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

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Received September 11, 2009; Revised Manuscript Received October 30, 2009

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, isophthaloylbenzyl amide group (I) was prepared through an electrostatic self-assembly and covalent fixation with a telechelic poly(THF) having N-phenylpyrroolidinium salt groups carrying a dicarboxylate counteranion containing the hydrogen-bonding unit (I). Another telechelic poly(THF) having an isophthaloylbenzyl amide group at the center position and having N-phenylpyrroolidinium 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 1H NMR and SEC techniques.

Introduction

Topologically appealing molecules such as catenanes and knots have continuously attracted broad academic interests and have recently been highlighted as new platforms for breakthroughs leading to future nanodevices and nanomachines. The self-assembly synthesis of catenanes and knots have a shape-persistent and robust structure that has been established by employing carefully designed components capable of forming a “just-fit-in-space” self-assembly through π-π interaction, metal coordination, or hydrogen-bonding interactions. Remarkable achievements by these protocols in recent years include simple to complex catenanes and knots, such as Borromean rings, Solomon link, and others.

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. In contrast, polymer catenanes and knots with long and flexible synthetic polymer components have still been a formidable synthetic challenge. 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. Therefore, previous attempts could isolate only less than 1% yield of polymer catenanes, though they could provide a unique opportunity to elucidate the topology effect on polymer properties.

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 or by effective end-linking processes of polymer precursors. 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 and in designing functional materials.

Thus, we have employed an electrostatic self-assembly and covalent fixation process, 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 isophthaloylbenzyl amide group, in such cyclic polymers either from an initiator or from a covalent fixation. The isophthaloylbenzyl 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. 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 benzyl amide group, I, has been prepared through an electrostatic self-assembly and covalent fixation with a telechelic poly(THF) having N-phenylpyrroolidinium salt groups carrying a dicarboxylate counteranion containing the hydrogen-bonding unit, I

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(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 I 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, \textit{kentro}-telechelic poly(THF) having an isophthaloyl benzylic amide group at the center position and \textit{N}-phenylpyrrolidinium salt end groups carrying a biphenyldicarboxylate counteranion, 2, has been prepared through the living polymerization of THF with an initiator formed \textit{in situ} by the reaction between a bifunctional acid chloride containing an isophthaloyl benzylic amide group and silver trifluoromethanesulfonate, AgO\textsubscript{3}SCF\textsubscript{3}, followed by the end-capping with \textit{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
solution containing an excess amount of sodium biphenyldicarboxylate. The subsequent covalent conversion of 2 in CHCl₃ 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 isophthaloylbenzylic amide and biphenyldicarboxylate groups at the opposite positions, II (Scheme 1).

¹H 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 DPₙ (x in the chemical formula in Scheme 1) of 30, (C₄H₈O)ₓ × 30 + C₄₅H₅₂N₂Oₓ 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 DPₙ (2y in the chemical formula in Scheme 1) of 20, (C₄H₈O) × 20 + C₆₀H₆₂N₂O₁₀ plus Na⁺ as 2542.43 (see S-Table 1 in Supporting Information 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 notably 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 corresponding telechelic polymer precursors with benzoate anions. 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 concluded that two types of cyclic poly(THF)s having a hydrogen-bonding unit have efficiently been produced.

Importantly, in the course of the synthesis of I, a noticeable 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 DPₙ (2x in the chemical formula in Scheme 1) of 20, (C₄H₈O) × 20 + C₆₀H₆₂N₂O₁₀ plus Na⁺ as 3027.07 (see S-Table 1 in Supporting Information for the summary of MALDI-TOF measurements.) These observations imply the formation of polymer [2]catenane.
product, I/I, during the polymer cyclization through the hydrogen-bonding interaction between the cyclic poly-(THF), I, and the open-chain telechelic precursor, I, 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, I, 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/I, from a simple dimeric cyclic polymer product. Nor could the SEC conclusively distinguish the polymer [2]catenane from the dimeric cyclic polymer product.

The reaction was carried out with the telechelic poly(THF) precursor, I, 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/I, is able to be confirmed by means of the mass spectroscopic analysis.

The reaction was carried out with the telechelic poly(THF) precursor, I, in the presence of the 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/I, is able to be confirmed by means of the mass spectroscopic analysis.

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, \((C_3H_8O)\times30 + C_{48}H_{52}N_4O_6 + Na^{+}\) 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\(_n\) (y in the chemical formula in Scheme 1) of 25, \((C_4H_8O)\times25 + C_{66}H_{68}N_4O_{10} + Na^{+}\) 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
components. Thus, the peak (assumed to be the adduct with Na\(^+\)) at 3323.08 corresponding to the [2]catenane, I/II, with the DP\(_n\) (x + 2y) in the chemical formula in Scheme 2 of 20, (C\(_{12}\)H\(_8\)O) \(\times\) 20 + C\(_{11}\)H\(_{12}\)N\(_8\)O\(_{16}\), plus Na\(^+\) as 3323.39. Moreover, a series of minor shoulder peaks assignable to the polymer [2]catenane, I/II, was detectable. For example, a peak (assumed to be the adduct with Na\(^+\)) at 3331.38 corresponds to the polymer [2]catenane, II/II, with the DP\(_n\) (4y) in the chemical formula in Scheme 1 of 16, (C\(_8\)H\(_5\)O) \(\times\) 16 + C\(_{13}\)H\(_{16}\)N\(_2\)O\(_2\) 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 fraction 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 precursors, i.e., the electrostatic interaction for the effective end-to-end polymer cyclization and the hydrogen-bonding interaction to entwine the two polymer chains. The formation of polymer [2]catenane product has been unequivocally demonstrated 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 Accompanying a Dicarboxylate Containing an Isophthaloylbenzylic Amide Group (I).** A THF solution (5 mL) of poly(THF) precursor accompanying trflate counteranions (1.010 g, see Supporting 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, 0.527 g, 1.11 \(\times\) 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 accompanying a dicarboxylate counteranion containing an isophthaloylbenzylic amide group, I (1.081 g, containing a small amount of water to avoid uncontrolled cyclic opening reaction).

\(^1\)H NMR (300 MHz, CDCl\(_3\)), \(\delta\) 1.32–1.67 (m, \(-\text{CH}_2\text{CH}_2\text{O}^-\)), 1.78–2.17 (m, \(-\text{NCH}_2\text{CH}_2\text{CH}_2\text{O}^-\), and pyrrolidine \(\beta\)-H), 3.07–3.60 (m, \(-\text{CH}_2\text{CH}_2\text{O}^-\)), 3.89–4.13 (m, 4H, pyrrolidine \(\alpha\)-H), 4.64 (s, 4H, \(-\text{CH}_2\text{NH}^-\)), 7.16 (d, \(J = 7.7\) Hz, 4H, Ar-\(H\) ortho to CH\(_2\)), 7.38–7.59 (m, 10H, \(-\text{NPh, isophthaloyl} 5-H\)), 7.74 (d, \(J = 7.7\) Hz, 4H, Ar-\(H\) meta to CH\(_2\)), 8.18 (d, \(J = 7.7\) Hz, 2H, isophthaloyl4-H, 6-H), 9.55 (s, 1H, isophthaloyl2-H), 10.27 ppm (s, 2H, \(-\text{CH}_2\text{NH}^-\)).

A weighed amount of the poly(THF) precursor, I (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

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**Figure 3.** SEC traces of (A) a cyclic poly(THF) having an isophthaloylbenzylic amide group (I) (solid line) and its linear analogue (broken line), (B) a cyclic poly(THF) having an isophthaloylbenzylic amide and biphenyl dicarboxylate 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, I (linear mode, matrix: dithranol with sodium trifluoroacetate; DP\(_n\) denotes the number of monomer units in the product).
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, \( \text{I} \). The acetone-insoluble fraction: 1H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 1.50–1.79 (m, \(-\text{C}_6\text{H}_4\text{CH}_2\text{O}-\)), 3.23–3.62 (m, \(-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}-\)), 4.31 (t, \(J = 6.2 \text{ Hz}\), \(-\text{C}_6\text{H}_4\text{NH}-\)), 4.68 (s, \(-\text{CH}_2\text{NH}-\)), 6.54–6.74 (m, NPh \(o\), \(p\)-H), 7.06 (s, \(-\text{CH}_2\text{NH}-\)), 7.17 (t, \(J = 6.7 \text{ Hz}\), NPh \(m\)-H), 7.41 (d, \(J = 7.3 \text{ Hz}\), Ar–\(H\) \(\text{ortho}\) to \(\text{CH}_2\)), 7.48 (t, \(J = 8.2 \text{ Hz}\), isophthaloyl \(5\)-H), 7.90–8.05 (m, Ar–\(H\) \(\text{meta}\) to \(\text{CH}_2\), isophthaloyl \(4\)-H, \(6\)-H), 8.24 (s, isophthaloyl \(2\)-H).

The acetone-soluble fraction: 1H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 1.32–1.67 (m, \(-\text{CH}_2\text{CH}_2\text{O}-\)), 3.07–3.60 (m, \(-\text{CH}_2\text{CH}_2\text{O}-\)), 4.35 (t, \(J = 6.2 \text{ Hz}\), 4H, \(-\text{CH}_2\text{NH}-\)), 4.71 (d, \(J = 5.2 \text{ Hz}\), 4H, \(-\text{CH}_2\text{NH}-\)), 6.53–6.74 (m, 6H, NPh \(o\), \(p\)-H), 6.85 (s, 2H, \(-\text{CH}_2\text{NH}-\)), 7.16 (d, \(J = 7.7 \text{ Hz}\), 4H, NPh \(m\)-H), 7.41 (d, \(J = 8.3 \text{ Hz}\), 4H, Ar–\(H\) \(\text{ortho}\) to \(\text{CH}_2\)), 7.55 (t, \(J = 8.0 \text{ Hz}\), 1H, isophthaloyl \(5\)-H), 7.92–8.10 (m, 6H, Ar–\(H\) \(\text{meta}\) to \(\text{CH}_2\), isophthaloyl \(4\)-H, \(6\)-H), 8.25 (s, 1H, isophthaloyl \(2\)-H), \(M_n\) (NMR) = 3200, \(M_d\) (SEC) = 2100.

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

<table>
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<th>entry</th>
<th>(I^\dagger) (mg)</th>
<th>(2^\ddagger) (mg)</th>
<th>(I/2) (mol/mol)</th>
<th>acetone-soluble fraction yield (mg) (%)</th>
<th>I–IIcovery</th>
<th>acetone-insoluble fraction yield (mg) (%)</th>
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<tr>
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<td>113</td>
<td>0.91</td>
<td>112 (41)</td>
<td>70:30</td>
<td>16 (7.1)</td>
<td>38:62</td>
</tr>
<tr>
<td>3</td>
<td>137</td>
<td>138</td>
<td>0.90</td>
<td>167 (61)</td>
<td>71:29</td>
<td>17 (5.7)</td>
<td>39:61</td>
</tr>
</tbody>
</table>

\(^\dagger\)See Experimental Section for experimental details. \(^\ddagger\) \(M_n = 3200\) (NMR). \(^\ddagger\) \(M_n = 2500\) (NMR). \(^\ddagger\) Determine by the NMR analysis (see also Figure 5).

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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, \( \text{I} \). The acetone-insoluble fraction: 1H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 1.50–1.79 (m, \(-\text{C}_6\text{H}_4\text{CH}_2\text{O}-\)), 3.23–3.62 (m, \(-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}-\)), 4.31 (t, \(J = 6.2 \text{ Hz}\), \(-\text{C}_6\text{H}_4\text{NH}-\)), 4.68 (s, \(-\text{CH}_2\text{NH}-\)), 6.54–6.74 (m, NPh \(o\), \(p\)-H), 7.06 (s, \(-\text{CH}_2\text{NH}-\)), 7.17 (t, \(J = 6.7 \text{ Hz}\), NPh \(m\)-H), 7.41 (d, \(J = 7.3 \text{ Hz}\), Ar–\(H\) \(\text{ortho}\) to \(\text{CH}_2\)), 7.48 (t, \(J = 8.2 \text{ Hz}\), isophthaloyl \(5\)-H), 7.90–8.05 (m, Ar–\(H\) \(\text{meta}\) to \(\text{CH}_2\), isophthaloyl \(4\)-H, \(6\)-H), 8.24 (s, isophthaloyl \(2\)-H).

The acetone-soluble fraction: 1H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 1.32–1.67 (m, \(-\text{CH}_2\text{CH}_2\text{O}-\)), 3.07–3.60 (m, \(-\text{CH}_2\text{CH}_2\text{O}-\)), 4.35 (t, \(J = 6.2 \text{ Hz}\), 4H, \(-\text{CH}_2\text{NH}-\)), 4.71 (d, \(J = 5.2 \text{ Hz}\), 4H, \(-\text{CH}_2\text{NH}-\)), 6.53–6.74 (m, 6H, NPh \(o\), \(p\)-H), 6.85 (s, 2H, \(-\text{CH}_2\text{NH}-\)), 7.16 (d, \(J = 7.7 \text{ Hz}\), 4H, NPh \(m\)-H), 7.41 (d, \(J = 8.3 \text{ Hz}\), 4H, Ar–\(H\) \(\text{ortho}\) to \(\text{CH}_2\)), 7.55 (t, \(J = 8.0 \text{ Hz}\), 1H, isophthaloyl \(5\)-H), 7.92–8.10 (m, 6H, Ar–\(H\) \(\text{meta}\) to \(\text{CH}_2\), isophthaloyl \(4\)-H, \(6\)-H), 8.25 (s, 1H, isophthaloyl \(2\)-H), \(M_n\) (NMR) = 3200, \(M_d\) (SEC) = 2100.

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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 \(\times 10^{-4}\) 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 \(\times 10^{-3}\) 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 \(\times 10^{-2}\) 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 \(-78 \text{ °C}\) and dried under vacuum. The yield was 1.940 g.

1H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 1.19–1.94 (m, \(-\text{CH}_2\text{CH}_2\text{O}-\)), 2.04–2.27 (m, \(-\text{NCH}_2\text{CH}_2\text{CH}_2\text{O}-\)), 2.27–2.45
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$_3$): $\delta$ 1.20–2.10 (m, –CH$_2$CH$_2$O–), 3.10–3.75 (m, –CH$_2$CH$_2$O–), 4.22–4.51 (m, 8H, –COOCH$_2$–), 4.71 (d, J = 6.0 Hz, 4H, –CH$_2$NH–), 6.60–6.72 (m, 6H, NPh o-p-H), 6.80–6.90 (2H, –CH$_2$NH–), 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′,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′,5′-H), 8.26 ppm (s, 1H, isophthaloyl 2-H), $M_n$(NMR) = 2900, $M_w$(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 isophthaloylbenzylc 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 II, 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$_3$): $\delta$ 1.47–2.15 (m, –CH$_2$CH$_2$O–), 3.22–3.61 (m, –CH$_2$CH$_2$O–), 4.26–4.48 (m, –COOCH$_2$–), 4.63–7.93 (m, –CH$_2$NH–), 6.58–6.79 (m, NPh α-p-H), 7.14–7.24 (m, NPh m-H), 7.42 (d,
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.

References and Notes


(12) For the synthesis of catenanes having large cyclic components through covalently entwined structural unit, see: (a) Únsal, O.; Godt, A. Chem.—Eur. J. 1999, 5, 1728–1733. (b) Shah, M. R.; Duda, S.; Müller, B.; Godt, A.; Malik, A. J. Am. Chem. Soc. 2003, 125, 5408–5414. The template synthesis could produce catenane products having large cyclic units in good yields. On the other hand, the catenate


