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ARTICLE

Synthesis and Topological Conversion of an 8-shaped Poly(THF) Having a Metathesis-Cleavable Unit at the Focal Position†

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ABSTRACT: A pair of 8-shaped poly(tetrahydrofuran)s, poly(THF)s, having a metathesis-cleavable olefinic unit of isomeric forms at the focal position, **IIa** and **IIb**, has been synthesized through an *electrostatic self-assembly and covalent fixation* (ESA-CF) process using a telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups carrying a tetracarboxylate counteranion containing a *trans*-3-hexenyl group, as equilibrated isomeric forms of **Ia** and **Ib**. The subsequent metathesis cleavage reaction of the olefinic group in **IIa** and **IIb** has been conducted with a second generation Grubbs catalyst in the presence of ethyl vinyl ether. The polymer topology was thus converted from a dicyclic 8-shape into two simple loops having the two distinctive sizes consisting of one and two prepolymer units, **IIIa** and **IIIb**, respectively, corresponding to the linking mode of the two prepolymer segments on the pair of carboxylate groups at either the neighboring or the remote sites of the tetracarboxylate. Moreover, MALDI−TOF mass analysis has been performed for a series of the SEC-fractionated metathesis cleavage products. The absence of any fraction corresponding to polymeric [2]catenane products implies that the entanglement of the two prepolymer segments does not occur even though they are placed spatially close to each other.

Introduction

Cyclic polymers have attracted growing interests in recent years.[1] A variety of effective and controlled synthetic protocols have now been developed for simple to complex cyclic polymers,[2,3] and renewed insights in static and dynamic properties have been revealed for cyclic polymers in contrast to their linear or branched counterparts.[4] New application potentials have been explored extensively from rheology modifiers[4d] to biomedical carriers,[4k] as well as to scaffolds for nanoobjects of unusual forms.[5]

Cyclic and multicyclic polymers having functional groups at the designated positions (*kyklo*-telechelics) are of a significant importance as precursors to construct complex and precisely designed polymer topologies.[6] We have so far reported an *electrostatic self-assembly and covalent fixation* (ESA-CF) process by using telechelic precursors having cyclic ammonium salt groups accompanying carboxylate counteranions having designated functional groups.[7] Not only simple cyclic but also multicyclic polymers having *pendant* reactive groups, including hydroxyl and olefinic groups, at the prescribed positions have been conveniently produced, and subsequently applied to the topological conversion into complex ring-linear and multicyclic constructions.[8] In particular, a *spiro*-type dicyclic, i.e., an 8-shaped, polymer having two *pendant* olefinic groups at the opposite positions of the two ring units has been prepared and subjected to an intramolecular metathesis condensation reaction to construct a doubly-*fused* tricyclic, δ-graph polymer topology.[8]

Moreover, we have prepared a pair of polymeric topological isomers comprised of dicyclic *fused* (θ-shaped) and *bridged* (manacle-shaped) constructions, which include a metathesis-cleavable olefinic group at the prescribed *inner* position in the specific segment component.[9] The subsequent topological conversion by an olefin-cleavage reaction through cross-metathesis was performed to allow the unequivocal assignment of the two isomeric topological forms of the starting θ-shaped and manacle-shaped polymers.[9]

In order to further extend the potential of the topological conversion by the metathesis cleavage process, we have now prepared a dicyclic 8-shaped polymer having an olefinic unit at the focal position. We have subsequently developed a selective process for the metathesis cleavage of the olefinic group placed in the 8-shaped polymer framework by empolying a second generation Grubbs catalyst (Scheme 1).[10] It is notable, in particular, that the two prepolymer chains tend to be placed spatially close to each other during the formation of the 8-shaped polymer construction. This might promote the mutual entanglement of the two randomly coiled polymer chains, leading subsequently to a catenated polymeric product by the subsequent metathesis cleavage of the focal position of the 8-shaped polymer (Scheme 2).[11,12] The structural analysis of the metathesis-cleaved products has been conducted after the SEC-fractionation, to elucidate whether polymeric [2]catenane products are formed. In this connection, we have shown an alternative means for the effective construction of polymer catenanes by making use of the hydrogen-bond interaction with a tailored telechelic precursor and subsequent polymer cyclization by the ESA-CF process.[13]

Results and Discussion

1. Synthesis of an 8-Shaped Poly(THF) Having an Olefinic Group at the Focal Position. A linear poly(THF) precursor (M_n(NMR) of 3.1 kDa, DP$_n$ of 36, corresponding to 180 skeletal bond atoms) having *N*-phenylpyrrolidinium salt groups and carrying triflate counteranions (**1**/triflate) was prepared by the process reported before,[14] and employed for the synthesis of a dicyclic 8-shaped polymer through an *electrostatic self-assembly*

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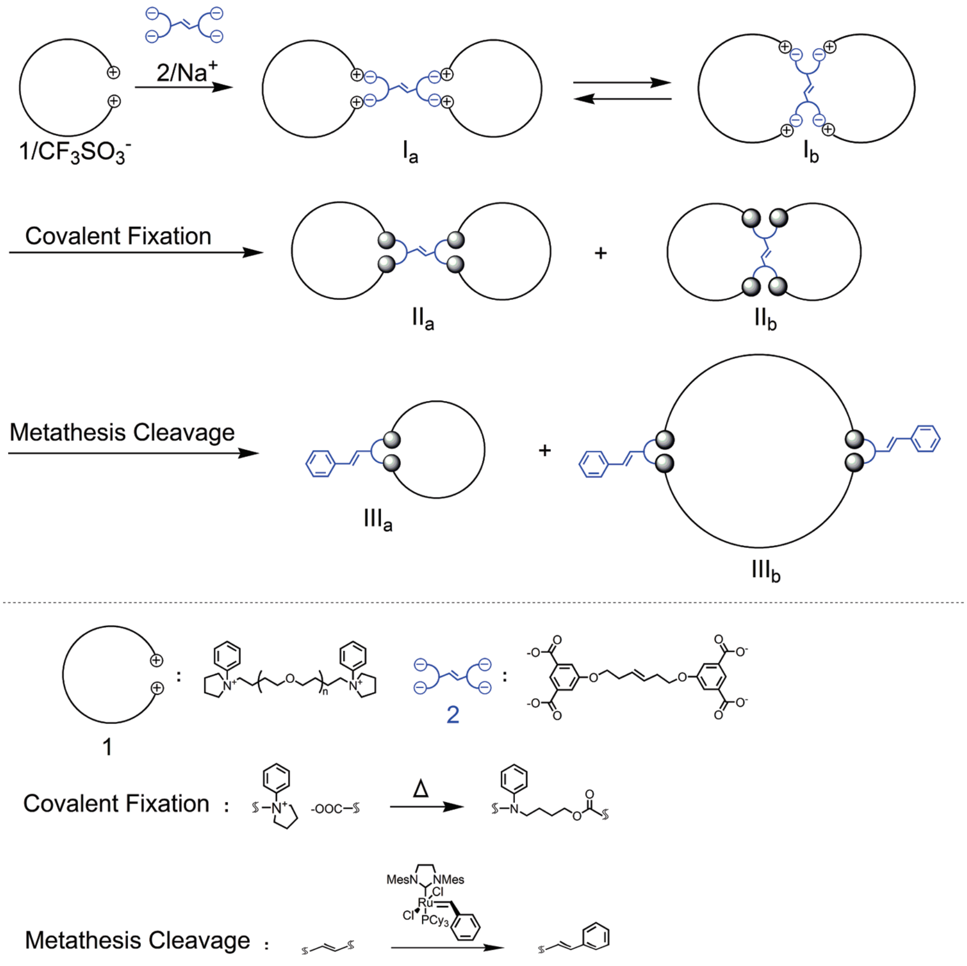
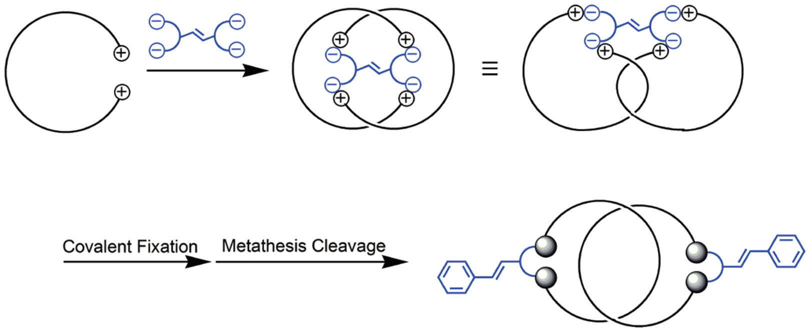
Scheme 1. Synthesis of an 8-Shaped Polymer Having an Olefinic Group at the Focal Position and the Topological Conversion by Metathesis Cleavage



Scheme 2. Formation of a Polymeric [2]Catenane Product through the Metathesis Cleavage of an Entangled 8-Shaped Polymer



and covalent fixation (ESA-CF) process after the ion-exchange reaction with a newly prepared tetracarboxylate containing a metathesis-cleavable olefinic group, i.e., 1,6-bis(3′,5′-dicarboxalatophenoxy)-*trans*-3-hexene, **2** (Scheme 1) (See also Supporting Information for the detailed synthetic procedure of **2**).[15]

An electrostatic polymer self-assembly comprised of two units of **1** and one unit of **2** was produced by precipitation of **1**/triflate into an aqueous solution containing an excess amount of **2** as a sodium salt form.[7] The ^{1}H NMR spectrum of the ion-exchanged product, **Ia** equilibrated with **Ib**, (Figure 1, top) showed signals derived from the components, **1** and **2**, due to the *N*-phenyl group at around 7.4−7.7 ppm and the pyrrolidinium groups at 2.02 and 2.28 ppm as well as the *trans*-3-hexenyl group at 5.55 ppm, respectively. Besides, the signal due to the isophthalate proton is visible at 8.35 ppm along with the signals due to the poly(THF) main chain at around 1.6 and 3.4 ppm.

It is notable that two types of the assembly having distinctive focal unit structures, **Ia** and **Ib**, were produced as seen in Scheme 1, corresponding to the connecting mode of the two prepolymers on a pair of either the neighboring or the remote carboxylate groups in **2**. Nevertheless, both products are regarded commonly as 8-shaped forms since the prepolymer chain of nearly 200 skeletal bond atoms is excessively large in comparison with the size of the focal tetracarboxylate, **2**.

In the obtained self-assemblies, **Ia** equilibrated with **Ib**, the cations and anions balance the charges. And a selective ring-opening reaction proceeded effectively through the nucleophilic substitution by carboxylate counteranions in dilution

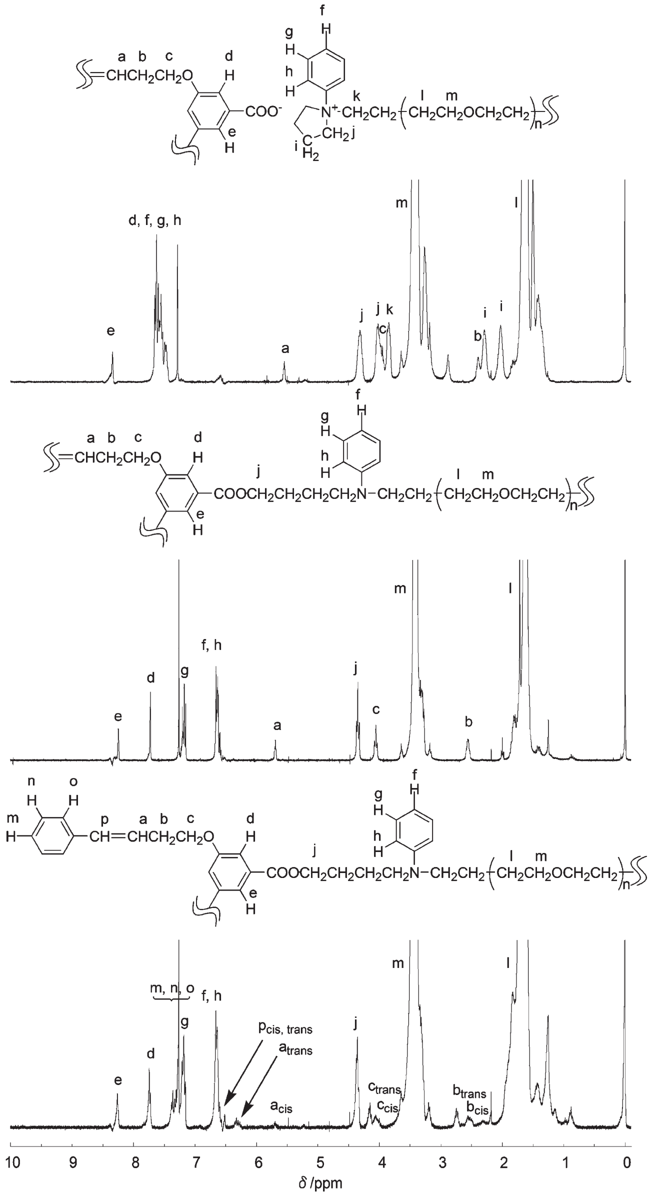


Figure 1. 300 MHz ^{1}H NMR spectra of (top) an electrostatic polymer self-assembly composed of poly(THF) having *N*-phenylpyrrolidinium salt groups at the chain ends, accompanying a tetracarboxylate counteranion having an olefinic group (**Ia** and **Ib**), (middle) the 8-shaped poly(THF) having an olefinic group at the focal position (**IIa** and **IIb**) and (bottom) the metathesis cleavage products (**IIIa** and **IIIb**). ($CDCl_3$, 40 °C).

condition (1.0 g/L) by reflux in $CHCl_3$ for 3 h. By subsequent column chromatography with silica gel, an 8-shaped poly(THF) having a 3-hexenyl unit and the two types of focal structures, **IIa** and **IIb**, was obtained. The random connection of the two prepolymers on the pair of carboxylate groups at either the neighboring or the remote side of the tetracarboxylate should produce **IIa** and **IIb** in a ratio of 1:2.

The ^{1}H NMR spectrum of the covalent conversion product, **IIa** and **IIb** (Figure 1, middle) showed signals due to the ester group at 4.35 ppm and *N*-phenyl group at 6.63 and 7.18 ppm, and due to the *trans*-3-hexenyl group on the tetracarboxylate unit at 2.56, 4.06, and 5.69 ppm, respectively. The signals due to the isophthalate group are also visible at 7.73 and 8.25 ppm. The difference of the linking mode of the polymer chains in **IIa** and **IIb** was not detectable.

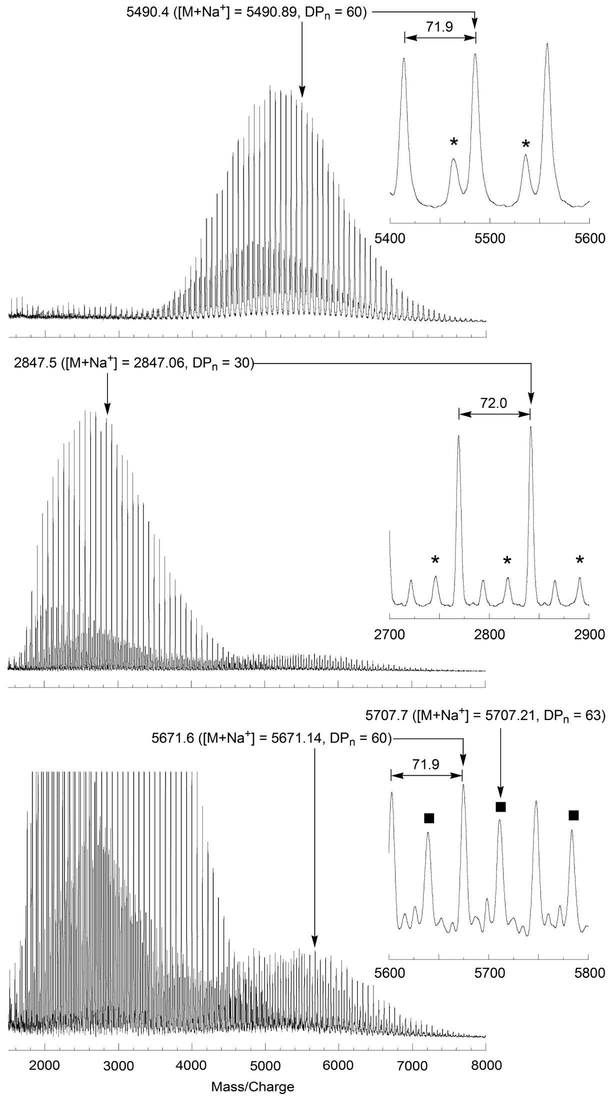


Figure 2. MALDI−TOF mass spectra of (top) an 8-shaped poly(THF) having an olefinic group at the focal position (**IIa** and **IIb**) and the metathesis cleavage products (**IIIa** and **IIIb**) focused on the lower (middle) and higher (bottom) mass areas (linear mode, matrix: dithranol with sodium trifluoroacetate, DP_n denotes the number of monomer units in the product). Key: (■) peak assignable to **IIa**/**IIb**; (∗) peak assignable to the H^+ adduct.

The MALDI−TOF mass spectrum of the 8-shaped products, **IIa** and **IIb** (Figure 2, top) showed a series of peaks corresponding to poly(THF) (peak interval of 72 mass units), and each peak corresponds exactly to the molar mass summing up the linking structure of the 8-shaped poly(THF)s having different focal point structures but identical molar masses, **IIa** and **IIb**, respectively. Thus, the peak (assumed to be the adduct with Na^+) at 5490.4 corresponds to the expected 8-shaped poly(THF), **IIa** and **IIb**, with DP_n (2*n* based on the chemical formula in Scheme 1) of 60, $(C_4H_8O) \times 60 + C_{70}H_{84}N_4O_{10}$ plus Na^+ as 5490.89.

SEC traces of the linear poly(THF) precursor analogue of **1**, obtained by the covalent conversion reaction with benzoate anions, and the 8-shaped product having the two units of **1** are compared in Figure 3 (top and middle, respectively). Both showed unimodal distributions (M_p(SEC) = 3.9 and 4.9 kDa, PDI = 1.23 and 1.13, respectively), and a notably larger hydrodynamic volume (3D size) was observed for the 8-shaped product than the linear analogue. A measure of the 3D size ratio of the 8-shaped polymer product against the

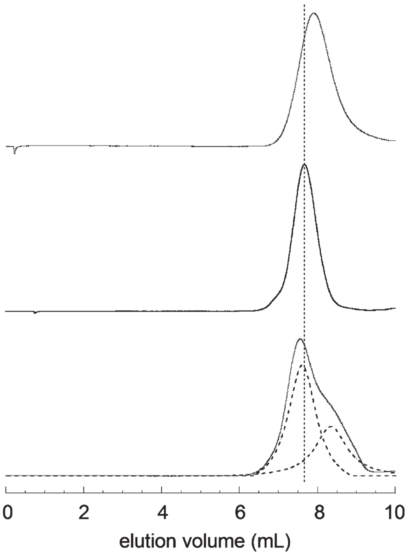
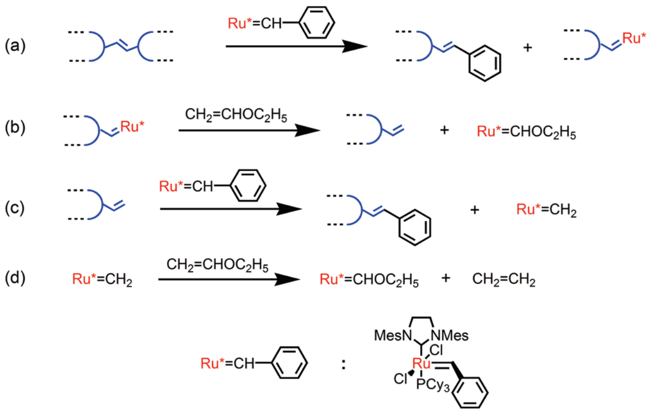


Figure 3. SEC traces of (top) a linear poly(THF) precursor analogue end-capped by benzoate counteranions, (middle) the 8-shaped poly(THF) having an olefinic group at the focal position (**IIa** and **IIb**) and (bottom) the metathesis cleavage products (**IIIa** and **IIIb**) with peak area-fitting by broken lines. (column, G3000HXL; eluent, THF 1.0 mL/min).

Scheme 3. Conversion of the 3-Hexenyl Group into a Benzylidene Group by the Metathesis Cleavage with a Second Generation Grubbs Catalyst



corresponding linear analogue of the same molecular weight, estimated as twice of the apparent peak molecular weight of **1**, was 0.63 and was comparable to those reported before.[7a,8,16] From these results, it was concluded that an 8-shaped poly(THF) having an olefinic unit at the focal position has efficiently been produced.

2. Topological Conversion of the 8-Shaped Poly(THF) by a Metathesis Cleavage Reaction. The 8-shaped poly(THF) having the two types of the focal structure, **IIa** and **IIb**, has been subjected to a metathesis cleavage reaction with a second generation Grubbs catalyst, and with the addition of ethyl vinyl ether, to cause the topological conversion into simple loops of the two distinctive sizes having either one or two prepolymer units, **IIIa** and **IIIb**, respectively (Scheme 1).[17]

In the present metathesis cleavage reaction, a 10-fold excess of the Grubbs catalyst was used against the 3-hexenyl group. In the following step, an excess amount of ethyl vinyl ether was added to extend the reaction further. Thus, in the initial stage, the 3-hexenyl groups in **IIa** and **IIb** were allowed to react with the Grubbs catalyst to form the two metathesis-cleaved products, one having a benzylidene unit together with another having a ruthenium-carbene unit, respectively (Scheme 3a).[18] The following addition of ethyl vinyl ether could transform the ruthenium-carbene unit into a vinylidene unit together with the deactivated ruthenium species having an oxyvinylidene unit (Scheme 3b).[18] Finally, the product having the vinylidene unit could react further with the remaining Grubbs catalyst to give the product having a more stable benzylidene unit by eliminating ethylene (Scheme 3, parts c and d).[19] Accordingly, we recovered the metathesis cleavage products, **IIIa** and **IIIb**, possessing almost exclusively the benzylidene unit.

The ^{1}H NMR spectrum of the metathesis cleavage products, **IIIa** and **IIIb** (Figure 1, bottom) showed that the signals for the *trans*-3-hexenyl group typically at 5.69 ppm (Figure 1, middle) diminished substantially. Instead, the signals due to *trans*- (major) and *cis*-forms (minor) of the 4-phenyl-3-butenoxy group appeared at 6.30 ppm and at 5.69 ppm, respectively.[20] And the latter was overlapped with the signal from the remaining 8-shaped polymer. Besides, the signal for the benzylidene group is visible at around 7.3−7.4 ppm. Moreover, the set of signals at around 4.15/4.06 and 2.75/2.53 ppm are assignable to *trans*- and *cis*-forms of the butenoxy group. The structural difference in **IIIa** and **IIIb** having distinctive ring sizes was thus not detectable.

On the other hand, MALDI−TOF mass spectra of the metathesis cleavage product (Figure 2, middle and bottom, focused on the lower and higher molar mass region, respectively) showed the presence of the two components corresponding to **IIIa** and **IIIb**, respectively. Thus, the two series of peaks both due to poly(THF) (peak interval of 72 mass units) were observed, and each peak corresponds exactly to the molar mass summing up the linking structure of the respective simple ring poly(THF)s having one or two prepolymer units, **IIIa** and **IIIb**, respectively. Thus, in Figure 2 (middle), the peak (assumed to be the adduct with Na^+) at 2847.5 corresponds to the expected ring poly(THF) having one benzylidene unit, **IIIa**, with the DP_n (*n* based on the chemical formula in Scheme 1) of 30, $(C_4H_8O) \times 30 + C_{42}H_{48}N_2O_5$ plus Na^+ as 2847.06. Also in Figure 2 (bottom), the peak (assumed to be the adduct with Na^+) at 5671.6 corresponds to another ring poly(THF) having two benzylidene units, **IIIb**, with DP_n (2*n* based on the chemical formula in Scheme 1) of 60, $(C_4H_8O) \times 60 + C_{84}H_{96}N_4O_{10}$, plus Na^+ as 5671.14. From these results, it is also shown that the molar mass of **IIIb** having two prepolymer units (5671.6, DP_n of 60) coincides with twice of that of **IIIa** having one prepolymer unit (2847.5 − Na, DP_n of 30) according to the topological conversion process depicted in Scheme 1. Moreover, the difference of the molar masses of **IIa**/**IIb** (5490.4 − Na, DP_n of 60) and **IIIb** (5671.6 − Na, DP_n of 60) corresponds exactly to the molar mass of the two benzylidene units. An additional series of peaks assignable to the 8-shaped polymer precursor, **IIa**/**IIb**, was noticeable in Figure 2 (bottom), presumably due to the higher ionization efficiency of **IIa**/**IIb** having a hexenyl group in comparison with **IIIb** having benzylidene units in the applied MALDI−TOF mass condition. Thus, the peak (assumed to be the adduct with Na^+) at 5707.7 is assignable to the 8-shaped poly(THF) precursor, **IIa**/**IIb**, with DP_n of 63.

The SEC trace of the metathesis cleavage product (Figure 3, bottom) further showed the presence of the two components corresponding to **IIIa** and **IIIb** having the larger and smaller 3D size, respectively. The former is noticeable as a shoulder at the smaller 3D size region of the main peak of the higher apparent molecular weight. The ratio of the two components was estimated through peak-fitting to be 39:61. (Figure 3, bottom, broken lines) The portion of **IIIa** formed

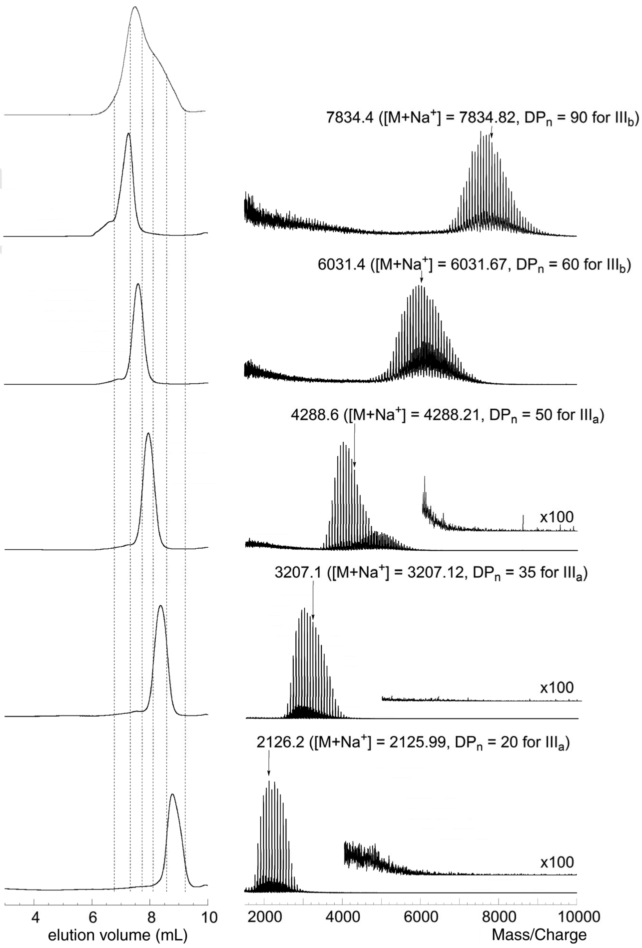


Figure 4. A series of (left) SEC traces and (right) MALDI−TOF mass spectra for the SEC-fractionated samples from the metathesis cleavage products (**IIIa** and **IIIb**). (For SEC, column: G3000HXL, eluent: THF 1.0 mL/min, For MALDI−TOF mass, linear mode, matrix: dithranol with sodium trifluoroacetate, DP$_n$ denotes the number of monomer units in the product.).

through the linking of the two neighboring carboxylate was marginally higher than one (1:2) assumed by the random linking process. By comparing the peak molecular weight of the 8-shaped polymer (M_p(SEC) = 4.9 kDa), **IIa**/**IIb**, with that of the simple ring polymer (M_p(SEC) = 5.5 kDa), **IIIb**, a noticeable enlargement of the 3D size was also confirmed.

Finally, we have elucidated whether any polymer [2]catenane products having identical molar mass with **IIIb** could be produced through the entanglement of the two prepolymer segments placed spatially close by each other. Such a polymeric catenane component, once formed, should possess substantially smaller 3D size than the corresponding linear or cyclic counterparts of the same length.[13,21] Therefore, we have conducted the fractionation of the metathesis cleavage product, **IIIa**/**IIIb**, by means of a preparative SEC technique, and a series of the fractions having different 3D sizes were recovered (Figure 4, left).

A series of ^{1}H NMR spectra for each fraction from the metathesis-cleaved product having different 3D sizes (S-Figure 1, in the Supporting Information) were practically unchanged and correspond to that of **IIIa**/**IIIb** shown before (Figure 1, bottom). On the other hand, MALDI−TOF mass spectra of a series of SEC-fractionated samples showed systematic variation of the peak pattern (Figure 4, right). It was evident that the larger 3D size fractions include the product **IIIb** as a major component, while the smaller 3D counterparts contain exclusively the other product, **IIIa**. In the smaller 3D size fractions, at the same time, any trace of signals were scarcely detectable for the higher molar mass region corresponding to the product **IIIb**, which is also equivalent to the polymeric [2]catenane product consisting of two units of **IIIa**. This result strongly implies, at least in the present system, that the entanglement of the two prepolymer segments appears reluctant to proceed even though they are placed spatially close by each other.

Conclusions

An 8-shaped poly(tetrahydrofuran), poly(THF), having a metathesis-cleavable olefinic unit at the focal position has been synthesized effectively through an *electrostatic self-assembly and covalent fixation* (ESA-CF) process using a telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups carrying a tetracarboxylate counteranion containing a *trans*-3-hexenyl group. The subsequent metathesis cleavage reaction of the olefinic group has been conducted with a second generation Grubbs catalyst in the presence of ethyl vinyl ether, to convert the polymer topology from a dicyclic 8-shape into a simple loop having either one or two prepolymer units, corresponding to the linking mode of the two prepolymer segments on the pair of carboxylate groups in either neighboring or remote side of the tetracarboxylate. Moreover, MALDI−TOF mass analysis has been performed for a series of SEC-fractionated metathesis cleavage products. The absence of any visible fraction corresponding to polymeric [2]catenane products implies that the entanglement of the two prepolymer segments appears reluctant to proceed even though they are placed spatially close by each other.

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Supporting Information Available: Text giving the experimental procedures in detail and a figure showing ^{1}H NMR spectra of the SEC-fractionated samples of the metathesis-cleaved products from the 8-shaped poly(THF) having an olefinic group. This material is available free of charge via the Internet at http://pubs.acs.org.

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