Tailored synthesis of branched polymers with poly(tetrahydrofuran) having an azetidinium salt end group

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SUMMARY: Monofunctional poly(tetrahydrofuran), (poly(THF)), having a 1-(diphenylmethyl)azetidinium end group (**1**) was prepared and subjected to an ion-coupling reaction with various mono- and plurifunctional carboxylates (**2a–j**). Multiarmed polymers having 2, 3, 4 and 6 arms were obtained in almost pure form by repeating a simple precipitation of a THF solution of **1** into an ice-cooled aqueous solution containing an excess amount of the relevant plurifunctional carboxylates (**2c–g**) as sodium salts. Another model-branched polymacromonomer was obtained in high yield through the macromolecular ion-coupling reaction of **1** with poly(sodium acrylate) (**2h**) of DP = 22. Moreover, the ion-coupling reaction of **1** with sodium (L)-tartarate (**2i**) or sodium 2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylate (**2j**) allowed one to introduce two hydroxyl groups at the center of a linear poly(THF) segment.

Introduction

The coupling reaction of an end-functionalized linear polymer precursor (telechelics) and a plurifunctional reagent has been considered as a potential method for the synthesis of well-defined branched polymer architectures[1–4] such as star polymers[5,6] and polymacromonomers[7,8]. We have reported a new macromolecular ion-coupling reaction using telechelic poly(THF)[9–13], polystyrene[14] and poly(dimethylsiloxane)[15] having a series of moderately strained cyclic onium salt groups such as 4-membered ammonium (azetidinium)[9,10], 5-membered ammonium (pyrrolidinium)[12,14,15], and 6-membered bicyclic ammonium (quinuclidinium) salts[12] and 5-membered sulfonium (tetrahydrothiophenium) salt groups[11,13]. The macromolecular reactions with the use of these telechelics are unique in contrast to direct coupling reactions of a living polymer with a plurifunctional coupling reagent. First, these telechelics are stable at ambient condition to allow full characterization and subsequent storage until use without any precautions. Secondly, they are capable of undergoing the ion-exchange reaction by precipitation into aqueous solution containing an excess of a desired anion. And thirdly, moderately strained cyclic onium salt groups can undergo selective ring-opening reaction by introducing an appropriate counter anion, i.e., a carboxylate having sufficient nucleophilic reactivity. Thus we have so far demonstrated the efficient synthesis of star polymers having up to 4-arms[10,11] as well as polymacromonomers[13] by a simple precipitation of a monofunctional poly(THF) having a 1,3,3-trimethylazetidinium salt or a tetrahydrothiophenium salt end group into aqueous solution containing plurifunctional carboxylates[16].

As an extension of the preceding studies, the present study aims at exploring further application possibilities of this macromolecular ion-coupling process by using a new monofunctional poly(THF) prepared with a readily available 1-(diphenylmethyl)azetidine, in place of the previous *N*-methyl- or *N*-(*t*-butyl)azetidine obtainable after multistep synthesis. In addition, choice of the substituent on the nitrogen atom of telechelics having cyclic ammonium salt groups could control its reactivity toward nucleophilic coupling reagents[17]. Also we refrain from using tetrahydrothiophene due to its ill odor and toxicological concern of tetrahydrothiophenium salts[18], though no toxicity of the reaction mixture of poly(THF) having a tetrahydrothiophenium salt end group was so far observed[13].

Experimental part

Reagents

THF was distilled from sodium diphenylketyl just before use. Methyl trifluoromethanesulfonate (methyl triflate) was purified by distillation over P_2O_5 just before use. 1-(Diphenylmethyl)azetidine (Aldrich; 98%) was used as received. 2,2′-Dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylic acid was prepared by a copper-catalyzed oxidative coupling reaction[19] of methyl 2-hydroxy-3-naphthoate, and subsequent hydrolysis under alkaline condition[20]. Sodium benzoate (**2a**), sodium terephthalate (**2c**) and sodium tartarate (**2i**) were used as received. Poly(sodium acrylate) (**2h**), MW = 2 100 with 10% residual carboxylic acid groups, from Scientific Polymer Products Inc., was used without further purification. Other sodium salts of plurifunctional carboxylic acids were synthesized by neutralization of the corresponding free acid with an equimolar amount of sodium hydroxide in aqueous solution.

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 either 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. ^{1}H NMR spectra were recorded with a JEOL JNM-AL300 apparatus in CDCl$_3$ at 40 °C. The chemical shifts were referenced from the signal of tetramethylsilane.

Synthesis of poly(THF) having a 1-(diphenylmethyl)-azetidinium salt end group (1)

Monofunctional poly(THF) having a 1-(diphenylmethyl)azetidinium salt end group was synthesized according to the slightly modified procedure reported previously[9]. Thus, to 100 ml of THF was added 0.49 g (3.0 mmol) of methyl triflate at 25 °C under nitrogen atmosphere. After a prescribed reaction period (12–14 min), a freshly prepared THF (20 ml) solution containing 2.0 g (9.0 mmol) of 1-(diphenylmethyl)-azetidine was added at once to the reaction solution. The resulting mixture was condensed by a rotary evaporator to a volume of ca. 10 ml, and the concentrated solution was added dropwise into 2 L of petroleum ether placed in an ice-NaCl salt bath (–15 °C). The formed precipitate (1) was collected by filtration, washed with cooled petroleum ether several times and finally dried in vacuo (yield, 3.9 g).

1: ^{1}H NMR (Fig. 1, top): δ = 1.46–1.72 (m, CH_2CH$_2$O), 1.84–1.96 (m, 2H), 2.48–2.66 (m, 1H), 3.32 (s, 3H), 3.25–3.55 (m, CH$_2$CH_2O), 3.62–3.72 (m, 2H), 4.42–4.55 (m, 2H), 4.78–4.90 (m, 2H), 5.65 (m, 1H), 7.45–7.62 (m, 10H). IR: 1259, 1031, 638 cm^{-1}.

Ion-coupling reaction of 1 *with a plurifunctional carboxylate*

The ion-coupling reaction of 1 with a plurifunctional carboxylate was performed as detailed before[10], but with a minor amendment. To an ice-cooled (<5 °C) aqueous solution (100 ml) containing 0.18 g (1.3 mmol) of sodium benzoate (2a) was added dropwise a THF solution (1 ml) of 0.2 g (0.067 mmol) of 1 under vigorous stirring. The resulting suspension was stirred for further 3 h. The formed precipitate (3a) was collected by filtration, washed with cold water several times and finally dried in vacuo. This precipitation treatment was repeated by three times to complete the reaction. The product 3a (0.12 g, 59%) was obtained.

3a: ^{1}H NMR: δ = 1.40–1.72 (m, CH_2CH$_2$O), 1.84–1.96 (m, 2H), 2.52 (t, J = 7.5 Hz, 2H), 2.68 (t, J = 7.5 Hz, 2H), 3.32 (s, 3H), 3.25–3.55 (m, CH$_2$CH_2O), 4.28 (t, J = 6.0 Hz, 2H), 4.79 (s, 1H), 7.10–7.60 (m, 13H), 7.89 (d, J = 9.0 Hz, 2H); IR: 1721 cm^{-1}.

The synthesis of 3b–j was carried out as in the synthesis of 3a under the conditions detailed in Tab. 1. The purities of 3a–j listed in Tab. 1 were determined by the relative values of the ^{1}H NMR signal intensities of 3 and 1 as well as GPC analysis.

3b: ^{1}H NMR: δ = 1.45–1.75 (m, CH_2CH$_2$O), 1.84–1.96 (m, 2H), 2.53 (t, J = 7.5 Hz, 2H), 2.68 (t, J = 7.5 Hz, 2H), 3.32 (s, 3H), 3.25–3.55 (m, CH$_2$CH_2O), 4.34 (t, J = 6.0 Hz, 2H), 4.79 (s, 1H), 7.08–7.40 (m, 10H), 8.00 (d, J = 9.0 Hz, 2H), 8.22 (d, J = 9.0 Hz, 2H); IR: 1727, 1530 cm^{-1}.

3c: ^{1}H NMR: δ = 1.40–1.72 (m, CH_2CH$_2$O), 1.84–1.96 (m, 4H), 2.53 (t, J = 7.5 Hz, 4H), 2.68 (t, J = 7.5 Hz, 4H), 3.32 (s, 6H), 3.25–3.55 (m, CH$_2$CH_2O), 4.32 (t, J = 6.3 Hz, 4H), 4.80 (s, 2H), 7.10–7.40 (m, 20H), 7.87 (s, 4H); IR: 1721 cm^{-1}.

3d: ^{1}H NMR: δ = 1.40–1.72 (m, CH_2CH$_2$O), 1.84–1.96 (m, 6H), 2.53 (t, J = 7.5 Hz, 6H), 2.65 (t, J = 7.5 Hz, 6H), 3.32 (s, 9H), 3.25–3.55 (m, CH$_2$CH_2O), 4.35 (t, J = 6.0 Hz, 6H), 4.80 (s, 3H), 7.08–7.40 (m, 30H), 8.62 (s, 3H); IR: 1731 cm^{-1}.

3e: ^{1}H NMR (Fig. 1, bottom): δ = 1.40–1.72 (m, CH_2CH$_2$O), 1.84–1.96 (m, 8H), 2.49 (t, J = 7.5 Hz, 8H), 2.59 (t, J = 7.5 Hz, 8H), 3.32 (s, 12H), 3.25–3.55 (m, CH$_2$CH_2O), 4.26 (t, J = 6.0 Hz, 8H), 4.78 (s, 4H), 7.08–7.38 (m, 40H), 7.73 (s, 2H); IR: 1728 cm^{-1}.

3f: ^{1}H NMR: δ = 1.40–1.80 (m, CH_2CH$_2$O), 2.40–2.60 (m, 16H), 3.00–3.10 (m, 2H), 3.32 (s, 12H), 3.25–3.65 (m, CH$_2$CH_2O), 3.88–4.10 (m, 8H), 4.76 (s, 4H), 7.10–7.38 (m, 40H); IR: 1737 cm^{-1}.

3g: ^{1}H NMR: δ = 1.40–1.72 (m, CH_2CH$_2$O), 2.30–2.60 (m, 24H), 3.32 (s, 18H), 3.20–3.65 (m, CH$_2$CH_2O), 3.85–4.04 (m, 12H), 4.76 (s, 6H), 7.06–7.42 (m, 60H); IR: 1741 cm^{-1}.

3h: ^{1}H NMR: δ = 1.40–1.72 (m, CH_2CH$_2$O), 2.30–2.70 (br, 4H), 3.32 (s, 3H), 3.15–3.60 (m, CH$_2$CH_2O), 3.70–4.10 (br, 2H), 4.85 (s, 1H), 7.05–7.50 (m, 10H); IR: 1734 cm^{-1}.

**3i:** ^{1}H NMR: δ = 1.40–1.72 (m, CH_2CH$_2$O), 1.85–1.95 (m, 4H), 2.45–2.65 (m, 8H), 2.99 (d, J = 7.5 Hz, 2H), 3.32 (s, 6H), 3.25–3.55 (m, CH$_2$CH_2O), 4.18 (d, J = 7.5 Hz, 2H), 4.23 (t, J = 6.0 Hz, 4H), 4.77 (s, 2H), 7.15–7.40 (m, 20H); IR: 1751 cm^{-1}.

3j: ^{1}H NMR: δ = 1.40–1.72 (m, CH_2CH$_2$O), 1.90–2.05 (m, 4H), 2.57 (t, J = 7.2 Hz, 4H), 2.74 (t, J = 6.0 Hz, 4H), 3.32 (s, 6H), 3.25–3.55 (m, CH$_2$CH_2O), 4.43 (t, J = 6.0 Hz, 4H), 4.83 (s, 2H), 7.10–7.44 (m, 26H), 7.80–7.88 (m, 2H), 8.42 (s, 2H), 10.72 (s, 2H); IR: 1682 cm^{-1}.

Results and discussion

1-(Diphenylmethyl)azetidine, having a bulky substituent on nitrogen, is now commercially obtainable as a termination reagent of living poly(THF) prepared with methyl trifluoromethanesulfonate as an initiator. The corresponding 1-(diphenylmethyl)azetidinium salt group was quantitatively introduced at one end of uniform-size poly(THF) ($\overline{M}_n$ = 3100) as in the reactions with other azetidines like 1,3,3-trimethylazetidine and 1-(t-butyl)azetidine (*Scheme 1*). ^{1}H NMR spectrum of obtained poly(THF) (1) (Fig. 1, top) proves the presence of the azetidinium salt end group, showing a typical AB pattern signals due to the endo-cyclic ammonium methylene protons at 4.42–4.55 ppm and 4.78–4.90 ppm, a singlet signal at 5.65 ppm due to the diphenylmethyne proton, and also a singlet signal

Scheme 1:
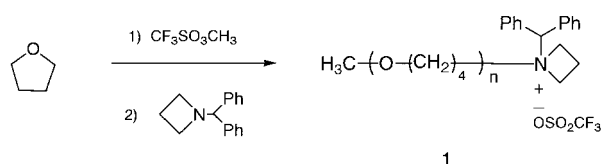
at 3.32 ppm due to the methoxy group originating from the initiator.

The subsequent ion-exchange and ring-opening reactions of thus obtained **1** was examined with sodium benzoate and *p*-nitrobenzoate (**2a** and **2b**, respectively) through the precipitation of **1** in THF solution into an ice-cooled aqueous solution containing an excess amount of **2a** or **2b** (*Scheme 2*; Tab. 1, entries 1 and 2).

The ion-exchange (and subsequent spontaneous ring-opening) reaction of **1** was incomplete after the first precipitation treatment, but proceeded to completion by repeating the precipitation treatment up to three times. Thus the ion-exchange efficiency of an azetidinium salt

group having a bulky substituent may be improved by the repetition of the precipitation procedure. GPC (Fig. 2) shows that the isolated product **3a** possesses unimodal and narrow molecular weight distribution, and the conductivity response due to the ionic end group in the starting **1** is completely removed. This indicates that the ring-opening reaction proceeded quantitatively as in the reactions with azetidinium salt groups of other substituent patterns. The ^{1}H NMR and IR spectroscopic analysis (detailed in Experimental part) also confirmed the quantitative ring-opening reaction. The ring-opening reaction of **1** was also examined by *p*-nitrobenzoate (**2b**) as a counter anion, which was previously observed to be significantly weaker nucleophile than **2a** during the ring-opening reaction of the 5-membered cyclic ammonium salt group at the end of poly(THF)[21]. In the case of the 4-membered cyclic azetidinium salt end group, on the other hand, **2b** was confirmed to be sufficiently reactive to cause a quantitative ring-opening reaction, as listed in Tab. 1 (entry 2).

We have then performed, based on the above results, the ion-coupling reaction of **1** with a series of *pluri*func-
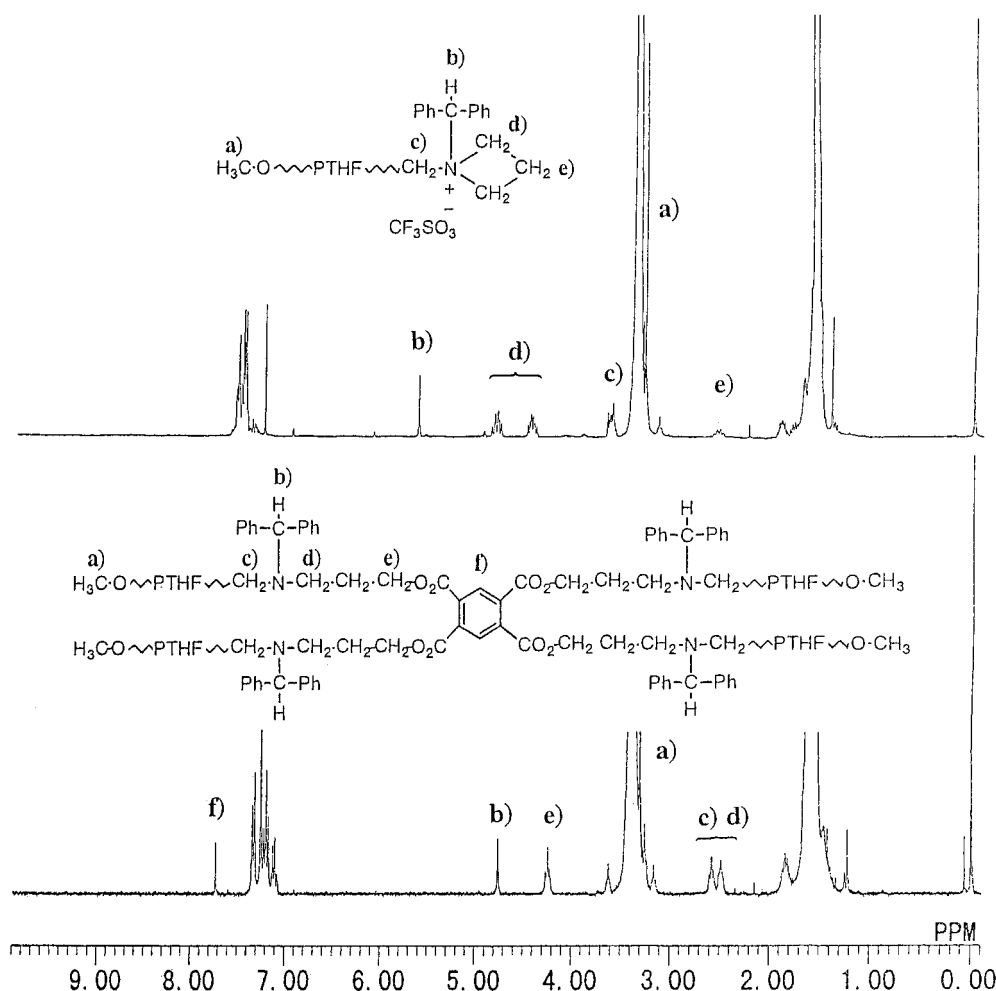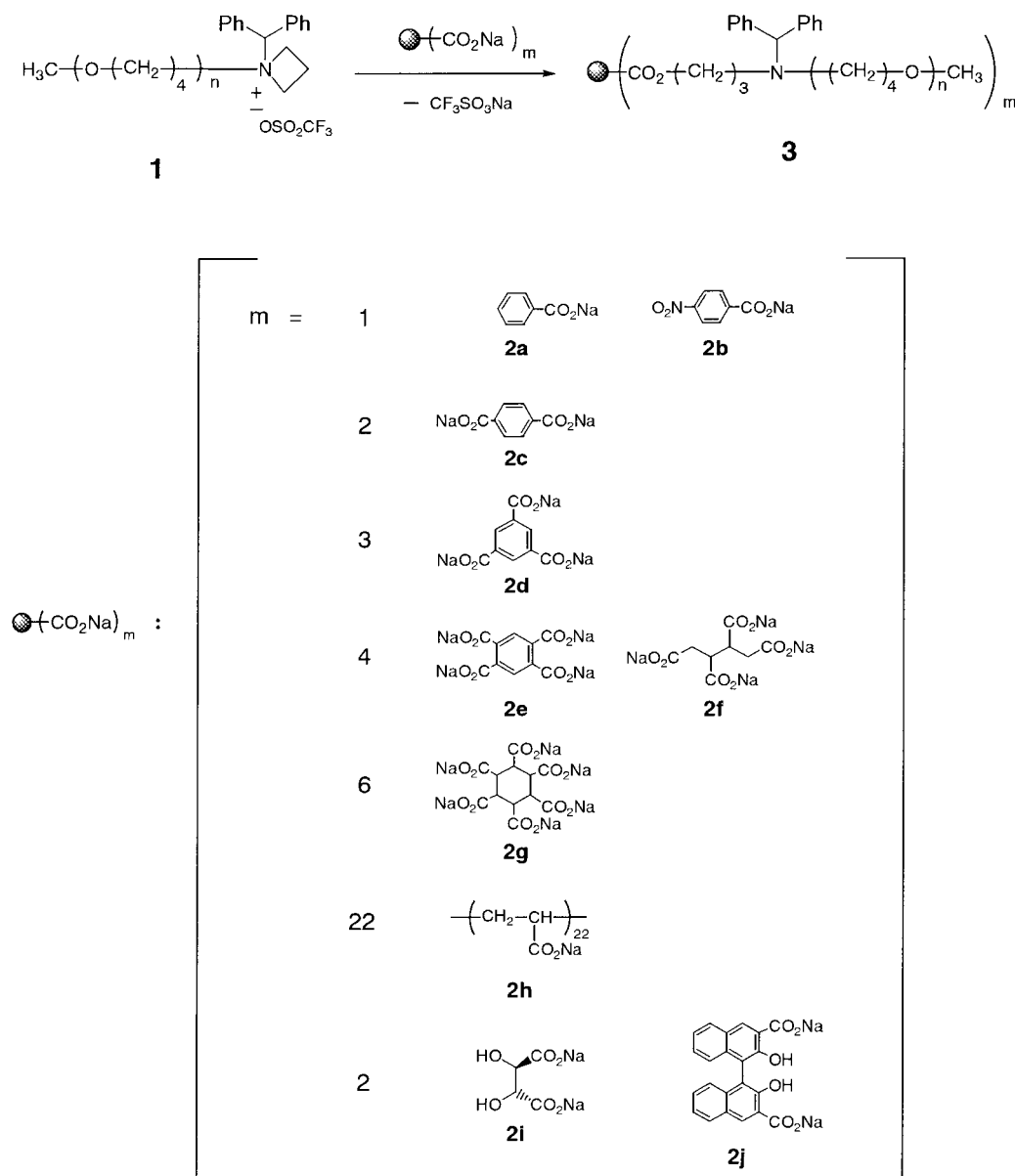

Fig. 1. ^{1}H NMR spectra of monofunctional poly(THF) having an azetidinium salt end group (**1**) (top) and 4-arm star poly(THF) (**3e**) (bottom). (Samples: see Tab. 1, CDCl₃, 40 °C)

Scheme 2:

1　→　**3**

m = 1 **2a**　**2b**

2 **2c**

3 **2d**

4 **2e**　**2f**

6 **2g**

22 **2h**

2 **2i**　**2j**

tional carboxylates. The relevant reaction of monofunctional poly(THF) having a 1,3,3-trimethylazetidinium salt end group with sodium terephthalate (**2c**), trimesate (**2d**) and pyromelitate (**2e**) has been previously reported to give the corresponding multiarmed polymers of up to 4-arms[10]. The ion-coupling reactions of **1** with these plurifunctional carboxylates (**2c–e**) were found to proceed as in the previous system, to give **3c**, **3d**, and **3e**, respectively, after repeating the precipitation three times. The GPC profiles for **3c–e** are collected in Fig. 2 (Tab. 1, entries 3–5). The products **3c–e** retain narrow molecular weight distributions, and the conductivity responses are completely eliminated, indicating that the ionic groups are not present. The molecular weight of **3c** was observed to be nearly twice that of the starting **1**, i. e., 3100. On the

other hand, the apparent molecular weights of **3d** and **3e**, i. e., 3- and 4-arm star polymers, were observed to be 7570 and 9450, respectively, which are significantly smaller than those obtained by multiplying the number of arms (3 and 4) with the molecular weight of starting **1**. This accords with the smaller hydrodynamic volume of **3d** and **3e** than that of the linear analogues. The structures of **3c–e** were also analysed by ¹H NMR spectroscopy. As an example, the ¹H NMR spectrum of the 4-arm star polymer **3e** is shown in Fig. 1 (bottom). The spectrum shows a singlet signal (7.73 ppm) due to the pyromelitate core unit, in addition to a triplet signal (4.26 ppm) due to the ester methylene protons of the arm segments. The signal intensity ratio between them agrees with the one expected for the 4-arm star polymer.

Tab. 1. Ion-coupling reactions between poly(THF) having an azetidinium salt end group (1) and plurifunctional carboxylates (2)[a]

Entry	Sodium[a] carboxylate (m)	Feed molar ratio of carboxylate groups in 2/1	Number of precipitations	Product[b]	Yield[c] in %	$\bar{M}_n$ (GPC)[d]	$\bar{M}_w/\bar{M}_n$[e]
1	2a (1)	20	3	3a	59	3040	1.21
2	2b (1)	10	2	3b	72	3070	1.19
3	2c (2)	20	3	3c	46	5620	1.14
4	2d (3)	20	3	3d	66	7570	1.13
5	2e (4)	40	3	3e	54	9450	1.10
6	2f (4)	10	5	3f	78	8250	1.15
7	2g (6)	10	4	3g	53	12300	1.05
8	2h (22)	10	3	3h	46	39500	1.40
9	2i (2)	20	5	3i	38	5260	1.18
10	2i (2)	20	7	3i	79	5560	1.13
11	2j (2)	10	1	3j	91	5650	1.11

[a]   Poly(THF) (1, $\bar{M}_n$(NMR) = 3100, 0,2 g) was employed, except for entry 10, where poly(THF) (1, $\bar{M}_n$(NMR) = 2900, 1,8 g) was used.
[b]   See Scheme 2.
[c]   The purity of each product was at least 95%, except for entries 6 and 8, where the purity was estimated to be 90%.
[d]   Determined by GPC with a calibration using polystyrene standards by a conversion factor of 0.556[22].
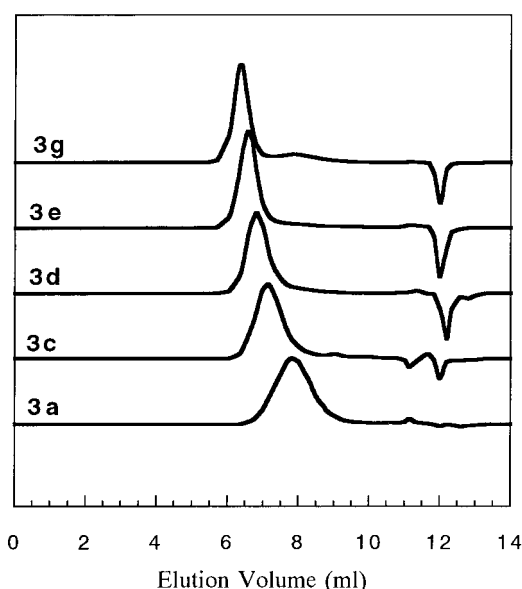[e]   Determined by GPC on the basis of polystyrene standards.

Fig. 2.   GPC (RI) traces of the ion-coupling products of 1 with monofunctional (3a), bifunctional (3c), trifunctional (3d), tetrafunctional (3e), and hexafunctional (3g) carboxylate. (Samples: see Tab. 1, column: TSK G3000HXL, eluent: THF, 1.0 mL/min)

In addition to the above reactions, new star polymers of 4- and 6-arms (3f and 3g) were prepared through the ion-coupling reaction of 1 with a tetra- and a hexacarboxylate (2f and 2g) (Tab. 1, entries 6 and 7). Both GPC (Fig. 2) and ¹H NMR analyses have shown the efficient production of the corresponding star polymers. The apparent molecular weight of 6-arm star polymer 3g observed by GPC analysis ($\bar{M}_n$(GPC) = 12300) is again smaller than the calculated one ($\bar{M}_n$(calc) = 18600). The ¹H NMR spectrum of 6-arm star polymer 3g shows that all the signals due to the azetidinium salt group in 1 were replaced by those due to the ester methylene protons appearing at 3.85–4.04 ppm.

The present ion-coupling reaction of 1 was then applied to the synthesis of a polymacromonomer through the macromolecular ion-coupling reaction with poly(sodium acrylate) (2h) of DP = 22 (Tab. 1, entry 8). As in the reaction of poly(THF) having a tetrahydrothiophenium end group[13], the corresponding polymacromonomer (3h) was obtained in a high yield. As the hydrodynamic volume of the polymacromonomers is consistently smaller than that of a linear polymer of identical molecular mass, the apparent molecular weight of the obtained branched polymers observed by GPC is accordingly smaller than the one calculated from the length and the number of the branch segment in the polymacromonomer (Tab. 1). Hence, the ion-exchange and ring-opening reaction of the azetidinium salt end groups with a series of plurifunctional carboxylates proceeds with high efficiency despite the bulky substituent on the nitrogen atom in 1.

This ion-coupling reaction has also been applied to the synthesis of centro-functional polymers, in which specific functional groups are located at the center position of a linear polymer chain. Thus, sodium salts of (L)-tartaric acid (2i) and 2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylic acid (2j) (racemic) were subjected to the reaction with 1 as in the relevant reactions shown above. Both ¹H NMR spectra of the corresponding products 3i and 3j show a doublet signal at 2.99 ppm ($J = 7.5$ Hz) for the former and a singlet signal at 10.72 ppm for the latter, respectively, due to two hydroxyl protons, in addition to a triplet signal (4.23 ppm for the former and 4.43 ppm for the latter, respectively) due to the ester methylene pro-

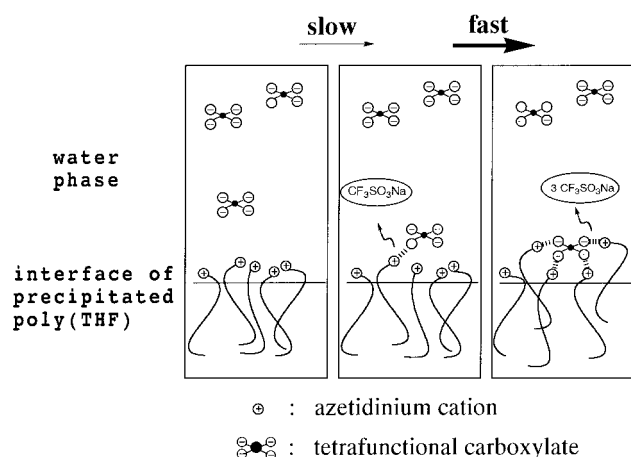⊕ : azetidinium cation

⊖●⊖ : tetrafunctional carboxylate

Fig. 3.   Schematic picture of the mechanism for the ion-coupling reaction of **1** with a tetrafunctional carboxylate

tons. The molecular weight of **3i** and of **3j** observed by GPC was nearly twice that of the starting **1** (Tab. 1, entries 9 and 11). These results indicate that centro-functional poly(THF)s having a diol group were obtained through the ion-coupling reaction of **1** with functional dicarboxylates (**2i** and **2j**). The reduced yield (38%) for **3i** (Tab. 1, entry 9) is apparently due to the multiple precipitation treatment in a small scale. The yield can, thus, be substantially improved (79%, Tab. 1, entry 10) by reaction in a large scale, even involving a multiple precipitation treatment.

The most remarkable feature of this branched polymer synthesis is the exceptionally high efficiency as well as the high selectivity during the ion-coupling process of **1** with plurifunctional carboxylates. This is ascribed to the interfacial process occurring between the precipitated polymer **1** with plurifunctional carboxylate anions in aqueous phase. As schematically shown in Fig. 3, hydrophilic azetidinium salt end groups tend to face the aqueous phase during the precipitation process, and once one carboxylate group in plurifunctional carboxylate anion has entered into an ion-exchange reaction with the azetidinium salt group of the polymer chain end, the plurifunctional carboxylate anion is fixed at the interface of the precipitated polymer/aqueous medium. In consequence, the remaining carboxylate groups become readily accessible to the azetidinium salt group of **1** to promote the further ion-exchange reaction by eliminating water-soluble salt species (i.e., sodium triflate) into the surrounding aqueous medium. Therefore, the present system provides a unique means to get exempt from the stoichiometry requirement between **1** and plurifunctional carboxylates, in contrast to the conventional coupling procedures applied to the synthesis of star polymers and polymacromonomers in homogeneous media.

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