Efficient Polymer Cyclization by Electrostatic Self-Assembly and Covalent Fixation with Telechelic Poly(tetrahydrofuran) Having Cyclic Ammonium Salt Groups[†]

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ABSTRACT: Uniform-size poly(tetrahydrofuran)s (poly(THF)s) having *N*-phenyl or *N*-methylpyrrolidinium salt end groups ($\mathbf{1_p}$ and $\mathbf{1_m}$, respectively) carrying a dicarboxylate counteranion have been prepared as ionic polymer precursors for an intramolecular cyclization reaction. Thus, 4,4′-biphenyldicarboxylate (**2a**) was first introduced quantitatively as a counteranion by repeated precipitation of the polymer precursor $\mathbf{1_p}$ into an aqueous solution containing dicarboxylate sodium salt. The efficient cyclization was confirmed with the ion-exchange product $\mathbf{I_pa}$ having the molecular weight ranging from 4 to 12 kg/mol in diluted THF. The polymer cyclization proceeded effectively also with $\mathbf{I_ma}$ having *N*-methylpyrrolidinium salt end groups. There was a pronounced effect upon changing the reaction solvent from THF to chloroform, acetone, toluene, and ethanol. A series of dicarboxylate salts, that is, terephthalate (**2b**), *o*-phthalate (**2c**), succinate (**2d**), adipate (**2e**), and *trans*-2-butene-1,4-dicarboxylate (**2f**), was then employed for the ion-exchange reaction. The ion-exchange reaction was quantitative with **2b** and **2c**, while the carboxylate content reached at most around 80% with **2d**, **2e**, and **2f** even after five precipitations. Nevertheless, the corresponding cyclic poly(THF)s **II** were obtained in high yields by the subsequent heat treatment of the precursors $\mathbf{I_pd}$−**f** and $\mathbf{I_pa}$−**c**. A partially ion-exchanged polymer precursor carrying mixed counteranions $\mathbf{I_p}$(**f**/triflate = 42/58) (42% *trans*-2-butene-1,4-dicarboxylate and 58% triflate) was then subjected to the reaction under dilution. Besides the unreacted $\mathbf{I_p}$(triflate), the cyclic polymer product $\mathbf{II_pf}$ was effectively produced through the exclusive formation of electrostatic self-assemblies by a single polymer precursor unit, in which cations and anions balance the charges.

Introduction

Cyclic polymer architectures are of increasing interest both in fundamental and applied fields of polymer science and technology since their absence of end groups should result in diverse novel polymer properties.[1−12] An efficient and practical means to construct cyclic polymer architectures, however, has been an ongoing challenge. This is in contrast to the remarkable achievements in the synthesis of well-defined branched polymer architectures having multiple end groups, such as star polymers,[13−15] polymacromonomers,[16−18] hyperbranched polymers,[19] and dendrimers.[20−22]

Straightforward polymer cyclization has so far been performed through an end-to-end linking reaction of an α,ω-bifunctional linear polymer precursor. This bimolecular process, however, requires strict stoichiometry between a polymer precursor and a small coupling reagent.[2,23−27] To avoid concurrent intermolecular chain extension, the reaction must be performed at high dilution to promote the intramolecular process. This, in turn, seriously reduces the rate of the bimolecular reaction. An alternative means to improve the polymer cyclization efficiency is a unimolecular, high dilution process using an α,ω-heterobifunctional polymer precursor.[28,29] Nevertheless, selective introduction of complementarily reactive groups at the opposite chain ends requires a multistep protection−deprotection process. Thus, its practical usefulness is limited.

We have recently developed an “electrostatic self-assembly and covalent fixation” process to efficiently construct a variety of unusual macromolecular architectures containing cyclic polymer units,[30−32] using telechelic poly(tetrahydrofuran)s (poly(THF)s) having cyclic ammonium salt groups carrying various pluricarboxylate counteranions. Upon dilution in an organic medium below a gram per liter, the ionically aggregated polymer precursors completely dissociate into the smallest assembly while cations and anions balance the charges (Scheme 1). Subsequent covalent fixation by ring opening of the cyclic ammonium salt group by a carboxylate counteranion produces a variety of unconventional polymer architectures comprising mono- and multicyclic polymer units. Herein, we report further details on this exceptionally efficient polymer cyclization using a variety of telechelic poly(THF)s having two types of pyrrolidinium salt groups and carrying different dicarboxylate counteranions (Scheme 2).

Experimental Section

Materials. Bifunctional poly(THF)s having *N*-phenyl- and *N*-methylpyrrolidinium salt end groups ($\mathbf{1_p}$ and $\mathbf{1_m}$, respectively) were prepared by the method detailed before.[30,31,33,34] Sodium benzoate (**2g**) (99.5%, Koso Chemical Co., Ltd.), sodium terephthalate (**2b**) (>99%, Tokyo Kasei Kogyo Co., Ltd.), and sodium succinate (**2d**) (>99%, Koso Chemical Co., Ltd.) were used as received. Other sodium salts, that is, 4,4′-biphenyldicarboxylate (**2a**), *o*-phthalate (**2c**), adipate (**2e**), and *trans*-2-butene-1,4-dicarboxylate (**2f**), were prepared quantitatively from the corresponding free acids (>97%, 99%, >99%, and

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[†] Dedicated to Professor Kiyokazu Imai in honor of his 75th birthday.

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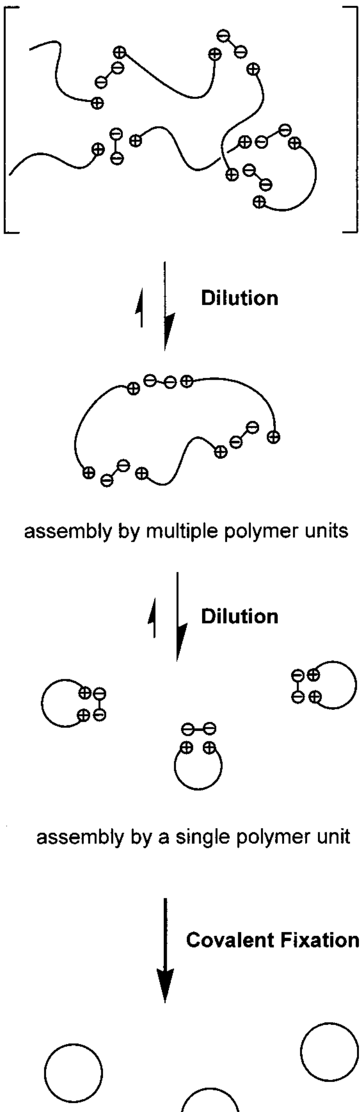
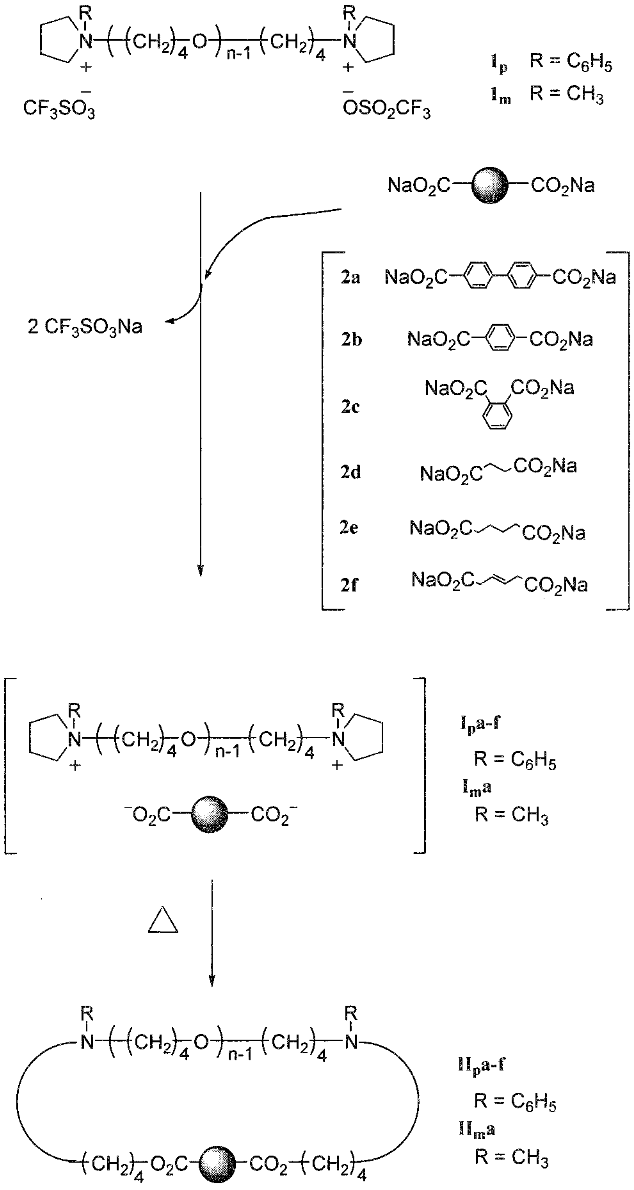
Scheme 1



Scheme 2



98%, respectively; Tokyo Kasei Kogyo Co., Ltd. (**2a**, **2e**, and **2f**) and Koso Chemical Co., Ltd. (**2c**)) with equimolar quantities of sodium hydroxide (93%, Koso Chemical Co., Ltd.) in water. THF (>99.5%, no stabilizer, Wako Pure Chemical Industries, Ltd.) was dried over sodium benzophenone ketyl and distilled just before use. Toluene (99%, Nacalai Tesque, Inc.) was distilled over calcium hydride. Chloroform (99%, Nacalai Tesque, Inc.) was dried over calcium chloride and then distilled under nitrogen atmosphere. Acetone (>99.5%, Kanto Chemical Co., Inc.) was dried over K_2CO_3 and then distilled under nitrogen atmosphere. Ethanol (>99%, Japan Alcohol Trading Co., Ltd.) was distilled over magnesium ethoxide. Unless noted otherwise, materials were obtained from commercial sources.

Ion-Exchange Reaction of 1.[33] Ion-exchange products $\mathbf{I_p}$**a**−**g** and $\mathbf{I_m}$**a**,**g** were obtained in good to excellent yields (52−99%) as in the following example. A THF solution (1.0 mL) of 0.30 g (0.071 mmol) of $\mathbf{1_p}$ was added dropwise to an ice-cooled (<5 °C) aqueous solution (120 mL) containing an excess amount of a sodium terephthalate (0.066 g, 5 equiv) under vigorous stirring. After 1 h, the precipitated ion-exchange product $\mathbf{I_p}$**b** was collected by filtration and dried in vacuo for up to 2 h. This precipitation treatment was repeated to complete the reaction ($\mathbf{I_p}$**b**, 0.23 g, 77% yield).

$\mathbf{I_p}$**a.** See ref 30.

$\mathbf{I_p}$**b.** ^{1}H NMR: see Figure 4 (top). IR: 1578 cm^{-1} (carboxylate anion).

$\mathbf{I_p}$**c.** ^{1}H NMR: δ 1.30−1.70 (m, CH_2CH$_2$O), 1.90−2.10 (m, 4 H, *endo*-NCH$_2$CH_2), 2.30−2.50 (m, 4 H, *endo*-NCH$_2$CH_2), 3.20−3.60 (m, CH$_2$CH_2O), 4.00−4.20 (m, 8 H, *exo*- and *endo*-NCH_2), 4.42−4.62 (m, 4 H, *endo*-NCH_2), 7.47 (dd, J = 6.0, 3.3 Hz, 2 H, Ar *m-H*), 7.50−7.72 (m, 10 H, NPh), 8.37 (dd, J = 6.0, 3.3 Hz, 2H, Ar *o-H*). IR: 1563 cm^{-1} (carboxylate anion).

$\mathbf{I_p}$**d.** ^{1}H NMR: δ 1.30−1.70 (m, CH_2CH$_2$O), 2.00−2.20 (m, 4 H, *endo*-NCH$_2$CH_2), 2.35−2.50 (m, 4 H, *endo*-NCH$_2$CH_2), 2.55 (s, 2.9 H, CH_2CO$_2^-$), 3.20−3.60 (m, CH$_2$CH_2O), 4.02−4.20 (m, 8 H, *exo*- and *endo*-NCH_2), 4.44−4.64 (m, 4 H, *endo*-NCH_2), 7.50−7.74 (m, 10 H, NPh). IR: 1556 cm^{-1} (carboxylate anion).

$\mathbf{I_p}$**e.** ^{1}H NMR: δ 1.30−1.70 (m, CH_2CH$_2$O), 2.00−2.15 (m, 4 H, *endo*-NCH$_2$CH_2), 2.20−2.30 (m, 3.3 H, CH_2CO$_2^-$), 2.35−2.50 (m, 4 H, *endo*-NCH$_2$CH_2), 3.20−3.60 (m, CH$_2$CH_2O), 4.02−4.20 (m, 8 H, *exo*- and *endo*-NCH_2), 4.50−4.66 (m, 4 H, *endo*-NCH_2), 7.50−7.74 (m, 10 H, NPh). IR: 1566 cm^{-1} (carboxylate anion).

$\mathbf{I_p}$**f.** ^{1}H NMR: δ 1.30−1.70 (m, CH_2CH$_2$O), 1.95−2.10 (m, 4 H, *endo*-NCH$_2$CH_2), 2.40−2.52 (m, 4 H, *endo*-NCH$_2$CH_2), 2.94−2.98 (br m, 3.4 H, CH_2CO$_2^-$), 3.20−3.60 (m, CH$_2$CH_2O), 4.02−4.20 (m, 8 H, *exo*- and *endo*-NCH_2), 4.44−4.60 (m, 4 H, *endo*-NCH_2), 5.66−5.74 (br m, 1.7 H, CH=), 7.48−7.76 (m, 10 H, NPh). IR: 1562 cm^{-1} (carboxylate anion).

$\mathbf{I_p}$**g.** See ref 33.

$\mathbf{I_m}$**a.** ^{1}H NMR: see Figure 3 (top). IR: 1533 cm^{-1} (carboxylate anion).

Table 1. Polymer Cyclization with Telechelic Poly(THF) Having Pyrrolidinium Salt Groups[a]

run	ionic polymer precursor[b] (dicarboxylate content in %)[c]	cyclic poly(THF)[b]	isolated yield (%)[d]	PDI[e]	M_p(SEC) × 10^{-3} [f]	M_p/M_p(**III**)[g]
1	$\mathbf{I_pa}$ (>95)	$\mathbf{II_pa}$	74 (93)[h]	1.09	3.7	0.79
2	$\mathbf{I_pa}$ (>95)	$\mathbf{II_pa}$	60 (88)[h]	1.22	6.5	0.87
3	$\mathbf{I_pa}$ (>95)	$\mathbf{II_pa}$	55 (84)[h]	1.20	10.3	0.87
4	$\mathbf{I_ma}$ (>95)	$\mathbf{II_ma}$	72	1.12	3.4	0.81
5	$\mathbf{I_pb}$ (>95)	$\mathbf{II_pb}$	73 (97)[h]	1.09	3.6	0.77
6	$\mathbf{I_pc}$ (>95)	$\mathbf{II_pc}$	73 (87)[h]	1.09	3.8	0.81
7	$\mathbf{I_pd}$ (75)	$\mathbf{II_pd}$	75 (94)[h,i]	1.13	3.8	0.81
8	$\mathbf{I_pe}$ (80)	$\mathbf{II_pe}$	64 (94)[h,i]	1.13	3.9	0.83
9	$\mathbf{I_pf}$ (80)	$\mathbf{II_pf}$	63[i]	1.11	3.5	0.75

[a] Ring opening was performed in THF at 66 °C for 3 h (runs 1−3 and 5−9) or in toluene at 80 °C for 20 h (run 4). [b] See Schemes 2 and 3. [c] Determined by ^{1}H NMR. [d] Isolated yields after purification by preparative TLC. [e] Determined by SEC on the basis of standard polystyrenes. [f] M_p(SEC): Apparent peak molecular weight determined by SEC relative to linear polystyrene standards by a conversion factor of 0.556 (ref 41). [g] A measure of the hydrodynamic volume ratio between cyclic poly(THF) and its linear analogue **III** (linear analogues prepared from the corresponding telechelic poly(THF) **I** carrying benzoate counteranions). M_p(**III**)(SEC): 4.7 × 10^3 (runs 1 and 5−9), 4.2 × 10^3 (run 4), 7.5 × 10^3 (run 2), 11.8 × 10^3 (run 3). [h] Yields in parentheses are estimated from reversed-phase chromatography of the crude products. [i] Values are based on the contents of the introduced dicarboxylate counteranions.

Table 2. Solvent and Temperature Effect on Cyclization of Telechelic Poly(THF) Having *N*-Phenylpyrrolidinium Salt Groups Carrying 4,4′-Biphenyldicarboxylate Counteranions[a]

run	solvent (bp/°C)	dielectric constant (ϵ)	cyclic polymer yield (%)[b]	PDI[c]
1	THF (66)	7.5	93	1.11
2	toluene (111)	2.4	80	>1.5
3	chloroform (61)	4.8	91	1.11
4	acetone (56)	21	89	1.17
5	ethanol (78)	25	0[d]	

[a] Ring opening was performed by refluxing in a solution at 0.2 [g/L] for 3 h. [b] Yield of the cyclic product of a single polymer precursor unit, estimated from the reversed-phase chromatograph peak area of the quantitatively recovered product. [c] Determined by SEC on the basis of polystyrene standards. [d] No reaction.

$\mathbf{I_mg}$. ^{1}H NMR: δ 1.55−1.75 (m, CH_2CH$_2$O), 2.20−2.30 (m, 8 H, *endo*-NCH$_2$CH_2), 3.27 (s, 6 H, OCH_3), 3.20−3.55 (m, CH$_2$CH_2O), 3.58−3.66 (m, 4 H, *exo*-NCH_2), 3.70−3.88 (m, 8 H, *endo*-NCH_2), 7.25−7.34 (m, 6 H, Ar *m,p-H*), 8.06−8.12 (m, 4 H, Ar *o-H*). IR: 1556 cm^{-1} (carboxylate anion).

Ring-Opening Reaction of Pyrrolidinium Salt End Groups in I. The covalently linked product **II** was recovered in an almost quantitative yield (as listed in Tables 1 and 2) by simply evaporating the solvent as in the following example. The ionic polymer precursor $\mathbf{I_pb}$ (0.10 g) was dissolved in 500 mL of THF (0.2 g/L) and was heated at 66 °C for 3 h. The reaction solvent was removed to yield 0.097 g (97%) of $\mathbf{II_pb}$, and the product was subjected to spectroscopic and chromatographic analyses. The recovered product (0.050 g) was further purified by preparative thin-layer chromatography (SiO$_2$, hexane/acetone = 2/1) to yield 0.037 g (73%) of pure cyclic poly(THF) $\mathbf{II_pb}$.

$\mathbf{II_pa}$. See ref 30.

$\mathbf{II_pb}$. ^{1}H NMR: see Figure 4 (bottom). IR: 1723 cm^{-1} (ester carbonyl).

$\mathbf{II_pc}$. ^{1}H NMR: δ 1.50−1.75 (m, CH_2CH$_2$O), 3.25−3.55 (m, CH$_2$CH_2O), 4.30 (t, J = 6.0 Hz, 4 H, CO$_2$CH_2), 6.58−6.70 (m, 6 H, NPh *o,p-H*), 7.14−7.20 (m, 4 H, NPh *m-H*), 7.51 (dd, J = 5.7, 3.3 Hz, 4 H, Ar *m-H*), 7.68 (dd, J = 5.7, 3.3 Hz, Ar *o-H*). IR: 1729 cm^{-1} (ester carbonyl).

$\mathbf{II_pd}$. ^{1}H NMR: δ 1.50−1.75 (m, CH_2CH$_2$O), 2.57 (s, 4 H, CH_2CO$_2$), 3.25−3.55 (m, CH$_2$CH_2O), 4.18 (t, J = 6.3 Hz, 4 H, CO$_2$CH_2), 6.58−6.70 (m, 6 H, NPh *o,p-H*), 7.14−7.20 (m, 4 H, NPh *m-H*). IR: 1737 cm^{-1} (ester carbonyl).

$\mathbf{II_pe}$. ^{1}H NMR: δ 1.50−1.75 (m, CH_2CH$_2$O), 2.20−2.40 (m, 4 H, CH_2CO$_2$), 3.25−3.55 (m, CH$_2$CH_2O), 4.08 (t, J = 6.0 Hz, 4 H, CO$_2$CH_2), 6.58−6.70 (m, 6 H, NPh *o,p-H*), 7.14−7.22 (m, 4 H, NPh *m-H*). IR: 1737 cm^{-1} (ester carbonyl).

$\mathbf{II_pf}$. ^{1}H NMR: δ 1.50−1.75 (m, CH_2CH$_2$O), 3.04−3.07 (m, 4 H, CH_2CO$_2$), 3.25−3.55 (m, CH$_2$CH_2O), 4.10 (t, J = 6.0 Hz, 4 H, CO$_2$CH_2), 5.64−5.70 (m, 2 H, CH=), 6.58−6.70 (m, 6 H, NPh *o,p-H*), 7.14−7.20 (m, 4 H, NPh *m-H*). IR: 1738 cm^{-1} (ester carbonyl).

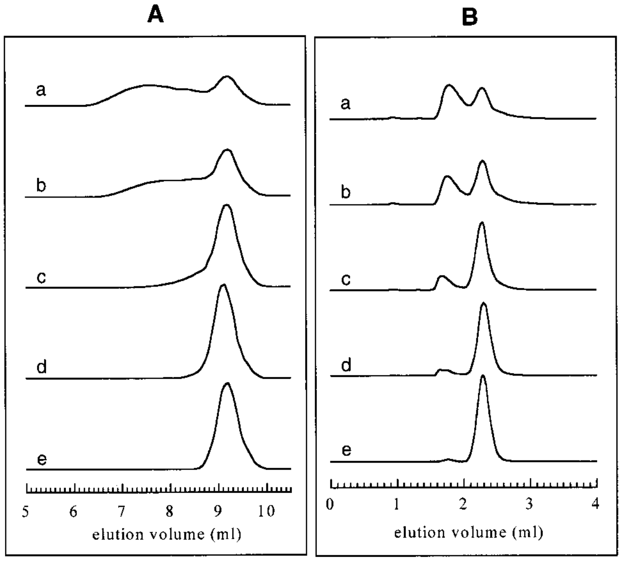


Figure 1. SEC traces (**A**, RI detector) and reversed-phase chromatography traces (**B**, UV detector) of the quantitatively recovered product of the ionically self-assembled polymer precursor $\mathbf{I_pa}$ after heating at various concentrations (a−d) and of the cyclic poly(THF) $\mathbf{II_pa}$ obtained after the purification by a preparative TLC procedure (e). Concentration of the precursor $\mathbf{I_pa}$ in THF: (a) 10.0 [g/L], (b) 5.0 [g/L], (c) 1.0 [g/L], and (d) 0.2 [g/L]. (Sample: run 1 in Table 1. SEC: column, TSK G4000HXL.)

$\mathbf{II_pg}$. See ref 33.

$\mathbf{II_ma}$. ^{1}H NMR: see Figure 3 (bottom). IR: 1720 cm^{-1} (ester carbonyl).

$\mathbf{II_mg}$. ^{1}H NMR: δ 1.50−1.75 (m, CH_2CH$_2$O), 2.21 (s, 6 H, NCH_3), 2.30−2.45 (m, 8 H, NCH_2) 3.30−3.55 (m, CH$_2$CH_2O), 4.33 (t, J = 7.5 Hz, 4 H, CO$_2$CH_2), 7.40−7.46 (m, 4 H, Ar *m-H*), 7.48−7.54 (m, 2 H, Ar *p-H*), 7.98−8.04 (m, 4 H, Ar *o-H*). IR: 1721 cm^{-1} (ester carbonyl).

Measurements. Size exclusion chromatography (SEC) measurements were performed using a Tosoh model CCPS equipped with a refractive index detector model RI 8020, a UV detector model UV 8020 at 254 nm, and a conductivity detector model CM 8010. A column of either TSK G3000HXL (300 mm × 7.8 mm i.d., 5 μm average particle size) or TSK G4000HXL (300 mm × 7.8 mm i.d., 5 μm average particle size) was employed with THF as an eluent at a flow rate of 1.0 mL/min at 40 °C. In a typical procedure, 40 μL of sample solution (sample concentration of 0.5 wt %) was injected. Reversed-phase chromatography measurements were conducted by an isocratic mode using a Tosoh model CCPS equipped with a

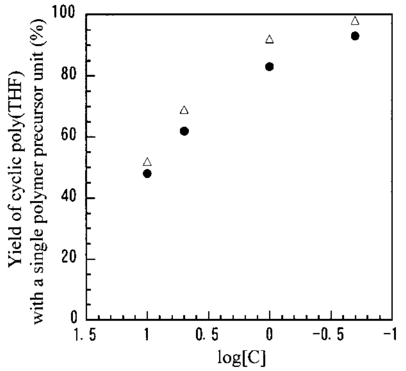


Figure 2. The experimental (●) and the theoretical (△) yields of cyclic poly(THF) **II$_p$a** with a single polymer precursor unit at different concentrations. The experimental and the theoretical yields of **II$_p$a** were estimated by reversed-phase chromatography (Figure 1B) and by the statistic equation given in the text, respectively. The concentration is given in a logarithmic scale (log[C]).

UV detector model UV 8020 at 254 nm. A C_{18} bonded silica column of TSK ODS-80TS (80 Å pore, 250 mm × 4.6 mm, 5 μm average particle size) was employed with a mixture of THF/CH_3CN/H_2O (66/25/9 in volume) at 25 °C. IR spectra were taken on a JASCO FT/IR-410 infrared spectrometer by casting the sample from a chloroform solution onto a NaCl plate. ^1H NMR spectra were recorded with a JEOL JNM-AL300 apparatus in $CDCl_3$ at 40 °C. The proton chemical shifts (ppm) were referenced from a signal of tetramethylsilane.

Results and Discussion

1. Electrostatic Self-Assembly and Covalent Fixation with Telechelic Poly(THF)s Having *N*-Phenyl- and Having *N*-Methylpyrrolidinium Salt Groups. We have recently shown that a cyclic poly(THF) is effectively produced by heating a uniform-size telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups carrying a dicarboxylate counteranion, that is, 4,4′-biphenyldicarboxylate (**I$_p$a**), under appropriate dilution.[30] This ionic polymer precursor **I$_p$a** tends to electrostatically self-assemble in solution, where the dissociation/association of ionic species depends on the concentration, while the cations and anions balance the charges (Scheme 1). SEC analysis after the heat treatment in an appropriately diluted THF solution ([C] = 0.2 g/L) showed that the cyclic poly(THF) had a narrow size distribution (PDI < 1.10) as in the polymer precursor unit and that it was produced almost quantitatively (Figure 1A, curve d). The cyclic structure of the product was unequivocally demonstrated by SEC and viscosity measurements as well as by ^1H NMR and vapor pressure osmometry (VPO) analyses.[30] The SEC and viscosity measurements agreed well with the theoretical hydrodynamic volume ratios for the cyclic product against its linear analogue **III$_p$g** (Scheme 3), which was prepared from a similar telechelic poly(THF) with benzoate counteranions (**I$_p$g**). VPO and ^1H NMR confirmed that the absolute molecular weights (corresponding to the total chain length, not the hydrodynamic volume) of the cyclic and linear poly(THF)s coincide with each other within experimental error. In addition, we have demonstrated[30] that reversed-phase chromatography is effective for separating a cyclic polymer from a linear analogue.[3,4,35–37] On the other hand, MALDI-TOF MS measurements of the present cyclic poly(THF)s

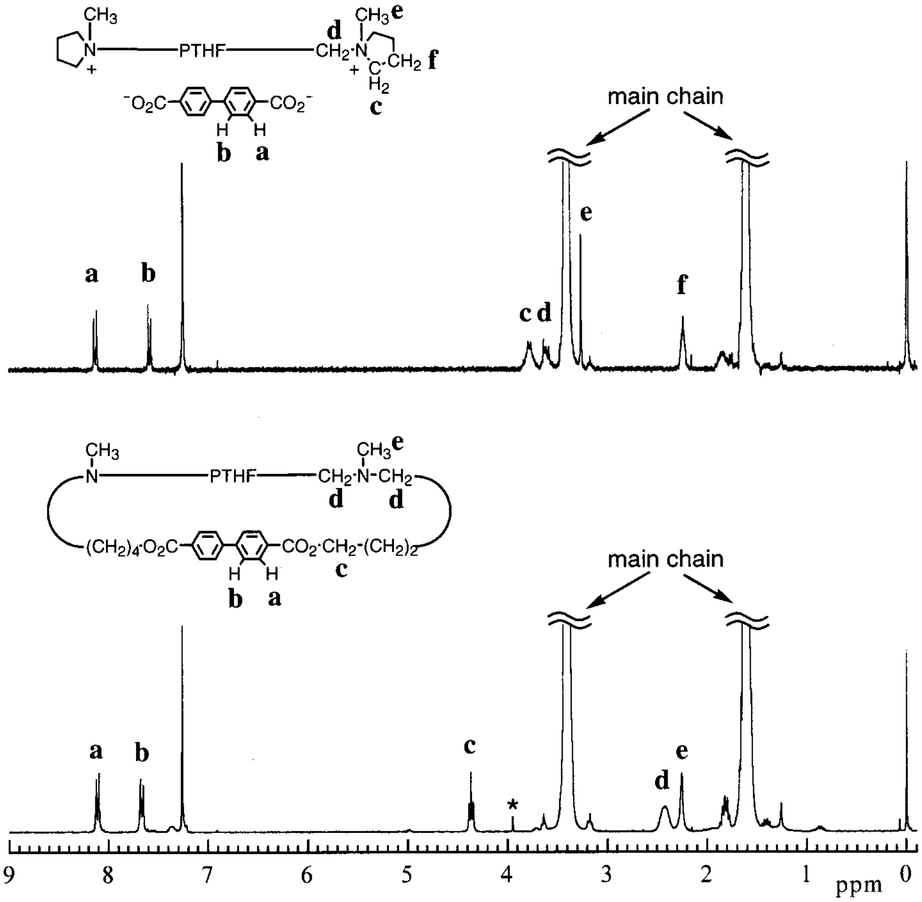


Figure 3. 300 MHz ^1H NMR spectra of an ion-exchange product of poly(THF) having *N*-methylpyrrolidinium salt end groups carrying 4,4′-biphenyldicarboxylate (**2a**) before (**I$_m$a**, top) and after (**II$_m$a**, bottom) the heat treatment. A singlet at 3.95 ppm (marked by *) is due to methyl ester protons produced by concurrent demethylation. (Sample: run 4 in Table 1, $CDCl_3$, 40 °C.)

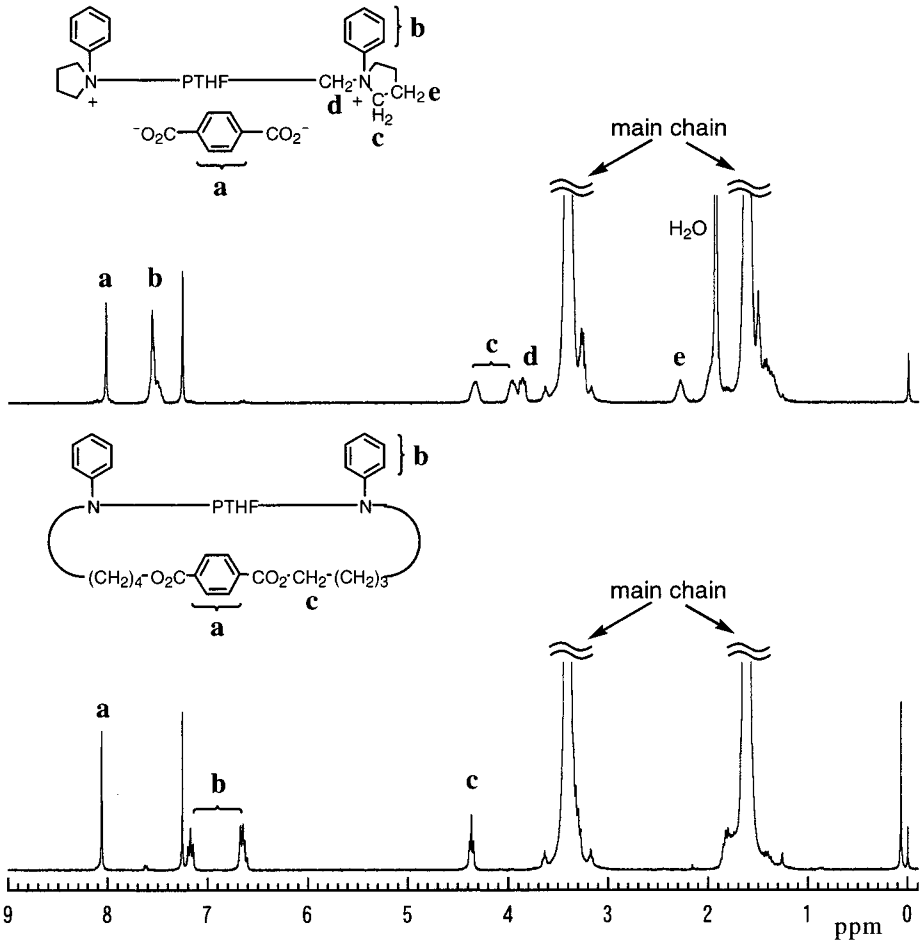
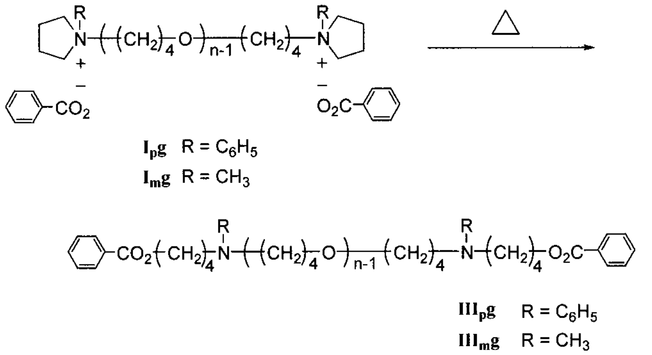


Figure 4. 300 MHz ^{1}H NMR spectra of an ion-exchange product of poly(THF) having *N*-phenylpyrrolidinium salt end groups carrying terephthalate (**2b**) before ($\mathbf{I_pb}$, top) and after ($\mathbf{II_pb}$, bottom) the heat treatment. (Sample: run 5 in Table 1, $CDCl_3$, 40 °C.)

Scheme 3



have so far been circumvented, due to the decomposition of the polymer products having laser-susceptible anilinobenzoate groups.

Moreover, the reversed-phase chromatograph (Figure 1**B**) of the crude product was bimodal with a broad peak at shorter retention time and a sharp peak at longer retention time. These two fractions correspond to a mixture of cyclic products from multiple polymer precursor units for the former and a cyclic product from a single polymer precursor unit for the latter. The content of the latter increases with further dilution (see also Figure 2, solid circle). This agrees with the SEC results in Figure 1**A**. By comparison of parts **A** and **B** of Figure 1, it is evident that more accurate yield values are obtained from reversed-phase chromatography. Thus, cyclization of $\mathbf{I_pa}$ proceeded with a yield as high as 93% at a concentration of 0.2 [g/L]; cyclic poly(THF) of more than 98% purity was obtained in 74% yield by subsequent purification by preparative thin-layer chromatography (TLC) (Table 1, run 1).

On the basis of the statistics for intramolecular cyclization and intermolecular chain extension processes by the end-reactive polymer precursor,[28,38] the ratio of the respective products formed at different concentrations can be estimated from the corresponding probability ratios, P_c and P_e, respectively, and is given by the following equation:

$$P_c/P_e = [3/2\pi\langle r_0^2\rangle]^{2/3}(\mathrm{MW}/[\mathrm{C}]\mathrm{NA})$$

where $\langle r_0^2\rangle$ (cm^2), [C] (g/mL), and NA are a mean square end-to-end distance of the polymer precursor, a polymer concentration in the cyclization reaction, and Avogadro's number, respectively. The theoretical yields of cyclic poly(THF) $\mathbf{II_pa}$ at different concentrations from the precursor $\mathbf{I_pa}$ (MW = 4700 g/mol) were thus estimated by assuming the end-to-end distance per unit mass for poly(THF), $r_0/\mathrm{MW}^{1/2}$, to be 0.09 nm(mol/g)$^{1/2}$,[39] at theta conditions. As evidently seen in Figure 2, the experimental yields are very close to the theoretical ones (open triangles), confirming the cation/anion stoichiometry in the electrostatically self-assembled polymer precursor system and the quantitative and selective chemical conversion process at the polymer precursor chain end.

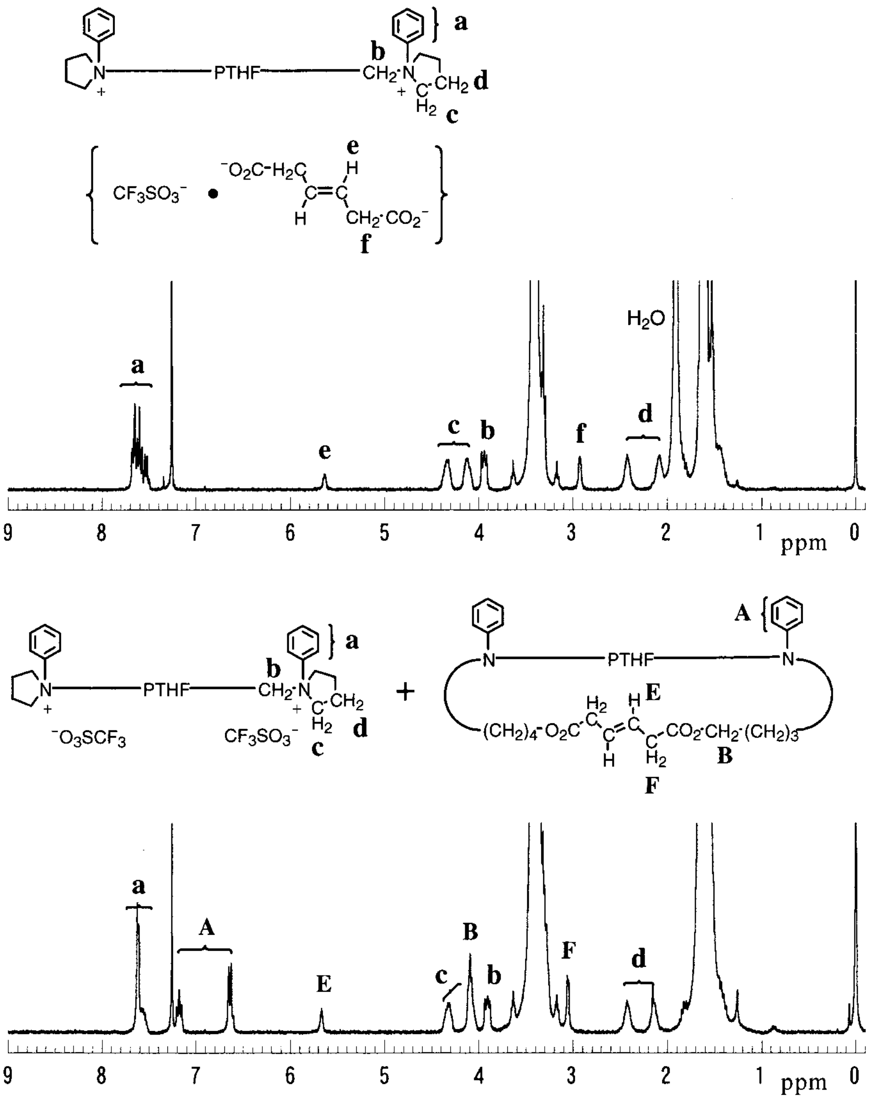


Figure 5. 300 MHz ^{1}H NMR spectra of a partially ion-exchanged poly(THF) precursor carrying mixed counteranions (58% triflate and 42% *trans*-2-butene-1,4-dicarboxylate) before (top) and after (bottom) the heat treatment. ($CDCl_3$, 40 °C.)

Another poly(THF) precursor having *N*-methylpyrrolidinium salt groups ($\mathbf{1_m}$) in place of *N*-phenylpyrrolidinium salt was also employed for the polymer cyclization reaction. Since a ring-opening reaction of the *N*-methylpyrrolidinium salt group takes place only at temperature higher than around 80 °C,[40] an ionic poly(THF) precursor $\mathbf{I_m a}$, prepared by the ion-exchange reaction of $\mathbf{1_m}$ with sodium 4,4′-biphenyldicarboxylate, was heated in toluene (Table 1, run 4). The ring-opening reaction was confirmed by ^{1}H NMR analysis of the quantitatively recovered crude product after evaporating the solvent (Figure 3, bottom). Thus, the resonances (marked **c**–**f**) due to the *N*-methylpyrrolidinium salt group of the polymer precursor (Figure 3, top) are completely replaced by a triplet at 4.37 ppm due to the ester methylene protons (marked **c**) and by a singlet at 2.26 ppm due to the *N*-methyl protons (marked **e**) on the amino-ester group. A small singlet at 3.95 ppm (marked by * in Figure 3, bottom), on the other hand, indicates that concurrent (<5%) demethylation occurs, as in the reaction with a benzoate counteranion.[40] The IR spectrum of the product also exhibited an absorption at 1720 cm^{-1} assignable to the ester carbonyl group formed by ring opening (not shown). In addition, the SEC showed a unimodal profile with a narrow size distribution (PDI = 1.15) for the quantitatively recovered product. Pure cyclic poly(THF) was isolated in a high yield (72%) by preparative TLC (Table 1, run 4).

The cyclization proceeded effectively for a series of telechelic poly(THF)s with molecular weights ranging from 4 to 12 kg/mol under appropriate dilution (0.2 [g/L]) in THF. Thus, cyclic poly(THF)s with ring sizes up to 260–800 members have been produced in good yields (Table 1, runs 1–3). Further decrease in the chain length of the polymer precursor, on the other hand, was circumvented, since recovery of the ion-exchange products after the precipitation became increasingly difficult due to their enhanced solubility in water.

2. Effect of Reaction Medium. Selective cyclization of a single polymer precursor unit $\mathbf{I_p a}$ will rely on selective formation of the smallest assembly from the ionically aggregated polymer precursor under appropriate dilution. Therefore, the polarity of the reaction solvent should affect this dissociation process. Thus, we examined the reaction in various solvents of different dielectric constant (ϵ), that is, toluene ($\epsilon = 2.4$), chloroform ($\epsilon = 4.8$), acetone ($\epsilon = 21$), and ethanol ($\epsilon = 25$) in place of THF ($\epsilon = 7.5$). The results are collected in Table 2. After heating at reflux in the respective solvents (bp = 111, 61, 56, and 78 °C, respectively) at a concentration of 0.2 [g/L] for 3 h (the reaction solution was always homogeneous throughout the reaction), the covalent

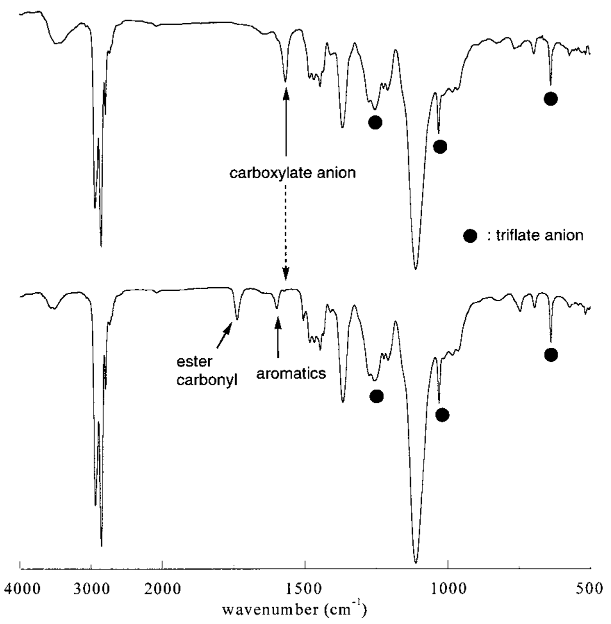
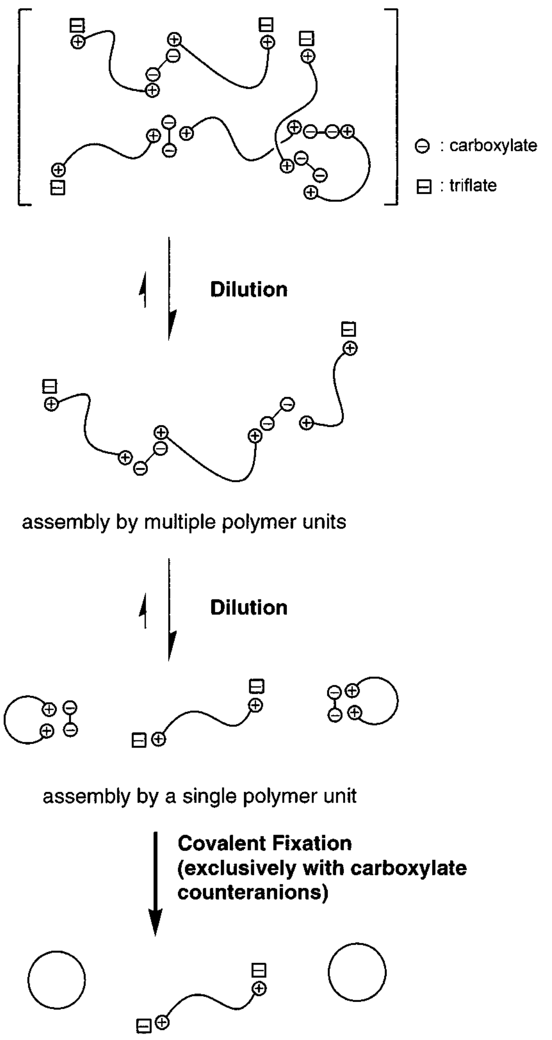


Figure 6. FT-IR spectra of a partially ion-exchanged poly(THF) precursor carrying mixed counteranions (58% triflate and 42% *trans*-2-butene-1,4-dicarboxylate) before (top) and after (bottom) the heat treatment.

Scheme 4



conversion reaction proceeded quantitatively in toluene, chloroform, and acetone. In contrast, no reaction was observed in ethanol. The solvation of carboxylate anions by ethanol through hydrogen bonds presumably suppresses the nucleophilicity of the carboxylate anion. SEC showed that the products obtained in chloroform and in acetone have narrow size distributions, as in THF. On the other hand, the SEC peak of the product obtained in toluene was broader (PDI > 1.5). The cyclic polymer yield of a single polymer precursor unit estimated by reversed-phase chromatography was also slightly lower in toluene (80% against 89−93% in chloroform and acetone). This implies that the ionically aggregated polymer precursor is not completely dissociated in the less-polar toluene solution. The polarity of the solvent is thus crucial for the efficient self-assembly and covalent conversion of the ionic polymer precursor, while telechelic ionomers tend to dissociate at higher temperature in an organic medium.

3. Effect of Dicarboxylate Counteranion and Unique Covalent Conversion Process with a Partially Ion-Exchanged Polymer Precursor. A series of aromatic and aliphatic dicarboxylate counteranions, that is, terephthalate, *o*-phthalate, succinate, adipate, and *trans*-2-butene-1,4-dicarboxylate (**2b**−**f**), were introduced by ion exchange of a telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups ($\mathbf{1_p}$). The results are collected in Table 1 (runs 5−9). The prepolymer $\mathbf{1_p}$ was precipitated in water (<5 °C) containing an excess amount of the corresponding sodium dicarboxylate salt, and the extent of the ion-exchange reaction was monitored by IR and ^{1}H NMR, as reported before.[30] Two precipitations were sufficient to cause almost complete ion exchange (>95%) with 4,4′-biphenyldicarboxylate (**2a**) and terephthalate (**2b**), while four or five precipitations were needed for *o*-substituted phthalate (**2c**). And for aliphatic dicarboxylates **2d**−**f**, the ion-exchange yield reached 70−80% at most after five precipitations. Aromatic dicarboxylates are therefore preferred to aliphatic ones in the present ion-exchange process, and 1,2-dicarboxylates are less efficient, presumably due to their steric hindrance.

The recovered ionic polymer precursors $\mathbf{I_p a}$−**f** were then heated in THF (0.2 [g/L]). The pyrrolidinium salt groups quantitatively ring-opened for each carboxylate counteranion, as typically shown for a polymer precursor $\mathbf{I_p b}$ (Figure 4). Even in the case of $\mathbf{I_p d}$−**f**, cyclic poly(THF)s having narrow size distributions were obtained in good yields, according to the content of the introduced dicarboxylate counteranions, as listed in Table 1 (runs 7−9).

Further insight into this unique covalent conversion process was obtained by the reaction of a partially ion-exchanged polymer precursor carrying mixed counteranions of a dicarboxylate anion and a triflate anion (Scheme 4). Thus, polymer precursor $\mathbf{I_p e}$ carrying 42% of *trans*-2-butene-1,4-dicarboxylate counteranion and 58% of a triflate anion (from a quaternary ammonium cation) was heated in dilute THF ([C] = 0.2 g/L). The triflate anion is not nucleophilic enough to ring-open the pyrrolidinium salt group at any temperature. The ^{1}H NMR and IR spectroscopic analysis of the quantitatively recovered product showed that while triflate counteranions remained intact, the carboxylate counteranions caused the quantitative ring-opening reaction. The ^{1}H NMR spectra in Figure 5 showed that a signal (marked by **f**) at 2.94 ppm due to the methylene protons of a *trans*-2-butene-1,4-dicarboxylate counteranion was re-

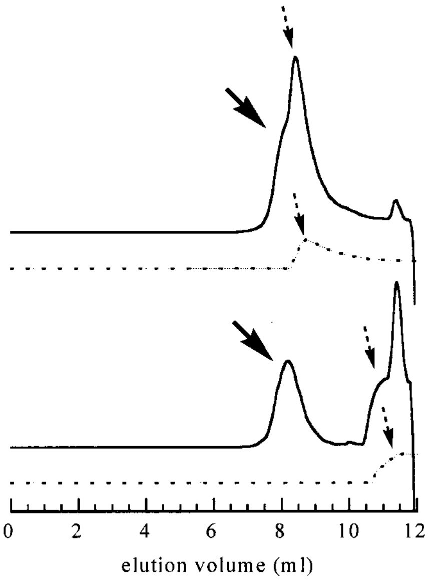


Figure 7. SEC traces of the quantitatively recovered product after the heat treatment of a partially ion-exchanged poly(THF) precursor carrying mixed counteranions (58% triflate and 42% *trans*-2-butene-1,4-dicarboxylate), measured at different polymer sample concentrations: 0.5 wt % (top) and 0.1 wt % (bottom). (Solid line: refractive index trace. Broken line: conductivity trace. Column: TSK G3000HXL.)

placed by a signal (marked by **F**) at 3.07 ppm due to the carboxylate ester formed after the heat treatment. At the same time, the signal due to unreacted pyrrolidinium salt groups carrying triflate counteranions is visible at 7.50−7.70 ppm.[33] By comparison of the signal intensities of *N*-phenyl protons at 6.60−6.70 and 7.15−7.20 ppm (marked by **A**) and ether methylene protons in the poly(THF) segment at 3.26−3.50 ppm, the extent of the cyclization reaction coincides with the initial benzoate anion content. The IR spectrum also showed that the absorption due to the carboxylate anion disappeared after the heat treatment, while those due to triflate anions remained intact (Figure 6).

Moreover, SEC (Figure 7) separated the covalently linked product from the ionically linked precursor accompanying the conductivity response, since the concentration-dependent elution delay took place for the latter due to the interaction of their ionic groups with the SEC gel bead surfaces.[34] The SEC trace of the covalently linked fraction is symmetric with a narrow size distribution (PDI = 1.11) and with a retention time identical to that of the purified cyclic polymer $\mathbf{II}_{\mathbf{p}}\mathbf{e}$ isolated by silica gel chromatography (Table 1, run 9). These results demonstrate that the covalently converted product consists of cyclic poly(THF) formed from a single polymer precursor unit, excluding any higher molecular weight products formed from multiple polymer precursor units. This corresponds to the exclusive formation of an electrostatically self-assembled single polymer precursor unit, in which cations and anions balance the charges (Scheme 4). Consequently, polymer cyclization is remarkably efficient regardless of the type of the dianionic counterion in the present electrostatic self-assembly and covalent fixation process.

Conclusion

A remarkably efficient polymer cyclization process has been demonstrated through the electrostatic self-assembly and covalent fixation strategy with bifunctional poly(THF)s having pyrrolidinium salt end groups carrying a dicarboxylate as counteranion. With dilution, a unique form of the ionically assembled polymer precursor consisting of a single polymer precursor unit has been produced. The subsequent covalent conversion through the quantitative ring opening of pyrrolidinium salt end groups upon heating produced selectively the corresponding cyclic polymers in high yields. The present process is simple and convenient and requires only a moderate dilution down to 0.2 g/L. Cyclization will also be of a practical potential since the solvent can conveniently be recycled from all nonvolatile polymer reagents used in the reaction. Thus, gram-scale samples of topologically unique polymers will be readily obtainable for the subsequent evaluation of various properties. Moreover, this novel process allows one to design diverse unprecedented polymer architectures comprising cyclic topologies through appropriate combinations of precursors and multifunctional carboxylates including those having other functional groups.[31]

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