

Ion-Coupling Synthesis of Polymacromonomer by Uniform Size Poly(tetrahydrofuran) Having a Cyclic Onium Salt End Group

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ABSTRACT: An ion-coupling reaction of a monofunctional poly(tetrahydrofuran) [poly(THF)] having a tetrahydrothiophenium salt end group (**1**) with poly(sodium acrylate) (**2**) was performed by a simple precipitation of a THF solution of **1** into an aqueous solution containing an excess amount of **2**. The coupling reaction took place efficiently to produce poly(THF) polymacromonomer through the ion-exchange reaction between **1** and **2** and the subsequent ring-opening reaction by the nucleophilic attack of the carboxylate anion toward the moderately strained cyclic onium salt end group of **1** at ambient condition.

Introduction

Model branched polymers such as star polymers and dendrimers have gained increasing attention from both academic and practical viewpoints.^{1–3} Novel and unique properties unattainable by conventional linear analogues are expected by such macromolecules with defined branch structures.

A polymacromonomer is another model branched polymer with high branch density exhibiting unique solution properties.^{4–10} So far, the preparation technique of a polymacromonomer has been limited to the homopolymerization of a macromonomer. However, the homopolymerization of a macromonomer is frequently circumvented by the unusually low concentration of polymerizable groups, such as vinyl groups, which decrease the apparent rate of polymerization, resulting in a product of only a limited degree of polymerization with a limited conversion of macromonomer. Besides, the control over the degree of polymerization, i.e., the number of the branch segments, of the polymacromonomer is difficult to achieve. A special reaction condition is thus required to compensate these disadvantages through the decrease of the apparent rate of termination due to the viscosity effect.⁴ In addition, the copolymerization of different macromonomers has scarcely been reported presumably due to the incompatibility of antagonistic polymer segments, resulting in a macroscopic phase separation in the reaction system.

In the present study, we propose a new alternative means to produce polymacromonomer by making use of monofunctional poly(THF) having a tetrahydrothiophenium salt group (**1**). In the preceding studies,¹¹ we have reported unique reactions with telechelic polymers having a series of cyclic onium salt groups, i.e., 4-membered, 5-membered cyclic and 6-membered bicyclic ammonium, and 5-membered cyclic sulfonium salt groups. In particular, we have demonstrated that a simple precipitation of telechelic polymer having a cyclic onium salt group into an aqueous solution containing a plurifunctional carboxylate, such as a 1,2,4,5-benzenetetracarboxylic acid sodium salt, caused a highly efficient coupling reaction of ionic groups at the interface between the precipitated polymer surface and the sur-

rounding aqueous medium to give a star polymer from a monofunctional prepolymer and a model network polymer from a bifunctional prepolymer, respectively, in high efficiency.¹² We have also applied this reaction system for the preparation of polymeric azoinitiator using an azo-containing bifunctional carboxylate¹³ and of cellulose-based graft copolymers using partly substituted sodium carboxymethylcellulose.¹⁴

As an extension of the preceding studies, the present study describes the macromolecular ion-coupling reaction of **1** with poly(sodium acrylate) (**2**) having degrees of polymerization of ca. 20 and 60. A simple precipitation of a THF solution of **1** into an aqueous solution containing **2** promotes the ion-exchange reaction between the two prepolymers, and the subsequent ring-opening reaction of a cyclic sulfonium salt group produces poly(THF) polymacromonomer of predefined branch segment numbers.

Experimental Section

(1) Materials. Poly(THF)s, having a tetrahydrothiophenium salt end group (**1**) of different molecular weights, were prepared by the method described before.^{15,16} (Note! Some tetrahydrothiophenium chlorides are reported to be toxic.¹⁷ Although no toxicity of the reaction mixture was observed in the course of the present study, the reaction solution should be handled carefully.) The molecular weight of **1** was estimated from the product yield/initiator ratio, since the GPC chromatogram of **1** itself suffered an elution delay and a peak tailing due to the interaction between the ionic end group of **1** and polystyrene gel of a GPC column as shown in Figure 1. The molecular weights of the three samples of **1** used in the present study were 2100, 2700, and 5400, respectively. Poly(sodium acrylate) samples, $M_n = 2100$ and 6000, both with 10% residual carboxyl group, **2**, from Scientific Polymer Products Inc., were used without further purification. Distilled water (Nacalai Tesque) and other reagents were used as received.

(2) Procedures. Into an ice-cooled (<5 °C) 300 mL aqueous solution containing a weighed amount of **2** was slowly added dropwise under vigorous stirring with a magnetic stirrer 3 mL of a THF solution of **1** (the weight ratio of **2/1** ranged from 0.8 to 10). The resulting suspension solution was then stirred for 1 h. The precipitate was recovered by filtration with a glass filter and finally dried in vacuo. An aliquot of the recovered product was then subjected to repeated precipitation into an aqueous solution containing a weighed amount of **2** by a similar manner.

(3) Measurements. GPC measurements were carried out with a Tohso Model CCPD high-performance liquid chromatograph equipped with a refractive index detector Model RI-8000, a UV detector Model UV-8000 at 254 nm, and a conductivity

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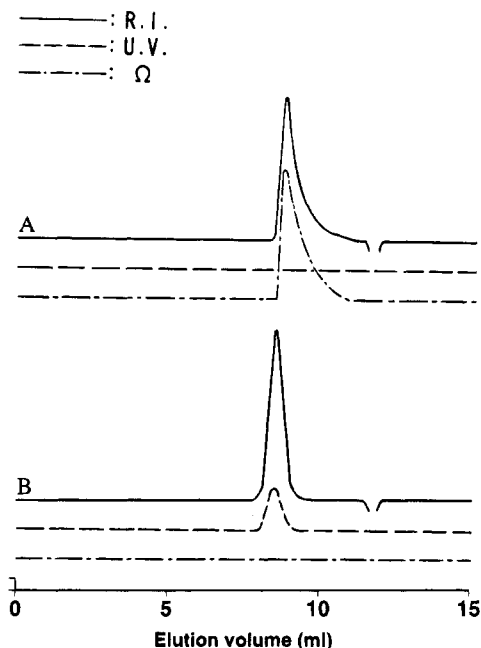


Figure 1. GPC traces of (A) **1** (sample: **1** of a MW of 5400) and (B) its ion-exchange and ring-opening product by benzoate anion (column, TSK G4000HXL; eluent, THF, 1.0 mL/min; RI, refractive index; UV, ultraviolet; Ω , conductivity traces).

detector Model CM-8010. A column of TSK G4000HXL was used with THF as an eluent at a flow rate of 1.0 mL/min. Light scattering (LS) measurements were performed by means of a dynamic light scattering spectrophotometer Model DLS-7000 (Otsuka Electronics) at 30 °C for $\lambda = 633$ nm in a benzene solution, and the weight-average molecular weight was determined through a Zimm plot. FT-IR spectra (40 scans) were taken on a Shimadzu Model FT-IR 8100 infrared spectrometer by casting the sample on a NaCl plate. $^1\text{H-NMR}$ spectra were recorded with a JEOL GX-270 apparatus in CDCl_3 at 40 °C.

Results and Discussion

A simple precipitation treatment was performed with a THF solution of poly(THF) having a tetrahydrothiophenium salt end group (**1**) into an ice-cooled (<5 °C) aqueous solution containing an excess amount of poly(sodium acrylate) (**2**). The recovered amount of the precipitated product was nearly identical to the charged amount of **1** in most cases.

Figure 2 shows an IR spectrum of the reaction product (**3**) together with that of the starting **1**. The absorption at 1730 cm^{-1} appeared in the spectrum of **3**, indicating the formation of an ester function through a counteranion-exchange reaction from a triflate to a carboxylate group on a tetrahydrothiophenium group, followed by a nucleophilic ring-opening reaction by the carboxylate anion. This counteranion-exchange reaction was confirmed also by the disappearance of the absorptions at 640 and 1025 cm^{-1} due to the triflate (sulfonate) anion along with the precipitation treatment. The relevant ring-opening reaction of a tetrahydrothiophenium group by a phenolate anion was previously utilized to produce nonionic macromolecular products with aryl cyclic sulfonium zwitterion compounds as monomers.¹⁸ $^1\text{H-NMR}$ inspection of **3** indicated also the formation of an ester group located in the vicinity of the main chain of **3** by the presence of an ester methylene signal at 4.00 ppm with notable signal broadening presumably due to the decrease of the transverse relaxation time, T_2 , caused by a decrease in the mobility of the main-chain segment after the grafting.

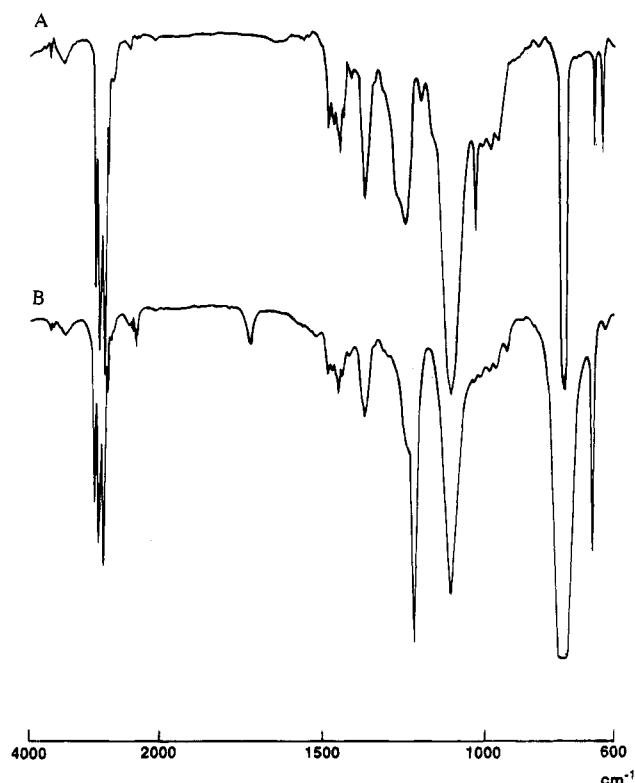


Figure 2. IR spectrum of (A) **1** (sample: **1** of a MW of 2100) and (B) **3** (sample: run 3 in Table 1).

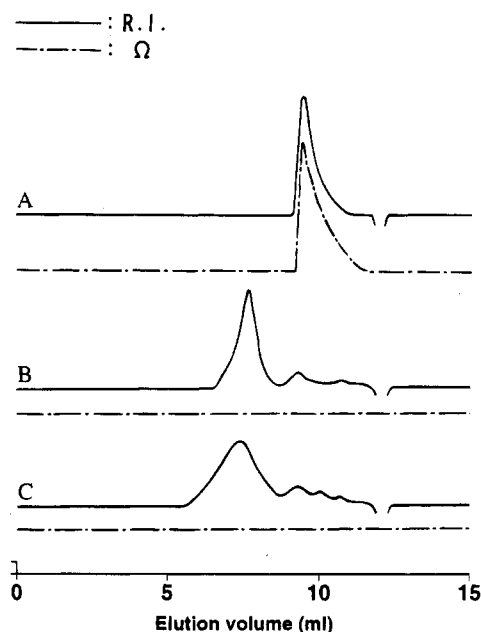


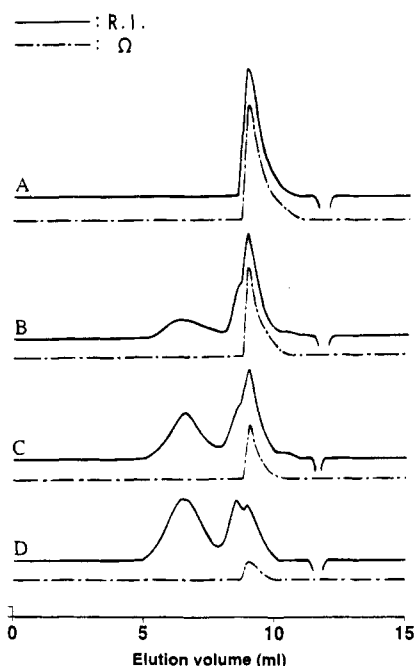
Figure 3. GPC traces of (A) **1** (sample: **1** of a MW of 2100) and (B and C) **3** (samples: (B) run 1, (C) run 3 in Table 1).

The results on GPC measurements of **3** obtained with **1** of a molecular weight of 2100 are listed in Figure 3 and in Table 1. The precipitation treatment only once in the reaction with **2** of a MW of 2100 or twice with **2** of a MW of 6000 produced **3** of significantly higher molecular weight than **1** in high yields. Indeed, the weight-average molecular weight of **3**, obtained through the coupling reaction between **1** of a MW of 2700 and **2** of a MW of 6000, was determined to be 1.44×10^5 by means of LS measurements. This value is close to the calculated one (1.73×10^5) from the MW of **1** (2700) and the degree of polymerization of **2** (64). This appears to indicate that the polymacromonomer, **3** possesses one

Table 1. Coupling Reaction between Poly(THF) Having a Tetrahydrothiophenium Salt End Group (1) and Poly(sodium acrylate) (2)

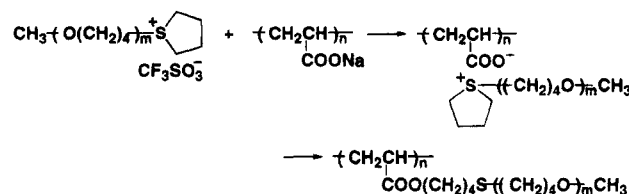
run ^a	pre-polymer ^b	feed ratio of 1 and 2 (g/g)	pre-cipitation time (h)	time (h)	recovered yield ^c (%)	polymacro-monomer yield ^d (%)
1	1a/2a	0.50/0.42	1	1	90	85
2	1a/2b	0.50/1.20	1	1	90	62
3	1a/2b	0.30/1.20	2	1	100	80
4	1b/2b	0.50/3.00	1	1	100	92
5	1c/2a	0.60/0.74	1	1	97	33
6	1c/2a	0.40/0.74	2	1	95	51
7	1c/2a	0.20/0.08	1	1	85	11
8	1c/2a	0.20/0.08	1	3	70	25
9	1c/2a	0.20/0.25	1	1	100	36
10	1c/2b	0.60/2.12	1	1	97	26
11	1c/2b	0.40/2.12	2	1	93	43
12	1c/2b	0.20/2.12	3	1	95	57
13	1c/2b	0.20/0.24	1	1	90	24
14	1c/2b	0.20/0.24	1	3	80	39
15	1c/2b	0.20/0.71	1	1	90	48

^a Molecular weight of prepolymers: 1a, 2100; 1b, 2700; 1c, 5400; 2a, 2100; 2b, 6000. ^b A repeated precipitation technique was applied for runs 2 and 3, 5 and 6, and 10–12. See also the Experimental Section. ^c Based on the feed amount of 1. ^d By GPC peak area ratio.

**Figure 4.** GPC traces of (A) 1 (sample: 1 of a MW of 5400) and (B–D) 3 (samples: (B) run 10, (C) run 11, and (D) run 12 in Table 1).

poly(THF) graft segment in each sodium acrylate residue in the starting 2. In addition, the complete consumption of an ionic end group in 1 after the coupling reaction with 2 was confirmed by the absence of conductivity in the product, 3. This indicates the ion-exchange reaction between 1 and 2, followed by the ring-opening reaction of the tetrahydrothiophenium salt end groups, to produce nonionic, covalent thioester groups in 3. Since an excess amount of 2 was charged in the reaction solutions, only a part of 2 takes part in the coupling reaction to produce a precipitated product comprising a polymacromonomer, 3, while the excess of 2 stays in the solution.

The results of the coupling reaction of 1 having a MW of 5400 are collected in Figure 4 and Table 1. The coupling reaction was found to be less efficient than the

Scheme 1

previous case using 1 of the lower MW. This is due to the decrease of the total concentration of the chain-end cyclic sulfonium group in 1 with the higher MW. A longer reaction time (compare runs 7 and 8 and runs 13 and 14 in Table 1) and/or a higher charge of 2 in the reaction medium (compare runs 7 and 9 and runs 13 and 15 in Table 1) marginally enhanced the coupling efficiency. The higher the concentration of 1 and 2 in the reaction medium, the higher the yield of the polymacromonomer, 3. (Compare runs 10 and 15 in Table 1.) Thus a part of ionic groups in 1 is considered to be located inside the precipitated polymer mass and will not be accessible to react the ionic groups of 2 in an aqueous medium. A repeated precipitation technique¹² was then performed, in which the product of the first precipitation, namely, the mixture of polymacromonomer, 3, and the unreacted 1, was dissolved again in THF and precipitated repeatedly into an aqueous solution containing 2. (Compare runs 2 and 3, runs 5 and 6, and runs 10–12 in Table 1.) By this procedure, the ionic groups originally located inside the precipitate mass are expected to relocate themselves toward the surface of the precipitate. As shown in Figure 4, the fraction of the polymacromonomer, 3, increased with the times of the precipitation treatment along with a decrease of the fraction of unreacted 1 possessing the conductivity response.

An additional GPC peak at a slightly higher MW region than that of 1 was observed. The content of this peak fraction increased with the repetition of the precipitation treatment. This fraction did not possess the conductivity response, and the elution position is almost identical to that of benzoate-terminated 1 shown in Figure 1. The hydrolysis of 3 and/or a direct nucleophilic ring-opening reaction of a tetrahydrothiophenium group by a hydroxide anion in an aqueous reaction medium is envisaged, since the precipitation of 1 into an aqueous NaOH solution produced a hydroxy-terminated poly(THF).

Conclusion

The present macromolecular ion-coupling reaction process, which exploits the unique properties of telechelic polymers having a specific cyclic onium salt group, provides an unconventional and facile means to produce a highly branched model polymer, i.e., a polymacromonomer. The ionic interaction between ionic groups located in the different prepolymers, one water-soluble and another water-insoluble, plays an important role in overcoming the adversarial steric congestion and in avoiding the requirement of stoichiometry of the reactive groups in the reaction system. The controlled conversion of the ionic bond to the covalent one through a ring-opening reaction of a cyclic onium salt group by the nucleophilic attack of a carboxylate counteranion can subsequently produce polymacromonomers in high yield.

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