79-5; **8b** (SRU), 126296-87-5; **8c** (copolymer), 126296-80-8; **8c** (SRU), 126296-88-6; **9a** (copolymer), 121778-04-9; **9a** (SRU), 121778-49-2; **9b** (copolymer), 126296-81-9; **9b** (SRU), 126296-89-7; **9c** (copolymer), 126296-82-0; **9c** (SRU), 126296-90-0; **10a** (copolymer), 126296-83-1; **10a** (SRU), 126327-52-4; **10b** (copolymer), 126296-84-2; **10b** (SRU), 126296-91-1; **10c** (copolymer), 126296-85-3; **10c** (SRU), 126296-92-2; 4-fluorobenzoyl chloride, 403-43-0; 2-aminophenol, 95-55-6; *m*-cresol, 108-39-4; 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, 83558-87-6; 4-fluorobenzoic acid, 456-22-4; 4,4′-amino-3,3′-hydroxybiphenyl, 2373-98-0; 3,3′-diamino-4,4′-dihydroxybiphenyl, 4194-40-5; 4-*tert*-butylphenol, 98-54-4.

Synthesis of Telechelic Poly(tetrahydrofuran) Having a Carboxyl Group by Using an Anion of Diethyl Malonate or Hydroxy Esters as Terminator

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ABSTRACT: Telechelic poly(tetrahydrofurans) (polyTHFs) having ester groups at each polymer end have been prepared by terminating living propagating species with an anion of diethyl malonate or of a hydroxy-containing ester. The resulting polymers have been converted into the corresponding telechelic polyTHFs having aliphatic or aromatic carboxyl groups by the hydrolysis and successive decarboxylation of the terminal diethyl malonate moiety or by the hydrolysis of the terminal ester moiety. The functionality of the resulting polyTHFs is close to 2.0, indicating that two carboxyl groups have quantitatively been introduced onto both polymer ends.

Introduction

Telechelic poly(tetrahydrofuran) (polyTHF) is an important building block for construction of various polymer materials such as a polyurethane and polyester. It is well-known that THF is polymerized by trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$) as a bifunctional initiator to give a living polymerization system having tetrahydrofuranium species at the polymer ends.[1]

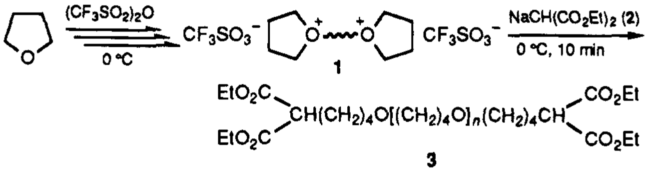
Telechelic polyTHFs having a variety of functional groups are usually prepared by reaction of the living propagating species with various nucleophiles.[2] Poly(oxytetramethylene) glycol, the most widely used telechelic polyTHF having terminal hydroxyl groups, can be synthesized by termination of the living species with water. Telechelic polyTHF of a bis-primary amine type can be produced by reaction of the living species with excess ammonia as terminator.[1]

Recently, much attention has been paid to telechelic polyTHFs having carboxyl groups. The telechelic polymer may be utilized as a starting material for various high-performance polymers with oxytetramethylene units in the main chain. In the previous paper, we have reported a new method for the preparation of telechelic polyTHFs having carboxyl groups, which involves a nucleophilic termination reaction of a ketene silyl acetal or a ketene bis(silyl acetal) with the living propagating species.[3] In relation to the present study, it has been reported that the oxidation of poly(tetrahydrofuran) glycol by a Cr(VI) compound gave telechelic polyTHF with a carboxylic acid group.[4]

The present paper describes a convenient synthesis of telechelic polyTHFs having carboxyl group using an anion of diethyl malonate or of a hydroxy-containing ester (hydroxy ester).[5] The introduction of carboxyl groups onto the polymer ends has been achieved by the following two reactions. The first is the termination of the living propagating species of THF with an anion (sodium salt) of diethyl malonate[6] or of a variety of hydroxy esters, giving rise to the corresponding end-capped telechelic polyTHFs having ester groups. The second is the conversion of the ester groups into carboxyl groups by hydrolysis and/or decarboxylation.

Results and Discussion

Synthesis of Telechelic PolyTHF Having Terminal Ester Groups by Using Sodium Diethyl Malonate as Terminator. THF was polymerized at 0 °C using $(CF_3SO_2)_2O$ as a bifunctional initiator to afford the living THF polymer **1**. The sodium salt of diethyl malonate, **2**, was very reactive toward the living ends of **1**, and the reaction was completed within 10 min at 0 °C. After work-up procedures, telechelic polyTHF **3** having a diethyl malonate moiety at both polymer ends was obtained.



The structure of **3** was confirmed by ^1H and ^{13}C NMR spectroscopies (Figure 1). The hydroxyl group would be contained as the terminal group in **3** if the living propagating species of THF was not quantitatively reacted with **2**. No signals due to the α-methylene carbon and β-me-

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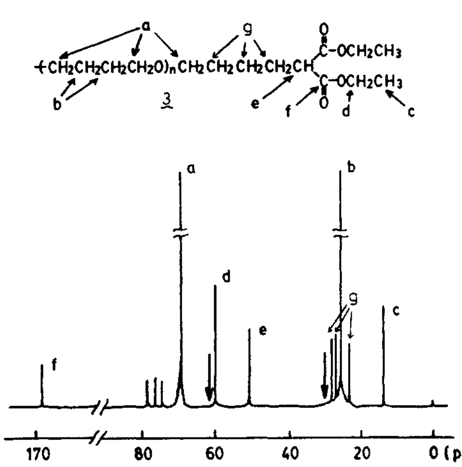


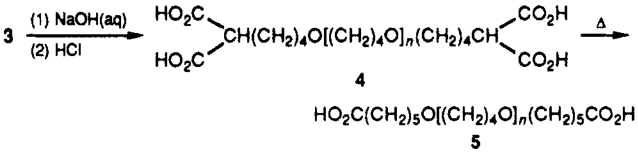
Figure 1. ^{13}C NMR spectrum of polyTHF **3** (entry 5) in $CDCl_3$.

thylene carbon to the terminal hydroxyl group of poly(tetrahydrofuran) glycol ($-CH_2OH$, 61.7 ppm) and ($-CH_2CH_2OH$, 29.5 ppm) in the ^{13}C NMR spectrum were detected (denoted by a downward arrow in Figure 1). These results indicate that the C–C bond-forming reaction occurred quantitatively between an anion of diethyl malonate and the living oxonium salt.

The effective introduction of diethyl malonate moiety onto the polymer ends was also confirmed by the absence of absorption due to hydroxyl group (ν_{OH} 3400 cm^{-1}) in the IR spectrum of **3**.

The gel permeation chromatography chart of the resulting telechelic polymer **3** showed the formation of a telechelic polymer with narrow molecular weight distribution ($M_w/M_n = 1.05$), which is inconsistent with the previous result of ring-opening polymerization of THF initiated by $(CF_3SO_2)_2O$.[1]

Hydrolysis and Decarboxylation of 3 to Telechelic PolyTHF Having a Terminal Carboxyl Group. The terminal ethyl ester groups of polymer **3** were converted into the corresponding carboxyl groups by alkaline hydrolysis followed by decarboxylation. Treatment of **3** with sodium hydroxide aqueous solution gave a polymer having sodium malonate moieties at the polymer ends. The polymer was subsequently transformed into the free carboxylic acid form **4**[7] by neutralization with hydrochloric acid. The resulting polyTHF **4** was then allowed to be decarboxylated by refluxing a toluene solution of **4** for 6 h, giving rise to polyTHF **5** having a carboxyl group at both ends.



$$\mathbf{3}\xrightarrow[\text{(2) HCl}]{\text{(1) NaOH(aq)}}(HO_2C)_2CH(CH_2)_4O[(CH_2)_4O]_n(CH_2)_4CH(CO_2H)_2\ \mathbf{4}\xrightarrow{\Delta}HO_2C(CH_2)_5O[(CH_2)_4O]_n(CH_2)_5CO_2H\ \mathbf{5}$$

The ^1H NMR spectrum of the resulting telechelic polyTHF indicates a characteristic triplet signal at 2.34 ppm, which is ascribed to the methylene protons adjacent to the terminal carbonyl carbon atom. Other signals' assignments are also given in Figure 2. The ^{13}C NMR spectrum of the polymer shows the complete conversion of the ethyl ester group into the corresponding carboxyl group (Figure 3). The signals at 13.1 and 59.9 ppm due to the ethyl group and the signal at 50.8 ppm due to the carbon of the ester carbonyl group in Figure 1 disappeared in Figure 3. The signal at 167.9 ppm due to the ester carbonyl carbon atom shifted to 173.6 ppm, which is assignable to the carbonyl carbon of the carboxylic acid. These data clearly indicate that the hydrolysis and successive decarboxylation took place quantitatively.

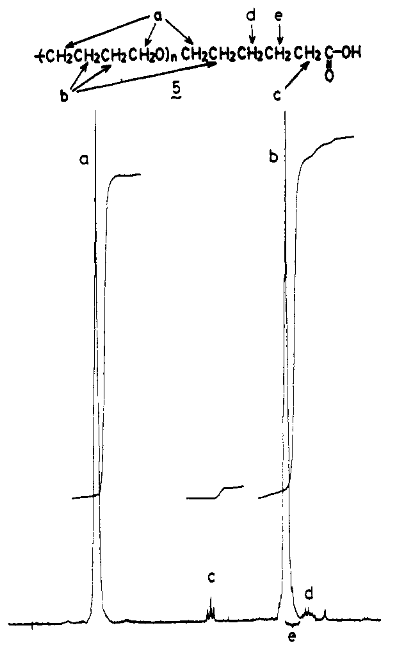


Figure 2. ^1H NMR spectrum of polyTHF **5** (entry 5) in $CDCl_3$ (250 MHz).

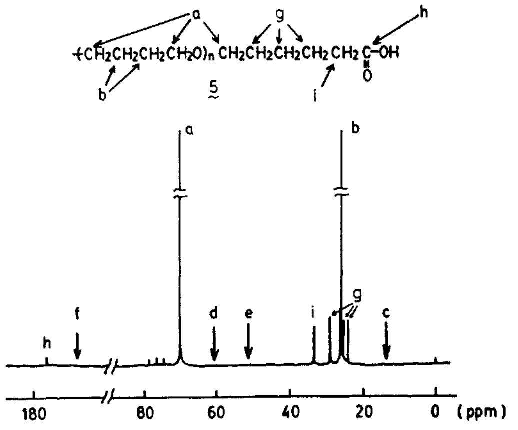


Figure 3. ^{13}C NMR spectrum of polyTHF **5** (entry 5) in $CDCl_3$.

The results of syntheses of telechelic polyTHF having carboxyl groups using sodium diethyl malonate as terminator are summarized in Table I. The molecular weight of the telechelic polyTHF can be easily controlled by changing the reaction time (entries 1–3) or the feed ratio of THF and $(CF_3SO_2)_2O$ (entries 4 and 5).

The functionality of **5** was determined by the combined results of the acid titration using a standard alkaline solution and the measurement of the molecular weight by means of vapor pressure osmometer (VPO). It is to be noted that the functionality of **5** was close to 2.0 in all runs; carboxyl groups were quantitatively introduced at both ends of polyTHF.

Fluorosulfonic anhydride ($(FSO_2)_2O$) also initiated the ring-opening polymerization of THF to give the living tetrahydrofuranium ions. The resulting living species were reacted with sodium diethyl malonate followed by hydrolysis and decarboxylation to afford the telechelic polyTHF having carboxyl groups (entry 6).

Synthesis of Telechelic PolyTHF Having a Terminal Ester Group by Using Sodium Alkoxides. It

Table I
Synthesis of Telechelic PolyTHF 5 Having a Terminal Carboxyl Group

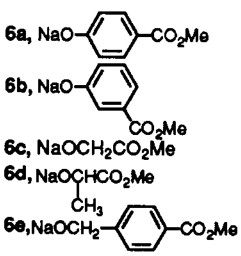
	polymerization					product		
entry	THF, mol	$(CF_3SO_2)_2O$, mmol	CH_2Cl_2, mL	temp, °C	time, min	polym 5, g	M_n[a]	functionality[b]
1	1.00	6.10		4	5	2.0	1430	1.96
2	1.00	6.10		4	10	6.9	2090	2.03
3	1.00	6.10		4	15	18.8	3800	1.95
4	1.26	12.5	295	0	60	3.0	640	2.00
5	2.02	11.8	238	0	60	13.3	2150[d]	1.95
6	1.00	10.0[c]		0	30	13.0	2660	1.94

[a] Determined by VPO. [b] Determined by M_n and acid titration values. [c] $(FSO_2)_2O$ was used as initiator. [d] The M_n value determined by integration of signals a and c in ^1H NMR (Figure 2) was 2180, which is very close to the value obtained by VPO.

has been shown that the living propagating species in the polymerization of THF react with various carbon nucleophiles such as ketene silyl acetal,[3] ketene bis(silyl acetal),[3] and sodium diethyl malonate to give the corresponding end-capped telechelic polyTHFs.

On the other hand, sodium phenoxide is known to react with the living tetrahydrofuranium species to afford polyTHF having phenyl ether moiety at the polymer end.[1b] Therefore, a similar reaction using an oxygen nucleophile as terminator has been applied to the preparation of telechelic polyTHF having a carboxyl group. A sodium salt of methyl hydroxybenzoate (**6a** and **6b**), methyl hydroxyacetate (**6c**), methyl hydroxylactate (**6d**), or methyl *p*-(hydroxymethyl)benzoate (**6e**) was chosen as the oxygen nucleophile. According to the present method of using hydroxy ester derivatives, telechelic polyTHFs having carboxyl groups can be obtained by the hydrolysis of the terminal ester group without a decarboxylation process.

$$\mathbf{1} \xrightarrow[0\ ^\circ C,\ 10\ min]{NaORCO_2Me\ (\mathbf{6})} \underset{\mathbf{7}}{MeO_2CRO(CH_2)_4O[(CH_2)_4O]_n(CH_2)_4ORCO_2Me} \xrightarrow[(2)\ HCl]{(1)\ NaOH(aq)} \underset{\mathbf{8}}{HO_2CRO(CH_2)_4O[(CH_2)_4O]_n(CH_2)_4ORCO_2H}$$



The polymerization of THF was performed in a similar manner using $(CF_3SO_2)_2O$ as a bifunctional initiator to give the living tetrahydrofuranium species. The termination reaction was carried out by adding a living polymerization solution to a sodium alkoxide solution. All these oxygen nucleophiles **6a**–**6e** were quite reactive toward the living ends **1**, and the termination reaction was complete within 10 min at 0 °C. The terminal methyl ester was successfully hydrolyzed by treating the polymer solution with an aqueous alkaline solution. The ^{13}C NMR spectrum of polyTHF having a hydroxybenzoic acid moiety showed the absence of α and β carbon atoms of the terminal hydroxyl group at 61.5 and 29.5 ppm, which would be detected in the case that the living species was not quenched quantitatively by **6a**. These results indicate the efficient introduction of a methyl hydroxybenzoate moiety into the polymer ends by using an oxygen nucleophile of the phenoxide type. Complete hydrolysis of the terminal methyl ester was confirmed by the absence of the signal due to the methyl carbon atom (51.3 ppm) in the ^{13}C NMR spectrum of the resulting polyTHF (Figure 4).

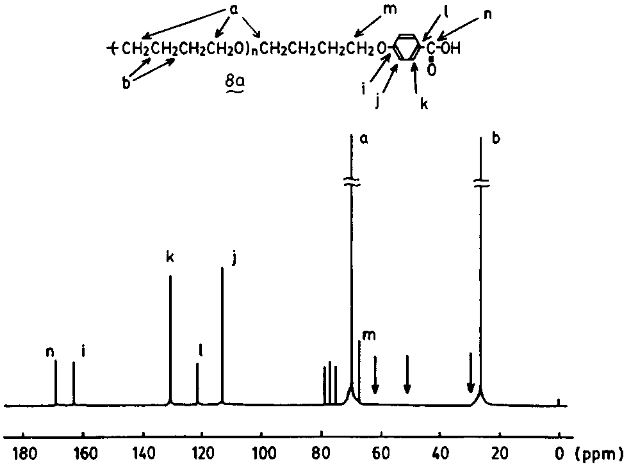


Figure 4. ^{13}C NMR spectrum of polyTHF **8a** (entry 7) in $CDCl_3$.

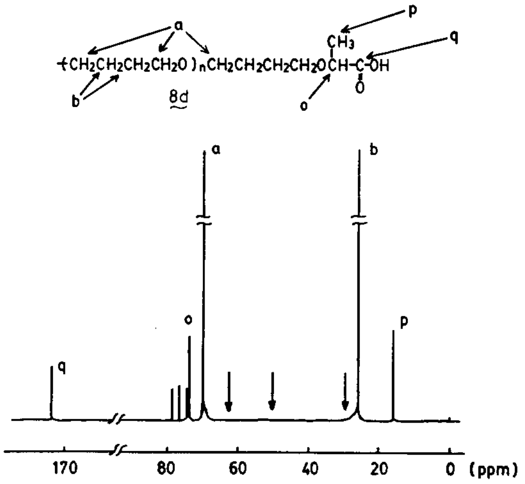


Figure 5. ^{13}C NMR spectrum of polyTHF **8d** (entry 14) in $CDCl_3$.

An alkoxide of primary or secondary hydroxy esters similarly reacted with the living tetrahydrofuranium species, giving rise to the corresponding telechelic polyTHFs. Figure 5 shows the ^{13}C NMR spectrum of polyTHF having lactic acid moieties at the polymer ends. The absence of the signals at 29.5 ppm ($-CH_2CH_2OH$), 50.5 ppm ($O{=}COCH_3$), and 61.5 ppm ($-CH_2OH$) indicates the quantitative introduction of a hydroxy ester moiety and the complete hydrolysis of the methyl ester giving rise to telechelic polyTHF. A bifunctional initiator $(FSO_2)_2O$ also gave similar results (entry 15).

The results of a termination reaction using a sodium salt of oxygen nucleophiles of various hydroxy ester derivatives are summarized in Table II.

Table II
Synthesis of Telechelic PolyTHFs 7 and 8 Using the Sodium Salt of a Hydroxy Ester

	polymerizn[a]			product		
entry	terminator	temp, °C	time, min	polym, g	M_n[b]	functionality[c]
7	**6a**	5	5	8.6	1270	1.96
8	**6a**	5	10	13.0[d]	2450	1.98
9	**6b**	0	10	7.6	1040	1.95
10	**6b**	0	20	10.2	1760	2.00
11	**6c**	0	20	6.9	1820	2.01
12	**6c**	0	30	11.4	2780	1.99
13	**6d**	5	5	9.1[d]	1650	1.99
14	**6d**	5	10	12.2	2130	1.98
15[e]	**6d**	0	20	10.6	1550	1.93
16	**6e**	0	20	6.1	1430	1.95
17	**6e**	0	40	13.3	3370	1.96

[a] Polymerization was carried out with 1.0 mol of THF and 6.10 mmol of $(CF_3SO_2)_2O$ under argon. [b] Determined by VPO. [c] Determined by M_n and acid titration values. [d] PolyTHF 7 having two terminal ester groups was isolated. Polymer **7a**: 19.4 g, M_n = 2440, functionality = 2.00. Polymer **7d**: 11.3 g, M_n = 1690, functionality = 2.02. [e] Polymerization was carried out with 1.0 mol of THF and 10.0 mmol of $(FSO_2)_2O$.

The molecular weight of the resulting telechelic polymers can be controlled by the reaction time or reaction temperature. The functionality of the polymers obtained was close to 2.0, which indicates that both the reaction of an alkoxide with the living species and the successive hydrolysis occurred quantitatively. Thus, by using various oxygen nucleophiles **6a–6e**, polyTHF telechelics having aliphatic or aromatic carboxylic acid groups can be obtained. It is also to be noted that polyTHF **7** having ester groups at the polymer ends is a useful prepolymer for the synthesis of a polyamide or polyester.

Experimental Section

Materials. Solvent CH_2Cl_2 was distilled over calcium hydride. THF was purified by distillation twice over sodium wire. Commercial reagents of CF_3SO_3H, P_2O_5, diethyl malonate, methyl *m*- and *p*-hydroxybenzoate, methyl hydroxyacetate, methyl lactate, and methyl *p*-(hydroxymethyl)benzoate were used without purification. $(CF_3SO_2)_2O$ was prepared according to the literature.[8]

Measurements. ^{13}C NMR spectra were recorded on a JEOL FX-60Q or Bruker AC-250P with Me_4Si standard using $CDCl_3$ as solvent. IR spectra were recorded on a Shimadzu IR-27G spectrometer. The molecular weight of polymers was measured by a Corona 115 vapor pressure osmometer in $CDCl_3$ at 30 °C. Gel permeation chromatographic (GPC) analysis was performed with poly(ethylene oxide) standard by using a Toyo Soda CCP&8000 liquid chromatograph under the following conditions: TSK-GEL G2500 HXL and TSK-GEL G4000 HXL columns with THF as eluent at a flow rate 1.0 mL/min at 40 °C.

Synthesis of Telechelic PolyTHF Having Carboxyl Groups by Using Sodium Diethyl Malonate. A typical procedure for the preparation of telechelic polyTHF (entry 1) is given as follows. Trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$; 1.72 g, 6.1 mmol) was added to THF (72.1 g, 1.0 mol) at 0 °C, and the resulting solution was stirred at 4 °C for 5 min under argon. To this solution was added a THF (40 mL) solution of sodium diethyl malonate (12.2 mmol), and the reaction mixture was stirred for 10 min. After diluting with toluene (100 mL), the reaction mixture was washed with water. The solvent was evaporated, and the residue was dried in vacuo to give telechelic polymer having diethyl malonate moieties at the polymer ends. To a THF (200 mL) solution of the resulting polymer (10 g) was added an aqueous solution of sodium hydroxide (20%), and the mixture was refluxed for 2 h. The hydrolyzed product was neutralized by adding 6 N hydrochloric acid and was extracted by toluene (100 mL) several times, and the solvent was removed in vacuo to give the polymer having malonic acid moiety. A toluene (200 mL) solution of the product was then refluxed for 6 h. After washing the mixture with water several times, the solvent was removed and the residue was dried in vacuo, giving rise to polyTHF having a terminal carboxyl group (2.0 g). For telechelic polyTHF **3** having terminal diethyl malonate groups, the data are as follows. ^1H NMR ($CDCl_3$): δ 1.26 ($\mathrm{CO_2CH_2C}\mathit{H}_3$, t, J = 7.1 Hz), 1.4–1.7 ($\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH(CO_2Et)_2}$, $(\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2})_n$), 3.3–3.5 ($\mathrm{C}\mathit{H}\mathrm{(CO_2Et)_2}$, $(\mathrm{OC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2)_n$), 4.19 ($\mathrm{CO_2C}\mathit{H}\mathrm{CH_3}$, q, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 13.1 ($\mathrm{(C{=}O)OCH_2}\mathit{C}\mathrm{H_3}$, 23.1, 27.6, 28.5 (each of $\mathrm{OCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH(CO_2Et)_2}$), 25.7 ($(\mathrm{OCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2})_n$), 50.8 ($\mathit{C}\mathrm{H(CO_2Et)_2}$), 59.9 ($\mathrm{(C{=}O)O}\mathit{C}\mathrm{H_2CH_3}$), 69.5 ($(\mathrm{O}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2})_n$), and 167.9 (C=O). For telechelic polyTHF **5** having terminal carboxyl groups, the data are as follows. ^1H NMR ($CDCl_3$): δ 1.4–1.6 ($\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CO_2H}$, $(\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2})_n$), 2.34 ($\mathrm{C}\mathit{H}_2\mathrm{CO_2H}$, t, J = 6.8 Hz), 3.42 ($(\mathrm{OC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2)_n$). ^{13}C NMR ($CDCl_3$): δ 23.3, 24.4, 28.1 (each of $\mathrm{OCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2CO_2H}$), 25.7 ($(\mathrm{OCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2})_n$), 32.3 ($\mathit{C}\mathrm{H_2CO_2H}$), 69.5 ($(\mathrm{O}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2})_n$), and 173.6 (C=O).

Titration of the Carboxyl Group. A telechelic polymer having a terminal carboxyl group was dissolved in 98% ethanol, and phenolphthalein was added as indicator. The resulting polymer solution was titrated with an ethanol solution of potassium hydroxide (0.2 N), which is calibrated by hydrochloric acid standard solution (0.2 N).

Synthesis of Telechelic PolyTHF Having a Carboxyl Group by Using an Anion of a Hydroxy Ester. A typical procedure for termination of living tetrahydrofuranium species with a sodium salt of hydroxy esters is given as follows. To THF (72.1 g, 1.0 mol) was added $(CF_3SO_2)_2O$ (1.72 g, 6.1 mmol) at 0 or 5 °C under argon, and the mixture was stirred for a desired reaction time. To this reaction mixture was added a THF (40 mL) solution of a sodium salt of hydroxy ester (12.2 mmol) at 0 °C, and the resulting mixture was stirred for 10 min. The mixture was diluted with toluene (100 mL) and washed with water. For entries 7–10, 16, and 17, in case of utilizing hydroxy-containing aromatic esters, the reaction mixture was evaporated to dryness, the residue was diluted with excess toluene or dichloromethane and insoluble materials (excess of the aromatic ester) were filtered off. The organic layer was concentrated to dryness and the residue was dried in vacuo, giving rise to polyTHF **7** having the ester moiety at the polymer ends.

Hydrolysis of PolyTHF Having a Terminal Hydroxy Ester and Titration of the Resulting Polymer. A telechelic polyTHF **7** was treated with 0.2 N ethanolic solution of potassium hydroxide (20 mL) by heating the solution at 80 °C for 1 h. The resulting solution was cooled to room temperature, and Bromthymol Blue was added as indicator. The excess potassium hydroxide was titrated with an aqueous solution of hydrochloric acid (0.2 N). For telechelic polyTHF **8a** having a benzoic acid moiety, the data are as follows. ^1H NMR ($CDCl_3$): δ 1.4–1.9 ($(\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2})_n$), 3.42 ($(\mathrm{OC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2)_n$), 4.05 ($\mathrm{C}\mathit{H}_2\mathrm{OAr}$, t, J = 6.1 Hz), 6.92, 8.02 (aromatic H, 4 H). ^{13}C NMR ($CDCl_3$): δ 25.7 ($(\mathrm{OCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2})_n$), 66.8 ($\mathit{C}\mathrm{H_2OAr}$), 69.5 ($(\mathrm{O}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2})_n$), 112.9, 121.1, 130.9, 162.1 (aromatic carbons), and 168.1 (C=O). For telechelic polyTHF **8d** having a lactic acid moiety, the data are as follows. ^1H NMR ($CDCl_3$): δ 1.44 ($\mathrm{OCH(C}\mathit{H}_3\mathrm{)CO_2H}$, d, J = 6.8 Hz), 1.61 ($(\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2})_n$), 3.42 ($(\mathrm{OC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2)_n$), 3.96 ($\mathrm{OC}\mathit{H}\mathrm{(CH_3)CO_2H}$, q, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 17.4 ($\mathrm{OCH(}\mathit{C}\mathrm{H_3)CO_2H}$), 25.7 ($(\mathrm{OCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2})_n$), 69.5 ($(\mathrm{O}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2})_n$), 73.4 ($\mathrm{O}\mathit{C}\mathrm{H(CH_3)CO_2H}$), 173.8 (C=O).

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(6) The anion of malonate has been used for the introduction of a carboxyl group in organic synthesis. An application to polymer synthesis has been reported. Sawamoto, M.; Enoki, T.; Higashimura, T. *Macromolecules* **1987**, *21*, 1.

(7) ^{13}C NMR ($CDCl_3$): δ 24.0, 28.7, 29.3 (each of $-OCH_2CH_2CH_2CH_2CH(CO_2H)_2$), 26.4 ($(OCH_2CH_2CH_2CH_2)_n$), 51.3 ($CH(CO_2H)_2$), 70.4 ($(OCH_2CH_2CH_2CH_2)_n$), 170.9 (C=O).

(8) Burden, J.; Farazmand, I.; Staley, M.; Tatlow, J. C. *J. Chem. Soc.* **1957**, 2574.

((Diethylamino)ethyl)chitins: Preparation and Properties of Novel Aminated Chitin Derivatives[1]

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ABSTRACT: Procedures for (diethylamino)ethylation of chitin with (diethylamino)ethyl chloride have been established. ((Diethylamino)ethyl)chitins (DEAE-chitins) were prepared in dispersion in organic solvents with a small amount of aqueous sodium hydroxide. Among the solvents examined, dimethyl sulfoxide was confirmed to be most suitable, and degrees of substitution above 1.2 were achieved. The substitution reactions in solution in aqueous sodium hydroxide also proceeded smoothly, and DEAE-chitins with substitution degrees above 1.4 were obtained. Addition of a phase-transfer catalyst to the aqueous solution enhanced the reaction efficiency considerably. The resulting DEAE-chitins exhibited highly improved affinity to water and organic solvents, and these properties were dependent on both the mode of preparation and substitution extent. The derivatives prepared in aqueous solution showed much better solubility and swelling; they were readily water soluble and swelled remarkably in common solvents such as benzene and alcohols. The separation behavior of these DEAE-chitins for organic dyes was studied, and those with high substitution degrees proved useful as adsorbents and separating materials.

Introduction

Much attention is currently being paid to chitin as an important biomass resource. It is produced in a huge amount annually in nature, but remains an almost unutilized resource. Recent rapid progress in chitin chemistry is revealing a high potential for developing new advanced materials on the basis of specific structure. Many efforts have been focused on exploration of various modes of chemical modifications to open the way to utilization.[2]

Introduction of additional amino groups into chitin is considered especially interesting because of the resulting strong cationic character due to the presence of the original and introduced amino groups. The utility of aminated polysaccharides such as ((diethylamino)ethyl)cellulose (DEAE-cellulose) and DEAE-Sephadex is well appreciated, and they have found many applications, especially for separation of biological components such as proteins and nucleic acids due to their high selectivity in adsorption.[3] Chitin itself is an amino polysaccharide and shows specific affinity for some proteins such as lectins,[4] and thus ((diethylamino)ethyl)chitin (DEAE-chitin) may possibly be another polycation useful in various fields as gels for effective bioseparation, supports for enzymes, chelating agents, ion exchangers, and water-soluble polycations for cosmetics and water treatment. (Diethylamino)ethylation of chitin has, however, attracted little attention thus far, and we have examined various factors influencing the reaction and established efficient preparative procedures. Some characteristic properties of the resulting DEAE-chitins are also discussed.

Experimental Section

General Procedures. Chitin was isolated from shrimp shells by the method reported before[5] and pulverized to 100-mesh pass. The degree of deacetylation was 0.10 as determined by conductometric titration. β-(Diethylamino)ethyl chloride hydrochloride was recrystallized from dioxane/ethanol (9:1). IR spectra were recorded on a JASCO IRA-1. NMR spectra were taken with a JEOL JNM-GX270, and chemical shifts are referenced to sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS). The degree of substitution was measured by conductometric titration with a Toa CM-40S conductivity meter. Absorption spectra were obtained with a JASCO Ubest-30. X-ray diffraction patterns were obtained with a Rigaku RAD-IA using nickel-filtered Cu Kα radiation. Elemental analyses were performed with a Yanaco MT-3 CHNcorder.

(Diethylamino)ethylation in Dispersion in Organic Solvents. A dispersion of 0.10 g of powdered chitin in 5 mL of an organic solvent was treated with 0.75 mL of 20% aqueous sodium hydroxide at a given temperature for 1 h. (Diethylamino)ethyl chloride hydrochloride [0.43 g (5 mol equiv per pyranose unit)] was added, and the mixture was stirred at the same temperature for 3 h. The mixture was then poured into 150 mL of acetone/methanol (7:3). The solid was washed with the same mixed solvent thoroughly and dried. DEAE-chitins were obtained as colorless to light brown powdery materials with substitution degrees of up to 1.27: IR (KBr) 2950 (C–H), 1660, 1560 cm^{-1} (C=O).

(Diethylamino)ethylation in Aqueous Solution. Powdered chitin (0.5 g) was dispersed in 10 mL of 42% aqueous sodium hydroxide, and the dispersion was left standing at room

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