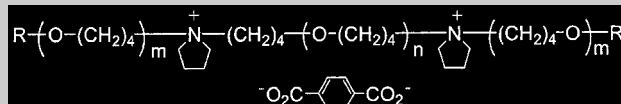


Communication: A novel and unusual polymer topology, i.e. *a-ring-with-two-branches*, has been constructed efficiently by making use of an interiorly functionalized poly(tetrahydrofuran) (poly(THF)) having two pyrrolidinium groups. The dicarboxylate counterion, i.e. terephthalate, was then introduced by an ion-exchange reaction of the interiorly located pyrrolidinium group. Subsequent heat treatment under appropriate dilution caused an efficient polymer cyclization to produce an *a-ring-with-two-*

branches polymer topology in high yield through the selective and quantitative ring-opening of the pyrrolidinium groups by the dicarboxylate counterion.



Designing an “A-Ring-with-Branches” Polymer Topology by Electrostatic Self-Assembly and Covalent Fixation with Interiorly Functionalized Telechelics^a Having Cyclic Ammonium Groups

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Introduction

The increasing diversity in polymer architectures has offered better opportunities in the development of novel polymer materials of unprecedented properties and functions, eventually leading to future nanotechnology.^[1,2] While a *linear* polymer architecture, possessing two chain ends, is a fundamental polymer topology, other polymer architectures possessing multiple chain ends and branch points, such as star polymers,^[3,4] polymacromonomers,^[5,6] hyperbranched polymers,^[7] and dendrimers,^[8,9] have become increasingly common. Another unique class of basic polymer architecture is a *cyclic* topology without any chain ends.^[10] Single and double cyclic, i.e. eight-shaped, polymer architectures have been realized so far.^[11–16] A wider variety of polymer topologies is envisaged by the combination of cyclic and linear polymer units. In this regard, a polymer of *a-ring-with-a-branch* structure, i.e. a tadpole polymer was also reported.^[14,15,17] Yet a practical and high yield synthesis of these class of polymers is an ongoing challenge.

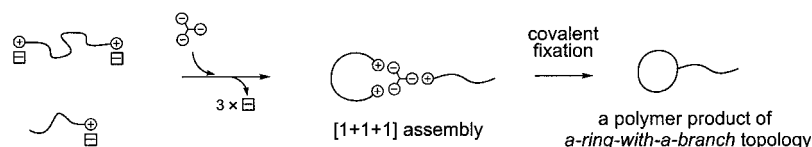
^a We propose herein the term “*eso-telechelics*” for a polymer precursor having interiorly located functional groups (*esoterikos* means *interior* in Greek).

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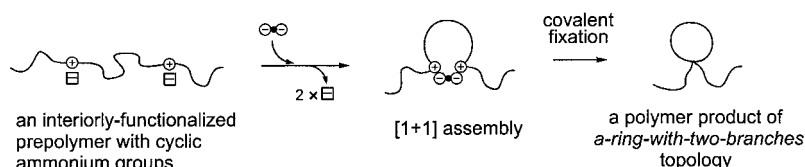
We recently developed an *electrostatic self-assembly and covalent fixation* process for the efficient construction of a variety of macromolecular architectures containing cyclic polymer units.^[15,18] In this method, we have utilized telechelic poly(THF)s with cyclic ammonium groups carrying various multi-carboxylate counterions.^[18] Under appropriate dilution, the ionic polymer precursors completely disaggregate^[18,19] into a smallest assembly, with balancing the charges between cations and anions. The subsequent covalent fixation through the ring-opening reaction of the cyclic ammonium groups by carboxylate counterions provides a variety of polymer architectures comprising a single or multiple cyclic polymer units.

We also demonstrated the effective construction of a polymer with *a-ring-with-a-branch* structure by making use of a spontaneous three-component self-assembly of mono- and bifunctional telechelics (Scheme 1) with a trifunctional counterion.^[15] As a further extension to the preceding studies, we report here on an efficient polymer cyclization of newly synthesized poly(THF) precursors having *interiorly located* pyrrolidinium groups, namely, *eso-telechelics*. Thus, an unusual polymer of *a-ring-with-two-branches* structure^[20,21] has been constructed effectively (Scheme 1).

A: From end-functionalized polymer precursors



B: From an interiorly-functionalized polymer precursor

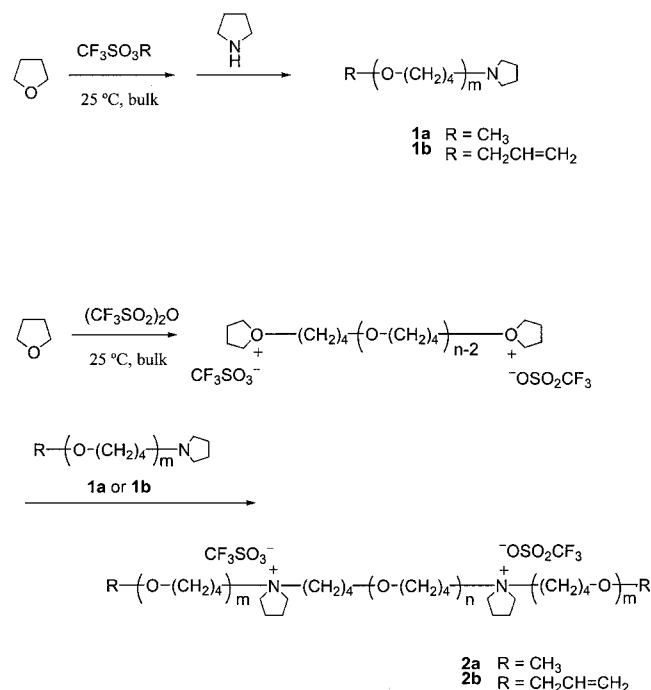


Scheme 1.

Experimental Part

Materials

Poly(THF)s having a tertiary amine, i.e. pyrrolidine end group (**1a** and **1b**) were synthesized by a cationic polymerization of THF initiated with either commercially available methyltrifluoromethane sulfonate (triflate) or in situ prepared allyl triflate,^[22,23] followed by a termination reaction with a secondary amine, i.e. pyrrolidine (Scheme 2).^[24] Sodium benzoate (Koso Chemical Co., Ltd.) and sodium terephthalate (Tokyo Kasei Kogyo Co., Ltd.) were used as received. Solvents were purified according to literature procedures.^[25] Trifluoromethanesulfonic anhydride (triflic anhydride) was distilled from P₂O₅ just before use. Unless otherwise noted, materials were obtained from commercial sources.



Scheme 2.

Preparation of Interiorly Functionalized Poly(THF) Having Pyrrolidinium Groups

Interiorly functionalized poly(THF)s having pyrrolidinium groups (**2a** and **2b**) were synthesized by a living polymerization technique (Scheme 2). A bifunctionally living poly(THF) was prepared by the cationic ring-opening polymerization of THF (25 mL) with trifluoromethanesulfonic anhydride (0.4 mmol) as the initiator at 25 °C. The subsequent end-capping reaction was conducted at around 10% monomer conversion to exclude chain-transfer reactions, by adding around 10% more of the equimolar quantities of **1a** and of **1b** (40 wt.-% solution in THF). **2a** and **2b** were subsequently isolated by precipitation into water cooled to 5 °C. Yields ranged from 1.5 g to 2.0 g.

2a: ¹H NMR (300 MHz, CDCl₃), see Figure 1.

IR (film): 1255, 1031, 639 cm⁻¹ (triflate anion).

2b: ¹H NMR (300 MHz, CDCl₃), see Figure 2 (top).

IR (film): 1261, 1031, 638 cm⁻¹ (triflate anion).

Ion-Exchange Reaction of 2

A detailed procedure of the ion-exchange reaction was described elsewhere.^[15,19] Ion-exchange products **2a(t)**, **2a(b)**, **2b(t)** and **2b(b)** (Scheme 3) were obtained by the repeated precipitation treatment of bifunctional poly(THF)s **2a** and **2b** into cold water (<5 °C) containing excess sodium terephthalate (**t**) or benzoate (**b**), respectively.

2a(t): ¹H NMR (300 MHz, CDCl₃): δ = 1.30–1.70 (m, CH₂CH₂O), 2.10–2.22 (m, 8 H), 3.32 (s, 6 H), 3.20–3.50 (m, CH₂CH₂O), 3.45–3.70 (m, 8 H), 8.02 (s, 4 H).

IR (film): 1563 cm⁻¹ (carboxylate anion).

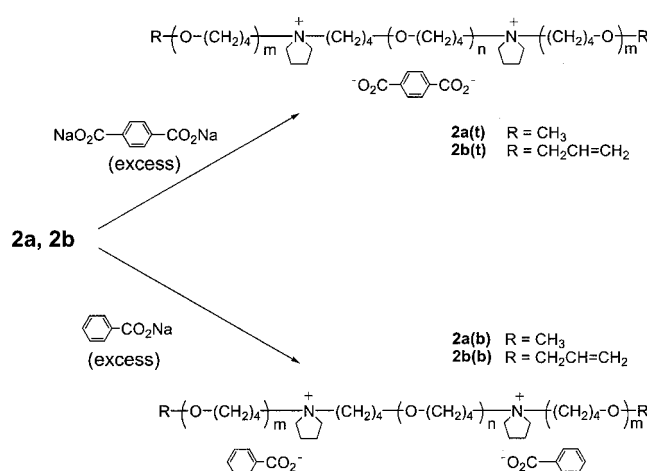
2a(b): ¹H NMR (300 MHz, CDCl₃): δ = 1.30–1.70 (m, CH₂CH₂O), 2.16–2.26 (m, 8 H), 3.32 (s, 6 H), 3.20–3.50 (m, CH₂CH₂O), 3.72–3.86 (m, 8 H), 7.20–7.35 (m, 6 H), 8.06–8.12 (m, 4 H).

IR (film): 1556 cm⁻¹ (carboxylate anion).

2b(t): ¹H NMR (300 MHz, CDCl₃), see Figure 2 (middle).

IR (film): 1558 cm⁻¹ (carboxylate anion).

2b(b): ¹H NMR (300 MHz, CDCl₃): δ = 1.30–1.70 (m, CH₂CH₂O), 2.18–2.28 (m, 8 H), 3.25–3.60 (m, CH₂CH₂O),



Scheme 3.

3.70–3.84 (m, 8 H), 3.96 (ddd, $J = 5.7, 1.5, 1.5$ Hz, 4 H), 5.15 (ddt, $J = 10.2, 1.5, 1.5$ Hz, 2 H), 5.26 (ddt, $J = 17.1, 1.5, 1.5$ Hz, 2 H), 5.91 (ddt, $J = 17.1, 10.2, 5.7$ Hz, 2 H), 7.20–7.35 (m, 6 H), 8.06–8.12 (m, 4 H).

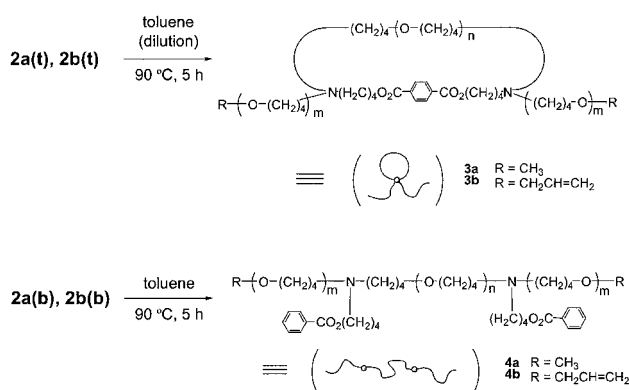
IR (film): 1556 cm^{-1} (carboxylate anion).

Ring-Opening Reaction of Pyrrolidinium Groups

Each of the ion-exchange products **2a(t)**, **2a(b)**, **2b(t)** and **2b(b)** (0.02–0.5 g) was dissolved in toluene at the prescribed concentration (0.1–5.0 g/L) and was heated at 90 °C for 5 h (Table 1). Covalently converted products **3a**, **4a**, **3b** and **4b** (Scheme 4) were recovered in almost quantitative yields simply after evaporating the solvent, and were subjected to spectroscopic and chromatographic analyses. The recovered products were further purified by means of preparative thin layer chromatography (TLC; SiO_2 , hexane/acetone 2:1) (48–55% isolated yield).

3a: ^1H NMR (300 MHz, CDCl_3) $\delta = 1.50$ – 1.70 (m, $\text{CH}_2\text{CH}_2\text{O}$), 2.36–2.52 (m, 12 H), 3.32 (s, 6 H), 3.25–3.52 (m, $\text{CH}_2\text{CH}_2\text{O}$), 4.35 (t, $J = 6.3$ Hz, 4 H), 8.08 (s, 4 H).

IR (film): 1721 cm^{-1} (ester).



Scheme 4.

4a: ^1H NMR (300 MHz, CDCl_3) $\delta = 1.50$ – 1.70 (m, $\text{CH}_2\text{CH}_2\text{O}$), 2.36–2.52 (m, 12 H), 3.32 (s, 6 H), 3.25–3.52 (m, $\text{CH}_2\text{CH}_2\text{O}$), 4.33 (t, $J = 6.3$ Hz, 4 H), 7.38–7.46 (m, 4 H), 7.50–7.56 (m, 2 H), 8.00–8.06 (m, 4 H).

IR (film): 1720 cm^{-1} (ester).

3b: ^1H NMR (300 MHz, CDCl_3), see Figure 2 (bottom).

IR (film): 1721 cm^{-1} (ester).

4b: ^1H NMR (300 MHz, CDCl_3) $\delta = 1.50$ – 1.70 (m, $\text{CH}_2\text{CH}_2\text{O}$), 2.42–2.54 (m, 12 H), 3.25–3.50 (m, $\text{CH}_2\text{CH}_2\text{O}$), 3.95 (ddd, $J = 5.7, 1.5, 1.5$ Hz, 4 H), 4.33 (t, $J = 6.6$ Hz, 4 H), 5.15 (ddt, $J = 10.2, 1.5, 1.5$ Hz, 4 H), 5.25 (ddt, $J = 17.1, 1.5, 1.5$ Hz, 2 H), 5.90 (ddt, $J = 17.1, 10.2, 5.7$ Hz, 4 H), 7.38–7.46 (m, 4 H), 7.52–7.58 (m, 2 H), 8.00–8.06 (m, 4 H).

IR (film): 1721 cm^{-1} (ester).

Measurements

Size-exclusion chromatography (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 G2000HXL or TSK G3000HXL was employed with THF as the eluent at a flow

Table 1. Polymer cyclization by interiorly functionalized poly(THF)s having pyrrolidinium groups. The ring-opening reaction of the pyrrolidinium groups was performed in a toluene solution (1.0 g/L) at 90 °C for 5 h.

Run	Polymer terminator ^{a)} [\bar{M}_n (NMR)]	Ionic polymer precursor ^{a)} [\bar{M}_n (NMR)] ^{b)}	A-ring-with-two-branches product ^{a)}	Isolated yield ^{c)} %	\bar{M}_n (NMR) ^{d)}	$M_p(\mathbf{3})/M_p(\mathbf{4})^e$	PDI ^{f)}
1	1a [1 900]	2a [7 800]	3a	60 (85)	8 000	0.79	1.05
2	1b [1 700]	2b [6 600]	3b	55 (80)	6 400	0.80	1.07

a) See Scheme 2 and 4.

b) Determined by means of ^1H NMR spectroscopy assuming a quantitative introduction of interiorly located pyrrolidinium groups.

c) Isolated yields after purification by means of preparative TLC. Yields in parentheses are estimated from the SEC peak area of the crude products.

d) Determined by means of ^1H NMR spectroscopy assuming a quantitative chemical conversion of interiorly located pyrrolidinium salt groups.

e) A measure of the hydrodynamic volume ratio between the poly(THF) of an a-ring-with-two-branches structure (**3**) and its linear analog **4**. M_p : Apparent-peak molecular weight determined by means of SEC with a calibration using linear polystyrene standards by a conversion factor of 0.556.^[28] The linear analogs were prepared from the corresponding poly(THF) **2** carrying benzoate counterions.

f) Determined by means of SEC on the basis of polystyrene standards.

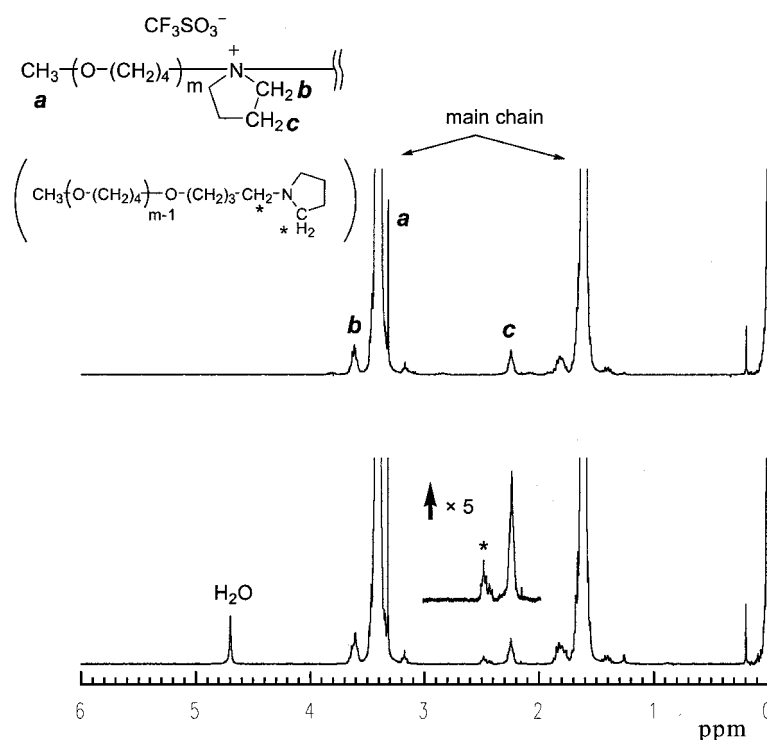


Figure 1. 300 MHz ¹H NMR spectra of an interiorly functionalized poly(THF) having pyrrolidinium groups (**2a**) before (top) and after (bottom) the addition of a drop of a NaOH/D₂O solution. (Sample: run 1 in Table 1; CDCl₃; 40 °C).

rate of 1.0 ml/min. IR spectra were taken on a JASCO FT/IR-410 infrared spectrometer by casting the sample from the chloroform solution on a NaCl plate. ¹H NMR spectra were recorded on a JEOL JNM-AL300 apparatus in CDCl₃ at 40 °C. The proton chemical shifts (ppm) were referenced to the signal of tetramethylsilane.

Results and Discussion

Preparation of Interiorly Functionalized Poly(THF)s Having Pyrrolidinium Groups

The two types of poly(THF) having interiorly located pyrrolidinium groups were synthesized by a two-stage procedure (Scheme 2 and Table 1). Thus in the first stage, the two types of monofunctionally living poly(THF) were prepared with either methyl triflate or allyl triflate.^[22, 23] They were subsequently terminated with a secondary amine, i.e. pyrrolidine, to produce the corresponding poly(THF)s **1a** and **1b** having a tertiary amine, i.e. *N*-substituted pyrrolidine, end group. In the second stage, they were subjected to an end-capping reaction of a bifunctionally living poly(THF), prepared by using triflic anhydride. Reaction products were recovered after precipitation into water cooled to 5 °C. The ¹H NMR spectra of the products recovered such (top in Figure 1 and 2, respectively) showed the formation of interiorly functionalized poly(THF)s **2a** and **2b** having pyrrolidinium groups.

Thus, signals at 3.50–3.68 ppm due to ammonium α -methylene protons and at 2.18–2.28 ppm due to ammonium β -methylene protons of the pyrrolidinium groups could be observed. A singlet at 3.32 ppm for **2a** is due to the methoxy group of **1a**, and signals at 5.91 (ddt, $J = 17.1, 10.2, 5.7$ Hz), 5.26 (ddt, $J = 17.1, 1.5, 1.5$ Hz), 5.15 (ddt, $J = 10.2, 1.5, 1.5$ Hz) and 3.96 (ddd, $J = 5.7, 1.5, 1.5$ Hz) ppm for **2b** are due to the allyloxy group of **1b**. Small signals for the remaining polymeric end-capping reagent **1a** or **1b**, used in slight excess with respect to the living chain end, become visible after the addition of a drop of an NaOH/D₂O solution into the NMR sample. Thus, the signals due to the α -methylene protons of the tertiary pyrrolidine group are noticeable at 2.40–2.50 ppm (marked with an asterisk), as seen in Figure 1 (bottom). Nevertheless, it was confirmed that the amounts of **1a** or **1b** present (around 10 wt.-%) are inert in the subsequent ion-exchange and ring-opening reactions of the interiorly located pyrrolidinium groups. **1a** and **1b** could be removed afterward by means of silica gel chromatography.

Synthesis of Poly(THF)s of "A-Ring-with-Two-Branched" Structure

A dicarboxylate, i.e. terephthalate, counterion was then introduced to the interiorly located pyrrolidinium groups in poly(THF)s **2a** and **2b** by ion-exchange reaction

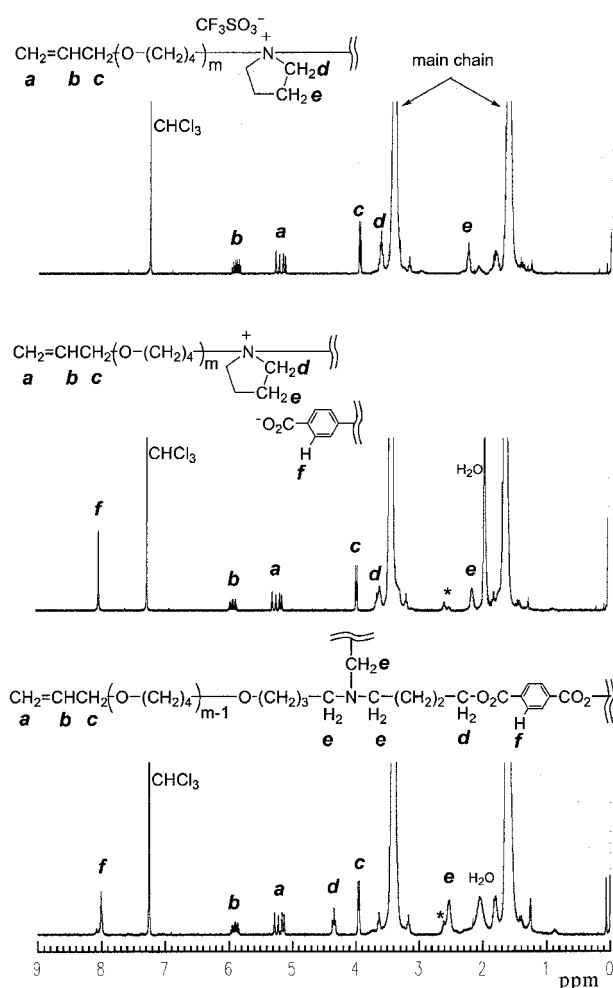


Figure 2. 300 MHz ^1H NMR spectra of an interiorly functionalized poly(THF) having pyrrolidinium groups (**2b**, top) and the ion-exchange product with sodium terephthalate before (**2b(t)**, middle) and after (**3b**, bottom) heat treatment. (Sample: run 2 in Table 1, CDCl_3 , 40°C , for the assignment of the signals marked with an asterisk, see Figure 1).

through a simple precipitation of the prepolymer solution into water ($<5^\circ\text{C}$) containing excess amounts of sodium terephthalate (Scheme 3). The ion-exchange reaction substituting the initial triflate anions with the dicarboxylate anion was readily monitored by means of IR and ^1H NMR spectroscopic analyses, as in the case of an end-functionalized (telechelic) poly(THF) with pyrrolidinium groups.^[15,19] The ^1H NMR spectrum of ion-exchange product **2b(t)** (Figure 2, middle) shows a singlet at 8.03 ppm due to the aromatic protons of the terephthalate counterion.

The subsequent heat treatment of the polymer precursor was performed in a toluene solution, to cause the ring-opening reaction of the interiorly located pyrrolidinium group by a nucleophilic attack of the carboxylate counterion (Scheme 4 and Table 1). The ^1H NMR analysis of the quantitatively recovered product showed that the nucleophilic attack of the carboxylate counterion

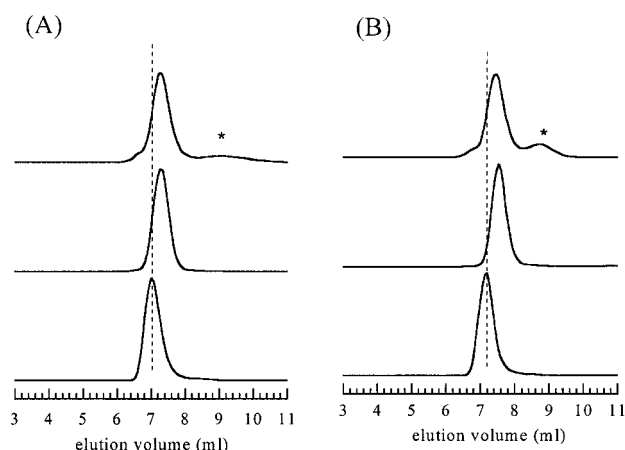


Figure 3. SEC traces of a series of poly(THF)s having methoxy end groups (**3a** and **4a**; (A)), and a series of poly(THF)s having allyloxy end groups (**3b** and **4b**; (B)). Top: the quantitatively recovered products of ionically self-assembled polymer precursors **2a(t)** (A) and **2b(t)** (B) after the heat treatment of a toluene solution (1.0 g/L). Middle: poly(THF)s of *a*-ring-with-two-branches structure **3a** (A) and **3b** (B), obtained after TLC purification. Bottom: linear analogs **4a** (A) and **4b** (B). (*: poly(THF)s having a tertiary pyrrolidine end group (**1a,b**) are detectable before purification. Sample: (A) run 1 and (B) run 2 in Table 1; column: TSK G3000HXL; eluent: THF, 1 ml/min).

occurred exclusively at the *endo*-methylene position of the pyrrolidinium group (Figure 2, bottom). Thus, after heat treatment, signals due to the interiorly located pyrrolidinium group of the polymer precursor were completely replaced by a triplet at 4.35 ppm due to the ester methylene protons and by signals at 2.40–2.50 ppm due to the amino *α*-methylene protons. Despite the presence of signals due to the tertiary pyrrolidine group of remaining **1b** (marked by an asterisk), quantitative ring opening was confirmed by comparing the corresponding signal intensities. During the nucleophilic reaction of the carboxylate counterions, the attack at the *exo*-methylene position on the interiorly located pyrrolidinium group did not take place at all, as in the case of the relevant end-functionalized poly(THF).^[15,18,19] The IR spectrum of the product also showed an absorption at 1720 cm^{-1} assignable to the ester carbonyl group of the ring-opened product (not shown).

The SEC showed a two-peak profile for the products recovered quantitatively after heat treatment of **2a(t)** and of **2b(t)** under appropriate dilution (1.0 g/L; Figure 3A and 3B, top). Thus, a major peak corresponds to the covalently converted product, while a minor broader peak corresponds to the remaining poly(THF)s **1a** and **1b**. The relative amount of the latter, around 10% as estimated from the SEC peak area ratio, agreed with the initial excess of **1a** or **1b** used in the end-capping reaction with the bifunctionally living poly(THF). No products deriving from side reactions were detectable. The major fractions, i.e. poly(THF)s of *a*-ring-with-two-branches structure **3a**

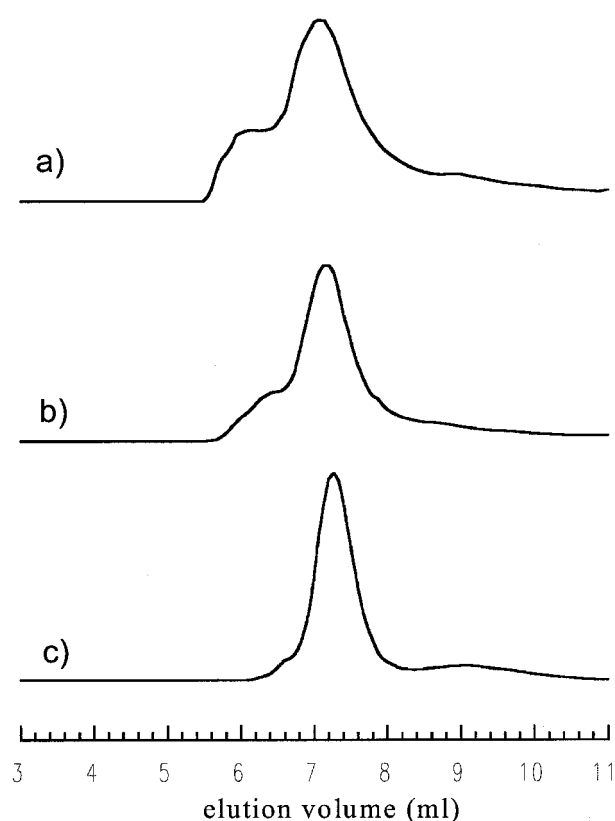


Figure 4. SEC traces of the quantitatively recovered products of ionically self-assembled polymer precursor **2a(t)** after heat treatment. Concentration of precursor **2a(t)** in toluene: (a) 20 g/L, (b) 4.0 g/L, (c) 1.0 g/L. (Sample: run 1 in Table 1; column: TSK G3000HXL; eluent: THF, 1.0 mL/min).

and **3b**, possess narrow size distributions ($PDI = 1.08-1.13$), and were readily isolated by means of TLC (Table 1). The absolute molecular weights (thus corresponding to their total chain length) of **3a** and **3b** were determined by means of 1H NMR spectroscopy as listed in Table 1. They were consistent with those of their linear analogs **4a** and **4b**, prepared from the identical polymer precursors but carrying benzoate counterions **2a(b)** and **2b(b)**, respectively. On the other hand, SEC (Figure 3, middle) revealed that the hydrodynamic volumes of **3a** and **3b** are notably smaller than those of **4a** and **4b** (bottom). The relevant results had been obtained previously in the end-functionalized poly(THF) system,^[15] where the absolute molecular weights for the cyclic and linear polymer products were consistent with each other by both vapor pressure osmometry (VPO) and NMR techniques.

These results indicate that a unique form of electrostatic self-assembly was selectively produced under dilution at 1.0 g/L, with balancing the charges between cations and anions (Scheme 1). The products were effectively converted into a permanent polymer structure of an *a*-ring-with-two-branches topology. The concurrent higher molecular weight fractions became noticeable at a higher concentration of 4.0 g/L, as shown in Figure 4.

Thus, in comparison with the case of the end-functionalized poly(THF),^[15, 18, 26] the cyclization product by a single polymer precursor unit was produced selectively even at higher concentration. This implies that a quantitative disaggregation of polymer precursors with interiorly located pyrrolidinium groups takes place at higher concentrations as compared to end-functionalized telechelics. Thus, the location of ionic groups at either the interior or end positions of the polymer chain appears to direct the equilibrium state of the ionically aggregated polymer precursors. The steric (exclusion-volume) effect by polymer chain segments is considered to play a dominant role in this process. Such a positional effect was also observed for an interiorly functionalized polymer with zwitterionic groups, which tends to form a smaller aggregate than the end-functionalized counterpart.^[27]

In conclusion, a novel polymer topology of an *a*-ring-with-two-branches structure has been constructed through the intramolecular polymer cyclization of newly synthesized polymer precursors having interiorly located cyclic ammonium groups. The inner location of the cyclic ammonium groups in the polymer chain was found to promote the formation of a self-assembly of a single polymer precursor unit. Moreover, functional groups were successfully introduced to the free branch ends of the polymer, and will be utilized to construct various complex polymer topologies. Studies toward this direction is now in progress in our laboratory.

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