Covalent Conversion of Cyclic Onium Salt End Groups of Poly(tetrahydrofuran) by Bulky Counteranions in the Absence and Presence of Macrocyclic Compounds

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ABSTRACT: A series of bulky carboxylates was introduced as a counteranion for *N*-methylpyrrolidinum salt end groups of poly(tetrahydrofuran), poly(THF), having molecular weights of ca. 5000. 4-(7,7,7-Triphenylheptoxy)benzoate was found to remain intact as a counteranion at ambient temperature but to cause the ring-opening reaction of pyrrolidinium groups at 90 °C to produce poly(THF) with bulky stopper groups in a pure form in 71% yield. The relevant ring-opening reaction also took place in the presence of such macrocyclics as 30-crown-10 and cyclodextrins, but an effective entrapping of cyclic components in polyrotaxanes was not achieved presumably because of the entropic repulsion between the two components.

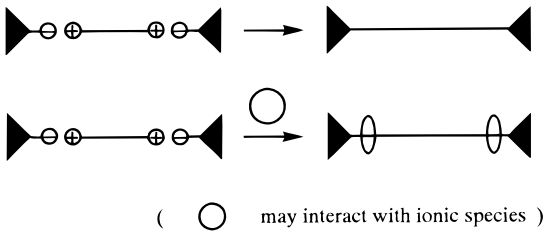
Introduction

Rotaxanes are topologically unique, supramolecular assemblies, consisting of a macrocyclic compound threaded by a linear compound having bulky stopper groups at both chain ends, preventing the spontaneous dissociation of these components. A number of intriguing methods have been developed in the past decade to achieve efficient synthesis of rotaxanes by utilizing, in particular, noncovalent attractive interactions between cyclic and linear components (or their precursor components).[1−4]

For macromolecular rotaxanes, in which a long-chain, flexible polymer molecule constitutes the linear component, a common synthetic process involves the polymerization of a low-molecular-weight monomer in the presence of an excess amount of the relevant macrocyclic compounds, i.e., as a solvent component in most cases and a subsequent end-capping reaction, if necessary, with appropriate bulky stopper compounds.[4−6] Although this process is versatile enough to provide a variety of macromolecular rotaxanes, full characterization of the linear component is inherently difficult to achieve. Another common process involves a preformed rotaxane compound possessing an additional functional group utilized for either the (co)polymerization reaction or the grafting reaction onto another polymeric reagent having complementary reactive groups.[7−9]

An alternative synthetic process which can offer, at least in principle, well-defined macromolecular rotaxanes is to combine the precharacterized linear, macrocyclic and stopper components. Only a few efficient processes by this synthetic principle have been reported so far. A notable example is a polyrotaxane synthesis through the complexation of a polyether, in particular poly(ethylene glycol), with cyclodextrins.[10−12] One should note, however, the effective molecular weight of the polyether component for the polyrotaxane formation is restricted to, at most, a few thousand even in this system, where an attractive hydrophobic interaction between the linear and cyclic component is exceptionally favorable for the complexation. This limitation can be accounted for by the fact that the longer the linear polymer component, the stronger the entropic repulsion is between the flexible polymer and macrocycles to prevent the thread of the latter into the former. Recently, noncovalent attractive interactions between either cyclic bipyridinium units and linear oligo(ethylene oxide) units[13−15] or crown ethers and linear polyurethanes[16] with hydrogen-bonding capability have been utilized to construct polypseudorotaxanes through the threading of macrocycles onto preformed linear polymers.[17]

Scheme 1



In this context, a novel process was examined in this study in which linear, macrocyclic, and stopper components can interact to form a self-assembly. An objective of this study is to test whether the subsequent covalent connection of the stopper component at the ends of the linear component in the presence of, and by interacting with, a macrocyclic component can efficiently produce macromolecular rotaxane structures (Scheme 1). Thus, we have synthesized a linear telechelic poly(tetrahydrofuran), poly(THF), having cyclic onium salt groups accompanying a series of bulky carboxylates as counter-

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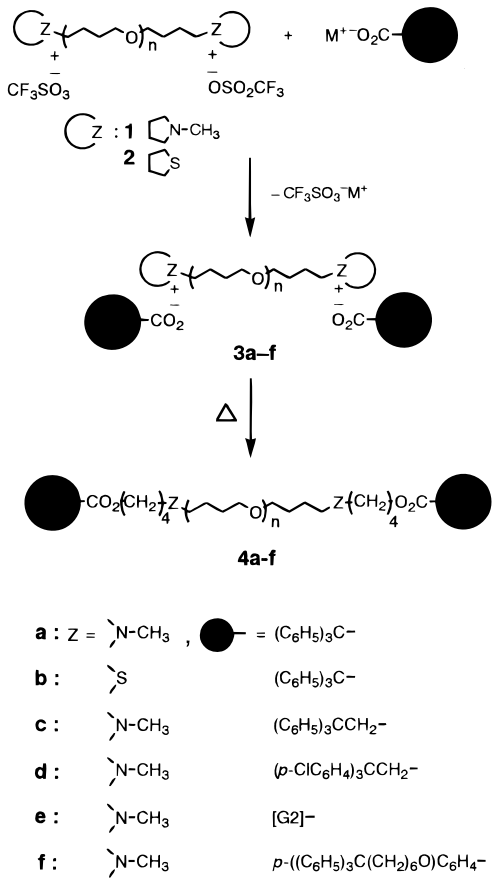
Scheme 2



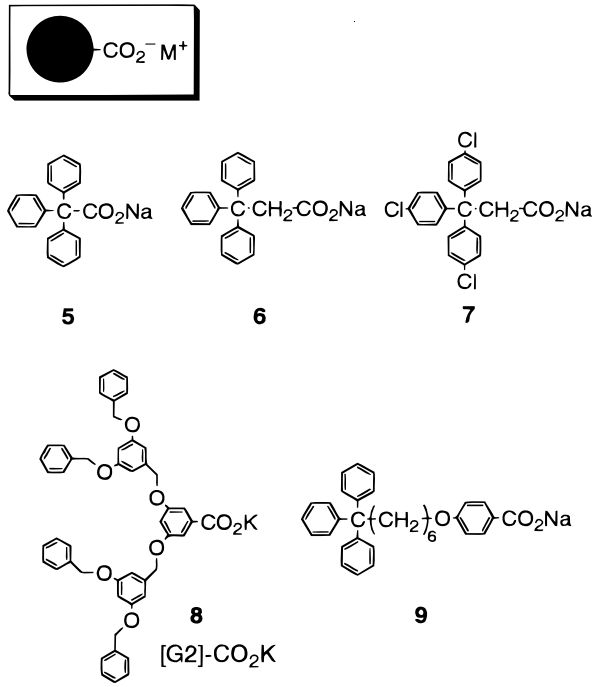
anions. The subsequent heating of the isolated telechelic polymers in the absence and presence of macrocycles has been performed to cause the ring-opening reaction of cyclic onium salt groups by nucleophilic attack of bulky carboxylate anions to convert the preformed ionic assembly to the covalently linked permanent structures.

Results and Discussion

Covalent Conversion of Cyclic Onium Salt End Groups of Poly(THF)s by Bulky Carboxylates. We have so far reported on such telechelics as poly(THF),[18–20] polystyrene,[21] and poly(dimethylsiloxane)[22] having moderately strained cyclic onium salt groups. They are unique in their macromolecular reactions in contrast to direct coupling reactions of a living polymer with coupling reagents. First, they are stable enough at ambient condition to allow full characterization and subsequent storage until use without any precautions. Second, they are capable of undergoing ion-exchange reactions by the precipitation into aqueous solutions containing excess desired anions. Third, the moderately strained cyclic onium salt groups can undergo selective ring-opening reactions by an appropriate counteranion, i.e., a carboxylate having sufficient nucleophilic reactivity, at ambient or elevated temperature.

Here, the reaction of two different cyclic onium salt end groups has been examined, i.e., five-membered cyclic ammonium (pyrrolidinium) (**1**) and sulfonium (tetrahydrothiophenium) (**2**) salt groups (Scheme 2), with a series of bulky carboxylates as counteranions (Scheme 3). First, a triphenylacetate anion (**5**), whose trityl group is reported to be bulky enough to prevent the dethreading of such macrocyclic compounds as 30-crown-10[23] and cyclodextrins,[24] was employed. The ion-

Scheme 3



exchange reaction of either **1** or **2** was performed by a simple addition of a THF solution of prepolymer into an ice-cooled aqueous solution containing an excess amount of sodium triphenylacetate (procedure A in the Experimental Section). The ^{1}H NMR spectrum of the recovered product with **2** showed a triplet signal (J = 6.3 Hz) at 4.22 ppm due to the ester methylene protons, indicating that the spontaneous ring-opening reaction of the tetrahydrothiophenium salt occurred at ambient temperature, as observed by other carboxylate counteranions, to give the covalently connected product **4b**. On the other hand, the telechelic poly(THF) having pyrrolidinium salt group **3a** was isolated with triphenylacetate as a counteranion. The subsequent heat treatment of **3a** at 100 °C, however, caused the decarboxylation reaction of the triphenylacetate anion to produce a triphenylmethane, instead of the expected ring-opening reaction.

Other commercially available bulky carboxylates, i.e., sodium salts of 3,3,3-triphenylpropionic acid (**6**) and 3,3,3-tris(4-chlorophenyl)propionic acid (**7**), were then employed for the ion-exchange and ring-opening reaction with **1** (Table 1). Because **6** and **7** were only slightly soluble in cooled water, we have performed the ion-exchange reaction through the precipitation of the mixture of **1** and an equimolar amount of **6** or **7** in THF solution into ice-cooled water (procedure B in the Experimental Section). The recovered product (**3c** and **3d**, from the reaction with **6** and **7**, respectively) was then subjected to heat treatment. Ion-exchange products **3c** and **3d** underwent a ring-opening reaction at 90 °C in toluene to form the covalently connected bulky end group on the poly(THF) segment. The produced poly(THF)s having bulky groups at both ends, **4c** and **4d**, were then purified by a preparative thin-layer chromatography (PTLC; SiO_2) finally isolated in 54% and 56% yields, respectively. The above ion-exchange and ring-opening reaction were confirmed by ^{1}H NMR and IR spectroscopic techniques. For example, the ^{1}H NMR spectrum of **4c** (Figure 1, bottom) showed a triplet signal (J = 6.3 Hz) at 3.78 ppm due to the ester methylene

Table 1. Ion-Exchange and Ring-Opening Reactions of Telechelic Poly(THF)s Having Cyclic Onium Salt Groups with Bulky Carboxylates

entry	telechelic[a] poly(THF)	carboxylate[b] anion	ion- exchange[c] product	yield (%)	covalently connected[c] product	yield (%)[d]	M_n[e] (GPC) (kg/mol)	M_w/M_n[f]
1	**1**	**5**	**3a**	94	**4a**	0		
2	**2**	**5**	**3b**		**4b**	91	5.0	1.18
3	**1**	**6**	**3c**	92	**4c**	56	4.0	1.12
4	**1**	**7**	**3d**	85	**4d**	54	4.2	1.13
5	**1**	**8**	**3e**	92	**4e**	59	5.9	1.06
6	**1**	**9**	**3f**	92	**4f**	71	4.5	1.09

[a] Molecular weight of **1** and **2** calculated by ^{1}H NMR: **1**, 4.5 (entries 1 and 6), 5.0 (entries 3 and 4) and 5.3 kg/mol (entry 5); **2**, 5.7 kg/mol. [b] See Scheme 3. [c] For the detailed reaction conditions, see the Experimental Section. [d] After purification by preparative thin-layer chromatography (SiO_2), except for entries 1 and 2. [e] Determined by GPC with the calibration using polystyrene standards by a conversion factor of 0.556.[28] [f] Determined by GPC on the basis of polystyrene standards.

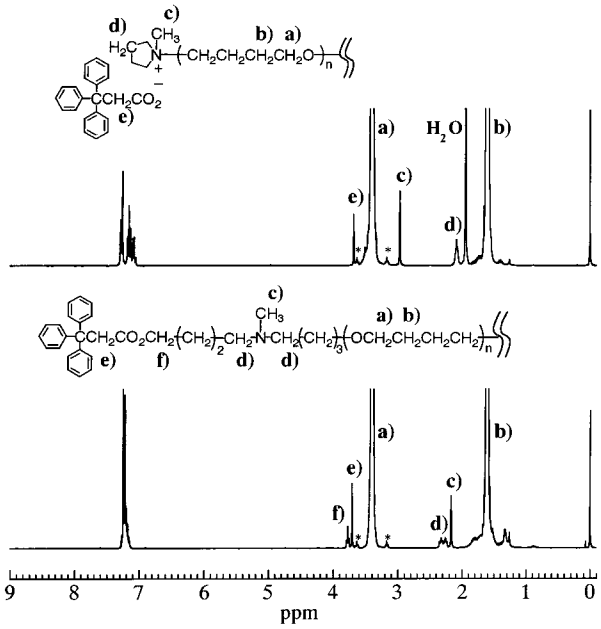


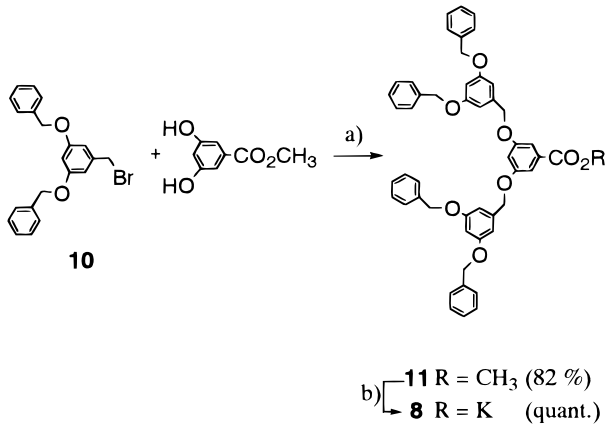
Figure 1. 300 MHz ^{1}H NMR spectra of poly(THF) having bulky carboxylate end groups before (**3c**; top) and after (**4c**; bottom) the heat treatment. (Samples, entry 3 in Table 1; in $CDCl_3$ at 40 °C; * = satellite signal).

protons and a singlet signal at 3.71 ppm due to α-methylene protons of a ester carbonyl group as well as signals at 2.17 ppm and 2.20−2.38 ppm due to *N*-methyl and *N*-methylene protons, respectively, in place of the signals at 2.97 ppm and 2.02−2.14 ppm due to pyrrolidinium salt groups observed in the spectrum of **3c** (Figure 1, top). IR spectroscopic analysis of **3c** and **4c** also indicated that the ion-exchange and ring-opening reactions took place. Thus, the absorption at 1577 cm^{-1} in the spectrum of **3c** due to the carboxylate counteranions is removed after the heat treatment, and that at 1737 cm^{-1} for ester groups appeared instead.

Two new bulky carboxylates were prepared in this study for potential blocking reagents: dendritic carboxylate **8** and *p*-(7,7,7-triphenylheptoxy)benzoate (**9**). The carboxylate **8** was prepared through the Williamson ether synthesis between Fréchet's dendritic benzyl bromide [G1]-Br[25] (**10**) and methyl 3,5-dihydroxybenzoate followed by hydrolysis of ester **11** with KOH in good yield (Scheme 4). The carboxylate **9** contains an alkoxyphenyl moiety which may interact with common macrocycles for rotaxane synthesis, i.e., cyclodextrins, and was synthesized in five steps from triphenylmethane in 48% total yield (Scheme 5).

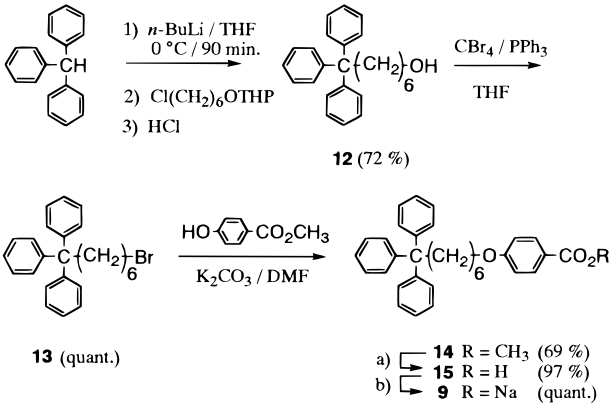
The ion-exchange reaction of **1** with **8** was performed through the precipitation of a mixture of **1** and **8** with

Scheme 4



Reagents: a) K_2CO_3, 18-crown-6, acetone; b) KOH, EtOH / THF.

Scheme 5



Reagents: (a) 1) KOH / EtOH , 2) H^+ (b) NaOH (1eq.) / aq. EtOH

an equimolar amount of ionic groups dissolved in THF into cooled water−MeOH (10:1 v/v). The ion-exchange product **3e** was recovered by filtration in 92% yield. The ^{1}H NMR spectrum (Figure 2, top) of **3e** showed signals due to the dendritic carboxylate (signals e−h as well as signals at 7.20−7.45 ppm) as well as signals a−c which were due to the pyrrolidinium group. The subsequent heat treatment of **3e** in toluene at 90 °C for 42 h caused the ring-opening reaction to produce **4e**. Poly(THF) having dendritic moieties at both ends was thus obtained in 59% isolated yield after purification by PTLC treatment. ^{1}H NMR spectrum (Figure 2, bottom) of **4e** showed a triplet signal (J = 6.6 Hz) at 4.31 ppm due to the ester methylene protons as well as signals at 2.22 ppm and 2.30−2.46 ppm due to *N*-methyl and *N*-methylene protons, respectively.

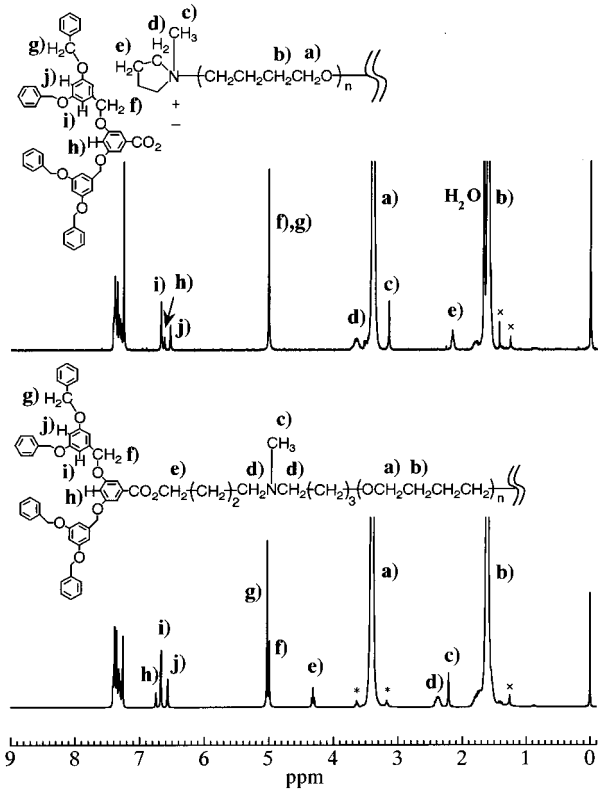


Figure 2. 300 MHz ^{1}H NMR spectra of poly(THF) having dendritic carboxylate end groups before (**3e**; top) and after (**4e**; bottom) the heat treatment. (Samples, entry 5 in Table 1; in $CDCl_3$ at 40 °C; * = satellite signal, × = impurity).

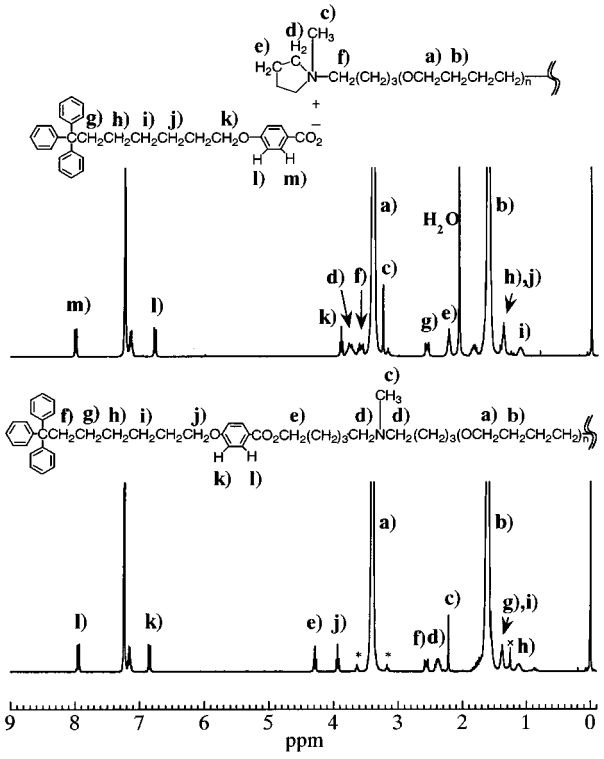


Figure 3. 300 MHz ^{1}H NMR spectra of poly(THF) having bulky carboxylate end groups before (**3f**; top) and after (**4f**; bottom) the heat treatment. (Samples, entry 6 in Table 1; in $CDCl_3$ at 40 °C; * = satellite signal, × = impurity).

The ion-exchange reaction of **1** with **9** was performed in a similar manner through the precipitation of a mixture of **1** and **9** with an equimolar amount of ionic groups dissolved in THF into ice-cooled water. The ion-exchange product **3f** was recovered by filtration in 92% yield. As observed in the cases of other carboxylates, the ^{1}H NMR spectrum (Figure 3, top) of **3f** showed signals due to the bulky carboxylate (signals e−h, as well as signals at 7.14−7.28 ppm) and signals a−c which were due to the pyrrolidinium group. The subsequent heat treatment of **3f** in toluene at 90 °C for 24 h caused the ring-opening reaction to produce **4f**, which was isolated in 71% yield after PTLC treatment. The ^{1}H NMR spectrum (Figure 3, bottom) of **4f** showed a triplet signal (J = 6.3 Hz) at 4.29 ppm due to ester methylene protons as well as the signals at 2.23 ppm and 2.32−2.44 ppm due to *N*-methyl and *N*-methylene protons, respectively. A GPC trace (Figure 4) of **4f** is unimodal with narrow polydispersity and showed a UV trace due to the phenyl groups in the bulky carboxylate group in **9**. The conductivity trace observed in **1** was, on the other hand, totally eliminated.

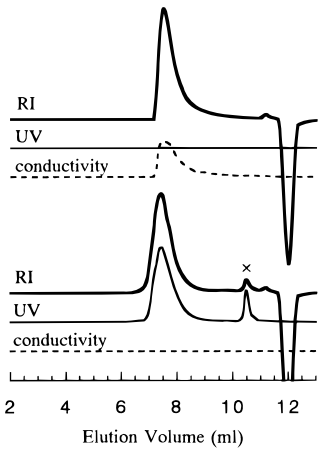


Figure 4. GPC traces of **1** (top) and poly(THF) (**4f**) having bulky carboxylate end groups (bottom). (Samples, entry 6 in Table 1; column, TSK-G3000HXL; eluent, THF; 1 mL/min; × = stabilizer in THF, 2,6-di-*tert*-butyl-4-methylphenol).

As reported previously,[20] the nucleophilic attack of the carboxylate anion took place predominantly at the *endo*-methylene position on the *N*-methylpyrrolidinium group, but the concurrent reaction at *N*-methyl position was detectable during the heat treatment of **3c**−**f**. The subsequent product, i.e., poly(THF) having a pyrrolidine end group, could be removed by a preparative thin-layer chromatography, and a series of poly(THF)s having bulky groups at both ends were isolated in pure forms.

Covalent Conversion of Cyclic Onium Salt End Groups of Poly(THF) by Bulky Carboxylates in the Presence of Macrocyclic Compounds. Among the series of bulky carboxylates examined above, **9** was chosen as the stopper precursor to test whether this covalent-fixation process can be applied for the efficient synthesis of macromolecular rotaxanes.

The covalent-fixation reaction of **3f** was carried out first in the presence of such macrocyclic ethers as 30-crown-10 (**16**) or dibenzo-30-crown-10 (**17**) in toluene solution. As listed in Table 2, the ring-opening reaction of **3f** proceeded as efficiently as it did in the absence of macrocycles with various concentrations except for the case in which 30-crown-10 was employed as a solvent. In this case, no ring-opening reaction was observed to occur, but in turn, this implies the interaction between the ionic groups and crown ethers. The reaction mixture was then precipitated into cold water to remove free 30-

Table 2. Covalent Fixation by a Bulky Counteranion on Pyrrolidinium Salt End Groups of Poly(THF) (3f) in the Presence of Crown Ethers[a]

entry	amount of **3f** (g)	crown ether type	crown ether feed (g)	feed ratio of **16** or **17**/**3f** (mol/mol)	toluene (mL)	ring-opening[b] yield (%)	rotaxane yield[b,c] **16** or **17**/**4f** (mol/mol)	rotaxane yield[b,c] threaded[d] **16** or **17** (%)
1	0.15	**16**	(0.056)	3	7.5	77	<0.025	<1
2	0.10	**16**	(0.25)	20	5.0	80	<0.05	<0.3
3	0.10	**16**	(0.25)	20	1.0	70	<0.2	<1
4	0.10	**16**	(1.4)	110	0	<5		
5	0.10	**17**	(0.05)	3	5.0	77	<0.2	<7
6	0.10	**17**	(0.3)	20	1.0	70	<0.2	<1

a) For the detailed reaction conditions, see the Experimental Section. b) Determined by ^{1}H NMR. c) The content of the crown ether component in the recovered polymer product was determined either after the first precipitation treatment (entries 1−3) or after the first recrystallization treatment (entries 5 and 6). d) Based on the feed amount of crown ether.

crown-10. In addition, free dibenzo-30-crown-10 could be removed by recrystallization from the reaction mixture. The ^{1}H NMR spectra of each fraction revealed that most of the free 30-crown-10 and dibenzo-30-crown-10 components were removed from the reaction mixture, but only a small portion of macrocyclic components remained in the polymer fraction. Any noticeable changes were observed in chemical shift values for either the crown ether component or the end groups of the linear poly(THF) component. GPC of the polymer fraction still showed residual low-molecular-weight component corresponding to the free or dethreaded crown ether. A further attempt by a chromatographic treatment to isolate a pure macromolecular rotaxane product was not successful. In Table 2, therefore, the uppermost approximation of the rotaxane yield value are presented. As also listed in Table 2, an increase in the feed ratio or the overall concentration of the reagents (or both) failed to improve the yield of macromolecular rotaxanes with crown ethers.

The ring-opening reaction of **3f** was also examined in the presence of a slight excess (1.6−1.7 equiv with respect to a pyrrolidinium end group) of β-cyclodextrin and of 2,6-dimethyl-β-cyclodextrin in either DMSO or toluene solution. The ring-opening reaction of a pyrrolidinium salt group took place only in a toluene solution and not in DMSO solution. The entrapping of the cyclodextrin component was not confirmed after the precipitation treatment of the reaction mixture into ice-cooled water.

In conclusion, although the ring-opening reaction of pyrrolidinium salt groups by nucleophilic attack of bulky carboxylate counteranions proceeds in the presence of the macrocycles to permanently connect bulky stopper components at the ends of poly(THF), the threading of macrocyclic components is apparently prevented under the present reaction conditions. This will be ascribed primarily to the entropic repulsion of the random-coiled linear component against macrocyclic components. In addition, one may note that the concentration of the cyclic ammonium salt end groups and aromatic tether in a bulky carboxylate is too low to form effectively the complex with crown ethers or cyclodextrins. The threading of macrocycles is thus kinetically disfavored. Consequently, the enthalpic interactions between pyrrolidinium salt end groups and crown ethers as well as between the aromatic tether and cyclodextrins appears to be insufficient to form a self-assembly of the three components involved.

Experimental Section

Reagents. Telechelic poly(THF) having pyrrolidinium salt end groups (**1**)[18] and tetrahydrothiophenium salt end groups (**2**)[19] were prepared by the method detailed previously. Triphenylacetic acid, 3,3,3-triphenylpropionic acid, and 3,3,3-tris(4-chlorophenyl)propionic acid were purchased, and their sodium salts were prepared by the standard neutralization method with sodium hydroxide. 6-Chlorohexyl 2-tetrahydropyranyl ether[26] and 30-crown-10 (**16**)[27] were prepared by the reported methods. Dibenzo-30-crown-10 (**17**) (Aldrich; 98%) and 2,6-dimethyl-β-cyclodextrin (Tokyo Chemical Industry Co., Ltd.) were used as received. THF was dried over sodium benzophenone ketyl and distilled just before use. Toluene and dimethyl sulfoxide (DMSO) were distilled from CaH_2. *n*-Butyllithium (hexane solution) was titrated as 1.6 M. Unless otherwise noted, materials were obtained from commercial sources.

Measurements. GPC measurements were performed using a Tosoh model CCPS equipped with a refractive index detector model RI 8020, a UV detector model UV 8020 at 254 nm, and a conductivity detector model CM 8010. A column of TSK G3000HXL was employed with THF as an eluent at a flow rate of 1.0 mL/min. 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 and ^{13}C NMR spectra were recorded with a JEOL JNM-AL300 apparatus in $CDCl_3$ or CD_3OD at 40 °C. The proton chemical shifts (ppm) were referenced from the signal of tetramethylsilane. The carbon chemical shifts (ppm) were referenced from the signal of the deuterated solvents: $CDCl_3$, 77.0; CD_3-OD, 49.0. Melting points were determined with a SEIKO DSC200 differential scanning calorimeter.

[G2]-CO_2CH_3 (11). Under a nitrogen atmosphere, an acetone (40 mL) solution of [G1]-Br[25] (**10**) (6.02 g, 15.8 mmol), methyl 3,5-dihydroxybenzoate (1.32 g, 7.9 mmol), K_2CO_3 (2.75 g, 19.7 mmol) and 18-crown-6 (0.42 g, 1.58 mmol) was heated with vigorous stirring at reflux temperature for 70 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated by a rotary evaporator. The residue was subjected to recrystallization from toluene−ethyl acetate ($^2/_1$) to give **11** (4.31 g, 71%) as a white solid. The mother liquid also gave **11** (0.65 g, 11%) by evaporation of the solvent followed by column chromatography on silica gel (toluene). **11**: mp 137 °C; ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 3 H), 4.99 (s, 4 H), 5.02 (s, 8 H), 6.57 (t, J = 2.1 Hz, 2 H), 6.67 (d, J = 2.1 Hz, 4 H), 6.76 (t, J = 2.4 Hz, 1 H), 7.10−7.46 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ 52.18, 70.20, 101.86, 106.51, 107.29, 108.57, 127.50, 127.97, 128.56, 132.15, 136.85, 138.95, 159.76, 160.27, 166.69; IR 1720 cm^{-1}. Anal. Calcd for $C_{50}H_{44}O_8$: C, 77.70; H, 5.74. Found: C, 77.88; H, 5.60.

[G2]-CO_2K (8). Under a nitrogen atmosphere, [G2]-CO_2CH_3 (**11**) (2.50 g, 3.2 mmol) was dissolved in a

refluxing mixture of 74 mL of absolute EtOH and 50 mL of THF. To this solution was added a 7.4 mL of a 10 N aqueous solution of KOH. After 2 h, the mixture was cooled to room temperature and concentrated to dryness. Water (ca. 50 mL) was added to the residue, and the insoluble part was collected by filtration The potassium salt (**8**) was obtained quantitatively (2.58 g) as a white solid. **8**: ^{1}H NMR ($CDCl_3$) δ 4.58 (s, 4 H), 4.67 (s, 8 H), 6.31 (t, J = 2.1 Hz, 2 H), 6.37 (t, J = 2.1 Hz, 1 H), 6.45 (d, J = 2.1 Hz, 4 H), 7.06−7.18 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ 69.73, 69.87, 101.54, 104.59, 106.53, 108.10, 127.50, 127.75, 128.39, 136.84, 139.46, 139.71, 159.29, 159.89, 173.35; IR 1574 cm^{-1}.

7,7,7-Triphenylheptanol (12). The procedure reported by Gibson et al.[26] was adopted with a slight modification. Under a nitrogen atmosphere, to a THF (80 mL) solution of triphenylmethane (7.82 g, 32.0 mmol) was added dropwise 24 mL of *n*-butyllithium (1.6 M in hexane, 38 mmol) at 0 °C over 50 min. After the solution was stirred at 0 °C for 45 min, 6-chlorohexyl 2-tetrahydropyranyl ether was added dropwise to the solution at 0 °C over 20 min. The reaction was allowed to proceed for 15 h, and water (20 mL) was added. The aqueous solution was extracted three times with chloroform and dried with $MgSO_4$. The yellow oil (14.7 g) obtained after the removal of the solvent by evaporation was redissolved in a mixture of chloroform and methanol (1:1 v/v 120 mL) and stirred at room temperature for 64 h after the addition of concentrated HCl (36%, 2 mL). Most of the solvent was then evaporated, and the residue was dissolved in 100 mL of methylene chloride. The solution was washed three times with water and dried with $MgSO_4$. After removal of the solvent by evaporation, the residue was subjected to column chromatography on silica gel with an eluent of hexane−ethyl acetate (grading from $^{10}/_1$ to $^4/_1$) to give **12** (8.02 g, 72%) as colorless oil. **12**: ^{1}H NMR ($CDCl_3$) δ 1.02−1.20 (m, 2 H), 1.20−1.42 (m, 4 H), 1.42−1.52 (m, 3 H), 2.50−2.60 (m, 2 H), 3.55 (t, J = 6.6 Hz, 2 H), 7.10−7.30 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 25.54, 25.64, 30.12, 32.68, 40.41, 56.59, 62.84, 125.68, 127.69, 129.18, 147.54; IR 3700−3100 (OH) cm^{-1}. Anal. Calcd for $C_{25}H_{28}O$: C, 87.16; H, 8.19. Found: C, 87.14; H, 8.07.

Methyl *p*-(7,7,7-Triphenylheptoxy)benzoate (14). Under a nitrogen atmosphere, to a mixture of **14** (3.47 g, 10.0 mmol) and carbon tetrabromide (4.21 g, 12.7 mmol) in 10 mL of THF was added triphenylphosphine (3.31 g, 12.6 mmol), and the reaction mixture was stirred at room temperature for 10 min. The reaction mixture was poured into water (30 mL) and extracted three times with ethyl acetate. The combined extracts were washed with water and dried with $MgSO_4$. After evaporating the solvent, the residue was subjected to column chromatography on silica gel with hexane−ethyl acetate ($^{10}/_1$) to give 1-bromo-7,7,7-triphenylheptane (**13**) (5.07 g) quantitatively as colorless oil. The bromide **13** was subjected to Williamson ether synthesis with methyl *p*-hydroxybenzoate without further purification, although ^{1}H NMR analysis indicated the presence of a trace of impurities. **13**: ^{1}H NMR ($CDCl_3$) δ 1.04−1.18 (m, 2 H), 1.22−1.42 (m, 4 H), 1.66−1.80 (m, 2 H), 2.50−2.60 (m, 2 H), 3.33 (t, J = 6.9 Hz, 2 H), 7.10−7.28 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 25.50, 27.99, 29.50, 32.72, 33.85, 40.33, 56.58, 125.73, 127.73, 129.17, 147.48.

Under a nitrogen atmosphere, a DMF (60 mL) solution of **13**, methyl *p*-hydroxybenzoate (1.53 g, 10.1 mmol) and K_2CO_3 (1.42 g, 10.3 mmol) was heated with vigorous stirring at 65 °C for 22 h. The reaction mixture was cooled to room temperature and poured into ice water (200 mL). Extractive workup with ethyl acetate followed by column chromatography on silica gel (hexane−ethyl acetate = $^5/_1$) afforded **14** (3.30 g, 69%) as a white solid. **14**: mp 90 °C; ^{1}H NMR ($CDCl_3$) δ 1.05−1.17 (m, 2 H), 1.34−1.44 (m, 4 H), 1.65−1.78 (m, 2 H), 2.52−2.62 (m, 2 H), 3.87 (s, 3 H), 3.93 (t, J = 6.3 Hz, 2 H), 6.86 (d, J = 8.7 Hz, 2 H), 7.10−7.28 (m, 15 H), 7.96 (d, J = 8.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.61, 25.82, 29.04, 30.06, 40.39, 51.77, 56.60, 68.05, 114.02, 122.33, 125.72, 127.72, 129.19, 131.52, 147.52, 162.87, 166.87; IR 1716 (C=O) cm^{-1}. Anal. Calcd for $C_{33}H_{34}O_3$: C, 82.81; H, 7.16. Found: C, 82.78; H, 7.26.

***p*-(7,7,7-Triphenylheptoxy)benzoic Acid (15).** To 40 mL of EtOH solution of **14** (0.70 g, 1.46 mmol) was added 1.5 mL of a 10 N aqueous KOH solution, and the reaction mixture was heated to reflux. The hydrolysis was complete (TLC) within 30 min. The reaction mixture was concentrated, and 1 N HCl (10 mL) was added. The product was extracted with ethyl acetate three times, and the combined extract was washed with water and dried with $MgSO_4$. After filtration, the solvent was removed by evaporation to yield 0.67 g (97%) of **15** as a white solid. **15**: mp 139 °C; ^{1}H NMR ($CDCl_3$) δ 1.05−1.21 (m, 2 H), 1.30−1.46 (m, 4 H), 1.67−1.80 (m, 2 H), 2.52−2.62 (m, 2 H), 3.95 (t, J = 6.3 Hz, 2 H), 6.89 (d, J = 9.0 Hz, 2 H), 7.13−7.30 (m, 15 H), 8.04 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.62, 25.83, 29.03, 30.06, 40.41, 56.62, 68.15, 114.17, 121.39, 125.74, 127.74, 129.20, 132.31, 147.53, 163.32, 171.80; IR 3400−2400 (OH), 1683 (C=O) cm^{-1}. Anal. Calcd for $C_{32}H_{32}O_3$: C, 82.73; H, 6.94. Found: C, 82.84; H, 6.96.

Sodium *p*-(7,7,7-Triphenylheptoxy)benzoate (9). To a 100 mL of EtOH solution of **15** (0.65 g, 1.41 mmol) was added 1 mL of an aqueous solution of NaOH (56 mg, 1.41 mmol), and the reaction mixture was stirred at room temperature for 19 h. The sodium salt (**9**) was obtained quantitatively (0.67 g) as a white solid after removal of the solvent under vacuum. **9**: ^{1}H NMR (CD_3OD) δ 1.03−1.15 (m, 2 H), 1.26−1.46 (m, 4 H), 1.60−1.74 (m, 2 H), 2.52−2.62 (m, 2 H), 3.92 (t, J = 6.3 Hz, 2 H), 6.81 (d, J = 9.0 Hz, 2 H), 7.10−7.30 (m, 15 H), 7.88 (d, J = 9.0 Hz, 2 H); ^{13}C NMR (CD_3OD) δ 26.83, 26.90, 30.18, 30.98, 41.45, 57.84, 68.84, 114.35, 126.78, 128.71, 130.31, 131.07, 132.06, 148.91, 162.37, 175.39; IR 1550 cm^{-1}.

Ion-Exchange Reaction of Poly(THF)s (1) and (2). *Procedure A (for **5**):* To an ice-cooled (<5 °C) aqueous solution (100 mL) containing a weighed amount of a sodium carboxylate (2 equiv with respect to pyrrolidinium salt end groups) was added dropwise a THF solution (0.6 mL) of 0.1 g of **1** with vigorous stirring. After 1 h, the precipitated ion-exchange product **3** was collected by filtration and dried in vacuo.

*Procedure B (for **6**−**9**):* A mixture of **1** and a sodium carboxylate with an equimolar amount of ionic groups was dissolved in THF and added dropwise to ice-cooled (<5 °C) water [or water−MeOH (10:1 v/v) for **8**] under vigorous stirring. After 1 h, the precipitated ion-exchange product **3** was collected by filtration and dried in vacuo.

3a: ^{1}H NMR ($CDCl_3$) δ 1.50−1.75 (m, CH_2CH$_2$O), 2.06−2.18 (m, 8 H), 3.03 (s, 6 H), 3.30−3.60 (m, CH$_2$CH_2O), 7.04−7.24 (m, 18 H), 7.45 (d, J = 6.0 Hz, 12 H); IR 1597 cm^{-1}.

3c: ^{1}H NMR ($CDCl_3$) δ 1.50−1.75 (m, CH_2CH_2O), 2.02−2.14 (m, 8 H), 2.97 (s, 6 H), 3.30−3.60 (m, CH_2CH_2O), 3.69 (s, 4 H), 7.05−7.32 (m, 30 H); IR 1577 cm^{-1}.

3d: ^{1}H NMR ($CDCl_3$) δ 1.50−1.75 (m, CH_2CH_2O), 2.04−2.18 (m, 8 H), 2.98 (s, 6 H), 3.25−3.60 (m, CH_2CH_2O), 3.58 (s, 4 H), 7.12−7.22 (m, 24 H); IR 1587 cm^{-1}.

3e: ^{1}H NMR ($CDCl_3$) δ 1.50−1.75 (m, CH_2CH_2O), 2.12−2.22 (m, 8 H), 3.16 (s, 6 H), 3.30−3.58 (m, CH_2CH_2O), 3.65−3.78 (m, 8 H), 5.02 (s, 24 H), 6.54 (t, J = 2.1 Hz, 4 H), 6.62 (t, J = 2.4 Hz, 2 H), 6.68 (d, J = 2.1 Hz, 8 H), 7.20−7.45 (m, 44 H); IR 1575 cm^{-1}.

3f: ^{1}H NMR ($CDCl_3$) δ 1.05−1.18 (m, 4 H), 1.30−1.44 (m, 8 H), 1.48−1.75 (m, CH_2CH_2O), 1.75−1.94 (m, 4 H), 2.16−2.28 (m, 8 H), 2.52−2.62 (m, 4 H), 3.25 (s, 6 H), 3.28−3.52 (m, CH_2CH_2O), 3.54−3.66 (m, 4 H), 3.66−3.88 (m, 4 H), 3.90 (t, J = 6.6 Hz, 4 H), 6.78 (d, J = 8.7 Hz, 4 H), 7.14−7.28 (m, 30 H), 8.00 (d, J = 8.7 Hz, 4 H); IR 1550 cm^{-1}.

4b: ^{1}H NMR ($CDCl_3$) δ 1.50−1.80 (m, CH_2CH_2O), 2.37 (t, J = 7.5 Hz, 4 H), 2.43 (t, J = 6.9 Hz, 4 H), 3.30−3.52 (m, CH_2CH_2O), 4.22 (t, J = 6.3 Hz, 4 H), 7.08−7.36 (m, 30 H); IR 1733 (C=O) cm^{-1}.

Synthesis of Poly(THF)s Having Bulky End Groups through Ring-Opening Reaction of Pyrrolidinium Salt Groups. A weighed amount of telechelic poly(THF) with bulky carboxylate counteranions (**3**) was dissolved in toluene under a nitrogen atmosphere. The reaction mixture was heated at 90 °C for 24 h (for **3a**, **3c**, **3d**, and **3f**) or 42 h (for **3e**) with stirring and concentrated to give the crude product quantitatively. The poly(THF) having bulky end groups (**4c**−**f**) was purified by preparative thin-layer chromatography (SiO_2, CH_2Cl_2−MeOH = $^{10}/_1$ or hexane−acetone = $^2/_1$).

4c: ^{1}H NMR ($CDCl_3$) δ 1.45−1.75 (m, CH_2CH_2O), 2.17 (s, 6 H), 2.20−2.38 (m, 8 H), 3.30−3.52 (m, CH_2CH_2O), 3.71 (s, 4 H), 3.78 (t, J = 6.3 Hz, 4 H), 7.14−7.26 (m, 30 H); IR 1737 (C=O) cm^{-1}.

4d: ^{1}H NMR ($CDCl_3$) δ 1.45−1.75 (m, CH_2CH_2O), 2.19 (s, 6 H), 2.20−2.40 (m, 8 H), 3.30−3.56 (m, CH_2CH_2O), 3.61 (s, 4 H), 3.81 (t, J = 6.3 Hz, 4 H), 7.11 (d, J = 8.7 Hz, 12 H), 7.24 (d, J = 8.7 Hz, 12 H); IR 1738 (C=O) cm^{-1}.

4e: ^{1}H NMR ($CDCl_3$) δ 1.45−1.75 (m, CH_2CH_2O), 2.22 (s, 6 H), 2.30−2.46 (m, 8 H), 3.30−3.52 (m, CH_2CH_2O), 4.31 (t, J = 6.6 Hz, 4 H), 5.00 (s, 8 H), 5.03 (s, 16 H), 6.57 (t, J = 2.1 Hz, 4 H), 6.67 (d, J = 2.1 Hz, 8 H), 6.75 (t, J = 2.1 Hz, 2 H), 7.24−7.42 (m, 44 H); IR 1717 (C=O) cm^{-1}.

4f: ^{1}H NMR ($CDCl_3$) δ 1.05−1.18 (m, 4 H), 1.30−1.44 (m, 8 H), 1.45−1.75 (m, CH_2CH_2O), 2.23 (s, 6 H), 2.32−2.44 (m, 8 H), 2.54−2.62 (m, 4 H), 3.28−3.52 (m, CH_2CH_2O), 3.94 (t, J = 6.3 Hz, 4 H), 4.29 (t, J = 6.3 Hz, 4 H), 6.85 (d, J = 9.0 Hz, 4 H), 7.10−7.28 (m, 30 H), 7.95 (d, J = 9.0 Hz, 4 H); IR 1714 (C=O) cm^{-1}.

Ring-Opening Reaction of 7 in the Presence of Crown Ethers. A mixture of a weighed amount of **7**, crown ether, and toluene was ultrasonicated for 15 min at room temperature (entries 1−3 in Table 2) or 50 °C (entries 5 and 6) and heated at 90 °C for 24 h with stirring. After being cooled to room temperature, the reaction solution of **7** and **16** (entries 1−4) was concentrated and subjected to reprecipitation from THF solution into cold water (<5 °C). Both the precipitate and the filtrate (after concentration) were dried in vacuo. The reaction mixture of **7** and **17** (entries 5 and 6) was allowed to cool to room temperature and to stand further for 24 h to recrystallize the excess of **17**. The recrystallized **17** was then separated by filtration, and the filtrate was concentrated and dried in vacuo.

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