Effective Synthesis of Polymer Catenanes by Cooperative Electrostatic/Hydrogen-Bonding Self-Assembly and Covalent Fixation

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ABSTRACT: The cooperative electrostatic and hydrogen-bonding self-assembly of polymer precursors and the subsequent covalent conversion have been demonstrated as an effective means for the synthesis of polymer catenanes. Thus, a cyclic poly(tetrahydrofuran), poly(THF), having a hydrogen-bonding, isophthaloylbenzylic amide group (**I**) was prepared through an *electrostatic self-assembly* and *covalent fixation* with a telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups carrying a dicarboxylate counteranion containing the hydrogen-bonding unit (**1**). Another telechelic poly(THF) having an isophthaloylbenzylic amide group at the center position and having *N*-phenylpyrrolidinium salt end groups carrying a biphenyl-dicarboxylate counteranion, **2**, was subsequently prepared and subjected to a covalent conversion reaction in the presence of the preformed cyclic poly(THF) having a hydrogen-bonding unit (**I**). A polymer [2]catenane comprised of the two different cyclic poly(THF) components, **I** and **II** (from **2**), has been isolated up to 7% yield as an acetone-insoluble fraction and unequivocally characterized by means of MALDI TOF mass spectroscopy together with ^{1}H NMR and SEC techniques.

Introduction

Topologically appealing molecules such as catenanes and knots have continuously attracted broad academic interests[1] and have recently been highlighted as new platforms for breakthrough functions leading to future nanodevices and nanomachines.[2] The self-assembly synthesis of catenanes and knots having a shape-persistent and robust structure has now been established by employing carefully designed components capable of forming a "just-fit-in-space" self-assembly through $\pi-\pi$ interaction,[3] metal coordination,[4] or hydrogen-bonding interactions.[5] Remarkable achievements by these protocols in recent years include simple to complex catenanes and knots, such as Borromean rings,[6] Solomon link,[7] and others.[8]

The construction of *polymer* catenanes and knots by DNA molecules has also been achieved by exploiting the complementary base-pair units and the subsequent enzymatic ligation process specifically applicable to the DNA process.[9] In contrast, *polymer* catenanes and knots with long and flexible synthetic polymer components have still been a formidable synthetic challenge.[10] The end-linking polymer cyclization requires dilution, which promotes an intramolecular process over an intermolecular chain extension but circumvents the associative pairing of polymer precursors. In addition, a long and flexible polymer chain tends to form a randomly coiled, thus contracted conformation, and the threading by another polymer chain appears ineffective, particularly in dilution.[11,12] Therefore, previous attempts could isolate only less than 1% yield of polymer catenanes,[10e−10g] though they could provide a unique opportunity to elucidate the topology effect on polymer properties.[13]

In recent years, however, a remarkable progress has been achieved in the controlled and effective synthesis of cyclic polymers either by ring-expansion polymerization with novel catalysts[14] or by effective end-linking processes of polymer precursors.[15,16] These encouraged us a renewed attempt for the effective synthesis of polymer catenanes, in particular by employing the cooperative action of a long-range electrostatic interaction and a directional hydrogen-bonding interaction, as has been exploited in biological processes[17] and in designing functional materials.[18]

Thus, we have employed an *electrostatic self-assembly* and *covalent fixation* process,[16] in which a variety of cyclic polymers have been produced effectively with polymer precursors having moderately strained cyclic ammonium salt end groups accompanying nucleophilic counteranions, typically carboxylates. We have subsequently introduced a hydrogen-bonding unit, i.e, an isophthaloylbenzylic amide group, in such cyclic polymers either from an initiator or from a counteranion. The isophthaloylbenzylic amide group has been recognized as an effective structural motif to form self-complementary and intertwined hydrogen-bonding pair to produce various shape-persistent catenanes and knots.[19] Accordingly, we have prepared two different cyclic polymers having the ring size of up to 150 atoms as components for a polymer [2]catenane (Scheme 1). It is notable that the combination of different cyclic polymer components provides the unequivocal mass spectroscopic support for the formation of the polymer [2]catenane. In contrast, the relevant polymer [2]catenane analogue comprised of the two identical cyclic polymer components is unable to be distinguished by their molar masses from a simple dimeric cyclic polymer.

Results and Discussion

1. Synthesis of Two Cyclic Polymer Components for a Polymer [2]Catenane. First, a cyclic poly(tetrahydrofuran), poly(THF), having a hydrogen-bonding, isophthaloyl benzylic amide group, **I**, has been prepared through an *electrostatic self-assembly* and *covalent fixation* with a telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups carrying a dicarboxylate counteranion containing the hydrogen-bonding unit, **1**

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<div align="center">**Scheme 1. Synthesis of Two Cyclic Polymer Components for a Polymer [2]Catenane**</div>
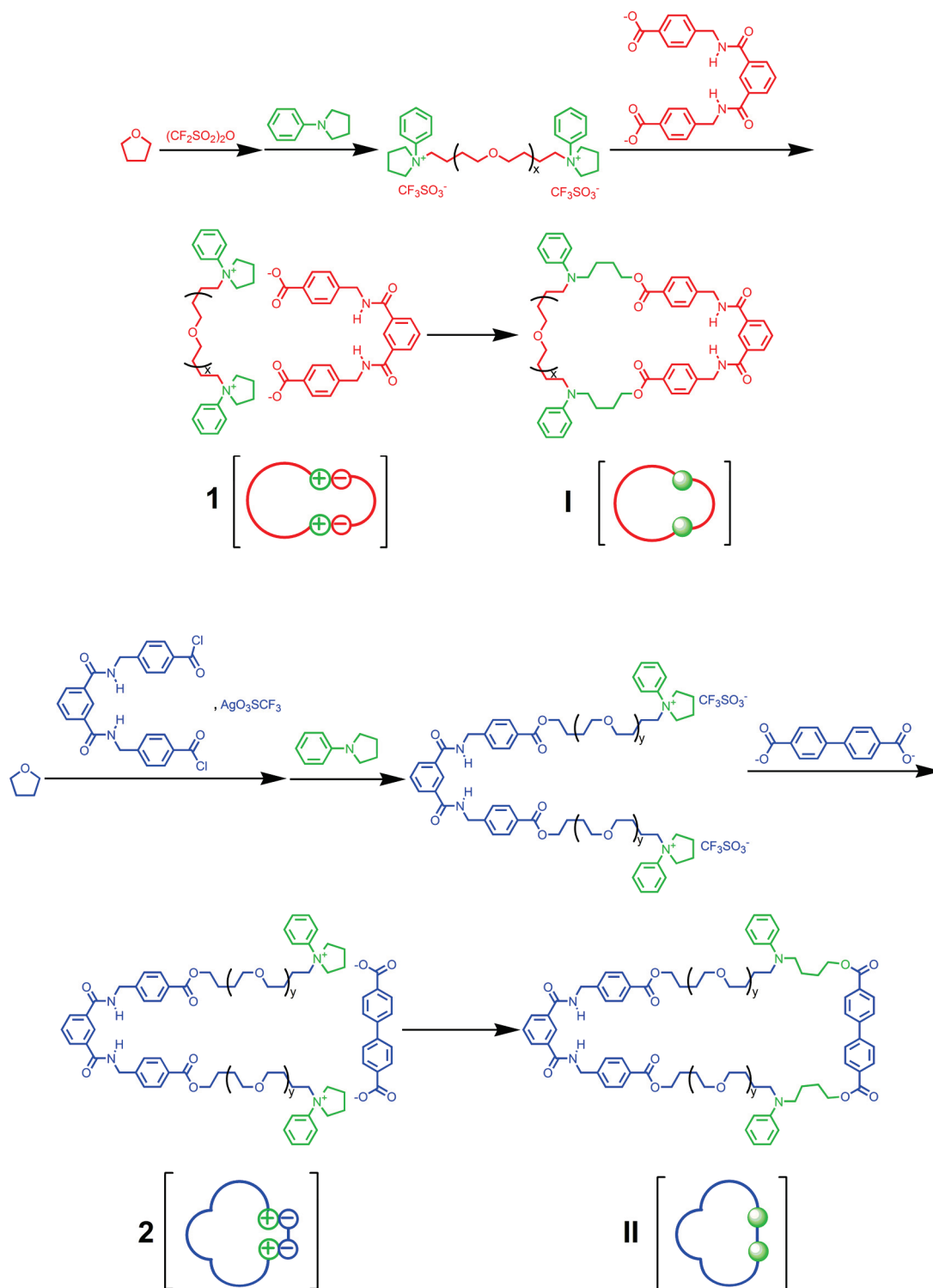
(Scheme 1, see Supporting Information for the synthesis of the precursor polymers and the counteranion). The cations and anions always balance the charges, and a selective ring-opening reaction by the nucleophilic substitution by carboxylate counteranions was performed by heating **1** in CHCl₃ under dilution (1.0 g/L) by reflux for 3 h. The subsequent purification by a flash chromatography with silica gel produced a cyclic poly(THF) having an isophthaloylbenzylic amide group, **I**.

Another center-functional, *kentro*-telechelic poly(THF) having an isophthaloyl benzylic amide group at the center position and *N*-phenylpyrrolidinium salt end groups

carrying a biphenyldicarboxylate counteranion, **2**, has been prepared through the living polymerization of THF with an initiator formed *in situ* by the reaction between a bifunctional acid chloride containing an isophthaloyl benzylic amide group and silver trifluoromethanesulfonate, AgO₃SCF₃, followed by the end-capping with *N*-phenylpyrrolidine (Scheme 1, see Supporting Information for the details of the synthetic procedure for a bifunctional acid chloride derivative). The subsequent counterion exchange reaction from triflate to biphenyldicarboxylate was performed by the precipitation of the poly(THF) precursor into an aqueous
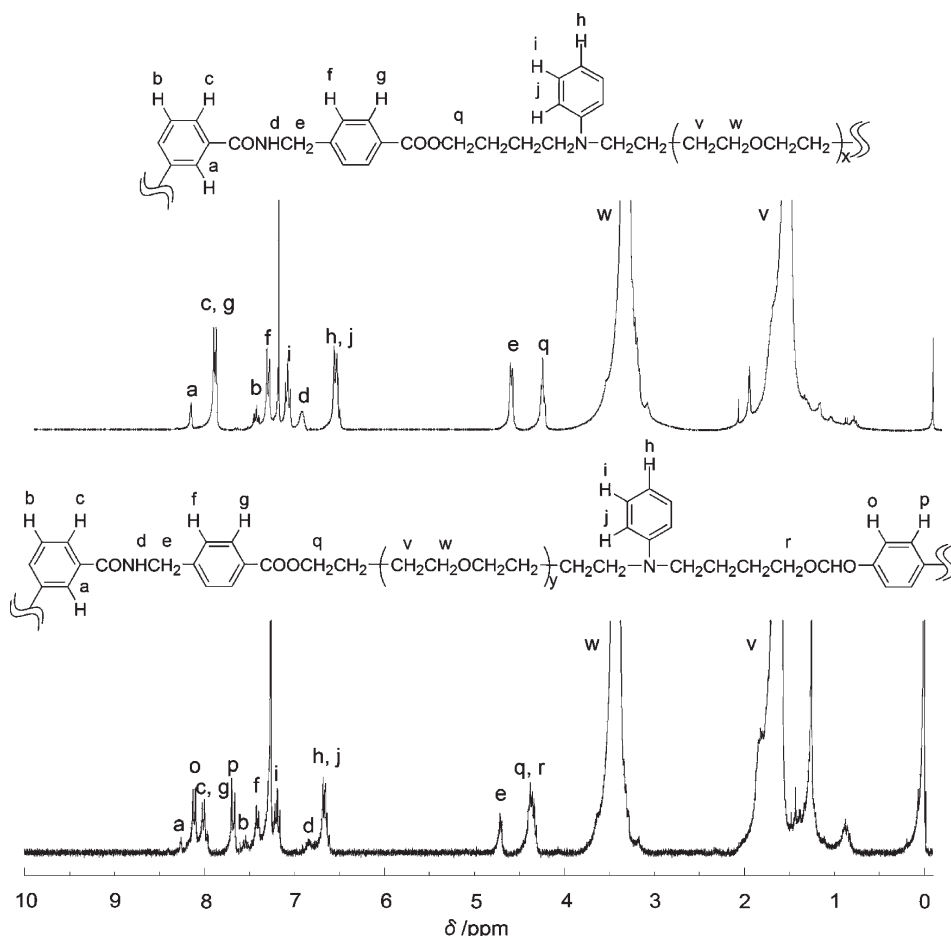
Figure 1. 300 MHz ^{1}H NMR spectra of (top) a cyclic poly(THF) having an isophthaloyl benzylic amide group (**I**) and (bottom) a cyclic poly(THF) having an isophthaloylbenzylic amide and biphenyldicarboxylate groups at the opposite positions (**II**) (CDCl$_3$, 40 °C).

solution containing an excess amount of sodium biphenyldi-carboxylate. The subsequent covalent conversion of **2** in CHCl$_3$ under dilution (1.0 g/L) by reflux for 3 h, followed by the purification through a flash chromatography with silica gel, afforded another cyclic poly(THF) having an iso-phthaloylbenzylic amide and biphenyldicarboxylate groups at the opposite positions, **II** (Scheme 1).

^{1}H NMR spectra of the two cyclic poly(THF)s, **I** and **II** (Figure 1, top and bottom, respectively), showed signals for both **I** and **II** due to the isophthaloyl group at 7.55/7.54 and 8.25/8.26 ppm and the benzylic groups at 4.71/4.71 and 7.16/7.19 ppm besides the overflowed signals due to the poly-(THF) main chain at 1.6 and 3.1 ppm. In addition, the signals due to the biphenyl protons are visible at 7.68 and 8.12 ppm only for the spectrum of **II** (Figure 1, bottom).

MALDI-TOF mass spectra of **I** and **II** (Figure 2, top and bottom, respectively) showed a series of peaks corresponding to poly(THF) (peak interval of 72 mass units), and each peak corresponds exactly to the molar mass summing up the linking structure of the respective cyclic poly(THF)s, **I** and **II**, respectively. Thus, the peak (assumed to be the adduct with Na$^+$) at 2967.08 corresponds to the expected cyclic poly(THF), **I**, with the DP$_n$ (x in the chemical formula in Scheme 1) of 30, (C$_4$H$_8$O) × 30 + C$_{48}$H$_{52}$N$_4$O$_6$ plus Na$^+$ as 2967.17 (Figure 2, top). Also, the peak (assumed to be the adduct with Na$^+$) at 2543.00 corresponding to the expected another cyclic poly(THF), **II**, with DP$_n$ (2y in the chemical formula in Scheme 1) of 20, (C$_4$H$_8$O) × 20 + C$_{66}$H$_{68}$N$_4$O$_{10}$, plus Na$^+$ as 2542.43 (see S-Table 1 in Supporting Informa-tion for the summary of MALDI-TOF measurements.)

SEC traces of **I** and **II** (Figure 3, A and B, solid lines, respectively) showed that both products possess unimodal distributions (PDI = 1.32 and 1.39, respectively) and a nota-bly smaller hydrodynamic volumes than those of the linear analogues (Figure 3, A and B, broken lines, respectively), obtained by the covalent conversion reaction of the corre-sponding telechelic polymer precursors with benzoate ani-ons. A measure of the hydrodynamic volume ratio of **I** and **II** against the corresponding linear analogue, determined by SEC from their apparent peak molecular weights, was 0.71 for both **I** and **II**, and this value is in good agreement with those reported before.[16g,16h] From these results, it was con-cluded that two types of cyclic poly(THF)s having a hydro-gen-bonding unit have efficiently been produced.

Importantly, in the course of the synthesis of **I**, a notice-able amount (up to 3% yields) of an acetone-insoluble fraction was isolated before the purification work-up by a flash chromatography. It is also remarkable that no acetone-insoluble fraction was isolated by the relevant polymer cyclization with the corresponding poly(THF) precursor without the hydrogen-bonding unit. The MALDI analysis of the acetone-insoluble fraction showed the mass peaks corresponding to the two units of a cyclic poly(THF), **I** (Figure 4). Thus, the peak (assumed to be the adduct with Na$^+$) at 3027.08 corresponds to twice of the cyclic poly-(THF), **I**, with the DP$_n$ (2x in the chemical formula in Scheme 1) of 20, (C$_4$H$_8$O) × 20 + C$_{96}$H$_{104}$N$_8$O$_{12}$ plus Na$^+$ as 3027.07 (see S-Table 1 in the Supporting Information for the summary of MALDI-TOF measurements.) These observations imply the formation of polymer [2]catenane
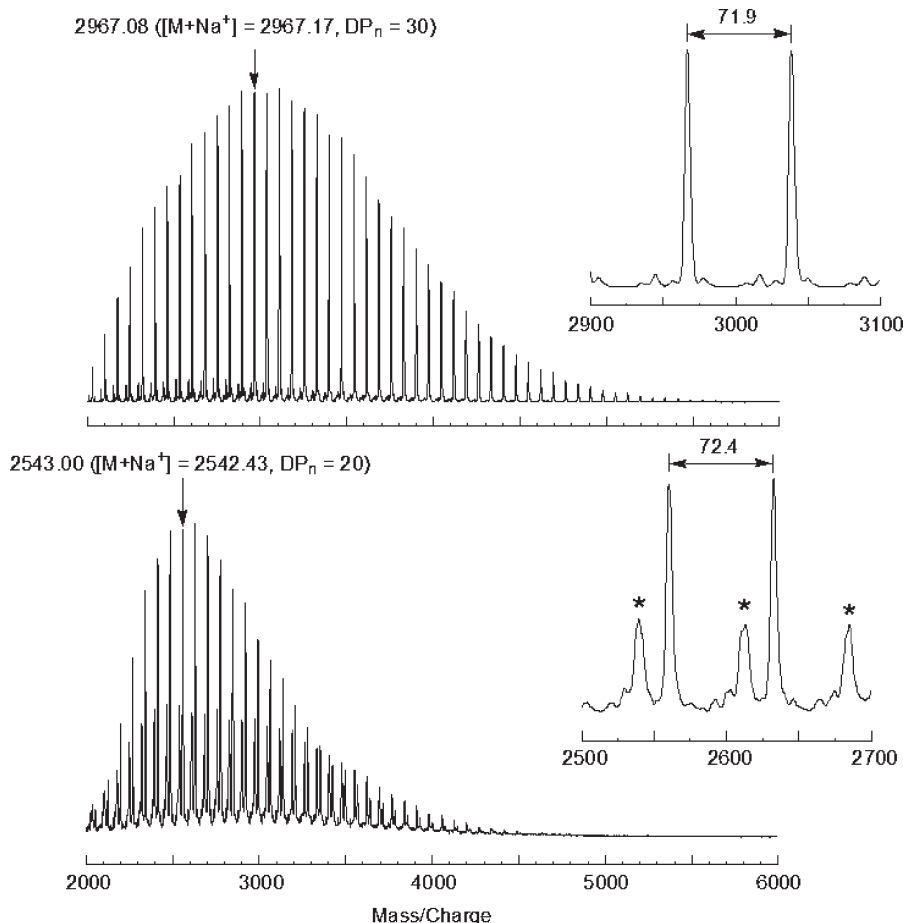
Figure 2. MALDI-TOF mass spectra of (top) a cyclic poly(THF) having an isophthaloylbenzylic amide group (**I**) and (bottom) a cyclic poly(THF) having an isophthaloylbenzylic amide and biphenyldicarboxylate groups at the opposite positions (**II**) (linear mode, matrix: dithranol with sodium trifluoroacetate; DP_n denotes the number of monomer units in the product; * indicates the peak assignable to the H^+ adduct).

product, **I/I**, during the polymer cyclization through the hydrogen-bonding interaction between the cyclic poly-(THF), **I**, and the open-chain telechelic precursor, **1**, having a hydrogen-bonding unit (Scheme 2). Unfortunately, mass spectroscopy could not distinguish the polymer [2]catenane product, **I/I**, from a simple dimeric cyclic polymer product. Nor could the SEC conclusively distinguish the polymer [2]catenane from the dimeric cyclic polymer product.

2. Synthesis of a Polymer [2]Catenane through the Cooperative Electrostatic/Hydrogen-Bonding Self-Assembly and Covalent Fixation. We have subsequently performed the covalent conversion reaction of the telechelic poly(THF) precursor, **2**, in the presence of the preformed cyclic poly-(THF) having a hydrogen-bonding unit, **I** (Scheme 2), since the formation of a polymer [2]catenane comprised of the two distinctive cyclic poly(THF)s, **I/II**, is able to be confirmed by means of the mass spectroscopic analysis.

The reaction was carried out with the telechelic poly(THF) precursor, **2**, in the presence of the cyclic poly(THF), **I** with the molar ration **I/2** of 0.6–0.9. The results are collected in Table 1. The acetone-insoluble fraction was isolated with notable yields of 5.7–7.1% in addition to the acetone-soluble fraction (40–60%). In the control experiment, the polymer cyclization of **2** was carried out in the presence of a simple cyclic poly(THF) without the hydrogen-bonding unit. The acetone-insoluble fraction was scarcely recovered (0.1%).

^{1}H NMR spectra of the acetone-soluble and acetone-insoluble fractions (Figure 5, top and bottom, respectively) showed that both fractions are commonly comprised of the two cyclic poly(THF)s, **I** and **II**. All signals were assignable to **I** or **II** in comparison with the two respective spectra of **I** and **II** given previously in Figure 1. The composition ratios in the acetone-soluble and the acetone-insoluble fractions were then determined and summarized in Table 1. Remarkably, the compositions of **I** and **II** in the acetone-soluble and insoluble fraction significantly differ from each other. And the latter is comprised of **I** and **II** in the ratio of about 2:3. This could be accounted for by that the acetone-insoluble fraction contains the polymer [2]catenane **II/II** in addition to the polymer [2]catenane **I/II**.

MALDI-TOF mass spectra of both the acetone-soluble and the acetone-insoluble fractions (Figure 6, top and bottom, respectively) showed commonly a series of peaks corresponding to poly(THF) with peak interval of 72 mass units. And for the acetone-soluble fraction, the observed molar mass for major peaks was assignable to **I** coincided with those shown in Figure 2 (top). For example, a peak (assumed to be the adduct with Na^+) at 2967.08 corresponds to the cyclic poly(THF), **I**, with the DP_n (x in the chemical formula in Scheme 1) of 30, $(C_4H_8O) \times 30 + C_{48}H_{52}N_4O_6$ plus Na^+ as 2967.17. In addition, a series of minor shoulder peaks was detectable and was assignable to the cyclic poly-(THF), **II**. For example, a peak (assumed to be the adduct with Na^+) at 2903.42 corresponds to the cyclic poly(THF), **II**, with the DP_n ($2y$ in the chemical formula in Scheme 1) of 25, $(C_4H_8O) \times 25 + C_{66}H_{68}N_4O_{10}$ plus Na^+ as 2902.96.

For the acetone-insoluble fraction, in contrast, a series of peak molar mass was assignable to the polymer [2]catenane comprised of the two cyclic poly(THF)s, **I** and **II**, as the
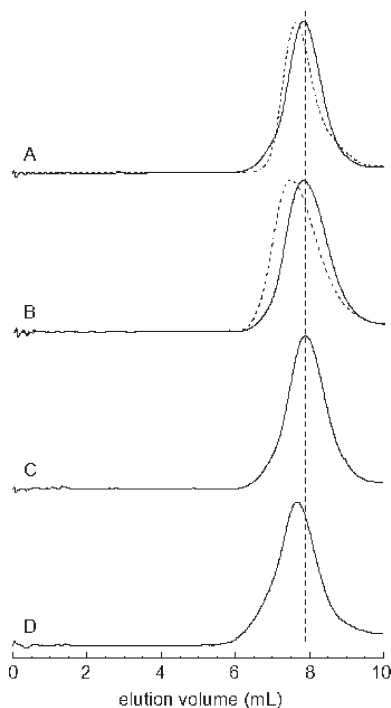
Figure 3. SEC traces of (A) a cyclic poly(THF) having an isophtha-loylbenzylic amide group (**I**) (solid line) and its linear analogue (broken line), (B) a cyclic poly(THF) having an isophthaloylbenzylic amide and biphenyldicarboxylate groups at the opposite positions (**II**) (solid line) and its linear analogue (broken line), and (C) the acetone-soluble and (D) the acetone-insoluble fraction obtained through the cooperative electrostatic/hydrogen-bonding self-assembly and covalent fixation by **2** in the presence of **I** (Tosoh G3000HXL, eluent: THF 1.0 mL/min).
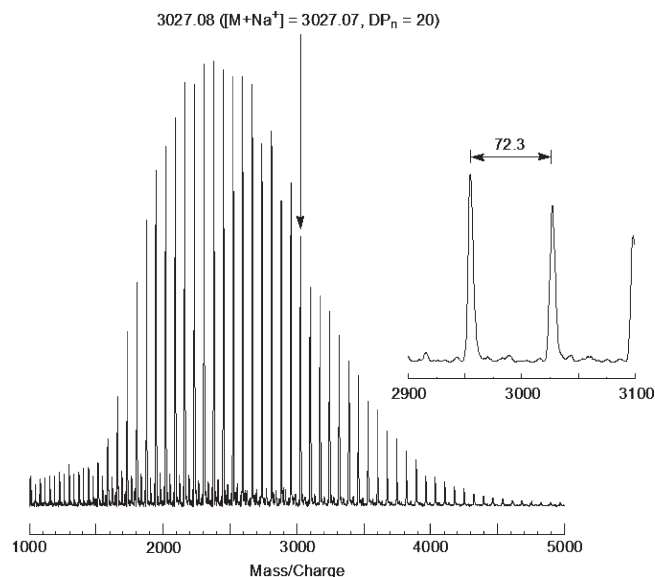

Figure 4. MALDI-TOF mass spectra of the acetone-insoluble fraction isolated during the synthesis of a cyclic poly(THF) (**I**) from a telechelic poly(THF) precursor, **1** (linear mode, matrix: dithranol with sodium trifluoroacetate; DP_n denotes the number of monomer units in the product).

components. Thus, the peak (assumed to be the adduct with Na^+) at 3323.08 corresponding to the [2]catenane composed of the poly(THF)s, **I** and **II**, with DP_n ($x + 2y$ in the chemical formula in Scheme 2) of 20, $(C_4H_8O) \times 20 + C_{114}H_{120}N_8O_{16}$, plus Na^+ as 3323.39. Moreover, a series of minor shoulder peaks assignable to the polymer [2]catenane, **II/II**, was

detectable. For example, a peak (assumed to be the adduct with Na^+) at 3331.38 corresponds to the polymer [2]cate-nane, **II/II**, with the DP_n ($4y$ in the chemical formula in Scheme 1) of 16, $(C_4H_8O) \times 16 + C_{132}H_{136}N_8O_{20}$ plus Na^+ as 3331.29 (see S-Table 1 in the Supporting Information for the summary of MALDI-TOF measurements).

The hydrodynamic volume of polymer [2]catenane was estimated by SEC comparison of the apparent molecular weights of cyclic poly(THF)s and of a polymer [2]catenane. As seen in Figure 3C,D, the acetone-soluble fraction showed the elution profile nearly unchanged from the cyclic poly-(THF)s, **I** and **II**, confirming that the acetone-soluble frac-tion is a mixture of the two cyclic poly(THF)s, **I** and **II**. The acetone-insoluble fraction showed, in contrast, a trace with the higher peak molecular weight ($M_p = 3000$) than either of the cyclic poly(THF)s, **I** ($M_p = 2400$) and **II** ($M_p = 2500$), while smaller than twice of the cyclic polymer component. The extent of the contraction of 3D size of the polymer catenane, thus estimated, was 0.68. This result is comparable with those reported by the simulation study.[13c]

Conclusions

We have shown that polymer [2]catenane has been produced by the cooperative noncovalent interaction of polymer pre-cursors, i.e., the electrostatic interaction for the effective end-to-end polymer cyclization and the hydrogen-bonding inter-action to entwine the two polymer chains. The formation of polymer [2]catenane product has been unequivocally demon-strated by means of mass spectroscopic analysis. Moreover, the unprecedentedly high yield of up to 7% has been demonstrated. Hence, this strategy will provide a promising means for the practical synthesis of a variety of polymer catenanes consisting of randomly coiled, long and flexible synthetic polymer segments of diverse chain structures, to allow further characterization and eventually the design of polymer materials of unique properties.

Experimental Section

1. Synthesis of a Cyclic Poly(THF) (I) from a Telechelic Poly(THF) Having *N*-Phenylpyrrolidinium Salt Groups Accom-panying a Dicarboxylate Containing an Isophthaloylbenzylic Amide Group (1). A THF solution (5 mL) of poly(THF) pre-cursor accompanying triflate counteranions (1.010 g, see Sup-porting Information for the synthetic procedures) was added dropwise under vigorous stirring into an ice-cooled aqueous solution (50 mL) including an excess amount of a sodium dicarboxylate containing an isophthaloylbenzylic amide group (**3**, 0.527 g, 1.11×10^{-3} mol, see Supporting Information for the synthetic procedures). The precipitated ion-exchange product was collected by filtration after stirring for 30 min and dried in vacuo for 2 h. This precipitation treatment was repeated twice to complete the ion-exchange reaction to give a telechelic poly-(THF) having *N*-phenylpyrrolidinium salt end groups accom-panying a dicarboxylate counteranion containing an isophtha-loylbenzylic amide group, **1** (1.081 g, containing a small amount of water to avoid uncontrolled cyclic opening reaction).

^{1}H NMR (300 MHz, CDCl$_3$): δ 1.32−1.67 (m, −C*H*$_2$CH$_2$O−), 1.78−2.17 (m, −NCH$_2$C*H*$_2$C*H*$_2$CH$_2$O−, and pyrrolidine β-*H*), 3.07−3.60 (m, −CH$_2$C*H*$_2$O−), 3.89−4.13 (m, 4H, pyrrolidine α-*H*), 4.64 (s, 4H, −C*H*$_2$NH−), 7.16 (d, *J* = 7.7 Hz, 4H, Ar-*H ortho* to CH$_2$), 7.38−7.59 (m, 10H, −NPh, isophthaloyl 5-*H*), 7.74 (d, *J* = 7.7 Hz, 4H, Ar-*H meta* to CH$_2$), 8.18 (d, *J* = 7.7 Hz, 2H, isophthaloyl 4-*H*, 6-*H*), 9.55 (s, 1H, isophthaloyl 2-*H*), 10.27 ppm (s, 2H, −CH$_2$N*H*−).

A weighed amount of the poly(THF) precursor, **1** (0.643 g), was then dissolved in CHCl$_3$ (643 mL) and was subjected to a heat treatment by reflux for 3 h. Thereafter, the solvent was removed by evaporation, and acetone (20 mL) was added at

Scheme 2. Synthesis of a Polymer [2]Catenane through the Cooperative Electrostatic/Hydrogen-Bonding Self-Assembly and Covalent Fixation
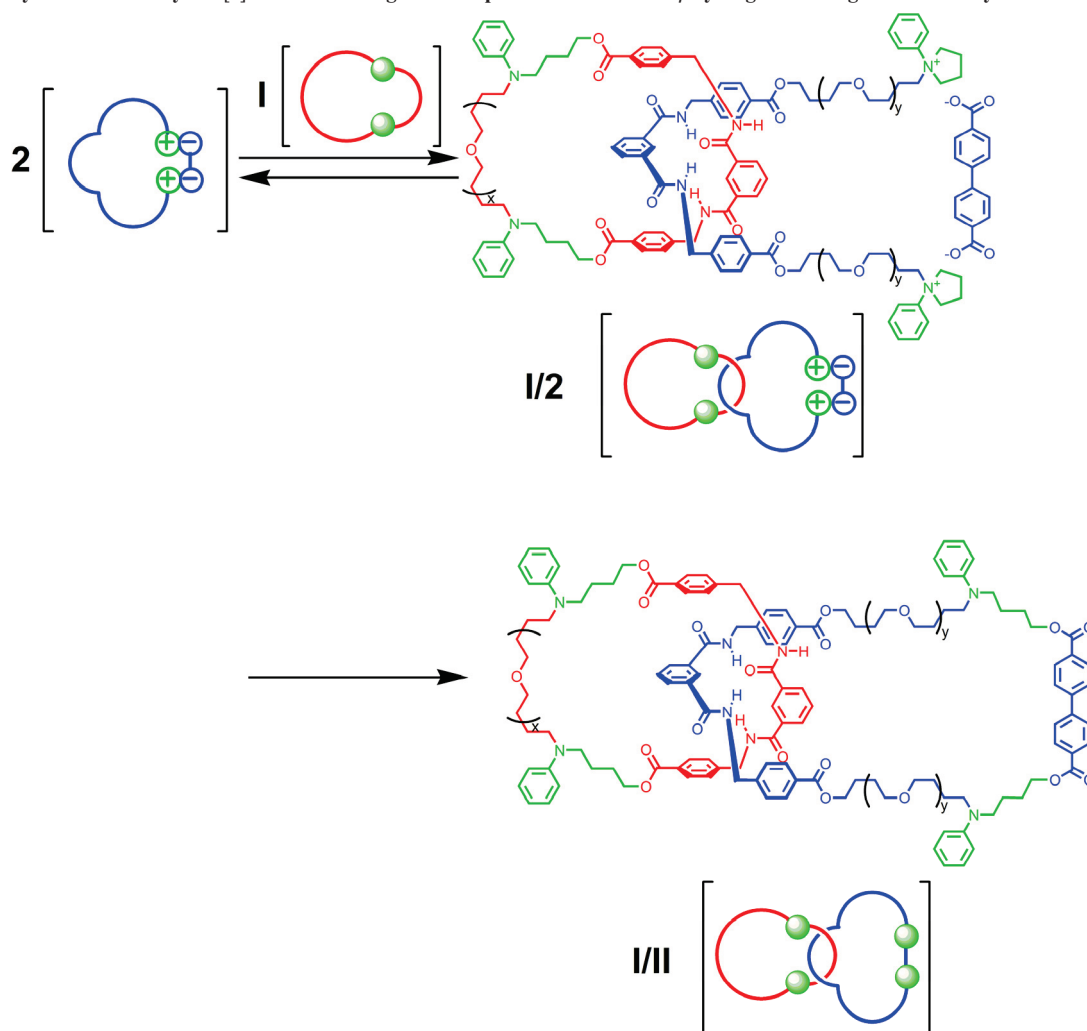
Table 1. Synthesis of Polymer [2]Catenanes through the Cooperative Electrostatic/Hydrogen-Bonding Self-Assembly and Covalent Fixation[a]

				acetone-soluble fraction		acetone-insoluble fraction	
entry	I^b (mg)	2^c (mg)	$I/2$ (mol/mol)	yield (mg) (%)	$I:II^d$	yield (mg) (%)	$I:II^d$
1	300	430	0.63	296 (49)	58:42	42 (5.8);	35:65
2	114	113	0.91	112 (41)	70:30	16 (7.1);	38:62
3	137	138	0.90	167 (61)	71:29	17 (5.7);	39:61

[a] See Experimental Section for experimental details. [b] M_n = 3200 (NMR). [c] M_n = 2500 (NMR). [d] Determine by the NMR analysis (see also Figure 5).

0 °C. The acetone-insoluble fraction was filtered (0.023 g), while the acetone-soluble fraction was subjected to the column chromatography on silica gel (hexane/acetone = 2/1) to yield 0.398 g, 62% of the cyclic poly(THF) product, **I**.

The acetone-insoluble fraction: ¹H NMR (300 MHz, CDCl₃): δ 1.50−1.79 (m, −CH_2CH_2O−), 3.23−3.62 (m, −CH_2CH_2O−), 4.31 (t, J = 6.2 Hz, −CH_2NH−), 4.68 (s, −CH_2NH−), 6.54− 6.74 (m, NPh o, p-H), 7.06 (s, −CH_2NH−), 7.17 (t, J = 6.7 Hz, NPh m-H), 7.41 (d, J = 7.3 Hz, Ar−H $ortho$ to CH_2), 7.48 (t, J = 8.2 Hz, isophthaloyl 5-H), 7.90−8.05 (m, Ar-H $meta$ to CH_2, isophthaloyl 4-H, 6-H), 8.24 (s, isophthaloyl 2-H).

The acetone-soluble fraction: ¹H NMR (300 MHz, CDCl₃): δ 1.32−1.67 (m, −CH_2CH_2O−), 3.07−3.60 (m, −CH_2CH_2O−), 4.35 (t, J = 6.2 Hz, 4H, −CH_2NH−), 4.71 (d, J = 5.2 Hz, 4H, −CH_2NH−), 6.53−6.74 (m, 6H, NPh o, p-H), 6.85 (s, 2H, −CH_2NH−) 7.16 (d, J = 7.7 Hz, 4H, NPh m-H), 7.41 (d, J = 8.3 Hz, 4H, Ar−H $ortho$ to CH_2), 7.55 (t, J = 8.0 Hz, 1H, isophthaloyl 5-H), 7.92−8.10 (m, 6H, Ar-H $meta$ to CH_2, isophthaloyl 4-H, 6-H), 8.25 (s, 1H, isophthaloyl 2-H). M_n(NMR) = 3200, M_n(SEC) = 2100.

2. Synthesis of a Poly(THF) Having an Isophthaloylbenzylic Amide Group at the Center Position and Having N-Phenylpyrrolidinium Salt Groups at the Chain Ends Accompanying a Biphenyldicarboxylate Counteranion (2). A weighed amount of a diacid chloride derivative containing an isophthaloylbenzylic amide group (**4**, 0.226 g, 4.82 × 10⁻⁴ mol, see Supporting Information for the synthetic procedures) was dissolved in 100 mL of dried THF. Thereupon, a THF solution (4 mL) of silver trifluoromethanesulfonate (0.494 g, 1.92 × 10⁻³ mol) was added at once. The precipitation of AgCl occurred immediately, and the polymerization was allowed to proceed at 25 °C for 4.0 min. The end-capping reaction was then carried out by adding N-phenylpyrrolidine (1.701 g, 1.155 × 10⁻² mol) and by stirring another 0.5 h. The reaction mixture was then filtered to remove AgCl, and the poly(THF) product was isolated by precipitation into hexane at −78 °C and dried under vacuum. The yield was 1.940 g.

¹H NMR (300 MHz, CDCl₃): δ 1.19−1.94 (m, −CH_2-CH_2O−), 2.04−2.27 (m, −NCH₂CH_2CH_2CH₂O−), 2.27−2.45
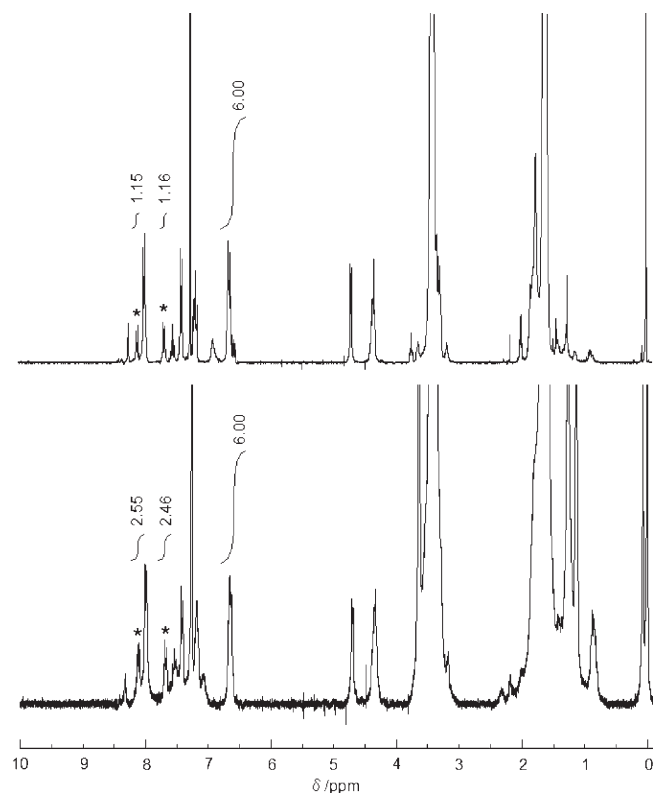
Figure 5. 300 MHz ^{1}H NMR spectra of (top) the acetone-soluble and (bottom) the acetone-insoluble fraction obtained through the cooperative electrostatic/hydrogen-bonding self-assembly and covalent fixation by the telechelic precursor, **2**, in the presence of the cyclic polymer, **I** (CDCl$_3$, 40 °C).

Figure 6. MALDI-TOF mass spectra of (top) the acetone-soluble and (bottom) the acetone-insoluble fraction obtained through the cooperative electrostatic/hydrogen-bonding self-assembly and covalent fixation by the telechelic precursor, **2**, in the presence of the cyclic polymer, **I** (linear mode, matrix: dithranol with sodium trifluoroacetate; DP$_n$ denotes the number of monomer units in the product).

(m, 4H, pyrrolidine β-*H*), 3.04−3.66 (m, −CH$_2$C*H*$_2$O−), 3.93−4.16 (m, 4H, pyrrolidine α-*H*), 4.32 (t, *J* = 6.4 Hz, 6H, −COOC*H*$_2$−), 4.68 (d, *J* = 5.5 Hz, 4H, −C*H*$_2$NH−), 7.39−7.79 (m, 15H, isophthaloyl 5-*H*, Ar−*H* *ortho* to CH$_2$, NPh-*H*), 7.88−8.22 ppm (m, 7H, isophthaloyl 2-*H*, 4-*H*, 6-*H*, Ar−*H* *meta* to CH$_2$). M_n(NMR) = 2500.

A weighed amount of the poly(THF) precursor described above, having *N*-phenylpyrrolidinium salt groups at the chain ends accompanying triflate counteranions (1.014 g), was dissolved in 8.0 mL of methanol and added dropwise under vigorous stirring into an ice-cooled aqueous solution (400 mL) containing an excess amount of sodium 4,4-biphenyldicarboxylate. The precipitated ion-exchange product was collected by filtration after stirring for 0.5 h and dried in vacuo. This precipitation treatment was repeated twice to give the ion-exchanged product, **2** (0.818 g, 81%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 1.02−1.75 (m, −CH$_2$-CH$_2$O−), 1.75−1.89 (m, 4H, −NCH$_2$C*H*$_2$C*H*$_2$CH$_2$O−), 1.89−2.07 (m, 4H, pyrrolidine β-*H*), 2.07−2.39 (m, 4H, −NCH$_2$C*H*$_2$CH$_2$CH$_2$O−), 3.07−3.72 (m, −CH$_2$C*H*$_2$O−), 3.72−4.10 (m, 4H, pyrrolidine α-*H*), 4.16−4.53 (m, 6H, −COOC*H*$_2$− and pyrrolidine α-*H*), 4.69 (d, *J* = 4.3 Hz, 4H, −C*H*$_2$NH−), 7.44−7.82 (m, 23H, Ar−*H* *ortho* to CH$_2$, isophthaloyl 5-*H*, 4, 4-biphenyldicarboxylate 2,2′,6,6′-*H*, NPh−*H*), 7.82−8.06 (m, 4H, 4,4-biphenyldicarboxylate 3,3′,5,5′-*H*), 8.06−8.31 ppm (m, 5H, Ar−*H* *meta* to CH$_2$, isophthaloyl 2-*H*, isophthal 2-*H*, 4-*H*, 6-*H*). M_n(NMR) = 2600.

3. Synthesis of a Cyclic Poly(THF) Having an Isophthaloyl-benzylic Amide and a Biphenyldicarboxylate Groups (II). A weighed amount of the poly(THF) precursor described above (**2**, 0.074 g) was dissolved in 740 mL of THF (0.1 g/L), and the solution was refluxed for 3 h. The product was isolated quantitatively (0.075 g) after the solvent was removed by evaporation and was further purified by preparative thin-layer
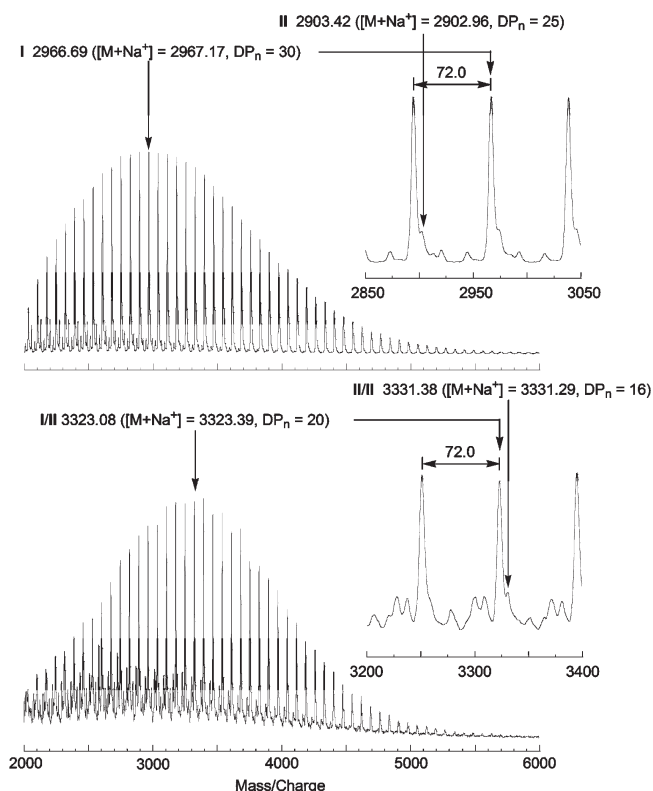
chromatography (SiO$_2$, hexane/acetone = 2/1) to yield 0.027 g (37%) of a cyclic poly(THF), **II**.

^{1}H NMR (300 MHz, CDCl$_3$): δ 1.20−2.10 (m, −C*H*$_2$CH$_2$O−), 3.10−3.75 (m, −CH$_2$C*H*$_2$O−), 4.22−4.51 (m, 8H, −COOC*H*$_2$−), 4.71 (d, *J* = 6.0 Hz, 4H, −C*H*$_2$NH−), 6.60−6.72 (m, 6H, NPh *o,p*-*H*), 6.80−6.90 (m, 2H, −CH$_2$N*H*−), 7.19 (t, *J* = 7.7 Hz, 4H, NPh *m*-*H*), 7.41 (d, *J* = 7.9 Hz, 4H, Ar-*H* *ortho* to CH$_2$), 7.54 (t, *J* = 7.7 Hz, 1H, isophthaloyl 5-*H*), 7.68 (d, *J* = 8.2 Hz, 4H, 4,4-biphenyldicarboxylate 2,2′,6,6′-*H*), 8.00 (m, 6H, isophthaloyl 4-*H*, 6-*H*, Ar-*H* *meta* to CH$_2$), 8.12 (d, *J* = 8.2 Hz, 6H, 4,4-biphenyldicarboxylate 3,3′,5,5′-*H*), 8.26 ppm (s, 1H, isophthaloyl 2-*H*). M_n(NMR) = 2900, M_n(SEC) = 2300.

4. Synthesis of a Polymer [2]Catenane by the Cooperative Electrostatic/Hydrogen-Bonding Self-Assembly and Covalent Fixation. A cyclic poly(THF) having a hydrogen-bonding unit, **I** (0.137 g), and a telechelic poly(THF) containing an isophthaloylbenzylic amide group at the center position and having *N*-phenylpyrrolidinium salt groups at the chain ends, accompanying a biphenyldicarboxylate counteranion, **2** (0.137 g), were mixed in 10 mL of CHCl$_3$. The solvent was once evaporated to promote the mixing of **I** and **2**, followed by adding once again CHCl$_3$ (138 mL). The solution was subsequently refluxed for 3 h. The reaction solvent was then removed by evaporation, and the acetone-insoluble fraction was isolated by adding acetone and by keeping at 0 °C. The yield was 0.017 g (5.7%). The acetone-soluble fraction was isolated by evaporating the solvent and was further purified by preparative thin-layer chromatography (SiO$_2$, hexane/acetone = 2/1). The yield was 0.167 g (61%).

The acetone-insoluble fraction: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.47−2.15 (m, −C*H*$_2$CH$_2$O−), 3.22−3.61 (m, −CH$_2$C*H*$_2$O−), 4.26−4.48 (m, −COOC*H*$_2$−), 4.63−79 (m, −C*H*$_2$NH−), 6.58−6.79 (m, NPh *o*, *p*-*H*), 7.14−7.24 (m, NPh *m*-*H*), 7.42 (d,

$J = 7.5$ Hz, Ar$-H$ *ortho* to CH$_2$), 7.43$-$7.63 (m, isophthaloyl 5-H), 7.69 (d, $J = 7.3$ Hz, 4,4-biphenyldicarboxylate 2,2′,6,6′-H), 7.87$-$8.08 (m, isophthaloyl 4-H, 6-H, Ar$-H$ *meta* to CH$_2$), 8.12 (d, $J = 7.9$ Hz, 4,4-biphenyldicarboxylate 3,3′,5,5′-H) ppm. M_n(NMR) = 8200, M_n(SEC) = 3800.

The acetone-soluble fraction: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.48$-$1.74 (m, $-$CH$_2$CH$_2$O$-$), 3.23$-$3.59 (m, $-$CH$_2$CH_2O$-$), 4.25$-$4.48 (m, $-$COOCH_2-), 4.70 (d, $J = 5.6$ Hz, $-$CH_2NH$-$), 6.54$-$6.71 (m, NPh *o*, *p-H*), 6.97$-$7.08 (m, $-$CH$_2$N$H-$), 7.13$-$7.26 (m, NPh *m-H*), 7.41 (d, $J = 7.5$ Hz, Ar$-H$ *ortho* to CH$_2$), 7.49$-$7.59 (m, isophthaloyl 5-H), 7.68 (d, $J = 8.4$ Hz, 4,4-biphenyldicarboxylate 2,2′,6,6′-H), 7.99 (m, $J = 8.4$ Hz, isophthaloyl 4-H, 6-H, Ar$-H$ *meta* to CH$_2$), 8.12 (d, $J = 8.4$ Hz, 4,4-biphenyldicarboxylate 3,3′,5,5′-H), 8.26 ppm (s, isophthaloyl 2-H). M_n(NMR) = 3800, M_n(SEC) = 2400.

4. Polymer Cyclization through Electrostatic Self-Assembly and Covalent Fixation in the Presence of a Cyclic Poly(THF) without the Hydrogen-Bonding Unit. A weighed amount of a cyclic poly(THF) without the hydrogen-bonding unit (0.095 g, see Supporting Information for the synthetic procedures) and a telechelic poly(THF) having an isophthaloylbenzylic amide group at the center position and having *N*-phenylpyrrolidinium salt groups at the chain ends, accompanying a biphenyldicarboxylate counteranion, **2** (0.094 g), were dissolved in 4 mL of CHCl$_3$. The solvent was once evaporated to promote the mixing of both poly(THF) precursors, followed by adding once again CHCl$_3$ (94 mL). The solution was subsequently refluxed for 3 h. Thereafter, the solvent was removed by evaporation, and the acetone-insoluble fraction was isolated by adding acetone and by keeping at 0 °C. The yield of the acetone-insoluble fraction was 0.2 mg (0.1%). The acetone-soluble fraction was isolated by evaporating the solvent and was further purified by preparative thin-layer chromatography (SiO$_2$, hexane/acetone = 2/1). The yield was 0.094 g (50%).

5. Measurements. ^{1}H NMR spectra were recorded with JEOL JNM-AL300 apparatus in D$_2$O, in CDCl$_3$, or in DMSO-d_6 at ambient temperature or 40 °C. The chemical shifts were referenced from the signal of solvent (D$_2$O) or tetramethylsilane. Size exclusion chromatography (SEC) measurements were performed with a Tosoh CCPS equipped with a refractive index detector model RI 8020. A column of TSK G3000HXL was employed with THF as an eluent at a flow rate of 1.0 mL/min. MALDI-TOF MASS spectra were taken on a Shimadzu AXIMA-CFR MASS spectrometer. The spectrometer was equipped with a nitrogen laser (λ = 337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by a linear-positive ion mode. The sample polymer solution (1 g/L) was prepared in THF. The matrix, dithranol (Aldrich) and sodium trifluoroacetate (Aldrich), was 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-cyanohydroxy-cinnamic acid dimer plus H$^+$ at 379.35.

Supporting Information Available: Synthetic procedures for dicarboxylate derivatives having isophthaloylbenzylic amide groups and for poly(THF) precursors for the preparation of cyclic poly(THF)s with and without a hydrogen-bonding unit. This material is available free of charge via Internet at http://pubs.acs.org.

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