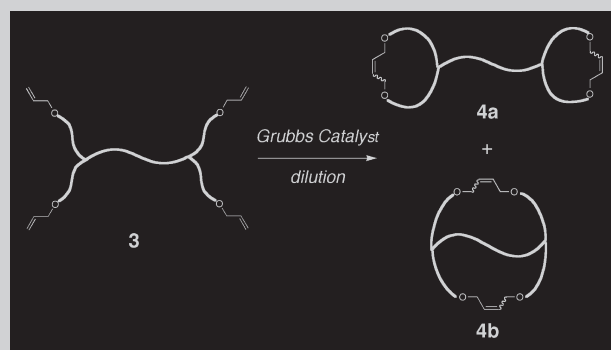


**Summary:** An H-shaped poly(tetrahydrofuran), poly(THF), having four terminal allyl groups was prepared through the covalent conversion of an ionically linked polymer assembly, comprised of four units of cationic poly(THF) having a pyrrolidinium salt and an allyl end group, and one unit of anionic poly(THF) having two dicarboxylate end groups. A pair of polymeric topological isomers, having double-cyclic, manacle, and  $\theta$ -shaped constructions, was subsequently produced under dilution through the intramolecular double metathesis condensation of four terminal allyl groups of the H-shaped precursor.



The formation of manacle-shaped and  $\theta$ -shaped architectures by the intramolecular double metathesis condensation of an H-shaped poly(tetrahydrofuran) with four terminal allyl groups.

# Synthesis of Polymeric Topological Isomers through Double Metathesis Condensation with H-Shaped Telechelic Precursors<sup>a</sup>

Dedicated to Prof. Kiyokazu Imai in honor of his 80th birthday

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## Introduction

Cyclic and multicyclic polymers have gained increasing attention, since these will realize unprecedented properties and functions because of their unique topologies, which are distinct from linear or branched counterparts.<sup>[1–7]</sup> We have recently reported an “electrostatic self-assembly and covalent fixation” process by making use of specifically designed linear and star telechelic polymer precursors having moderately strained cyclic ammonium salt end groups carrying appropriately nucleophilic counteranions like carboxylates.<sup>[8–11]</sup> A variety of single cyclic and multicyclic,

i.e., such double-cyclics as figure 8-shaped,  $\theta$ -shaped, and a triple-cyclic trefoil-shaped, polymer constructions have been effectively produced by this methodology.

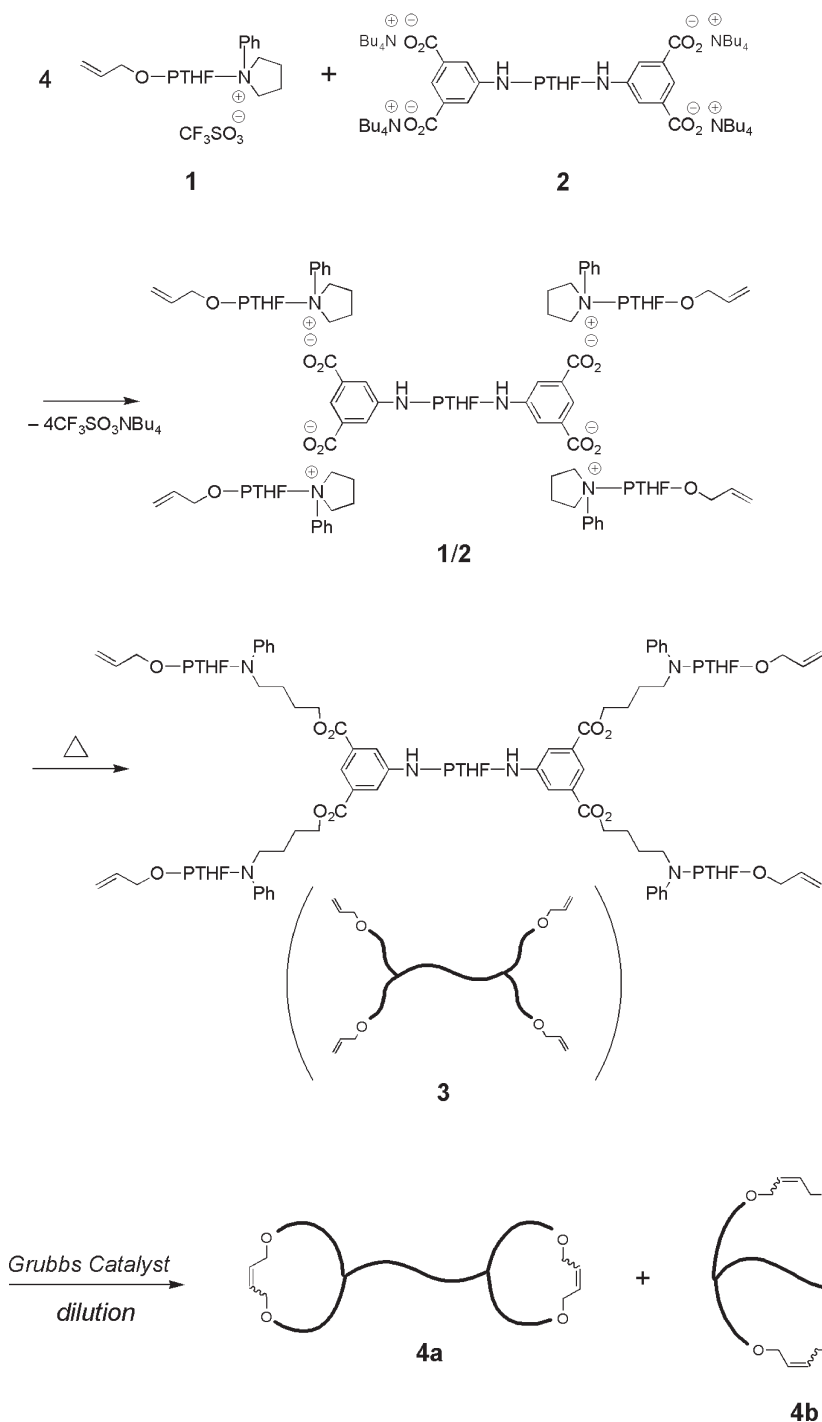
It has been recognized that a pair of dicyclic manacle-shaped and  $\theta$ -shaped polymers were formed simultaneously either from an assembly comprised of linear bifunctional precursors carrying trifunctional carboxylates, or from star trifunctional precursors carrying bifunctional carboxylates, respectively, in which cations and anions balance the charges.<sup>[8,12,13]</sup> These products are identical in their molecular weights and in their chemical compositions, but distinctive in their segment connectivity. Hence, such polymeric products are identified as constitutional isomers, more specifically, topologically distinctive constitutional isomers.<sup>[7]</sup> Moreover, a reversed-phase liquid chromatography (RPC) technique has been revealed as an effective means for the separation of these polymeric isomers.<sup>[8,12,13]</sup>

<sup>a</sup> Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.

It is remarkable that such multicyclic topological isomers are often formed by the equimolar combination reaction between linear or star telechelic polymer precursors with polyfunctional end-linking reagents.<sup>[7]</sup>

The pair of manacle- and  $\theta$ -shaped polymers is obtainable alternatively by the intramolecular end-linking reaction of an H-shaped polymer precursor. Hence, in the present study, we have conducted a double metathesis

condensation with a newly prepared H-shaped poly(tetrahydrofuran), poly(THF), having four terminal allyl groups, **3**, for the production of the polymeric topological isomers having  $\theta$ - and manacle-constructions (Scheme 1). The relevant intramolecular metathesis condensation of a linear poly(THF) having allyl end groups has been recently performed under dilution in the presence of a Grubbs catalyst, ruthenium(II) dichloride phenylmethylene bis(tricyclohex-



Scheme 1.

ylphosphine)  $[\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})]$ , to produce a cyclic poly(THF) effectively.<sup>[14]</sup> It is also worth noting that the intramolecular metathesis condensation of small- to medium-size molecules having multiple olefinic groups has been employed for the construction of a variety of complex loop topologies.<sup>[15–18]</sup>

The  $\theta$ - and manacle-shaped polymeric isomers obtainable by the present metathesis process will be of a particular interest, since they are interconvertible with each other by applying the cross-metathesis reaction,<sup>[19,20]</sup> to provide useful thermodynamic insights on these topological isomers based on randomly coiled, flexible polymer segments.

## Experimental Part

Experimental procedures and  $^1\text{H}$  NMR spectra of the cationic poly(THF) precursor, **1** (S-Figure 1), the anionic poly(THF) precursor, **2** (S-Figure 2), and the isolated double-cyclic poly(THF) topological isomers, **4a** and **4b** (S-Figure 3) are available as *Supporting Information*. Please refer to the footnote on the first page of this article.

## Results and Discussion

### Synthesis of H-Shaped Poly(THF) having Four Terminal Allyl Groups, **3**

An H-shaped polymer is a basic branched model polymer possessing two junction points, along with multi-armed star polymers possessing one junction point.<sup>[21,22]</sup> In the present study, a functional H-shaped polymer precursor having four terminal allyl groups, **3**, has been newly prepared through an “electrostatic self-assembly and covalent fixation” technique.<sup>[8–11]</sup> First, a cationic poly(THF) precursor, having both an *N*-phenylpyrrolidinium salt and an allyl end group, **1**, carrying triflate counteranions, and an anionic polymer precursor, having two dicarboxylate end groups, **2**, carrying tetrabutylammonium counteranions, were prepared, respectively. An ionically linked polymer assembly, **1/2**, comprised of four units of **1** and one unit of **2** was subsequently prepared by the ion-coupling reaction through the coprecipitation of a THF solution of the mixture of **1** and **2** (slightly excess of **1** was charged for the complete ion-exchange reaction of **2**) into aqueous solution to remove tetrabutylammonium triflate from the precipitated product, **1/2** (Scheme 1).

The ionically linked product, **1/2**, was isolated by simple filtration, and subsequently heated to reflux in THF for 3 h to cause the ring-opening reaction of the pyrrolidinium salt groups in **1** by carboxylate anions in **2** (Scheme 1). The H-shaped polymer precursor, **3**, was finally isolated by means of a preparative size exclusion chromatography (SEC) fractionation technique to remove the excess of unreacted **1**.

The  $^1\text{H}$  NMR comparison of the ionically linked precursor, **1/2**, and the isolated H-shaped poly(THF), **3** (Figure 1,

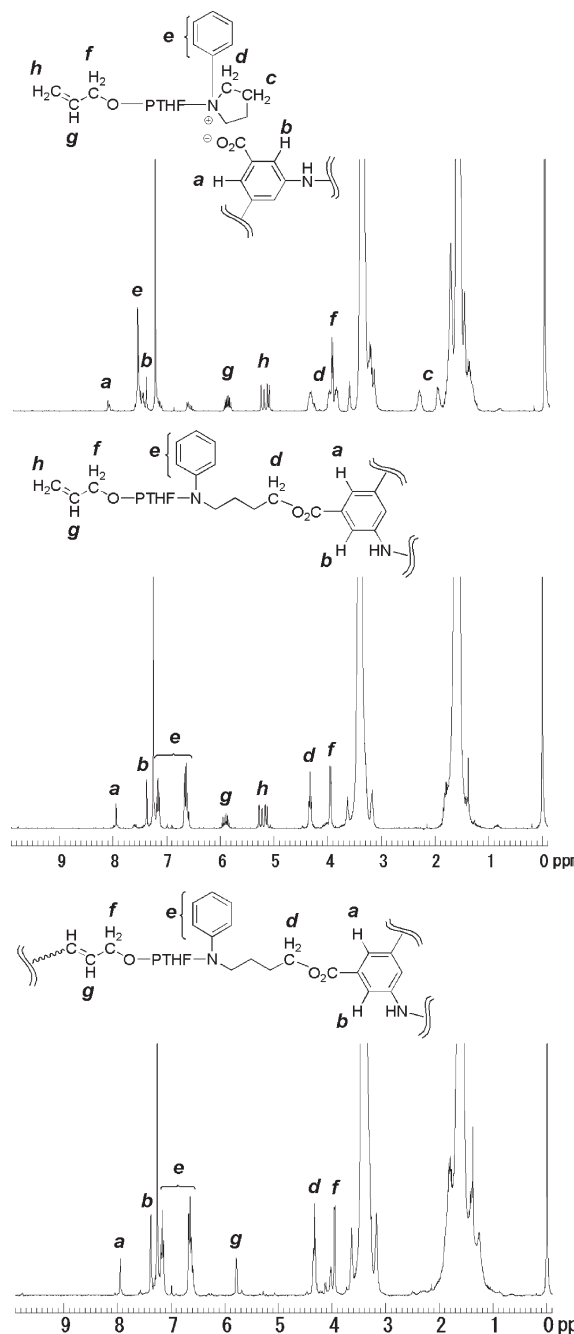


Figure 1. 300 MHz  $^1\text{H}$  NMR spectra (in  $\text{CDCl}_3$ ) of the ionically linked polymer precursor (**1/2**; top), the H-shaped poly(THF) having four terminal allyl groups (**3**; middle), and the metathesis condensation product (bottom).

top and middle) showed that the signals attributed to the *N*-phenylpyrrolidinium salt group of **1/2** are replaced by a triplet signal at 4.33 ppm arising from the ester methylene protons and by signals at 7.14–7.19 and 6.59–6.67 ppm arising from the *N*-phenyl protons on the amino-ester group. IR analysis also showed the formation of ester groups ( $\nu(\text{C}=\text{O}) = 1735\text{ cm}^{-1}$ ) in **3** after the heating of **1/2**.

SEC measurements of the H-shaped polymer product, **3** (Figure 2, C), together with the linear precursor analogues

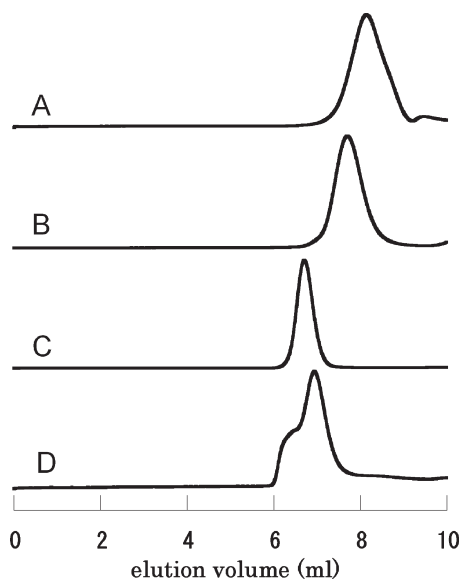


Figure 2. SEC traces (RI) of linear poly(THF) precursor analogues (**1** with end groups ring-opened by benzoate anions; A, and **2** with methyl ester end groups; B), the H-shaped poly(THF) having four terminal allyl groups (**3**; C) and the product after the metathesis condensation (**4**; D) (column: TSK G3000HXL, eluent: THF, flow rate:  $1 \text{ mL} \cdot \text{min}^{-1}$ ).

of **1** and **2** (Figure 2, A and B) showed that **3** possesses a distinctly higher apparent molecular weight ( $\bar{M}_p = 11\,600$ ) than each of the linear precursor analogues ( $\bar{M}_p(\mathbf{1}) = 2\,600$  and  $\bar{M}_p(\mathbf{2}) = 4\,200$ ). Moreover, the branched structure of **3** having a constricted hydrodynamic volume was evidenced

by the apparent molecular weight of **3** ( $\bar{M}_p = 11\,600$ ) being noticeably smaller than its calculated molecular weight (14 600), corresponding to four units of **1** and one unit of **2**. Matrix-assisted laser desorption–ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements, on the other hand, have so far been unsuccessful, presumably because of ineffective ionization of the present products having molecular weights higher than  $10^4$ .

#### Double Metathesis of H-Shaped Poly(THF) having Four Terminal Allyl Groups, **3**

The intramolecular metathesis condensation process has now been recognized as a remarkably versatile synthetic means for the construction of a variety of complex loop topologies.<sup>[14–18,23]</sup> In the present study, the metathesis condensation of **3** was performed in dichloromethane solution at a concentration of  $0.20 \text{ g} \cdot \text{L}^{-1}$  under reflux for 48 h, using a Grubbs catalyst charged at 0.8 eq. of allyl groups in **3** (Scheme 1). The effective metathesis condensation was confirmed to proceed even under applied dilution.

Hence,  $^1\text{H}$  NMR spectroscopy of the product recovered after the metathesis condensation (Figure 1, bottom) showed the signals attributed to inner alkenic groups (*cis* and *trans* signals at 5.78 and 5.68 ppm, and at 3.95 and 4.03 ppm, respectively), in place of the signals attributable to the allyl group of **3** at 5.20 and 5.90 ppm, and at 3.95 ppm, respectively.

The SEC of the metathesis condensation product (Figure 2, D) showed a slightly broadened but nearly

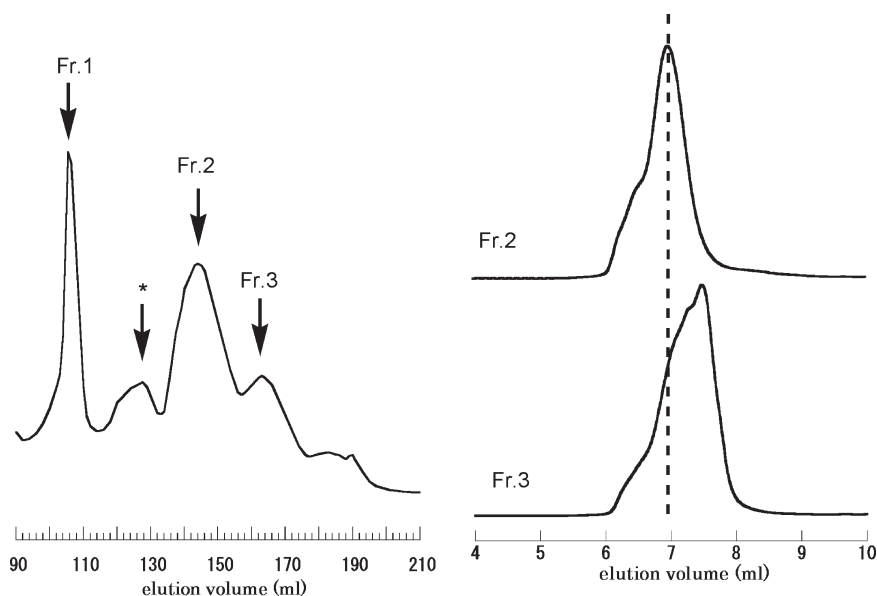


Figure 3. (Left) An RPC trace (UV, 254 nm) of the metathesis condensation product from **3** (column: JAIGEL-ODS-AP, eluent: THF/ $\text{CH}_3\text{CN}$  (51/49, v/v), flow rate:  $2.0 \text{ mL} \cdot \text{min}^{-1}$ , \* = peak for the unassignable product), and (Right) SEC traces (RI) of fraction 2 (top) and fraction 3 (bottom) in the metathesis condensation product from **3**, isolated by the preparative RPC technique (column: TSK G3000HXL, eluent: THF, flow rate:  $1 \text{ mL} \cdot \text{min}^{-1}$ ).

symmetrical main peak, which is accompanied by a minor shoulder peak at the higher-molecular-weight region attributable to the concurrent intermolecular metathesis condensation. The apparent molecular weight of the main peak ( $\bar{M}_p = 11\,400$ ) was observed nearly unchanged from that of precursor, **3**, which implies that intramolecular polymer cyclization has occurred.

As shown in Scheme 1, the two polymeric topological isomers, having manacle- and  $\theta$ -constructions, **4a** and **4b**, respectively, can be obtained by the intramolecular metathesis condensation of **3**. If the linking of the four terminal groups took place randomly, the  $\theta$ - and manacle-isomers could be formed in the ratio of 2/1 (i.e., the  $\theta$ -isomer is the major product).

The reversed-phase chromatography (RPC) technique has been applied to show the formation of these polymeric topological isomers.<sup>[8,12,13]</sup> The RPC of the metathesis product (Figure 3 (left)) showed the two fractions (fractions 2 and 3) corresponding to the relevant polymeric topological isomers (**4a** and **4b**, respectively), besides an additional fraction 1 corresponding to the higher-molecular-weight component formed through the intermolecular metathesis condensation (confirmed by SEC). Hence, fraction 2 was recovered as a major component (43% yield) and fraction 3 was recovered as a minor component (20% yield). <sup>1</sup>H NMR spectra of both fractions (S-Figure 3 in Supporting Information) coincided with each other, and also with that before the fractionation (Figure 1, bottom).

The SEC comparison of the two fractions (Figure 3 (right)) showed, on the other hand, that fraction 2 is noticeably larger in its hydrodynamic volume than fraction 3. Since the manacle-polymer is considered larger in its hydrodynamic volume than the  $\theta$ -polymer,<sup>[8,12,13]</sup> fraction 2 could be assigned as the manacle-isomer **4a** and fraction 3 as the  $\theta$ -isomer **4b**, respectively.

These results imply that during this intramolecular metathesis condensation, the two allyl groups at the near neighborhood positions preferentially reacted with each other to form a manacle-isomer. This is contrary to the hypothetical random combination of the four terminal allyl groups, by which  $\theta$ - and manacle isomers could be formed in the ratio of 2/1. It is also notable that this non-statistic selectivity is in contrast to the relevant "electrostatic self-assembly and covalent fixation" process, where manacle- and  $\theta$ -isomers were formed in the ratio near to those expected from the statistic combination of linear or star-shaped polymer precursors and the end-linking reagents.<sup>[8,12,13]</sup>

In conclusion, a double metathesis condensation was conducted with an H-shaped poly(THF) having four terminal allyl groups, which was prepared through the covalent conversion of an ionically linked polymer assembly, comprised of four units of a cationic precursor having both a pyrrolidinium salt and an allyl end group, and one unit of an anionic counterpart having two dicarboxylate end groups. The formation of a pair of double-cyclic polymeric topo-

logical isomers of manacle- and  $\theta$ -constructions was confirmed by <sup>1</sup>H NMR, SEC, and RPC analyses of the products. Further investigations into the interconversion reaction of the manacle- and  $\theta$ -shaped topological isomers through the cross-metathesis process are in progress in our laboratory.

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