, **IIb**, and **IIc** and the relevant precursors, SEC of **Ic** and the star precursor, IR of **IIIa**, **IIIb**, **IIIc**, **IVa**, and **IVb** and the relevant precursors (PDF)

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Notes

The authors declare no competing financial interest

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■ DEDICATION

[‡]This paper is dedicated to the memory of Professor Teiji Tsuruta (1920–2015).

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