

Synthesis of polymeric topological isomers through electrostatic self-assembly and covalent fixation with telechelic poly(THF) having cyclic ammonium salt groups^{†‡}

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Abstract: A pair of macromolecular constitutional isomers having topologically distinctive constructions, ie θ -shaped and manacle-shaped polymers, has been synthesized through covalent conversion of an electrostatic polymer self-assembly comprised of bifunctional linear poly(tetrahydrofuran) [poly(THF)] having *N*-phenylpyrrolidinium salt end groups carrying tricarboxylate counteranions (1) under various dilutions. The presence of the two constitutional polymeric isomers was revealed by means of a reverse-phase liquid chromatography (RPLC) technique. Moreover, size-exclusion chromatography (SEC) confirmed that one major component possesses notably larger hydrodynamic volume than another, and is assigned as a manacle-shaped isomer while a minor component as a θ -shaped isomer. Further details of this unique process were investigated by RPLC analysis of topological isomer products obtained from a series of poly(THF) precursors, 1, having different molecular weights.

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Keywords: polymeric topological isomers; self-assembly; telechelics; ring polymers

INTRODUCTION

Novel macromolecular architectures comprised of monocyclic and polycyclic polymer units with optional free branches are of increasing interest.^{1–6} Besides a simple ring construction, there exist three dicyclic polymer topologies,⁷ ie figure-of-eight-shaped, θ -shaped and manacle-shaped polymer constructions. Synthetic attempts to realize such unusual polymer topologies are an ongoing challenge in fundamental polymer chemistry.^{6,8} We have recently reported on an 'electrostatic self-assembly and covalent fixation' process, making use of specifically designed telechelic polymer precursors having moderately strained cyclic ammonium salt end-groups carrying appropriate nucleophilic counteranions like carboxylates.^{6,9–17} A variety of single cyclic, and multicyclic, ie such double-cyclics as figure-of-eight-shaped, θ -shaped as well as a triple-cyclics, polymer constructions have been effectively produced by this methodology.

Moreover, we have found that two of three dicyclic topologies, namely a pair of topological isomers of θ -shaped and manacle-shaped polymers, are formed from an assembly comprised of bifunctional linear precursors and trifunctional carboxylates, in which cations and anions balance the charges (Scheme 1).⁹ They are identical in their molecular weights and in their chemical compositions but distinctive in their topological connectivity.^{5,18,19} It should be noted that such topological isomers are often encountered in multicyclic polymer products through the equimolar combination of linear or branched polymer precursors with polyfunctional end-linking reagents.⁵

Herein we report the details on the formation of topologically distinctive polymeric isomers, ie θ -shaped and manacle-shaped polymers, through the 'electrostatic self-assembly and covalent fixation' process by employing a series of bifunctional linear precursors having different molecular weights (Scheme 1).

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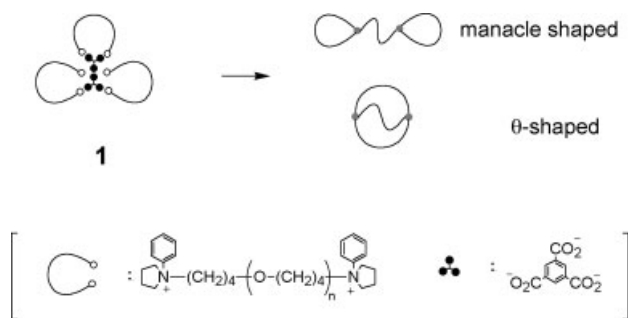
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Scheme 1. Formation of manacle-shaped and θ -shaped polymeric topological isomers.

EXPERIMENTAL

Materials and procedures

A series of bifunctional linear poly(THF)s having *N*-phenylpyrrolidinium salt end-groups carrying trimesate counteranions (**1**) were prepared by the method detailed previously.⁹ The covalently linked products, comprised of θ -shaped and manacle-shaped poly(THF)s were prepared as in the following example. The ionic polymer precursor **1** (0.059 g) was dissolved in 300 ml of THF (0.2 g l⁻¹) and heated to reflux (bath temp of 90 °C) for 3 h. The reaction solvent was removed, and the recovered product (0.053 g) was further purified by preparative thin layer chromatography (SiO₂, hexane/acetone = 2/1) to yield 0.037 g (80%) of θ -shaped and manacle-shaped poly(THF)s.

Measurements

Size Exclusion Chromatography (SEC) measurements were performed using a Tosoh Model CCPS instrument equipped with a refractive index detector Model RI 8020, a UV detector Model UV 8020 at 254 nm, and a conductivity detector Model CM 8010. A column of either TSK G3000HXL (300 mm \times 7.8 mm ID, 5 μ m average particle size) or TSK G4000HXL (300 mm \times 7.8 mm ID, 5- μ m average particle size) was employed with THF as an eluent at a flow rate of 1.0 ml min⁻¹ at 40 °C. In a typical procedure, 40 μ l of sample solution (sample concentration 0.5 wt%) was injected. Reverse-phase liquid chromatography (RPLC) measurements were conducted by an isocratic mode using a Tosoh Model CCPS instrument equipped with a UV detector Model UV 8020 at 254 nm. A C₁₈-bonded silica column of TSK ODS-80TS (80 Å pore, 250 mm \times 4.6 mm, 5- μ m average particle size) was employed with a mixture of THF/CH₃CN (50/50 in v/v) at 25 °C. IR spectra were taken on a JASCO FT/IR-410 infrared spectrometer by casting the sample from a chloroform solution onto a NaCl plate. ¹H NMR spectra were recorded with a JEOL JNM-AL300 apparatus in CDCl₃ at 40 °C. The proton chemical shifts (ppm) were referenced from the signal of tetramethylsilane.

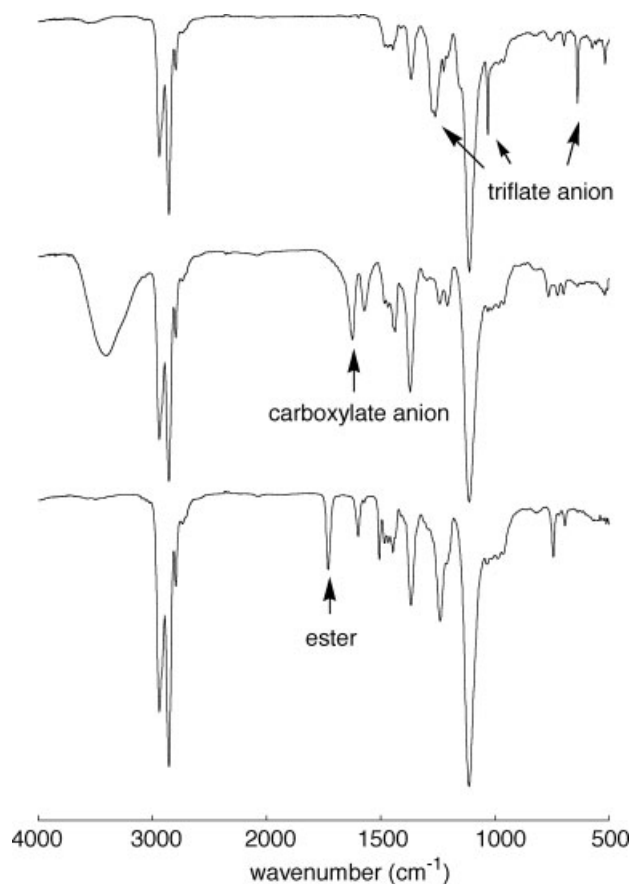


Figure 1. IR spectra of (top) the poly(THF) precursor carrying triflate counteranions, (middle) the ion-exchange product with trimesate counteranions, **1**, and (bottom) the product after the heat treatment under dilution. (Sample: run 3 in Table 1).

RESULTS AND DISCUSSION

A pair of topological isomers of θ -shaped and manacle-shaped constructions were synthesized from the polymer precursor/counteranion assembly, namely an assembly comprised of three bifunctional linear polymer precursor having ammonium salt end groups carrying two trifunctional carboxylate as counteranions (**1**) (Scheme 1). Assembly **1** was prepared from a series of poly(THF) precursors having different molecular weights carrying trifluoromethane sulfonate (triflate) counteranions, through the ion-exchange reaction by precipitation into aqueous solution containing the trifunctional trimesate anions as the sodium salt form. IR spectra of the products before and after the ion-exchange reaction (Fig 1, top and middle panels, respectively) showed that the counteranion was replaced quantitatively from triflate by trimesate. The subsequent covalent conversion was conducted by the heat treatment under reflux in THF solution at various dilutions toward 0.05 g l⁻¹. The recovered products were subjected to preparative thin layer chromatography (TLC) on silica gel to remove any residual ionic species, and the isolated products were examined by means of IR, ¹H NMR, SEC and RPLC techniques. IR spectra of the product after the heat treatment (Fig 1, bottom panel) showed the ring-opening reaction of

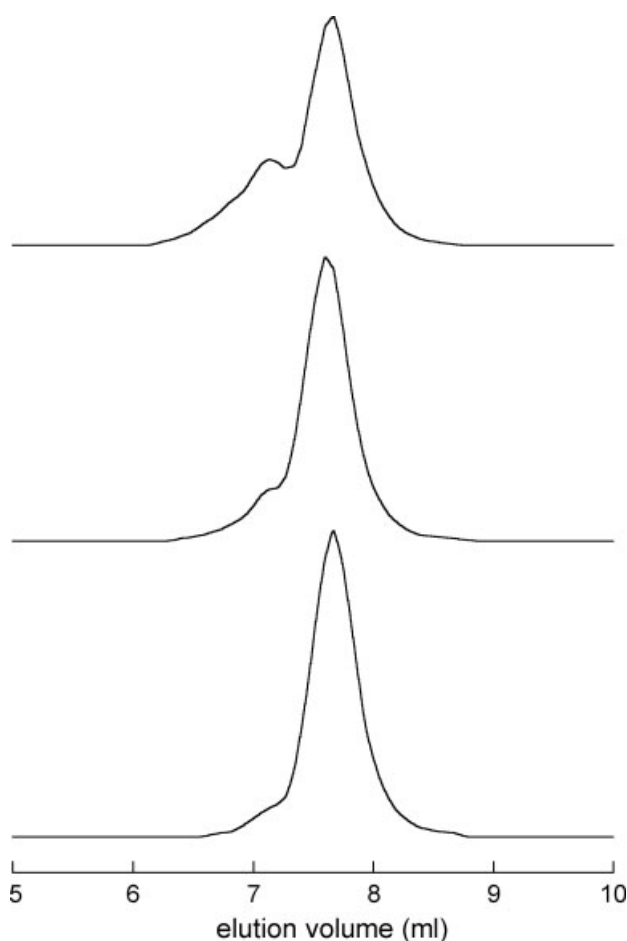


Figure 2. SEC traces (refractive index) of the products from the assembly by telechelic poly(THF) with trimesate counteranion, **1**, after the heat treatment. Concentration of the **1** in THF: (top) 2.0 g l^{-1} , (middle) 0.5 g l^{-1} , and (bottom) 0.2 g l^{-1} . Samples: runs 3, 5 and 7 in Table 1, TSK G4000HXL, eluent: THF, 1.0 ml min^{-1}).

five-membered pyrrolidinium salt groups by carboxylate counteranions to produce amino-ester groups. In addition, ^1H NMR of the purified product from **1** (presented in the preceding report⁹) also showed a quantitative and selective ring-opening reaction of pyrrolidinium salt groups at the polymer precursor chain ends by carboxylate counteranions, irrespective of the dilution.

Size-exclusion chromatography (SEC) showed that the size (or hydrodynamic volume) distribution of the product obtained from **1** becomes narrower by eliminating larger size fractions along with progressive dilution (Fig 2), and the size of the product showing at 0.2 g l^{-1} between two and three times that of the starting linear polymer precursor (Fig 3), consistent with cyclization. Moreover, RPLC revealed that the product obtained from **1** consisted of two components, irrespective of their molecular weights, and that the ratio of the two components varied with the molecular weight of the polymer precursor (Fig 4). It was also found that the larger molecular weight fractions formed from multiple precursor aggregates at increasing concentrations eluted earlier than the two isomer components (not shown).

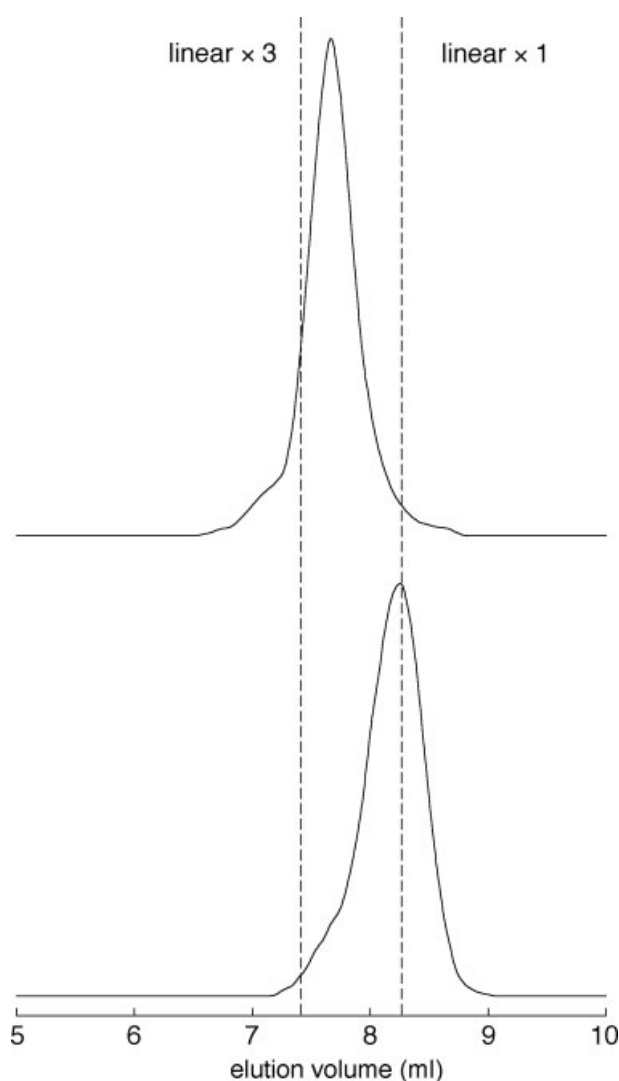


Figure 3. SEC traces (refractive index) of (top) the product from the assembly by telechelic poly(THF) with trimesate counteranion, **1**, after the heat treatment, and (bottom) the starting poly(THF) precursor. Sample; run 3 in Table 1. The poly(THF) precursor sample for SEC measurement was prepared by ion-exchange reaction of the precursor carrying triflate counteranions with benzoate, and subsequent heat treatment in order to avoid chromatographic anomaly due to polymer samples containing ionic moieties.

The subsequent fractionation of the two fractions and SEC examination confirmed that the major component is larger in size than the other, thus assignable to a manacle-shaped product while the other assigned as θ -shaped product, as was described in a preliminary report.⁹

The combination of the bifunctional precursor chain ends by carboxylate counteranions in **1** proceeds stepwise as shown in Scheme 2. Both manacle- and θ -shaped products are formed through four intermolecular and two intramolecular reactions within the assembly consisting of three polymer precursors and two carboxylate anions. A random linking process would produce the two isomers in a ratio of 3:2. The manacle-shaped product was indeed observed as the major component, while its relative amount was constantly higher than that estimated by random combination (Table 1). It is

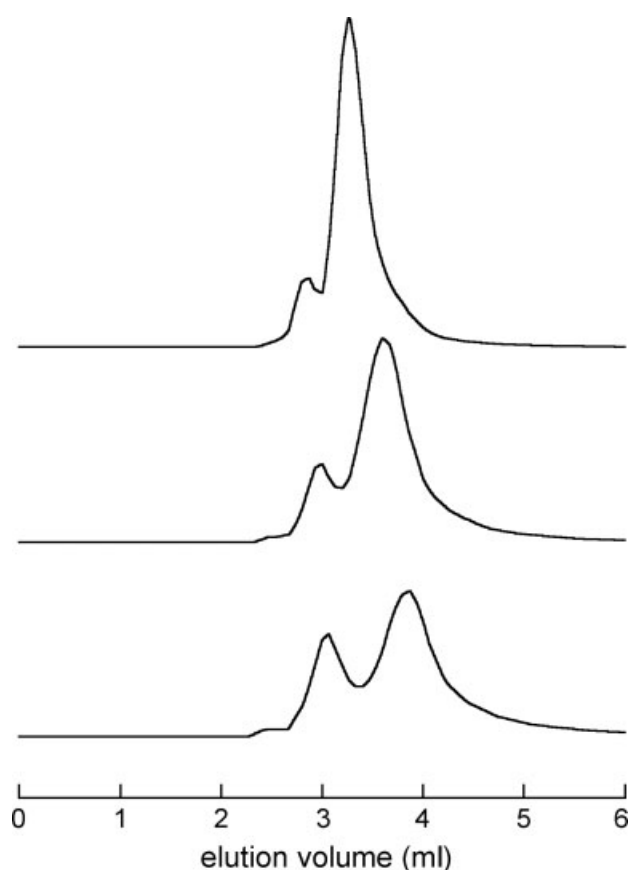
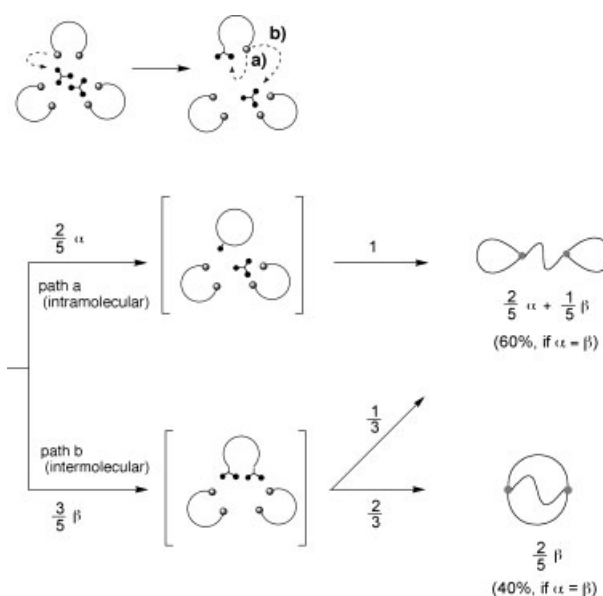


Figure 4. RPLC traces (UV) of the products from the assembly by telechelic poly(THF) with trimesate counteranion, **1**, after the heat treatment. Molecular weight (NMR) of the poly(THF) precursor in **1**: (top) 3300 g mol⁻¹ (middle) 5200 g mol⁻¹ and (bottom) 6800 g mol⁻¹. Sample; runs 2, 9 and 10 in Table 1, TSK ODS-80TS, eluent: THF/CH₃CN (50/50 in v/v), isocratic; 0.75 mL min⁻¹.

assumed that the two chain ends of the polymer precursor readily come into contact with each other, and thus the intramolecular reaction could occur



Scheme 2. Covalent conversion process of the electrostatically self-assembled polymer precursor, **1**.

more rapidly than the intermolecular process within the assembly. Consequently, the kinetically favoured intramolecular coupling could lead to preferential formation of two identical polymer cycles, each having an additional carboxylate group, followed by the intermolecular coupling to form a manacle-shaped product. In contrast, a θ -shaped product should be formed through four intermolecular reactions initially, followed by two intramolecular steps. The preference factor of the intramolecular cyclization against intermolecular combination, α/β , shown in Scheme 2, is given in the last column of Table 1. It is clear that the longer the chain of the polymer precursor in **1**, the more random the covalent conversion proceeded (runs 2, 9 and 10 in Table 1). However, the

Table 1. Synthesis of manacle- and θ -shaped poly(THF)s by electrostatic self-assembly and covalent fixation^a

Run	Precursor ^b (M_n (NMR) $\times 10^{-3}$) ^c	Conc (g l ⁻¹)	Isolated yield (%) ^d	M_p (SEC) $\times 10^{-3}$ ^e	$\frac{M_p \text{ (SEC)}^f}{M_n \text{ (NMR)}}$	θ /manacle isomer ratio ^g	α/β^h
1	1 (3.3)	0.05	38	7.3	0.73	11/89	7.6
2	1 (3.3)	0.1	85	7.6	0.77	10/90	8.5
3	1 (3.3)	0.2	85	7.6	0.77	11/89	7.6
4	1 (3.3)	0.3	69	7.3	0.73	10/90	8.5
5	1 (3.3)	0.5	74	7.3	0.73	12/88	6.8
6	1 (3.3)	1	77	7.3	0.73	13/87	6.2
7	1 (3.3)	2	78	7.6	0.77	16/84	4.8
8	1 (4.3)	0.2	80	9.4	0.73	17/83	4.4
9	1 (5.2)	0.1	84	11.9	0.76	16/84	4.8
10	1 (6.8)	0.1	63	14.1	0.69	28/72	2.1

^a Ring-opening was performed in THF at 66 °C for 3 h.

^b See Scheme 1.

^c Determined by ¹H NMR based on the signal ratio between the end-groups and the poly(THF) chain in g mol⁻¹.

^d Isolated yields after purification by preparative TLC.

^e M_p (SEC): apparent peak molecular weight determined by SEC relative to linear polystyrene standards by a conversion factor of 0.556 in g mol⁻¹.²⁰

^f A measure of the hydrodynamic volume ratio between manacle-shaped poly(THF), including minor portion of θ -shaped poly(THF), and their corresponding linear polymers. M_n (NMR): three times that of M_n of **1**.

^g Determined from reversed-phase liquid chromatography.

^h A preference factor of the intramolecular cyclization against intermolecular combination during the covalent conversion process. See also Scheme 2.

extent of dilution in the reaction solution during the covalent conversion process affected the isomer ratio less significantly (runs 1–7 in Table 1).

CONCLUSION

We present a novel polymer materials design through electrostatic self-assembly and covalent fixation with a unique polymer assembly comprised of telechelic poly(THF) having ammonium salt end groups carrying trimesate counteranions. It can provide unprecedented topology control of polymer materials and, moreover, the precise positioning of functional groups within the flexible polymer framework. Since natural proteins often achieve their diverse and specific functions through fine-tuning of the location of functional groups within the polypeptide framework, our strategy will offer a unique opportunity to develop synthetic polymer materials of unprecedented properties and functions.

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