Designing Unusual Polymer Topologies by Electrostatic Self-Assembly and Covalent Fixation

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Abstract: A novel protocol for designing a variety of topologically unique multicyclic polymer architectures, such as mono-, bi-, and tricyclic polymers as well as topological isomers, has been proposed on the basis of an electrostatic self-assembly of polymer precursors having five-membered cyclic ammonium salt groups accompanying plurifunctional carboxylate counteranions. Upon dilution in an organic medium at a concentration of below a gram per liter, the multiple aggregates of the polymer precursors completely dissociate into a smallest assembly, and cations and anions balance the charge. The subsequent covalent fixation through the ring-opening reaction of cyclic ammonium salt groups by carboxylate counteranions provides an efficient means for a variety of polymer architectures comprising mono- and multicyclic polymer units.

Introduction

Precise control of polymer architectures in either linear, branched, or cyclic forms is often a prerequisite of unprecedented properties and functions by advanced polymer materials.[1−3] In contrast to a significant progress recently observed for the synthesis of such branched polymers as star polymers,[4] comb polymers,[5] and dendrimers,[6,7] as well as such linear polymers as monodisperse polymers[8,9] and block copolymers,[10] an efficient and practical synthesis of a variety of polymer architectures composed of large cyclic units is still a challenging subject due to the inherent difficulty in discriminating intra- and intermolecular reactions between reactive groups located at the specific positions (mostly chain ends) of polymers. An efficient polymer cyclization is also a basis for achieving such topologically unique polymer architectures as knots and catenanes, as intriguingly synthesized with single-stranded DNA molecules,[11−14] while single-stranded DNA molecules assume exclusively unbranched topologies.

Thus, in a single-polymer cyclization, a bimolecular end-to-end cyclization of an α,ω-bifunctional linear polymer precursor must be performed in high dilution under strictly stoichiometric conditions between the polymer precursor and the low-molecular-weight coupling reagent, limiting its practical usefulness.[15−17] Alternative means to improve the cyclization efficiency include a unimolecular, high-dilution process incorporating α,ω-heterobifunctional polymer precursors[18−21] and another incorporating polymer-supported reagents to exploit their interfacial reaction.[22] Nevertheless, a practical high-yield process to provide versatile polymer topologies comprising multicyclic polymer units or both cyclic and linear polymer units has been an ongoing challenge.

We have now developed a conceptually novel process to realize efficient synthesis of such topologically unique polymer architectures through an electrostatic self-assembly of polymer precursors having cyclic onium salt groups (Schemes 1 and 2). Moderately strained cyclic ammonium or sulfonium salt groups introduced at the chain ends of hydrophobic monodisperse polymers exhibit unique physicochemical and organochemical properties. Those properties are Coulombic interaction through their ionic end groups and a ring-opening capability after a quantitative ion-exchange reaction with suitable anions, such as a carboxylate, in which the nucleophilicity of the carboxylate anion is enhanced as such in phase-transfer catalyst systems (Scheme 2).[23] An efficient synthesis of well-defined branched and network polymers by use of such telechelic polymers has

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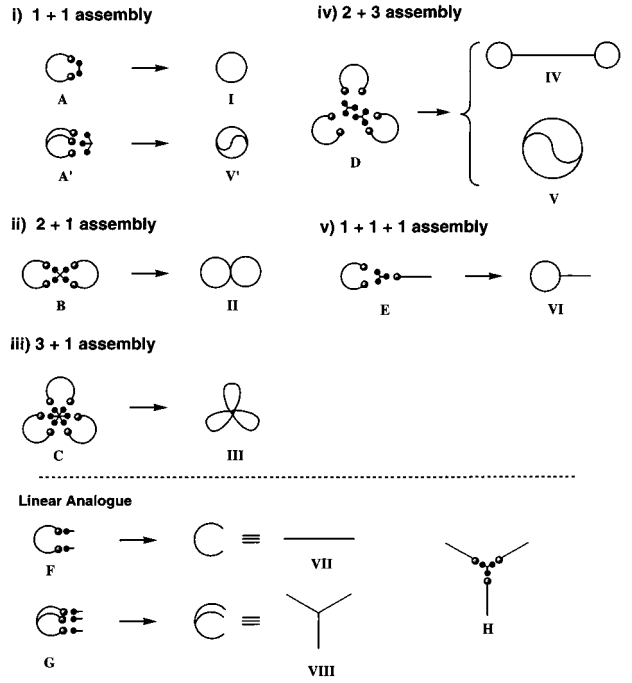
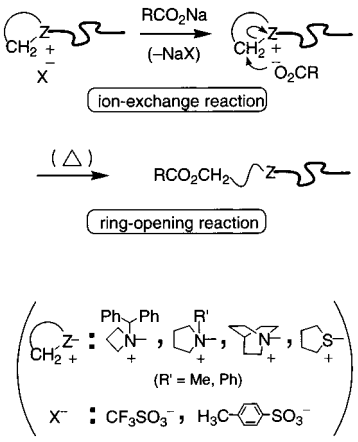
Scheme 1



Scheme 2

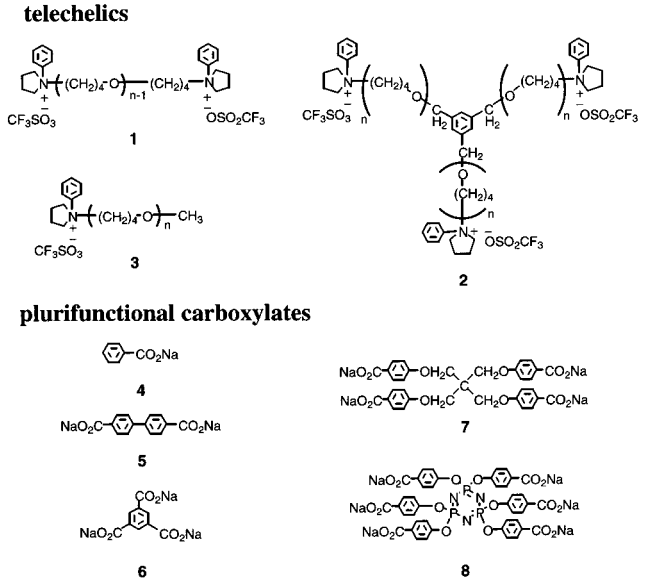


been reported.[24−29] Here we have applied these polymer precursors to achieve an efficient one-step formation of well-defined polymers comprising mono- or multicyclic polymer units. Our strategy is, as shown in Scheme 1, reliant on electrostatic self-assembly of bifunctional, as well as trifunctional, hydrophobic polymer precursors having plurifunctional carboxylates as a coupling reagent in an organic medium.

Results and Discussion

1. Electrostatic Self-Assembly of Polymer Precursors. We have prepared bi- and trifunctional poly(tetrahydrofuran)s,

Scheme 3



(PTHFs), having five-membered ammonium salt groups, **1** and **2**, shown in Scheme 3, through the reaction of a bi- or trifunctionally living PTHF with 1-phenylpyrrolidine, respectively. Both **1** and **2** accompany trifluoromethanesulfonate counteranions, which are readily replaced by a desired carboxylate counteranion, also shown in Scheme 3, through a simple precipitation of a tetrahydrofuran (THF) solution of **1** or **2** into an ice-cooled aqueous solution containing an excess amount of a carboxylate as a sodium salt form. The ion-exchange reaction could be followed by IR and ^{1}H NMR spectrometry. For example, ^{1}H NMR spectra of the ion-exchange products **A**, **B**, **C**, and **D** (top in Figures 1, 2, 3, and 4, respectively) prepared from **1** ($M_n = 4.3 \times 10^3$, number-average molecular weight) and di-, tetra-, hexa-, and tricarboxylate (**5**, **7**, **8**, and **6**, respectively) showed signals due to aromatic protons from the corresponding carboxylate counteranions. Thus, the ionic balance between the polymer precursor and the carboxylate in the product, corresponding to the molar ratio of 1:1, 2:1, 3:1, and 3:2, respectively, was confirmed to be achieved. In the IR spectra of the products, the absorptions at 1254, 1031, and 638 cm^{-1} due to a trifluoromethanesulfonate anion were removed after the ion-exchange process, as shown in Figure 5 (middle).

2. Covalent Conversion of Electrostatically Self-Assembled Polymer Precursors. The covalent conversion of a series of electrostatically assembled polymer precursors was performed by heating in organic solutions. When the reaction was conducted either in bulk or in concentrated solution, insoluble gel products were produced quantitatively, except for the reaction between **1** and dicarboxylate **5**. When the reactions were repeated in more dilute solutions, the product after reaction eventually became totally soluble. And remarkably, the three-dimensional size distribution in solution [hydrodynamic volumes examined by size-exclusion chromatography (SEC)] of the quantitatively recovered crude products approached the same level of uniformity as in the precursor polymer analogues (**VII** and **VIII**) independently prepared from **1** and **2** with sodium benzoate (**4**), respectively. Typical examples of the formation of **A** from **1** and **5** and of **B** from **1** and **7** are shown in Figures 6 and 7, respectively. These results indicate that a unique form of the assembly product was produced upon appropriate dilution through the complete dissociation of multiple aggregates of

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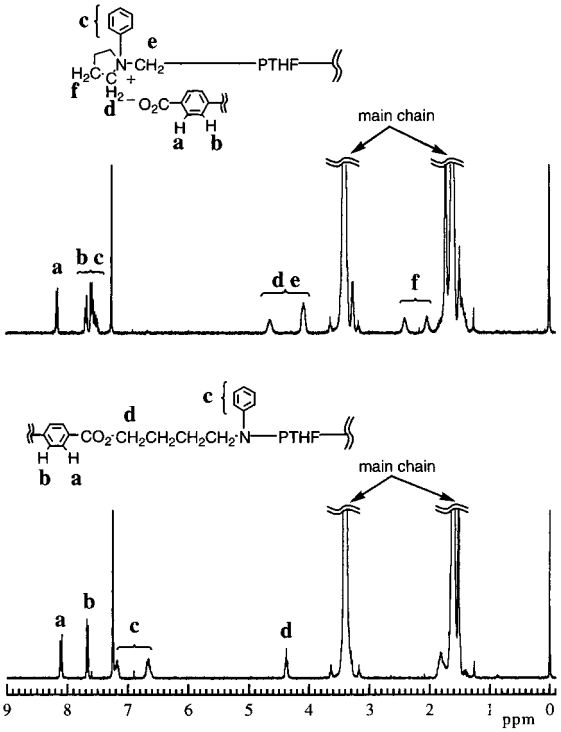

Figure 1. 300 MHz ^{1}H NMR spectra of the ion-exchange product of bifunctional PTHF **1** with sodium 4,4′-biphenyldicarboxylate (**5**) before (**A**, top) and after (**I**, bottom) the heat treatment (sample, run 1 in Table 1; $CDCl_3$; 40 °C).

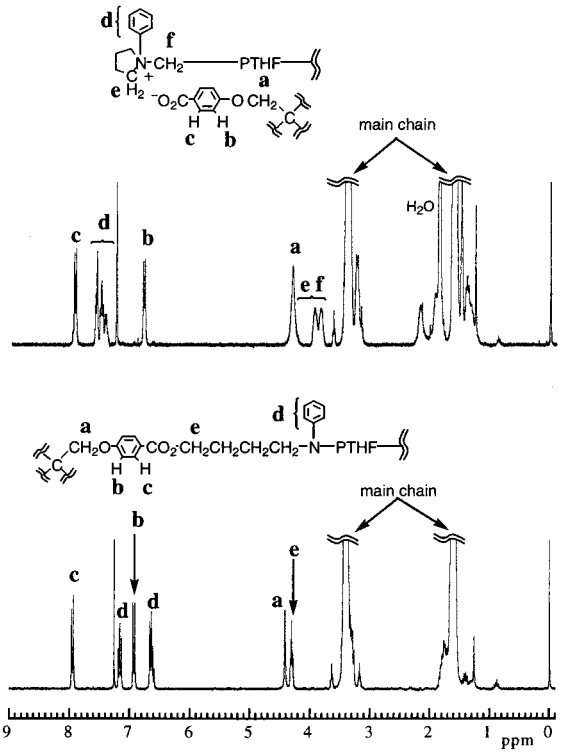

Figure 2. 300 MHz ^{1}H NMR spectra of the ion-exchange product of bifunctional PTHF **1** with sodium tetracarboxylate **7** before (**B**, top) and after (**II**, bottom) the heat treatment (sample, run 2 in Table 1; $CDCl_3$; 40 °C).

polymer precursors, and cations and anions balance the charge (Scheme 4).[30]

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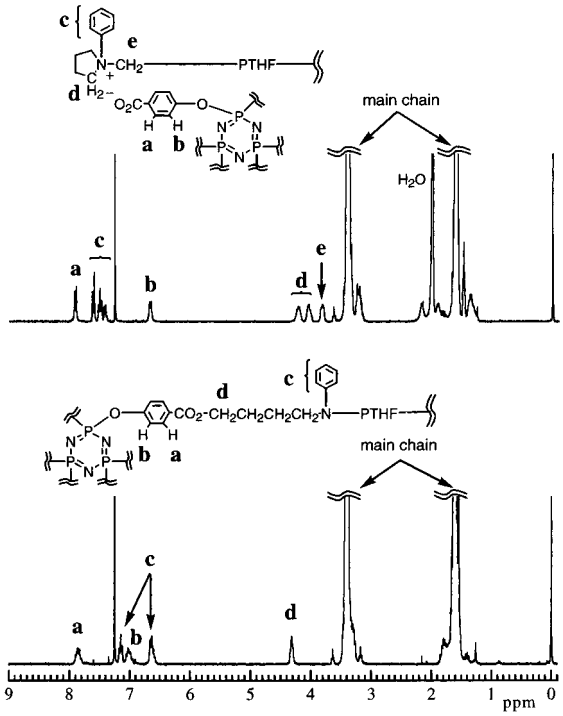


Figure 3. 300 MHz ^{1}H NMR spectra of the ion-exchange product of bifunctional PTHF **1** with sodium hexacarboxylate **8** before (**C**, top) and after (**III**, bottom) the heat treatment (sample, run 3 in Table 1; $CDCl_3$; 40 °C).

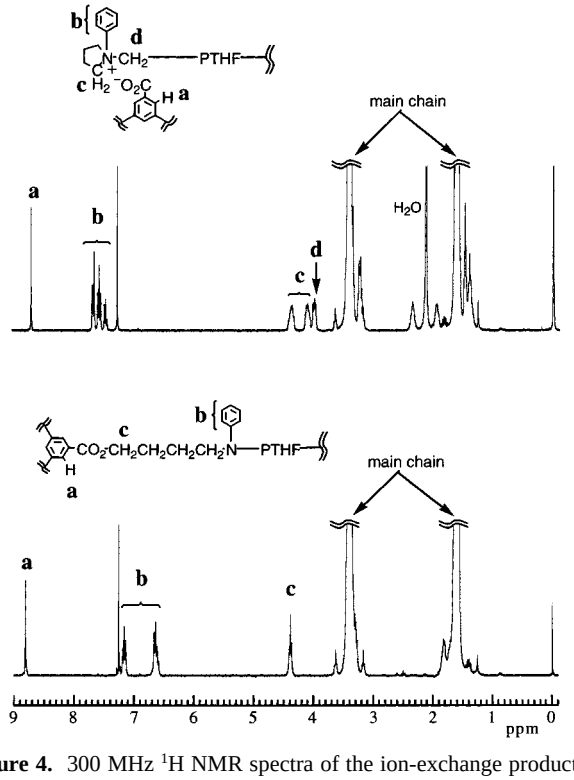


Figure 4. 300 MHz ^{1}H NMR spectra of the ion-exchange product of bifunctional PTHF **1** with sodium trimesate (**6**) before (**D**, top) and after (mixture of **IV** and **V**, bottom) the heat treatment (sample, run 5 in Table 1; $CDCl_3$; 40 °C).

3. Mono-, Bi-, and Tricyclic Polymers. On the basis of the principle shown above, a series of topologically unique polymer architectures consisting of mono-, bi-, and tricyclic units (**I**, **II**, and **III** in Scheme 1) were constructed through the covalent fixation of the relevant electrostatically assembled polymer precursors. The assembled precursors **A**, **B**, and **C**, prepared

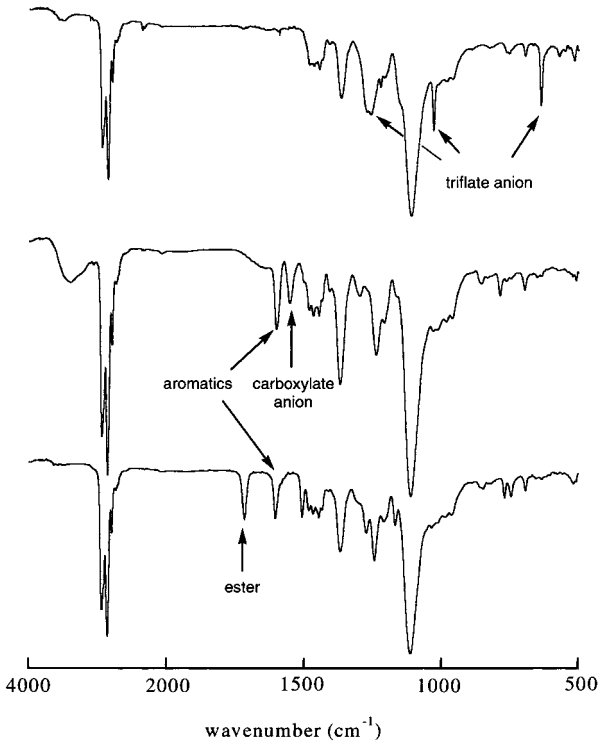


Figure 5. IR spectra of a bifunctional PTHF **1** (top) and the ion-exchange product with sodium tetracarboxylate **7** before (**B**, middle) and after (**II**, bottom) the heat treatment (sample, run 2 in Table 1).

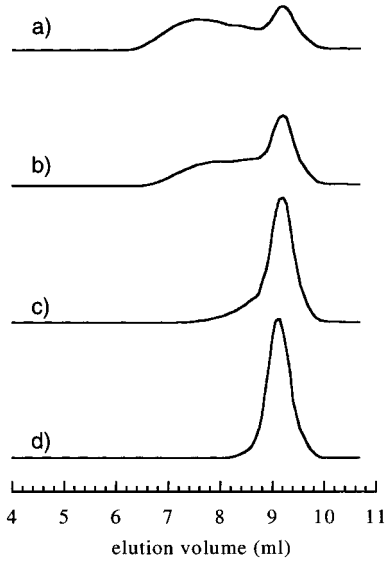


Figure 6. SEC traces (RI, refractive index, detector) of the quantitatively recovered crude product from bifunctional PTHF **1** and sodium 4,4′-biphenyldicarboxylate (**5**) after the heat treatment. Concentration of the precursor **A** in THF: (a) 10 g/L; (b) 5.0 g/L; (c) 1.0 g/L; (d) 0.2 g/L (sample, run 1 in Table 1; column, TSK G4000HXL; eluent, THF; 1.0 mL/min).

from **1** with dicarboxylate **5**, tetracarboxylate **7**, and hexacarboxylate **8**, respectively, were subjected to heat treatment at 66 °C for 3 h in THF (0.1−0.2 g/L). The reaction solutions were homogeneous throughout the process at these concentrations. The quantitatively recovered crude products were then subjected to preparative thin-layer chromatography to remove any residual ionic polymer compounds. ^{1}H NMR spectroscopic analysis of the purified products, namely **I**, **II**, and **III** (bottom in Figures 1, 2, and 3), confirmed that all pyrrolidinium salt groups were converted to aminoester groups through the ring-opening

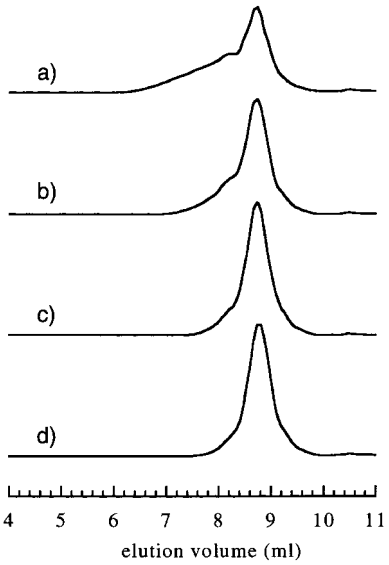
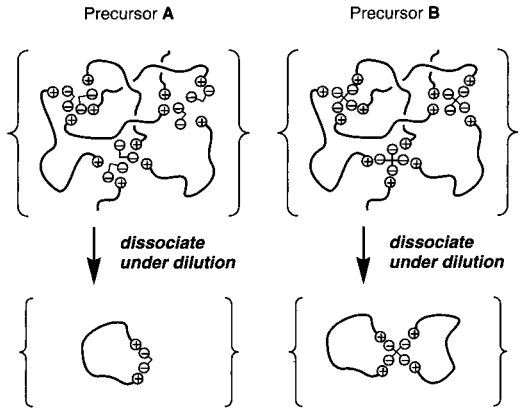


Figure 7. SEC traces (RI, refractive index, detector) of the quantitatively recovered crude product from bifunctional PTHF **1** and sodium tetracarboxylate **7** after the heat treatment. Concentration of the precursor **A** in THF: (a) 2.0 g/L; (b) 0.5 g/L; (c) 0.2 g/L; (d) 0.1 g/L (sample, run 2 in Table 1; column, TSK G4000HXL; eluent, THF; 1.0 mL/min).

Scheme 4



reaction. IR spectra of products **I** (Figure 5 bottom), **II,** and **III** exhibit an absorption at 1720 cm^{-1} that is assignable to ester carbonyl groups.

The molecular weight (thus, corresponding to its total chain length) of **I**, which was determined by vapor pressure osmometry (VPO) technique and by ^{1}H NMR, is naturally indistinguishable from that of its linear analogue **VII**, which was prepared from the identical polymer precursor **1** and sodium benzoate (**4**) (runs 1 and 4 in Table 1), because the difference in the molecular weight between the former and the latter is as small as two by the two hydrogen atoms. On the other hand, SEC analysis showed that the product **I** (Figure 8c; run 1 in Table 1) retained uniform size distribution (PDI = 1.09, polydispersity index), and its hydrodynamic volume was notably smaller than that of the corresponding linear analogue **VII** (Figure 8d; run 4 in Table 1). Besides SEC results, the viscosity measurement of the cyclic PTHF **I** (concentration = 0.50 g/dL) in *N*-methylpyrrolidone at 30 °C) showed a significantly lower inherent viscosity than that of **VII** from the identical polymer precursor. The inherent viscosity ratio, $[\eta]_{\text{inh(CYCLIC)}}/[\eta]_{\text{inh (LINEAR)}}$, was determined to be 0.647, which is very close to the theoretical intrinsic viscosity ratio, $[\eta]_{\text{(CYCLIC)}}/[\eta]_{\text{(LINEAR)}}$, of

Table 1. Synthesis of PTHFs Comprising Cyclic Polymer Units by Electrostatic Self-Assembly and Covalent Fixation[a]

run	telechelic PTHF[b] (functionality)	plurifunctional carboxylate[b] (functionality)	electrostatically assembled precursor[b]	covalently linked product[b]	isolated yield[c] (%)	M_n (VPO) ($\times 10^3$)	M_n (NMR)[d] ($\times 10^3$)	M_n(SEC)[e] /M_n(NMR)	PDI[f]
1	**1** (2)	**5** (2)	**A**	**I**	74 (91)	4.3	4.3	0.79	1.09
2	**1** (2)	**7** (4)	**B**	**II**	65 (78)	7.8	8.8	0.69	1.07
3	**1** (2)	**8** (6)	**C**	**III**	61 (82)	11	13	0.65	1.07
4	**1** (2)	**4** (1)	**F**	**VII**	67	4.3	4.4	1.00	1.09
5	**1** (2)	**6** (3)	**D**	**IV**, **V**	67 (89)	11[g]	13, 13	0.89, 0.57	1.11[g]
6	**2** (3)	**6** (3)	**A′**	**V′**	52 (79)	ND[h]	14	0.61	1.06
7	**2** (3)	**4** (1)	**G**	**VIII**	85	ND[h]	14	0.93	1.12
8	**1** (2), **3** (1)	**6** (3)	**E**	**VI**	ND[h] (90)	ND[h]	9.0	0.76	1.19

[a] Ring-opening reaction of pyrrolidinium salt end groups in the assembled precursors was performed at reflux temperatures in THF for 3 h (runs 1−5, 7, and 8) or in THF/acetone (1/1, v/v) for 5 h (run 6). Concentrations of the assembled precursors: 0.06 g/L (run 8), 0.1 g/L (run 2), 0.2 g/L (runs 1, 3, 5, and 6), 5.0 g/L (run 7), and 10 g/L (run 4). [b] See Schemes 1 and 3. Molecular weights of **1**, **2**, and **3**: 4.3×10^3 (runs 1−5), 14×10^3 (runs 6 and 7), 5.6×10^3 (run 8, **1**), and 2.5×10^3 (run 8, **3**). [c] Isolated yields are for purified products by preparative TLC (SiO_2; hexane/acetone = 2/1). Yields in parentheses are estimated from the SEC peak areas of the crude products. [d] Determined by ^{1}H NMR, assuming quantitative chemical conversion of polymer end groups. [e] M_n(SEC)/M_n(NMR): A measure of the hydrodynamic volume ratio between cyclic-containing polymers and their corresponding linear polymers. M_n(SEC) was determined by SEC with a calibration using linear polystyrene standards by a conversion factor of 0.556.[33] [f] Determined by SEC on the basis of polystyrene standards. [g] Determined as a mixture of **IV** and **V**. [h] Not determined.

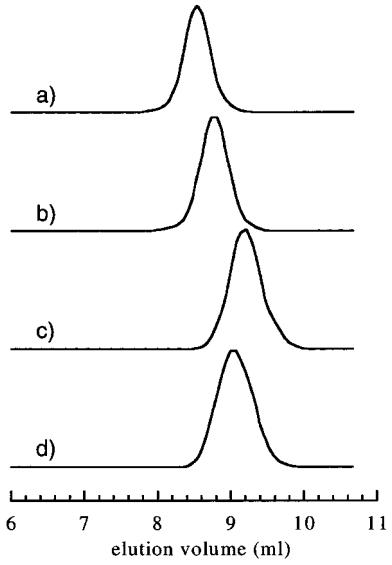


Figure 8. SEC traces (RI detector) of the purified reaction product of bifunctional PTHF **1** with sodium hexacarboxylate **8** (**III**, a), sodium tetracarboxylate **7** (**II**, b), sodium 4,4′-biphenyldicarboxylate (**5**) (**I**, c), and sodium benzoate (**4**) (**VII**, d), after the heat treatment (samples, runs 1−4 in Table 1; column, TSK G4000HXL; eluent, THF; 1.0 mL/min).

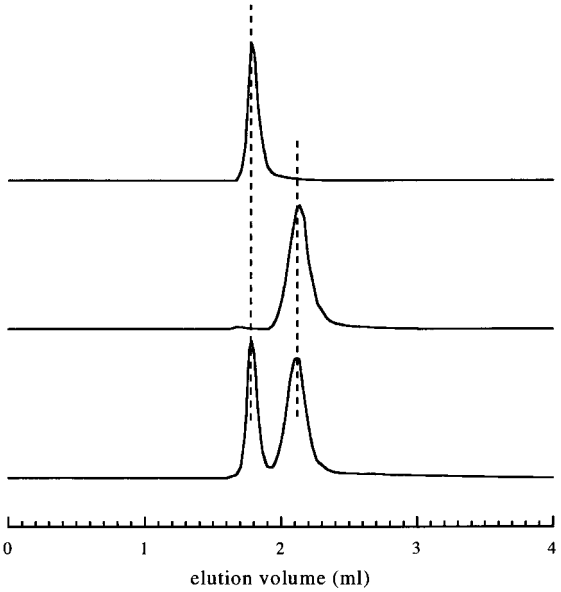


Figure 9. Reversed-phase chromatography traces (UV detector) of a cyclic PTHF **I** (middle), of the linear analogue **VII** (top), and of the mixture of **I** and **VII** (bottom) (samples, runs 1 and 4 in Table 1; column, TSK ODS-80TS (8 nm pore, 75 mm × 4.6 mm, 5 μm pore size); eluent, THF/CH_3CN = 50/50 (v/v), isocratic; 1.0 mL/min).

0.66.[31] Furthermore, the cyclic product **I** and the relevant linear product **VII** could be distinguished by means of a reversed-phase high-pressure liquid chromatography (RPC), in which the topology of the polymer product dictates the elution property (Figure 9).

SEC analysis of products **II** (Figure 8b) and **III** (Figure 8a) showed their apparent molecular weights to be significantly larger than that of their linear precursor analogue **VII**, but smaller than those of the twice (for **II**) and of the three times (for **III**) of **VII** (runs 2 and 3 in Table 1), respectively, although retaining their uniform size distributions (PDI = 1.07). On the other hand, the actual molecular weights of **II** and of **III**, which were determined by VPO technique and by ^{1}H NMR (assuming quantitative chemical conversion of polymer end groups) coincide, within experimental error, with those of the twice (for **II**) and of the three times (for **III**) of its linear precursor analogue **VII**, respectively (Table 1). These results evidently show the formation of unique forms of the polymer assemblies **B** and **C** under dilution, comprised of two units of **1** and one unit of **7**, and of three units of **1** and one unit of **8**, respectively. Subsequent heat treatment of these precursors could lead to bi- and tricyclic polymers **II** and **III** through the covalent fixation by the ring-opening reaction of pyrrolidinium salt groups.

4. Preparation and Separation of Topological Isomers.[11] Next, an assembled precursor **D** was prepared from bifunctional polymer precursor **1** and tricarboxylate **6** and was subjected to heat treatment at 66 °C for 3 h in THF (0.2 g/L). As in the reactions described above, no gelation occurred at this condition. Remarkably, the covalent linkage between the two pyrrolidinium groups in **1** and the three carboxylate groups in **6** can produce the two topologically different polymer architectures, **IV** and **V**, shown in Scheme 1. The random combination of cations and anions in **1** and **6** will produce **IV** and **V** in a ratio of 3:2. The size, that is, the hydrodynamic volume, of **IV** is considered to be marginally larger than that of **V**. In addition, the dielectric property of the two topological isomers, **IV** and **V**, should be distinct from each other because the spatial alignments of polar groups (*N*-phenyl groups) in **IV** and **V** are different. And RPC

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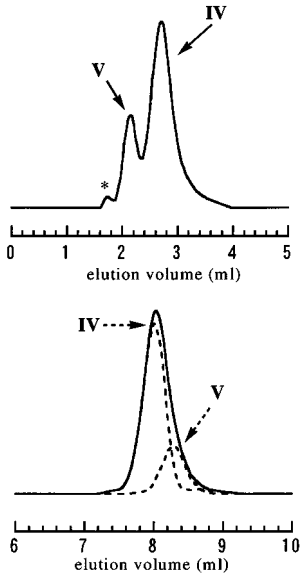
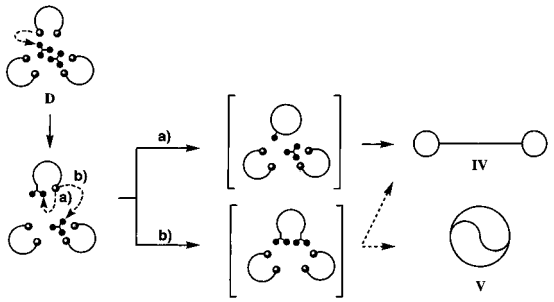


Figure 10. SEC and RPC traces (bottom and top, respectively; ultraviolet detector at 254 nm) of the product of bifunctional PTHF **1** with sodium trimesate (**6**) (mixture of **IV** and **V**) after the preparative thin-layer chromatography treatment to remove any residual ionic polymer compounds (sample, run 5 in Table 1. SEC: column, TSK G4000HXL; eluent, THF; 1.0 mL/min. RPC: column, TSK ODS-80TS (8 nm pore, 75 mm × 4.6 mm, 5 μm pore size); eluent, THF/CH_3CN = 49/51 (v/v), isocratic; 1.0 mL/min). The broken line in the SEC profile shows the deconvoluted profiles for **IV** and **V** of the respective elution volumes and of the ratio of 78:22 estimated by RPC. The peak marked by an asterisk (*) is that of an unassigned fraction.

Scheme 5



(Figure 10 top) showed that the covalent fixation product of **D** is, indeed, composed of two components which were subsequently separated by means of fractionation. ^{1}H NMR and IR of the two fractions were identical to each other and showed the quantitative ring-opening reaction of the pyrrolidinium salt groups by the carboxylate groups in **6** (Figure 4 bottom). The SEC analysis of the covalent fixation product of **D** (as a mixture of **IV** and **V**, Figure 10 bottom) showed a consistent peak profile which is convoluted from the two components, **IV** and **V**, of the respective elution volumes and of the ratio of 78:22, estimated by the RPC method above. Thus, the intramolecular process to produce **IV** is slightly favored in this covalent fixation process of **D** (path a in Scheme 5). The molecular weights of **IV** and **V**, as a mixture, determined by VPO technique and by ^{1}H NMR (assuming quantitative chemical conversion of polymer end groups) coincide, within experimental error, with that of the three times (thus 13×10^3, run 5 in Table 1) of its precursor analogue **VII**. These results are consistent with the formation of a self-assembled product by dilution, consisting of three units of **1** and two units of **6**. Subsequent heat treatment of the assembled precursor **D** could lead to topological isomers **IV** and **V** through the covalent fixation by the ring-opening reaction

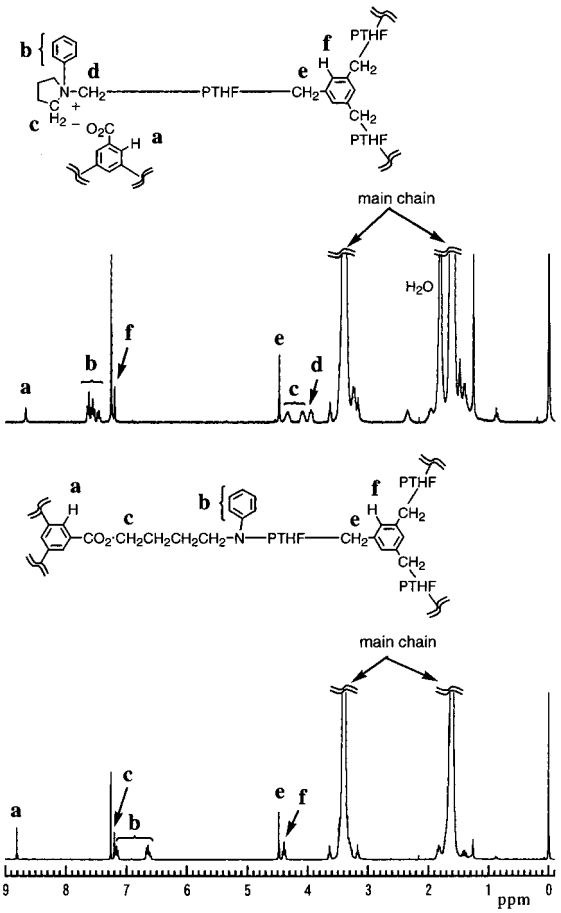


Figure 11. 300 MHz ^{1}H NMR spectra of the ion-exchange product of trifunctional PTHF **2** with sodium trimesate (**6**) before (**A′**, top) and after (**V′**, bottom) the heat treatment (sample, run 6 in Table 1; $CDCl_3$; 40 °C).

of pyrrolidinium salt groups. Moreover, one form of these two topological isomers, namely **V′** of the identical topology as **V**, has been produced by an alternative process in which the covalent conversion of the assembled precursor **A′** was obtained from a trifunctional PTHF having *N*-phenylpyrrolidinium salt end groups (**2**) ($M_n = 14 \times 10^3$) and a trifunctional carboxylate **6** (Scheme 1, and run 6 in Table 1). ^{1}H NMR spectroscopic analysis of **V′** (Figure 11 bottom) confirmed that all pyrrolidinium salt groups in **A′** (top in Figure 11) were converted to aminoester groups through the ring-opening reaction. In addition, SEC analysis showed that the product **V′** (top in Figure 12) retained a uniform size distribution (PDI = 1.06), and its hydrodynamic volume was notably smaller than that of its open-chain analogue, that is, star PTHF **VIII** (Figure 12 bottom, and run 7 in Table 1).

5. Reshuffling in Electrostatically Self-Assembled Polymer Precursors. Furthermore, this novel strategy has been applied for topology design of polymer architectures comprising both cyclic and linear units (i.e., possessing free chain ends). Thus, an equimolar amount of the assembled precursor **D**, obtained from **1** ($M_n = 5.6 \times 10^3$) and tricarboxylate **6**, and another precursor **H**, obtained from monofunctional PTHF having an *N*-phenylpyrrolidinium salt end group (**3**) ($M_n = 2.5 \times 10^3$) (Scheme 2) and **6**, were mixed and subjected to covalent fixation under relevant dilution (0.06 g/L) (run 8 in Table 1). The spontaneous reshuffling between the electrostatically assembled precursors **D** and **H**[26] can produce a new polymer assembly **E** (Schemes 1 and 6) because in dilution, the polymer precursor and the carboxylate units tend to form a self-assembled product

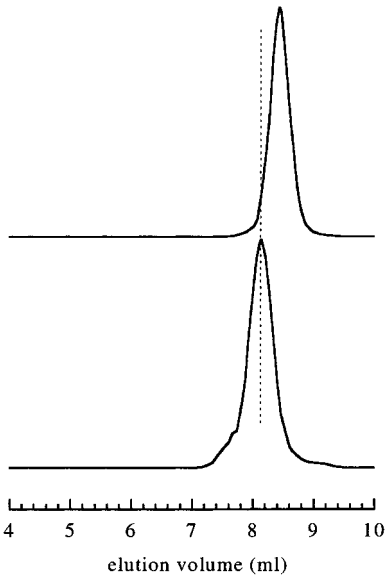
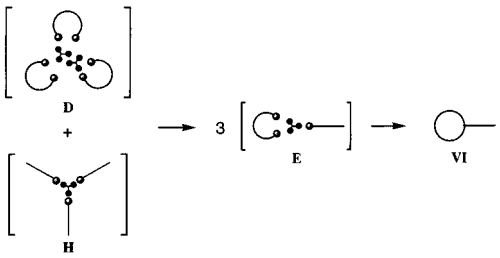


Figure 12. SEC traces (RI detector) of the purified reaction product of trifunctional PTHF **2** with sodium trimesate (**6**) (**V′**, top) and with sodium benzoate (**4**) (**VIII**, bottom) after the heat treatment (samples, runs 6 and 7 in Table 1; column, TSK G4000HXL; eluent, THF; 1.0 mL/min).

Scheme 6



having the smallest number of components and having a balanced charge of cations and anions. The quantitative ring-opening reaction of the pyrrolidinium salt groups was confirmed by IR and ^{1}H NMR (Figure 13) spectroscopic analysis. The SEC profile of the product is compared to the mixture of the multicyclic PTHF (a mixture of the two topological isomers **IV** and **V**) and star PTHF, obtained separately from **D** and **H**, respectively. As shown in Figure 14, an equimolar mixture of the multicyclic PTHF (mixture of **IV** and **V**) and star PTHF[24] gives a two-peak profile composed of the two fractions with equal peak areas (top). On the covalent conversion, the SEC profile of the quantitatively recovered crude products approached being a single peak upon dilution of the reaction solution. These results agree with the selective formation of **VI**, which is composed of both cyclic and linear units by the covalent fixation of **E**, produced from the mixture of the assembled precursors **D** and **H** through a reshuffling process, that is, the dissociation of multiple aggregates of polymer precursors and reassembly to form a self-assembled product with the smallest number of the components and having a balanced charge of cations and anions.

Conclusion

A remarkably efficient polymer cyclization process has been developed to produce a variety of topologically unique polymers composed of mono-, bi-, and tricyclic units, as well as topological isomers, through the electrostatic self-assembly and covalent fixation strategy with a series of mono-, bi-, and

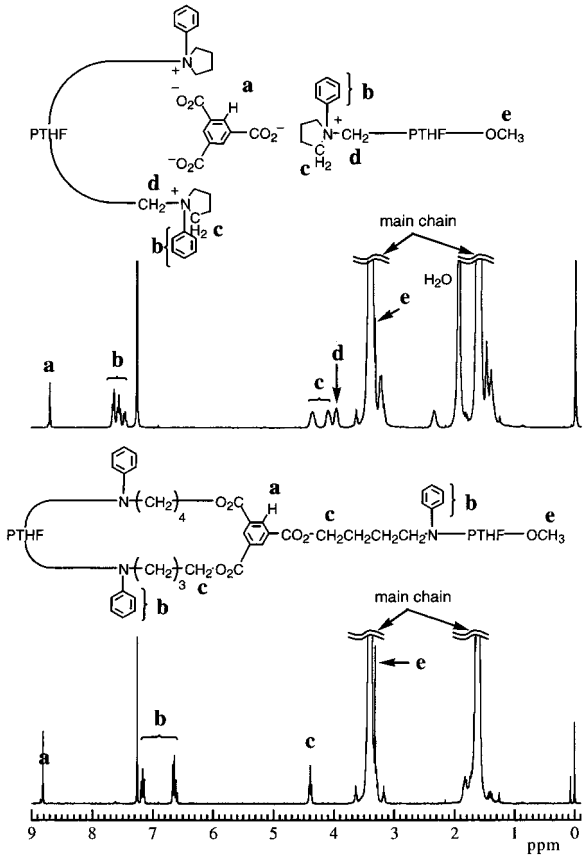


Figure 13. 300 MHz ^{1}H NMR spectra of the mixture of the ion-exchange products **D**, prepared from bifunctional PTHF **1** with sodium trimesate (**6**) and **H**, prepared from monofunctional PTHF **3** with sodium trimesate (**6**), namely an assembled precursor **E** before (top) and after (**VI**, bottom) the heat treatment (sample, run 8 in Table 1; $CDCl_3$; 40 °C).

trifunctional PTHFs having pyrrolidinium salt end groups accompanying plurifunctional carboxylates as a counteranion. By diluting the precursor solution, a unique form of the electrostatically assembled polymer precursor with the smallest number of the components and having a balanced charge of cations and anions has been produced, and subsequent covalent conversion through the quantitative ring-opening reaction of pyrrolidinium salt end groups by the heat treatment produced the corresponding topologically unique polymers in exceptionally high yields. A series of products was relevantly characterized by IR and ^{1}H NMR, showing the chemical structure formed by the covalent fixation process, and by VPO, showing the absolute mass (or the number of polymer precursor units) of the final products. In particular, the resolution of the topological isomers has been accomplished by means of reversed-phase HPLC technique. Hence, the reported strategy will provide a powerful means to design a variety of novel polymer architectures comprising cyclic topologies.

Experimental Section

Reagents. Mono- and bifunctional PTHFs having *N*-phenylpyrrolidinium salt end groups (**3** and **1**, respectively) were prepared by the method detailed before.[24] The molecular weights of the samples used in the present study were 4.3×10^3, 5.8×10^3 (for **1**), and 2.5×10^3 (for **3**), respectively. Sodium salts of a tetracarboxylic acid and a hexacarboxylic acid (**7** and **8**, respectively) were prepared by the method detailed before.[24] Sodium benzoate (**4**) (Koso Chemical Co., Ltd.) was used as received. Sodium salts of 4,4′-biphenyldicarboxylic acid and 1,3,5-benzenetricarboxylic acid (trimesic acid) (**5** and **6**, respectively)

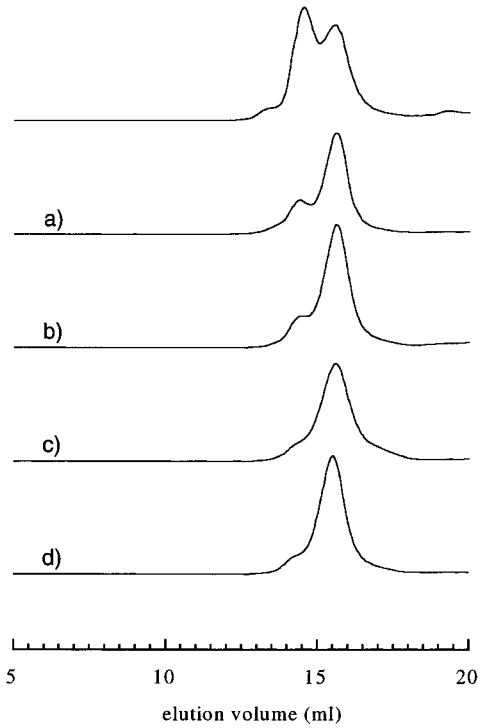


Figure 14. SEC traces (RI detector) of the mixture of **IV** and **V** (as a mixture) and **VII** (the forward and the backward peaks, respectively; top), prepared independently from the precursors **D** and from **H**, respectively, and of the quantitatively recovered crude product from the mixture of the precursors **D** and **H** after the heat treatment (a−d). Concentration of the precursors in THF: (a) 0.6 g/L; (b) 0.25 g/L; (c) 0.13 g/L; (d) 0.06 g/L (sample, run 8 in Table 1; column, 2 × TSK G4000HXL; eluent, THF; 1.0 mL/min).

were prepared quantitatively from the commercially available corresponding free acids using an equimolar quantity of sodium hydroxide in water. THF was dried over sodium benzophenone ketyl and distilled just before use. Acetone was dried with potassium carbonate and distilled before use. Trifluoromethanesulfonic anhydride (triflic anhydride) was distilled from P_2O_5 just before use. Unless otherwise noted, the materials were obtained from commercial sources.

Preparation of Trifunctional PTHF Having *N*-Phenylpyrrolidinium Salt End Groups (2). Trifunctional PTHF having *N*-phenylpyrrolidinium salt end groups (**2**) was prepared from a trifunctionally living PTHF produced by 1,3,5-tris(trifluoromethanesulfonyloxymethyl)-benzene as an initiator, prepared in situ from 1,3,5-tris(hydroxymethyl)-benzene and triflic anhydride in the presence of 2,6-di-*tert*-butylpyridine, according to the reported method,[32] and subsequent end-capping reaction with *N*-phenylpyrrolidine. **2:** $M_n = 14 \times 10^3$; ^{1}H NMR ($CDCl_3$) δ 1.45−1.70 (m, CH_2CH$_2$O), 2.08−2.18 (m, 6H), 2.36−2.46 (m, 6H), 3.28−3.58 (m, CH$_2$CH_2O), 3.88−3.96 (m, 6H), 4.02−4.12 (m, 6H), 4.28−4.40 (m, 6H), 4.48 (s, 6H), 7.20 (s, 3H), 7.50−7.65 (m, 15H)

Electrostatic Self-Assembly and Covalent Fixation of Telechelic PTHF Having *N*-Phenylpyrrolidinium Salt Groups. To an ice-cooled (<5 °C) aqueous solution (200 mL) containing an excess amount of a sodium carboxylate (**4**−**8**) (4−15 equiv) was added dropwise a THF solution (5.0 mL) of 0.5 g of **1**, **2**, or **3** under vigorous stirring. After 1 h, the precipitated ion-exchange product (electrostatically self-assembled PTHF) was collected by filtration and dried in vacuo. This precipitation treatment was repeated to complete the reaction. The electrostatically self-assembled products (**A**−**F**) were then dissolved in THF (for **A**−**F**) or in THF/acetone (1/1) (for **A′**) at the prescribed concentration (0.1−10 g/L) and were heated at reflux temperature for 3−5 h. The covalently linked products (**I**−**V**, **V′**, **VII**, and **VIII**) that were recovered quantitatively by evaporating the solvent were directly subjected to spectroscopic and chromatographic analyses in most cases. The products were further purified by preparative thin-layer chromatography (SiO_2, hexane/acetone = 2/1) (52−85% yield). **VII**: ^{1}H NMR ($CDCl_3$) δ 1.50−1.75 (m, CH_2CH$_2$O), 3.24−3.55 (m, CH$_2$CH_2O), 4.35 (t, J = 6.0 Hz, 4H), 6.58−6.68 (m, 6H), 7.14−7.20 (m, 4H), 7.38−7.46 (m, 4H), 7.52−7.58 (m, 2H), 8.00−8.04 (m, 4H); IR 1721 cm^{-1}. **VIII**: ^{1}H NMR ($CDCl_3$) δ 1.50−1.75 (m, CH_2CH$_2$O), 3.24−3.55 (m, CH$_2$CH_2O), 4.35 (t, J = 6.0 Hz, 6H), 4.48 (s, 6H), 6.58−6.68 (m, 9H), 7.14−7.22 (m, 6H), 7.20 (s, 3H), 7.39−7.46 (m, 6H), 7.52−7.58 (m, 3H), 8.00−8.04 (m, 6H); IR 1721 cm^{-1}. The topological isomers **IV** and **V** were separated by means of fractionation with an analytical RPC apparatus by repeating the experimental procedure.

Reshuffling in Electrostatically Self-Assembled Polymer Precursors D and H and the Subsequent Ring-Opening Reaction of *N*-Phenylpyrrolidinium Salt End Groups. An equimolar amount of the electrostatically self-assembled products **D** and **H** were dissolved in THF at the prescribed concentration (0.06−0.6 g/L for the total amount of the polymer precursors) and were heated at reflux temperature for 5 h. The covalently linked product **VI** recovered quantitatively by evaporating the solvent was directly subjected to spectroscopic and chromatographic analyses.

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 system of single or two sets of TSK G4000HXL was employed with THF as the eluent at a flow rate of 1.0 mL/min. RPC measurements were performed by an isocratic mode using a Tosoh model CCPS equipped with a UV detector, model UV 8020, at 254 nm. A C18 bonded-silica column of TSK ODS-80TS (8 nm pore, 75 mm × 4.6 mm, 5 μm pore size) was employed with a mixture of THF and CH_3CN premixed in the ratio of 49/51 or 50/50 (v/v). The number-average molecular weights of cyclic and linear polymers were determined by vapor pressure osmometry (VPO) performed on a Corona NA 117 in benzene at 40 °C. The inherent viscosities of cyclic and linear polymer samples were measured in *N*-methylpyrrolidone at 30 °C using an Ostwald viscometer. IR spectra were recorded on a JASCO FT/IR-410 infrared spectrometer by casting the sample from the chloroform solution on a NaCl plate. ^{1}H NMR spectra were taken on a JEOL JNM-AL300 apparatus in $CDCl_3$ at 40 °C. The proton chemical shifts (ppm) were referenced from the signal of tetramethylsilane.

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