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# Synthesis of Polymeric Topological Isomers Having $\theta$- and Manacle-Constructions with Olefinic Groups at Designated Positions

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ABSTRACT: Dicyclic polymers having $\theta$- and manacle-constructions with olefinic groups at the designated positions have been synthesized through electrostatic self-assembly and covalent fixation using linear precursors having either a pendant or an inner olefinic groups. The formation of the two constitutional isomers having $\theta$- and manacle-constructions has been confirmed by reversed-phase chromatography (RPC) coupled with the matrix assisted laser desorption/ionization time-of-flight (MALDI TOF) mass analysis and by the metathesis cleavage of the inner olefinic group included at the specific position of the two isomer frameworks.

## Introduction

Cyclic and multicyclic polymers, distinct from their linear and branched counterparts by the absence of free chain ends in their topologies, have gained increasing attention, since they could realize unprecedented properties and functions owing to their unique topologies.[1−8] Besides a simple loop (ring) and a loop-and-branch (tadpole)[9] topologies, a series of dicyclic polymers having either 8-,[10−14] $\theta$-,[12,15] or manacle-constructions[12,16,17] have now been obtainable by new synthetic protocols. Remarkably, two of the three dicyclic polymers having $\theta$- and manacle-constructions are formed simultaneously either from three units of a *bifunctional* linear polymer precursor and two units of a *trifunctional* end-linking reagent[12,16] or from two units of a *trifunctional* star polymer precursor and three units of a *bifunctional* end-linking reagent (Scheme 1).[17] The pair of dicyclic polymer products are, thus, identical in their molecular weights and in their chemical compositions, but they are distinctive in their segment connectivity. Hence, these are identified as topologically distinctive constitutional isomers.[18−23]

Such a pair of dicyclic polymers have subsequently been prepared[12,16,17] by an *electrostatic self-assembly and covalent fixation* process with a polymeric self-assembly either from a linear bifunctional or a star-trifunctional precursor having moderately strained cyclic ammonium salt end groups, carrying trifunctional or bifunctional carboxylate counteranions, respectively (Scheme 1). The pair of polymeric topological isomers has also been formed in intramolecular double-metathesis condensation with H-shaped polymer precursor having four allyl terminal groups.[24]

The introduction of relevant functional groups at the prescribed positions in such dicyclic polymer constructions could offer further opportunities not only to construct more complex polymer topologies but also to elucidate their basic geometrical properties. In this regard, we have recently reported a dicyclic, 8-shaped telechelic polymer having two allyl groups at the opposite positions in the two ring units, and the subsequent intramolecular metathesis condensation to produce a doubly fused, tricyclic, i.e., $\delta$-graph polymer.[25]

As an extension of the preceding studies, we show here the preparation of different types of functional dicyclic polymers having either $\theta$- or manacle-constructions, in which two pendant allyl groups or an inner olefinic group are introduced at the designated positions in these dicyclic polymer frameworks (Scheme 2). The formation of the two constitutional isomers has been confirmed by the reversed-phase chromatography (RPC) coupled with MALDI TOF mass analysis, as well as by the metathesis conversion of the two reactive isomer components having either $\theta$- or manacle-constructions.

## Experimental Section

**Preparation of Polymer Precursors.** A poly(THF) precursors having *N*-phenylpyrrolidinium salt end groups (**I**, $M_p$(SEC) = 8700, PDI = 1.24), dicarboxylate end groups (**II**, $M_p$(SEC) = 3500, PDI = 1.22) and *N*-phenylpyrrolidinium salt end groups containing an allyloxy group at the center position ($\mathbf{I_f}$, $M_p$(SEC) = 3200, PDI = 1.31) were prepared by the method detailed before (Scheme 3).[9,24,25]

A poly(THF) with an inner olefinic group and dicarboxylate end groups ($\mathbf{II_f}$, $M_p$(SEC) = 7200, PDI = 1.18) was prepared through the metathesis condensation of a poly(THF) precursor having a dimethyl isophthalate and an allyl end group (**1**) (Scheme 3). Thus, into 300 mL of dry THF was added an allyl trifluoromethanesulfonate initiator in methylene chloride (30 mL), prepared in situ from allyl alcohol (0.79 g, 13.6 mmol) and trifluoromethanesulfonic anhydride (3.45 g, 12.2 mmol) in the presence of 2,6-di-*tert*-butylpyridine (3.05 g, 16.0 mmol), to react at 25 °C for 10 min to produce a monofunctionally living poly(THF). Thereupon, dimethyl 5-aminoisophthalate (9.42 g, 45.1 mmol, in 60 mL of THF) was added to cause an end-capping reaction. The crude product of **1** was recovered by precipitation into ice cooled (<5 °C) hexane, and the residual dimethyl 5-aminoisophthalate was removed by the repeated centrifugation from the chloroform solution. The produced poly(THF) having a dimethyl isophthalate and an allyl end group, **1**, was finally isolated by precipitation into methanol in a dry ice/acetone bath. The yield was 20.1 g. The MALDI TOF mass spectrum of **1** is shown in Figure 1 (top). $^1$H NMR spectra (S-Figure 1, top) and SEC trace (S-Figure 2, top) are shown in the Supporting Information. $^1$H NMR (CDCl$_3$): $\delta$ 1.46−1.77 (m, C*H*$_2$-CH$_2$O), 3.25−3.58 (m, CH$_2$C*H*$_2$O), 3.91 (s, 6H, COOC*H*$_3$), 3.95−3.98 (m, 2H, CH$_2$=CHC*H*$_2$), 5.08−5.31 (m, 2H, C*H*$_2$=CHCH$_2$), 5.83−6.00 (m, 1H, CH$_2$=C*H*CH$_2$), 7.41 (s, 2H, Ar−*H ortho* to N), 7.96 (s, 1H, Ar−*H para* to N). MALDI−TOF mass: 3155.6 (obsd), 3155.39 (calcd for DP$_n$ = 40 with Na$^+$). $M_p$(SEC) = 3600, PDI (SEC) = 1.16.

Then, a poly(THF) having a dimethyl isophthalate and an allyl end group, **1**, (1.02 g, 0.27 mmol) and the first generation Grubbs catalyst (Strem Chem., 99.0 mg, 0.12 mmol) were dissolved in 25

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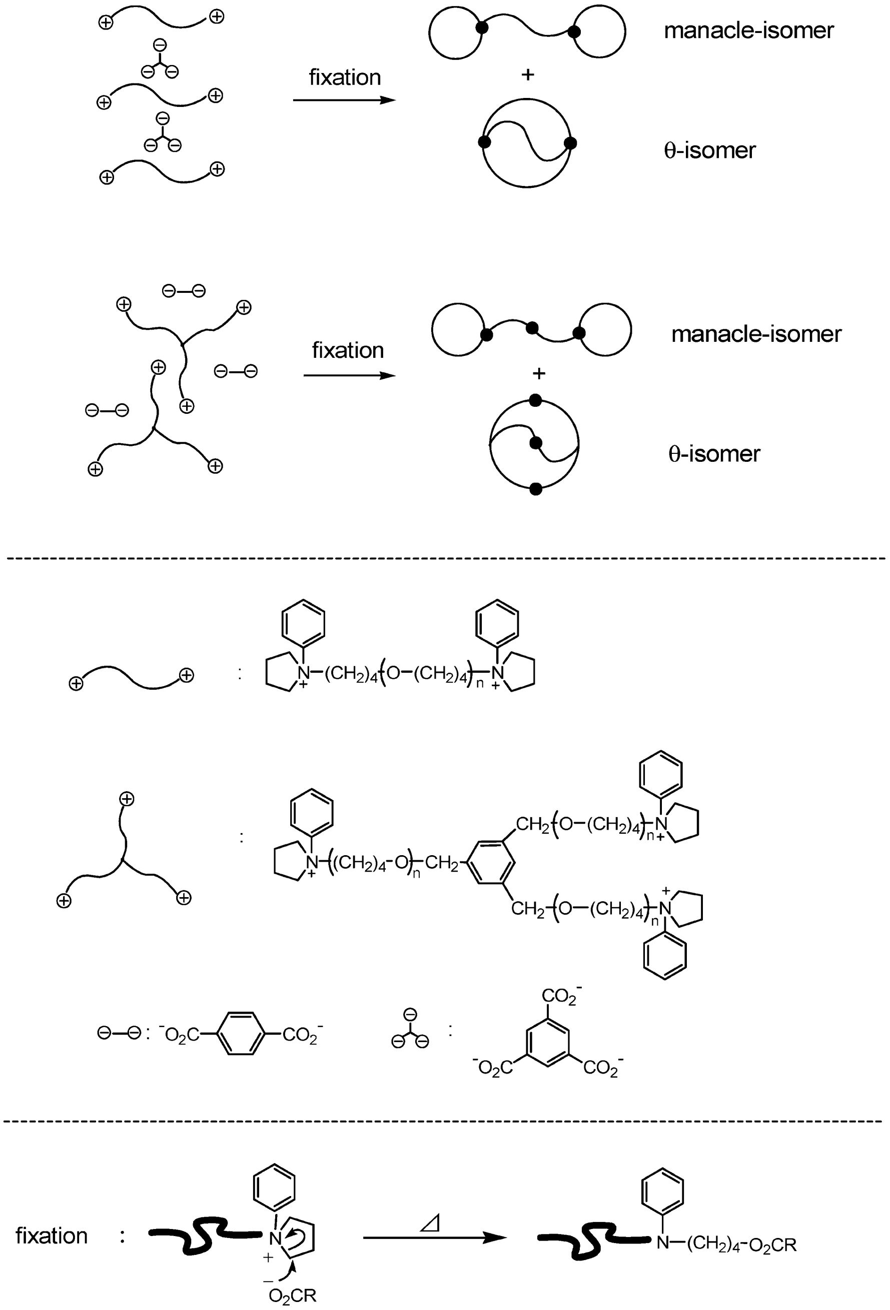
**Scheme 1. Polymeric Topological Isomers Having *θ*- and Manacle-Constructions by Electrostatic Self-Assembly and Covalent Fixation**

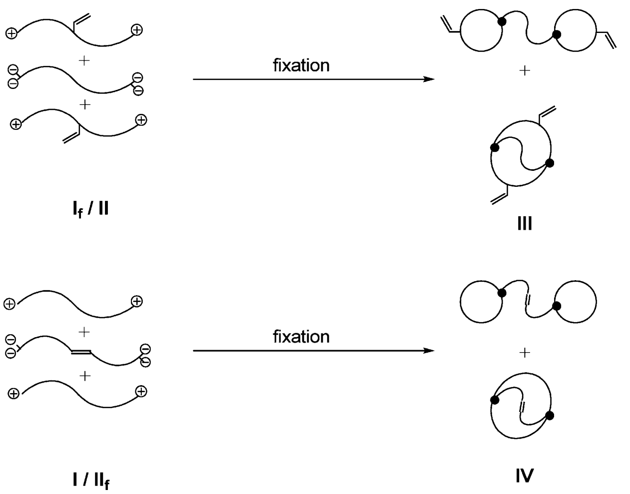


mL of methylene chloride. The solution was heated to reflux for 48 h. After the solvent was removed by evaporation, the product was recovered by the reprecipitation from THF/*n*-hexane in a dry ice/acetone bath. The crude product (1.03 g) was further purified by the preparative SEC fractionation to give a poly(THF) having an inner olefinic group and dimethyl phthalate end groups, **2**. The yield was 0.38 g. MALDI TOF mass spectrum of **2** is shown in Figure 1 (bottom). $^1$H NMR spectrum (S-Figure 1, middle) and SEC trace (S-Figure 2, bottom) are shown in Supporting Information. $^1$H NMR ($CDCl_3$): $\delta$ 1.47−1.76 (m, $CH_2CH_2O$), 3.27−3.54 (m, $CH_2CH_2O$), 3.92 (s, 12H, $COOCH_3$), 3.94−3.98 (m, 4H × 0.89, *cis*-CH=CHC*H*$_2$), 4.01−4.05 (m, 4H × 0.11, *trans*-CH=CHC*H*$_2$), 5.66−5.73 (m, 2H × 0.08, *trans*-C*H*=C*H*), 5.76−5.82 (m, 2H × 0.92, *cis*-C*H*=C*H*), 7.42 (s, 4H, Ar-*H ortho* to N), 7.98 (s, 2H, Ar-*H para* to N). MALDI−TOF mass: 6260.3 (obsd), 6260.77 (calcd for $DP_n = 80$ with $Na^+$). $M_p$(SEC) = 7200, PDI (SEC) = 1.18.

The subsequent alkaline hydrolysis of dimethyl phthalate end groups of **2** was performed as follows. Into a THF solution of **2** (0.38 g in 6 mL) was added a NaOH (82 mg) solution in ethanol/water (3 mL/3 mL) to proceed the reaction at ambient temperature for 48 h. After neutralization by $HCl_{aq}$, the product, poly(THF) having an inner olefinic group and dicarboxylic acid end groups, **3**, was recovered after precipitation into an acidic aqueous solution. The yield was 0.36 g. $^1$H NMR spectrum is shown in S-Figure 1 (bottom) in Supporting Information. $^1$H NMR ($CDCl_3$): $\delta$ 1.48−1.77 (m, $CH_2CH_2O$), 3.27−3.55 (m, $CH_2CH_2O$), 3.93−3.98 (m, 4H × 0.94, *cis*-CH=CHC*H*$_2$), 4.00−4.04 (m, 4H × 0.06, *cis*-CH=CHC*H*$_2$), 5.71−5.75 (m, 2H × 0.04, *trans*-C*H*=C*H*), 5.75−5.81 (m, 2H × 0.96, *cis*-C*H*=C*H*), 7.44 (s, 4H, Ar−*H ortho* to N), 8.02 (s, 2H, Ar−*H para* to N).

**Electrostatic Self-Assembly and Covalent Fixation of Cationic and Anionic Telechelic Precursors to Produce Polymeric Topological Isomers Having *θ*- and Manacle-Constructions.** Two types of electrostatic self-assemblies of cationic and anionic telechelic precursors, $\mathbf{I_f}$/**II** and **I**/$\mathbf{II_f}$, were prepared by a coprecipitation procedure. Thus, for a typical example, an equimolar amount of a cationic telechelic precursors **I** (117 mg, 15 × $10^{-3}$ mmol) carrying triflate counteranions and an anionic counterpart $\mathbf{II_f}$ (58 mg, 7.9 × $10^{-3}$ mmol) carrying tetra-*n*-butylammonium counter-

**Scheme 2. Preparation of Dicyclic Telechelic Polymers Containing Pendant or Inner Olefinic Groups at the Prescribed Positions**

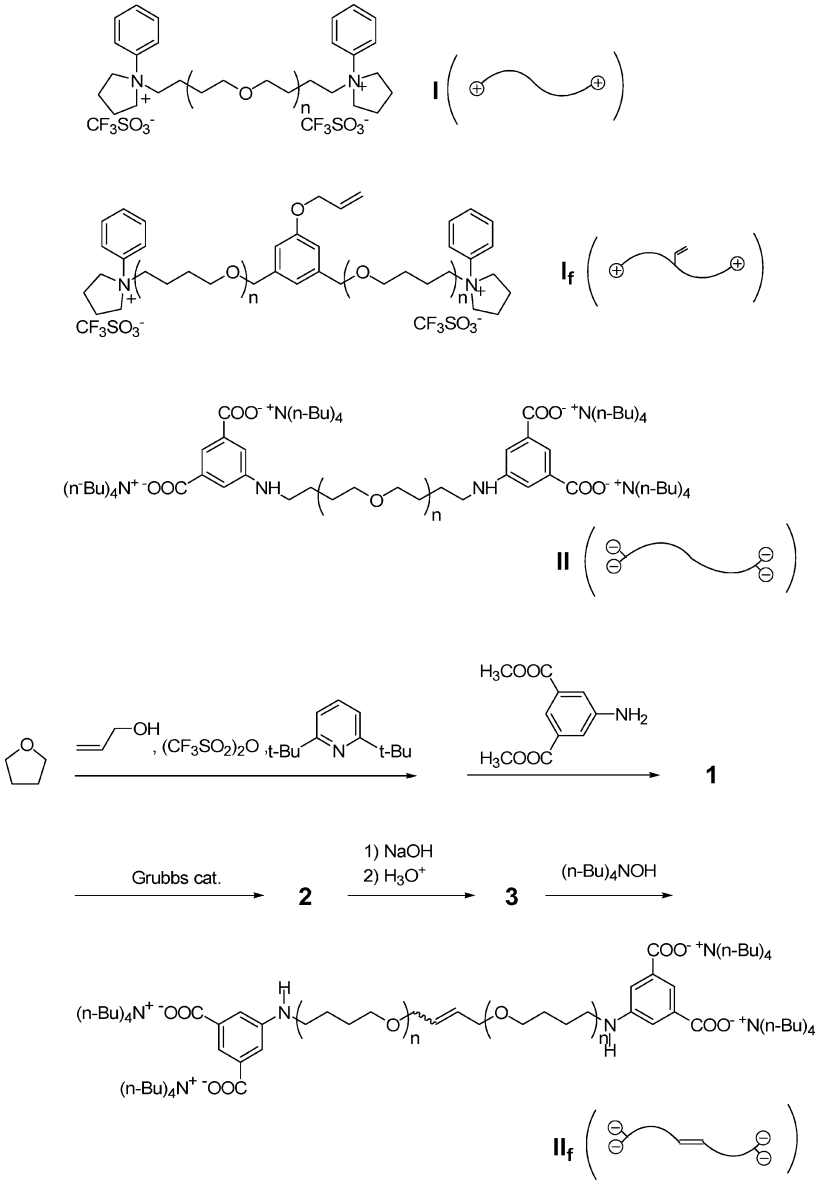


anions, prepared by the titration of **3** with tetra-*n*-butyl ammonium hydroxide (10% methanol solution, Tokyo Kasei Co.), were mixed in THF (6 mL), and the solution was added dropwise into an ice-cooled (<5 °C) water (250 mL) under vigorous stirring. After 0.5 h, the precipitated electrostatic polymer−polymer assembly (**I**/**II**$_f$) was collected by filtration (193 mg, containing a small portion of water to avoid uncontrolled ring-opening reaction of the end groups in **I**). $^1$H NMR ($CDCl_3$): $\delta$ 1.46−2.13 (m, C$\mathit{H}_2$CH$_2$O), 2.20−2.43 (m, 8H, *endo*-NCH$_2$C$\mathit{H}_2$), 3.32−3.59 (m, CH$_2$C$\mathit{H}_2$O), 3.72−3.84 (m, 8H, NC$\mathit{H}_2$), 3.93−3.97 (m, 4H, *cis*-CH═CHC$\mathit{H}_2$), 3.97−4.09 (m, 8H, *exo*-NC$\mathit{H}_2$CH$_2$), 4.09−4.26 (m, 8H, *endo*-NC$\mathit{H}_2$CH$_2$), 5.73−5.84 (m, 2H, *cis*- and *trans*-C*H*═C*H*), 7.38 (s, 4H, Ar−*H ortho* to NH), 7.44−7.64 (m, 20H, NPh *ortho, meta, para-H*), 7.95 (s, 2H, Ar−*H para* to NH).

As for **I**$_f$/**II**, $^1$H NMR ($CDCl_3$): $\delta$ 1.48−1.61 (m, C$\mathit{H}_2$CH$_2$O), 3.17−3.41 (m,CH$_2$C$\mathit{H}_2$O), 3.75 (m, 4H, *endo*-NC$\mathit{H}_2$CH$_2$), 4.04−4.25 (m, 8H, *exo*-NC$\mathit{H}_2$CH$_2$), 4.45 (s, 4H, ArC$\mathit{H}_2$O), 4.54 (d, 2H, $J$ = 5.1 Hz, CH$_2$═CHC$\mathit{H}_2$OAr), 5.24−5.43 (m, 2H, C$\mathit{H}_2$═CHCH$_2$-OAr), 5.94−6.11 (m, 1H, CH$_2$═C*H*CH$_2$OAr), 6.82 (s, 2H, Ar−*H ortho* to OCH$_2$CH═), 6.84 (s, 1H, Ar−*H para* to OCH$_2$CH═), 7.39 (s, 4H, Ar−*H* ortho to NH), 7.45−7.62 (m, 10H, N*Ph ortho-*, *meta-*, *para-H*), 7.96 (s, 2H, Ar−*H para* to NH).

An electrostatic self-assembly of cationic and anionic telechelic precursors (**I**/**II**$_f$, 193 mg) was then dissolved in 1 L of THF and heated at 66 °C for 5 h. The reaction solvent was removed by evaporation, and the product was subjected to the flush column

**Scheme 3. Preparation of Cationic (I and I$_f$) and Anionic (II and II$_f$) Telechelic Precursors**



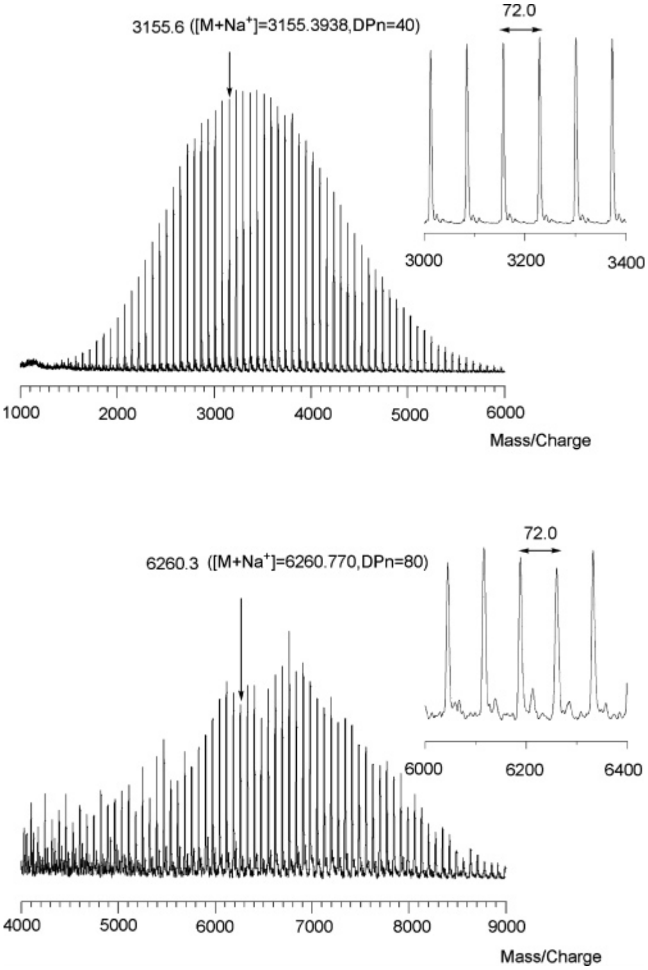


**Figure 1.** MALDI−TOF mass spectra of poly(THF) having a dimethylester and an allyl end groups, **1**, (top) and poly(THF) having an inner olefinic group and dimethylester end groups, **2**, (bottom). (linear mode, matrix: dithranol with sodium trifluoroacetate).

chromatography on silica gel with hexane/acetone (2/1 in vol/vol). The covalently converted product, **IV**, was finally isolated by freeze-drying from benzene solution. The yield was 105 mg. $^1$H NMR (CDCl$_3$): $\delta$ 1.48−1.98 (m, C*H*$_2$CH$_2$O), 3.24−3.63 (m, CH$_2$C*H*$_2$O), 3.93−4.00 (m, 4H, *cis*-CH$_2$=CHC*H*$_2$), 4.33 (t, 4H, $J$ = 6.3 Hz, COOC*H*$_2$), 5.77−5.82 (m, 2H, *cis*- and *trans*-C*H*=C*H*), 6.61−6.72 (m, 12H, NPh *ortho, para-H*), 7.14−7.23 (m, 8H, NPh *meta-H*)), 7.38 (s, 4H, Ar−*H ortho* to NH), 7.95 (s, 2H, Ar−*H para* to NH).

By the similar procedure from **I$_f$**/**II**, the covalently converted product, **III** was obtained. $^1$H NMR (CDCl$_3$): $\delta$ 1.48−1.61 (m, C*H*$_2$CH$_2$O), 3.24−3.63 (m, CH$_2$C*H*$_2$O), 4.33 (t, 4H, $J$ = 6.3 Hz, COOC*H*$_2$), 4.45 (s, 4H, ArC*H*$_2$O), 4.54 (d, 2H, $J$ = 5.1 Hz, CH$_2$=CHC*H*$_2$OAr), 5.24−5.43 (m, 2H, C*H*$_2$=CHCH$_2$OAr), 5.94−6.11 (m, 1H, CH$_2$=C*H*CH$_2$OAr), 6.61−6.72 (m, 12H, NPh *ortho, para-H*), 6.82 (s, 2H, Ar−*H ortho* to OCH$_2$CH=), 6.84 (s, 1H, Ar−*H para* to OCH$_2$CH=), 7.14−7.23 (m, 8H, Ar−*H meta* to NH), 7.38 (s, 4H, Ar−*H ortho* to NH), 7.95 (s, 2H, Ar−*H para* to NH). Yield: 47%.

**Separation and Metathesis Transformation of Polymeric Topological Isomers Having *θ*- and Manacle-Constructions.** RPC fractionation of the covalently converted product, **III**, was performed using a Tosoh model CCPC equipped with a UV detector model UV 8020 at 254 nm. A column of TSK ODS-80Ts (8 nm pore, 150 mm × 4.6 mm i. d., 5 $\mu$m average particle size) was employed with THF/CH$_3$CN (60/40, vol/vol) as an eluent at a flow rate of 1.0 mL/min. The two fractions having the shorter and the longer retention times (**IIIa** and **IIIb**, respectively) were recovered by evaporating the solvent and subjected to MALDI TOF mass analysis. SEC fractionation was applied for the covalently converted product, **IV**, by means of JAI model LC-908W apparatus with a refractive index detector model RI-5, using a tandem set of two JAIGEL-3H-AF columns. RPC fractionation with the UV detector was circumvented by the strongly UV-absorbing components, presumably catalyst residues in the product, **IV**. A sample solution of ca. 50 mg of **IV** in 3 mL THF was injected. The eluent was THF at a flow rate of 3.5 mL/min. The two fractions having the larger and the smaller hydrodynamic (**IVa** and **IVb**, respectively) volumes were recovered by evaporating the solvent. A stabilizer for the SEC eluent, i.e., 2,6-di-*tert*-butyl-4-methylphenol, was removed by precipitation of the product into petroleum ether cooled at −78 °C. The yields of the former and the latter were 24 mg and 14 mg, respectively, from 57 mg of **IV**. By an additional experiment, 45 mg of **IVa** and 28 mg of **IVb** were isolated, respectively, from 140 mg of **IV**. $^1$H NMR spectra of both fractions are shown in S-Figure 3 in the Supporting Information.

The metathesis transformation of the two fractions (**IVa** and **IVb**) was subsequently performed. Thus, the polymer precursor (**IVb**, 24 mg, $1.0 \times 10^{-3}$ mmol), allyl benzene (18 mg, 0.16 mmol) and a Grubbs catalyst (2 mg, $2.6 \times 10^{-3}$ mmol) were mixed in methylene chloride (7 mL) to react for 48 h at 40 °C. The product, **Vb**, was isolated by the precipitation into precooled hexane. The yield was 14 mg. $^1$H NMR (acetone-d$_6$): $\delta$ 1.05−1.93 (m, C*H*$_2$-CH$_2$O), 3.24−3.58 (m, CH$_2$C*H*$_2$O), 3.90−3.97 (m, 4H, *cis*-CH=CHC*H*$_2$), 4.22−4.33 (m, COOC*H*$_2$ and CH=CHC*H*$_2$Ph), 5.74−5.98 (m, 2H, *cis*- and *trans*-C*H*=C*H*), 6.64−6.77 (m, 12H, NPh *ortho*- and *para-H*), 7.07−7.17 (m, 8H, NPh *meta-H*), 7.59 (s, 4H, Ar−*H ortho* to N), 7.59−7.89 (m, CH$_2$Ph *ortho*-, *meta*-, and *para-H*), 7.89 (s, 2H, Ar−*H para* to N).

**Measurements.** $^1$H NMR spectra were recorded on a JEOL JNM-AL300 apparatus in CDCl$_3$ or in acetone-$d_6$. The proton chemical shift (ppm) was referenced to the signal of tetramethylsilane. Size exclusion chromatography (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 (300 mm × 7.8 mm i.d., 5 $\mu$m average particle size) was employed with THF as an eluent at a flow rate 1.0 mL/min at 40 °C. In a typical procedure, 40 $\mu$L of sample solution (sample concentration of 0.5 wt %) was injected. MALDI−TOF mass 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(10*H*)-anthracenone (dithranol, Aldrich) and sodium trifluoroacetate (Aldrich), was dissolved in THF (10 and 1 g/L, respectively). The polymer solution (50 $\mu$L) was then mixed with 50 $\mu$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 plus H$^+$ at 5734.62, insulin $\beta$ plus H$^+$ at 3497.96 and α-cyanohydroxycinnamic acid dimer plus H$^+$ at 379.35.

## Results and Discussion

**Preparation of Dicyclic Polymers Having *θ*- and Manacle-Constructions with Olefinic Groups at Designated Positions.** A pair of polymeric constitutional isomers possessing $\theta$- and manacle-constructions have so far been obtained from electrostatic self-assemblies with a linear bifunctional or a star trifunctional telechelic precursor (Scheme 1)[12,16,17] and from an H-shaped telechelic precursor.[24] Each polymeric isomer component could be separated either by means of a reversed-phase chromatography (RPC) technique operated at near critical condition,[12,16] or by means of a size exclusion chromatography (SEC).[17] The relative ratio of the two isomers was estimated by their RPC peak areas, and was in accord with the statistic estimation based on the random combination in the end-linking process.[26] The subsequent SEC measurements showed that one isomer is noticeably larger in its hydrodynamic volume

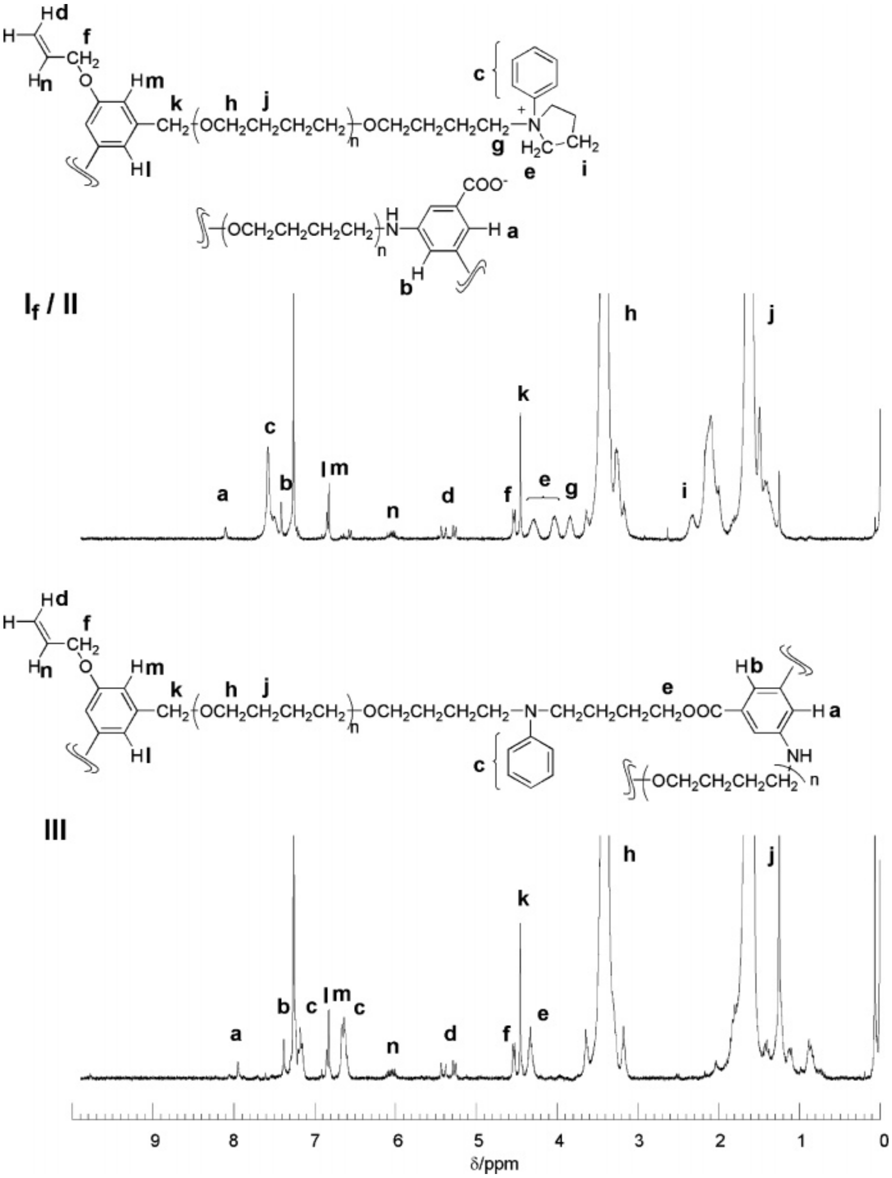


**Figure 2.** 300 MHz $^1$H NMR spectra of the electrostatic self-assembly product between poly(THF) having a pendant olefinic group at the center position and pyrrolidinium salt end groups (**I**$_\mathrm{f}$) and poly(THF) having dicarboxylate end groups (**II**) (top), and the covalent conversion product (**III**) (bottom). (CDCl$_3$, 40 °C).

than another. On the basis of these observations, we have provisionally assigned one component having the larger hydrodynamic volume as a manacle-isomer, and another having smaller hydrodynamic volume as a *θ*-isomer, respectively.[12,16,17,24]

In the present study, we have prepared a series of cationic polymer precursors, i.e., a linear poly(THF) ($M_\mathrm{p}$(SEC) = 8700) having *N*-phenylpyrrolidinium salt end groups (**I**) and a linear functional poly(THF) ($M_\mathrm{p}$(SEC) = 3200) having an additional allyloxy group at the center position (**I**$_\mathrm{f}$), as well as anionic counterparts, i.e., a telechelic poly(THF) ($M_\mathrm{p}$(SEC) = 3500) having dicarboxylate end groups (**II**) and a functional telechelic poly(THF) ($M_\mathrm{p}$(SEC) = 7200) having an additional inner olefinic group (cis/trans ratio of ca. 9/1) (**II**$_\mathrm{f}$).[27] The subsequent ion-exchange reaction between precursors **I** and **I**$_\mathrm{f}$, initially carrying trifluoromethanesulfonate (triflate) counteranions, and **II** and **II**$_\mathrm{f}$, initially carrying tetrabutylammonium countercations, was conducted by a simple coprecipitation procedure (Scheme 2).[28] Thus, a THF solution containing an equimolar amount of **I** (or **I**$_\mathrm{f}$) and **II** (or **II**$_\mathrm{f}$), was prepared by monitoring with $^1$H NMR, and was precipitated into ice-cooled water to remove tetrabutylammonium trifluoromethanesulfonate. An electrostatic polymer−polymer assembly (**I**$_\mathrm{f}$/**II** and **I**/**II**$_\mathrm{f}$) was recovered by simple filtration, and was subjected to the heat treatment at 66 °C for 5 h (for both **I**$_\mathrm{f}$/**II** and **I**/**II**$_\mathrm{f}$) under appropriate dilution (0.1 g/L for **III** and 0.2 g/L for **IV**, respectively, in THF) in order to maintain the self-assembly consisting of the smallest number of cationic and anionic units, i.e., two units of **I** and one unit of **II**, in which cations and anions balance the charges.[9] Covalently linked products (**III** and **IV**) were obtained in the yields of up to 72% for **III** and up to 81% for **IV**, respectively.

The $^1$H NMR comparison of the ionic self-assemblies, **I**$_\mathrm{f}$/**II** and **I**/**II**$_\mathrm{f}$, and the covalently converted **III** and **IV** (Figure 2 and 3, respectively) showed that the signals attributed to the *N*-phenylpyrrolidinium salt group of both **I**$_\mathrm{f}$/**II** and **I**/**II**$_\mathrm{f}$ at 3.7−3.8, and 7.4−7.6 ppm are replaced by a triplet signal at 4.34 ppm for both **III** and **IV** arising from ester methylene protons, and signals at 6.6−6.7 and 7.1−7.2 ppm arising from the *N*-phenyl protons on the aminoester group. Aromatic protons due to 5-aminoisophthalate anion/ester groups are visible at 7.38 and 7.95 ppm for both **III** and **IV**. IR analysis also showed the formation of ester groups (1717 cm$^{-1}$ in **III** and

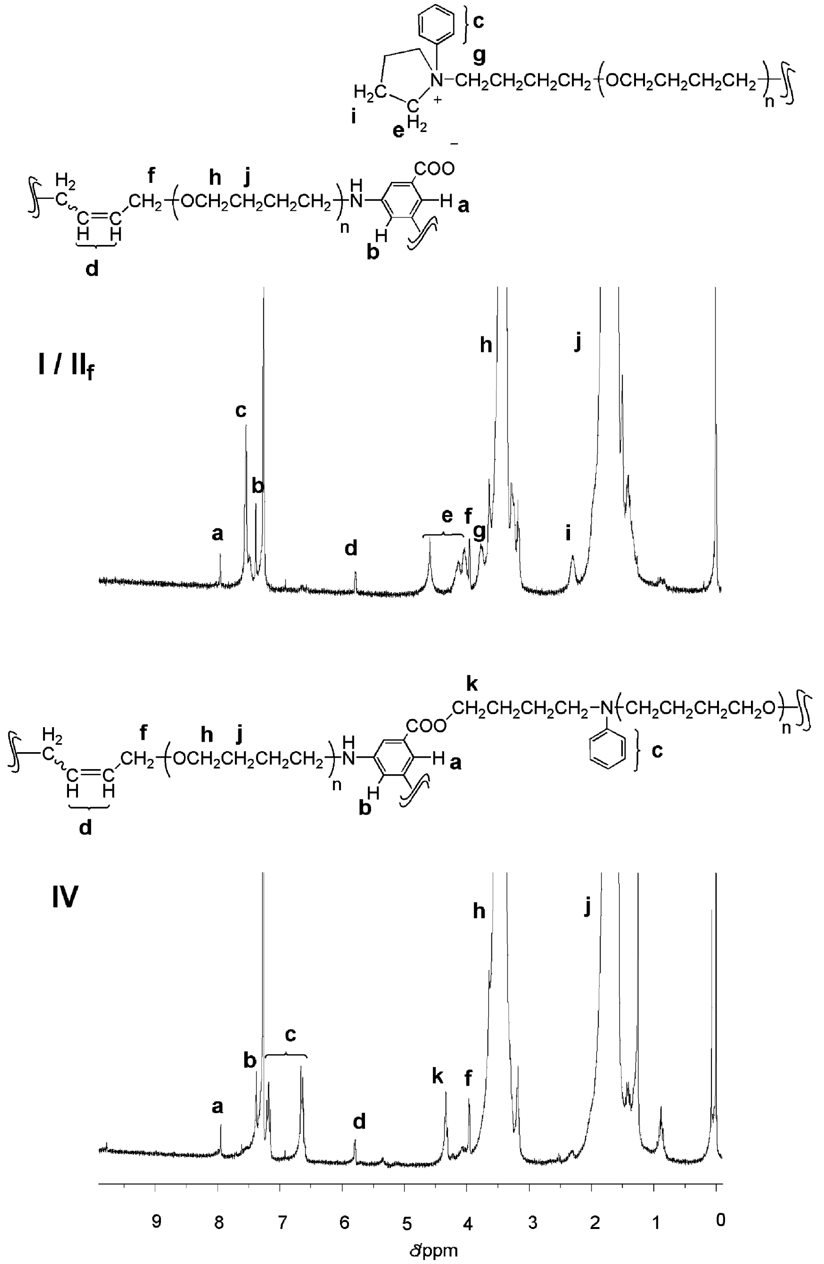


**Figure 3.** 300 MHz $^1$H NMR spectra of the electrostatic self-assembly product between poly(THF) having pyrrolidinium salt end groups (**I**) and poly(THF) having an inner olefinic group and dicarboxylate end groups ($\mathbf{II}_\mathrm{f}$) (top), and the covalent conversion product (**IV**) (bottom). ($CDCl_3$, 40 °C).

1725 cm$^{-1}$ in **IV**) replacing the carboxylate absorption (1595−1597 cm$^{-1}$) in $\mathbf{I}_\mathrm{f}$/**II** and **I**/$\mathbf{II}_\mathrm{f}$. Pendant allyl protons in **III** and inner olefinic protons in **IV** are also visible at 4.54 and 5.2−5.5 ppm for the former and 3.9−4.0 ppm for the latter, respectively.

The SEC analysis of the products **III** and **IV** showed a unimodal peak, and with a noticeable tailing toward the larger hydrodynamic volume region for **IV** (Figure 4, A and B). And the products **III** and **IV** possesses distinctively higher apparent molecular weight ($M_\mathrm{p}$ = 6900 for **III** and $M_\mathrm{p}$ = 15 300 for **IV**, respectively) than each of the precursor analogues ($M_\mathrm{p}(\mathbf{I}_\mathrm{f})$ = 3200 and $M_\mathrm{p}(\mathbf{II})$ = 3500, and $M_\mathrm{p}(\mathbf{I})$ = 8700 and $M_\mathrm{p}(\mathbf{II}_\mathrm{f})$ = 7200, respectively). Nevertheless, the hydrodynamic volume of the product, estimated from the apparent peak molecular weight, $M_\mathrm{p}$, by SEC, was notably smaller than that of the relevant linear polymer having the same molecular weight. Thus, the sum of the two of $\mathbf{I}_\mathrm{f}$ and one of **II** is 9900 (indeed, $M_\mathrm{n}$ estimated by NMR was 10000), and the two of **I** and one of $\mathbf{II}_\mathrm{f}$ is 24600, respectively. The product having the contracted hydrodynamic volume, compared with the linear analogue, is consistent with its multicyclic structure. Indeed, the ratio of the apparent molecular weight, i.e., the measure of the hydrodynamic volume, of products **III** and **IV** against the linear polymer analogue possessing the same molecular weight was 0.69 and 0.62, respectively, and these values were close to the reported ones (0.69−0.77).[29]

**Chromatographic, Spectroscopic and Chemical Assignment of Polymeric Topological Isomers Having *θ*- and Manacle-Constructions.** The presence of the two constitutional isomers in both dicyclic products **III** and **IV** has subsequently been confirmed through the reversed-phase liquid chromatography (RPC)/mass spectroscopy (MALDI TOF) technique, as well as through the chemical transformation analyses. First, product **III** was subjected to reversed-phase chromatography (RPC),[4,12] and the presence of two components has been confirmed under an optimized condition, i.e., THF/$CH_3CN$ (60/

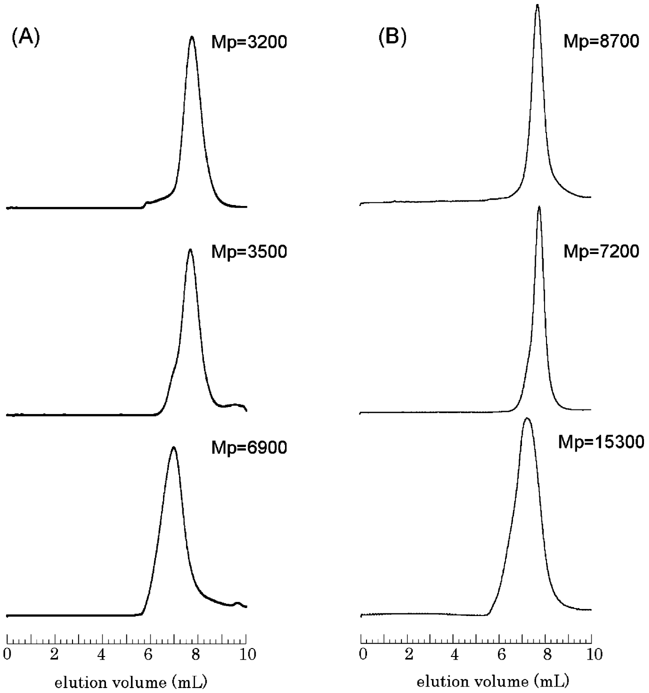


**Figure 4.** SEC traces (RI) of [**A**] a cationic poly(THF) precursor analogue (**I$_f$**, with end groups ring-opened by benzoate anion) (top), an anionic poly(THF) precursor analogue (**II**, with methyl ester end group) (middle), and the covalent conversion product (**III**) (bottom), and [**B**] a cationic poly(THF) precursor analogue (**I**, with end groups ring-opened by benzoate anion) (top), an anionic Poly(THF) precursor analogue (**II$_f$**, with methyl ester end group) (middle), and the covalent conversion product (**IV**) (bottom). (TSK G3000HXL, eluent = THF 1.0 mL/min)

40 in vol/vol) as an eluent (Figure 5, inset). The two fractions were then recovered and subjected to MALDI TOF mass analysis (Figure 5). In both fractions, three sets of a series of peaks corresponding to poly(THF) (peak interval of 72 mass units) were detected. And significantly, a series of major peaks corresponds exactly to the molar mass summing up the additional fragment groups in **III**, while other two sets of a series of minor peaks were not assignable so far. Thus, for example, **IIIa**, the peak (the mass/charge assumed to be the adduct with Na$^+$) at 4049.0 corresponds to the expected dicyclic polymeric isomer product having either a $\theta$- or manacle-constructions, with the DP$_n$ of 50, $(C_4H_8O) \times 50 + C_{78}H_{88}N_6O_{10}$, plus Na$^+$ as 4050.03. And another fraction, **IIIb**, the peak (the mass/charge assumed to be the adduct with Na$^+$) at 6393.2 corresponds to another dicyclic polymeric isomer product, with the DP$_n$ of 70, $(C_4H_8O) \times 70 + C_{78}H_{88}N_6O_{10}$, plus Na$^+$ as 6392.17. This is indicative of the presence of the two components having identical series of molar masses, i.e., topological isomers, in the polymer product **III**.

The two components having the larger and the smaller hydrodynamic volume were observed also in the product **IV** by a higher resolution SEC measurement (Figure 6, inset). And the two fractions having the larger and the smaller hydrodynamic volume, **IVa** and **IVb**, were subsequently separated by means of preparative SEC technique (Figure 6). Both fractions showed coincident $^1$H NMR spectra (S-Figure 3 in Supporting Information) with each other despite the notable difference in their hydrodynamic volumes estimated by SEC (Figure 5, middle and bottom). And the two fractions showed the equivalent DP$_n$ values, estimated based on the proton peak area ratio between *N*-phenyl groups of the linking units and poly(THF) main chain methylene units.

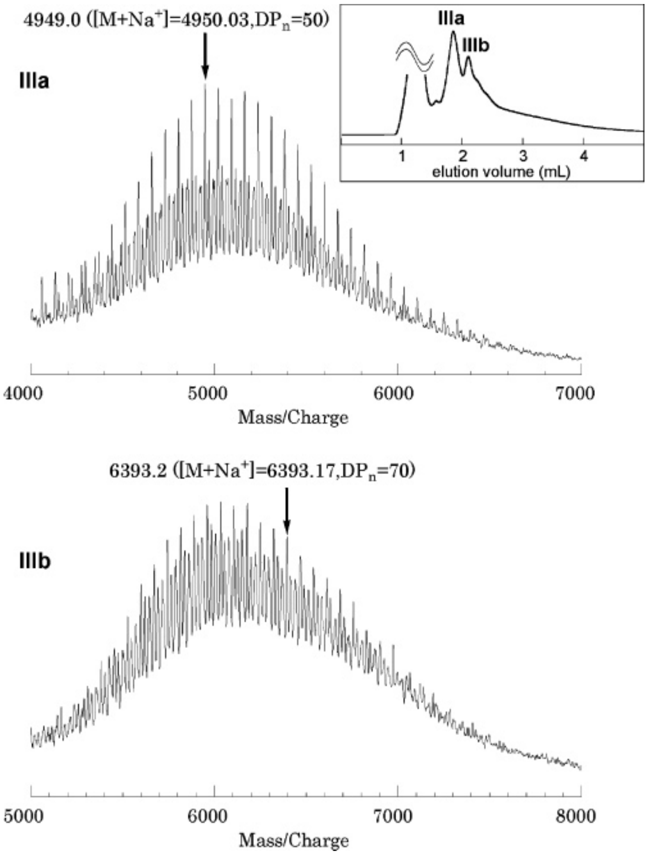


**Figure 5.** RPC trace (the inset, the overflowed peak is due to residual low molar mass impurities) of the covalent conversion product comprised of manacle- and $\theta$-isomers (**III**), and MALDI−TOF mass spectra of the recovered two fractions having a lower (top, **IIIa**) and a higher (bottom, **IIIb**) elution volume, respectively. (linear mode, matrix: dithranol with sodium trifluoroacetate).

As shown in Scheme 2, the two polymeric topological isomers having manacle- and $\theta$-constructions, **IVa** and **IVb**, respectively, are obtainable through the covalent conversion of **I/II$_f$**. And if the linking of the terminal groups took place randomly, the $\theta$- and manacle-isomers could be formed in the ratio of 2/1 (thus the $\theta$-isomer as a major product). Accordingly, one product **IVb** was recovered as a major component (47% yield), while another **IVa** as a minor component (29% yield), respectively.

The two fractions having the larger and the smaller hydrodynamic volumes, **IVa** and **IVb**, respectively, were isolated and subjected to the cross-metathesis reaction with excess allyl benzene in the presence of the first generation Grubbs catalyst (Scheme 4). By the selective chain cleavage of the olefinic group with a cross metathesis reaction,[30] the manacle-isomer will produce two units of a tadpole-shape product having a significantly reduced SEC size with the half DP$_n$. On the other hand, the $\theta$-isomer will produce a two-tail tadpole product having a comparable or even larger SEC size with the unchanged DP$_n$. Hence, the SEC examination of each fraction before and after the cross-metathesis, i.e., the chain cleavage, reaction could provide the direct assignment of each topological isomer. Allyl benzene was chosen because the relevant inner olefinic compound, 1,4-diacetoxy-2-butene, has been reported to undergo an effective cross-metathesis reaction with allyl benzene to give 1-acetoxy-4-phenyl-2-butene.[31] The reaction products **Va** (from **IVa**) and **Vb** (from **IVb**) were recovered in appreciable yields after purification (24% for **Va** and 60% for **Vb**, respectively). And $^1$H NMR spectra of **Va** and **Vb** coincided with each other, showing the signals attributed to the benzylmethylidene group

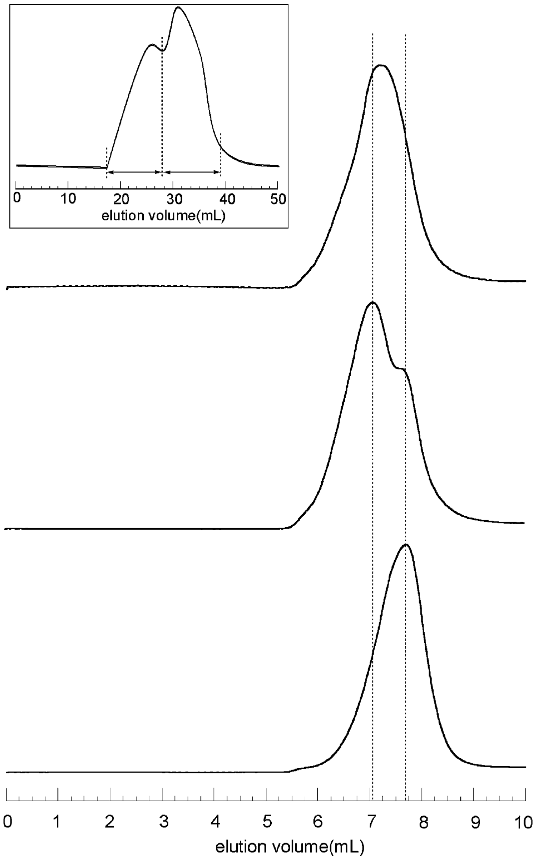
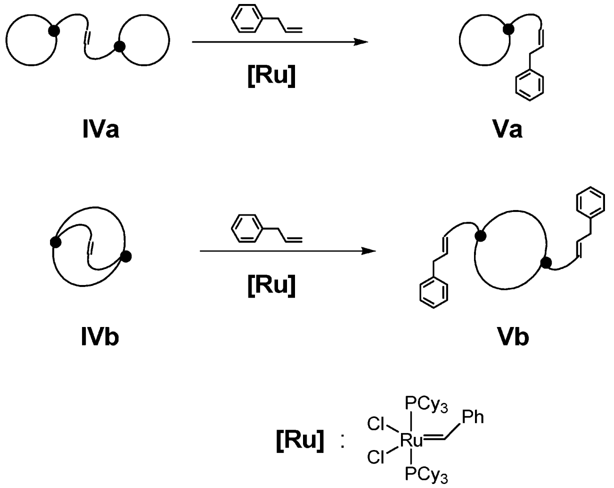


**Figure 6.** SEC traces of the covalent conversion product comprised of manacle- and $\theta$-isomers (**IV**) (top), where the inset shows a chromatogram obtained during the fractionation by the preparative SEC with higher resolution condition (see Experimental Section for details) and the recovered fraction having the larger (middle) and the smaller (bottom) hydrodynamic volumes (TSK G3000HXL; eluent = THF 1.0 mL/min).

**Scheme 4. Metathesis Transformation of Polymeric Topological Isomers Having $\theta$- and Manacle-Constructions Containing an Inner Olefinic Group**



at 4.22−4.33 and 7.59−7.89 ppm (S-Figure 4 in Supporting Information).

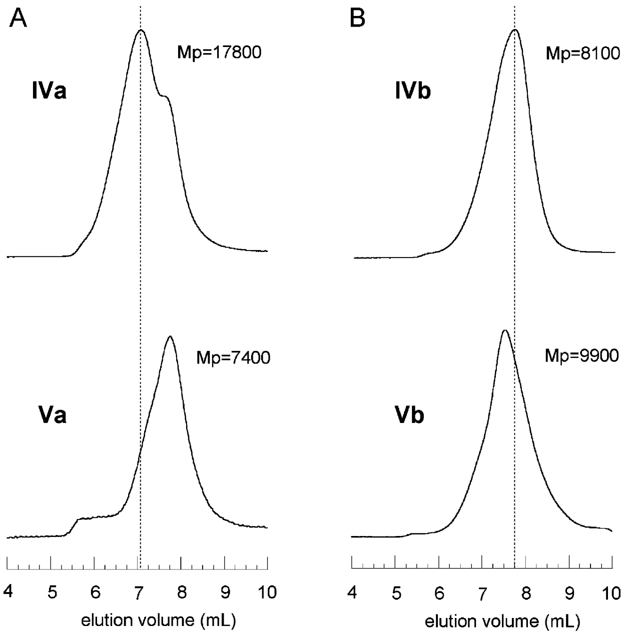


**Figure 7.** SEC traces (RI) of (**A**) the fraction having the larger hydrodynamic volume (**IVa**) and (**B**) the fraction having the smaller hydrodynamic volume (**IVb**) before (top) and after (bottom) the cross-metathesis reaction with allylbenzene. (TSK G3000HXL; eluent = THF 1.0 mL/min).

SEC comparison of the product, **Va**, with the starting **IVa** (Figure 7, A) showed a significant reduction of the hydrodynamic volume (from $M_p$ = 17 800 for **IVa** to $M_p$ = 7200 for **Va**) along with the reaction. In contrast, the relevant product, **Vb**, from **IVb** showed a nearly unchanged or even slightly increased hydrodynamic volume (from $M_p$ = 8100 for **IVb** to $M_p$ = 9900 for **Vb**) after the reaction. These results accord with the process shown in Scheme 4, and we have conclusively assigned an isomer having the larger hydrodynamic volume as the manacle-form, and another having the smaller hydrodynamic volume as a $\theta$-form, respectively.

## Conclusion

Dicyclic polymers having either $\theta$- or manacle-constructions have been prepared through electrostatic polymer self-assembly and covalent fixation using linear precursors having a pendant or an inner olefinic group. The formation of the two constitutional isomers has been confirmed by the reversed-phase chromatography (RPC) coupled with MALDI TOF mass analysis, as well as by the metathesis conversion of the two reactive isomer components. Since dicyclic polymers having functional groups are now available for the synthesis of various more complex multicyclic polymers, unequivocal assignment of the two isomers should promote further developments of topological polymer chemistry.

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**Supporting Information Available:** Figures showing the $^1$H NMR spectra and SEC traces of the precursors **1**, **2**, and **3** for the preparation of **II$_f$**, $^1$H NMR spectra of **IVa** and **IVb** (the larger and the smaller hydrodynamic fraction of **IV**) and their cross-metathesis products **Va** and **Vb**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The relative ratio of manacle- and $\theta$-isomers produced by random combination should be 3:2, and the ratio of 70−80:30−20 was observed. See refs 16 and 17.

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(29) In the preceding studies (refs 12, 16 and 17), the manacle-isomer having presumably the larger size was considered as a major product by random combination. In the present process, however, the $\theta$-isomer having presumably the smaller size is considered as a major component. This may account for the smaller hydrodynamic volume ratio observed here (0.69 and 0.62) in comparison with those found before (0.69−0.77).

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