Polyurethanes with a New Diol Segment. Synthesis of Polyurethanes Containing a Norbornene Moiety and Their Reactions with Thiols

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ABSTRACT: Polyaddition of 5-norbornene-2,2-dimethanol (NDM) with methylenebis(phenyl isocyanate) (MDI) was carried out in THF in the presence of DABCO at 60 °C to obtain the corresponding polyurethane **3a** (Y, 100%; $\overline{M}_n$, 27 000). Similarly, polyurethane **3b** was also prepared from hexamethylene diisocyanate (HDI) in the presence of dibutyltin dilaurate (Y, 100%; $\overline{M}_n$, 6000). The polymers were characterized by spectral data on the basis of the results of the model compounds, which were synthesized by the reactions of NDM and phenyl or butyl isocyanates. The polymerization conditions (reaction time, concentration, and catalyst) were examined in terms of molecular weight and yield of the polyurethanes. DSC data of the polyurethanes showed that they had comparatively high T_gs (**3a**, 170 °C; **3b**, 71 °C). As an example of the functionalization of the polyurethanes **3**, a (2-hydroxyethyl)thio group was introduced quantitatively into **3a** by the radical addition of 2-mercaptoethanol to the norbornene moiety at 80 °C for 18 h. Meanwhile, **3a** was treated with 1,2-ethanedithiol at 60 °C for 62 h to give the cross-linked polymer quantitatively under the radical conditions.

Introduction

Polyurethanes are typical thermoplastic elastomers and are of interest from the viewpoint of variety of molecular design, easy molding, and other characteristics. Syntheses of functional polyurethanes containing reactive groups have been of considerable interest because of the variety of their applicability to adhesives, photopolymerizable compounds, etc.[1]

We have recently studied the synthesis of novel functional polyurethanes using unique 1,3-diols with reactive groups.[2] 5-Norbornene-2,2-dimethanol (NDM) is one of the 1,3-diols, which is readily preparable from cyclopentadiene and acrolein in two steps[3] and has an interesting structure with a reactive olefin and a rigid skeleton. In consideration of this specific structure, NDM has been used for the preparation of the corresponding spiroorthocarbonate[4] and oxetane, their polymers,[5] etc.

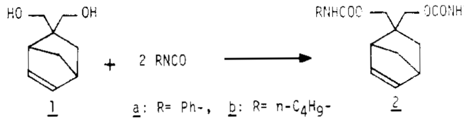
In this paper, preparation and characterization of polyurethanes with NDM as a diol segment and polymer reactions of the polyurethanes with thiols are described.

Results and Discussion

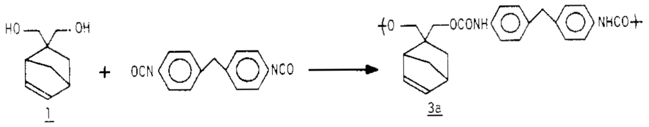
Preparation of Model Compounds. In order to study the general scope of the polyaddition reaction of NDM toward aryl and alkyl diisocyanates and to identify the structures of polyurethanes, model compounds corresponding to the repeating units were synthesized by DABCO-catalyzed reactions of NDM with phenyl or *n*-butyl isocyanates in THF.

The model compounds (**2a** and **2b**; Scheme I) were characterized by IR and ^{1}H NMR spectra and elemental analyses. The most characteristic IR absorption band appeared at 1690 cm^{-1} as carbamate carbonyl stretching. No isocyanate absorption was observed at 2260 cm^{-1}. In the ^{1}H NMR spectra in dimethyl-d_6 sulfoxide (DMSO-d_6) of **2a**, two kinds of proton signals (NH) of carbamate groups, appearing at 9.45 and 9.50 ppm, suggest exo and endo carbamate groups placed under different environments in the norbornene structure. A broad proton signal from the two carbamate NHs of **2b** was observed around 6.6–7.1 ppm. In the ^{13}C NMR spectra of **2a** and **2b**, carbon signals of the norbornene structures were assigned by reference to the shift data of **1**. These spectral data were in good accordance with the structure of the model compounds.

Scheme I



Scheme II



Polymerization. On the basis of the results of the model reactions, polyaddition of NDM with aryl or alkyl diisocyanates was carried out in solution to afford polyurethanes containing the norbornene moiety as the diol segment. The effects of reaction time, concentration, and catalyst on the polymerization were studied.

An equimolar mixture of NDM and methylenebis(4-phenyl isocyanate) (MDI) was treated with a catalytic amount of 1,4-diazabicyclooctane (DABCO) (2 mol %) at 60 °C in tetrahydrofuran (THF; Scheme II). The structure of the polyurethane obtained as a white powder was determined by IR and NMR spectra. The IR spectrum of the polyurethane **3a** was similar to that of the model compound **2a**. Characteristic strong bands appeared at 3300 cm^{-1} (NH stretching band) and 1710 cm^{-1} (carbonyl stretching band). The ^{1}H NMR (DMSO-d_6) spectrum of polyurethane **3a** showed characteristic signals due to the olefinic proton of the norbornene moiety around

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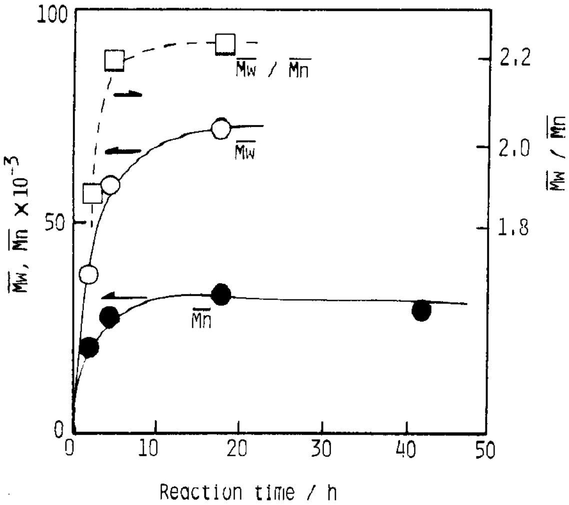


Figure 1. Effect of reaction time on polyaddition of NDM to MDI: 60 °C, NDM (1×10^{-3} mol), MDI (1×10^{-3} mol), DABCO (2×10^{-5} mol) in THF (2 mL).

6.10 ppm and two carbamate NH protons at 9.34 and 9.40 ppm.

Reaction Time. Figure 1 shows plots of number-average and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) vs reaction time in the polymerization in THF in the presence of DABCO at 60 °C. The reaction mixture became viscous within 1 h, and after 2 h the yield of the polymer was quantitative. Under these conditions, $\overline{M}_n$ reached 30 000 for 10–20 h, during which $\overline{M}_w/\overline{M}_n$ also increased to ca. 2.2.

Generally, polyaddition of diols and diisocyanates is known to follow roughly second-order kinetics, first order in the concentration of each functional group.[6] In this case, the $\overline{M}_n$ of polyurethane–reaction time curve becomes linear. But in the polymerization conditions shown in Figure 1, an initial fast increase of $\overline{M}_n$ decreased because an increase of the viscosity of the reaction system due to the progress of the polymerization presumably retarded the reaction rate.

Concentration. $\overline{M}_n$ and yield of **3a** obtained in the reaction at 60 °C for 4.5 h are indicated as a function of the concentration in Figure 2. The $\overline{M}_n$ and yield increased significantly with an increase of the concentration as expected. Consequently, [NDM] must be more than 0.3 mol/L in order to obtain the polymer with both $\overline{M}_n$ more than 10 000 and yield more than 90%.

Catalyst. It is known that polyadditions of diols with diisocyanates are catalyzed by alkylamines such as DABCO and organometallic salts such as dibutyltin dilaurate (DBTDL) or stannous octanate (SO) and that a combination of such amines and tin catalysts shows a synergetic effect.[6] Results of the polyaddition of NDM and MDI using these catalysts are summarized in Table I. The best yield and $\overline{M}_n$ were observed with use of DBTDL. But little difference in the catalytic activity among these catalysts was observed, because the primary diol (NDM) and the aryl diisocyanate (MDI) were so reactive that these catalysts showed almost similar activity under the conditions.

The polyaddition of NDM was carried out with hexamethylene diisocyanate (HDI; Scheme III). IR and ^{1}H NMR spectra of the polymer obtained as white powder were also similar to those of the model compound **2b**. The $\overline{M}_n$ of the polyurethane **3b** was lower than that of **3a**. This may be due to the difference in the reactivity of the isocyanate group between MDI and HDI. When DABCO was used instead of DBTDL, the yield of the insoluble polymer in *n*-hexane–ether mixed solvent was only 50% under similar conditions; DABCO was less active than DBTDL. The difference in activities of the catalysts was clearly confirmed in this polymerization with HDI, probably because DABCO activates mainly hydroxy groups whereas DBTDL activates both hydroxy and isocyanate groups. Lower reactivity of HDI than MDI made the activity difference between DABCO and DBTDL clear.

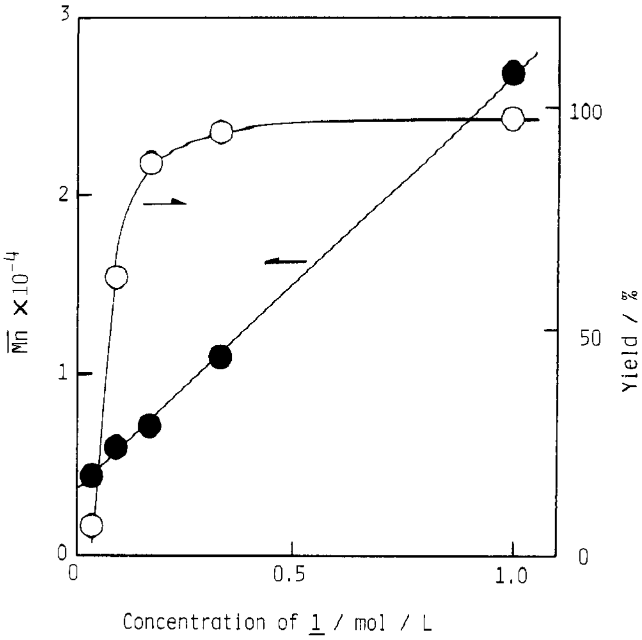


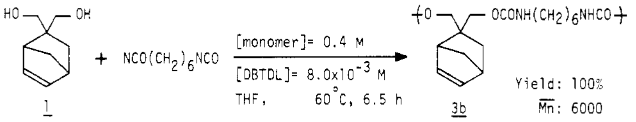
Figure 2. Effect of concentration on polyaddition of NDM to MDI: 60 °C, for 4.5 h, DABCO (1 mol % based on monomer) in THF, $\overline{M}_n$ (●); yield of insoluble polymer in hexane–ether (○).

Table I
Effect of Catalysts on Polyaddition of NDM to MDI[a]

catalyst[b]	DABCO	DABCO + SO	DBTDL
yield,[c] %	90	90	98
$\overline{M}_n$[d]	5800	6100	6600

[a] At 60 °C, for 4.5 h, NDM (1.0×10^{-3} mol), MDI (1.0×10^{-3} mol) in THF (6.0 mL). [b] Catalyst = 4.0 mol % based on NDM. [c] Insoluble part in *n*-hexane–ether (1:1). [d] Measured by GPC based on polystyrene standard.

Scheme III



Properties of the Polyurethanes. The solubilities of the polyurethanes were examined and are summarized in Table II. Both **3a** and **3b** were soluble in most polar aprotic solvents and showed a similar behavior except for in acetic acid.

The melting (T_m) and glass transition (T_g) temperatures of the polyurethanes were determined by differential scanning calorimetry (DSC). DSC data of these polymers are listed in Table III. The T_g of **3a** was higher than that of the same carbon number polyurethanes prepared from MDI and 1,9-dihydroxynonane (72 °C) or 1,3-propanediol (119 °C).[7] This may be attributed to the difference in the rigidity of the diol moiety. **3b** showed a lower T_g than that of **3a**, as it is well-known that flexible alkylene groups of the diisocyanate moiety in poly-

Table II
Solubility of Polyurethanes[a]

polym	DMF	H_2SO_4	CF_3COOH	dioxane	THF	$PhNO_2$	AcOH	$CHCl_3$	acetone
3a	++	++	++	++	++	+ −	− −	− −	− −
3b	++	++	++	++	++	+ −	++	− −	− −

[a] At room temperature, (++) soluble, (+ −) soluble by heating, (− −) insoluble.

Table III
Thermal Properties of Polyurethanes

			temp, °C		
polym	T_m,[a] °C	T_g, °C	5% wt loss[b]	10% wt loss[b]	residual wt[b] at 500 °C, %
3a	227	170	265	275	9.3
3b	169	71	245	262	1.0

[a] Polymer melting temperatures were obtained from DSC curves. [b] Weight losses were obtained in TGA in helium (heating rate: 10 °C/min).

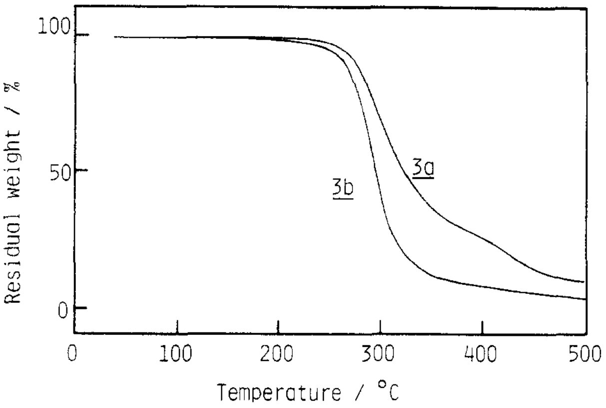
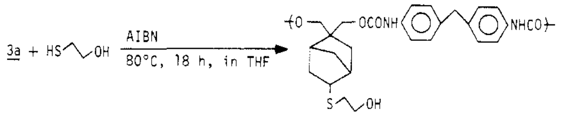


Figure 3. TGA curves of **3a** and **3b** in helium (60 mL/min) at a heating rate of 10 °C/min.

Scheme IV



urethanes make T_g low in comparison with arylene groups. The thermal stability of those polyurethanes was evaluated by thermogravimetric analysis (TGA). The TGA curves of **3a** and **3b** are shown in Figure 3, and thermal stability data are listed in Table III.

These polymers containing alkylene linkages showed relatively good thermal stability for polyurethanes, undoubtedly due to their structural rigidity.

Addition of Thiols to Norbornene Moieties in the Polyurethane. Functional groups on polymeric backbones can modify the physical properties of polymers or serve as reaction sites for further modification of the polymer. The incorporation of the hydroxyl group into polymers has been found useful in the synthesis of polymeric supports and reagents[8] and in coating applications requiring cross-linking reactions and adhesion promotion.[9]

Since thiols add radically to the olefinic bond of norbornene and its skeleton does not undergo rearrangement, as it does under the ionic conditions,[10] radical addition of a thiol with a hydroxyl group to the norbornene moiety was selected for the modification of the preformed norbornene polyurethane.

Addition of 2-mercaptoethanol to **3a** (Scheme IV) was carried out with 2,2′-azobis(isobutyronitrile) (AIBN) as initiator in THF at 80 °C, and the hydroxyl group containing polymer(s) was obtained in 72% yield. Incorporation of the (2-hydroxyethyl)thio group was 90% based on the olefin bond, determined by elemental analysis.

A cross-linking reaction was attempted by using a dithiol. In the radical addition of 1,2-ethanedithiol to **3a** under similar conditions to those above, a cross-linked polymer was obtained quantitatively. The result of elemental analysis showed that a 1,2-ethylenedithio unit was quantitatively introduced.

Thus, in this paper, novel polyurethanes with norbornene moieties have been prepared and characterized. In addition, introduction of functional groups with a hydroxythiol and cross-linking with a dithiol by radical addition have been carried out by utilizing reactive norbornene moieties.

Experimental Section

Materials. Methylenebis(4-phenyl isocyanate) (MDI, from Tokyo Kasei) was purified by recrystallization from *n*-hexane and dried in a vacuum desiccator at room temperature. Commercially available hexamethylene diisocyanate (HDI, from Tokyo Kasei), phenyl isocyanate, *n*-butyl isocyanate, 1,2-ethanedithiol, and 2-mercaptoethanol were purified by fractional distillation under reduced pressure. Tetrahydrofuran (THF) was dried over calcium hydride and was fractionally distilled before use. 1,4-Diazabicyclooctane (DABCO) was purified by recrystallization from *n*-hexane. Extrapure-grade dibutyltin dilaurate (DBTDL), stannous octanoate (SO), and 2,2′-azobis(isobutyronitrile) (AIBN) were used without further purification.

Preparation of 5-Norbornene-2,2-dimethanol (1). The preparation of **1** was carried out with a modification of the method of Bruson et al.[3] A mixture of 50.9 g (0.42 mol) of 5-norbornene-2-carboxaldehyde (from Aldrich), 101.0 g (1.25 mol) of 37% aqueous formaldehyde, and 200 mL of methanol was heated at 77 °C for 0.5 h in an oil bath under nitrogen. To the refluxing mixture was added dropwise with stirring over a period of 2.5 h 107.5 g of 35% KOH solution (0.67 mol). After refluxing for 1 h, the mixture was allowed to cool to room temperature. Ether (100 mL) was added to the mixture, and the resulting precipitate was removed by filtration. The filtrate was extracted three times with ether. The combined organic layer was washed with water and dried over anhydrous magnesium sulfate. After the drying agent was filtered off, the filtrate was concentrated under a reduced pressure to give a cake, which was recrystallized from benzene to yield 40.7 g (63.4%) of **1**: mp 111.2–112.0 °C (lit.[3] mp 113–114 °C); IR (KBr) 3250, 3040, 2910, 2850, 1565, 1460, 1405, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) 6.10 (t, 2 H, –CH=CH–), 3.83 (s, 2 H, $-CH_2O-$), 3.53 (dd, 2 H, $-CH_2O-$), 2.94–2.82 (m, 2 H, >CH–), 2.62 (s, 2 H, –OH), 1.51–0.71 (m, 4 H, $-CH_2-$) ppm; ^{13}C NMR ($CDCl_3$) 137.00 and 135.05 (–CH=), 77.11 and 70.23 ($-CH_2OH$), 48.54 (>C<), 46.89 ($-CH_2-$), 44.50 and 41.96 (>CH–), 32.85 ($-CH_2-$) ppm.

Preparation of 5-Norbornene-2,2-dimethanol Bis(*N*-phenylcarbamate), Model Compound 2a. In a 50-mL round-bottom flask equipped with a reflux condenser with a calcium chloride tube were placed 2.42 g (20.4 mmol) of phenyl isocyanate, 1.57 g (10.2 mmol) of **1**, and 20 mL of a solution of DABCO in THF (2.0×10^{-5} mol/mL), and the mixture was stirred in an oil bath at 60 °C for 2 h. THF was removed using a rotary evaporator, and the resulting residue (crude yield 95%) was recrystallized three times from benzene to yield 1.83 g (45.7%) of **2a**: mp 167.0–168.9 °C; IR (KBr) 3240, 3050, 1690, 1600, 1500 cm^{-1}; ^1H NMR (DMSO-d_6) 9.50 and 9.45 (s, 1 H × 2, –NH–), 7.57–6.70 (m, 8 H, Ph), 6.33–5.96 (m, 2 H, –CH=CH–), 4.25 and 3.89 (s, 2 H × 2, $-CH_2O-$), 2.95–2.26 (m, 2 H, >CH–), 1.88–0.71 (m, 4 H, $-CH_2-$) ppm; ^{13}C NMR (DMSO-d_6) 153.25 and 153.11 (–OCONH–), 138.78 and 137.27 (–CH=), 133.86, 128.15, 121.96 and 118.21 (Ph), 67.23 and 66.60 ($-CH_2O-$), 46.52 ($>C<$), 45.98 ($-CH_2-$), 45.54 and 41.64 ($>CH-$), 32.24 ($-CH_2-$) ppm. Anal. Calcd for $C_{23}H_{24}N_2O_4$: C, 70.39; H, 6.16; N, 7.14. Found: C, 70.48; H, 5.81; N, 7.40.

Preparation of 5-Norbornene-2,2-dimethanol Bis(*N*-*n*-butylcarbamate), Model Compound 2b. In a 10-mL round-bottom flask equipped with a reflux condenser with a calcium chloride tube were placed 0.991 g (10.0 mmol) of *n*-butyl isocyanate, 0.771 g (5.0 mmol) of **1**, and 5.4 mL of a solution of DABCO in THF (2.0×10^{-5} mol/mL), and the mixture was stirred in an oil bath at 80 °C for 3.5 h. The solvent was then removed using a rotary evaporator, and the residual product (crude yield 98%) was recrystallized three times from benzene to give 0.866 g (45.4%) of **2b**: mp 41.5–44.0 °C; IR (KBr) 3350, 3050, 1690, 1525 cm^{-1}; ^1H NMR (DMSO-d_6) 7.12–6.62 (m, 2 H, NH), 6.24–5.80 (m, 2 H, $-CH{=}CH-$), 4.01 and 3.63 (s, 2 H × 2, $-CH_2O-$), 3.11–2.40 (m, 6 H, $-NHCH_2-$, $>CH-$), 1.43–0.33 (m, 18 H, $-CH_2CH_2CH_3$, $-CH_2-$) ppm; ^{13}C NMR (CD_3CN) 157.52 ($-NHCOO-$), 138.51 and 135.30 ($-CH{=}$), 68.48 and 67.70 ($-CH_2O-$), 47.81 ($-CH_2-$), 47.37 ($>C<$), 46.93 ($-CH_2-$), 43.33 and 41.23 ($>CH-$), 33.43, 32.85 and 20.62 ($-CH_2-$), 14.09 ($-CH_3$). Anal. Calcd for $C_{19}H_{32}N_2O_4$: C, 64.74; H, 9.15; N, 8.51. Found: C, 64.47; H, 9.27; N, 7.99.

Typical Procedure for the Preparation of Polyurethanes. **1** (0.154 g, 1 mmol), MDI (0.250 g 1 mmol), a solution of DABCO in THF (0.02M, 1 mL), and THF (1 mL) were placed in a glass ampule. After repeated degassing and evacuating, the ampule was sealed off and then heated at 60 °C for 4.5 h in an oil bath. The mixture was allowed to cool to room temperature and was poured into a large amount of *n*-hexane–diethyl ether mixed solvent (200 mL, 1:1) to precipitate polymer. After the mixture was allowed to stand overnight, the precipitate was collected by filtration and dried under a reduced pressure at room temperature. The polymer obtained was a white powder. **3a**: IR (film) 3300, 3050, 1710, 1595, 1520 cm^{-1}; ^1H NMR (DMSO-d_6) 9.43 and 9.38 (s, 1 H × 2, NH), 7.45–6.90 (dd, 8 H, phenylene), 6.31–5.93 (m, 2 H, $-CH{=}CH-$), 4.40–4.10 (m, 2 H, $-CH_2O-$), 3.94–3.69 (m, 4 H, $-CH_2O-$, $-CH_2-$), 2.96–2.64 (m, 2 H, $>CH-$), 1.87–1.13 (m, 3 H, $-CH_2-$, $-CH-$), 1.06–0.52 (m, 1 H, $>CH-$) ppm; ^{13}C NMR (DMSO-d_6) 153.67 and 153.52 ($-NHCOO-$), 137.59 (Ph), 137.05 and 135.44 ($-CH{=}$), 134.22, 128.67, and 118.72 (Ph), 67.55 and 66.97 ($-CH_2O-$), 46.84 ($-C-$), 46.35 ($-CH_2-$), 45.91 and 42.01 ($>CH-$), 40.70 and 32.61 ($-CH_2-$) ppm. **3b**: IR (film) 3300, 3050, 1690, 1525 cm^{-1}; ^1H NMR (DMSO-d_6) 7.1–6.7 (m, 2 H, NH), 6.27–5.87 (m, 2 H, $-CH{=}CH-$), 4.70–2.40 (m, 10 H, $-CH_2O-$, $-NHCH_2-$, $>CH-$), 1.96–0.40 (m, 12 H, $-CH_2-$) ppm.

Addition of 2-Mercaptoethanol to 3a. **3a** (0.992 g, 2.45 mmol), 2-mercaptoethanol (0.230 g, 2.94 mmol), AIBN (0.0223 mg, 0.135 mmol), and THF (10 mL) were placed in a glass ampule. After repeated degassing and evacuating, the ampule was sealed off and then heated at 80 °C for 18 h in an oil bath. The mixture was allowed to cool to room temperature and poured into methanol (300 mL) to precipitate the polymer. The gummy precipitate was collected by decantation and further purified via repeated precipitation from THF solution into *n*-hexane–ether mixed solvent (1:1 (v/v)) to yield 0.852 g (72.0%) of **5** (white powder): IR (film) 3260, 1690, 1595, 1520 cm^{-1}; ^1H NMR (DMSO-d_6) 9.5–9.2 (br s, 2 H, HN), 7.5–6.8 (dd, 8 H, phenylene), 4.7–3.3 (m, 9 H, $-OH$, $-CH_2OH$, $-CH_2O-$, $-CH_2-$), 3.00–0.6 (m, 11 H, $-SCH_2-$, $>CHS-$, $>CH-$, $-CH_2-$) ppm; ^{13}C NMR (DMSO-d_6) 153.4 ($-NHCOO-$), 136.6, 135.1, 128.4 and 118.4 (Ph), 66.2, 64.9 and 60.7 ($-CH_2O-$), 46.7 ($>C<$), 44.9 ($-SCH<$), 43.7 and 42.9 ($>CH-$), 40.9 ($-CH_2-$), 37.8 ($-CH_2S-$), 35.9, 34.1, and 33.5 ($-CH_2-$) ppm. Anal. Found: C, 64.06; H, 6.16; N, 5.86; S, 6.31. (2-Hydroxyethyl)thio group was introduced into 90% of the olefin bond, which was determined by the elemental analysis.

Cross-Linking of 3a with 1,2-Ethanedithiol. **3a** (2.011 g, 4.97 mmol), 1,2-ethanedithiol (0.112 g, 1.19 mmol), AIBN (0.0247 mg, 0.15 mmol), and THF (30 mL) were placed in a glass ampule. After repeated degassing and evacuating, the ampule was sealed off and then heated at 60 °C in an oil bath. Gelation occurred immediately, and the mixture was allowed to stand for 14 h at the same temperature. The mixture was subjected to Soxhlet extraction with THF (150 mL) for 29 h to remove excess dithiol. The Soxhlet thimble containing the washed polymer was dried under reduced pressure at room temperature until its weight became constant: yield 2.13 g (99.8%). Anal. Found: C, 68.06; H, 6.72; N, 5.72; S, 3.88. The elemental analysis data showed that the 1,2-ethylenedithio unit was quantitatively introduced to the polymer.

Measurement. ^1H NMR spectra were recorded with a JEOL JNM PMX-60SI spectrometer using tetramethylsilane as an internal standard (solvent DMSO-d_6). IR spectra were measured by a Jasco IRA-2 spectrometer. Number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights and their distributions were obtained by gel permeation chromatography (GPC). GPC analysis of polymers was performed at 35 °C with a Toyo Soda HPLC CCCP & 8000 system equipped with three polystyrene gel columns (TSK gel G2000, G2500, and G300) and a data-processing system. Tetrahydrofuran (THF) was used as the GPC solvent. The melting and glass transition temperatures of polymers were determined from differential scanning calorimetry curves obtained with a Rigaku Denki Co. TG-DSC-8089E-1 thermobalance analyzer. Thermogravimetry (TG) was performed with the same analyzer, in helium (60 mL/min) at a heating rate of 10 °C/min.

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Registry No. **1**, 6707-12-6; **2a**, 126615-58-5; **2b**, 126644-58-4; **3a** (copolymer), 126615-59-6; **3a** (SRU), 126615-63-2; **3b** (copolymer), 126615-60-9; **3b** (SRU), 126615-64-3; (**3a**)(1,2-ethanedithiol) (copolymer), 126644-59-5; DBCO, 280-57-9; DBTDL, 77-58-7; SO, 1912-83-0; 5-norbornene-2-carboxaldehyde, 5453-80-5; formaldehyde, 50-00-0; phenyl isocyanate, 103-71-9; *n*-butyl isocyanate, 111-36-4.