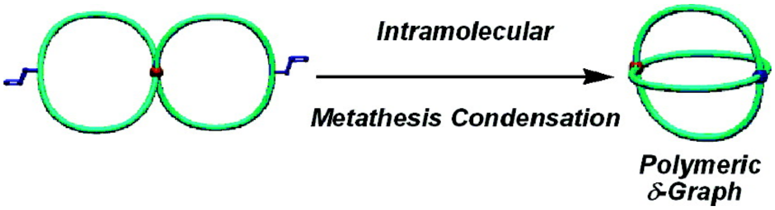
Article

# Construction of Polymeric δ-Graph: A Doubly Fused Tricyclic Topology

Yasuyuki Tezuka, and Kohsuke Fujiyama

*J. Am. Chem. Soc.*, **2005**, 127 (17), 6266-6270• DOI: 10.1021/ja042198j • Publication Date (Web): 08 April 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES

# Construction of Polymeric $\delta$-Graph: A Doubly Fused Tricyclic Topology

Yasuyuki Tezuka* and Kohsuke Fujiyama

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

Received December 27, 2004; E-mail: ytezuka@o.cc.titech.ac.jp

---

***Abstract:*** A doubly fused tricyclic polymer architecture, corresponding to a $\delta$-graph, has been constructed effectively through metathesis polymer cyclization (MPC) of an 8-shaped dicyclic polymer precursor having two allyl groups placed at opposite positions of the two rings of the 8-shaped structure. The 8-shaped polymer precursor has been obtained through the covalent conversion of an electrostatic self-assembly (composed of two units of the linear poly(tetrahydrofuran)s, poly(THF)s, having pyrrolidinium salt end groups and having a pendant allyl group at the middle of the chain, carrying a tetrafunctional carboxylate counteranion) by the heating treatment under appropriate dilution to cause the ring-opening reaction of pyrrolidinium salt groups by carboxylate anions.

---

## Introduction

Topologically attractive molecules have been an ongoing synthetic challenge.[1] Remarkable achievements have recently been observed in the construction of complex loop topologies, either based on DNA chains[2] or on intriguing artificial molecular motifs through their self-assembly processes, leading to knots[3] and catenanes,[4] including a Borromean ring.[5] Besides scientific interests, these are now recognized as a prototype of molecular devices and molecular machines to realize nanotechnology.[6] Multiply fused loop topologies have been another class of appealing synthetic targets. These include such doubly fused loops as $\alpha$, $\beta$, $\gamma$, and $\delta$-graph constructions[7] as well as further complex and topologically significant constructions such as a triply fused $K_{3,3}$ and a quadruply fused $K_5$ graphs (Scheme 1).[8] The construction of such unique molecular architectures has been attained, in which their chemical structures can be represented by the molecular graphs equivalent to $K_{3,3}$ and $K_5$ graphs.[8]

In these molecular structures, however, the flexible conformational motion of the skeletal segments between junctions is seldom achieved, although such a property is considered as a characteristic feature of topological geometry. On the contrary, randomly coiled macromolecular structures consisting of long and flexible *synthetic* polymer segments are regarded as more relevant to topological geometry. These topological structures are characterized first by their principal geometric parameters, i.e., the absence or the presence (and the number) of termini (end groups) and junctions (branch points).[9] For example, the topology of a flexible-ring polymer molecule is characterized by the absence of termini and is regarded as equivalent to that of a triangle or square but distinctive as that of an open-chain linear polymer molecule having two termini. Such topological graphic representation of flexible polymer molecules is in contrast with that of small (or shape-persistent) molecules, in which each bond length and bond angle is considered as an

---

(1) (a) Flapan, E. *When topology meets chemistry. A topological look at molecular chirality*; Cambridge University Press: Cambridge, UK, 2000. (b) Sauvage, J.-P.; Dietrich-Buchecker, C. Eds. *Molecular catenanes, rotaxanes and knots*; Wiley-VCH: Weinheim, Germany, 1999. (c) Semlyen, J. A., Ed. *Cyclic Polymers*, 2nd ed.; Kluwer: Dordrecht, The Netherlands, 2000. (d) Walba, D. M. *Tetrahedron* **1985**, *41*, 3161−3212. (e) Chambron, J.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Top. Curr. Chem.* **1993**, *165*, 131−162.

(2) (a) Seeman, N. C. *Angew. Chem., Int. Ed.* **1998**, *37*, 3220−3238. (b) Sa-Ardyen, P.; Jonoska, N.; Seeman, N. C. *J. Am. Chem. Soc.* **2004**, *126*, 6648−6657 and references therein.

(3) (a) Safarowsky, O.; Nieger, M.; Fröhlich, R.; Vögtle, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 1616−1618. (b) Perret-Aebi, L.-E.; von Zelewsky, A.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4482−4485. (c) Lukin, O.; Kubota, T.; Okamoto, Y.; Kaufmann, A.; Vögtle, F. *Chem. Eur. J.* **2004**, *10*, 2804−2810 and references therein.

(4) Wang, L.; Vysotsky, M. O.; Bogdan, A.; Bolte, M.; Boehmer, V. *Science* **2004**, *304*, 1312−1314 and references therein.

(5) (a) Chichak, K. S.; Cantrill, S. J.; Pease, A. R.; Chiu, S.-H.; Cave, G.W. V.; Atwood, J. L.; Stoddart, J. F. *Science* **2004**, *304*, 1308−1312. (b) Mao, C.; Sun, W.; Seeman, N. C. *Nature* **1997**, *386*, 137−138. (c) C. A. Schalley, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 4399−4401.

(6) (a) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines: A Journey into the Nanoworld*; Wiley-VCH: Weinheim, Germany, 2003. (b) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391. (c) Badjic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845−1849. (d) Lehn, J.-M. *Science* **2002**, *295*, 2400−2403. (e) Seeman, N. C. *Nature* **2003**, *421*, 427−431. (f) Shin, W. M.; Quispe, J. D.; Joyce, G. F. *Nature* **2004**, *427*, 618−621. (g) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4098. (h) Rowan, S. J.; Cantrill, S. J.; Cousins, G.R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 898−952.

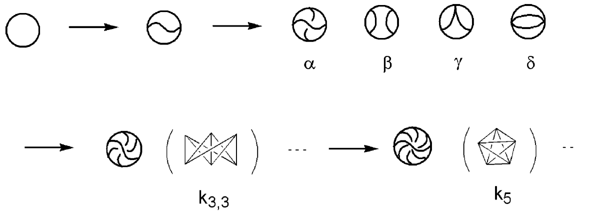
(7) (a) Essam, W.; Fisher, M. E. *Rev. Mod. Phys.* **1972**, *43*, Suppl., 271−282. (b) Balaban, A. T. *Rev. Roum. Chim.* **1973**, *18*, 635−653. For some examples of polycycloalkanes having doubly fused tricyclic topologies, (c) Rasmussen, D. R.; Radom, L. *Chem. Eur. J.* **2000**, *6*, 2470−2483. (d) Takemura, H.; Kon, N.; Yasutake, M.; Nakashima, S.; Shinmyuzu, T.; Inazu, T. *Chem. Eur. J.* **2000**, *6*, 2334−2337. (e) Takimiya, K.; Thorup, N.; Becher, J. *Chem. Eur. J.* **2000**, *6*, 1947−1954. For shape-persistent multiply fused loop topologies, (f) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402−413. (g) Yoshizawa, M.; Kusukawa, T.; Fujita, M.; Yamaguchi, K. *J. Am. Chem. Soc.* **2000**, *122*, 6311−6322.

(8) For a $K_{3,3}$ topology, (a) Chen, C.-T.; Gantzel, P.; Siegel, J. S.; Baldridge, K. K.; English, R. B.; Ho, D. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2657−2660. For a $K_5$ topology, (b) Kuck, D. *Liebigs Ann. Recl.* **1997**, 1043−1057.

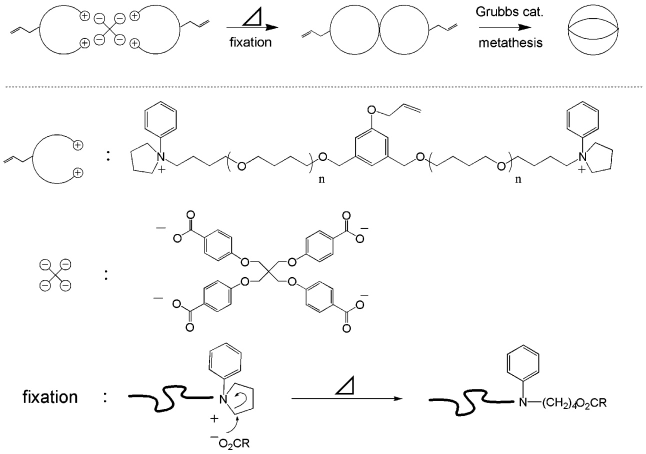
(9) Tezuka, Y.; Oike, H. *J. Am. Chem. Soc.* **2001**, *123*, 11570−11576.

10.1021/ja042198j CCC: $30.25

***Scheme 1.*** Fused Loop Topologies



***Scheme 2.*** Synthesis of Polymeric δ-Graph



invariant Euclidian geometric parameter. Hence, unique insights on intrinsic properties of flexible nonlinear polymer molecules may be obtained through the topological geometry elucidation.[9]

We have recently developed an “electrostatic self-assembly and covalent fixation” process by making use of specifically designed linear or star telechelic polymer precursors having moderately strained cyclic ammonium salt end groups carrying appropriately nucleophilic counteranions such as carboxylates.[10] A variety of single cyclic polymers of different segment components[10a,f−g] and having specific functional groups at designated positions, i.e., cyclic macromonomers[10l] and cyclic telechelics (*kyklo*-telechelics),[10n] have been effectively produced. Moreover, multicyclic polymers having spiranic-loop topologies, i.e., double-cyclic eight-shaped[10a,f] and tricyclic trefoil-shaped[10a] constructions as well as those having singly fused double-cyclic $\theta$-shaped[10a,h] constructions, have been prepared by a direct extension of this self-assembly process. However, multicyclic polymers having doubly fused tricyclic topologies (Scheme 1) have thus far been a challenge, since these constructions are geometrically less symmetric compared with the above-mentioned examples, and are hardly obtainable through a one-step combination of linear or star polymer precursors with end-linking reagents.

Here, we present a first and effective construction of a doubly fused tricyclic loop polymer architecture, **3**, i.e., $\delta$-graph, by combining the “self-assembly and covalent fixation” process[10] and the “metathesis polymer cyclization” with a Grubbs catalyst[11] (Scheme 2). Thus, we have prepared an 8-shaped polymer precursor, **2**, having two allyl groups placed at opposite ends of the two ring units in the 8-shaped structure through the covalent conversion of the electrostatic self-assembly, **1**, composed of two units of a linear polymer precursor having *N*-phenylpyrrolidinium salt end groups and an allyl group at the center of the chain, accompanying one unit of tetrafunctional carboxylate counteranion (Scheme 2). The subsequent intramolecular metathesis condensation of the two allyl groups in **2** could effectively produce a polymeric $\delta$-graph, **3**.[12]

## Results and Discussion

A linear poly(THF) precursor ($M_n$(NMR) of 5000, corresponding to 350 skeletal bond atoms), having *N*-phenylpyrrolidinium salt end groups and an allyl group at the center of the chain, was prepared according to the method reported previously.[13] The subsequent ion-exchange reaction of the pyrrolidinium salt end groups was conducted by the precipitation of the poly(THF) precursor, initially carrying triflate counteranions, into aqueous solution containing an excess of tetracarboxylate anions as a sodium salt form. Such a symmetrical tetracarboxylate was chosen to avoid the formation of isomeric 8-shaped products.

The recovered ion-exchanged product, **1**, was then dissolved in THF under various dilutions. At the concentration of 0.125 g/L, an assembly consisting of two units of the poly(THF) precursor and one unit of a tetracarboxylate counteranion is produced by the de-assembly of the ionically aggregated form (Scheme 2).[11b] The subsequent covalent conversion was performed by heating to reflux in THF for 3 h to cause the ring-opening reaction of the pyrrolidinium salt groups by each carboxylate group in the counteranion (Scheme 2).[14] The 8-shaped polymer precursor, **2**, was obtained in 89% yield after purification by column chromatography with silica gel.

The metathesis condensation reaction of **2** was performed in methylene chloride solution under reflux at the concentration of 0.10 g/L in the presence of a Grubbs catalyst,[11] charged at 1.5 equiv of allyl groups in the 8-shaped polymer precursor. Despite the low concentration ($10^{-5}$ M) of allyl groups of **2** in the reaction solution, the quantitative reaction proceeded within 48 h.[15] The $\delta$-graph polymer product, **3**, was isolated in 67% yield after purification by precipitation into *n*-hexane at −78 °C.

---

(10) (a) Oike, H.; Imaizumi, H.; Mouri, T.; Yoshioka, Y.; Uchibori, A.; Tezuka, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9592−9599. (b) Tezuka, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2905−2917. (c) Tezuka, Y.; Oike, H. *Prog. Polym. Sci.* **2002**, *27*, 1069−1122. (d) Tezuka, Y.; Oike, H. *Macromol. Rapid Commun.* **2001**, *22*, 1017−1029. (e) Oike, H.; Mouri, T.; Tezuka, Y. *Macromolecules* **2001**, *34*, 6592−6600. (f) Oike, H.; Hamada, M.; Eguchi, S.; Danda, Y.; Tezuka, Y. *Macromolecules* **2001**, *34*, 2776−2782. (g) Tezuka, Y.; Mori, K.; Oike, H. *Macromolecules* **2002**, *35*, 5707−5711. (h) Tezuka, Y.; Tsuchitani, A.; Yoshioka, Y.; Oike, H. *Macromolecules* **2003**, *36*, 65−70. (i) Tezuka, Y.; Tsuchitani, A.; Oike, H. *Polym. Int.* **2003**, *52*, 1579−1583. (j) Oike, H.; Washizuka, M.; Tezuka, Y. *Macromol. Rapid Commun.* **2001**, *22*, 1128−1134. (k) Tezuka, Y.; Tsuchitani, A.; Oike, H. *Macromol. Rapid Commun.* **2004**, *25*, 1531−1535. (l) Oike, H.; Mouri, T.; Tezuka, Y. *Macromolecules* **2001**, *34*, 6229−6234. (m) Oike, H.; Uchibori, A.; Tsuchitani, A.; Kim, H.-K.; Tezuka, Y. *Macromolecules* **2004**, *37*, 7595−7601. (n) Oike, H.; Kobayashi, S.; Mouri, T.; Tezuka, Y. *Macromolecules* **2001**, *34*, 2742−2744.

(11) (a) Tezuka, Y.; Komiya, R. *Macromolecules* **2002**, *35*, 8667−8669. (b) Tezuka, Y.; Komiya, R.; Washizuka, M. *Macromolecules* **2003**, *36*, 12−17. (c) Trunka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. For the application of metathesis condensation to construct complex loop topologies, (d) Bogdan, A.; Vysotsky, M. O.; Ikai, T.; Okamoto, Y.; Böhmer, V. *Chem. Eur. J.* **2004**, *10*, 3324−3330. (e) Badjic, J. D.; Cantrill, S. J.; Grubbs, R. H.; Guidry, E. N.; Orenes, R.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3273−3278.

(12) Although the metathesis condensation of **2** produces a linking group containing 6 skeletal atoms between the two junction points, we consider the loop length of polymer segments (350 skeletal atoms) is large enough to assume the product **3** as a $\delta$-graph construction.

(13) Oike, H.; Kobayashi, S.; Tezuka, Y.; Goethals, E. J. *Macromolecules* **2000**, *33*, 8898−8903.

(14) Oike, H.; Imamura, H.; Imaizumi, H.; Tezuka, Y. *Macromolecules* **1999**, *32*, 4819−4825.

(15) The concentration of **2** at 0.1 g/L was chosen since the reaction at 0.15 g/L gave the product showing the noticeable higher molecular weight fraction in SEC.

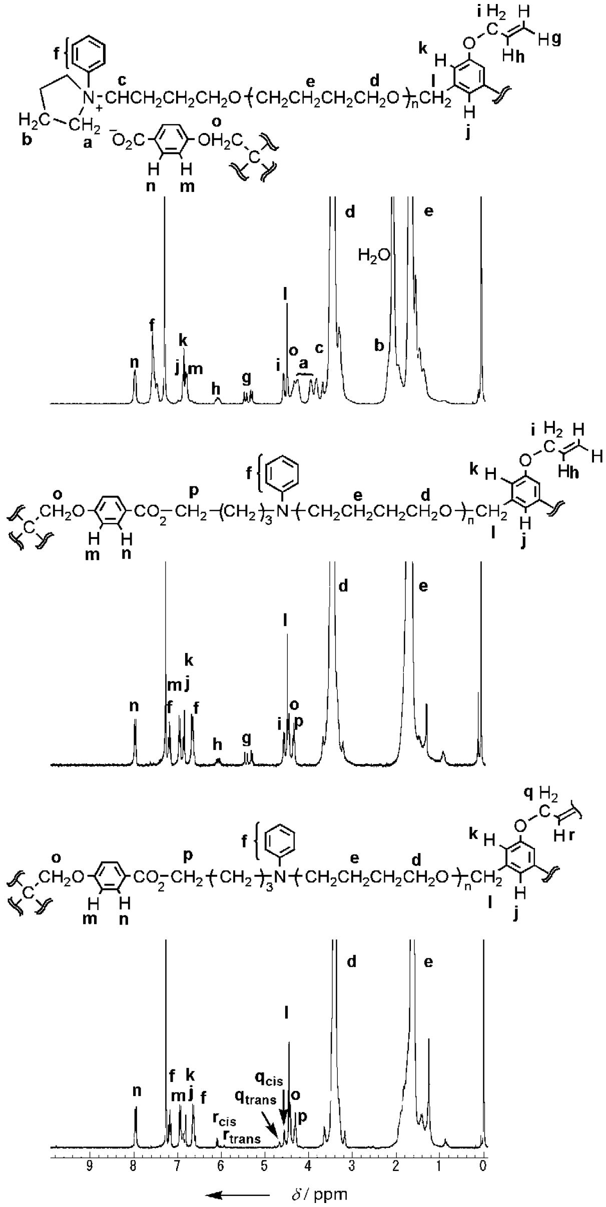


*Figure 1.* 300 MHz $^1$H NMR spectra of the ionically self-assembled product carrying a tetracarboxylate counteranion (**1**; top), the 8-shaped poly(THF) precursor having two allyl groups (**2**; middle) and the *δ*-graph poly(THF) obtained by the metathesis condensation (**3**; bottom). ($CDCl_3$).

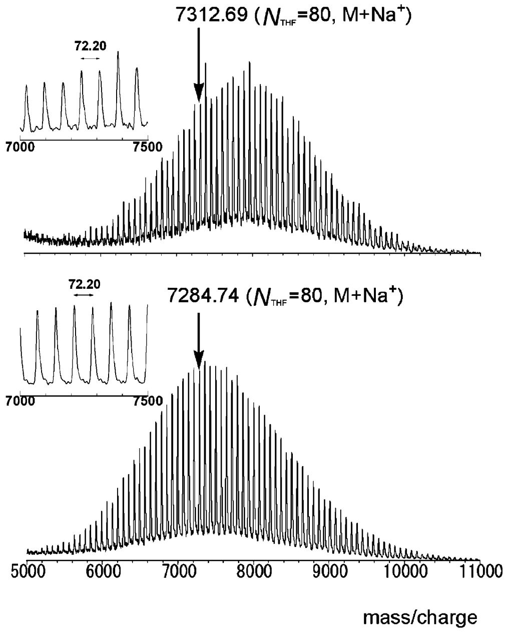


*Figure 2.* MALDI-TOF MS spectra of the 8-shaped poly(THF) precursor having two allyl groups (**2**; top) and the *δ*-graph poly(THF) obtained by the metathesis condensation (**3**; bottom). (linear mode, matrix: dithranol with sodium trifluoroacetate).

The $^1$H NMR comparison of the ionically self-assembled precursor, **1**, and the subsequent covalent 8-shaped poly(THF), **2**, (Figure 1, top and middle) confirmed the selective ring-opening reaction of the pyrrolidinium salt end groups by carboxylate groups in the symmetrical tetrafunctional counteranion. Thus, a set of signals due to the *endo*- and *exo*-methylene protons on the *N*-phenyl pyrrolidinium salt group in **1** are replaced after the heating by a triplet signal at 4.30 ppm due to the ester methylene protons. In addition, signals at 7.15−7.20 and 6.63−6.66 ppm appeared due to the *N*-phenyl protons on the amino-ester group. After the metathesis reaction (Figure 1, bottom), moreover, the signals due to the allyl groups in **2** at 5.05 and 5.35 ppm, and at 4.54 ppm, respectively, are totally removed, and those due to the inner olefinic unit (cis and trans signals at 6.09 and 5.94 ppm, and at 4.56 and 4.67 ppm, respectively) appeared instead. The efficient metathesis condensation was thus confirmed to take place even under applied dilution.

The *δ*-graph poly(THF), **3**, and its 8-shaped precursor, **2**, were then compared by MALDI-TOF MS spectroscopy (Figure 2, top and bottom). The *δ*-graph product, **3**, showed a uniform series of peaks corresponding to poly(THF) (peak interval of 72 mass units); each peak corresponds exactly to the molar mass summing up the linking structure produced by the metathesis condensation reaction of allyl groups in the 8-shaped precursor, **2**. As an example, the peak (assumed to be the adduct with $Na^+$) at 7284.74 corresponds to the product with the number of monomer THF units, $N_{THF}$ of 80, $(C_4H_8O) \times 80 + C_{93}H_{96}N_4O_{14}$, plus $Na^+$ as 7284.297. The 8-shaped polymer precursor, **2**, also showed a major series of the peaks corresponding to the $Na^+$ adduct. Thus, the peak (assumed to be the adduct with $Na^+$) at 7312.69 corresponds to the product with the $N_{THF}$ of 80, $(C_4H_8O) \times 80 + C_{95}H_{100}N_4O_{14}$, plus $Na^+$ as 7312.328. Since the *δ*-graph poly(THF) product, **3**, is produced from the 8-shaped precursor, **2**, by the elimination of an ethylene molecule, their molecular weights differ by 28 mass units. This was confirmed by the two TOF MS spectra shown in Figure 2. These results unequivocally indicate the formation of *δ*-graph poly(THF)s, **3**, having a series of monomer THF units.

The hydrodynamic volumes, corresponding to the three-dimensional (3D) size of the randomly coiled polymers, are dependent on their topologies.[16] Thus, SEC measurements were carried out to observe the topology effect on the 3D size of the obtained polymer products (Figure 3). The results are summarized in Table 1. First, the 8-shaped product, **2**, was compared with its linear precursor (Figure 3, top and middle). The peak

---

[16] (a) Gorbunov, A. A.; Vakhrushev, A. V. *Polymer* **2004**, *45*, 6761−6770. (b) Gorbunov, A. A.; Vakhrushev, A. V. *Polymer* **2004**, *45*, 7303−7315. (c) Arrighi, V.; Gagliardi, S.; Dagger, A. C.; Semlyen, J. A.; Higgins, J. S.; Shenton, M. J. *Macromolecules* **2004**, *37*, 8057−8065 and references therein.

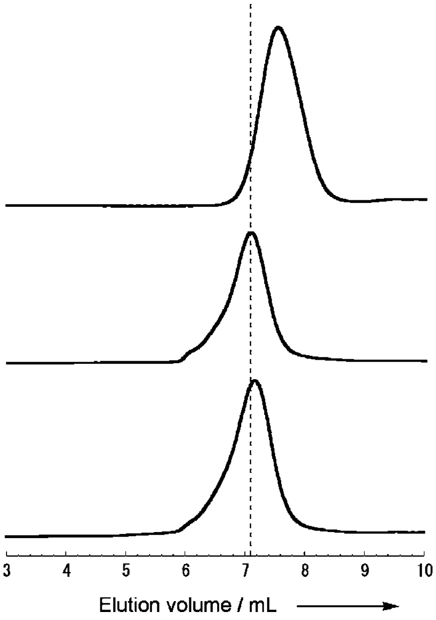


***Figure 3.*** SEC traces (RI) of a linear poly(THF) precursor analogue (top), the 8-shaped poly(THF) precursor having two allyl groups (**2**; middle) and the δ-graph poly(THF) obtained by the metathesis condensation (**3**; bottom). (TSK G3000HXL, eluent: THF, 1.0 mL/min)

***Table 1.*** SEC Analysis of 8-Shaped and δ-Graph Polymers

| liner poly(THF) precursor | | | 8-shaped polymer | | | δ-graph polymer | | |
|---|---|---|---|---|---|---|---|---|
| $M_n$(NMR)[a] | $M_p$(SEC)[b] | PDI[c] | $M_p$(SEC)[b] | PDI[c] | $M_p$(SEC)/ $M_n$(NMR)[d] | $M_p$(SEC)[b] | PDI[c] | $M_p$(SEC)/ $M_n$(NMR)[d] |
| 5000 | 4800 | 1.11 | 7800 | 1.16 | 0.82 | 7000 | 1.18 | 0.63 |

[a] The number-average molecular weight determined by NMR. [b] The peak-molecular weight determined by SEC with a calibration using linear polystyrenes by a conversion factor of 0.056.[19] [c] The polydispersity index determined by SEC. [d] A measure of the hydrodynamic volume ratio between the 8-shaped and linear polymers, and the δ-graph and linear polymers.

molecular weight, $M_p$(SEC), as a measure of the hydrodynamic volume of the products in solution, of the 8-shaped product ($M_p$(SEC) = 7800) was notably higher, but less than twice that of the linear precursor ($M_p$(SEC) = 4800), indicative of the formation of the cyclic product having the smaller 3D size than the linear counterpart of the relevant chain length.[17] Moreover, the ratio between the $M_p$(SEC) and the number-average molecular weight obtainable by NMR, $M_n$(NMR), i.e., $M_p$(SEC)/$M_n$(NMR), was taken as a quantitative measure of the hydrodynamic volume ratio between the 8-shaped and the corresponding linear polymers. The degree of the contraction of the 3D size for the 8-shaped polymer against the linear counterpart was thus estimated to be 0.82.

The δ-graph product, **3**, obtained subsequently by the metathesis condensation of the 8-shaped precursor, **2** (Figure 3, bottom), retained a nearly symmetrical SEC profile, with its hydrodynamic volume marginally smaller ($M_p$(SEC) = 7000) than that of **2**.[18] The degree of the contraction of the 3D size for the δ-graph polymer against the linear counterpart was subsequently estimated to be 0.63. It is remarkable that the observed degree of the contraction for the δ-graph polymer is in the same range of the θ-shaped polymer having a singly fused, double cyclic topology (0.61−0.63).[10h] This could be accounted for by the repulsive interaction between densely emanating branches, i.e., four arms from two junctions, or by the exclusion volume effect by the presence of the four polymer chains within the restricted loop structure.

## Conclusions

A doubly fused tricyclic, δ-graph poly(THF) has been synthesized in satisfactory yields through the intramolecular metathesis condensation of the 8-shaped polymer precursor having two allyl groups in the presence of a Grubbs catalyst. Further applications of metathesis condensation or other coupling processes with multicyclic polymer precursors obtainable by an "electrostatic self-assembly and covalent fixation" process are now in progress to construct various multicyclic polymer topologies, including α, β, and γ graphs and ultimately $K_{3,3}$ graph.

## Experimental Section

**Materials.** A linear poly(THF) precursor having *N*-phenylpyrrolidinium salt end groups and an allyl group at the center of the chain was prepared according to the method reported previously (the number-average molecular weight by NMR, $M_n$(NMR), of 5000 and PDI of 1.11).[13] $^1$H NMR spectrum of the poly(THF) precursor is shown in S-Figure 1 (Supporting Information). The molecular weight measurements by SEC and by MALDI-TOF MS techniques were performed after the covalent conversion of the pyrrolidinium salt end groups by the ring-opening reaction with benzoate counteranion. MALDI-TOF MS spectrum of the obtained poly(THF) is shown in S-Figure 2 (Supporting Information). A tetracarboxylate sodium salt used in the present study was prepared as reported before.[14] A Grubbs catalyst, ruthenium(II) dichloride phenylmethylene bis(tricyclohexylphosphine) [$RuCl_2(PCy_3)_2({=}CHPh)$], was purchased from Aldrich, and used without further purification. THF (99.5%, Kanto Chemical Co., Inc.) was distilled over Na wire. Methylene chloride (99.0%, Kanto Chemical Co., Inc.) was distilled over $CaH_2$. Other reagents were used as received otherwise noted.

**Preparation of 8-Shaped Poly(THF) Having Two Allyl Groups.** A linear poly(THF) precursor having *N*-phenylpyrrolidinium salt end groups and an allyl group at the center of the chain (69.5 mg, 16.3 × $10^{-3}$ mmol) was dissolved in 1.0 mL of THF, and the resulting solution was added dropwise into an ice-cooled aqueous solution (100 mL) containing tetracarboxylate sodium salt (95.2 mg). The precipitate of ion-exchanged product, **1**, was collected by filtration, and the yield was 70.8 mg, which contains a small amount of water to prevent uncontrolled ring-opening reaction. Then, **1** (39.2 mg) was dissolved in 320 mL of THF and heated to reflux for 3 h. The covalent-converted product was isolated by evaporating the solvent and was purified by column chromatography with silica gel. The yield of **2** thus obtained was 34.9 mg. $^1$H NMR of **1** ($CDCl_3$): δ 1.32−1.78 (m, $CH_2CH_2O$), 3.30−3.60 (m, $CH_2CH_2O$), 3.79 (m, 8H, *endo*-$NCH_2$), 3.91 (m, 8H, *exo*-$NCH_2$), 4.21 (m, 8H, *endo*-$NCH_2$), 4.29 (s, 8H, $CCH_2O$), 4.60 (s, 8H, $ArCH_2O$), 4.54 (d, 4H, $J$ = 3.9 Hz, $=CHCH_2OAr$), 5.26−5.44 (m, 4H, $CH_2{=}CHCH_2OAr$), 5.98−6.10 (m, 2H, $CH_2{=}CHCH_2OAr$), 6.77 (d, 8H, $J$ = 7.8 Hz, Ar-*H* meta to $CO_2^-$), 6.82 (s, 4H, Ar-*H* ortho to $OCH_2CH{=}$), 6.85 (s, 2H, Ar-*H* para to $OCH_2CH{=}$), 7.44−7.55

---

(17) Theoretical and simulation studies are awaited to show systematically the relationship between various multicyclic polymer topologies and their three-dimensional sizes. For a simple ring polymer, Bloomfield, V.; Zimm, B. H. *J. Chem. Phys.*, **1966**, *44*, 315−323.

(18) The small peak tailing toward the higher molecular weight region was noticeable for **2** and for **3**, along with the increase of their PDIs in comparison with that of the linear precursor analogue. This is presumably due to the presence of minor side products formed by the intermolecular combination of polymer precursors. Also, during the isolation procedure of **3** (the recovery yield of 67.3%), the lower molecular weight component tends to be lost as shown by the increase of the $M_n$(NMR) of **3** (11200) from that of **2** (9500).

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

(m, 20H, N*Ph*), 7.95 (d, 8H, $J$ = 7.5 Hz, Ar-*H* ortho to $CO_2^-$). $^1$H NMR of **2** ($CDCl_3$): $\delta$ 1.45−1.89 (m, C*H*$_2$CH$_2$O), 3.23−3.60 (m, CH$_2$C*H*$_2$O), 4.30 (t, 8H, $J$ = 6.6 Hz, CO$_2$C*H*$_2$), 4.43 (s, 8H, CC*H*$_2$O), 4.46 (s, 8H, ArC*H*$_2$O), 4.54 (d, 4H, $J$ = 5.1 Hz, =CHC*H*$_2$-OAr), 5.26−5.44 (m, 4H, C*H*$_2$=CHCH$_2$OAr), 5.99−6.10 (m, 2H, =C*H*CH$_2$OAr), 6.63−6.66 (m, 12H, Ar-*H* ortho and para to N), 6.82 (s, 4H, Ar-*H* ortho to OCH$_2$CH=), 6.85 (s, 2H, Ar-*H* para to OCH$_2$-CH=), 6.94 (d, 8H, $J$ = 8.7 Hz, Ar-*H* meta to CO$_2$), 7.18 (t, 8H, $J$ = 7.8 Hz Ar-*H* meta to N), 7.96 (d, 8H, $J$ = 8.7 Hz, Ar-*H* ortho to CO$_2$).

**Intramolecular Metathesis Condensation of 8-Shaped Poly(THF) Having Two Allyl Groups.** An 8-shaped poly(THF) precursor having two allyl groups, **2**, (30.0 mg, $3.47 \times 10^{-3}$ mmol) and the Grubbs catalyst (2.47 mg, $3.01 \times 10^{-3}$ mmol) were dissolved in 300 mL of methylene chloride. The solution was heated to reflux for 48 h. After the solvent was removed by evaporation, the product was subjected to the reprecipitation from THF/*n*-hexane cooled in a dry ice/acetone bath. The yield was 20.2 mg (67.3%). $^1$H NMR of **3** ($CDCl_3$): $\delta$ 1.49−1.82 (m, C*H*$_2$CH$_2$O), 3.22−3.59 (m, CH$_2$C*H*$_2$O), 4.31 (t, 8H, $J$ = 5.4 Hz, CO$_2$C*H*$_2$), 4.43 (s, 8H, CC*H*$_2$O), 4.46 (s, 8H, ArC*H*$_2$O), 4.56 (m, 3H, =CHC*H*$_2$OAr, cis isomer), 4.67 (m, 1H, =CHC*H*$_2$OAr, trans isomer), 5.94 (m, =C*H*CH$_2$OAr trans isomer), 6.09 (m, =C*H*CH$_2$OAr cis isomer), 6.64−6.66 (m, 12H, Ar-*H* ortho and para to N), 6.82 (s, 4H, Ar-*H* ortho to OCH$_2$CH=), 6.88 (s, 2H, Ar-*H* para to OCH$_2$CH=), 6.94 (d, 8H, $J$ = 9.9 Hz, Ar-*H* meta to CO$_2$), 7.18 (t, 8H, $J$ = 7.7 Hz Ar-*H* meta to N), 7.95 (d, 8H, $J$ = 9.3 Hz, Ar-*H* ortho to CO$_2$).

**Measurements.** $^1$H NMR spectra were recorded with a JEOL JNM-AL300 apparatus in $CDCl_3$ at ambient temperature. The proton chemical shifts (ppm) were referenced from the signal of tetramethylsilane. MALDI-TOF MS spectra were taken on a SHIMADZU AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser ($\lambda$ = 337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by a linear-positive ion mode. The sample polymer solution (1 g/L) was prepared in THF. The matrix, 1,8-dihydroxy-9(10H)anthracenone (dithranol, Aldrich) and sodium trifluoroacetate (Aldrich), were dissolved in THF (25 and 2 g/L, respectively). The polymer solution (50 $\mu$L) was then mixed with 250 $\mu$L of the matrix solution. A 1 $\mu$L portion of the final solution was deposited onto a sample target plate and allowed to dry in air at room temperature. Mass values were calibrated by the three-point method with insulin $\beta$ (Sigma-Aldrich) at 3497.0 (plus $H^+$), bovine insulin (Sigma-Aldrich) at 5733.5 (plus $H^+$), and myoglobin (Sigma-Aldrich) at 16950.9 (plus $H^+$). SEC measurements were performed using a Tosoh model CCPS equipped with a refractive index detector model RI 8020 and a UV detector model UV 8020 at 254 nm. A column of TSK G3000HXL was employed with THF as an eluent at a flow rate of 1.0 mL/min. In a typical procedure, 40 $\mu$l of sample solution (sample concentration of 1 wt %) was injected.

**Acknowledgment.** This paper is dedicated to Professor Teiji Tsuruta in honor of his 85th birthday. We thank Professor. H. Oike (Tokyo University of Agriculture and Technology) and Dr. K. Adachi for helpful discussions and assistance for the preparation of the manuscript. We are also grateful to Professor M. Kakimoto for our access to the NMR apparatus. This work was supported partly by a grant from the Ministry of Education, Science and Culture, Japan (13450377).

**Supporting Information Available:** $^1$H NMR spectrum of the poly(THF) precursor having *N*-phenylpyrrolidinium salt groups and an allyl group at the center of the chain (S-Figure 1) and MALDI-TOF MS spectrum of the poly(THF) precursor having *N*-phenylpyrrolidinium salt groups and an allyl group at the center of the chain, after the ion-exchange reaction with benzoate to cause the ring-opening reaction (S-Figure 2) This material is available free of charge via Internet at http://pubs.acs.org.

JA042198J