Self-Polyaddition of Six-Membered Cyclic Carbonate Having Fmoc-Protected Amino Group: Novel Synthetic Method of Polyhydroxyurethane

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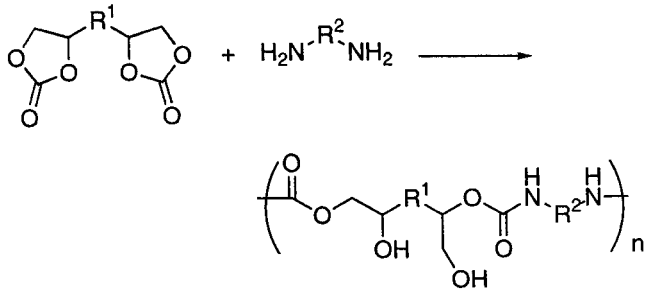
ABSTRACT: This article deals with the self-polyaddition of 3-(1,3-dioxan-2-one-5-yl)propyl 2-(9-fluorenylmethoxycarbonylamino)ethyl thioether by the deprotection of the 9-fluorenylmethyoxycarbonyl (Fmoc) group with *N*,*N*-diisopropylethylamine, 4-(dimethylamino)pyridine, or triethylamine as a novel synthetic method of a polyhydroxyurethane. The polymer with higher yields and M_n's was obtained by using *N*,*N*-diisopropylethylamine and 4-(dimethylamino)pyridine than triethylamine. Fmoc deprotection and stability of the cyclic carbonate group were elucidated to optimize the condition by using the model compounds, 3-cyclohexylpropyl 2-(9-fluorenylmethoxycarbonylamino)ethyl thioether and 3-(1,3-dioxan-2-one-5-yl)propyl ethyl thioether.

Introduction

Polyhydroxyurethanes exhibit useful characteristics such as high water absorption and thermal stability,[1] which are superior to commercial polyurethanes produced by the polyaddition of diisocyanates with diols. Polyhydroxyurethanes can be synthesized by the polyaddition of bis(five-membered cyclic carbonate)s with diamines (Scheme 1).[2−9] Bis(six-membered cyclic carbonate)s undergo polyaddition with diamines much faster than five-membered ones to give higher molecular weight polymers.[3] Stoichiometric balance is important to achieve the efficient polyaddition, i.e., a precisely equivalent molar ratio between bis(cyclic carbonate)s and diamines is necessary to obtain high-molecular-weight polyhydroxyurethanes possessing enough mechanical strength. Impurities cause unequality between the two monomers, resulting in decrease of molecular weight. In polyester synthesis, hydroxycarboxylic acids are sometimes employed to maintain equality between two different functional groups.[10,11] These monomers are practically useful because they eliminate the need for precise weighing, especially in an industrial plant. In this study, we have designed a novel monomer having six-membered cyclic carbonate and fluorenylmethoxycarbonyl (Fmoc)-protected amino groups. The monomer was used to synthesize a polyhydroxyurethane by deprotection of the Fmoc group. We have chosen the Fmoc group among numerous protective groups for the amino group,[12] because it can be cleaved with a tertiary amine under mild conditions, which are inert to a cyclic carbonate group.[12,13]

Scheme 1



Results and Discussion

Monomer Synthesis. 2-(9-Fluorenylmethoxycarbonylamino)ethanethiol, $FmocNH(CH_2)_2SH$, was prepared according to the literature.[14,15] The 5-allylated six-membered cyclic carbonate, 5-(2-propenyl)-1,3-dioxan-2-one, was prepared from triphosgene and 2-allylpropane-1,3-diol, which was synthesized by $LiAlH_4$ reduction of allylmalonic acid diethyl ester.[16] The monomer possessing six-membered cyclic carbonate and Fmoc-protected amino groups, 3-(1,3-dioxan-2-one-5-yl)propyl 2-(9-fluorenylmethoxycarbonylamino)ethyl thioether (**1**), was synthesized by radical addition of $FmocNH(CH_2)_2SH$ and the 5-allylated six-membered cyclic carbonate in 10% yield (Schemes 2 and 3). 3-Cyclohexylpropyl 2-(9-fluorenylmethoxycarbonylamino)ethyl thioether (**2**) and 3-(1,3-dioxan-2-one-5-yl)propyl ethyl thioether (**3**) were also synthesized as the model compounds in 50 and 82% yields, respectively (Schemes 2 and 3). Compound **3** was obtained in a better yield than **1** and **2** using AIBN at 60 °C overnight. No reaction of $FmocNH(CH_2)_2SH$ took place with the 5-allylated six-membered cyclic carbonate under similar conditions. Overnight reaction at 80 °C caused deprotection of the Fmoc group.

Cleavage of Fmoc Group as the Model Reaction. The Fmoc group of **2** was removed by treatment with 10 mol % of *N*,*N*-diisopropylethylamine, 4-(dimethylamino)pyridine, or triethylamine in dimethyl-d_6 sulfoxide (DMSO-d_6, initial reagent concentration: 1 M) at 30 °C for 24 h as shown in Scheme 4. Figure 1 depicts the ^1H NMR spectra of **2** and the reaction mixture obtained by *N*,*N*-diisopropylethylamine treatment. The methylene and methine proton signals (*k* and *l*) of the

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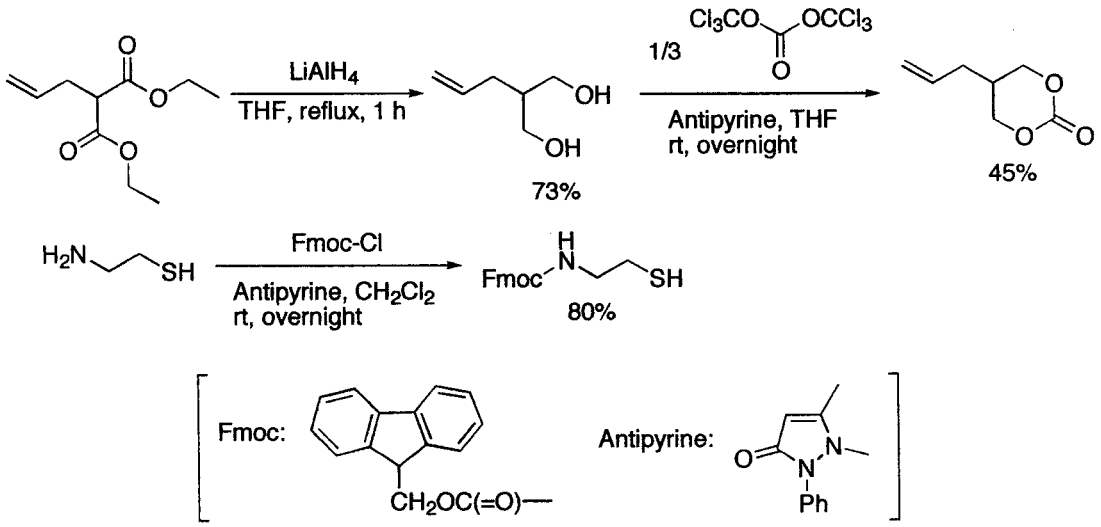
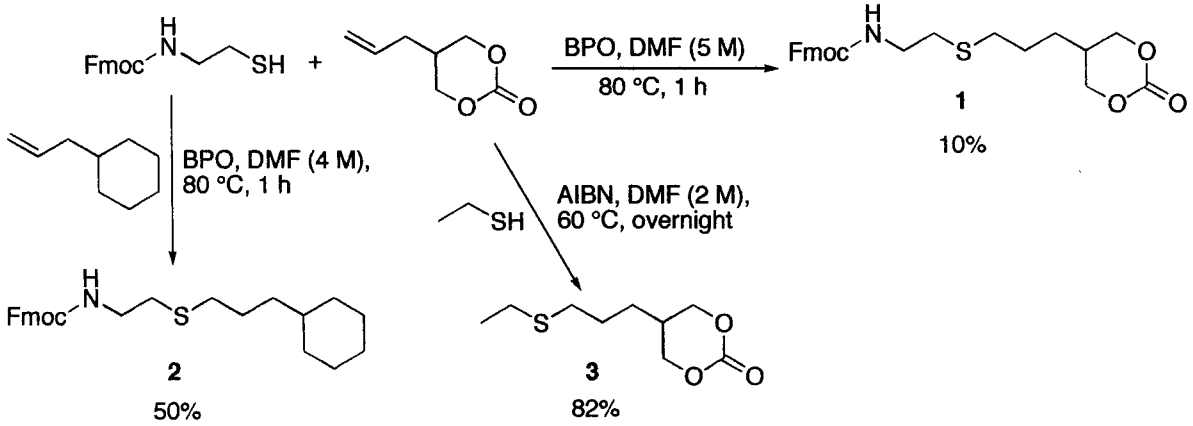
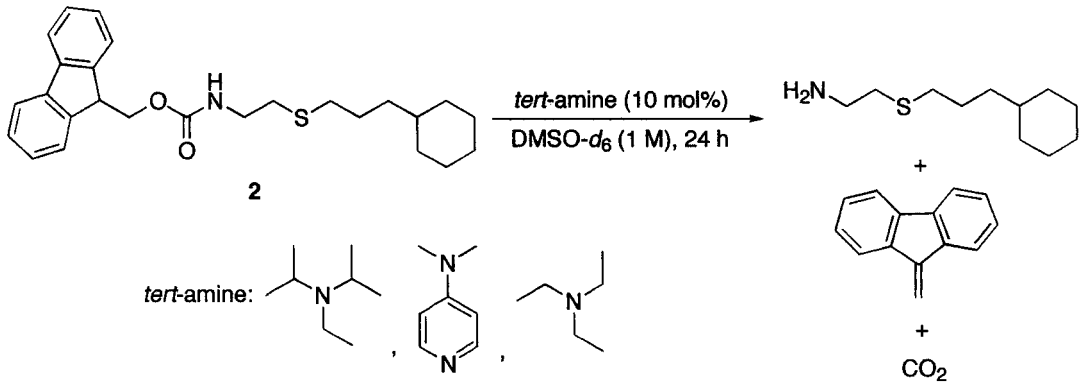
Scheme 2



Scheme 3



Scheme 4



Fmoc group disappeared, and the exo-methylene proton signal (*k′*) of dibenzofulvene appeared at 6.28 ppm, indicating the Fmoc group was completely cleaved under the above-mentioned conditions. It has been reported that six-membered cyclic carbonates undergo anionic polymerization with a tertiary amine as an initiator.[17] To investigate the stability of the six-membered cyclic carbonate group in the presence of *N*,*N*-diisopropylethylamine, 4-(dimethylamino)pyridine, or triethylamine, 10 mol % of the *tert*-amine was added to a solution of **3** in DMSO-d_6 (initial reagent concentration: 1 M), and the resulting mixture was stirred at 30, 50, and 70 °C for 14 days. In the cases of *N*,*N*-diisopropylethylamine and 4-(dimethylamino)pyridine, no significant change was observed by ^{1}H NMR spectroscopy at 30 and 50 °C for 14 days except a small unassignable peak at 4.07 ppm (Figure 2). High-performance liquid chromatography (HPLC) was also employed to investigate the conversion of the six-membered cyclic carbonate group. The conversions in the presence of *N*,*N*-diisopropylethylamine and 4-(dimethylamino)pyridine at 50 °C in 14 days were less than 1%. However, conversion of the six-membered cyclic carbonate group was confirmed at 70 °C by HPLC, which became 55% of the original after 7 days. On the other hand, triethylamine rapidly converted the six-membered cyclic carbonate group even at 30 °C. These results were also supported by ^{1}H NMR spectral analysis.

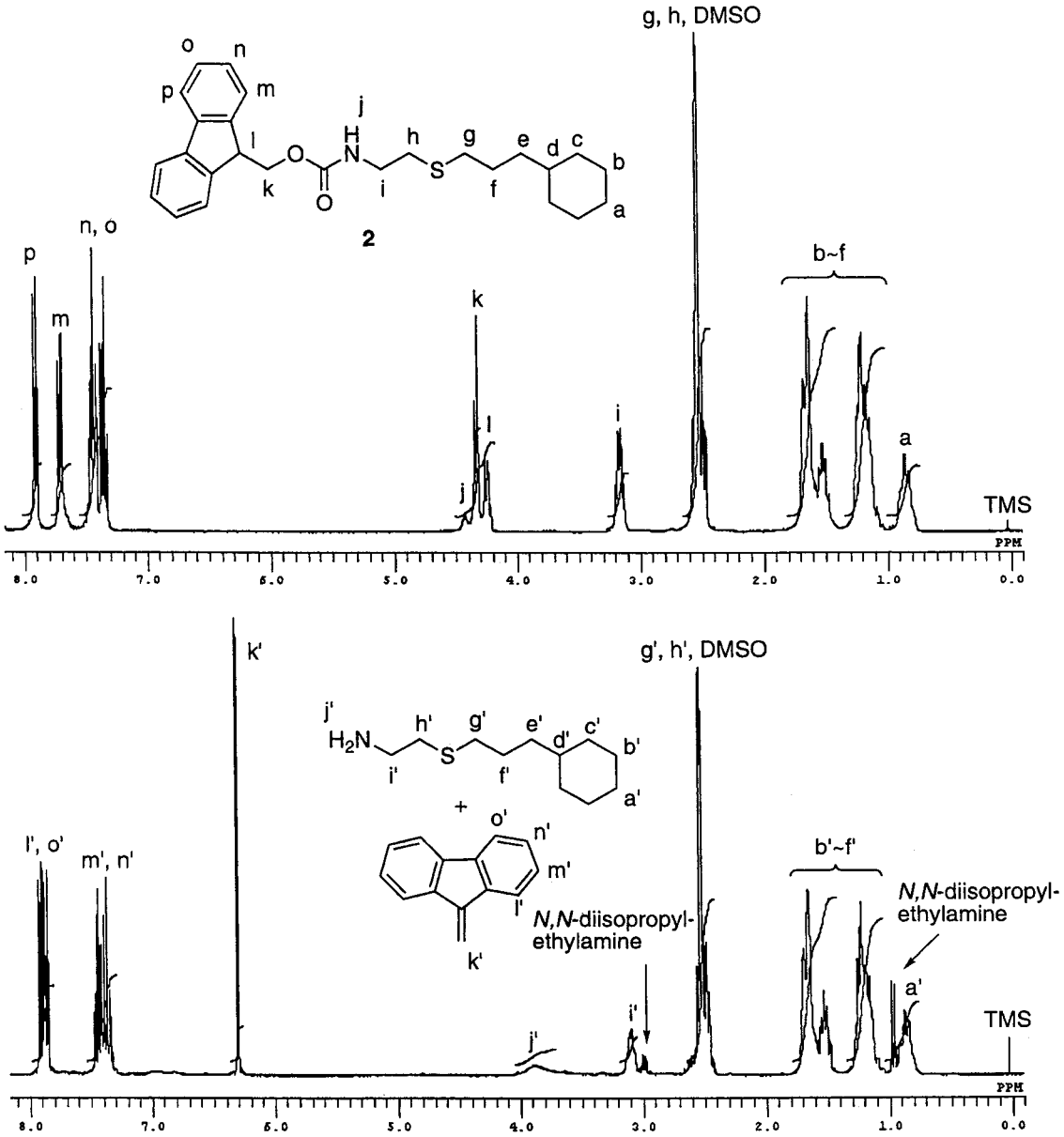


Figure 1. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **2** (above) and the mixture obtained by the reaction of **2** with 10 mol % of *N*,*N*-diisopropylethylamine in DMSO-d_6 (initial reagent concentration 1 M) at 30 °C for 24 h (below).

Self-Polyaddition. The self-polyaddition of the monomer (**1**) having a six-membered cyclic carbonate and the Fmoc protected amino group was carried out in DMSO-d_6 with an initial reagent concentration of 1 M at 30, 50, and 70 °C for 14 days by adding 10 mol % of *N*,*N*-diisopropylethylamine, 4-(dimethylamino)pyridine, or triethylamine to obtain the corresponding polyhydroxyurethane (Scheme 5). The polymer was precipitated with ether to purify. It was proceeded several times until no signal assignable to dibenzofulvene was observed in NMR spectrum. The structure of the obtained polymer was examined by ^{1}H NMR and IR spectroscopy. Figure 3 depicts the ^{1}H NMR spectrum of the obtained polyhydroxyurethane, in which all of the signals could be reasonably assigned. The IR spectrum of the polymer showed strong absorption peaks based on hydroxyl and urethane carbonyl groups at 3350 and 1700 cm^{-1}, respectively. No carbonyl absorption attributable to cyclic carbonate moiety was observed around 1730 cm^{-1}. Figure 4 depicts the relationships between the reaction time and conversion of the carbonate group at 30 and 50 °C in the presence of *N*,*N*-diisopropylethylamine. The conversion of **1** was determined by the ^{1}H NMR integration ratio of the β-methine proton of cyclic carbonate group to the total phenyl protons of dibenzofulvene. For the evaluation of the monomer to polymer conversion, no further purification of the polymer was employed. As summarized in Table 1, the carbonate group of **1** converted quantitatively in 14 days in every case except runs 3 and 9. In these two cases, the reaction mixture separated into two phases during the reaction, and finally a yellowish mass precipitated. The mass was insoluble in DMSO, tetrahydrofuran, acetone, and chloroform. The M_n of the polymer decreased as the reaction temparature rose. Although the conversions of cyclic carbonate group reached 100% in runs 1, 2, and 4−8, the yields and M_n's of the polymer depended on the *tert*-amines. *N*,*N*-Diisopropylethylamine and 4-(dimethylamino)pyridine afforded the polymer with higher yields and M_n's than triethylamine. Triethylamine is more nucleophilic than the other amines. The higher nucleophilicity may result in some side reactions such

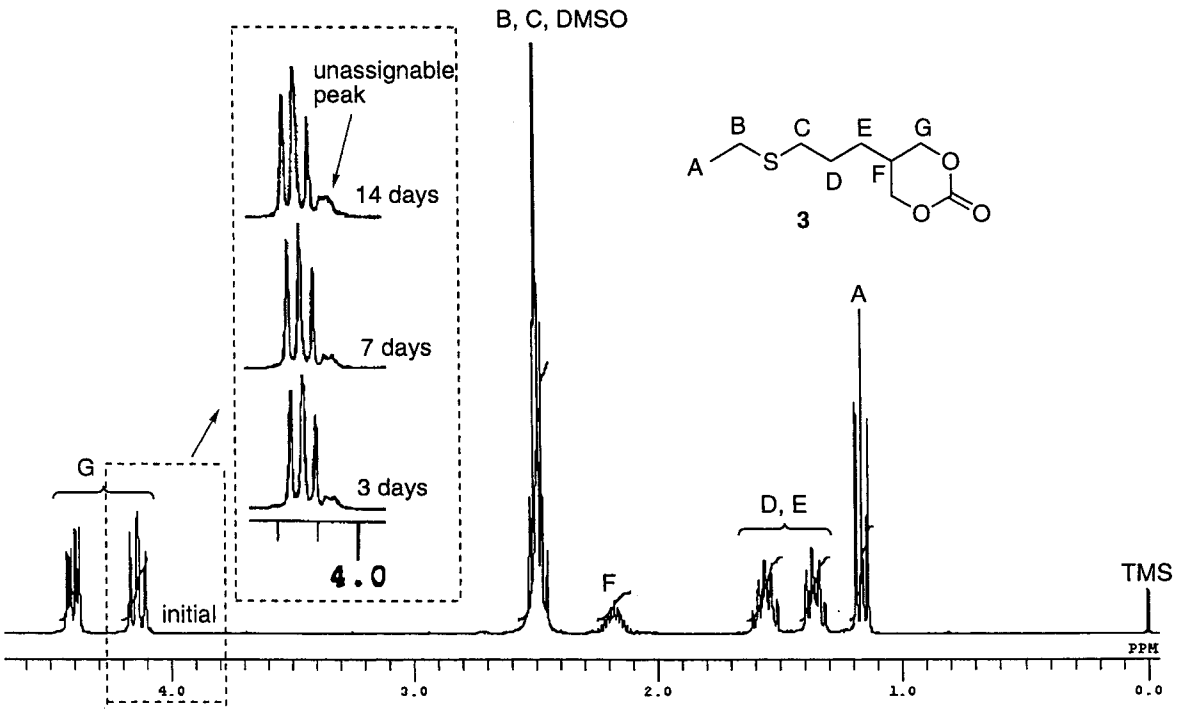


Figure 2. ^{1}H NMR spectral changes (300 MHz, $CDCl_3$) of **3** in the presence of 10 mol % of *N*,*N*-diisopropylethylamine at 50 °C.

Scheme 5

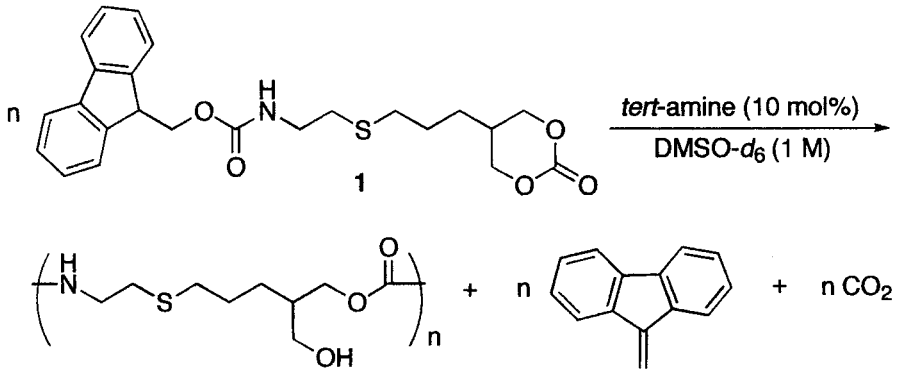


Table 1. Polyaddition of 1 in the Presence of *tert*-Amine[a]

run	*tert*-amine	temp (°C)	conv[b] of cyclic carbonate group (%)	yield[c] (%)	M_n[d]	M_w/M_n[d]
1	*N*,*N*-diisopropylethylamine	30	100	98	11000	1.2
2	*N*,*N*-diisopropylethylamine	50	100	97	8000	1.2
3	*N*,*N*-diisopropylethylamine	70	*e*	*e*	*e*	*e*
4	4-(dimethylamino)pyridine	30	100	97	10500	1.2
5	4-(dimethylamino)pyridine	50	100	95	7700	1.2
6	4-(dimethylamino)pyridine	70	100	95	6700	1.2
7	triethylamine	30	100	90	5500	1.1
8	triethylamine	50	100	90	5200	1.1
9	triethylamine	70	*e*	*e*	*e*	*e*

[a] Initial concentration of **1** (1 M) in DMSO-d_6, *tert*-amine 10 mol %, time 14 days. [b] Determined by ^{1}H NMR. [c] Ether-insoluble part. [d] Determined by GPC. [e] Could not be determined.

as attack at the carbonate carbonyl group. 4-(Dimethylamino)pyridine could afford the polymer even at 70 °C (run 6). Figure 5 depicts the typical GPC diagram of the polyhydroxyurethane obtained by self-polyaddition of **1**. The glassy transition temperature of the obtained polyhydroxyurethane in the presence of *N*,*N*-diisopropylethylamine at 30 °C was determined to be −23 °C.

In summary, we presented the self-polyaddition of a monomer having six-membered cyclic carbonate and amino groups, whose Fmoc protective group was cloven by a tertiary amine in situ as a novel synthetic method of a polyhydroxyurethane.

Experimental Section

Measurements. NMR spectra were recorded on a JEOL LA-300 spectrometer (300 MHz), using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$) or DMSO-d_6. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer. The melting points were measured by a Yanako micro melting point apparatus. Conversion of six-membered cyclic carbonate group of **3** was estimated by high-

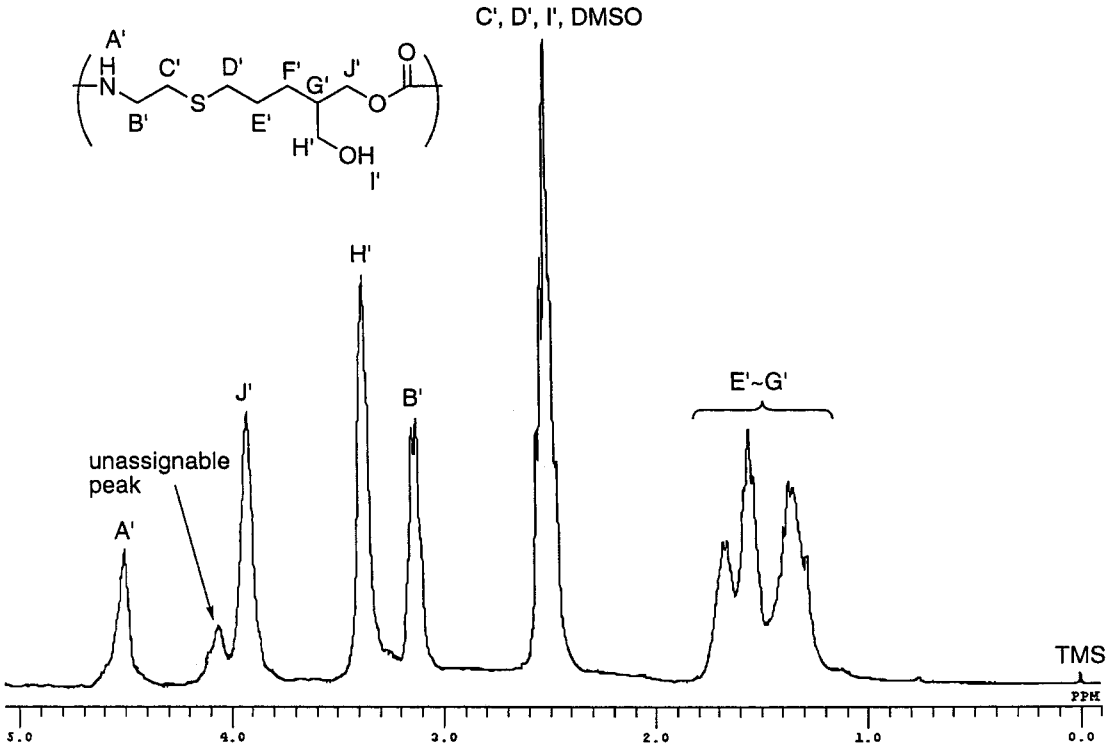


Figure 3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the polyhydroxyurethane obtained by the polyaddition of **1** in the presence of 10 mol % of *N*,*N*-diisopropylethylamine at 30 °C for 14 days.

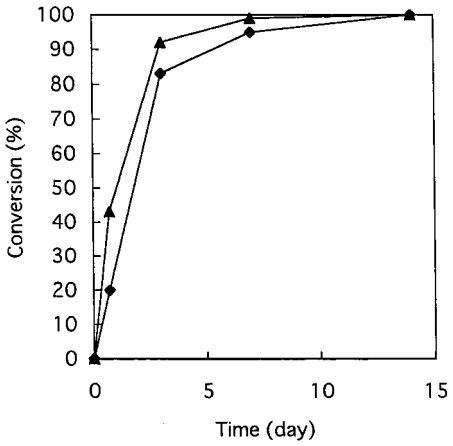


Figure 4. Time−conversion relationships of the cyclic carbonate group of **1** in the reaction at 30 °C (◆) and at 50 °C (▲) in DMSO-d_6 (initial reagent concentration 1 M) in the presence of 10 mol % of *N*,*N*-diisopropylethylamine.

performance liquid chromatography (HPLC) with a JASCO Gulliver 1500 system equipped with a silica gel column (JASCO finepak Sil-5), detected with 254 nm UV light, eluted by 2-propanol. Number- and weight-average molecular weights (M_n and M_w) were estimated by gel permeation chromatography (GPC) with a Tosoh HLC-8020 system equipped with three consecutive polystyrene gel columns (TSKgel G5000HXL, TSKgel G4000HXL, and TSKgel G2500HXL), detected with refractive index, eluted by 10 mmol/L solution of lithium bromide in *N*,*N*-dimethylformamide with a flow rate of 1 mL/min at 40 °C, and calibrated by polystyrene standards. The glassy transition temperature was estimated by differential scanning calorimetry (DSC) with TA Instruments 2920 modulated DSC with a scanning rate of 10 °C/min.

Materials. *N*,*N*-Diisopropylethylamine and triethylamine were distilled over CaH_2 and stored under nitrogen before use. Other chemicals were reagent grade and used without further purification.

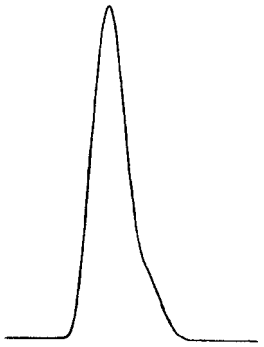


Figure 5. Typical GPC diagram of the polyhydroxyurethane obtained by self-polyaddition of **1**.

2-(9-Fluorenylmethoxycarbonylamino)ethanethiol. To a solution of 2-aminoethanethiol (15.00 g, 0.19 mol) and 2,3-dimethyl-1-phenyl-5-pyrazolone (36.60 g, 0.19 mol) in CH_2Cl_2 (194 mL) was added a solution of 9-fluorenylmethyl chloroformate (50.30 g, 0.19 mol) in CH_2Cl_2 (100 mL) dropwise at 0 °C. After the addition, the solution was stirred at room temperature overnight and washed with an adequate amount of water. After removal of the solvent, the residue was purified by column chromatography (eluent; ethyl acetate/*n*-hexane = 1/2, volume ratio) to obtain a white solid. Yield 46.6 g (80.0%). ^{1}H NMR ($CDCl_3$): δ 1.31 (1H, t, J = 8.5 Hz, SH), 2.55−2.70 (2H, m, CH_2SH), 3.25−3.40 (2H, m, NHCH_2), 4.15−4.30 (1H, m, CH), 4.35−4.50 (2H, m, CH_2O), 5.23 (1H, s, NH), 7.25−7.45 (4H, m, Ph), 7.50−7.65 (2H, m, Ph), 7.70−7.80 (2H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 24.73 (CH_2SH), 43.85 ($NHCH_2$), 47.17 (CH), 66.51 (CH_2O), 119.89 (Ph), 124.89 (Ph), 126.94 (Ph), 127.60 (Ph), 141.20 (Ph), 143.75 (Ph), 156.20 (C=O). IR (KBr): 1267, 1450, 1544, 1695, 2567, 2885, 2932, 3065, 3330 cm^{-1}. Mp 124.5−125.5 °C. Anal. Calcd for $C_{17}H_{17}NSO_2$: C, 68.20; H, 5.72; N, 4.68; S, 10.71. Found: C, 68.67; H, 5.83; N, 4.22; S, 10.42.

2-Allylpropane-1,3-diol. To a suspension of $LiAlH_4$ (25.00 g, 0.66 mol) in THF (200 mL) was added a solution of allylmalonic acid diethyl ester (33.00 g, 0.16 mol) in THF (25 mL) dropwise at 0 °C. After the addition was completed, the

mixture was refluxed for 1 h. The reaction mixture was cooled to 0 °C, and ethyl acetate (125 mL) and then saturated Na_2SO_4 aqueous solution were added dropwise to the mixture. The mixture was filtered and the precipitate was washed thoroughly with THF (150 mL) twice. After removal of the solvent, the crude product was distilled under vacuum (100−105 °C/4 mmHg) to obtain colorless liquid. Yield 14.0 g (73.0%). ^{1}H NMR ($CDCl_3$): δ 1.82−1.88 (1H, m, CH), 2.02−2.09 (2H, m, =CHCH_2), 3.34 (2H, s, OH × 2), 3.61−3.66 (2H, m, CH_2OH), 3.76−3.79 (2H, m, CH_2OH), 5.02−5.09 (2H, m, CH_2=CH), 5.72−5.86 (1H, m, CH_2=C*H*). ^{13}C NMR ($CDCl_3$): δ 32.43 (CH_2=CH*C*H_2), 41.70 (*C*HCH$_2$OH), 65.07 (CH_2OH), 116.52 (*C*H_2=CH), 136.13 (CH_2=*C*H). IR: 1100, 1240, 1640, 3080, 3350 cm^{-1}. Anal. Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 62.11; H, 10.57.

5-(2-Propenyl)-1,3-dioxan-2-one. To a solution of 2-allylpropane-1,3-diol (7.00 g, 0.06 mol) and 2,3-dimethyl-1-phenyl-5-pyrazolone (22.70 g, 0.12 mol) in THF (240 mL) was added a solution of triphosgene (5.96 g, 0.02 mol) in THF (50 mL) dropwise at 50 °C. After the addition, the solution was cooled to room temperature and stirred overnight. The reaction mixture was filtered and concentrated by rotary evaporation and then dissolved in chloroform (100 mL). The solution was washed with aqueous hydrochloric acid (3.5 wt %, 200 mL) and an adequate amount of water. After removal of the solvent, the residue was purified by column chromatography (eluent; ethyl acetate/*n*-hexane = 2/1, volume ratio) to obtain colorless liquid. Yield 3.85 g (44.9%). ^{1}H NMR ($CDCl_3$): δ 2.15−2.20 (2H, m, =CHCH_2), 2.25−2.38 (1H, m, CH), 4.11−4.18 (2H, m, CH_2O), 4.42−4.47 (2H, m, CH_2O), 5.12−5.18 (2H, m, CH_2=CH), 5.67−5.81 (1H, m, CH_2=C*H*). ^{13}C NMR ($CDCl_3$): δ 31.65 (*C*HCH$_2$O), 32.26 (CH_2=CH*C*H_2), 71.51 (CH_2O), 117.05 (*C*H_2=CH), 135.49 (CH_2=*C*H), 148.42 (C=O). IR (NaCl): 1180, 1640, 1750, 3080 cm^{-1}. Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.22; H, 7.18.

3-(1,3-Dioxan-2-one-5-yl)propyl 2-(9-Fluorenylmethoxycarbonylamino)ethyl Thioether (1). A solution of 2-(9-fluorenylmethoxycarbonylamino)ethanethiol (5.00 g, 0.02 mol), 5-allyl-1,3-dioxan-2-one (2.37 g, 0.02 mol), and benzoyl peroxide (0.41 g, 0.002 mol) in DMF (4 mL) was prepared in a 10 mL ampule. After dissolved oxygen was removed under vacuum, the ampule was sealed and heated at 80 °C with stirring for 1 h. The reaction mixture was dissolved in ethyl acetate (100 mL) and washed with an adequate amount of water. After removal of the solvent, the residue was purified by column chromatography (eluent; ethyl acetate/*n*-hexane = 2/1, volume ratio) to obtain a colorless liquid. Yield 0.75 g (10.2%). ^{1}H NMR ($CDCl_3$): δ 1.35−1.70 (4H, m, SCH_2C*H*$_2$C*H*$_2$), 2.05−2.20 (1H, m, $SCH_2CH_2CH_2C$*H*), 2.45−2.05 (2H, t, J = 6.5 Hz, S*C*$H_2CH_2CH_2$), 2.05−2.15 (2H, t, J = 6.5 Hz, S*C*H_2-CH_2NH), 3.25−3.40 (2H, q, J = 6.5 Hz, SCH_2C*H*$_2$NH), 4.10−4.20 (2H, m, CH_2CHC*H*$_2$OC=O), 4.20−4.30 (1H, m, C*H*CH$_2$-OC(=O)NH), 4.30−4.45 (2H, m, CH_2CHC*H*$_2$OC=O), 4.30−4.45 (2H, m, C*H*$_2$OC(=O)NH), 5.43 (1H, s, NH), 7.25−7.45 (4H, m, fluorene ring), 7.50−7.60 (2H, m, fluorene ring), 7.70−7.80 (2H, m, fluorene ring). ^{13}C NMR ($CDCl_3$): δ 26.01 (SCH_2C*H*$_2$-CH_2CH), 26.35 (SCH_2CH_2C*H*$_2CH$), 30.62 (S*C*$H_2CH_2CH_2CH$), 31.14 (S*C*H_2CH_2NH), 31.74 ($SCH_2CH_2CH_2C$H), 40.07 (SCH_2C*H*$_2$-NH), 46.96 (*C*HCH$_2$OC(=O)NH), 66.47 (*C*H_2OC(=O)NH), 71.62 (CH_2CHC*H*$_2$OC=O), 119.78 (fluorene ring), 124.86 (fluorene ring), 126.77 (fluorene ring), 127.51 (fluorene ring), 141.04 (fluorene ring), 143.64 (fluorene ring), 148.32 (OC(=O)O), 156.20 (OC(=O)NH). IR (NaCl): 1262, 1447, 1530, 1696, 1730, 2847, 2918, 3064, 3350 cm^{-1}. Anal. Calcd for $C_{24}H_{27}NSO_5$: C, 65.28; H, 6.16; N, 3.17; S, 7.26. Found: C, 65.27; H, 6.15; N, 3.20; S, 7.20.

3-Cyclohexylpropyl 2-(9-Fluorenylmethoxycarbonylamino)ethyl Thioether (2). The title compound was synthesized from 2-(9-fluorenylmethoxycarbonylamino)ethanethiol and allylcyclohexane in a similar manner as **1**. Yield 49.5%. Mp 89.5−90.5 °C. ^{1}H NMR (DMSO-d_6): δ 0.75−1.75 (15H, m, CH_2CH_2C$_6$*H*$_{11}$), 2.40−2.60 (4H, m, CH_2SCH_2), 3.05−3.25 (2H, m, NHCH_2), 4.20−4.27 (1H, m, C*H*CH$_2$O), 4.27−4.35 (2H, m, CH_2O), 7.25−7.50 (4H, m, Ph), 7.60−7.75 (2H, m, Ph), 7.80−7.95 (2H, m, Ph).^{13}C NMR (DMSO-d_6): δ 25.78 (C_6H_{11}), 26.14 ($CH_2CH_2C_6H_{11}$), 26.43 (C_6H_{11}), 30.74 ($SCH_2CH_2CH_2C_6H_{11}$), 31.23 ($CH_2C_6H_{11}$), 32.78 (C_6H_{11}), 35.99 ($NHCH_2CH_2S$), 36.69 (C_6H_{11}), 40.33 ($NHCH_2$), 46.72 (*C*HCH_2O), 65.31 (CH_2O), 120.10 (fluorene ring), 125.13 (fluorene ring), 127.02 (fluorene ring), 127.58 (fluorene ring), 140.74 (fluorene ring), 143.87 (fluorene ring), 156.02 (C=O). IR (KBr): 1262, 1447, 1531, 1696, 2848, 2918, 3065, 3351 cm^{-1}. Anal. Calcd for $C_{26}H_{33}NSO_2$: C, 73.72; H, 7.85; N, 3.31; S, 7.57. Found: C, 74.00; H, 7.62; N, 3.27; S, 7.51.

3-(1,3-Dioxan-2-one-5-yl)propyl Ethyl Thioether (3). A solution of 5-allyl-1,3-dioxan-2-one (0.90 g, 0.006 mol), ethyl mercaptan (0.40 g, 0.006 mol), and 2,2′-azobis(isobutyronitrile) (0.10 g, 0.0006 mol) in DMF (3 mL) was prepared in a 10 mL ampule. After dissolved oxygen was removed under vacuum, the ampule was sealed and heated at 60 °C with stirring overnight. The reaction mixture was dissolved in ethyl acetate (100 mL) and washed with an adequate amount of water. After removal of the solvent, the residue was purified by column chromatography (eluent; ethyl acetate/*n*-hexane = 2/1, volume ratio) to obtain a colorless liquid. Yield 1.07 g (82.0%). ^{1}H NMR ($CDCl_3$): δ 1.26 (3H, t, J = 7.0 Hz, CH_3), 1.45−1.55 (2H, m, SCH_2C*H*$_2$), 1.60−1.75 (2H, m, C*H*$_2$CH), 2.20−2.30 (1H, m, CH), 2.50−2.60 (4H, m, C*H*$_2$SC*H*$_2$), 4.05−4.20 (2H, m, CH_2O), 4.40−4.50 (2H, m, CH_2O).^{13}C NMR ($CDCl_3$): δ 15.00 (CH_3), 25.10 (SCH_2CH_2), 26.01 (CH_3CH_2), 26.26 (*C*H_2CH), 30.30 (S*C*H_2CH_2), 30.72 (CH), 71.85 (CH_2O × 2), 148.32 (C=O). IR (KBr): 770, 1180, 1641, 1750, 3081 cm^{-1}. Anal. Calcd for $C_9H_{16}SO_3$: C, 52.91; H, 7.89; S, 15.70. Found: C, 52.70; H, 7.77; S, 15.50.

Polyaddition of 1. To a solution of **1** (1.00 g, 0.0034 mol) in DMSO (3.40 mL) was added *N*,*N*-diisopropylethylamine (0.044 g, 0.00034 mol), and the resulting mixture was heated at 30 °C for 14 days. The reaction mixture was poured into ether (200 mL) to precipitate a polymer. It was separated by filteration, washed thoroughly with ether, and dried under vacuum. Yield 0.74 g (100%). ^{1}H NMR (DMSO-d_6): δ 1.20−1.80 (5H, m, SCH_2C*H*$_2C$*H*$_2C$*H*), 2.35−2.62 (4H, m, CH_2SCH_2), 3.01−3.21 (2H, m, NHCH_2), 3.21−3.50 (2H, m, CH_2OH), 3.80−4.00 (2H, m, CH_2OC=O), 4.06 (1H, s, OH), 4.50 (1H, s, NH).^{13}C NMR (DMSO-d_6): δ 27.04 (*C*H_2CH_2CH), 27.40 (CH_2CH_2CH), 31.25 (S*C*$H_2CH_2CH_2$), 31.66 (S*C*H_2CH_2N), 39.91 (CH), 40.18 (SCH_2CH_2N), 61.17 (CH_2OH), 64.68 (*C*H_2OC=O) 156.83 (C=O). IR (KBr): 1100, 1450, 1700, 2880, 2915, 3350 cm^{-1}.

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References and Notes

(1) Polyhydroxyurethane films obtained from 2,2-bis[*p*-(1,3-dioxolane-2-one-4-yl-methoxy)phenyl]propane and 4,9-dioxadodecane-1,12-diamine absorb water more than 30 wt %, while commercial polyurethane CRISVON 9004 [hard type polyurethane (Dainippon Ink and Chemicals, Inc.)] less than 2%. The thermal decomposition temperatures of the polyhydroxyurethane are 32−88 °C higher than that of the commercial polyurethane (259 °C).

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