Synthesis of θ-Shaped Poly(THF) by Electrostatic Self-Assembly and Covalent Fixation with Three-Armed Star Telechelics Having Cyclic Ammonium Salt Groups†

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ABSTRACT: A series of θ-shaped poly(tetrahydrofuran), poly(THF), of different molecular weights were effectively synthesized by an electrostatic self-assembly and covalent fixation process using a three-armed, star telechelic precursor having *N*-phenylpyrrolidinium salt groups carrying a trimesate, 1,3,5-benzene tricarboxylate, counteranion (**1**/trimesate). Under appropriate dilution in acetone, θ-shaped poly(THF)s (**2**) were obtained in 40−49% isolated yields through the covalent conversion of an electrostatic self-assembly of a single polymer precursor unit with retaining the balance of the charges between cations and anions. The isolated product was unequivocally characterized by means of ^{1}H NMR, IR, SEC as well as a reversed-phase chromatography (RPC), and MALDI−TOF MASS techniques.

Introduction

Novel macromolecular architectures comprised of monocyclic and polycyclic polymer units with optional free branches are of an increasing interest.[1−6] As for three dicyclic polymer topologies,[7] i.e., 8-shaped, θ-shaped, and manacle-shaped polymer constructions, synthetic attempts have so far been restricted on 8-shaped polymers.[8−11] Thus, an equimolar coupling reaction was performed between two units of linear bifunctionally living polymers and tetrafunctional coupling reagent under dilution.[8,9] An alternative approach of unimolecular double cyclization process was reported by Deffieux et al.,[10] and a cyclic polymer precursor having a functional group was prepared by Kubo et al. for the subsequent linking by a bifunctional coupling reagent under equimolar conditions.[11]

We have recently developed an "electrostatic self-assembly and covalent fixation" process for the effective synthesis of monocyclic and, moreover, three dicyclic polymer structures.[12,13] Thus, an 8-shaped polymer was effectively produced by using a self-assembly composed of two units of a bifunctional linear polymer precursor having cyclic ammonium salt end groups carrying one unit of tetracarboxylate as a counteranion.[12,14] Moreover, two other dicyclic polymers, i.e., a mixture of θ-shaped and manacle-shaped polymeric isomers, were prepared through a self-assembly composed of three units of a bifunctional linear polymer precursor having cyclic ammonium salt end groups carrying two unit of tricarboxylate as counteranions (Scheme 1).[12] Each of the two topological isomers could be identified and subsequently isolated by means of reversed-phase chromatography (RPC).

We have also shown a preliminary result on the selective synthesis of a θ-shaped polymer from a self-assembly composed of a trifunctional star-shaped polymer precursor having cyclic ammonium salt end groups (**1**) carrying a tricarboxylate as a counteranion (Scheme 1).[12] In the present paper, we show details on the synthesis of θ-shaped polymers of various molecular weights. Remarkable solvent effects were observed on the covalent conversion process of the electrostatically self-assembled precursor. The isolated θ-shaped polymer product was unequivocally characterized by NMR, IR, SEC as well as reversed-phase liquid chromatography (RPC), and MALDI−TOFF MASS techniques.

Experimental Section

Materials. Trifunctional star-shaped poly(THF)s having *N*-phenylpyrrolidinium salt end groups (**1**/triflate)[13] as well as their ion-exchange products with benzoate (**1**/benzoate) and subsequent three-armed star-shaped poly(THF)s (molecular weights of 7 300, 9 600, and 11 900 by ^{1}H NMR) were prepared by the method detailed before.[15] Sodium trimesate was prepared by mixing the corresponding free acids (5.00 g, 0.024 mol, Tokyo Kasei Kogyo Co. Ltd.) with an equimolar quantity of sodium hydroxide (93%, Koso Chemical Co., Ltd.) in water. After removing water in vacuo, the product (with a trace of water) was recovered quantitatively (7.68 g). Sodium benzoate (99.5%, Koso Chemical Co., Ltd.) was used as received. THF (>99.5%, no stabilizer, Wako Pure Chemical Industries, Ltd.) was dried over sodium benzophenone ketyl and distilled just before use. Chloroform (99%, Nacalai Tesque, Inc.) was dried over calcium chloride and then distilled under a nitrogen atmosphere. Acetone (>99.5%, Kanto Chemical Co., Inc.) was dried over K_2CO_3 and then distilled under a nitrogen atmosphere. Ethanol (>99%, Japan Alcohol Trading Co., Ltd.) was distilled over magnesium ethoxide. Unless noted otherwise, materials were obtained from commercial sources.

Synthesis of θ-Shaped Polymers (**2**). An ion-exchange reaction of **1**/triflate was conducted as in the following example. A THF solution (1.0 mL) of 0.200 g (0.026 mmol) of **1**/triflate was added dropwise to an ice-cooled (<5 °C) aqueous solution (120 mL) containing an excess amount of a sodium trimesate (0.083 g, 10 equiv) under vigorous stirring. After 1 h, the precipitated ion-exchange product was collected by filtration and dried in vacuo for up to 1.5 h. This precipitation treatment was repeated three times to give **1**/trimesate, 0.173 g (containing a trace amount of residual water to avoid uncontrolled ring-opening reaction), with 94% ion-exchange yield.

† Dedicated to Professor Eric Goethals in recognition of his contribution to polymer chemistry at the occasion of his 65th birthday.

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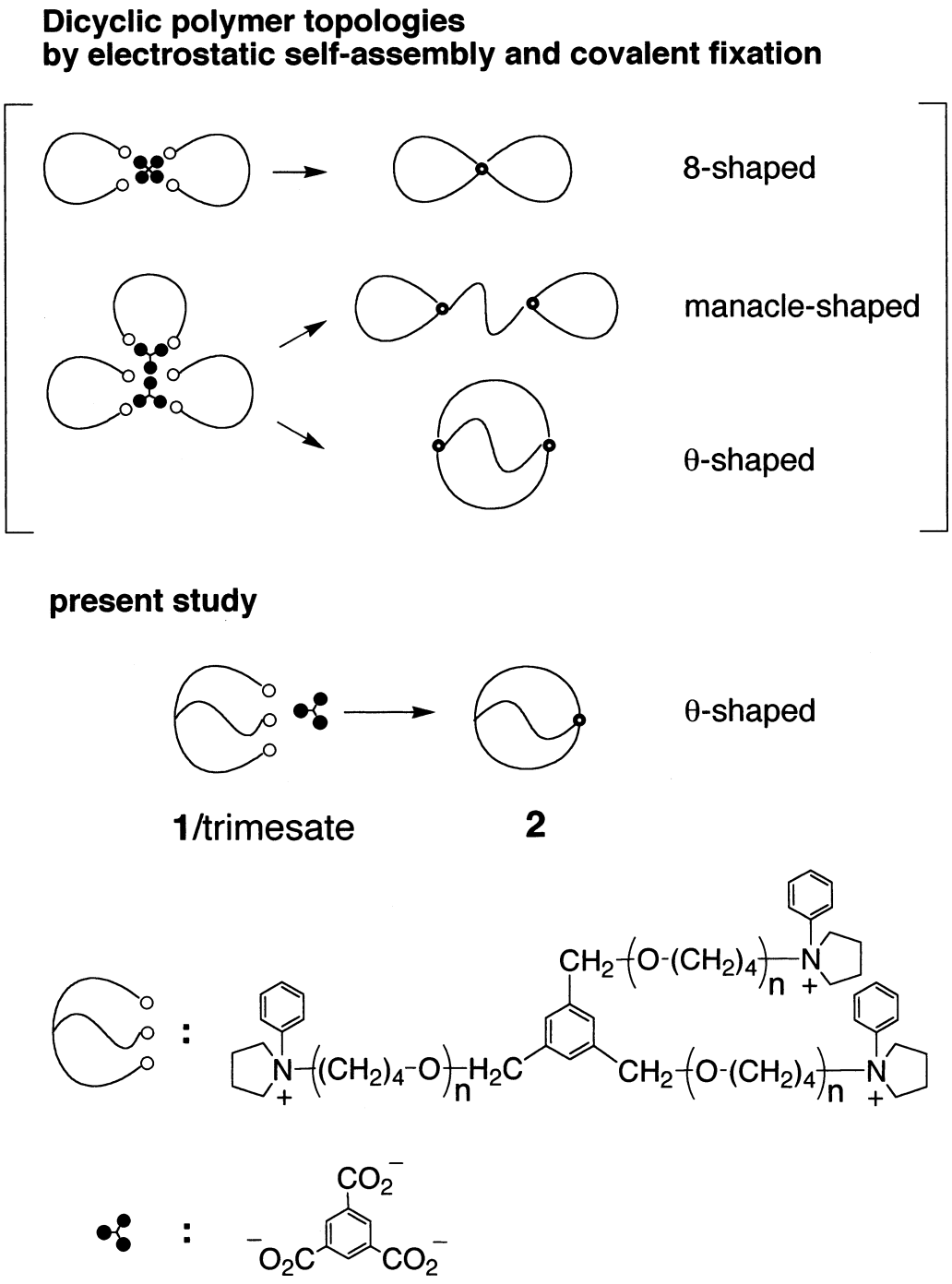
Scheme 1



1/trimesate: ^{1}H NMR δ 1.46−1.73 (m, CH_2CH$_2$O), 1.88−2.02 (m, 6H, *endo*-NCH$_2$CH_2), 2.31−2.45 (m, 6H, *endo*-NCH$_2$CH_2), 3.28−3.57 (m, CH$_2$CH_2O), 4.00−4.19 (m, 12H, *endo*-, *exo*-NCH_2), 4.48 (s, 6H, ArCH_2O), 4.41−4.58 (m, 6H, *endo*-NCH_2), 7.20 (s, 3H, Ar−*H* ortho to CH$_2$O), 7.41−7.73 (m, 15H, NPh), 8.71 (s, 3H, Ar−*H* ortho to CO_2^-).

The covalently-linked θ-shaped polymers (**2**) were prepared as in the following example. The ionic polymer precursor **1**/trimesate (0.025 g) was dissolved in 250 mL of acetone (0.1 g/L) and was heated to reflux (bath temperature of 90 °C) for 18 h. The reaction solvent was removed, and the recovered product (0.023 g) was further purified by preparative thin-layer chromatography (SiO_2, hexane/acetone = 2/1) to yield 0.011 g (49%) of θ-shaped poly(THF) **2**.

2: ^{1}H NMR δ 1.46−1.76 (m, CH_2CH$_2$O), 3.24−3.54 (m, CH$_2$CH_2O), 4.39 (t, J = 6.0 Hz, 6H, CO$_2$CH_2), 4.48 (s, 6H, ArCH_2O), 6.58−6.70 (m, 9H, Ar−*H* ortho and para to N), 7.12−7.22 (m, 9H, Ar−*H* meta to N, and Ar−*H* ortho to CH$_2$O), 8.82 (s, 3H, Ar−*H* ortho to CO$_2$CH$_2$).

Measurements. SEC measurements were performed using a Tosoh model CCPS 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 TSK G4000HXL (300 mm × 7.8 mm i.d., 5 μm average particle size) was employed with THF as an eluent at a flow rate of 1.0 mL/min at 40 °C. In a typical procedure, 40 μL of sample solution (sample concentration of 0.5 wt %) was injected. Reversed-phase chromatography measurements were conducted by an isocratic mode using a Tosoh model CCPS equipped with a UV detector model UV 8020 at 254 nm. A C_{18} bonded silica column of TSK ODS-80TS (80 Å pore, 250 mm × 4.6 mm, i.d., 5 μm average particle size) was employed with a mixture of THF/CH$_3$CN (1/1 in volume) 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. ^{1}H NMR spectra were recorded with a JEOL JNM-AL300 apparatus in $CDCl_3$ at 40 °C. The proton chemical shifts (ppm) were referenced from a signal of tetramethylsilane. MALDI−TOF MASS spectra were taken on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer is equipped with a nitrogen laser (λ = 337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV in linear-positive ion mode. The 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 also dissolved in THF (10 and 1 g/L, respectively). The polymer solution (50 μL) was then mixed with 50 μL of the matrix solution. A 1 μL 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 two-point method with insulin β plus H^+ at 3497.96 and α-cyano-hydroxycinnamic acid dimer plus H^+ at 379.35.

Results and Discussion

Electrostatic Self-Assembly and Covalent Fixation of Star Telechelic Poly(THF). We have recently developed an effective polymer cyclization process by an "electrostatic self-assembly and covalent fixation" by making use of linear bifunctional polymer precursors having cyclic ammonium salt end groups carrying a dicarboxylate counteranion.[12,14,16−20] A key feature of this process is the balance of the charges between cations at polymer chain ends and carboxylate counteranion species and the subsequent covalent conversion through the ring-opening reaction of moderately strained cyclic ammonium salt groups by the nucleophilic attack of carboxylate counteranions. As an extension of this principle, we have employed a trifunctional star-shaped poly(THF) precursor having cyclic ammonium salt end groups (**1**) carrying a tricarboxylate counteranion to produce a θ-shaped polymer construction (Scheme 1).

Trifunctional star-shaped poly(THF) precursors of different molecular weights were prepared according to the method reported elsewhere.[15] Thus, a trifunctional initiator for the living polymerization of THF was prepared in situ by the reaction of 1,3,5-tris(hydroxymethyl)benzene with trifluoromethanesulfonic anhydride in the presence of a proton trap. The subsequent living polymerization of THF followed by the termination with *N*-phenylpyrrolidine affords a star-shaped poly(THF) precursor having *N*-phenylpyrrolidinium salt groups (**1**/triflate). The anion-exchange reaction from a triflate toward such carboxylate as a monofunctional benzoate and a trifunctional trimesate proceeded by the repeated precipitation of the poly(THF) precursor (**1**/triflate) solution into an aqueous solution containing carboxylate anion in its sodium salt form. An ionic assembly of **1**/trimesate was thus isolated in high recovery yield. A relevant ion-exchange product with benzoate, **1**/benzoate, was also prepared from the same precursor, **1**/triflate, as a reference sample. The subsequent ring-opening reaction of **1**/benzoate at an elevated temperature produced a star-shaped polymer, retaining the narrow molecular weight distributions (PDI = 1.10−1.15).[15]

The heating treatment of **1**/trimesate was conducted in various solvents under dilution at 0.1−0.2 g/L. While the gelation was observed in bulk or at higher concentration, the reaction at dilution proceeded homogeneously. Thus, the deassembly of an aggregate of **1**/trimesate tended to proceed, and a unique assembly was formed, comprising a single polymer precursor unit carrying a single trimesate counteranion to balance the charges between cations and anions. The subsequent heat treatment under dilution produced a θ-shaped polymer product.

A remarkable solvent effect was observed on the covalent conversion process, i.e., the ring-opening reaction of *N*-phenylpyrrolidinium salt group by a trimesate counteranion in comparison with the previous polymer cyclization by the relevant bifunctional linear poly(THF) carrying a biphenyldicarboxylate counteranion.[18] First, the ring-opening reaction failed to occur at all in ethanol as in the previous system. This is ascribed to the hydrogen bonding of ethanol to carboxylate to suppress the nucleophilic reactivity. In chloroform, moreover, the reaction by trimesate did not proceed at all, in contrast with a quantitative reaction by biphenyldicarboxylate. The choice of chloroform as solvent is thus decisive either to suppress or to cause the ring-opening reaction, by recognizing lower nucleophilicity of a trimesate (pK_a = 2.98) than a biphenyldicarboxylate (pK_a = 3.77).[21,22]

The ring-opening reaction by a trimesate took place both in THF and in acetone, as in the previous biphenyldicarboxylate system.[18] It is remarkable that the reaction by the trimesate proceeded notably faster in THF than in acetone. Thus, the quantitative ring-opening reaction took place in THF after 3 h, while the conversion remained at 48% in acetone. On the contrary, such kinetic discrimination was not observed in the previous system by a biphenyldicarboxylate,[18] where the reaction completed within 3 h both in THF and in acetone. The lower nucleophilic reactivity of a trimesate than a biphenyldicarboxylate will be again attributable to this solvent effect.

SEC also showed another notable solvent effect by comparing the products obtained in THF, in acetone, and in their mixtures (Table 1). Thus, a SEC profile of the product obtained in THF showed a noticeable shoulder fraction at higher molecular weight region (Figure 1). On the other hand, the products obtained in THF/acetone mixtures showed, as compared in Figure 1, a narrower peak profile by eliminating higher molecular weight fractions. This accords with that the deassembly of **1**/trimesate to a single polymer unit tends to proceed more effectively in a polar solvent of acetone (ϵ = 21) than in THF (ϵ = 7.5), where oligomeric self-assemblies remain and subsequently converted to covalently fixed products.

Characterization of θ-Shaped Polymers. A series of θ-shaped poly(THF)s, **2**, of different molecular weights were thus synthesized in acetone (Table 1). These products were isolated in 40−49% yields after purification by preparative TLC to remove any residual ionic species. The products were then characterized by means of IR, ^{1}H NMR, SEC as well as PRC, and MALDI−TOF MASS techniques. First, IR and ^{1}H NMR showed a quantitative ring-opening reaction to produce amino-ester groups at each chain ends of star-shaped polymer precursors (Supporting Information, S-Figure 1).

SEC showed that the θ-shaped product, **2**, was significantly smaller in its size than the relevant star-shaped polymer possessing nearly equal molecular weights (thus total chain lengths) (Figure 2, left). The relative size ratio, corresponding to their hydrodynamic volumes, between the θ-shaped and the star-shaped polymers was within the range of 0.71−0.75, as estimated from their SEC peak molecular weights (Table 1). The three-dimensional size of a θ-shaped polymer is constricted by linking three chain ends of a star polymer

Table 1. Synthesis of θ-Shaped Poly(THF)s by Electrostatic Self-Assembly and Covalent Fixation[a]

run	M_n(NMR) of precursor **1** $\times 10^{-3}$ [b]	solvent[c]	concn (g/L)	time (h)	isolated yield (%)[d]	M_p(SEC) $\times 10^{-3}$ [e]	PDI[f]	$M_p(\theta)/M_p$(star)[g]	M_p(SEC)/M_n(NMR)[h]
1	7.3	acetone	0.1	18	49	4.4	1.10	0.71	0.61
2	11.9	acetone	0.1	18	42	7.4	1.07	0.71	0.63
3	9.6	acetone	0.1	18	40	5.6	1.16	0.75	0.60
4	9.6	THF/acetone (1/2)	0.2	12	71	6.2	1.41	n.d.[i]	n.d.
5	9.6	THF/acetone (1/1)	0.2	12	65	6.2	1.24	n.d.	n.d
6	9.6	THF/acetone (2/1)	0.2	12	67	6.2	1.24	n.d.	n.d.
7	9.6	THF	0.2	3	54	6.5	1.31	n.d.	n.d.

[a] Ring-opening was performed under reflux in respective solvents. [b] See Scheme 1. M_n(NMR): determined by ^{1}H NMR based on the signal ratio between the end groups and the poly(THF) chain. [c] Values in parentheses are volume ratios. [d] Isolated yields after purification by preparative TLC. [e] M_p(SEC): apparent molecular weight determined by SEC relative to linear polystyrene standards by a conversion factor of 0.556 (ref 35). [f] Determined by SEC on the basis of standard polystyrenes. [g] A measure of the hydrodynamic volume ratio between θ-shaped poly(THF)s and star-shaped precursor analogues prepared from the corresponding star-shaped poly(THF) carrying benzoate counteranions. Determined by SEC. [h] A measure of the hydrodynamic volume ratio between θ-shaped poly(THF)s and their corresponding linear poly(THF) analogues. [i] n.d. = not determined.

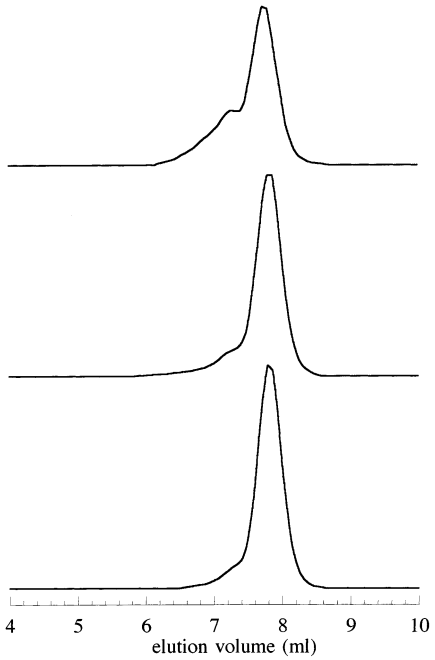


Figure 1. SEC traces (RI) of the product from **1**/trimesate after the heat treatment, in THF at 0.2 g/L (top), in THF/acetone (50/50 in v/v) at 0.2 g/L (middle), and in acetone at 0.1 g/L (bottom) (samples; runs 7, 5, and 3 in Table 1; TSK G4000HXL, eluent: THF, 1.0 mL/min).

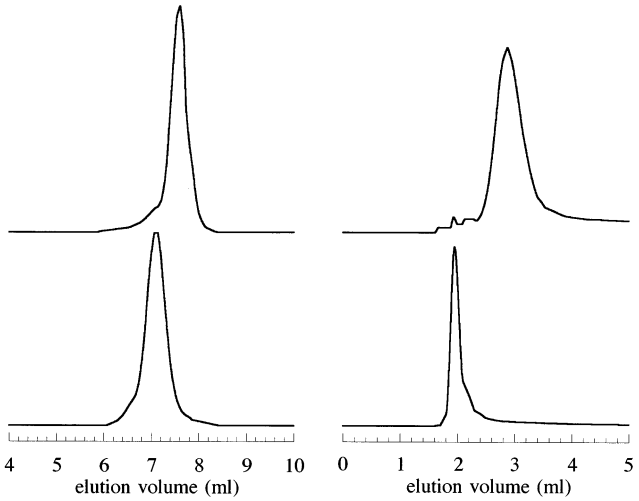


Figure 2. SEC (left) and RPC (right) traces of a θ-shaped poly(THF) (top) and a star-shaped analogue (bottom) (SEC (RI): sample; run 3 in Table 1; TSK G4000HXL, eluent: THF, 1.0 mL/min; RPC (UV): sample; run 1 in Table 1, TSK ODS-80TS, eluent: THF/CH_3CN (50/50 in v/v), isocratic; 1.0 mL/min).

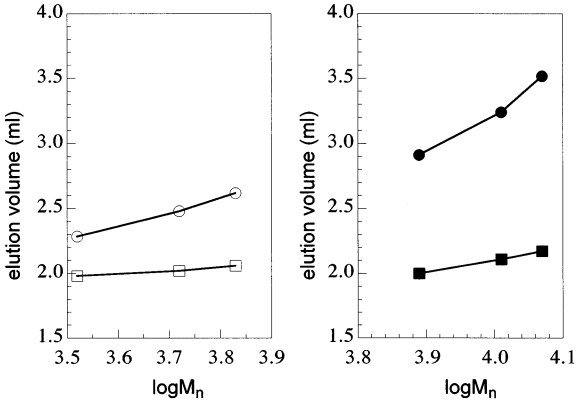


Figure 3. Relationships between the molecular weight and the RPC elution volume for (right) θ-shaped poly(THF)s (●) and star-shaped analogues (■) and for (left) cyclic poly(THF)s (○) and linear analogues (□) (samples; runs 1, 3, and 2 in Table 1 for θ-polymers, TSK ODS-80TS, eluent: THF/CH_3CN (50/50 in v/v), isocratic; 1.0 mL/min).

precursor, and the extent of the constriction is more significant than in the cyclic polymer formation from the linear polymer precursor (the size ratio of cyclic/linear polymers is around 0.8 estimated by SEC).[23−27] Since the star-shaped polymer is constricted in its size in comparison with its linear analogue, θ-shaped polymers are significantly compact in their three-dimensional structures. Thus, indeed, the relative size ratio between the θ-shaped and the linear polymers was estimated in the range 0.60−0.63 (Table 1).

RPC was also conducted on the obtained θ-shaped poly(THF)s, in comparison with their star-shaped polymer analogues (Figure 2, right), to check the purity of the isolated products.[28−34] The isolated θ-shaped polymer showed a nearly unimodal RPC profile with only a trace of side products, whose elution volume corresponds to that of the star-shaped poly(THF) analogue. This is indicative of the high uniformity of the product both in the chemical composition and in the topological structure.

Moreover, the RPC elution behavior of a pair of θ-shaped and star-shaped poly(THF)s of different molecular weights was compared with that of the relevant pair of simple cyclic and linear counterparts (Figure 3). It is shown that θ-shaped and single cyclic poly(THF)s eluted after the corresponding star-shaped and linear analogues, respectively, and the difference in the elution volumes in the pair of θ-shaped and star-shaped poly-

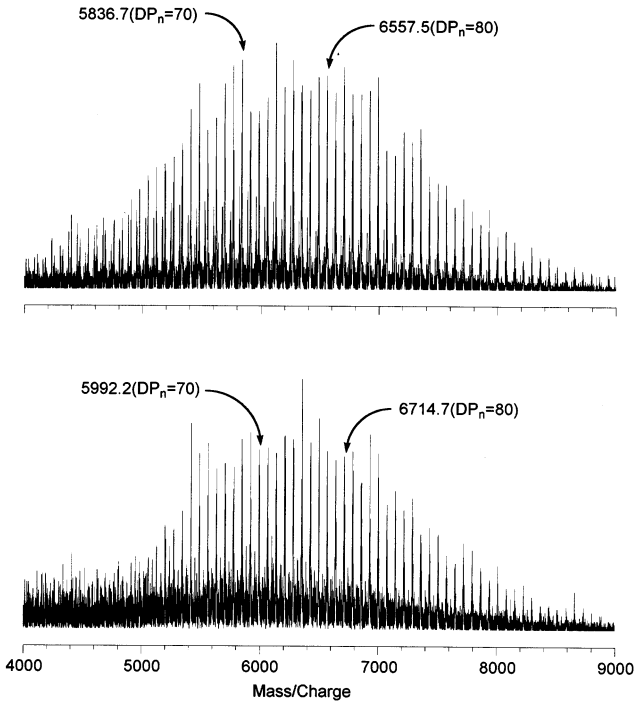


Figure 4. MALDI−TOF MASS spectra of (top) a θ-shaped poly(THF) and of (bottom) a star-shaped analogue (sample; run 1 in Table 1 for the θ-polymer; linear mode, matrix: dithranol with sodium trifluoroacetate).

mers was larger than that in the pair of cyclic and linear counterparts. The topological change in the former pair is more significant than in the latter pair by decreasing the number of chain ends from 3 to 0 in the former against 2 to 0 in the latter. In addition, the constriction of the three-dimensional size from the star to θ-shaped polymers is more significant than from linear to cyclic polymers.

Finally, the θ-shaped poly(THF), **2**, and its star-shaped precursor analogue were examined by a MALDI−TOF MASS spectroscopy (Figure 4). The θ-shaped polymer product 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 ring-opening reaction of three *N*-phenylpyrrolidinium groups by a trimesate anion. As an example, the peak (assumed to be the adduct with Na^+) at 5836.7 corresponds to the product with the DP_n of 70, $(C_4H_8O) \times 70 + C_{48}H_{51}N_3O_6$, plus Na^+ as 5836.451. A minor series of peaks having smaller molecular weights (by 22 mass units) were also observed, corresponding to the adduct with H^+. The star-shaped product, obtained from the identical poly(THF) precursor, **1**, but carrying benzoate counteranions, also showed a series of the peaks corresponding to the Na^+ adduct. Thus, the peak (assumed to be the adduct with Na^+) at 5992.2 corresponds to the product with the DP_n of 70, $(C_4H_8O) \times 70 + C_{60}H_{63}N_3O_6$, plus Na^+ as 5992.679. Since both θ-shaped and star-shaped poly(THF)s are produced from the identical precursor **1**, after the ion exchange by either a trimesate or three benzoate counteranions, their molecular weights differ by 156 mass units. This was confirmed by the two TOF MASS spectra shown in Figure 4.

To conclude, θ-shaped polymers of different molecular weights were synthesized in practical yields. The electrostatic self-assembly and covalent fixation process was proven to be an effective means to produce such an unusual polymer architecture. Further studies in progress in our laboratory include the topology effect on static and dynamic polymer properties and the synthesis of not only dicyclic but also tricyclic polymer constructions.

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Supporting Information Available: S-Figure 1: IR (top) and ^1H NMR (300 MHz) (bottom) spectra of a θ-shaped poly(THF) (sample; run 3 in Table 1, NMR; $CDCl_3$, 40 °C). This material is available free of charge via the Internet at http://pubs.acs.org.

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