Macromolecular Ion-Coupling Reactions with Uniform-Size Poly(THF) Having Cyclic Onium Salt End Groups

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ABSTRACT: A series of mono- and bifunctional telechelic poly(THF)s having various cyclic onium salt groups, i.e., tetrahydrothiophenium (**1a** and **2a**), 1-methylpyrrolidinium (**1b** and **2b**), and quinuclidinium (**1c** and **2c**), were prepared and subjected to an ion-coupling reaction with poly(styrene-*co*-sodium acrylate) (**3**) having different carboxylate contents. The coupling reaction was found to take place efficiently by the simple precipitation of a THF solution of the mixture of **1** (or **2**) and **3** into cooled water to produce graft (from **1** and **3**) and network (from **2** and **3**) copolymers, respectively, through the ion-exchange reaction between the prepolymers and the subsequent ring-opening reaction by the nucleophilic attack of the carboxylate anion toward the cyclic onium salt group either at an ambient condition (**1a** and **2a**) or at an elevated temperature (**1b**, **2b**, **1c**, and **2c**).

Introduction

Uniform-size polymers with a suitably reactive end group are commonly produced through the modification of an end group of a living polymer and are considered as important macromolecular building blocks for the synthesis of precisely designed block and graft copolymers with control of their properties which are pronouncedly influenced by their phase separation morphology due to the incompatibility of the polymer segments.[1-3]

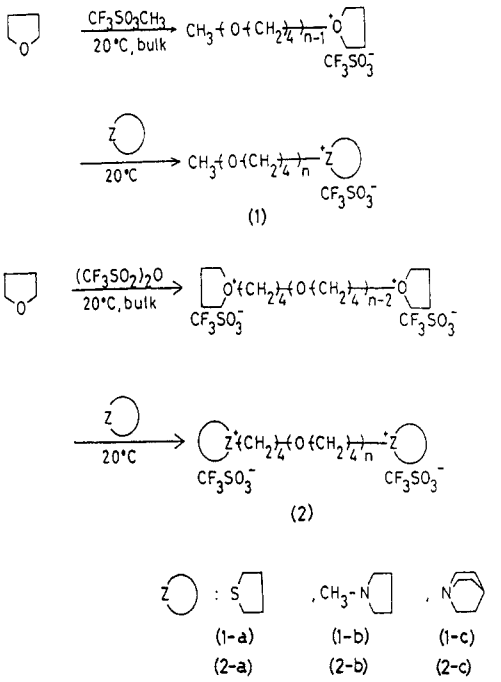
However, the incompatible nature of different polymer chains frequently causes a significant decrease of the apparent reactivity of functional groups located on the different polymers due to the repulsive interaction and the eventual phase separation of the immiscible polymer components. In addition, polymer–polymer reactions are sometimes too sluggish for practical applications due to the low initial concentration of the functional groups.

Although highly reactive living polymers have been utilized to address these problems, the reaction at the living end group is frequently beyond control, particularly in polymer–polymer reactions, and the handling of living polymers usually requires cumbersome experimental apparatus, which limits practical applications.

We have recently reported a synthesis of uniform-size poly(tetrahydrofuran) [poly(THF)] having uniquely reactive end groups, namely such moderately strained cyclic onium salt groups as 4-membered (azetidinium),[4] 5-membered cyclic (pyrrolidinium),[5] and 6-membered bicyclic (quinuclidinium)[6] ammonium salts as well as 5-membered cyclic sulfonium (tetrahydrothiophenium)[7] salt groups. These cyclic onium salt groups are readily introduced either at a single chain end or at both chain ends through the reaction of the corresponding cyclic amines or a sulfide with the oxonium salt end group of a living poly(THF), which is produced with a triflic acid ester or a triflic anhydride as initiator (see Scheme I).

The following unique features are noted for these poly(THF)s with a series of cyclic onium salt end groups;[1]

Scheme I



1. They are sufficiently stable during common isolation and characterization procedures, and no specific precautions are required for handling and storage.

2. When the molecular weight exceeds a few thousand, they become readily soluble in organic solvents but insoluble in water, since the lipophilic nature of the polymer chain prevails in the solubility property despite the presence of ionic end groups.

3. On the other hand, the aggregation of the ionic end groups takes place in organic solvents to increase the local concentration of the ionic end group despite the low overall concentration.

4. The cyclic onium salt end group initially accompanies a counteranion with a weak nucleophilic reactivity, such as triflate anion, but which can be replaced by another by an anion-exchange reaction. The anion-exchange reaction indeed takes place simply by the precipitation of a THF

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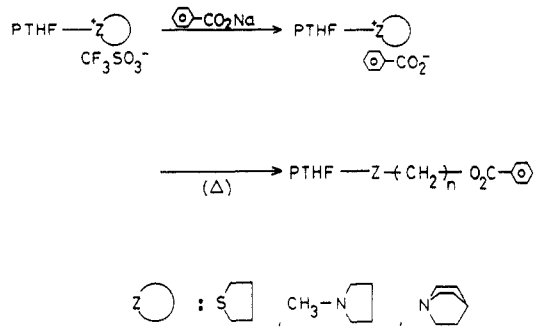
Scheme II



solution of the telechelic poly(THF) into an aqueous solution containing an excess amount of another anion as a salt form.[5]

5. In particular, a carboxylate anion was found to be a sufficiently strong nucleophile to cause the selective ring-opening reaction of a series of cyclic onium salt groups. Thus, the 4-membered cyclic ammonium and the 5-membered cyclic sulfonium salt undergo a quantitative ring-opening reaction at an ambient condition to produce the corresponding amino ester and thioester groups, respectively.[5,6] The 5-membered cyclic and 6-membered bicyclic ammonium salts are stable with carboxylate as a counteranion at an ambient condition, while the former can cause a ring-opening reaction at 100 °C and the latter at 130 °C, respectively.[5,7] Thus, one can control the ring-opening reaction of these cyclic onium salt end groups by an appropriate choice of the ring structure of a cyclic onium salt, the type of counteranion, and the reaction temperature (see Scheme II).

By making use of these unique characteristics of telechelic polymers with cyclic onium salt groups, we have so far reported (1) the modification reaction of the end group by the simple precipitation of telechelic poly(THF)s into an aqueous solution containing a carboxylate compound with another functional group, such as sodium methacrylate, to produce a poly(THF) macromonomer,[6] (2) the synthesis of such model polymers as star polymers and model networks by the simple precipitation of mono- and bifunctional telechelic poly(THF) into an aqueous solution containing an excess amount of a plurifunctional carboxylate salt,[8] and (3) the grafting reaction onto water-soluble polymers containing carboxylate salt groups, such as sodium (carboxymethyl)cellulose, by the precipitation of monofunctional telechelic poly(THF) into an aqueous solution containing a polymeric carboxylate.[7]

As an extension of the preceding studies, the present paper reports on the macromolecular ion-coupling reaction of telechelic poly(THF)s having a series of cyclic onium salt groups with a hydrophobic polymer containing a carboxylate salt group, namely, poly(styrene-*co*-sodium acrylate) of less than 5 mol % carboxylate content. The strong ionic interaction between the end group of the telechelic poly(THF) and carboxylate groups along the polystyrene chain is expected to overcome the repulsive interaction between these two incompatible polymer segments to cause an efficient coupling reaction by the enhancement of the apparent reactivity of functional groups located on the separate polymer segments.

Experimental Section

(1) Materials. (1-1) Poly(THF) Having Cyclic Onium Salt End Groups (1 and 2). A series of mono- and bifunctional poly(THF)s having cyclic onium salt end groups (1 and 2) were synthesized according to the reported procedure,[5] where living poly(THF)s with mono- and bifunctionality were prepared by the cationic ring-opening polymerization technique with methyl trifluoromethanesulfonate (methyl triflate) and trifluoromethanesulfonic anhydride (triflic anhydride) as initiator, respectively. The subsequent termination reaction by tetrahydrothiophene, 1-methylpyrrolidine, and quinuclidine produced the corresponding uniform-size poly(THF)s having cyclic onium salt groups, respectively (Scheme I). Series of 1 and 2 used in the present study are listed in Table I.

Table I
Telechelic Poly(THF)s Having Various Cyclic Onium Salt Groups

sample	functionality[a]	end group[b]	M_n (DP)[c]
1a	M	T	4400 (71)
1b	M	P	4400 (71)
1c	M	Q	5400 (87)
2a	B	T	6600 (106)
2b	B	P	3900 (63)
2c	B	Q	6100 (98)

[a] M, monofunctional; B, bifunctional poly(THF). (See also Scheme I.) [b] T, tetrahydrothiophenium; P, 1-methylpyrrolidinium; Q, quinuclidinium end group. (See also Scheme I.) [c] By GPC with the calibration using polystyrene standard samples by a conversion factor of 0.556.[9]

Table II
Poly(styrene-*co*-sodium acrylate)s Having Various Carboxylate Contents

sample	acrylate content,[a] mol %	M_n (DP)[b]	N_a[c]
3a	1.2	72000 (690)	8.3
3b	3.7	74000 (710)	26
3c	5.3	76000 (730)	39

[a] By titration. [b] By GPC using poly(styrene-*co*-acrylic acid)s with the calibration by polystyrene standard samples. [c] Average number of acrylate groups per a polymer chain.

(1-2) Poly(styrene-*co*-sodium acrylate) (3). A mixture of 10 mL of styrene and a predetermined amount of acrylic acid was placed in an ampule containing 0.06 g of azobis(isobutyronitrile). The solution was flushed with nitrogen for several minutes, and the sealed ampule was placed in a water bath thermostated at 60 °C for 6 h. The reaction mixture was then poured into 1 L of methanol, purified further by reprecipitation from a benzene/methanol system, and finally freeze-dried from benzene solution. The acrylate content in the copolymer was determined by means of a titration technique, where 20 mL of the THF solution containing a weighed amount of the copolymer (ca. 0.1 g) was titrated by 0.01 N NaOH solution with phenolphthalein as an indicator.

Then 2.0 g of poly(styrene-*co*-acrylic acid) was dissolved in 20 mL of benzene and poured dropwise into 1 L of methanol solution containing 0.1 mol of sodium phenoxide, which was prepared by the reaction of sodium metal with phenol in ethanol solution. The precipitate was recovered and washed with methanol and dried under reduced pressure. The complete conversion of the acrylic acid group in the copolymer to the sodium salt group was confirmed by IR inspection of the product, where the absorption at 1700 cm^{-1} disappeared and instead an absorption at 1600 cm^{-1} appeared due to the conversion of the free carboxylic acid group to the carboxylate salt group. A series of 3 produced in the present study are listed in Table II.

(2) Procedures. (2-1) Ion-Exchange Reaction of Poly(THF) Having Cyclic Onium Salt Groups (1 and 2). Sodium benzoate (0.3 g) was dissolved in 200 mL of deionized water cooled below 5 °C. Thereupon a 3-mL THF solution containing 0.3 g of 1 (or 2) was added dropwise in 10 min under vigorous stirring to form the precipitate. The suspended solution was then stirred for another 1 h. The product was recovered by filtration and purified by repeated precipitation from a THF/water(<5 °C) system.

The heating treatment of the product was carried out in a vacuum desiccator thermostated at 100 °C for the product from **1b** and **2b** and at 130 °C for the product from **1c** and **2c**.

(2-2) Ion-Coupling Reaction of Poly(THF) Having Cyclic Onium Salt Groups (1 and 2) with Poly(styrene-*co*-sodium acrylate) (3). (2-2-1) Synthesis of Graft Copolymers. A mixture of **1a** (or **1b** or **1c**) and **3** with an equimolar amount of

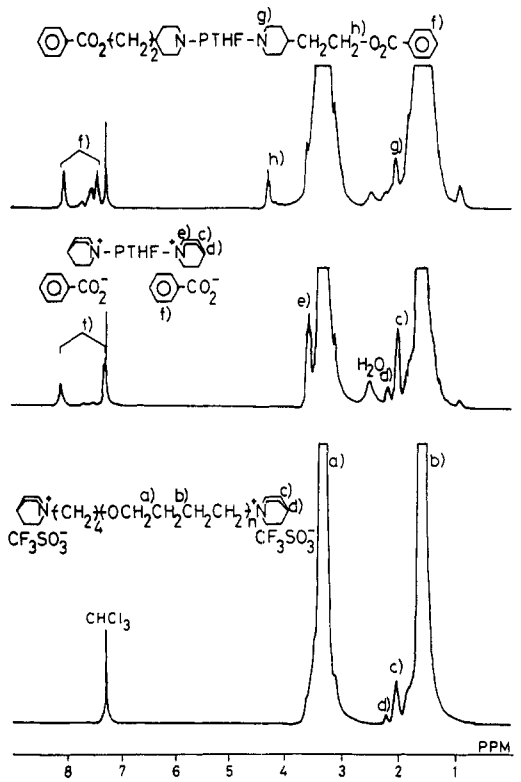


Figure 1. 270-MHz ^{1}H NMR spectra of poly(THF) having quinuclidinium salt end groups (bottom) and the ion-exchange product with benzoate before (middle) and after (top) the heating treatment at 130 °C (sample **2c** in Table I, $CDCl_3$, 40 °C).

ionic groups was dissolved in THF (ca. 5 wt %) and added dropwise during 10 min into 100 volumes of deionized water cooled below 5 °C under vigorous stirring. The precipitated product was recovered by filtration and was subjected to either heating treatment or repeated precipitation by the identical procedure up to five times. The heating treatment was carried out with a vacuum desiccator as described in the previous section.

(2-2-2) Synthesis of Network Copolymers. The procedure was identical to those described for the synthesis of graft copolymers, but using **2a** (or **2b** or **2c**) in place of **1**. In the case of the reaction with **2b** and **2c**, the precipitation treatment was repeated by using a part of the sample employed in the preceding precipitation treatment (see Table IV). The gel product thus obtained was then extracted with THF for 10 h using a Soxhlet apparatus.

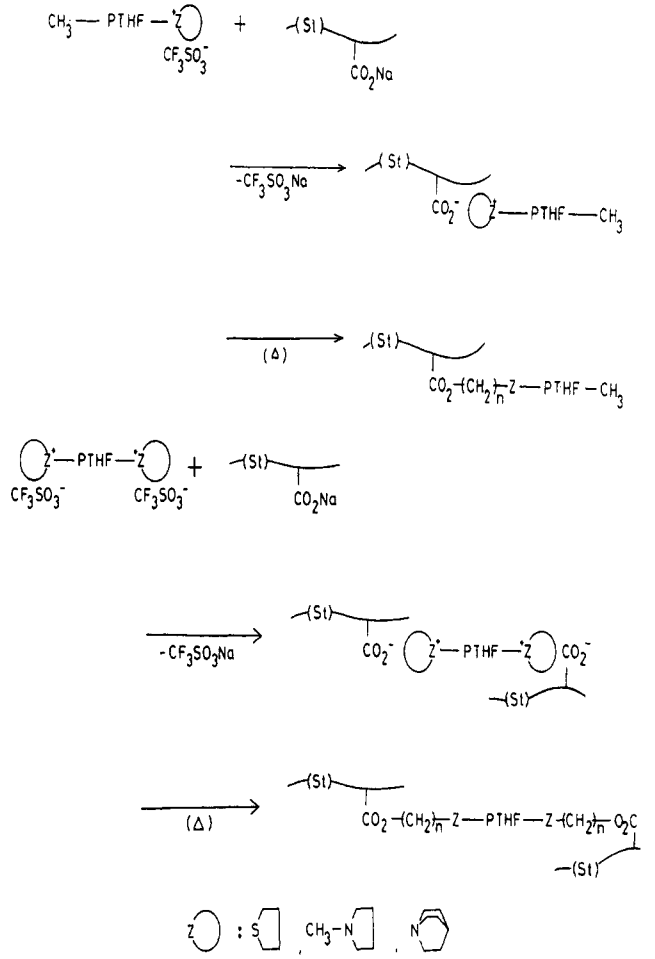
(3) Measurements. ^{1}H NMR spectra were recorded with a JEOL GX-270 apparatus in $CDCl_3$ at 40 °C. FT-IR spectra (40 scans) were taken on a Shimadzu Model FT-IR 8100 infrared spectrophotometer either by casting the sample on a NaCl plate or by mixing the sample with KBr powder. GPC measurements were carried out with a Tohso Model CCPD high-performance liquid chromatograph equipped with a refractive index detector Model RI 8000 and with a column of either TSK G3000HXL, TSK G4000HXL, or TSK G50000HXL. THF was used as an eluent at the flow rate of 1.0 mL/min. Calibration was obtained by using a series of standard polystyrene samples with the conversion factor of 0.556 for poly(THF) samples.[9]

Results and Discussion

(1) Ion-Exchange and Ring-Opening Reactions. Three types of cyclic onium salt groups were introduced at either one end or both ends of uniform-size poly(THF). These are 5-membered cyclic sulfonium (tetrahydrothiophenium) (**1a** and **2a**), 5-membered cyclic ammonium (1-methylpyrrolidinium) (**1b** and **2b**), and 6-membered bicyclic ammonium (quinuclidinium) (**1c** and **2c**) salt groups.

The ring-opening reactivity of these cyclic onium salt groups by a carboxylate anion was examined by introducing it as a counteranion. It has been shown in the preceding

Scheme III



study[5] that the nucleophilic reactivity of the carboxylate anion, when introduced as a counteranion of the onium salt groups of poly(THF) chain ends, is remarkably enhanced in comparison with that of the low molecular weight salt analogue in aqueous medium. This is accounted for by the desolvation of water molecules at the hydrophobic poly(THF) chain ends to form a "naked" anion which commonly exhibits enhanced reactivity in phase-transfer catalyst systems.

The ion-exchange reaction was performed simply by the precipitation of a poly(THF) having cyclic onium salt groups into an aqueous solution containing an excess of sodium benzoate (Scheme II). As reported previously,[5,6] **1a** and **2a** underwent a quantitative ring-opening reaction at an ambient condition to produce the corresponding thioester groups, while **1b** and **2b** quantitatively formed amino ester groups in a ring-opening reaction at 100 °C. The quinuclidinium group in **1c** and **2c** was found to be stable even at 100 °C but caused a ring-opening reaction at 130 °C as indicated by ^{1}H NMR spectroscopic analysis shown in Figure 1, where the presence of a quinuclidinium end group in **2c** is confirmed by signals at 2.09 and 2.27 ppm for the methylene and methine protons at the β and γ positions of quaternary ammonium group, respectively (Figure 1, bottom). The subsequent exchange of the counteranion from triflate to benzoate is indicated by phenyl proton signals at 7.3–8.2 ppm (Figure 1, middle). Finally, the ring-opening reaction of the quinuclidinium group by nucleophilic attack of a benzoate anion during the heating treatment at 130 °C is evident from a notable change in the spectrum (Figure 1, top), where a triplet signal appears at 4.37 ppm due to the formation of ester methylene groups as well as the change of the phenyl proton signal pattern. The presence of the 6-membered cyclic amine (piperidine) skeleton is also indicated by a signal

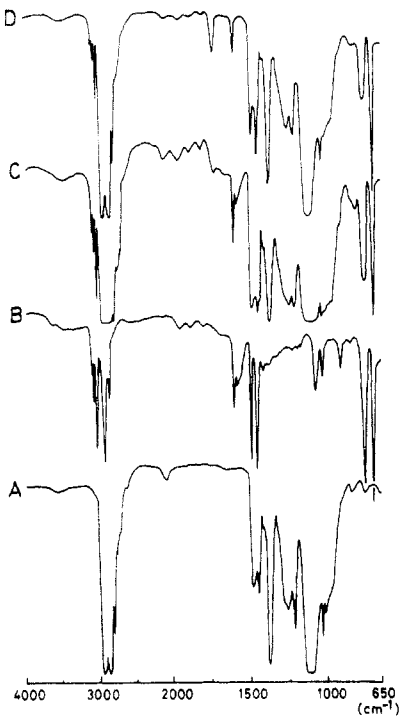


Figure 2. IR spectra of poly(THF) having a 1-methylpyrrolidinium salt end group (A), poly(styrene-*co*-sodium acrylate) (B), and the coupling product before (C) and after (D) the heating treatment at 100 °C (run 11 in Table III).

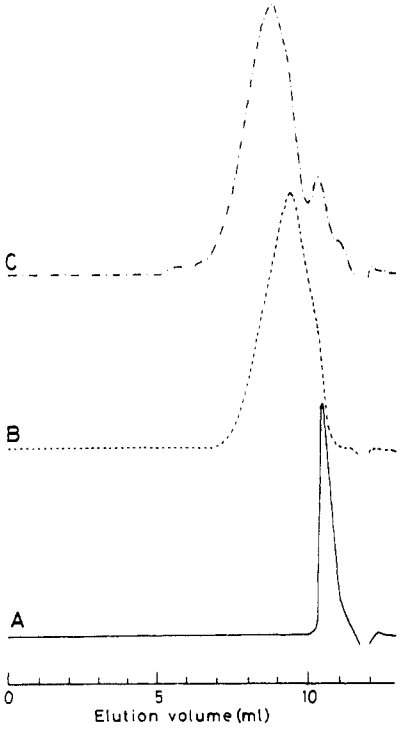


Figure 3. GPC traces of poly(THF) having a 1-methylpyrrolidinium salt end group (A), poly(styrene-*co*-acrylic acid) (B), and the coupling product after the heating treatment at 100 °C (C) (run 11 in Table III; TSK G5000HXL column; THF as eluent at 1.0 mL/min).

at 2.09 ppm for methylene protons at the α position of the amine nitrogen. Further kinetic details of the ring-opening process of a series of cyclic onium salt groups at the poly(THF) chain ends will be reported separately.

GPC measurements of the product before and after the heating treatment indicated the absence of noticeable degradation during the heating treatments.

(2) Synthesis of Graft Copolymers. A series of poly(THF)s having cyclic onium salt end groups, **1** and **2**, were then subjected to the ion-coupling reaction with poly(styrene-*co*-sodium acrylate) **3** having different carboxylate contents up to ca. 5 mol %. Since both prepolymers are readily soluble in THF, the coupling reaction was performed through the precipitation of the THF solution containing both prepolymers of equimolar content of ionic groups into cooled water (Scheme III). Optimum experimental conditions in the precipitation procedure, i.e., the poly(THF) prepolymer concentration in THF solution, the temperature of water, and the addition rate of the prepolymer solution into water, were chosen to form a finely dispersed suspension in the aqueous reaction medium.

During this procedure, the ion-exchange reaction between the two ionic groups located on the separate prepolymers is expected to occur by expelling sodium triflate into the surrounding aqueous medium to combine the prepolymers with an ionic interaction. The subsequent ring-opening reaction either at an ambient condition or at an elevated temperature is expected to transform the nature of the bond between the prepolymers to the covalent type through nucleophilic attack of the carboxylate counteranion on the cyclic onium salt end groups.

Figure 2 shows IR spectra of the coupling product between **1b** and **3b** before and after the heating treatment at 100 °C for 24 h, together with those of the starting prepolymers. The spectrum for the product before the heating treatment shows simply overlapping absorptions of starting prepolymers, while after the heating treatment the absorption at 1740 cm^{-1} due to the formation of ester groups appears along with the disappearance of the

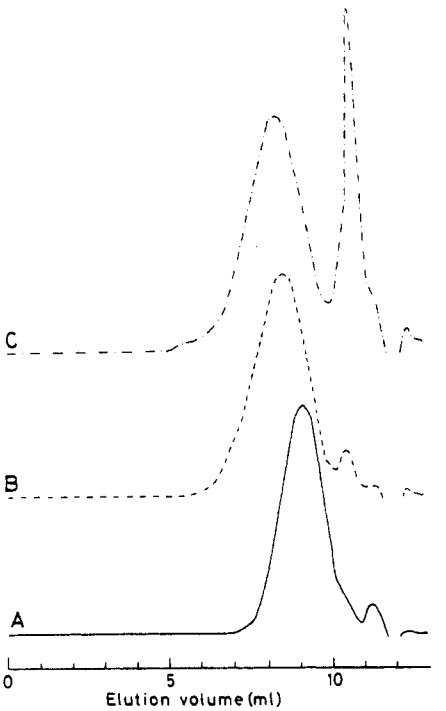


Figure 4. GPC traces of the coupling products between poly(THF) having a tetrahydrothiophenium salt end group and a series of poly(styrene-*co*-sodium acrylate) with different carboxylate contents [runs 1 (A), 4 (B), and 7 (C) in Table III; TSK G5000HXL column; THF as eluent at 1.0 mL/min).

absorption at 1600 cm^{-1} due to the carboxylate salt group, without any additional change in the spectrum. This indicates that the selective ring-opening reaction of the pyrrolidinium salt groups in **1b** took place by nucleophilic attack of the carboxylate anion in **3b** to transform the ionic bond between the prepolymers to a covalent nature.

The ion-exchange and the subsequent ring-opening reactions of the cyclic onium salt groups were also confirmed to occur with **1a** and **1c** at an ambient condition and at 130 °C, respectively. Thus, the ring-opening

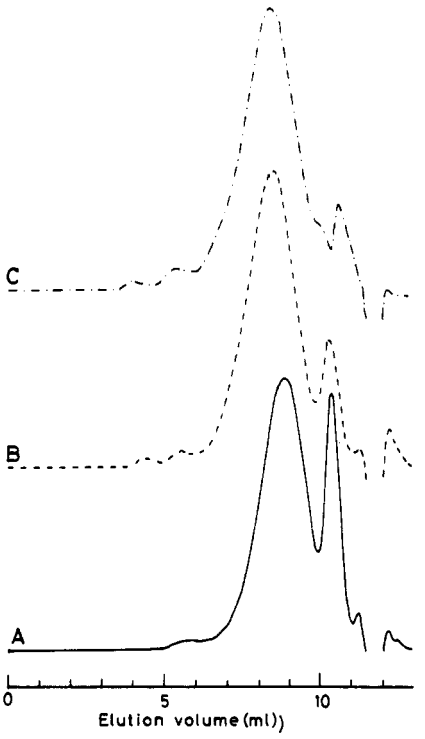


Figure 5. GPC traces of the coupling products between poly(THF) having a quinuclidinium salt end group and poly(styrene-*co*-sodium acrylate) by a repeated precipitation method [runs 13 (A), 14 (B), and 15 (C) in Table III; TSK G5000HXL column; THF as eluent at 1.0 mL/min).

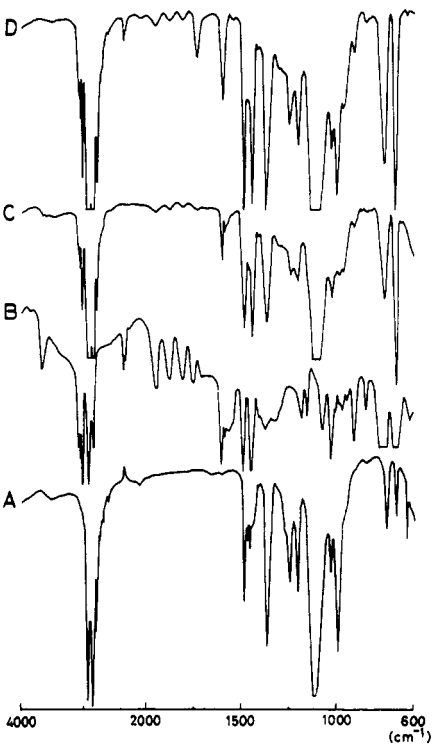


Figure 6. IR spectra of poly(THF) having quinuclidinium salt end groups (A), poly(styrene-*co*-sodium acrylate) (B), and the coupling product before (C) and after (D) the heating treatment at 130 °C (run 8 in Table IV).

reactions of the cyclic onium salt groups by a carboxylate located on the polystyrene segment were confirmed to proceed in the same fashion as with a low molecular weight benzoate anion.

The results of GPC measurements for the reaction products recovered after the precipitation into water are shown in Figures 3–5. As is clearly seen in Figure 3, the molecular weight of a major fraction in the product is evidently higher than that of the starting **3**, though a minor fraction of unreacted **1** was also observed. This indicates the occurrence of the coupling reaction in the present procedure to form a polystyrene-*graft*-poly(THF). In Figure 4, GPC traces are given for the products from the reaction between **1a** and a series of **3** with different carboxylate contents. The molecular weight of a major fraction in the product was observed to be higher with the increase of the carboxylate content in **3**, indicating the increase of the number of the graft segments in the products. On the other hand, the increase of the carboxylate content in **3** resulted in the decrease in the efficiency of the coupling reaction, as noticed from the increase of the fraction corresponding to the unreacted **1a**.

The coupling efficiency was found to be improved by means of a repeated precipitation technique, which was previously applied to the synthesis of star polymers using a poly(THF) having another cyclic onium salt group.[8] Thus, the product recovered after the first precipitation was dissolved in THF and was again subjected to the identical precipitation procedure. As demonstrated in Figure 5, the coupling efficiency was improved with increases of the times of the precipitation treatment, and polystyrene-*graft*-poly(THF) of the increased number of the graft segments was obtained in high yields.

In Table III, the results of the ion-coupling reaction between a series of **1** and **3** by means of a repeated precipitation technique are summarized. The recovered yield in each precipitation procedure was as high as 90%

Table III
Coupling Reaction between Monofunctional Poly(THF)s Having Various Cyclic Onium Salt Groups and Poly(styrene-*co*-sodium acrylate)s

run	prepolymers[a]	feed ratio of 1 and 3 g/g	precipitn times	recovd yield, %	graft copolymer		
					MW[b] × 10⁻³	N_a[c]	DP of graft
1	**1a/3a**	0.10/0.20	1	96.7			
2	**1a/3a**	0.10/0.20	3	86.7			
3	**1a/3a**	0.10/0.20	5	73.3	108	8.3	71
4	**1a/3b**	0.10/0.06	1	93.8			
5	**1a/3b**	0.10/0.06	3	75.0			
6	**1a/3b**	0.20/0.12	5	75.0	190	26	71
7	**1a/3c**	0.22/0.10	1	93.8			
8	**1a/3c**	0.22/0.10	3	87.5			
9	**1a/3c**	0.22/0.10	5	78.1	246	39	71
10	**1b/3b**	0.17/0.10	1	85.2			
11	**1b/3b**	0.17/0.10	3	70.4			
12	**1b/3b**	0.17/0.10	5	59.3	190	26	71
13	**1c/3b**	0.10/0.05	1	93.3			
14	**1c/3b**	0.10/0.05	3	66.7			
15	**1c/3b**	0.10/0.05	5	46.7	216	26	87

[a] See also Tables I and II. [b] Calculated from M_n's of prepolymers and N_a. [c] Average number of graft segments per polymer chain.

Table IV
Coupling Reaction between Bifunctional Poly(THF)s Having Various Cyclic Onium Salt Groups and Poly(styrene-*co*-sodium acrylate)s

run	prepolymers[a]	feed ratio of 2 and 3, g/g	precipitn times	recovd yield, %	network copolymer: gel cont,[b] %	network copolymer: poly(THF) conv,[c] %	network copolymer: segment ratio,[d] (DP/DP)
1	**2a/3a**	0.04/0.10	1	91.4	97.9	92.0	83/106
2	**2a/3b**	0.05/0.06	1	92.7	93.9	88.8	27/106
3	**2a/3c**	0.08/0.05	1	90.9	86.4	77.9	19/106
4	**2b/3b**	0.14/0.20	1	94.1	84.4	62.1	
5[e]			3	88.6	92.5	81.8	
6[e]			5	80.0	93.9	85.1	27/63
7	**2c/3b**	0.21/0.20	1	92.7	79.0	59.9	
8[e]			3	85.1	89.6	80.0	
9[e]			5	76.7	96.2	92.5	27/98

[a] See also Tables I and II. [b] Obtained after a Soxhlet extraction. [c] Calculated from the feed weight of 1 and the gel content. (See also the text.) [d] Segment lengths between the cross-linking points [polystyrene/poly(THF)]. [e] Repeated precipitation using a sample subjected to the preceding precipitation treatment.

and the polystyrene-*graft*-poly(THF) of the predetermined number of the graft segment and of the defined graft segment length was produced in high yields.

(3) Synthesis of Network Copolymers. With the use of bifunctional poly(THF)s, **2**, in the present coupling reaction with a series of **3**, the gel products were obtained either simply after the isolation at ambient condition with **2a** or after the heating treatment with **2b** and **2c**. An example of the IR analysis for the reaction product is shown in Figure 6, where the absorption at 1740 cm^{-1} appears after the heating treatment at 130 °C along with the disappearance of the absorbance at 1600 cm^{-1} due to the conversion of the carboxylate salt group to the ester group without any noticeable side reactions during the heating treatment. This indicates that the precipitation of a THF solution of the mixture of **2c** and **3b** into water produced first the ion-exchange product, in which both prepolymers were connected by an ionic bond, and the subsequent heating treatment at 130 °C converted it to the covalent bond to form a polystyrene–poly(THF) network copolymer.

A series of gel products were thus obtained and were subjected to the extraction treatment with THF. The extract was examined by ^1H NMR spectroscopy to contain solely unreacted poly(THF) prepolymers **2**. In Table IV, the gel content in the products and the amount of **2** incorporated into the gel are collected together with the recovered yields of the products after each precipitation procedure.

The recovered yield after each precipitation procedure reached as high as 90%. The gel content was observed to increase with the times of the precipitation procedure to approach near completion, indicating the improvement of the coupling efficiency by the repeated precipitation technique, as was the case for the graft copolymer synthesis with **1**. Since the reaction with **2a** produced insoluble gel products even after the first precipitation procedure, the products were directly subjected to the extraction treatment, while products from the reaction with **2b** and **2c** remained soluble in THF before the heating treatment, allowing repeated precipitation. The gel content in the product after the first precipitation treatment appears to be slightly higher with **2a** than with **2b** and **2c**. It was also observed from the reaction with **2a** that higher carboxylate content in **3** gave lower gel content in the product.

Thus, the present reaction process, in particular with **2b** and **2c**, provides a highly efficient means to produce network copolymers comprised of different polymer segments, where the soluble nature of the coupling products through the ionic bond allows one to perform the repeated precipitation to improve the coupling efficiency in the reaction. This is in contrast to the common network formation processes, where a serious retardation usually occurs after the gel point due to the difficulty of the mutual diffusion of the polymeric reagents.

Studies of the swelling behavior as well as of the microphase structure of the present network products consisting of the two immiscible segments are currently in progress in our laboratory.

Conclusion

The present macromolecular ion-coupling process, which makes use of the unique reactivities of telechelic polymers having a series of cyclic onium salt groups, is considered to be a simple and efficient method to produce well-defined graft and network copolymers consisting of inherently incompatible segments. The ionic interaction between the salt groups located in the prepolymers plays an important role in overcoming the repulsive interaction of the incompatible segments, which are otherwise likely to cause a microscopic phase separation to disturb the reaction between the prepolymers. Controlled conversion of the ionic bond to the covalent bond is achieved by an approproate choice of a cyclic onium salt group, a counteranion, and a reaction temperature to result in the selective formation of the coupling products in high yields.

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