Bis(triflate ester)s Having an Additional Functional Group: Initiators for the Preparation of α,ω,*kentro*-Telechelic Poly(THF)s[1]

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Introduction

Uniform-size polymers having functional groups at the desired positions along the chain are of significant importance as macromolecular building blocks to construct novel and unconventional polymer architectures.[2] Although a variety of *end*-functionalized polymers such as telechelics and macromonomers have so far been synthesized,[3,4] such polymer precursors as those having *inner*-functional groups have scarcely been reported despite their potential utility as macromolecular building blocks. We have recently reported an efficient preparation of such *center*-functional poly(THF)s through the linking reaction between a monofunctionally telechelic poly(THF) having a cyclic onium salt group and a dicarboxylate having an additional functional group such as a diol group.[5]

An alternative means for the preparation of *center*-functional polymers is to develop new initiators. Such an initiator system can provide further opportunity to produce, in combination with an appropriate end-capping reaction, α,*ω*,*kentro*-telechelic polymers.[1] Thus, in the present paper, we report on a novel bifunctional initiator having an additional functional group for *center*-functional poly(THF)s and α,*ω*,*kentro*-telechelic poly(THF)s.

The present study is based on a recently reported efficient method to prepare living poly(THF)s by a novel initiator prepared in situ from a functional alcohol and trifluoromethanesulfonic anhydride (triflic anhydride).[6,7] We have applied this process for the preparation of bi- and trifunctionally living poly(THF)s by using multifunctional benzylic alcohols.[8] As an extension of the preceding studies, we report here on the polymerization of THF with a series of bifunctional initiators having an additional functional group prepared in situ from functional diols and the synthesis of *center*-functional poly(THF)s as well as α,*ω*,*kentro*-telechelics.

Results and Discussion

1. Polymerization of THF by in situ Prepared Bifunctional Triflates Having an Additional Functional Group. Mono- and bifunctionally living poly(THF)s have so far been prepared by in situ generated triflate esters from allyl alcohol,[6,7] benzyl alcohol,[8] and a benzylic diol (1,4-bis(hydroxymethyl)benzene)[8] (Scheme 1). The resonance stabilization of the cationic charge developed on the allylic or benzylic carbon atom at the transition state of the initiation process (i.e., the nucleophilic substitution of the triflate ester by a THF molecule) apparently effectuates a living polymerization of THF. Thus, we have first examined a series of diols, listed in Scheme 2, including bis(allylic alcohol)s and substituted bis(hydroxymethyl)benzenes to generate the corresponding triflate esters for the polymerization of THF.

First, *cis*- and *trans*-2-butene-1,4-diol (**1** and **2**, respectively) were reacted with triflic anhydride in the presence of 2,6-di-*tert*-butylpyridine (DTBP) in dichloromethane at 0 °C. The corresponding bis(triflate ester)s were confirmed to be produced in 3 h. Then THF was added after the solution was warmed at 25 °C. The polymerization reaction was allowed to proceed for 10 min and was then terminated with sodium methoxide up to 10% of monomer conversion, excluding the chain transfer reaction.[9] Although SEC analysis of the produced poly(THF) exhibited a unimodal profile with a narrow molecular weight distribution (PDI = 1.07−1.14), ^{1}H NMR analysis showed the incomplete incorporation of the olefinic group originating from **1** or **2** (functionality = 0.46−0.53). Moreover, the concurrent *cis*−*trans* isomerization of olefinic groups, i.e., from *cis* to *trans* form up to 15% and from *trans* to *cis* up to 20%, was observed in both poly(THF)s produced from **1** and from **2**, respectively. An intramolecular cyclization process through a nucleophilic substitution reaction of an allyloxy group with an allyl triflate group during a key initiation step[10] is assumed to be involved as shown in Scheme 3. On the other hand, the mechanism of the *cis*−*trans* isomerization is obscure at present.

In the case of *trans*-3-hexene-1,6-diol (**3**) as a precursor of a bifunctional initiator (entry 1 in Table 1), the initiation was sluggish, though the corresponding bis(triflate ester) was formed quantitatively. Thus, even after 20 min, 55% of the triflate ester remained unreacted. The SEC of the obtained poly(THF) shows a broad molecular weight distribution (PDI = 1.45), while ^{1}H NMR shows a quantitative incorporation of an olefinic group in the product. The type of alkyl groups in in situ formed triflate esters has been shown to exert a significant steric effect.[7] Thus, the rate of initiation by in situ prepared *n*-butyl triflate is notably slower than the relevant ethyl triflate. Furthermore, the homoallyl group in **3** is no longer capable of stabilizing any cationic charge, developed on the triflate ester methylene carbon atom at the transition state of the initiation process, in contrast to allyl or benzyl triflates. The incapability of the norbornene derivatives from **4** or from **5** to give any polymer product will also be ascribed to both steric and electronic effects.

In contrast, a bis(triflate ester) from 2-butyne-1,4-diol (**6**) was found to produce a bifunctionally living poly(THF). As shown in Figure 1 (bottom), the ^{1}H NMR spectrum of the obtained poly(THF) **VIa**, after the termination with sodium methoxide, shows a singlet at 4.16 ppm due to propargyl protons in addition to a singlet at 3.32 ppm due to methoxy end groups. The signal intensity ratio of the former against the latter is close to that predicted from the chemical formula. Besides, the SEC (Figure 1, top) shows a narrow molecular weight distribution (PDI = 1.11) of the

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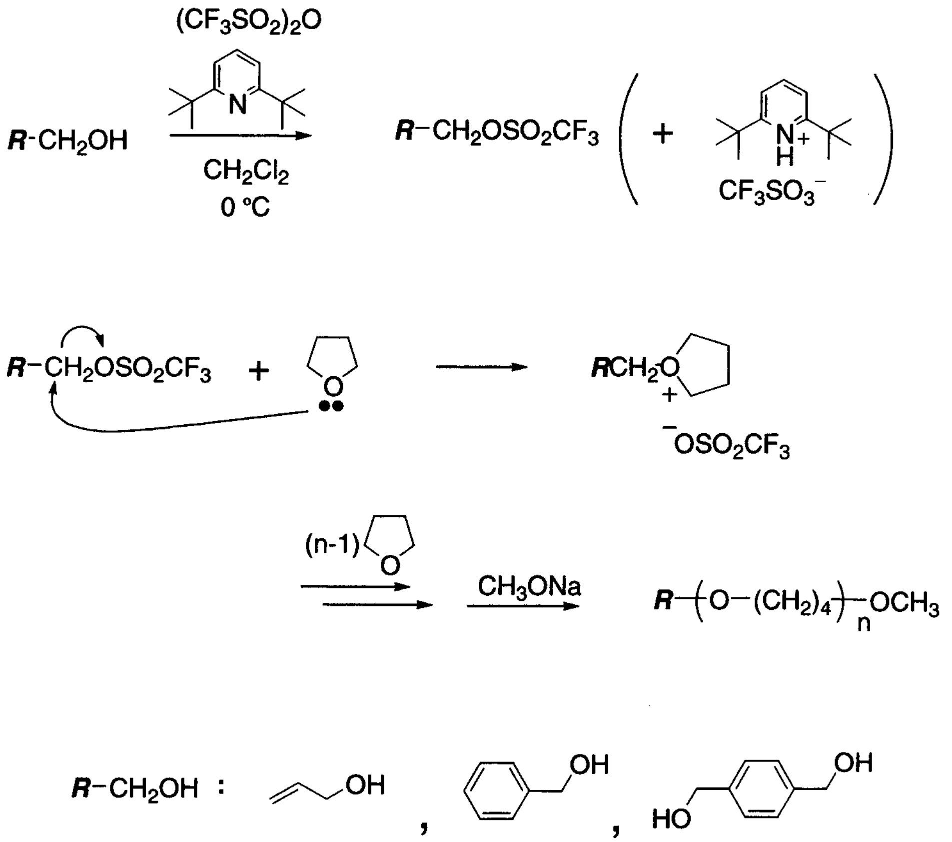
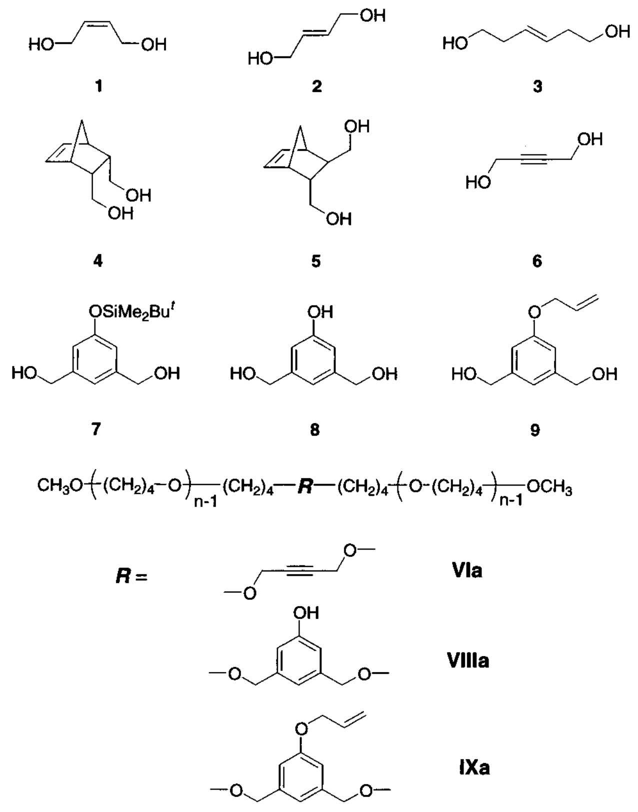
Scheme 1



Scheme 2



obtained poly(THF). These are typical features of a living polymerization process, namely the rapid and quantitative initiation, by the bis(triflate ester) prepared in situ from **6**.

In addition, a substituted bis(hydroxymethyl)benzene, namely 1-(*tert*-butyldimethylsiloxy)-3,5-bis(hydroxymethyl)benzene (**7**), was synthesized as a precursor for a triflate initiator (Scheme 4). A bis(triflate ester) was formed in dichloromethane at 0 °C as confirmed by ^{1}H NMR analysis. The polymerization proceeded by subsequent addition of THF to this initiator solution warmed at 25 °C. The ^{1}H NMR spectrum (Figure 2, bottom) of the obtained poly(THF) **VIIIa**, after the termination with sodium methoxide (entry 2 in Table 1), shows signals at 6.77 and 6.73 ppm due to phenyl protons, a singlet at 4.43 ppm due to benzylic methylene protons from the center unit originating from **7**, and also a singlet at 3.32 ppm due to the methoxy groups originating from the terminator. The *tert*-butyldimethylsilyl protecting group was found to have been totally removed during precipitation of the reaction mixture into water. Thus, the ^{1}H NMR spectrum shows a broad singlet at 6.52 ppm due to a phenolic hydroxy proton, which disappears after the addition of D_2O. The SEC (Figure 2, top) of **VIIIa** shows a unimodal profile with a narrow molecular weight distribution (PDI = 1.19) indicative of a living polymerization by rapid initiation. The introduction of a *tert*-butyldimethylsilyl protecting group on the phenolic hydroxy group in **7** is a prerequisite to achieve a living polymerization of THF, since a triflate ester formed from unprotected 1-hydroxy-3,5-bis(hydroxymethyl)benzene (**8**) failed to produce poly(THF) with a well-defined structure. On the other hand, the initiator from 1-allyloxy-3,5-bis(hydroxymethyl)benzene (**9**) was found to produce a bifunctionally living poly(THF) (entry 4 in Table 1 and Figure 3) as in the case with **7**, though the bis(triflate ester) of **9** gradually decomposed to form an insoluble, unassignable product in the absence of THF.

Scheme 3

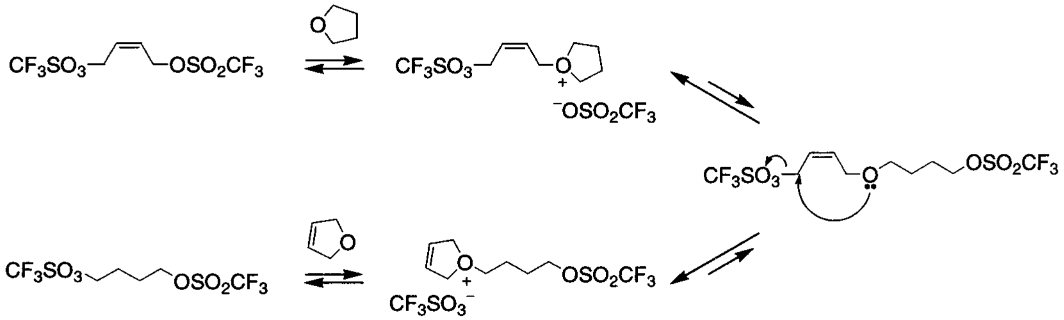


Table 1. Synthesis of *center*-Functional Poly(THF)s by Functional Bis(triflate ester) Initiators Prepared in situ[a]

entry	diol[b]	poly(THF)[b]	M_n(NMR)[c]	M_n(SEC)[d]	PDI[e]
1	**6**	**VIa**	4800	5000	1.11
2	**7**	**VIIIa**	5900	6100	1.19
3	**7**	**VIIIb**	5700	5800[f]	1.11
4	**9**	**IXa**	7200	7400	1.07

[a] Typical reaction conditions: preparation of triflate esters: alcohol, 0.74×10^{-3} mol; $(CF_3SO_2)_2O$, 1.49×10^{-3} mol; DTBP, 2.23×10^{-3} mol; CH_2Cl_2, 3 mL; 0 °C, 1 h. polymerization: THF, 30 mL; 25 °C; 10 min (entries 1−3) or 11 min (entry 4). [b] See Schemes 2 and 5. [c] Determined by ^{1}H NMR spectroscopy assuming the functionality of 1.0 for the *center*-functional group. [d] Determined by SEC with the calibration using polystyrene standards by a conversion factor of 0.556.[19] [e] Determined by SEC on the basis of polystyrene standards. [f] Estimated from the corresponding poly(THF) obtained after the ion-exchange and subsequent ring-opening reaction with sodium benzoate.

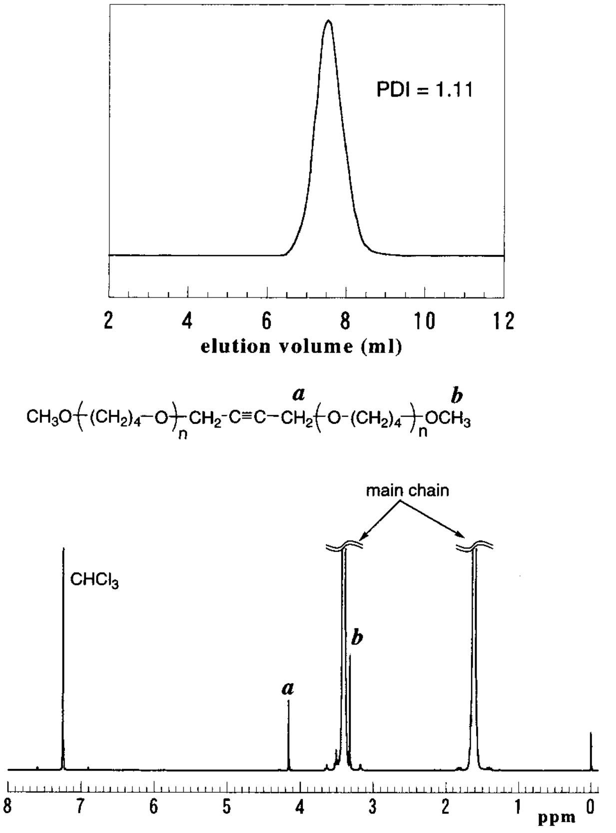


Figure 1. SEC trace (RI, top) and 300 MHz ^{1}H NMR spectrum (bottom) of poly(THF) **VIa** prepared from bis(triflate ester) of 2-butyne-1,4-diol (**6**) (sample: entry 1 in Table 1; column for SEC: TSK G3000HXL; eluent: THF, 1 mL/min; solvent for NMR: $CDCl_3$, 40 °C).

2. Synthesis and Reactions of α,ω,*kentro*-Telechelic Poly(THF). On the basis of above results, we have carried out the synthesis of a novel telechelic poly(THF) having an additional functional group at the center position of the polymer chain. Thus, a bifunctionally living poly(THF) obtained with a bis(triflate ester) from **7** was end-capped with *N*-phenylpyrrolidine (entry 3 in Table 1). The relevant mono- and bifunctionally telechelic poly(THF)s have been recently prepared for a versatile prepolymer to synthesize various polymer architectures.[11−15] The ^{1}H NMR spectrum (Figure 4, top) of the obtained poly(THF) **VIIIb** shows the presence of the *N*-phenylpyrrolidinium salt end groups as evidenced by typical AB pattern signals due to the *endo*-cyclic ammonium methylene protons at 4.04−4.12 ppm and at 4.26−4.36 ppm, by multiplets at 3.86−3.94 ppm due to the *exo*-cyclic ammonium methylene protons, and by mulitplets at 7.50−7.66 ppm due to the aromatic protons. In addition, a broad singlet at 6.50 ppm due to the hydroxy group as well as three singlets at 6.77, 6.73, and 4.43 ppm, due to the initiator fragment, is also clearly visible. The quantitative end-capping reaction was confirmed by comparing the signal intensity ratio of the pyrrolidinium end groups against those from the center unit originating from **7**.

Furthermore, the ion-exchange reaction and subsequent ring-opening reaction of *N*-phenylpyrrolidinium salt end groups in **VIIIb** were conducted with sodium benzoate, as in the mono- and bifunctionally telechelic poly(THF)s (Scheme 5).[12] The ^{1}H NMR spectra of the ion-exchange product before and after the heat treatment are compared in Figure 4 (middle and bottom, respectively). The quantitative ion-exchange reaction and the subsequent ring-opening reaction of *N*-phenylpyrrolidinium salt by heat treatment were thus confirmed. During the transformation of the end groups, the signals due to the center unit, such as a signal at 6.46 ppm, remain intact, demonstrating the high chemoselectivity in the ring-opening reaction of the *N*-phenylpyrrolidinium salt group. In addition, the SEC profile (Figure 5, bottom) of the obtained poly(THF) after the heat treatment is compared with that of starting **VIIIb** (Figure 5, top). The elution delay and the peak tailing observed for **VIIIb** are ascribed to the interaction between the ionic end groups and SEC gel beads surfaces and subsequently eliminated completely after the covalent conversion of ionic groups by the heat treatment. In consequence, the symmetrical and unimodal profile with low polydispersity index (PDI = 1.11) was obtained.

In conclusion, functional bis(triflate ester)s have been successfully applied in situ for the synthesis of bifunctionally living poly(THF)s for *center*-functional poly(THF)s. Subsequent end-capping reaction with a suit-

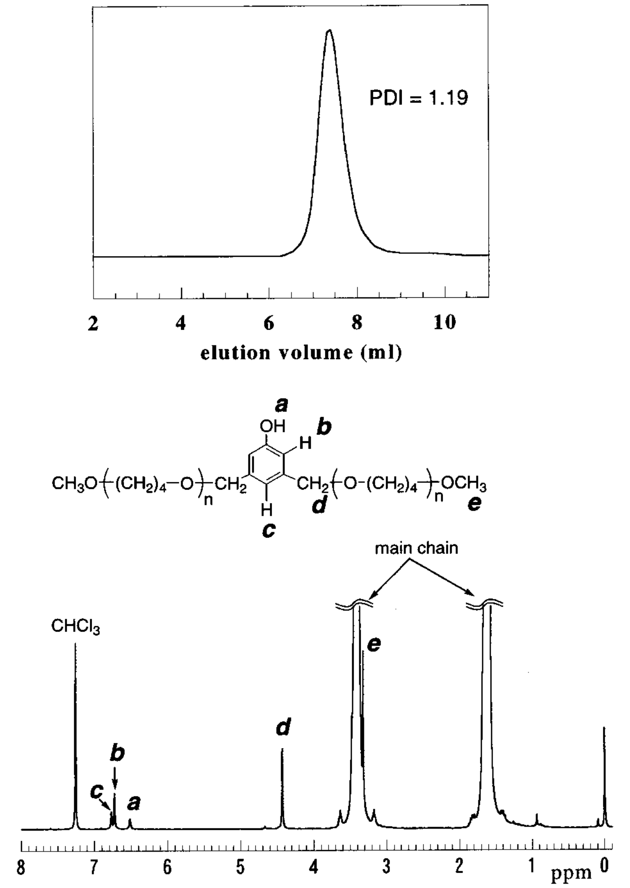
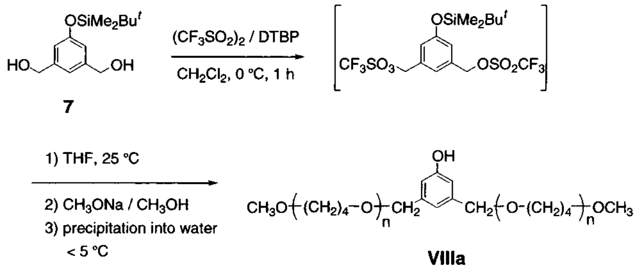


Figure 2. SEC trace (RI, top) and 300 MHz ^1H NMR spectrum (bottom) of poly(THF) **VIIIa** prepared from bis(triflate ester) of 1-(*tert*-butyldimethylsiloxy)-3,5-bis(hydroxymethyl)benzene (**7**) (sample: entry 2 in Table 1; column for SEC: TSK G3000HXL; eluent: THF, 1 mL/min; solvent for NMR: $CDCl_3$, 40 °C).

Scheme 4



able nucleophile such as moderately strained cyclic amine produced a novel telechelic poly(THF) having an additional hydroxy group at the center position of the polymer chain. Further studies on the use of these new telechelics for the construction of a variety of unique polymer architectures are currently in progress.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled just before use. Dichloromethane (CH_2Cl_2) and 2,6-di-*tert*-butylpyridine (DTBP; Aldrich, 97%) were distilled from CaH_2. Trifluoromethanesulfonic anhydride (triflic anhydride) was purified by distillation over P_2O_5 just before use. *cis*-2-Butene-1,4-diol (**1**) (Tokyo Chemical Industry Co., Ltd.), 2-butyne-1,4-diol (**6**) (Tokyo Chemical Industry Co., Ltd.), and sodium methoxide (28% in methanol) were used as received. *trans*-2-Butene-1,4-diol (**2**),[16] 1-(*tert*-butyldimethylsiloxy)-3,5-bis(hydroxymethyl)benzene (**7**),[17] and *N*-phenylpyrrolidine[12] were prepared as reported. *trans*-3-Hexene-1,6-diol (**3**), 5-norbornene-2-*endo*,3-*endo*-dimethanol (**4**), 5-norbornene-2-*endo*,3-*exo*-dimethanol (**5**), 1-hydroxy-3,5-bis(hydroxymethyl)benzene (**8**), and 1-allyloxy-3,5-bis(hydroxymethyl)benzene were prepared from the corresponding precursors, *trans*-2-butene-1,4-dicarboxylic acid, *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride, *cis*-5-norbornene-2-*endo*,3-*exo*-dicarboxylic acid, dimethyl 5-hydroxyisophthalate, and dimethyl 5-allyloxyisophthalate by reduction with $LiAlH_4$ in 46%, 43%, 91%, 62%, and 81% isolated yield, respectively. Dimethyl 5-allyloxyisophthalate was prepared by Mitsunobu reaction[18] from dimethyl 5-hydroxyisophthalate and allyl alcohol in 88% isolated yield.

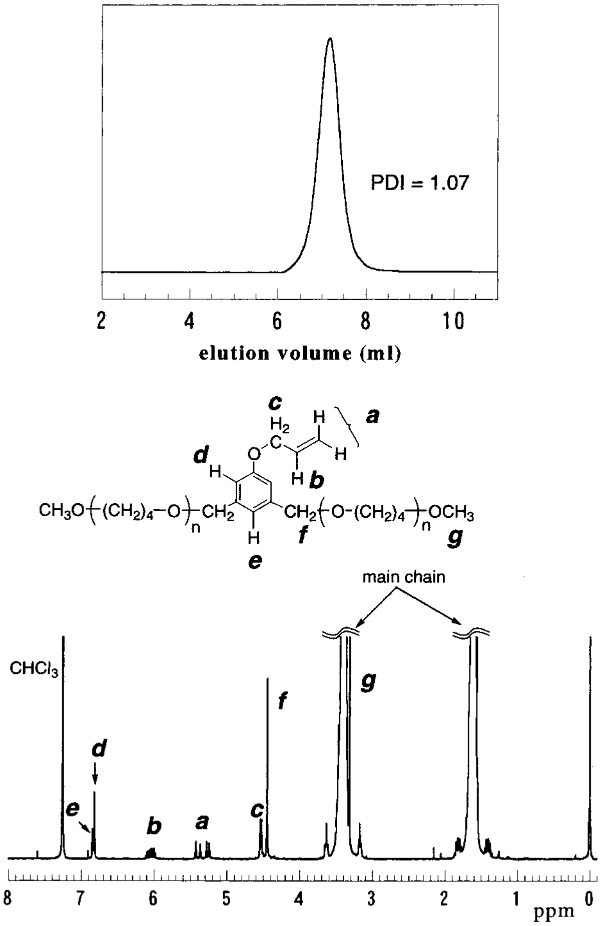


Figure 3. SEC trace (RI, top) and 300 MHz ^1H NMR spectrum (bottom) of poly(THF) **IXa** prepared from bis(triflate ester) of 1-allyloxy-3,5-bis(hydroxymethyl)benzene (**9**) (sample: entry 2 in Table 1; column for SEC: TSK G3000HXL; eluent: THF, 1 mL/min; solvent for NMR: $CDCl_3$, 40 °C).

Preparation of Initiator and Subsequent Polymerization of THF. A typical procedure is as follows. In a dried two-necked flask, 3 mL of CH_2Cl_2, 0.25 mL of DTBP (1.11×10^{-3} mol), and 0.125 mL of triflic anhydride (0.74×10^{-3} mol) were placed at 0 °C. To this solution was added a diol (0.37×10^{-3} mol) under vigorous stirring, and the mixture was stirred for 1 h at 0 °C. The solution was warmed at 25 °C; thereupon 50 mL of THF was introduced. The polymerization was carried out at 25 °C for the prescribed reaction time and was terminated with sodium methoxide (28% in methanol, 1 mL) up to 10% of monomer conversion,[9] excluding the chain transfer reaction. The polymer was quantitatively recovered by precipitation into water in an ice−water bath and dried *in vacuo*. If needed, the polymer was further purified by the reprecipitation into methanol or into petroleum ether in an ice−salt bath.

Preparation of α,ω,*kentro*-Telechelic Poly(THF) VIIIb. A bifunctionally living poly(THF) was prepared by a bis(triflate

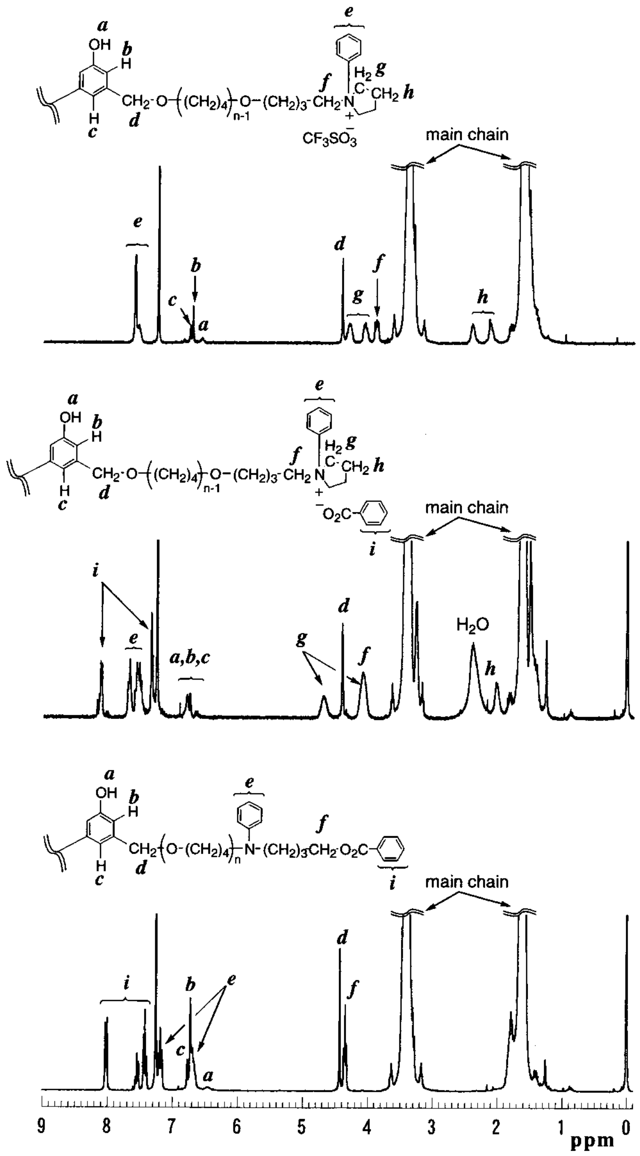


Figure 4. The 300 MHz ^{1}H NMR spectra of α,ω,*kentro*-telechelic poly(THF) (**VIIIb**, top) and the ion-exchange product with sodium benzoate before (middle) and after (bottom) heat treatment (sample: entry 3 in Table 1, $CDCl_3$, 40 °C).

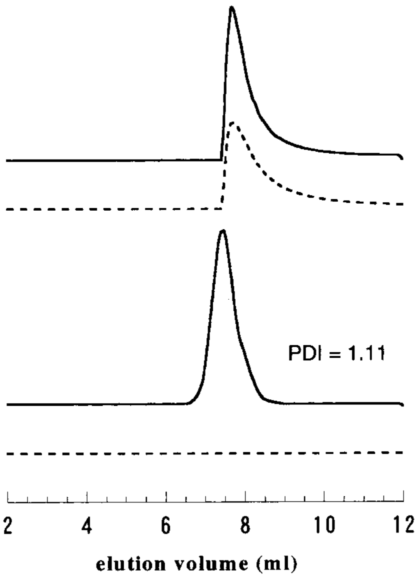
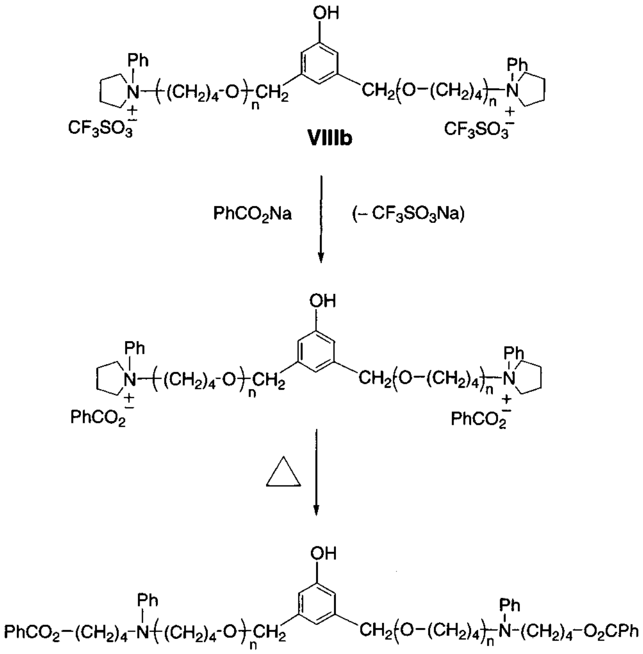


Figure 5. SEC traces of α,ω,*kentro*-telechelic poly(THF) (**VIIIb**, top) and the ion-exchange product with sodium benzoate after heat treatment (bottom) (sample: entry 3 in Table 1; column: TSK G3000HXL; eluent: THF, 1 mL/min; solid line: refractive index trace; broken line: conductivity trace).

Scheme 5



ester) as an initiator, prepared from 1-(*tert*-butyldimethylsiloxy)-3,5-bis(hydroxymethyl)benzene (**7**) (0.40 g, 1.5 × 10^{-3} mol) and triflic anhydride (0.84 g, 3.0 × 10^{-3} mol) in the presence of DTBP (0.90 g, 4.7 × 10^{-3} mol), according to the method detailed above. The polymerization was allowed to proceed for 7 min and subsequently terminated with an excess amount of *N*-phenylpyrrolidine (2.3 g, 15.6 × 10^{-3} mol). The produced trifunctional poly(THF) **VIIIb** was precipitated first in petroleum ether in an ice−salt bath and recovered after subsequent precipitation into water in an ice−water bath.

Ion-Exchange and Ring-Opening Reaction of *N*-Phenylpyrrolidinium Salt End Groups of VIIIb. To an ice-cooled (<5 °C) aqueous solution (200 mL) containing an excess amount of a sodium benzoate (20 equiv) was added dropwise THF solution (10 mL) of 0.4 g of trifunctional poly(THF) **VIIIb** under vigorous stirring. After 1 h, the precipitated ion-exchange product was collected by filtration and dried in vacuo. This precipitation treatment was repeated four times to complete the ion-exchange reaction. This ion-exchange product was then subjected to a heat treatment in THF at reflux temperature for 3 h. After removal of the solvent, the ring-opening product was collected.

Measurements. SEC measurements were performed using a Tosoh model CCPS equipped with a refractive index detector model RI 8020, a UV detector model UV 8020 at 254 nm, and a conductivity detector model CM 8010. A column of TSK G3000HXL was employed with THF as an eluent at a flow rate of 1.0 mL/min. IR spectra were taken on a JASCO FT/IR-410 infrared spectrometer by casting a sample from a 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 (ppm) were referenced from a signal of tetramethylsilane.

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References and Notes

(1) An “α,*ω*,*kentro*-telechelics” refers to a novel telechelic (thus, end-reactive) polymer precursor, possessing an additional functional grous at the center (“*kentro* in Greek”) position of the chain. We propose the term “α,*ω*,*kentro*-telechelics”, since the usage of the Greek “*kentro*” is apparently consistent with the Greek-based term “*telechelics*”. This class of telechelics has previously been reported, without referring to the terminology. See: Deffieux, A.; Schappacher, M. *Macromolecules* **1995**, *28*, 2629−2636.

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