

Head-to-Tail Regularity of Polyurethanes from *p*-Isocyanatobenzyl Isocyanate and Ethylene Glycol by a Distannoxane Catalyst

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(Received December 7, 2000; Accepted April 24, 2001)

ABSTRACT: An ordered polyurethane with high head-to-tail (H-T) regularity (up to 93%) was prepared by polyaddition reaction of *p*-isocyanatobenzyl isocyanate (**1**) with ethylene glycol (**2**) using 1,3-bis(isothiocyanate)-1,1,3,3-tetrabutyl-distannoxane as catalyst. Polymerizations were conducted in *N,N*-dimethylformamide (DMF) at -40°C in the presence of distannoxane by mixing both monomers all at once. The microstructure of polymers obtained was investigated by ^1H and ^{13}C NMR spectroscopy, and it was found that the polymers had the expected H-T ordered structure. The ordered polyurethane with 93% H-T regularity showed higher melting point and crystallinity compared to the polymers with lower H-T regularity.

KEY WORDS Polyurethane / Constitutional Isomerism / Head-to-Tail Regularity / Nonsymmetric Monomer / *p*-Isocyanatobenzyl Isocyanate / Distannoxane / Structure-Property Relationship /

Structure-property relationships arising from constitutional isomerism are not well known for condensation polymers.^{1,2} We have been interested in developing a synthetic method for constitutional isomeric condensation polymers from nonsymmetric monomers² and in clarifying structure-property relationships between constitutional isomers.^{3,4}

Recently, we reported the first example of an ordered (head-to-head (H-H) or tail-to-tail (T-T)) polyurethane synthesis, that is, H-H or T-T polyurethane from *p*-isocyanatobenzyl isocyanate (**1**) and ethylene glycol (**2**).⁵ Furthermore, we found that head-to-tail (H-T) polyurethane (H-T content: 83%) was produced from **1** and **2** in the presence of organotin catalysts.⁶ The synthesis of an H-T polymer from a nonsymmetric monomer and a symmetric monomer requires strong deactivation of the second functional group on the symmetric monomer by reaction of the first functional group,¹ and there are only a very few, such as H-T polyurea from bis(4-nitrophenyl) carbonate and 2-(4-aminophenyl)ethylamine and H-T polyamide from succinic anhydride and 2-(4-aminophenyl)ethylamine in the presence of a condensing agent.^{7,8}

The regularity or lack of regularity in polymers affects their properties because of large differences in ability to crystallize. Higher ordered H-T polyurethane from **1** and **2** was expected to have properties that were

superior to the lower H-T one.

The article investigates how the H-T regularity of polyurethanes from **1** and **2** changes depending on polymerization conditions, especially polymerization temperatures and catalysts. Furthermore, the effects of constitutional isomerism on thermal properties and crystallinity are also discussed.

EXPERIMENTAL

Materials

N,N-Dimethylformamide (DMF) was stirred over anhydrous CuSO_4 for 4 days at room temperature, purified by vacuum distillation, and stored over Molecular Sieves 4A-1/16. Tetrahydrofuran (THF) and toluene were purified by the usual method. Methanol and ethylene glycol were stirred over anhydrous Na_2SO_4 for 4 days at room temperature, purified by distillation and stored over Molecular Sieves 4A-1/16. *p*-Isocyanatobenzyl isocyanate (**1**) was prepared by the reported method.⁵ Triethylamine (TEA) was stirred over potassium hydroxide for 4 days at room temperature and purified by distillation. Dibutyltin dilaurate (DBTL) was used as received. Dibutyltin dichloride and dibutyltin oxide as the precursors of distannoxane derivatives were used as received. All operations were carried out under N_2 atmosphere.

Synthesis of 1,3-Dichloro-1,1,3,3-Tetrabutyl-distannoxane (3a)

A solution of sodium hydroxide (3.20 g, 80.0 mmol) in methanol (40 mL) was slowly added to a solution of dibutyltin dichloride (24.0 g, 80.0 mmol) in methanol (20 mL). The solution was stirred at room temperature for 1 h. A white precipitate was filtered off, washed with water/methanol several times, and dried *in vacuo*. The yield was 21.67 g (98%). Mp 110–111°C (lit.⁹ 110–112°C).

Synthesis of 1-Chloro-3-Hydroxy-1,1,3,3-Tetrabutyl-distannoxane (3b)

A solution of sodium hydroxide (1.60 g, 40.0 mmol) in methanol (20 mL) was added slowly to a solution of **3a** (12.0 g, 21.71 mmol) in methanol (300 mL). The mixture was stirred at room temperature for 18 h, and the precipitate was filtered off and dried *in vacuo*. This crude product was dissolved in hexane, poured into water, and extracted with hexane. The organic layer was dried over MgSO₄ and distilled under reduced pressure. The yield was 9.63 g (83%). Mp 100–101°C (lit.⁹ 109–121°C).

Synthesis of 1-Hydroxy-3-Isothiocyanato-1,1,3,3-Tetrabutyl-distannoxane (3d)

A solution of sodium thiocyanate (0.387 g, 4.0 mmol) in ethanol was added to a solution of **3b** (1.07 g, 4.0 mmol) in ethanol (50 mL). The mixture was heated for 10 min. The mixture was concentrated *in vacuo*, poured into water, and extracted with hexane. The organic layer was dried over MgSO₄ and distilled under reduced pressure. The yield was 0.93 g (83%). Mp 109–111°C (lit.¹⁰ 123–134°C).

Synthesis of Dibutyltin Diisothiocyanate

Dibutyltin dichloride (7.517 g, 24.74 mmol) was dissolved in absolute ethanol (16 mL) at room temperature. Sodium thiocyanate (4.01 g, 49.5 mmol) in ethanol (34 mL) at room temperature was added to this solution. The mixture was stirred at room temperature for 1 h. Precipitated sodium chloride was filtered off, and the solvent was distilled under reduced pressure. Recrystallization from toluene afforded white needles. The yield was 6.89 g (80%). Mp 142–144°C (lit.¹⁰ 142–142.5°C).

Synthesis of 1,3-Bis(isothiocyanato)-1,1,3,3-Tetrabutyl-distannoxane (3c)

Dibutyltin isothiocyanate (5.58 g, 16.0 mmol) and dibutyl oxide (3.98 g, 16.0 mmol) were dissolved in toluene (30 mL). The mixture was stirred at 100°C for 1 h, and an almost clear solution was obtained. The

solvent was removed under reduced pressure, and the product was recrystallized from hexane to afford white needles. The yield was 3.92 g (41%). Mp 79–81°C (lit.¹⁰ 83.5–84.5°C).

Synthesis of N-Phenyl(hydroxy)alkylurethane (5a–5c)

General procedure. 1,3-Propanediol (7.16 g, 100.0 mmol) and DBTL (0.316 g, 0.50 mmol) in THF (50 mL) were slowly added to phenylisocyanate (1.19 g, 10.00 mmol) at 0°C. This mixture was stirred at room temperature for 20 h, poured into water, and extracted with ethyl acetate. The organic layer was dried over MgSO₄ and concentrated *in vacuo*. The crude compound was purified by column chromatography (Wakogel C-300, ethyl acetate/hexane as an eluent). The yield was 1.61 g (82%) of colorless viscous liquid. IR (KBr, cm⁻¹): ν 1708 (C=O), 2961 (CH₂), 3310 (NH), 3390 (OH). ¹H NMR (600 MHz, DMF-*d*₇, δ): 1.85(m, 2H, –CH₂–CH₂–CH₂–OH), 3.64(q, 2H, –CH₂–CH₂–CH₂–OH), 4.23 (t, 2H, –CH₂–CH₂–CH₂–OH), 4.61 (t, 2H, –CH₂–CH₂–CH₂–OH), 7.02–7.62 (m, 5H, –C₆H₅), 9.58 (s, 1H, –NH–). ¹³C NMR (600 MHz, DMF-*d*₇, δ): 27.2, 62.5, 65.9, 119.7, 123.8, 130.3, 141.4, 155.5. Anal. Calcd. for C₁₀H₁₃NO₃: C, 61.53; H, 6.71; N, 7.18. Found: C, 61.69; H, 6.69; N, 7.07.

N-Phenyl-(2-hydroxy)ethylurethane (5a)

Yield: 85%, colorless viscous liquid. IR (KBr, cm⁻¹): ν 1711 (C=O), 2953 (CH₂), 3316 (NH), 3380(OH). ¹H NMR (600 MHz, DMF-*d*₇, δ): 3.73(q, 2H, –CH₂–CH₂–OH), 4.17(t, 2H, –CH₂–CH₂–OH), 4.93(t, 1H, –CH₂–CH₂–OH), 7.02–7.63 (m, 5H, –C₆H₅), 9.67 (s, 1H, –NH–). ¹³C NMR (600 MHz, DMF-*d*₇, δ): 61.6, 67.8, 119.7, 123.8, 130.3, 141.3, 155.5. Anal. Calcd. for C₉H₁₁O₃: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.36; H, 6.26; N, 7.69.

N-Phenyl-(4-hydroxy)butylurethane (5c)

Yield: 69%. Mp 58–61°C. IR (KBr, cm⁻¹): ν 1708 (C=O), 2949 (CH₂), 3310 (NH), 3390 (OH). ¹H NMR (600 MHz, DMF-*d*₇, δ): 1.59 (m, 2H, –CH₂–CH₂–CH₂–CH₂–OH), 1.73 (m, 2H, –CH₂–CH₂–CH₂–CH₂–OH), 3.57 (br, 2H, –CH₂–CH₂–CH₂–CH₂–OH), 4.15 (t, 2H, –CH₂–CH₂–CH₂–CH₂–OH), 4.52 (br, 2H, –CH₂–CH₂–CH₂–CH₂–OH), 7.02–7.62 (m, 5H, –C₆H₅), 9.58(s, 1H, –NH–). ¹³C NMR (600 MHz, DMF-*d*₇, δ): 27.2, 62.5, 65.9, 119.7, 123.8, 130.3, 141.4, 155.5. Anal. Calcd. for C₁₁H₁₅NO₃: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.36; H, 7.22; N, 6.57.

Synthesis of Alkylenebis(N-phenylcarbamate) (6a–6c)

General procedure. 1,3-Propanediol (1.52 g, 20.0 mmol) and DBTL (0.632 g, 1.00 mmol) in THF (20 mL) were added to phenylisocyanate (4.89 g, 41.0 mmol) at room temperature. The mixture was refluxed for 20 h. The solvent was removed under reduced pressure. The product was recrystallized from ethyl acetate to afford colorless needles. The yield was 5.27 g (84%). Mp 138°C. IR (KBr, cm^{-1}): ν 1707 (C=O), 2970 (CH_2), 3335 (NH). ^1H NMR (600 MHz, $\text{DMF-}d_7$, δ): 2.05 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 4.25 (t, 4H, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 7.03–7.63 (m, 10H $-\text{C}_6\text{H}_5$), 9.67 (s, 2H, $-\text{NH}-$). ^{13}C NMR (δ , $\text{DMF-}d_7$): 30.1, 62.7, 119.7, 123.9, 130.3, 141.3, 155.4. Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_4$: C, 64.96; H, 5.77; N, 8.91. Found: C, 65.13; H, 5.73; N, 8.83.

Ethylenebis(N-Phenylcarbamate) (6a)

Yield: 76%. Mp 154–155°C. IR (KBr, cm^{-1}): ν 1711 (C=O), 2973 (CH_2), 3344 (NH). ^1H NMR (600 MHz, $\text{DMF-}d_7$, δ): 4.40 (s, 4H, $-\text{CH}_2-$), 7.03–7.66 (m, 10H, $-\text{C}_6\text{H}_5$), 9.79 (s, 2H, $-\text{NH}-$). ^{13}C NMR (600 MHz, $\text{DMF-}d_7$, δ): 64.3, 119.8, 123.9, 130.1, 140.9, 155.1. Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 63.79; H, 5.31; N, 9.20.

Butylenebis(N-Phenylcarbamate) (6c)

Yield: 82%. Mp 182–183°C. IR (KBr, cm^{-1}): ν 1703 (C=O), 2970 (CH_2), 3321 (NH). ^1H NMR (600 MHz, $\text{DMF-}d_7$, δ): 1.77 (m, 4H, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 4.19 (t, 4H, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 7.02–7.63 (m, 10H, C_6H_5), 9.61 (s, 2H, $-\text{NH}-$). ^{13}C NMR (600 MHz, $\text{DMF-}d_7$, δ): 27.1, 65.5, 119.7, 123.9, 130.3, 141.3, 155.5. Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.73; H, 6.10; N, 8.37.

Synthesis of H-T Polyurethanes (4a–4e)

A solution of **1** (0.871 g, 5.0 mmol) in DMF (2 mL) at room temperature was added to one of **2** (0.310 g, 5.0 mmol) and **3c** (0.030 g, 0.05 mmol) in DMF (18 mL). It was stirred for 20 h. The resulting polymer solution was poured into methanol. The polymer was filtered off and dried at 50°C *in vacuo* for 1 d. The yield was 0.920 g (78%). Head-to-tail content of polymer **4c** was 82%. IR (KBr, cm^{-1}): ν 1705 (C=O), 2956 (CH_2), 3322 (NH). ^1H NMR (600 MHz, $\text{DMF-}d_7$, δ): 4.24–4.40 (m, 6H, $-\text{CH}_2-$), 7.29–7.66 (m, 4H, $-\text{C}_6\text{H}_4-$), 7.67 (br, 1H, $-\text{CH}_2-\text{NH}-\text{CO}_2-$), 9.74 (br, 1H, $-\text{C}_6\text{H}_4-\text{NH}-\text{CO}_2-$). ^{13}C NMR (600 MHz, $\text{DMF-}d_7$, δ): 45.4, 64.2, 64.4, 64.6, 119.8, 129.3, 135.6, 139.9, 155.2, 158.1. M_w (M_w/M_n)=26000 (2.6). Anal. Calcd. for $(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_4)_n$: C, 55.93; H, 5.12; N, 11.86. Found: C, 55.19; H, 5.15; N, 11.61. Polymers **4a**, **b**, **d**, **e** were also prepared as described above.

Synthesis of H-T Polyurethanes (4f–4l)

A solution of **1** (0.523 g, 3.0 mmol) in DMF (2 mL) at -40°C was added to one of **2** (0.186 g, 3.0 mmol) and **3c** (0.018 g, 0.03 mmol) in DMF (1 mL) and stirred for 5 h at this temperature. This solution was allowed to warm from -40°C to room temperature and was stirred for 20 h. The polymer was isolated as described above. The yield was 0.588 g (83%). Head-to-tail content of polymer **4k** was 93%. IR (KBr, cm^{-1}): ν 1706 (C=O), 2956 (CH_2), 3325 (NH). ^1H NMR (600 MHz, $\text{DMF-}d_7$, δ): 4.24–4.40 (m, 6H, $-\text{CH}_2-$), 7.29–7.66 (m, 4H, $-\text{C}_6\text{H}_4-$), 7.67 (br, 1H, $-\text{CH}_2-\text{NH}-\text{CO}_2-$), 9.74 (br, 1H, $-\text{C}_6\text{H}_4-\text{NH}-\text{CO}_2-$). ^{13}C NMR (600 MHz, $\text{DMF-}d_7$, δ): 45.4, 64.2, 64.4, 64.6, 119.8, 129.3, 135.7, 139.8, 155.2, 158.1. M_w (M_w/M_n)=27000 (2.1). Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_4$: C, 55.93; H, 5.12; N, 11.86. Found: C, 55.15; H, 5.41; N, 11.73.

Polymers **4f**, **g**, **h**, **i**, **j** were also prepared as described above. Random polyurethane **4l** was prepared by the reported method.⁵

Model Reaction of Phenyl Isocyanate and Diols with Various Methylene Units

General procedure. A solution of **2** (0.310 g, 5.0 mmol) and **3c** (0.03 g, 0.05 mmol) in THF (10 mL) was added to a solution of phenyl isocyanate in THF (2 mL). The mixture was stirred for 1 h at room temperature or -40°C , and the solvent was removed *in vacuo*. The ratio of products was estimated from the urethane-proton ratio of compound **5** and **6** by ^1H NMR spectroscopy.

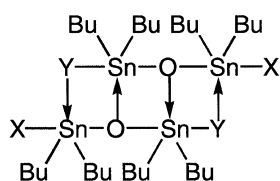
Measurements

Infrared spectra were recorded on a Perkin–Elmer PARAGON 1000 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded in *N,N*-dimethylformamide- d_7 ($\text{DMF-}d_7$) on a JEOL Lambda-600 instrument. Regularity of the polymers was determined by ^{13}C NMR (an inversed gated decoupling method) from the signal areas of methylene groups. Thermogravimetric (TG) analysis was performed on a MAC Science TG-DTA 2000 s at a heating rate $10^\circ\text{C min}^{-1}$ under Ar. Differential scanning calorimetry (DSC) was performed by a MAC Science DSC 3200 s at a heating rate of $10^\circ\text{C min}^{-1}$ under Ar. Gel permeation chromatography (GPC) analysis was carried out by a Tosoh 8020 system (α M column \times 2, LiCl (0.4 wt%) using DMF as an eluent) on the basis of standard polystyrenes. Wide-angle X-Ray diffraction (WAXD) of powdered samples was performed using Rigaku RU-200B Cu- K_α radiation. WAXD traces were obtained by wide-angle diffractometry with step width and fixed time programmed for $0.5^\circ\text{C min}^{-1}$ using a powder sample on a glass plate.

Table I. Regularity of polyurethanes obtained in the presence of **3**^a

Polymer No.	Catalyst No.	Content Ratio of H-T Units ^b	\overline{M}_w^c	$\overline{M}_w/\overline{M}_n^c$	Yield ^d
		%			%
4a	3a	76	25000	2.6	71
4b	3b	75	16000	2.1	75
4c	3c	82	26000	3.7	78
4d	3d	80	21600	2.6	71
4e ^e	3c	75	10000	2.6	74

^aConditions: **1**, 5 mmol; **2**, 5 mmol; DMF, 20 mL; catalyst, [**3**]/[**1**]=0.01; time, 20 h; temp., r.t. ^bMeasured by ¹³C NMR in DMF-*d*₇ with reversed gate decoupling at room temperature. ^cEstimated by GPC[DMF with LiCl (0.4 wt%), PSt. Standard]. ^dIsolated yield after precipitation into MeOH. ^ePolymerization carried out with 1,3-propanediol instead of **2**.



3a; X=Cl, Y=Cl
3b; X=Cl, Y=OH
3c; X=NCS, Y=NCS
3d; X=NCS, Y=OH

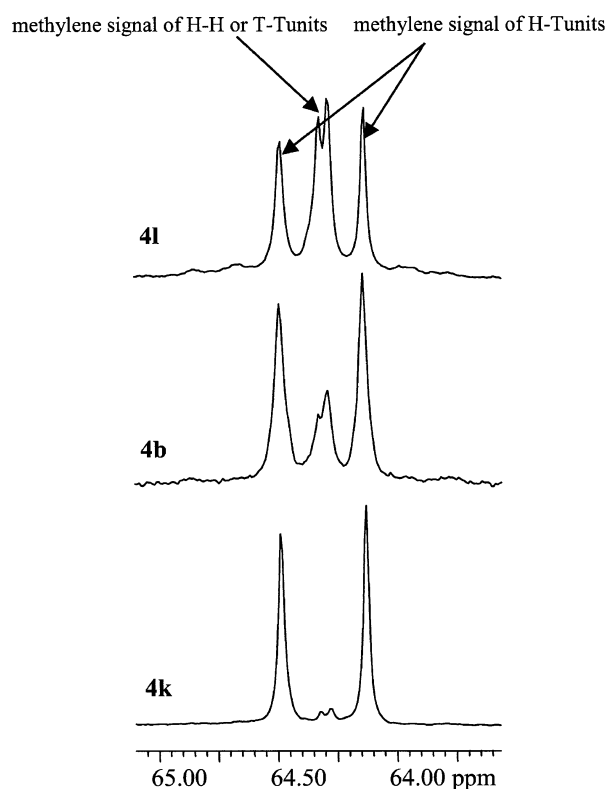
Scheme 1.

RESULTS AND DISCUSSION

Otera *et al.* reported that in distannoxane-catalyzed urethane synthesis from isocyanate and alcohol, alkoxydistannoxane is formed at first.¹¹ Thus, leaving groups (X and Y) of 1,3,3,3-tetraalkyldistannoxanes X(R₂)SnOSn(R₂)Y were expected to play important roles in the formation of alkoxydistannoxane. Distannoxanes **3** with various leaving groups such as Cl, OH, and NCS were prepared for preparation of polyurethanes (Scheme 1). From a previous report,⁶ a butyl group was chosen as an alkyl substituent of distannoxane.

Synthesis of H-T Polymers

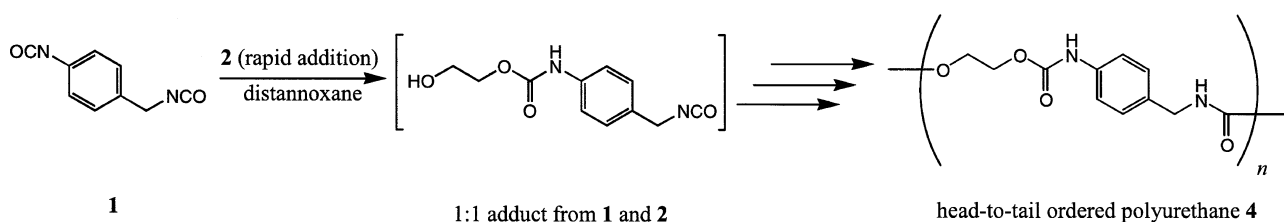
Polymerization of **1** with **2** was carried out in DMF at room temperature for 20 h in the presence of distannoxane. Polymers **4** were isolated as white fibrous materials by pouring the polymerization solution into methanol. The results are summarized in Table I. The structures of polyurethanes **4** were characterized by IR, ¹H NMR, and ¹³C NMR spectroscopies and elemental analysis. IR spectra showed characteristic absorptions at 3300 and 1705 cm⁻¹ due to NH and C=O stretching, respectively. Elemental analysis supported the formation of expected polymers. ¹H NMR spectra had aromatic protons at 7.1–7.5 ppm and urethane protons at 7.5 and 9.7 ppm. Figure 1 shows ¹³C NMR spectra of methylene groups in polymers **4**. According to previous

**Figure 1.** ¹³C NMR spectra (methylene region) of polymers **4b**, **4k**, and **4l** in DMF-*d*₇ measured at 80°C.

studies,^{5,6} signals at 64.2 and 64.6 ppm were assigned to carbon nuclei in methylene groups for H-T units and signals at 64.4 ppm for H-H or T-T units. H-T regularity in polymers **4** was estimated from the ratio: [the intensity of H-T methylene peaks] / [the intensity of whole methylene peaks].

Catalyst **3b** containing OH groups as a leaving group gave ordered polymer **4b** with 75% H-T content, with regularity comparable to that of polymer **4a** catalyzed by **3a**. Higher H-T regularity of polymers was obtained in the presence of **3c** and **3d** containing NCS groups. Sn–NCS bond in distannoxane has high polarity that promotes the formation of alkoxydistannoxane of **2**.¹¹ Thus, a 1:1 adduct from **1** and **2** was formed readily at the initial stage of polymerization (Scheme 2).

The selectivity of functional groups is improved by



Scheme 2.

Table II. Regularity of polyurethanes obtained in the presence of **3c**^a

Polymer No.	Temp. ^b °C	Content Ratio of H-T Units ^c %	\bar{M}_w ^d	\bar{M}_w/\bar{M}_n ^d	Yield ^e %
4f	-10	85	15100	2.4	73
4g	-30	87	11000	2.2	74
4h	-40	88	11200	2.2	73
4i	-50	88	7100	2.4	74

^aConditions: **1**, 3 mmol; **2**, 3 mmol; DMF, 12 mL; catalyst, [**3c**]/[**1**]=0.01. ^bThe reaction was carried out at room temperature for 20 h after cooling the solution to -10°C to -50°C for 5 h. ^cMeasured by ¹³C NMR in DMF-*d*₇ with reversed gate decoupling at room temperature. ^dEstimated by GPC[DMF with LiCl (0.4 wt%), PSt. Standard]. ^eIsolated yield after precipitation into MeOH.

Table III. Regularity of polyurethanes obtained in the presence of **3c**

Polymer No.	Content Ratio of H-T Units ^d %	\bar{M}_w ^e	\bar{M}_w/\bar{M}_n ^e	Yield ^f %
4j ^a	92	14000	2.1	79
4k ^b	93	27000	2.1	83
4l ^c	52	24000	2.7	74
4b	76	16000	1.8	75

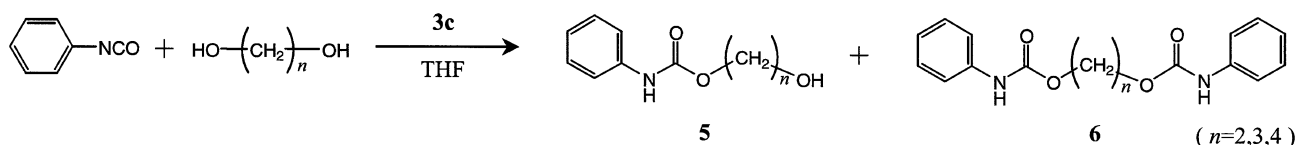
^aConditions: **1**, 3 mmol; **2**, 3 mmol; DMF, 6 mL; catalyst, [**3c**]/[**1**]=0.01. ^bConditions: **1**, 3 mmol; **2**, 3 mmol; DMF, 3 mL; catalyst, [**3c**]/[**1**]=0.01. These reactions (**4j**, **4k**) were carried out at room temperature for 20 h after cooling the solution to -40°C for 5 h. ^cCatalyst: triethylamine. ^dMeasured by ¹³C NMR in DMF-*d*₇ with reversed gate decoupling at 80°C. ^eEstimated by GPC[DMF with LiCl (0.4 wt%), PSt. Standard]. ^fIsolated yield after precipitation into MeOH.

decreasing polymerization temperature because of differences in activation of free energy. The effects of the polymerization temperature on the H-T content were thus investigated. Polymerization in the presence of **3c** was carried out by varying the temperature from -10°C to -50°C for 5 h and at room temperature for 20 h. The results are summarized in Table II. H-T regularity, 82% at room temperature, increased with decreasing temperature, and the H-T regularity reached 88% at -40°C. \bar{M}_w of polymers decreased to 7000 with decrease in temperature.

To minimize the effects of oligomers on H-T regularity, polymers **4** with higher molecular weights were prepared in higher monomer concentrations. The results are shown in Table III. The polymerization proceeded smoothly, giving polymer **4k** with 27000 of \bar{M}_w , and H-T regularity reached 93%. Polymers **4j** and **4k** were partially insoluble in DMF at room temperature, but soluble on heating. This low solubility of polymers **4j** and **4k** compared to other lower H-T polymers is attributable to higher H-T regularity of the re-

sulting polymers. Thus, both polymerization temperature and monomer concentration should affect H-T content of polymers **4**, and lower temperature and higher monomer concentration should give higher H-T content.

We studied the probability of the formation of H-T polymer from other diols except for **2** by the following model reactions. Reactions of phenyl isocyanate and various diols with different numbers of methylene units n ($n=2,3,4$) were carried out in the presence of **3c** at room temperature and -40°C as shown in Scheme 3. Product ratios of 1:1 adducts (**5**) and 2:1 adducts (**6**) from PhNCO and diol were determined by ¹H NMR spectroscopy (Table IV). Product **5** was formed dominantly in the case of **2** ($n=2$), and product ratios of **6** decreased as the number of methylene units increased. With 1,4-butanediol ($n=4$), the product ratio of **5** and **6** was the theoretical value obtained when equal reactivity of diols was assumed, that is, **5**:**6**=2:1. Reaction temperature slightly influenced product ratio in the case of **2**. These findings suggest that compound **2** appears

**Scheme 3.****Table IV.** Model reaction of phenyl isocyanate and diols with various methylene units^a

No.	<i>n</i>	Temp. °C	Product ratio ^b	
			5	6
1	2	r.t.	90	10
2	2	-40	93	7
3	3	r.t.	72	28
4	3	-40	74	26
5	4	r.t.	67	33
6	4	-40	68	32

^aConditions: diol, 5 mmol; phenyl isocyanate; 5 mmol, THF; 12 mL; reaction time, 1 h. ^bDetermined by ¹H NMR.

Table V. Thermal properties of polyurethanes 4

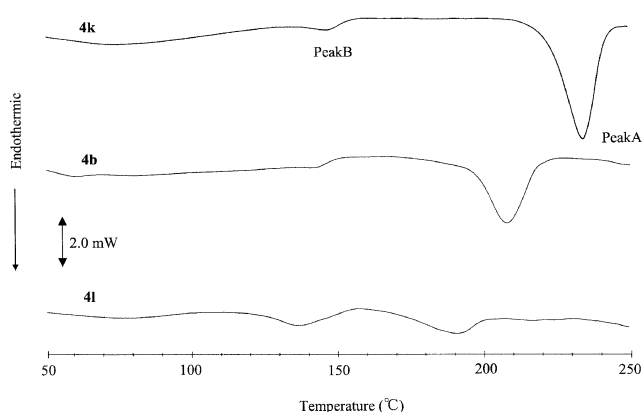
Polymer No.	<i>T</i> _{m1} ^a		ΔH mJ mg ⁻¹	<i>T</i> _g ^a		<i>T</i> ₅ ^b °C
	lst. heating			2nd. heating		
	°C	°C	°C	°C		
4b	141	208	49	90	240	
4k	147	234	68	98	242	
4l	136	190	24	98	241	

^aObtained by DSC under nitrogen atmosphere at heating rate of 10°C min⁻¹. *T*_m; melting temperature, *T*_g; glass transition temperature. ^bFive percent weight loss temperature by TG measurement under nitrogen atmosphere with heating rate of 10°C min⁻¹.

somewhat specific in the reactivity of an OH group in comparison with other diols. In fact, H-T regularity of the resulting polymer **4e** was 75% when polymerization was carried out from **1** with 1,3-propanediol (*n*=3) in the presence of **3c**. This value is lower than that of polymer **4c**.

Properties of H-T Polymers

Thermal properties of polymers were examined by thermogravimetry (TG) and differential scanning calorimetry (DSC). The results are summarized in Table V. Rapid weight loss of all polymers **4** started at around 240°C. Thermal degradation behavior was almost the same despite different chain regularities. DSC traces of the first-heating process for polymers **4** with various regularities are illustrated in Figure 2. Large and small endothermic peaks in DSC traces of polymer **4k** appeared at 147°C and 234°C, respectively, probably related to dual populations of primary and secondary crystals, which is characteristic of prior crystallization history.^{12,13} As reported previously,⁶ peak B (endothermic peak at lower temperature) is associated with thermodynamically unstable crystallites, and peak A seems attributable to a highly ordered orientation. The temperature of peak A (endothermic peak at

**Figure 2.** DSC traces of the first-heating for polymers **4b**, **4k**, and **4l**.

higher temperature) in DSC traces of polymer **4b** was lower than that of polymer **4k**. On the other hand, small endothermic peaks were observed at 136°C and 190°C in DSC traces of random polymer **4l**, indicating low crystallinity. As shown in Table V, the temperature of the endothermic peak A and values of enthalpy change (ΔH) increased with H-T regularity. No endothermic peak was observed in second-heating DSC traces of polymer **4b**, **4k**, and **4l**, indicating only typical glass transition profiles. Once the as-made polymers were melted, no crystalline could be formed during cooling

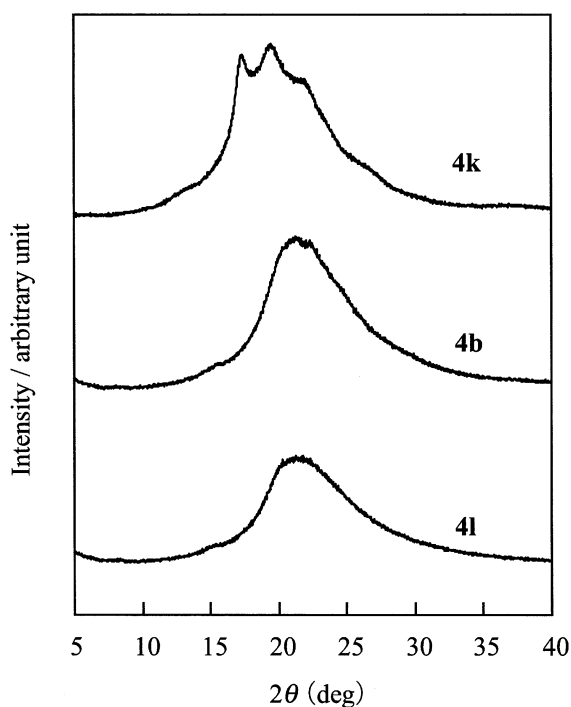


Figure 3. WAXD intensity curves of as-made samples for polymers **4b**, **4k**, and **4l**.

process. Chain mobility seems to be restricted by hydrogen bonds between intermolecular or intramolecular urethane bonds. Hydrogen bonds formed during cooling from the melting would restrict chain movement and hinder formation of regular chain conformations.

We investigated the structures of as-made **4b**, **4k**, and **4l** by WAXD analysis. WAXD profiles of as-made polymers **4b**, **4k**, and **4l** are illustrated in Figure 3. Several peaks of reflection indicate that **4k** is a semi-crystalline polymer, the same as an H-H or T-T ordered polyurethane,⁵ but the location of each reflection peak is different, showing that crystallites of **4k** differ from those of H-H or T-T ordered polyurethane. On the other hand, polymers **4b** and **4l** show amorphous profiles. WAXD refractions of **4k** differed from those of **4b** and **4l**, meaning that higher content of the H-T regularity changes the packing structure of the crystallite in polyurethane.

CONCLUSIONS

We successfully prepared H-T polyurethane from

1 and **2** using a 1,3-bis(isothiocyanate)-1,1,3,3-tetraabutyldistannoxane as catalyst. H-T regularity of polyurethane was improved to 93% at low temperature -40°C . Thermal properties and crystallinity of polyurethane **4k** were different from those of polyurethanes **4b** and **4l** with low H-T regularities. In the series of investigations of ordered polyurethanes, constitutional isomerism was found to have strong effect on the physical properties of a polymer, such as the thermal property and crystallinity.

Acknowledgments. The New Energy and Industrial Technology Development Organization (NEDO) financially supported this study, which was conducted as a project on Technology for Novel High-Functional Materials and sponsored by the Agency of Industrial Science and Technology (AIST).

REFERENCES

1. F. T. Gentle and U.W. Suter, "Comprehensive Polymer Science," G. Allens and J. C. Bevington, Ed., Pergamon, Oxford, 1989, vol. 5, p 97.
2. M. Ueda, *Prog. Polym. Sci.*, **24**, 699 (1999).
3. L. Li, H. Seino, K. Yonetake, and M. Ueda, *Macromolecules*, **32**, 3851 (1999).
4. L. Li, T. Hayakawa, K. Yonetake, and M. Ueda, *Macromol. Chem. Phys.*, **201**, 1667 (2000).
5. A. Nishio, A. Mochizuki, J. Sugiyama, K. Takeuchi, M. Asai, K. Yonetake, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 2106 (2000).
6. A. Nishio, A. Mochizuki, J. Sugiyama, K. Takeuchi, M. Asai, K. Yonetake, and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 416 (2001).
7. M. A. Schmucki, P. Pino, and U. W. Suter, *Macromolecules*, **18**, 823 (1985).
8. M. Ueda, T. Morishima, M. Kakuta, and J. Sugiyama, *Macromolecules*, **25**, 6580 (1992).
9. R. Okawara and M. Wada, *J. Organomet. Chem.*, **1**, 81 (1963).
10. M. Wada, M. Nishio, and R. Okawara, *J. Organomet. Chem.*, **3**, 70 (1965).
11. J. Otera, T. Yano, and R. Okawara, *Organometallics*, **5**, 1167 (1986).
12. R.W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).
13. G. C. Alfonso, E. Pedemonte, and L. Ponzetti, *Polymer*, **20**, 104 (1979).