Macromolecules **1999,** *32,* 4819−4825

Tailored Synthesis of Branched and Network Polymer Structures by Electrostatic Self-Assembly and Covalent Fixation with Telechelic Poly(THF) Having *N*-Phenylpyrrolidinium Salt Groups

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Received February 2, 1999; Revised Manuscript Received May 10, 1999

ABSTRACT: Uniform size poly(THF)s having *N*-phenylpyrrolidinium salt as a single and both end groups (**1** and **2**) were synthesized as a reactive precursor to produce star polymers, polymacromonomers, and model networks through the "electrostatic self-assembly and covalent fixation" technique. The *N-phenyl*pyrrolidinium salt group was found to undergo a ring-opening reaction exclusively by a series of carboxylate counteranions at an appropriately elevated temperature, in contrast to the case of the *N*-methylpyrrolidinium salt group, which caused a concurrent demethylation by a nucleophilic attack of carboxylate anions on the *N*-methyl group. In particular, even a weak nucleophile such as *p*-nitrobenzoate counteranion was able to cause a quantitative ring-opening reaction at 80 °C, in contrast to the unreactive *N-methyl*pyrrolidinium salt group at the same conditions. The improved selectivity as well as reactivity in the ring-opening reaction of *N*-phenylpyrrolidinium salt group allowed one to utilize **1** and **2** to produce effectively covalently linked star polymers, polymacromonomers, and model networks, first by the isolation of the ionically linked polymer assemblies formed through the ion-exchange reaction of either **1** or **2** with polycarboxylate salts and the subsequent heat treatment of them.

Introduction

A variety of noncovalent forces have recently been exploited to construct artificial supramolecular assemblies of unusual chemical structures to realize unconventional and biomimetic functions.[1] Noncovalent forces such as hydrogen bonds[2] and metal coordination bonds[3] have been frequently applied for the production of supramolecular assemblies from, in most examples, low-molecular weight building blocks.

A Coulombic interaction based on a long-range attractive or repulsive electrostatic force may also be utilized to construct supramolecular assemblies. Hydrophobic macromolecules containing organic salt moieties may offer a unique opportunity to provide attractive interaction between ion pairs to cause an efficient molecular association in organic medium or in bulk. This principle has been industrially exploited in ionomer materials.[4]

We have proposed a novel polymer reaction process, in which such a self-assembly principle is applied to construct ionically preorganized macromolecular architectures that otherwise were difficult or impossible to make and subsequently converting them into covalently linked permanent polymer structures.[5] In particular, we have utilized electrostatic interaction operating between moderately strained cyclic onium salt groups introduced as the end groups of hydrophobic macromolecules and polycarboxylate counteranions. Thus, a series of cyclic onium salt end groups, including four- and five-membered cyclic and six-membered bicyclic ammonium salt groups as well as a five-membered cyclic sulfonium salt group, have been introduced as end groups on uniform-size polymers (telechelics) such as poly(THF),[6−8] polystyrene,[9] and poly(dimethylsiloxane).[10] It has been revealed that the five-membered cyclic ammonium (pyrrolidinium) salt group, such as an *N*-methylpyrrolidinium salt group, is of a particular interest, since it is stable to be isolated with carboxylates as counteranions at ambient condition but undergoes a ring-opening reaction by the nucleophilic attack of a carboxylate counteranion at an appropriately elevated temperature to convert an ionic group into a covalent ester group. The efficient synthesis of star and model network poly(dimethylsiloxane)s has been reported with use of mono- and bifunctional telechelics, respectively, through the isolation of the ionically linked preorganized polymer assembly and subsequent covalent conversion process.[9]

It has been observed, however, in the course of above studies that a S_N2 process between the *N-methyl*pyrrolidinium salt group and carboxylate anions often accompanied, besides the ring-opening reaction, a demethylation reaction through the nucleophilic attack at the *N*-methyl carbon. On the other hand, a Hofmann-type elimination was negligible under the usual ring-opening reaction condition. Consequently, the electrostatic self-assembly and covalent fixation process with use of telechelics having *N-methyl*pyrrolidinium salt groups has often limited its synthetic scope within carefully selected combination of polymer precursors and carboxylates.[11]

Thus in the present study, we have synthesized a new alternative polymer precursor, in which *N-methyl* group on a pyrrolidinium salt group was replaced by a *N-phenyl* group. Since the nucleophilic substitution reaction on the phenyl group is strongly suppressed, the ring-opening reaction on aliphatic endo methylene groups will be favored to occur. Furthermore, the ring-opening reaction will be promoted by introducing an aniline derivative group, which is a better leaving group than an alkylamino group in the S_N2 reaction. We then demonstrate the improved synthetic process of star

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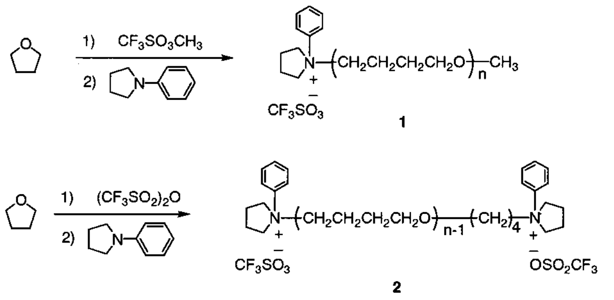
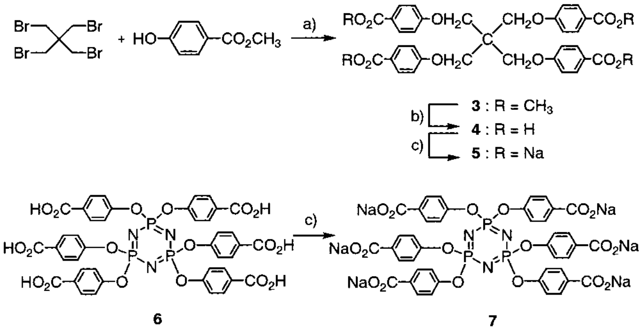
10.1021/ma990139y CCC: $18.00

Scheme 1

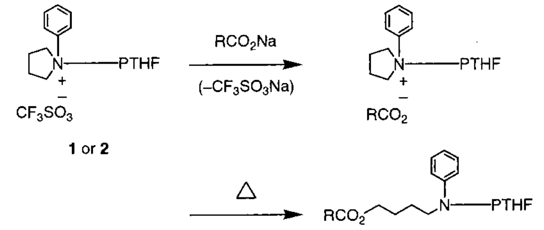


Scheme 2



Reagents: a) K_2CO_3 / DMF; b) 1) KOH / EtOH, THF 2) H^+; c) NaOH (1eq.) / aq. EtOH

Scheme 3



polymers, polymacromonomers, and model networks of poly(THF) through the electrostatic self-assembly and subsequent covalent fixation strategy with telechelic poly(THF)s having *N-phenyl*pyrrolidinium salt groups (Schemes 1–3).

Experimental Section

Reagents. Sodium benzoate (Koso Chemical Co., Ltd.) was used as received. Sodium salts of *p*-anisic acid, *p*-nitrobenzoic acid, and 1,3,5-benzenetricarboxylic acid (trimesic acid) were prepared quantitatively from the commercially available corresponding free acid with an equimolar quantity of sodium hydroxide in water. Poly(sodium acrylate), MW = 2100 with 10% residual carboxylic acid group, from Scientific Polymer Products Inc. was used without further purification. THF was dried over sodium benzophenone ketyl and distilled just before use. Dimethylformamide (DMF) and pyrrolidine were distilled from CaH_2. Ethanol (EtOH) was distilled from magnesium ethoxide. Unless otherwise noted, materials were obtained from commercial sources.

Preparation of *N*-Phenylpyrrolidine The procedure described in the literature[12] was adopted with a slight modification. A mixture of sodium amide (23.4 g, 0.6 mol) and pyrrolidine (90 mL) was refluxed for 15 min. Bromobenzene (47.1 g, 0.3 mol) was then added dropwise over 2 h. The resulting mixture was refluxed for further 4 h, cooled in an ice bath, and treated with 75 mL of water. The mixture was extracted three times with CH_2Cl_2, and the organic layer was washed with saturated $NaHCO_3$ aqueous solution and dried with K_2CO_3. After removal of the solvent, the residue was distilled under reduced pressure to give 34.5 g (78%) of *N*-phenylpyrrolidine, bp 72–74 °C/0.7 Torr (lit.[13] bp 70 °C/0.58 Torr). Spectrum data were identical in the literature.[13]

Preparation of Poly(THF) Having *N*-Phenylpyrrolidinium Salt End Groups (1 and 2). Mono- and bifunctional poly(THF)s having *N*-phenylpyrrolidinium salt end groups (**1** and **2**, respectively) were synthesized according to the reported procedure,[14] where living poly(THF)s with mono- and bifunctionality were prepared by the cationic living ring-opening polymerization technique with methyl trifluoromethanesulfonate and trifluoromethanesulfonic anhydride as initiator, respectively. The subsequent termination reaction by *N*-phenylpyrrolidine (4 equiv) produced the uniform-size poly(THF)s having *N*-phenylpyrrolidinium salt end groups (**1** and **2**). Telechelics **1** and **2** were precipitated in cold (−15 °C) petroleum ether, filtered, and dried in vacuo.

Preparation of Tetracarboxylic Acid, Sodium Salt (5). (a) Tetraester (3). Under a nitrogen atmosphere, a DMF (100 mL) solution of pentaerythrityl tetrabromide (5.11 g, 13.4 mmol), methyl *p*-hydroxybenzoate (8.00 g, 52.6 mmol), and K_2CO_3 (21.9 g, 157 mmol) was heated under vigorous stirring at 90 °C for 92 h. The reaction mixture was cooled to room temperature, and most of the solvent was removed under reduced pressure. H_2O (100 mL) was added to the residue, and extractive workup with CH_2Cl_2 afforded **3** (8.56 g, 97%). **3**: mp 200 °C. ^1H NMR ($CDCl_3$): δ 3.87 (s, 12 H), 4.41 (s, 8 H), 6.93 (d, J = 9.0 Hz, 8 H), 7.96 (d, J = 9.0 Hz, 8 H). ^{13}C NMR ($CDCl_3$): δ 44.8, 51.8, 66.5, 114.2, 123.4, 131.6, 162.1, 166.6. IR: 1708 cm^{-1}. Anal. Calcd for $C_{37}H_{36}O_{12}$: C, 66.06; H, 5.39. Found: C, 65.66; H, 5.30.

(b) Tetracarboxylic Acid (4). Under a nitrogen atmosphere, **3** (3.00 g, 4.46 mmol) was dissolved in a refluxing mixture of 80 mL of absolute EtOH and 60 mL of THF. To this solution was added 48 mL of 10 N aqueous KOH solution. After 2 h, the mixture was cooled to room temperature and concentrated to dryness. The residue was dissolved in 40% aqueous EtOH (40 mL) and acidified with glacial acetic acid to give the partially protonated product which precipitated from solution. This partially neutralized precipitate was collected by suction filtration and dissolved in THF (30 mL), and trimethylsilyl chloride (1.73 g) was added to the solution. This mixture was stirred at room temperature for 30 min and precipitated into water (200 mL). The precipitate of fully protonated product was collected by suction filtration and dried to give tetracarboxylic acid **4** (2.44 g, 90%) as a white solid. **4**: mp >300 °C. ^1H NMR (DMSO-d_6): δ 4.39 (s, 8 H), 7.05 (d, J = 9.0 Hz, 8 H), 7.85 (d, J = 9.0 Hz, 8 H),11.5–13.5 (brs, 4 H).^{13}C NMR (DMSO-d_6): δ 44.2, 66.3, 114.3, 123.4, 131.1, 161.8, 166.7. IR: 3600–2200, 1696 cm^{-1}.

(c) Tetracarboxylic Acid, Sodium Salt (5). To a 100 mL aqueous solution containing 0.63 g of NaOH (16 mmol) was added 2.4 g of **4** (3.9 mmol), and the reaction mixture was stirred at room temperature for 18 h. The sodium salt **5** was obtained quantitatively (2.7 g) after filtration and removal of the solvent in vacuo. **5:** ^1H NMR (D_2O) δ 4.51 (s, 8 H), 7.05 (d, J = 8.7 Hz, 8 H), 7.82 (d, J = 8.7 Hz, 8 H). IR (KBr) 1546 cm^{-1}.

Preparation of Hexacarboxylic Acid, Sodium Salt (7). To a 200 mL aqueous solution containing 0.55 g of NaOH (12.5 mmol) was added 2.22 g of **6**[15] (2.06 mmol), and the reaction mixture was stirred at room temperature for 5 h. The sodium salt **7** was obtained quantitatively (2.46 g) after filtration and removal of the solvent in vacuo. **7**: ^1H NMR (D_2O) δ 6.94 (d, J = 6.6 Hz, 12 H), 7.84 (d, J = 6.6 Hz, 12 H). IR (KBr) 1574 cm^{-1}.

Electrostatic Self-Assembly and Covalent Fixation of Telechelic Poly(THF) Having *N*-Phenylpyrrolidinium Salt Groups. To ice-cooled (<5 °C) aqueous solution (200 mL) containing an excess amount of a sodium carboxylate (ranged from 20 to 100 equiv) was added dropwise THF solution (1.0 mL) of 0.2 g of **1** or **2** under vigorous stirring. After 1 h, the precipitated ion-exchange product (electrostatically self-assembled poly(THF)) was collected by filtration and dried in vacuo for up to 2 h. This precipitation treatment was repeated to complete the reaction. The amount of water contained in the product (up to 50%) was determined after the complete

Table 1. Coupling Reaction between Telechelic Poly(THF) Having *N*-Phenylpyrrolidinium Salt Groups (1 and 2) and Various Carboxylates

run	telechelic poly(THF) type	telechelic poly(THF) $M_n \times 10^{-3}$ (GPC)[a]	carboxylate (functionality)	precipitation (no. of times)	recovered yield (%)	product yield (%)[b]	$M_n \times 10^{-3}$ (GPC)[a]	swelling degree (%)[c]
1	1	4.9	benzoate, Na (1)	3	56	100	4.9	*f*
2	1	4.9	*p*-methoxybenzoate, Na (1)	3	ND[d]	100	5.1	*f*
3	1	6.2	*p*-nitrobenzoate, Na (1)	4	90	100	6.0	*f*
4	1	6.2	trimesate, Na (3)	2	66	93	15.1	*f*
5	1	2.4	poly(sodium acrylate) (22)	2	49	92	14.5	*f*
6	1	4.9	poly(sodium acrylate) (22)	3	64	95	28.6	*f*
7	2	4.5	trimesate, Na (3)	2	100	98	*e*	447
8	2	4.5	**5** (4)	1	100	98	*e*	460
9	2	4.5	**7** (6)	1	96	97	*e*	378
10	2	6.2	trimesate, Na (3)	2	100	98	*e*	470
11	2	6.2	**5** (4)	1	100	99	*e*	454
12	2	7.6	trimesate, Na (3)	2	91	97	*e*	554
13	2	7.6	**5** (4)	1	97	95	*e*	546
14	2	7.6	**7** (6)	1	100	97	*e*	483

[a] Determined by GPC with the calibration using polystyrene standards by a conversion factor of 0.556.[16] [b] Runs 1−6, by GPC; runs 7−14, gel content, after the heat treatment. [c] In THF, 25 °C. [d] ND = not determined. [e] Gelation. [f] No gelation.

drying of a small part of the sample. The electrostatically self-assembled products were then subjected to a heat treatment at 80 °C for 5 h. An insoluble, but swollen, gel product was obtained from **2** and subjected to an extractive treatment with THF to estimate a gel content.

Coupling Product of 1 with Sodium Benzoate after the Heat Treatment (Sample; Run 1 in Table 1). ^{1}H NMR ($CDCl_3$): δ 1.45−1.80 (m, CH_2CH$_2$O), 3.32 (s, 3 H), 3.20−3.55 (m, CH$_2$CH_2O), 4.35 (t, J = 6.3 Hz, 2 H), 6.60−6.70 (m, 3 H), 7.12−7.22 (m, 2 H), 7.23 (dd, J = 7.5, 7.5 Hz, 2 H), 7.53 (d, J = 7.5 Hz, 1 H), 8.02 (d, J = 7.5 Hz, 2 H). IR: 1721 cm^{-1}.

Coupling Product of 1 with Sodium *p*-Methoxybenzoate after the Heat Treatment (Sample; Run 2 in Table 1). ^{1}H NMR ($CDCl_3$): δ 1.45−1.80 (m, CH_2CH$_2$O), 3.32 (s, 3 H), 3.20−3.55 (m, CH$_2$CH_2O), 3.85 (s, 3 H), 4.32 (t, J = 6.3 Hz, 2 H), 6.60−6.70 (m, 3 H), 6.91 (d, J = 8.7 Hz, 2 H), 7.12−7.22 (m, 2 H), 7.97 (d, J = 8.7 Hz, 2 H). IR: 1715 cm^{-1}.

Coupling Product of 1 with Sodium Trimesate after the Heat Treatment (Sample; Run 4 in Table 1). ^{1}H NMR ($CDCl_3$): δ 1.45−1.80 (m, CH_2CH$_2$O), 3.32 (s, 9 H), 3.20−3.55 (m, CH$_2$CH_2O), 4.39 (t, J = 6.3 Hz, 6 H), 6.60−6.70 (m, 9 H), 7.12−7.22 (m, 6 H), 8.81 (s, 3 H). IR: 1730 cm^{-1}.

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 or TSK G4000HXL 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 unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM-AL300 apparatus in $CDCl_3$, DMSO-d_6, or D_2O 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; DMSO-d_6, 39.5. Melting points were determined with a SEIKO DSC200 differential scanning calorimeter. The degree of swelling (by weight) for a series of network products was determined by comparing the weight of the dry network with that of the swollen network samples after immersion in THF at ambient temperature. The swelling values obtained by three experiments were averaged.

Results and Discussion

1. Synthesis of Telechelic Poly(THF) Having *N*-Phenylpyrrolidinium Salt Groups.

N-Phenylpyrrolidine was prepared in good yield (78%) by a single-step reaction involving bromobenzene, sodium amide, and pyrrolidine according to the literature.[12] An *N*-phenylpyrrolidinium salt end group was then introduced quantitatively at a single or both chain ends of poly(THF)s through the termination reaction of a mono- and bifunctional living poly(THF) with *N*-phenylpyrrolidine, respectively. The ^{1}H NMR spectrum (Figure 1, top) confirms the presence of the *N*-phenylpyrrolidinium salt end group from typical AB pattern signals due to the *endo* cyclic ammonium methylene protons at 4.04−4.14 and 4.26−4.36 ppm and signals at 3.86−3.96 ppm due to the *exo* cyclic ammonium methylene protons as well as signals at 7.50−7.66 ppm due to the aromatic protons. A singlet signal at 3.32 ppm due to the methoxy group originating from the initiator is also visible in the case of the monofunctional poly(THF). Mono- and bifunctional telechelic poly(THF)s (**1** and **2**, respectively) were readily isolated and were stable at ambient condi-

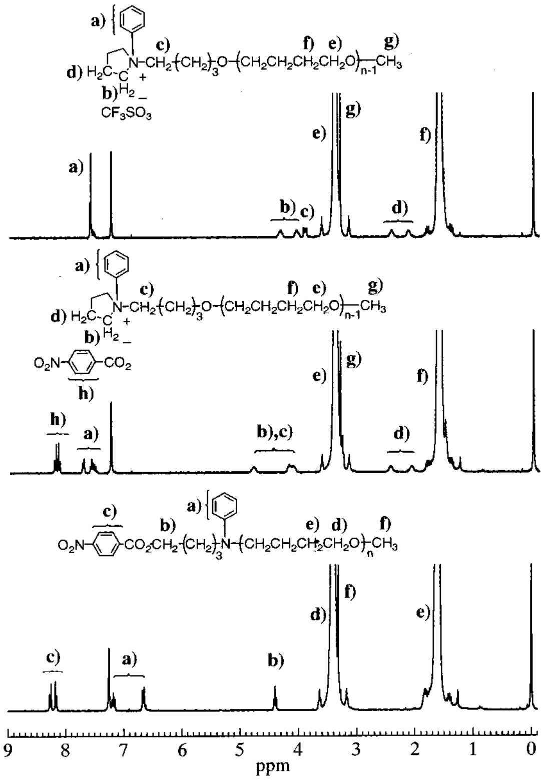


Figure 1. The 300 MHz ^{1}H NMR spectra of poly(THF) having an *N*-phenylpyrrolidinium salt end group (**1**; top) and the coupling product with sodium *p*-nitrobenzoate before (middle) and after (bottom) the heat treatment (sample: run 3 in Table 1, $CDCl_3$, 40 °C).

tions to be subjected to the full spectroscopic and chromatographic characterization. They could also be stored until use without any precautions.

2. Ring-Opening Reaction of *N*-Phenylpyrrolidinium Salt Groups. The counteranion exchange reaction of the *N*-phenylpyrrolidinium salt end group was carried out from an initial trifluoromethanesulfonate (triflate) counteranion into three different benzoate anions. They are *p*-methoxybenzoate ($pK_a = 4.47$), unsubstituted benzoate ($pK_a = 4.20$), and *p*-nitrobenzoate ($pK_a = 3.42$), of different nucleophilic reactivities. The ion-exchange reaction was completed by repeating the precipitation of THF solution of **1** or **2** into an ice-cooled aqueous solution containing an excess amount of a prescribed sodium carboxylate.

The ion-exchange product isolated by filtration was subsequently subjected to a heat treatment, to compare the ring-opening reactivity of the *N-phenyl*pyrrolidinium salt group with that of the *N-methyl* counterpart. It has been shown before that the *N*-methylpyrrolidinium salt end group failed to undergo the ring-opening reaction with *p*-nitrobenzoate counteranion even at 100 °C for 24 h, while unsubstituted benzoate and *p*-methoxybenzoate caused the ring-opening reaction, but accompanying the demethylation reaction up to 21% depending on the heat conditions.[11]

^{1}H NMR spectra of the ion-exchange product between **1** and sodium *p*-nitrobenzoate before and after the heat treatment are compared in Figure 1. The quantitative ion-exchange reaction is evidenced by the two sets of doublet signals at 8.16 and 8.22 ppm due to the *p*-nitrobenzoate anion, as well as by the change of the signal pattern for the *N*-phenyl protons on pyrrolidinium salt group at 7.40−7.80 ppm.

The subsequent heat treatment at 80 °C for 2 h caused a complete ring-opening reaction of *N*-phenylpyrrolidinium salt by the nucleophilic attack of a carboxylate counteranion at the *endo* position of the five-membered pyrrolidinium ring. As shown in Figure 1, the signals due to the *N*-phenyl protons on the pyrrolidinium salt group are replaced after the heat treatment by a triplet signal at 4.40 ppm due to the ester methylene protons and by signals at 7.16−7.22 and 6.60−6.70 ppm due to the *N*-phenyl protons on the amino-ester group. There are only assignable signals visible in the spectrum, demonstrating high chemoselectivity in the ring-opening reaction of the *N*-phenylpyrrolidinium salt group. In addition, unsubstituted benzoate and *p*-methoxybenzoate counteranions also caused a quantitative and selective ring-opening reaction of an *N*-phenylpyrrolidinium salt group (Table 1, runs 1 and 2).

The enhanced ring-opening reactivity of the *N*-phenylpyrrolidinium salt group was furthermore noticed by the partial (up to 40%) ring-opening reaction even by the complete dehydration of the ion-exchange product in vacuo. On the other hand, the hydrated (up to until ca. 3 wt % residual water) product showed no sign of the ring-opening reaction at ambient temperature. Hence, the ion-exchange products were stored in a refrigerator until use after drying treatment for a short period (1 or 2 h) in vacuo at ambient temperature in order to prevent uncontrolled ring-opening reaction.

3. Tailored Synthesis of Branched and Network Polymers with Poly(THF) Having *N*-Phenylpyrrolidinium Salt End Groups. 3.1. Synthesis of Star Polymers and Polymacromonomers. The ion-exchange reaction of monofunctional telechelics **1** with a tricarboxylate (trimesate) and with poly(sodium acrylate) was performed to produce a polymer assembly combined through an electrostatic interaction. The subsequent covalent conversion of such a noncovalent polymer assembly was then attempted by a simple heat treatment.

The ion-exchange reaction of **1** with sodium trimesate was performed by the repeated precipitation of **1** into an ice-cooled aqueous solution containing an excess amount of a sodium trimesate. The subsequent heat treatment of ionically linked polymer assembly at 80 °C for 2 h caused the selective ring-opening reaction to give a covalently linked star polymer of three-arms in high yield. The quantitative ion-exchange and ring-opening reaction was confirmed by ^{1}H NMR and IR spectroscopic analysis (not shown). GPC analysis showed the narrow size distribution of the star polymer (PDI = 1.22) as in the precursor polymer **1** (PDI = 1.12) The molecular weight (M_n = 15 100) of the resulting star polymer estimated by GPC was notably higher than that of the precursor **1** (M_n = 6200). Since the hydrodynamic volume of star polymers is smaller than that of linear polymers of identical molecular weight, it is reasonable to observe the apparent peak molecular weight of the star polymer by GPC is lower than that calculated by the number of branch arms.

We have reported the ion-coupling synthesis of a polymacromonomer with use of monofunctional poly(THF) having a five-membered cyclic sulfonium (tetrahydrothiophenium) salt end group and of poly(sodium acrylate).[7] Since the tetrahydrothiophenium salt group is reactive enough to undergo the spontaneous ring-opening reaction by a carboxylate counteranion at ambient conditions, an ionically linked polymer assembly could not be isolated as an intermediate. Instead, a covalently linked polymacromonomer was directly produced after the ion-exchange reaction and the subsequent isolation of the product. Thus, the isolation of the electrostatically assembled precursor will provide a unique opportunity for the further synthetic application of polymacromonomer synthesis. In addition, the previous attempts to prepare the relevant polymacromonomers with use of telechelic poly(THF) and poly(dimethylsiloxane) having an *N-methyl*pyrrolidinium salt end group have been circumvented due to the extensive demethylation caused by carboxylate anions in the poly(acrylate) component.

Therefore, in the present study, a monofunctional poly(THF) having an *N-phenyl*pyrrolidinium salt end group (**1**) was utilized in the macromolecular ion-exchange reaction with poly(sodium acrylate) (MW = 2100) through the repeated precipitation of **1** into an ice-cooled aqueous solution containing an excess amount of poly(sodium acrylate). As shown in the IR spectrum (Figure 2, middle), the ion-exchange reaction generates an absorption at 1550 cm^{-1} due to carboxylate anions, by eliminating those at 1030 and 639 cm^{-1} due to triflate anions. No sign of the ring-opening reaction was detected for the isolated ion-exchange product, i.e., electrostatically assembled polymacromonomer precursor, from the absence of the absorption due to ester carbonyl groups. The absorption at 1720 cm^{-1} appears only after the heat treatment by replacing that at 1550 cm^{-1}, while the rest of the spectrum remained intact. The covalent fixation process between **1** and poly(sodium acrylate) can also be observed by ^{1}H NMR spectroscopic analysis,

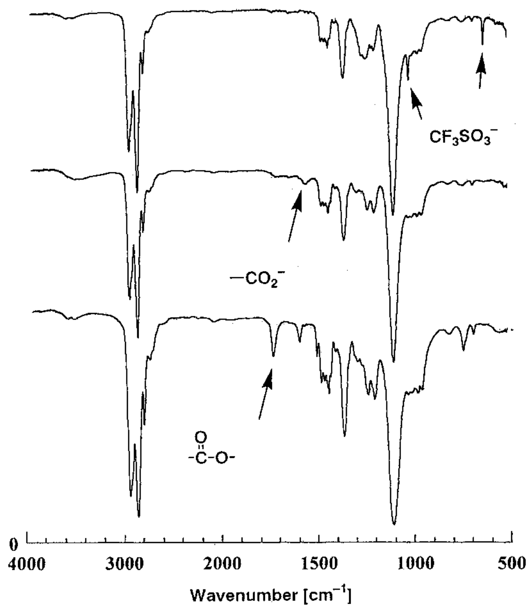


Figure 2. FT-IR spectra of poly(THF) having an *N*-phenylpyrrolidinium salt end group (**1**; top) and the coupling product with poly(sodium acrylate) before (middle) and after (bottom) the heat treatment (sample: run 6 in Table 1).

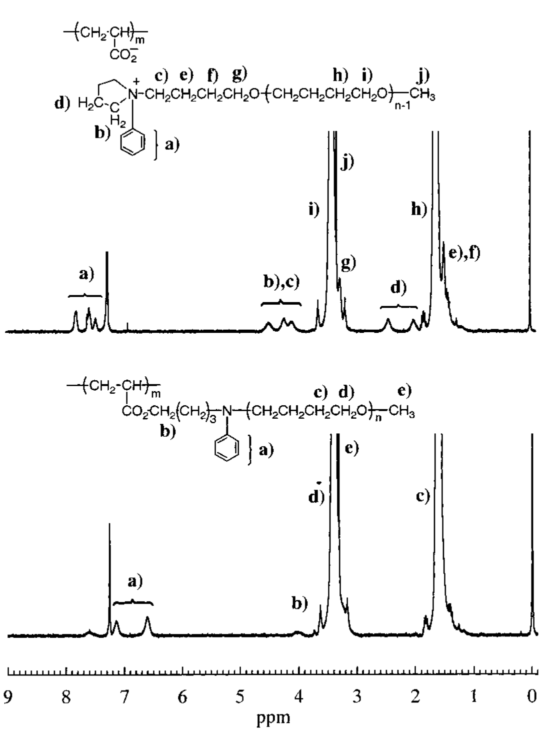


Figure 3. The 300 MHz ^{1}H NMR spectra of the coupling products of **1** with poly(sodium acrylate) before (top) and after (bottom) the heat treatment (sample: run 6 in Table 1, CDCl$_3$, 40 °C).

as shown in Figure 3. Signals at 6.54−6.68 and 7.10−7.20 ppm due to the *N*-phenyl protons on the aminoester group as well as a broad signal at 3.80−4.15 ppm due to the ester methylene protons become clearly visible after the heat treatment, by replacing the signals due to the *N*-phenyl protons on the pyrrolidinium salt group observed before the heat treatment.

The GPC results are shown in Figure 4. The produced covalently linked poly(THF) polymacromonomer possesses significantly higher molecular weight than that of the precursor **1**, and the conductivity response observed in **1** is completely eliminated. The apparent size distribution for the macromonomer was found to be relatively narrow (PDI = 1.28), which coincided with the case of polymacromonomers from poly(THF) having a tetrahydrothiophenium salt end group. These results obviously indicate that the covalently linked polymacromonomer has been effectively produced with **1** via the isolation of electrostatically assembled polymacromonomer precursor.

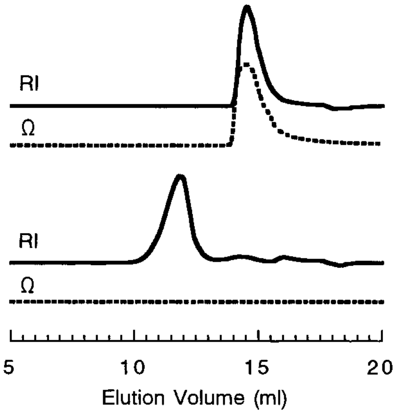


Figure 4. GPC traces of **1** (top) and the coupling product with poly(sodium acrylate) after the heat treatment (bottom) (sample: run 5 in Table 1; column: TSK G4000HXL; eluent: THF, 1 mL/min; RI: refractive index; Ω: conductivity).

3.2. Synthesis of Model Networks. The “model network” synthesis by poly(dimethylsiloxane) having *N-methyl*pyrrolidinium salt end groups via electrostatic self-assembly and covalent fixation process has been recently described.[10] It should be noted, however, that the previous attempts to prepare the relevant poly(THF) model networks with use of telechelic poly(THF) having *N-methyl*pyrrolidinium salt groups has failed to produce gel products (network) in high yield. This is apparently due to the concurrent demethylation in the reaction of telechelic poly(THF) having *N-methyl*pyrrolidinium groups. Therefore, poly(THF) having *N-phenyl*pyrrolidinium salt end groups (**2**) was utilized in the present study to undergo the ion-exchange and subsequent covalent fixation reaction with polycarboxylates. The ion-exchange reaction of **2** with a series of tri-, tetra-, and hexacarboxylates listed in Table 1 was performed by a simple precipitation procedure as described in the previous sections. The pseudonetwork products were thus formed, in which poly(THF) segments are combined through the Coulombic interaction between *N*-phenylpyrrolidinium cations and carboxylate anions. IR spectroscopic analysis confirmed the quantitative ion-exchange reaction from the absorption at 1550 cm^{-1} due to the carboxylate anions which appeared after the reaction, by replacing those at 1030 and 639 cm^{-1} due to triflate anions (Figure 5, top and middle). All pseudonetwork products were found to be soluble in CHCl$_3$, THF, and other common organic solvents, allowing one to perform the full characterization by means of a solution ^{1}H NMR spectroscopy. Figure 6 shows ^{1}H NMR spectra of the polymer assembly formed between **2** and tri-, tetra-, and hexacarboxylates. As for example, a singlet signal due to trimesate is visible at 8.68 ppm, and its intensity is close to one-fifth of that of the *N*-phenyl protons on the pyrrolidinium salt group, indicating quantitative ion-exchange reaction to occur. The complete ion-exchange reaction was confirmed also in the case of tetra- and hexacarboxylate with **2**.

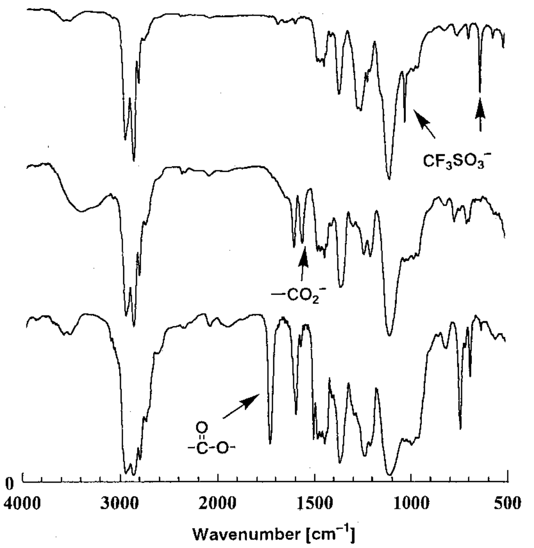


Figure 5. FT-IR spectra of poly(THF) having *N*-phenylpyrrolidinium salt end groups (**2**; top) and the coupling product with sodium trimesate before (middle) and after (bottom) the heat treatment (sample: run 7 in Table 1).

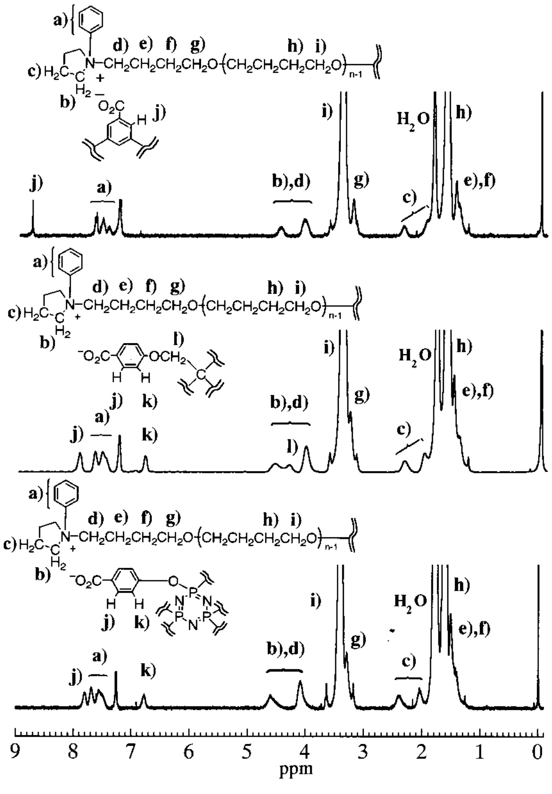


Figure 6. The 300 MHz ^{1}H NMR spectra of the coupling products of **2** with sodium trimesate (top), tetracarboxylate **5** (middle), and hexacarboxylate **7** (bottom) before the heat treatment (samples: runs 7–9 in Table 1, $CDCl_3$, 40 °C).

A series of ionically linked pseudonetworks were then subjected to the heat treatment in bulk at 80 °C, to convert the ionic interaction into the covalent linkage. All products became no more soluble but swollen in any solvents. The gel content was nearly quantitative in all cases (Table 1). The selective ring-opening reaction was confirmed to occur by the IR spectroscopic analysis of the products. The absorption at 1730 cm^{-1} due to the ester carbonyl groups appeared after the heat treatment, by replacing that at 1550 cm^{-1} due to the carboxylate anions (Figure 5, bottom), while the rest of the spectrum remained intact. Thus, the obtained network products are considered as “model networks”, in which both the number of the segment at the junction points and the length of the segments between the junction points are precisely defined. The former number corresponds to the functionality of the carboxylate used, and the latter length corresponds to the molecular weight of **2**.

To get further insight into the “model networks” prepared in the present study, the swelling degrees of a series of network products of different structural parameters were measured and listed in the last column of Table 1. It is obvious that the higher the molecular weight of the prepolymer **2**, the higher the swelling degree. Besides, the network product with hexacarboxylate showed significantly lower swelling degree compared with those with tri- and tetracarboxylates. On the other hand, the swelling degrees of the network products obtained either with tricarboxylate (trimesate) or tetracarboxylate **5** are scarcely different. This is presumably due to the significant difference in the chemical structure of junction points produced either from trimesate or **5** used in the present study (Scheme 2). The latter is apparently larger in its size compared to the former. And this will account for the disagreement in the swelling behavior with the previous poly(dimethylsiloxane) network obtained either with tricarboxylate (trimesate) or tetracarboxylate (i.e., pyrromelitate), where the network product with trimesate showed distinctly higher swelling degree compared with those with pyrromelitate.

In conclusion, the present study demonstrated that the electrostatic self-assembly and covalent fixation strategy by making use of the telechelic poly(THF)s having *N*-phenylpyrrolidinium salt groups can provide an efficient means for the synthesis of branched poly(THF)s as well as “model network” poly(THF)s. The highly selective ring-opening reaction of pyrrolidinium salt end groups of telechelic poly(THF) has been achieved by the introduction of an *N-phenyl* substituent in place of the *N-methyl* substituent.

Acknowledgment. Authors are grateful to Professor M. Kakimoto, Tokyo Institute of Technology, for our access to the NMR apparatus. Financial support from General Sekiyu Research & Development Encouragement & Assistance Foundation is gratefully acknowleged. This work was supported partly by grants from the Ministry of Education, Science and Culture, Japan (10875189, 10305066, 11695040).

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MA990139Y