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END-CAPPING REACTION OF TRIFLUORO-METHANESULFONIC ANHYDRIDE-INITIATED LIVING POLY(TETRAHYDROFURAN) WITH LITHIUM OR SODIUM SALT OF METHYL *p*-HYDROXYBENZOATE: IDENTIFICATION OF SIDE PRODUCTS AND SYNTHESIS OF BENZOIC ACID-TERMINATED TELECHELIC POLY(TETRAHYDROFURAN)

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NOTE

END-CAPPING REACTION OF TRIFLUOROMETHANESULFONIC ANHYDRIDE-INITIATED LIVING POLY(TETRAHYDROFURAN) WITH LITHIUM OR SODIUM SALT OF METHYL *p*-HYDROXYBENZOATE: IDENTIFICATION OF SIDE PRODUCTS AND SYNTHESIS OF BENZOIC ACID-TERMINATED TELECHELIC POLY(TETRAHYDROFURAN)

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Key Words: Poly(tetrahydrofuran), Benzoic Acid, Telechelic Polymer, Living Polymer, Trifluoromethanesulfonic Anhydride, Ring-Opening Polymerization, Cationic Polymerization

ABSTRACT

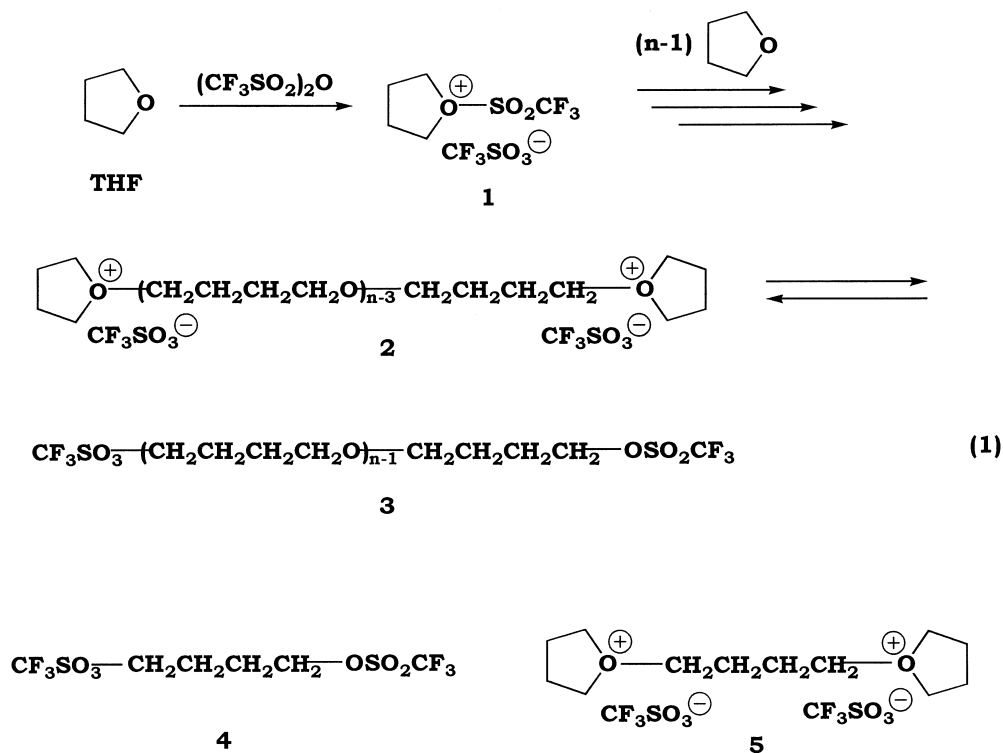
In order to synthesize telechelic poly(tetrahydrofuran) [poly(THF)] with benzoic acid terminal groups (**9**), the reaction of bifunctional living cationic poly(THF) initiated by trifluoromethanesulfonic anhydride with lithium or sodium salt of methyl *p*-hydroxybenzoate was performed in THF solvent at 0°C. The product was found to be the mixture of telechelic

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poly(THF) with the benzoate ends (**8**) and oligomers with the same benzoate moieties (**10** and **11**). Alkaline hydrolysis of the mixture of the polymer and the oligomers and the subsequent treatment of the hydrolyzed products with water enabled us to recover the telechelic poly(THF) with benzoic acid ends (**9**) without contamination by any oligomeric products.

INTRODUCTION

Poly(tetrahydrofuran) [poly(THF)] is of commercial importance as the soft segment of thermoplastic polyurethane and polyester elastomers [1]. Since Smith and Hubin reported the simple synthesis of bifunctional living poly(THF) by the ring-opening cationic polymerization of THF with use of the anhydride of trifluoromethanesulfonic acid $[(CF_3SO_2)_2O]$ [2] (Equation 1), the end-capping reactions of the living poly(THF) with nucleophilic terminators have been often utilized for the preparation of a variety of functional polymers and model polymers of particular structures [3,4]. The examples include telechelic polymers [5-16], block copolymers [17-22], network polymers [23-25], and ionomers [26-30] of well-defined structures.



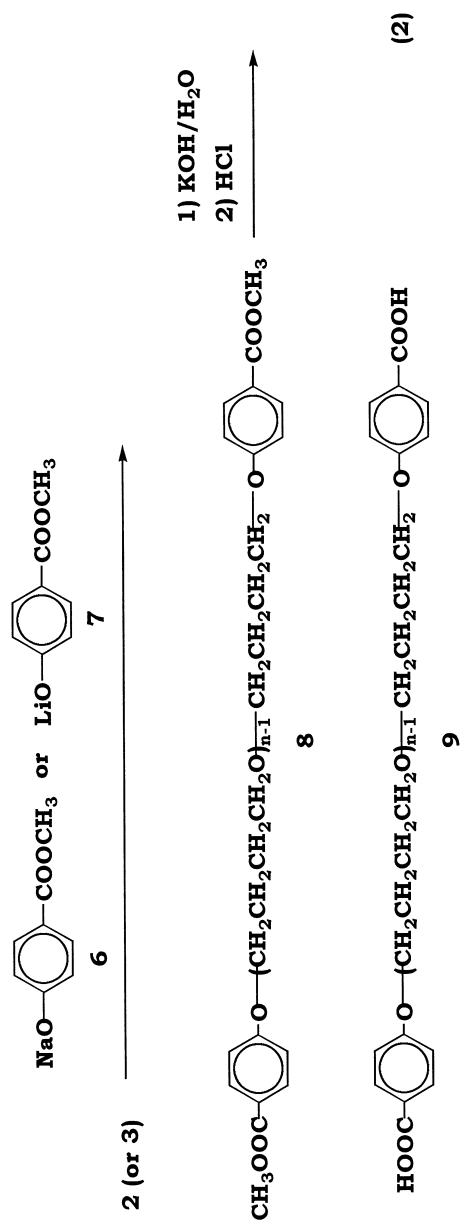
The later publication by Smith's group [31] described that two oligomeric intermediates, tetramethylene bistriflate (**4**) and a bisoxonium ion salt (**5**), was formed in the $(\text{CF}_3\text{SO}_2)_2\text{O}$ -initiated living polymerization of THF. The former species initiated living propagation of THIF at much slower rate than its ionic counterpart (**1**) and hence, the obtained poly(THF) exhibited a bimodal molecular weight distribution (MWD). The latter intermediate was formed during the polymerization when high initial $(\text{CF}_3\text{SO}_2)_2\text{O}$ concentration was employed. These facts suggest that the corresponding side products might be produced in the course of the terminating reactions employed for the syntheses of the above-mentioned polymers [5-30]. It is rather surprising, therefore, that none of the previous studies observed the formation of the side products derived from the species **4** and **5** [5-30].

Noting this problem, we decided to reinvestigate the possible formation of side products in the end-capping reaction of the living poly(THF) initiated by $(\text{CF}_3\text{SO}_2)_2\text{O}$. The reaction of the living poly(THF) with alkali metal salts of methyl *p*-hydroxybenzoate (**6** and $(\text{CF}_3\text{SO}_2)_2\text{O}$; Equation 2) [11] was chosen for this investigation because of the following two reasons; (1) the phenoxide-type terminator is known to react with both the oxonium ion propagating species (2) and the ester counterpart (3) of THF to give the phenyl ether terminal [32, 33] and hence the oligomers **4** and **5** would be also converted into the corresponding stable product [31]. (2) The product benzoate-capped poly(THF) (**8**) is the precursor of the benzoic acid-terminated telechelic poly(THF) (**9**) (Equation 2) [11]; because benzoic acid moieties form stable dimers, the benzoic acid-terminated telechelic polymers have recently received much attention for constructing new supramolecular polymer assembly [34-36]. In addition to detection and identification of the oligomeric products, we explored a simple way to separate the undesirable side products from the acid-terminated telechelic polymer (**9**).

EXPERIMENTAL

Materials

THF (Wako Pure Chemicals) was dehydrated over molecular sieves (4A 1/16) for several days, and refluxed and then distilled three times over lithium aluminum hydride before used. $(\text{CF}_3\text{SO}_2)_2\text{O}$ was prepared and purified according to the literature [37]. The lithium and sodium salts **6** and **7** were prepared by the reactions of methyl *p*-hydroxybenzoate with sodium hydride and with lithium hydride, respectively, in THF at room temperature, and purified by washing with THF.



Polymerization and End-Capping Reaction

Bulk polymerization of THF with $(\text{CF}_3\text{SO}_2)_2\text{O}$ was carried out according to the procedures described by Smith and Hubin [2]. The polymerization was initiated by injecting neat $(\text{CF}_3\text{SO}_2)_2\text{O}$, via dry syringes, into the purified THF (90 mL) at 0°C and the reaction mixture was stirred for 10 minutes at this temperature. The polymerization was quenched by adding a THF solution of excess amount of **6** or **7** at 0°C as reported by Kobayashi *et al.* [11] The mixture was filtered to remove insoluble residue and the filtrate was evaporated to dryness to give the product. The product was purified by reprecipitation in cold water ($\sim 2^\circ\text{C}$; ca. 900 mL) from THF (20 mL) to remove the unreacted salt (**6** or **7**) completely. Conversion of THF was obtained gravimetrically: ca. 12% ($[(\text{CF}_3\text{SO}_2)_2\text{O}]_0 = 0.080 \text{ mol/L}$); ca. 4% ($[(\text{CF}_3\text{SO}_2)_2\text{O}]_0 = 0.014 \text{ mol/L}$). Fractions containing the oligomeric products were separated from the polymeric products by preparative GPC in chloroform on a Jasco Trirotar-11 chromatograph equipped with a polystyrene gel columns (Shodex H2000P) and a refractive index detector. For VPO measurement, the polymer samples were further purified by freeze-drying from benzene.

Conversion of Ester End into Benzoic Acid Moiety and Removal of Side Products

To a solution of ester-capped polymer **8** (5.0 g) in ethanol (40 mL) was added 0.5 mol/L-KOH ethanol solution (100 mL) and water (10 mL), the solution was heated to 85°C with magnetic stirring for 3 hours. The resulting mixture was cooled to room temperature and evaporated to dryness. The residue was washed with water (300 mL) to remove the oligomeric salts, and the insoluble polymeric salt was collected by filtration. The polymer was dissolved in ethanol (200 mL), and the 0.1 mol/L-hydrochloric acid was added to the solution to convert the potassium salt end into the benzoic acid moiety. The mixture was filtered to remove an insoluble by-product (KCl), and the filtrate was evaporated to dryness. The recovered polymer was purified by reprecipitation in cold water ($\sim 2^\circ\text{C}$; ca. 900 mL) from THF (20 mL); yield: ca. 1.2 g.

Measurements

The MWD of the products was measured by GPC in tetrahydrofuran on a Shimadzu LC-10AD chromatograph equipped with three polystyrene gel columns (Shodex 80M \times 2 and KF-203.5) and a refractive index (RI) detector. The \bar{M}_n , and \bar{M}_w/\bar{M}_n values were calculated from chromatograms based on a

polystyrene calibration. The GPC measurements for the determination of the relative molar fractions of oligomers and polymers in the products were carried out in chloroform on a Shimadzu LC-10AD chromatograph equipped with three polystyrene gel columns (Shodex K-804L \times 3) and a Hitachi L-7400 UV detector (254 nm) [31]. The integral intensities of UV traces of oligomers and polymers were measured by the weighing method. VPO measurement was conducted on a Hitachi 117-type osmometer in benzene at 40°C. ^1H NMR spectra were recorded on Jeol EX-270 instrument in CDCl_3 at room temperature with tetramethylsilane as an internal standard. The carboxyl content of the polymers was measured by alkaline titration with 0.1 mol/L-ethanolic KOH in ethanol with phenolphthalein as an indicator.

RESULTS AND DISCUSSION

The THF polymerizations was initiated with $(\text{CF}_3\text{SO}_2)_2\text{O}$ and terminated with the phenoxide salts (Equation 2). Figure I shows the MWD of the products obtained with **6** or **7** [measured by gel-permeation chromatography (GPQ)]. Both

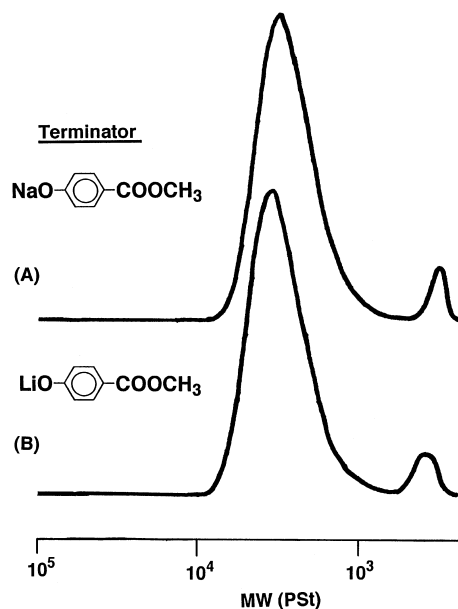


Figure 1. MWD curves of the products obtained by quenching the living polymerization of THF initiated by $(\text{CF}_3\text{SO}_2)_2\text{O}$ with terminator **6** (A) and terminator **7** (B).

the products consist of a polymeric fraction and an oligomeric fraction, and the MWD of the former is relatively narrow (polydispersity ratio, $= \bar{M}_w/\bar{M}_n = \sim 1.2$; Table 1). To analyze the oligomer structure, the oligomer fraction separated from the polymeric fraction by preparative GPC. During the measurement of the preparative GPC chromatograms, the oligomeric fraction was found to involve two kinds of oligomers [designated as fraction **I** (lower elution volume) and **II** (higher elution volume)] and they were separated from each other and subjected to NMR measurement.

Figure 2 shows ^1H NMR spectra of the two oligomers produced with the terminator **7**. The absorptions of the oligomer **I** (spectrum A) are attributable to the structure of a unimer of THF with the benzoate terminals (**10**). For example, peaks **d** and **e** are due to the methylene chain protons, and peaks **a**, **b**, and **c** are ascribed to the protons of the methyl benzoate ester. On the other hand, the signals of oligomer **11** (spectrum B) are consistent with the structure of a dimer of THF with the same benzoate terminals (**11**). The peaks due to the three kinds of the methylene groups, **d**, **e**, and **f**, were observed, and the signals of the benzoate ester was detected as peaks **a**, **b**, and **c**. The numbers in the Figure 2 indicate the relative signal intensities, with peak **c** as a standard (the value of relative intensity to be 4.0), determined from peak areas; those in parentheses show the calculated values based on the assigned structures (**10** and **11**). The agreement between the calculated and observed values is satisfactory. The oligomers obtained with the terminator **6** had identical structures to those with **7**.

To obtain the relative content of the oligomeric products against the polymeric fraction, we measured the UV traces of the MWD curves of the products in the GPC measurements (see Experimental). The relative molar fractions of oligomeric and polymeric parts were determined by the integrated intensities of each fraction [31]. As shown in Table 2, the relative molar fractions of the mixture of the oligomers **10** and **11** were the values of 29-27 at different initial concentrations of the initiator and with different terminators (**6** and **7**). The contents of the oligomers in the total products are apparently similar to those observed by Smith *et al* under the similar reaction conditions [31].

These results indicate that oligomeric intermediates indeed generated in the $(\text{CF}_3\text{SO}_2)_2\text{O}$ -initiated living polymerization of THF, and they formed the side products (**10** and **11**) in the course of the end-capping reaction of the living polymers. The oligomer **10** was most likely formed by the reaction of the monomeric bistriflate ester **4** with the phenoxide terminators. The oligomer **11** may be derived from the corresponding dimeric species. Under the present reaction conditions, the trimeric side products based on the species **5** were not formed.

TABLE 1. Characterization of Poly(THF)s with Benzoate Ester or Benzoic Acid Terminals (**8** and **9**)^{a)}

Polymer	Code	Terminator	End Group	\overline{M}_n (GPC) ^{b)}	$\overline{M}_w/\overline{M}_n$ (GPC) ^{b)}	\overline{M}_n (VPO) ^{c)}	\overline{M}_n (NMR) ^{d)}	\overline{M}_n (Tit.) ^{e)}	\overline{M}_n (Calc.) ^{f)}
8	i	6	-COOCH ₃	3980	1.22	2090	2040 ^{g)}	-	2030
8	ii	7	-COOCH ₃	3860	1.22	2070	2180 ^{g)}	-	2010
9	iii	- ^{b)}	-COOH	6160	1.19	-	2920 ^{h)}	2870	-

a) Polymerizations were carried out in bulk ([THF]₀ = 12 mol/L) with (CF₃SO₂)₂O (0.080 mol/L) at 0°C for 10 min.

b) By GPC with polystyrene calibration.

c) By VPO.

d) By ¹H NMR spectroscopy; determined from the peak intensity ratio **2f**(**b+c**) in Figure 3 [see ^{d)} and ^{b)}].

e) By Alkaline titration with ethanolic KOH.

f) \overline{M}_n (Calc.) = \overline{DP}_n (Calc.) x 72.12 + 12.01 x 16 + 1.01 x 14 + 16.00 x 5;

\overline{DP}_n (Calc.) = [THF]₀/[(CF₃SO₂)₂O]₀ [molar fraction of polymer **8** to the total products] x conversion (%) / 100.

g) \overline{M}_n (NMR) = \overline{DP}_n (NMR) x 72.12 + 12.01 x 16 + 1.01 x 14 + 16.00 x 5; \overline{DP}_n (NMR) = **2f**(**b+c**) + 1

[see Figure 3(A)].

h) Obtained from polymer **8** (sample code ii)

i) \overline{M}_n (NMR) = \overline{DP}_n (NMR) x 72.12 + 12.01 x 14 + 1.01 x 10 + 16.00 x 5; \overline{DP}_n (NMR) = **2f**(**b+c**) + 1

[see Figure 3(B)].

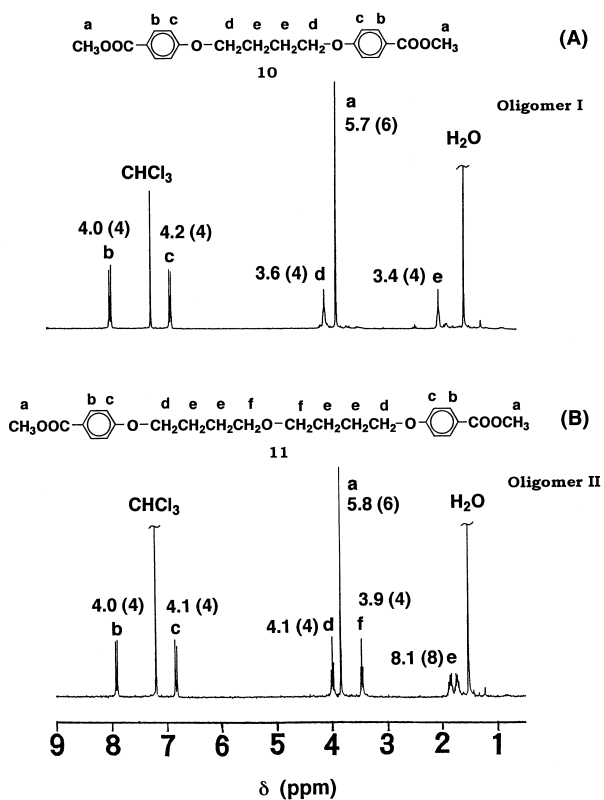


Figure 2. ^1H NMR spectra of oligomer I (A) and oligomer II (B) obtained with terminator 7.

TABLE 2. Product Fraction^a) Measured by UV (254 nm)
Trace of GPC Chromatograms^b)

Terminator	$[(\text{CF}_3\text{SO}_2)_2\text{O}]_0$, mol/L	Relative Molar Fraction	
		Mixture of Oligomers 10 and 11	Polymer 8
6	0.014	29	71
6	0.080	28	72
7	0.080	27	73

a) Polymerizations were carried out in bulk ($[\text{THF}]_0 = 12$ mol/L) with $(\text{CF}_3\text{SO}_2)_2\text{O}$ at 0°C for 10 min.

b) See EXPERIMENTAL.

It is not clear why similar side products have not been detected in a number of previous studies with the end-capping reactions of the same living polymer under the similar reaction conditions [5-30]. One possible reason is, as Smith *et al* already pointed out [31], the use of less resolvable GPC columns for low molecular weight fractions. Another reason might be solubility of the side products in water; almost all the work-up and purification procedures of the products include washing with water and/or reprecipitation in water [5-30], and therefore the by-products that were soluble in water were removed from the main polymeric fraction prior to the MWD and structural analyses. Thanks to their less solubility in water, the oligomers **10** and **11** were recovered even after the treatment with water (see Experimental).

We then analyze the structure of the polymeric fraction (Figure 1). Figure 3(A) depicts the ^1H NMR spectrum of the polymer obtained with the terminator **7**, along with the peak assignments, which exhibits the poly(THF) main chain absorptions (peaks **e** and **f**) and the signals of the terminal methyl benzoate ester (peaks **a**, **b**, and **c**) and the methylene group adjacent to the pbenoxy moiety (peak **d**). On the basis of the peak intensity ratio of the methylene of the poly(THF) chain (peak **f**) to the two terminal aromatic groups (peaks **b** and **c**), the number-average molecular weight $[\overline{M}_n(\text{NMR})]$ was determined (Table 1). The $[\overline{M}_n(\text{NMR})]$ values for both the polymers obtained with the terminator **6** and **7** are very close to the \overline{M}_n 's obtained by vapor pressure osmometry \overline{M}_n (VPO)], indicating that each polymer chain possesses two benzoate esters as the end groups. The (VPO) values are also in good agreement with the calculated \overline{M}_n 's based on the monomer conversion and the initiator fraction used for the polymer formation ($[(\text{CF}_3\text{SO}_2)_2\text{O}]_0 \times$ [molar fraction of polymer **8** to the total products]; see Table 2). This result shows that the polymer fractions in the products generated in a living manner. Although Kobayashi *et al.* have already prepared the same benzoate-capped poly(THF) by the use of the terminator **6** under the similar conditions and the corresponding benzoic acid-telechelic polymer thereby [11], they have not described the formation of the side products (see above).

To remove the side products from the target benzoic acid-capped poly(THF) (**9**) by a simple way, we treated the mixture of the oligomers (**10** and **11**) and the ester-capped polymers (**8**) with an alkaline solution and the resulting salt mixture was washed with water (see Experimental), from which only the polymeric salt was left as a precipitate. The obtained polymeric salt was then converted to the acid form and analyzed by GPC and NMR. The GPC chromatogram of the acid polymer exhibited no peaks due to the oligomeric fractions and its MWD was narrow ($\overline{M}_w/\overline{M}_n = 1.19$) (Table 1). Figure 3(B) illustrates ^1H

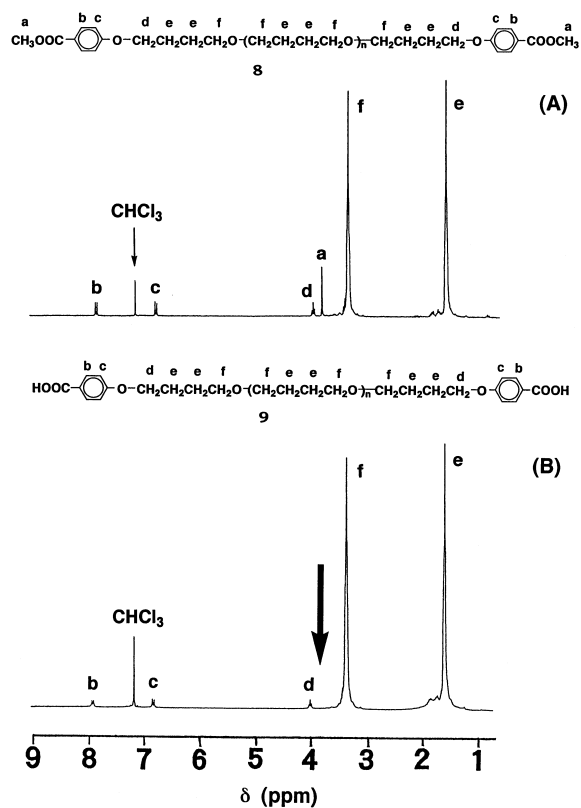


Figure 3. ^1H NMR spectra of polymer **8** obtained with terminator **7** (A) and polymer **9** (B).

NMR spectrum of the polymer. The ester methyl signal **a** in spectrum A is now completely absent in spectrum B as shown by a thick arrow, whereas all other absorptions remain intact during the reaction. The intensity ratio of peak **f** (the main chain methylene) to peaks **b** and **c** (the benzene ring) gave $\bar{M}_n(\text{NMR})$ for the polymer **9** (Table 1). The $\bar{M}_n(\text{NMR})$ value is in good agreement with the \bar{M}_n obtained by alkaline titration $\bar{M}_n(\text{Titr.})$.

CONCLUSION

The oligomeric side products **10** and **11** were found to form in the synthesis of the benzoate ester-terminated telechelic poly(THF) **8** by the reaction of bifunctional living poly(THF) initiated by $(\text{CF}_3\text{SO}_2)_2\text{O}$ with the phenoxide salt

terminators **6** and **7**. The side products were successfully removed by alkaline hydrolysis of the mixture of the ester-terminated poly(THF) and the oligomers followed by washing the hydrolyzed products with water to give the pure benzoate acid-terminated telechelic poly(THF) **9**.

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