Figure 2. Representative optical polarization micrographs (100×) of the nematic texture displayed by PMC-11 after annealing at 162 °C (on cooling scan) for 30 min.

acteristic smectic mesophase upon annealing were unsuccessful so far.

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Registry No. IB, 123640-26-6; IA, 123640-27-7; OC-9, 123640-28-8; OC-6, 123640-29-9; MC-11, 123640-32-4; MC-11 (homopolymer), 123640-37-9; 4′-acetobenzo-15-crown-5, 41757-95-3; benzo-15-crown-5, 14098-44-3; acetic anhydride, 108-24-7; 4′-carboxybenzo-15-crown-5, 56683-55-7; 4,4′-dihydroxybiphenyl, 92-88-6; 10-undecen-1-yl tosylate, 51148-67-5; 4-(11-hydroxyundecan-1-yloxy)-4′-hydroxybiphenyl, 123640-30-2; 11-bromoundecan-1-yl acetate, 30295-23-9; 4-[(11-methacryloylundecan-1-yl)oxy]-4′-hydroxybisphenyl, 123640-31-3.

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Synthesis of Telechelic Poly(tetrahydrofuran) Having a Carboxyl Group Using Ketene Silyl Acetal as a Terminator

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ABSTRACT: Telechelic poly(tetrahydrofurans) (polyTHFs) having a carboxyl or an ester group were synthesized. The living polymerization of THF was achieved with trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$) as initiator, and living propagating species thus formed were terminated with a nucleophile such as a ketene silyl acetal or a ketene bis(silyl acetal) without a catalyst. The structures of polymers were confirmed by IR and ^1H and ^{13}C NMR spectroscopy. Molecular weight was determined by vapor pressure osmometry and ^1H NMR. The functionality of these telechelic polyTHFs having two terminal ester groups was close to 2.0, as determined by ^1H NMR analysis. These telechelic polyTHFs of methyl and trimethylsilyl esters were converted to telechelic polyTHFs having carboxylic acid groups by alkaline hydrolysis.

Introduction

Telechelic polymers are those with reactive groups at both ends. They become increasingly important for practical use, e.g., as a prepolymer for block copolymers or a cross-linking agent. For the preparation of these telechelic polymers, living polymerizations can be most conveniently employed since functional groups are readily introduced via the termination of living propagating species.

Smith and Hubin described the polymerization of THF using trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$) as a bifunctional initiator, which proceeds via living propagating species.[1] They obtained telechelic polyTHFs of glycol and diamine type by terminating the living species

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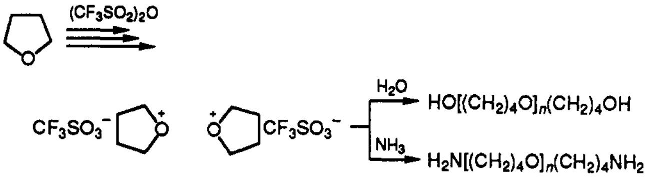
Table I
Synthesis of Telechelic PolyTHF Having Terminal Ester Groups

	polymerization[a]				characterization of 5				
entry	$(CF_3SO_2)_2O$, mmol	THF, mmol	CH_2Cl_2, mL	yield of 5 (g)	DP[b]	M_n[b]	M_n[c]	M_w/M_n[d]	functionality[b]
1	0.955	58.7	25.4	0.32	1.62	366	382		1.99
2	0.950	96.2	22.7	0.46	3.16	477	490	1.37	1.95
3	0.592	82.9	13.5	0.46	8.90	892	880	1.27	1.97
4	0.592	101	11.9	1.20	26.0	2120	2050	1.12	1.98

[a] Polymerization was carried out at 0 °C for 1 h. [b] From ^1H NMR. DP denotes *n* values of 5 calculated by taking the terminal group into account. [c] From VPO. [d] From GPC calibrated with polystyrene standard.

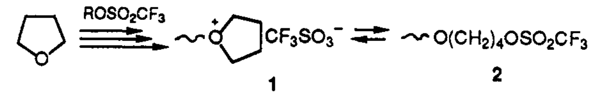
with water and ammonia, respectively. Telechelic polyTHFs having a variety of functional groups could be synthesized by reaction of various nucleophiles with living propagating species.[2]



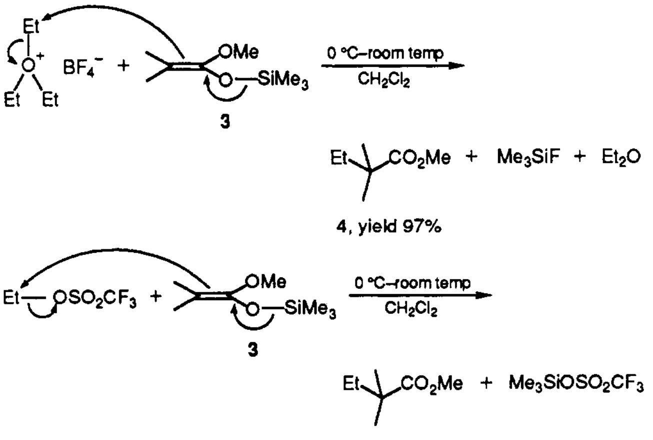
In order to prepare the hitherto unknown telechelic polyTHF having a carboxyl group at the both ends, we paid attention on the nucleophilic reactivity of a ketene silyl acetal **3**. It is well-known that a ketene silyl acetal reacts with various electrophiles a catalyst such as a metal fluoride and a Lewis acid are used.[3] Webster et al. used a ketene silyl acetal as initiator for the living polymerization of methyl methacrylate ("group-transfer polymerization").[4] We wish to report the first synthesis of telechelic polyTHFs having carboxyl groups, in which the living propagating species of THF were reacted with a ketene silyl acetal as a nucleophilic terminator.[5]

Result and Discussion

Model Reaction. An anhydride or ester of a superacid such as CF_3SO_3H gives a living polymerization system for THF, in which the living species are normally in equilibrium between oxonium ions **1** and covalently bonded esters **2**.[1,6]

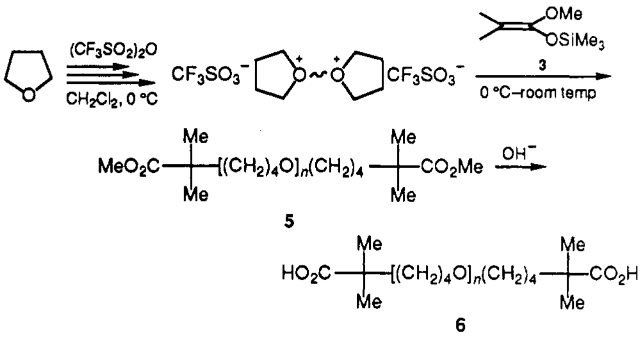


Two model reactions were carried out to examine the reactivity of ketene silyl acetal **3** where triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) and ethyl trifluoromethanesulfonate (CF_3SO_3Et) are model compounds of species **1** and **2**, respectively.



In both reactions the expected compound, methyl 2,2-dimethylbutanoate (**4**), was quantitatively formed without a catalyst, and hence, **3** was taken to have enough reactivity toward the living propagating species of THF, regardless of the nature of the living species.

Synthesis of Telechelic PolyTHF Having a Terminal Ester Group. The ring-opening polymerization of THF was performed with $(CF_3SO_2)_2O$ as a bifunctional initiator in CH_2Cl_2 at 0 °C for 1 h to produce the living propagating species of THF. Then **3** was added to the polymerization mixture at 0 °C and allowed to react for 3 days at room temperature. After workup procedures, telechelic polyTHF **5**, having methyl ester groups at both ends, was obtained.



The structure of **5** was confirmed by IR and ^1H and ^{13}C NMR spectroscopy. Hydroxyl group would be contained in the terminal groups of **5** if the living propagating species of THF was not quantitatively reacted with **3**. Neither a characteristic peak of the hydroxyl group (ν(O–H), 3400 cm^{-1}) in the IR spectrum of **5** nor a signal due to the methylene carbon adjacent to the terminal hydroxyl group of polyTHF glycol ($\sim CH_2OH$, 61.7 ppm) in the ^{13}C NMR spectrum was detected. These results indicate that the amount of the terminal hydroxyl group is very small, if any, within the sensitivity of IR and ^{13}C NMR spectroscopy. However, more sensitive 400-MHz ^1H NMR spectroscopy showed the presence of terminal methylene protons adjacent to hydroxyl groups in very small amounts. A very small triplet peak b at 3.64 ppm is assigned to protons $\sim CH_2OH$. Other signal assignments are given in Figure 1. Thus, the functionality, i.e., the number of ester groups per molecule **5**, was calculated from the ratio of integrated area of the signals a and b. The degree of polymerization (DP) of **5** was calculated from the ratio of integrated area of the signals a and c. The results of synthesis and characterization of **5** are summarized in Table I. The molecular weight of **5** could be controlled mainly by the concentrations of the initiator and THF. The molecular weight values of **5** calculated by ^1H NMR analysis agreed well with those obtained by vapor pressure osmometry (VPO). The functionality of **5** was close to 2.0 in all runs; a methyl ester group was quantitatively introduced at both ends of polyTHF. It is observed that M_w/M_n values were always narrow, which may be explained as follows. The

Table II
One-Pot Synthesis of Telechelic PolyTHF Having Terminal Carboxylic Acid Groups

	polymerization[a]				characterization of 6			
entry	$(CF_3SO_2)_2O$, mmol	THF, mmol	CH_2Cl_2, mL	yield of 6 (g)	DP[b]	M_n[b]	M_w/M_n[c]	functionality[b]
5	0.914	91.7	22.7	0.43	3.08	477	1.11	1.97
6	0.585	85.6	13.5	0.73	16.0	1410	1.27	2.00

[a] Polymerization was carried out at 0 °C for 1 h. [b] From ^1H NMR. DP denotes *n* value of 6 calculated by taking the terminal group into account. [c] From GPC calibrated with polystyrene standard.

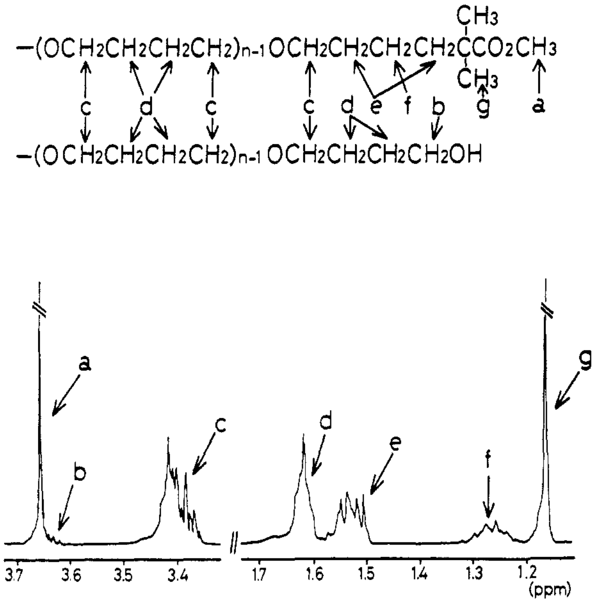


Figure 1. 400 MHz ^1H NMR spectrum of polyTHF having terminal ester group 5 (entry 2).

polymerization of THF almost reached monomer–polymer equilibrium[6] under the reaction conditions when the terminator 3 was added, and/or the actual polymerization system might involve only oxonium propagating species 1 (without ester species 2), and hence, the termination was relatively fast.

Hydrolysis of the Ester Group to Telechelic PolyTHF Having a Terminal Carboxylic Acid Group. The terminal methyl esters of polymer 5 were converted into the corresponding carboxyl groups by alkaline hydrolysis. Thus, treatment of 5 with potassium hydroxide in isopropyl alcohol gave polymers with potassium carboxylate terminals, which were subsequently transformed into the free carboxylic acid form by neutralization with hydrochloric acid. Figures 2 and 3 show ^1H and ^{13}C NMR spectra of the polymer samples before (5) and after (6) hydrolysis. Comparisons between spectra A and B in Figures 2 and 3 show the complete conversion of the methyl esters into the corresponding carboxyl groups. The signals at 3.68 ppm in Figure 2A and at 53.0 ppm in Figure 3A due to the ester methyl group completely disappear in Figures 2B and 3B, respectively. The signal at 180.0 ppm due to the ester carbonyl group shifted to 183.9 ppm, which is assignable to the carbonyl group of the carboxylic acid. The degree of polymerization (DP) of THF and the functionality of the hydrolysis product were determined in a similar manner as for 5 by ^1H NMR spectroscopy. The DP was calculated from the ratio of the integrated areas of the signal at 1.17 ppm and the signal at 3.42 ppm. The functionality was calculated from the ratio of integrated areas of the signal at 1.17 ppm and the signal at 3.64 ppm. The DP and the functionality of 6 (entry 2) are 3.31 and 1.98, respectively, which agree well with the values obtained before hydrolysis.

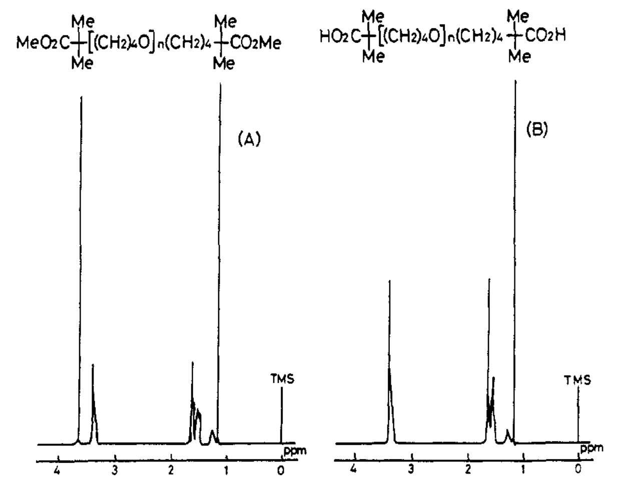
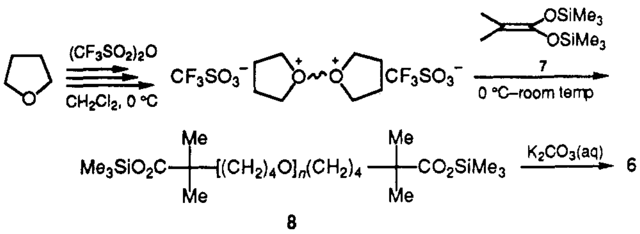


Figure 2. 400 MHz ^1H NMR spectra of (A) polyTHF having terminal ester group 5 (entry 2) and (B) the hydrolysis product of 5.

One-Pot Synthesis of Telechelic PolyTHF Having a Terminal Carboxylic Acid Group. For the preparation of telechelic polyTHF having a carboxylic acid group in one pot, a ketene bis(silyl acetal) 7 was used instead of 3 since the silyl ester group of the product polymer 8 can be easily hydrolyzed to give 6.



The structure of 6 was confirmed by IR and ^1H and ^{13}C NMR spectroscopy. The degree of polymerization of THF and the functionality of 6 were determined similarly (Table II). Two functionalities of 6 were 1.97 and 2.00, which implies that carboxylic acid group was quantitatively introduced at both ends of polyTHF. The narrow M_w/M_n values terminated by 7 are probably understood similarly to the cases of terminator 3.

Experimental Section

Materials. Solvent CH_2Cl_2 was purified by distillation twice over calcium hydride. A commercial reagent of THF was purified by distillation three times over lithium aluminum hydride before use. A commercial reagent of CF_3SO_3Et was purified by distillation. A commercial reagent of $(CF_3SO_2)_2O$ was purified by distillation over P_2O_5. $Et_3O^+BF_4^-$ was prepared according to the literature.[7] Ketene silyl acetal 3 and ketene bis(silyl acetal) 7 were prepared according to the literature.[8,9] All procedures were carried out under nitrogen.

Model Reactions. To the CH_2Cl_2 solution (10 mL) containing 0.595 g (3.13 mmol) of $Et_3O^+BF_4^-$, 0.819 g (4.70 mmol) of ketene silyl acetal 3 was added at 0 °C under nitrogen. The reaction mixture was allowed to stand at room temperature for 3 days to give methyl 2,2-dimethylbutanoate (4) (yield 97%). The yield

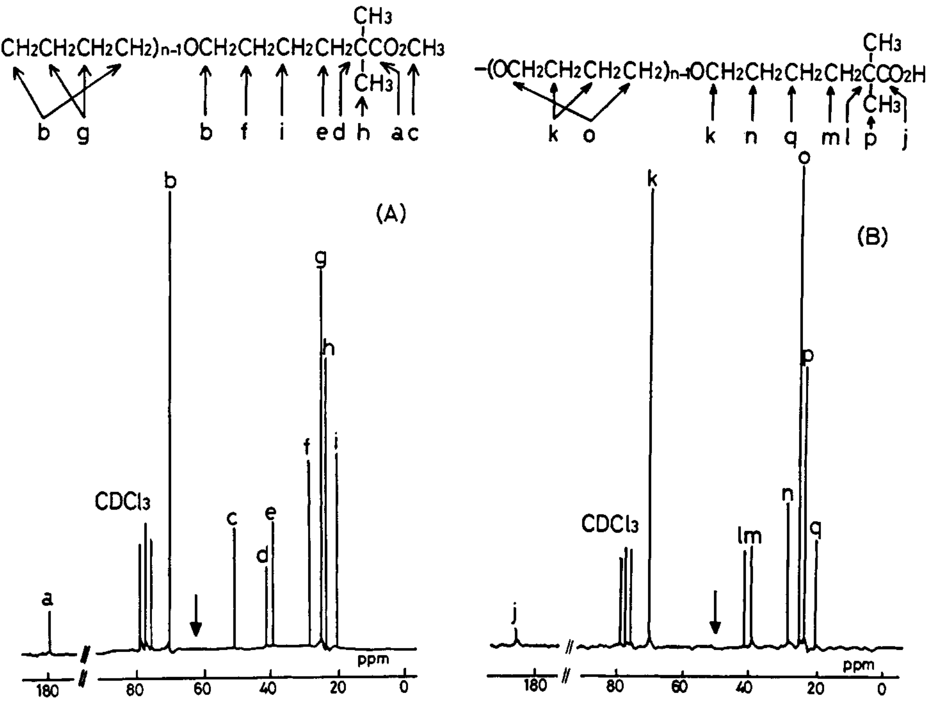


Figure 3. 22.6 MHz ^{13}C NMR spectra of (A) polyTHF having terminal ester group **5** (entry 2) and (B) the hydrolysis product of **5**.

of **4** was determined by gas chromatographic analysis. Similarly, the reaction of CF_3SO_3Et with **3** gave **4** quantitatively: ^{1}H NMR ($CDCl_3$) δ 0.8 (s, CH_3C, 3 H), 1.1 (t, CH_3CH_2, 6 H), 1.6 (q, CH_2C, 2 H), 3.6 (s, OCH_3, 3 H); IR (neat) 1730 cm^{-1} ($\nu_{C=O}$).

Synthesis of Telechelic PolyTHF Having Terminal Ester Groups. A typical run was as follows (entry 4). To the solution of 7.27 g (101 mmol) of THF in 11.9 mL of CH_2Cl_2, 0.167 g (0.592 mmol) of $(CF_3SO_2)_2O$ was added at 0 °C under nitrogen. The polymerization of THF was carried out for 1 h at 0 °C. To the polymerization mixture, 1.15 g (6.60 mmol) of ketene silyl acetal **3** was added at 0 °C and the mixture was stirred at room temperature for 3 days. Then the mixture was poured into a $^1/_2$ N HCl aqueous solution (30 mL) and extracted three times with 30 mL of diethyl ether. The organic layer was washed with saturated $NaHCO_3$ aqueous solution and with water. Then the organic layer was separated and dried over $MgSO_4$ for 1 day, followed by evaporation, and the residue was separated by using a silica gel column with CH_2Cl_2 for the removal of methyl isobutylate derived from the excess amount of **3** to give 1.2 g of **5**: ^{1}H NMR ($CDCl_3$) δ 1.2 (s, 12 H), 1.2–1.3 (m, 4 H), 1.5–1.6 (m, 8 H), 1.6–1.7 [br, 104.4 H ($4n - 4$, $n = 27.1$, n is the degree of polymerization of THF)], 3.3–3.5 [br, 108.4 H ($4n$, $n = 27.1$)], 3.7 (s, 6 H); IR (neat) 1730 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{122.1}H_{242.2}O_{31.0}$: C, 66.44; H, 11.07. Found: C, 66.14; H, 11.22.

Hydrolysis of the Ester Group to Telechelic PolyTHF Having Terminal Carboxylic Acid Groups. A typical run was as follows. A mixture of 0.11 g (0.22 mmol) of **5** (entry 2) and 0.40 g (7.1 mmol) of KOH in 25 mL of isopropyl alcohol was refluxed. The reaction was monitored spectroscopically by the disappearance of the IR peak at 1730 cm^{-1} due to the ester group. After 12 h, the mixture was poured into water (200 mL), and the solution was acidified at pH 5.0 with dilute HCl and extracted with CH_2Cl_2 (50 mL × 3). Then the organic layer was dried over $MgSO_4$ overnight followed by evaporation. The residue was dried in vacuo to give 0.050 g of the hydrolysis product of **5** (48% yield).

One-Pot Synthesis of Telechelic PolyTHF Having Terminal Carboxylic Acid Groups. A typical run was as follows (entry 6). To a THF solution (6.17 g, 85.6 mmol) in 13.5 mL of CH_2Cl_2, 0.165 g (0.585 mmol) of $(CF_3SO_2)_2O$ was added at 0 °C under nitrogen. The polymerization of THF was carried out at 0 °C for 1 h. To the polymerization mixture, 1.53 g (6.47 mmol) of ketene bis(silyl acetal) **7** was added at 0 °C and the mixture was stirred at room temperature for 6 days. Then 20 mL of saturated K_2CO_3 aqueous solution was added to the mixture which was extracted with diethyl ether (30 mL × 3). The organic layer was washed with a $^1/_2$ N HCl solution and dried over $MgSO_4$ for 1 day, followed by evaporation. The residue was separated by using a silica gel column with CH_2Cl_2 to give 0.734 g of **6**: ^{1}H NMR ($CDCl_3$) δ 1.2 (s, 12 H), 1.2–1.3 (m, 4 H), 1.5–1.6 (m, 4 H), 1.6–1.7 [br, 60.0 H ($4n - 4$, $n = 16.0$, n is the degree of polymerization of THF)], 3.3–3.5 [br, 64.0 H ($4n$, $n = 16.0$)]; IR (neat) 3400–2600 cm^{-1} (ν_{O-H}), 1700 cm^{-1} ($\nu_{C=O}$).

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a 400-MHz JEOL JNM-GX400 spectrometer and a 22.6-MHz Hitachi R-900 spectrometer, respectively. IR spectra were recorded on a Hitachi 260-50 spectrometer. Gas chromatographic analysis was performed by using a Shimadzu GC-6A gas chromatograph. The molecular weight of polymers was measured by a Corona 117 vapor pressure osmometer in chloroform at 40 °C. Gel permeation chromatographic (GPC) analysis was performed by using a JASCO TRIROTOR with an RI detector under the following conditions: Shodex K-802 column or AC-803 column with chloroform eluent at a flow rate of 1.0 or 0.5 mL/min.

Registry No. **3**, 31469-15-5; **4**, 813-67-2; **5**, 123359-36-4; **6**, 123359-37-5; $EtO^+BF_4^-$, 368-39-8; $EtOSO_2CF_3$, 425-75-2.

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