Synthesis and Characterization of Ordered Poly(urethane−urea)s from *p*-Isocyanatobenzyl Isocyanate and 4-Aminophenylethyl Alcohol

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ABSTRACT: The ordered (-abcd-) poly(urethane−urea) was prepared by the polyaddition reaction of two nonsymmetric monomers, *p*-isocyanatobenzyl isocyanate (XabX) (**1**) with 4-aminophenylethyl alcohol (YcdY) (**2**) in the presence of dibutyltin dilaurate as a catalyst. The polymerization was conducted in *N*,*N*-dimethylformamide (DMF) at 0 °C by mixing both monomers all at once, producing the ordered poly(urethane−urea) with a number-averaged molecular weight of 49 000. Authentic ordered and random poly(urethane−urea)s were prepared to verify the structure of the ordered polymer. The microstructure of polymer obtained was investigated by ^{1}H and ^{13}C NMR spectroscopy, and the expected (-abcd-) ordered structure was confirmed. The constitutional regularity influenced the solubility, crystallinity, and thermal and mechanical properties of polymers. Furthermore, the model reactions were studied in detail to demonstrate the feasibility of polymer formation.

Introduction

Structure−property relationships arising from constitutional isomerism are not well-known for condensation polymers.[1,2] Therefore, it is important to establish the method for the synthesis of ordered polymer from nonsymmetric monomers and to clarify the structure−property relationships between condensation polymers with different regularities. However, the synthesis of ordered polymeric repeating units of -(abcc)- or -(abccbacc)- from nonsymmetric (XabX) and symmetric (YccY) monomers is difficult by the one-step method and generally requires a multistep synthetic approach. Here -ab- and -cc- represent the nonsymmetric and symmetric monomeric units in the chain, respectively, and X and Y are the functional groups in the polymerization reaction.

We have been interested in the synthesis of ordered polymers from nonsymmetric monomers by direct polycondensation and have reported the successful syntheses of various ordered polymers from symmetric and nonsymmetric monomers.[2] The structure−property relationships between constitutional isomeric poly(amide−ester)s obtained from isophthaloyl chloride or adipoyl chloride and 4-(2-aminoethyl)phenol have been established.[3,4] Recently, the successful synthesis of ordered polyurethanes -(abccbacc)- or -(abcc)- by polyaddition of a symmetric monomer, ethylene glycol (YccY), with a nonsymmetric monomer, *p*-isocyanatobenzyl isocyanate **(1)**, was reported.[5,6] The head-to-head or tail-to-tail ordered polyurethane showed a high crystallinity, while the crystallinity of the corresponding random polyurethane was very low.

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Our next target was the synthesis of ordered polyurethanes from two nonsymmetric monomers, XabX and YcdY. 4-Aminophenylethyl alcohol **(2)** was selected as a nonsymmetric nucleophilic monomer because of the large difference of nucleophilicity between the hydroxyl group and the amino group to an isocyanate group.

We now report the synthesis and properties of ordered (-abcd-) poly(urethane−urea) by polyaddition reaction of two nonsymmetric monomers, **1** (XabX) and **2** (YcdY), using dibutyltin dilaurate as a catalyst.

Experimental Section

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 triethylamine (TEA) were purified by the usual method. Phenyl isocyanate (**3**), benzyl isocyanate (**4**), benzylamine (**5**), and aniline (**6**) were purified by vacuum distillation. Methanol and 2-phenylethanol (**7**) 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] 4-Aminophenylethyl alcohol (**2**) was purified by recrystallization from toluene. The other reagents were used as received. All reactions were carried out under a N_2 atmosphere.

1-Phenyl-3-benzylurea (8). To solution of **5** (0.322 g, 3.0 mmol) in THF (12 mL) was added phenyl isocyanate (0.357 g, 3.0 mmol). The solution was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and the product was recrystallized from ethyl acetate to afford white needles. The yield was 0.56 g (83%); mp172−173 °C. IR (KBr, cm^{-1}): ν 1635 (C═O), 3326 (NH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 4.30 (d, CH_2, J = 5.9 Hz, 2H), 6.60 (t, NH, J = 6.1 Hz, 1H), 6.89 (t, Ar, 1H), 7.21−7.41 (m, Ar, 9H), 8.51 (s, NH, 1H).^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 42.7, 117.7, 121.1, 126.7, 127.1, 128.3, 128.6, 140.3, 140.4, 155.2.

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Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C,74.27; H,6.06; N,12.25.

1,3-Dibenzylurea (9). This compound was prepared from **4** and **5** as described above. The yield was 0.644 g (89%). Recrystallization from ethyl acetate gave white needles; mp173−175 °C. IR (KBr, cm^{-1}): ν 1628 (C═O), 3322 (NH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 4.23 (d, CH_2, J = 5.9 Hz, 4H), 6.43 (t, NH, J = 6.1 Hz, 2H), 7.21−7.30 (m, Ar, J = 7.2, 10H). ^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 42.7, 126.5, 127.0, 128.2, 140.8, 158.1. Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.82; H, 6.62; N, 11.58.

1,3-Diphenylurea (10). To a solution of **6** (0.279 g, 3.0 mmol) and TEA (0.03 g, 3.9 mmol) in THF (12 mL) was added phenyl isocyanate (0.357 g, 3.0 mmol). The solution was refluxed for 15 h, after which the solvent was removed under reduced pressure. The product was recrystallized from ethyl acetate to afford white needles. The yield was 0.439 g (69%); mp 246−248 °C. IR (KBr, cm^{-1}): ν 1649 (C═O), 3289 (NH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 6.96 (t, Ar, J = 7.3 Hz, 2H), 7.27 (t, Ar, J = 9.9 Hz, 4H), 7.45 (d, Ar, J = 7.7 Hz, 4H), 8.64 (s, NH, 2H).^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 118.2, 121.8, 128.8, 139.7, 152.5. Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.38; H, 5.55; N, 13.10.

Phenethyl-*N*-phenylcarbamate (11). This compound was prepared from phenyl isocyanate and 2-phenylethanol and DBTL as described above. The yield was 0.625 g (88%). Recrystallization from hexane gave white needles; mp 83−84 °C. IR (KBr, cm^{-1}): ν 1701 (C═O), 3356 (NH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.94 (t, CH_2, J = 7.0 Hz, 2H), 4.29 (t, CH_2, J = 7.0 Hz, 2H), 6.98 (t, Ar, J = 7.7 Hz, 1H), 7.20−7.50 (m, Ar, 9H), 9.59 (s, NH, 1H).^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 34.7, 64.7, 118.2, 122.3, 126.3, 128.4, 128.7, 128.8, 138.1, 139.1, 153.5. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.60; H, 6.18; N, 5.72.

Competitive Reaction of 3 and 4 with 5. To a solution of **5** (0.322 g, 3.0 mmol) and TEA (0.030 g, 0.3 mmol) in THF (12 mL) was added **3** and **4** at −20 °C. After mixing, the solution was stirred for 1 h at room temperature, after which the solvent was removed in vacuo. The ratio of products was estimated by ^{1}H NMR spectroscopy.

Other Competitive Reactions. Other competitive reactions were carried out in a similar way as described above.

Model Compounds: 4-(3-Phenylureido)phenethyl-(*N*-phenylcarbamate) (12). A solution of **2** (0.686 g, 5.0 mmol), **3** (1.191 g,10.0 mmol), and DBTL (0.316 g, 0.5 mmol) in THF (30 mL) was refluxed for 13 h. The solvent was removed under reduced pressure, and the product was recrystallized from DMF/toluene to afford white needles. The yield was 1.44 g (77%); mp 227−229 °C. IR (KBr, cm^{-1}): ν 1637, 1693 (C═O), 3311 (NH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.88 (t, CH_2, J = 6.8 Hz, 2H), 4.27 (t, CH_2, J = 7.0 Hz, 2H), 6.94−7.45 (m, Ar, 14H), 8.60 (s, NH, 1H), 8.62 (s, NH, 1H), 9.69 (s, NH, 1H). ^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 34.1, 64.8, 118.1, 118.4, 121.7, 122.3, 128.7, 128.7, 129.2, 131.3, 138.0, 139.1, 139.7, 152.5, 153.5. Anal. Calcd for $C_{22}H_{21}N_3O_3$: C, 70.38; H, 5.64; N, 11.19. Found: C, 70.40; H, 5.61; N, 11.15.

4-(3-Benzylureido)phenethyl-(*N*-benzylcarbamate) (13). A solution of **2** (0.686 g, 5.0 mmol), **4** (1.33 g,10.0 mmol), and DBTL (0.316 g, 0.5 mmol) in THF (30 mL) was refluxed for 13 h. The solvent was removed under reduced pressure, and the product was recrystallized from DMF/toluene to give white needles. The yield was 1.77 g (88%); mp 191−193 °C. IR (KBr, cm^{-1}): ν 1638, 1683 (C═O), 3289 (NH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.78 (t, CH_2, J = 6.8 Hz, 2H), 4.13 (t, CH_2, J = 5.9 Hz, 2H), 4.16 (d, CH_2, J = 5.9 Hz, 2H), 4.29 (d, CH_2, J = 5.9 Hz, 2H), 6.57 (t, NH, J = 6.0 Hz, 1H), 7.09−7.33 (m, Ar, 14H), 7.65 (t, J = 6.0 Hz, NH, 1H), 8.48 (s, NH, 1H).^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 34.3, 42.7, 43.7, 64.6, 117.8, 126.7, 126.9, 127.1, 128.2, 128.3, 129.0, 130.7, 138.7, 139.8, 140.4, 155.3, 156.4. Anal. Calcd for $C_{24}H_{25}N_3O_3$: C, 71.44; H, 6.25; N, 10.41. Found: C, 71.37; H, 6.22; N, 10.35.

4-(3-Phenylureido)phenethyl-(*N*-benzylcarbamate) (14). A solution of **2** (0.686 g, 5.0 mmol)) and **3** (0.596 g, 5.0 mmol) in THF (30 mL) was stirred at room temperature for 1 h. Compound **4** (0.666 g, 5.0 mmol) and DBTL (0.158 g, 0.25 mmol) were added to the solution, and the solution was refluxed for 15 h. The solvent was removed under reduced pressure. The residue was recrystallized from ethyl acetate to afford white needles. The yield was 1.66 g (85%); mp 204−206 °C. IR (KBr, cm^{-1}): ν 1636, 1685 (C═O), 3304 (NH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.80 (t, CH_2, J = 6.8 Hz, 2H), 4.14 (d, CH_2, J = 7.0 Hz, 2H), 4.16 (d, CH_2, J = 6.2 Hz, 2H), 6.94−7.45 (m, Ar, 14H), 7.66 (t, NH, J = 6.1 Hz, 1H), 8.58 (s, NH, 1H), 8.61 (s, NH, 1H). ^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 34.3, 43.7, 64.5, 118.1, 118.2, 121.7, 126.7, 126.9, 128.2, 128.7, 129.1, 131.5, 137.9, 139.7, 139.8, 152.5, 156.4. Anal. Calcd for $C_{23}H_{23}N_3O_3$: C, 70.93; H, 5.95; N, 10.79. Found: C, 70.92; H, 5.94; N, 10.74.

4-(3-Benzylureido)phenethyl-(*N*-phenylcarbamate) (15). A solution of **2** (0.686 g, 5.0 mmol) and **4** (0.666 g, 5.0 mmol) in THF (30 mL) was stirred at 60 °C for 1 h. Then, compound **3** (0.596 g, 5.0 mmol) and DBTL (0.158 g, 0.25 mmol) were added to the solution, and the solution was refluxed for 15 h. After removing the solvent under reduced pressure, the product was recrystallized from ethyl acetate to produce white needles. The yield was 1.60 g (78%); mp 187−189 °C. IR (KBr, cm^{-1}): ν 1630, 1695 (C═O), 2969 (CH_2), 3320 (NH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.85 (t, CH_2, J = 7.0 Hz, 2H), 4.24 (t, CH_2, J = 7.0 Hz, 2H), 4.29 (d, CH_2, J = 5.9 Hz, 2H), 6.56 (t, NH, J = 5.9 Hz, 1H), 6.95−7.46 (m, Ar, 14H), 8.48 (s, NH, 1H), 9.58 (s, NH, 1H). ^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 34.0, 42.7, 64.8, 117.9, 118.2, 122.3, 126.7, 127.1, 128.2, 128.6, 129.0, 130.5, 138.8, 139.1, 140.3, 153.5, 155.2. Anal. Calcd for $C_{23}H_{23}N_3O_3$: C, 70.93; H, 5.95; N, 10.79. Found: C, 70.93; H, 5.94; N, 10.68.

1-[4-(Isocyanatomethyl)phenyl]-3-(4-hydroxyethyl)-phenylurea (16) and 1-[4-(Methoxycarbonylaminomethyl)phenyl]-3-(4-hydroxyethyl)phenylurea (17). A solution of **2** (0.686 g, 5.00 mmol) in toluene (10 mL) and DMF (3 mL) was added dropwise over a period of 30 min to a solution of **1** (2.666 g, 15.30 mmol) in toluene (25 mL) cooled with an ice bath. The mixture was stirred at 0 °C for 2 h, and the precipitate **16** was collected and dried under vacuum. The yield was 1.40 g (90%). To confirm the structure, compound **16** was reacted with methanol. A solution of **16** (0.314 g, 1.01 mmol), methanol (0.949 g, 29.6 mmol), and DBTL (0.035 g, 0.05 mmol) in DMF (1.5 mL) was stirred at room temperature for 20 h. Product **17** was isolated by pouring the solution into water. The yield was 0.32 g (92%); mp 194−196 °C. IR (KBr, cm^{-1}): ν 1637, 1700 (C═O), 2931 (CH_2), 3309 (NH), 3380 (OH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.65 (t, CH_2, J = 7.2 Hz, 2H), 3.54 (s, CH_3, 3H), 3.56 (t, CH_2, J = 6.2 Hz, 2H), 4.10 (d, CH_2, J = 6.2 Hz, 2H), 4.59 (t, OH, J = 5.1 Hz, 1H), 7.11 (d, Ar, J = 8.4 Hz, 2H), 7.14 (d, Ar, J = 8.4 Hz, 2H), 7.33 (d, Ar, J = 8.4 Hz, 2H), 7.37 (d, Ar, J = 8.1 Hz, 2H), 7.59 (t, NH, J = 5.9 Hz 1H), 8.51 (s, NH, 1H), 8.56 (s, NH, 1H). ^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 38.4, 43.4, 51.3, 62.3, 118.2, 127.6, 129.1, 132.9, 133.1, 137.6, 138.5, 152.6, 156.9. Anal. Calcd for $C_{18}H_{21}N_3O_4$: C, 62.96; H, 6.16; N, 12.24. Found: C, 62.95; H, 6.16; N, 11.96.

Authentic Ordered Poly(urethane−urea) (4a). A solution of **16** (0.364 g, 1.17 mmol) and DBTL (0.037 g, 0.06 mmol) in DMF (9 mL) was stirred for 20 h at room temperature. The polymer solution was poured into methanol (1:1 v/v). The polymer was filtered off and dried at 70 °C in vacuo for 1 day. The yield was 0.305 g (84%). IR (KBr, cm^{-1}): ν 1666, 1694 (C═O), 3286 (NH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.81−2.83 (t, CH_2, 2H), 4.12−4.13 (d, CH_2, 2H), 4.16−4.19 (t, CH_2, 2H), 7.13−7.17 (t, 5H), 7.35−7.38 (t, Ar, 4H), 8.34 (s, NH, 1H), 8.36 (s, NH, 1H). ^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 34.0, 64.2, 118.1, 118.3, 127.2, 128.6, 131.4, 132.9, 137.6, 138.1, 152.3, 155.9. M_n (M_w/M_n) = 22 600 (2.72). Anal. Calcd for $(C_{17}H_{17}N_3O_3{\cdot}0.3H_2O)_n$: C, 64.46; H, 5.56; N, 13.27. Found: C, 64.46; H, 5.45; N, 13.28.

Ordered Poly(urethane−urea) (4b). To a solution of 1 (0.523 g,3.0 mmol) in DMF (5 mL) was added a solution of **2** (0.412 g, 3.0 mmol) in DMF (7 mL) at 0 °C, and the solution was stirred for 3 h at this temperature. This solution was allowed to warm to room temperature. Then, DBTL (0.15 mmol, 0.095 g) was added to the resulting solution. After

stirring the solution for 20 h, the resulting polymer solution was poured into methanol. The polymer was filtered off and dried at 70 °C in vacuo for 1 day. The yield was 0.834 g (89%). IR (KBr, cm^{-1}): ν 1666, 1694 (C═O), 3286 (NH). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.81−2.84 (t, CH_2, 2H), 4.12−4.13 (d, CH_2, 2H), 4.16−4.19 (t, CH_2, 2H), 7.13−7.17 (t, 5H), 7.35−7.38 (t, Ar, 4H), 8.35 (s, NH, 1H), 8.37 (s, NH, 1H). ^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 34.0, 64.2, 118.1, 118.3, 127.2, 128.6, 131.4, 132.9, 137.6, 138.1, 152.3, 155.9. M_n (M_w/M_n) = 48 800 (2.60). Anal. Calcd for $(C_{17}H_{17}N_3O_3 \cdot 0.2\ H_2O)_n$: C, 64.83; H, 5.52; N, 13.34. Found: C, 64.75; H, 5.52; N, 13.33.

Random Poly(urethane−urea) (4c). A solution of **1** (0.261 g, 1.50 mmol) in DMF (10 mL) was added slowly to a solution of **2** (0.412 g, 3.0 mmol) in DMF (2 mL) over a period of 3 h at room temperature and stirred for 3 h. To this solution was added **1** (0.261 g, 1.5 mmol) and DBTL (0.095 g, 0.15 mmol) at room temperature. After stirring the solution for 20 h, the polymer was isolated as described above. The yield was 0.896 g (96%). IR (KBr, cm^{-1}): ν 1666, 1694 (C═O), 3286 (NH).^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 2.78−2.91 (m, CH_2, 2H), 4.11−4.29 (m, CH_2, 4H), 6.35−7.40 (m, 9H), 8.19−9.18 (s, NH, 2H). ^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 34.0, 64.2, 118.1, 118.3, 127.2, 128.6, 131.4, 132.9, 137.6, 138.1, 152.3, 155.9. M_n (M_w/M_n) = 50 600 (2.89). Anal. Calcd for $(C_{17}H_{17}N_3O_3 \cdot 0.3\ H_2O)_n$: C, 64.46; H, 5.56; N, 13.27. Found: C, 64.52; H, 5.51; N, 13.28.

Measurements. The infrared spectra were recorded on a Perkin-Elmer PARAGON 1000 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were measured in DMF-d_7 on a JEOL Lambda-600 instrument. The regularities of the polymers were determined using ^{13}C NMR (inversed gated decoupling method) from the signal areas of the methylene groups. Thermogravimetric (TG) analysis was performed on a MAC Science TG-DTA 2000s at a heating rate of 10 °C min^{-1} under Ar. Differential scanning calorimetry (DSC) was performed by a MAC Science DSC 3200s at a heating rate 10 °C min^{-1} under Ar. Gel permeation chromatography (GPC) analysis was carried out by a Tosoh 8020 system (αM+ α6000 + α4000, 0.1 mM LiBr + 0.1 mM phosphoric acid (0.4 wt %) using DMF as an eluent) calibrated with polystyrene standard. A wide-angle X-ray diffraction (WAXD) of powdered samples was performed by using Rigaku RU-200B Cu Kα radiation. WAXD traces were obtained by the wide-angle diffractometry method with step width and fixed time programmed for 0.5 °C min^{-1} using a powder sample on a glass plate.

Mechanical tests were carried out with films made from the synthesized polymer powders. The film was prepared by casting from a 10% DMF solution (by weight) on a glass plate. The glass plate was heated at 150 °C for 4 h in a nitrogen atmosphere, and then the film was peeled off, follow by 190 °C for 1 h in a nitrogen atmosphere.

Dynamic mechanical thermal analysis was carried out using a Seiko Instrument Inc. DMS 120 running tensile mode at an oscillation frequency of 10 Hz at a heating rate of 5 °C min^{-1}. Thermal mechanical analysis was performed on a Seiko Instruments Inc. TMA/SS 100 running tensile mode at a heating rate of 10 °C min^{-1}.

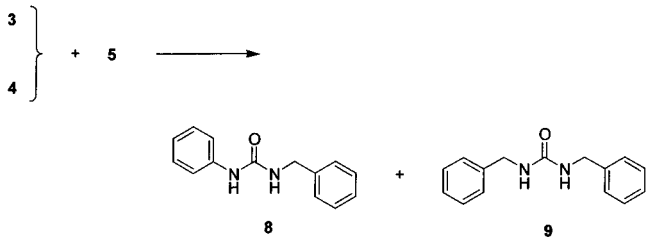
Results and Discussion

According to the theoretical treatments on the synthesis of ordered polymer from two nonsymmetric monomers (XabX and YcdY), the polymer with -bacd- order is obtained when the reaction rate between -aX and Yc- groups is faster than any other elementary reactions.[7] In this case, the first intermediate is XbacdY, which will later polymerize stoichiometrically to the fully ordered (-bacd-) polymer. Therefore, the choice of nonsymmetric nucleophile reacting with nonsymmetric diisocyanate **1** is important in the preparation of the ordered polymer from two nonsymmetric monomers by polyaddition reaction.

The reactivity of the isocyanate group toward nucleophiles such as alcohols and amines depends on the electron density of the carbon atom of isocyanates. Aromatic isocyanates have higher reactivity than aliphatic isocyanates because the resonance between the aromatic ring and isocyanates decreases the electron density of the carbon atom of isocyanate.[8] Therefore, the reactivity difference between aromatic and aliphatic isocyanates toward amines was studied. The competitive reactions of isocyanates such as phenyl isocyanate (**3**) and benzyl isocyanate (**4**) with benzylamine (**5**) or aniline (**6**) were carried out under various conditions to determine whether selective addition occurs or not (Scheme 1). The molar ratios of products 1-phenyl-3-benzylurea (**8**) and 1,3-dibenzylurea (**9**) obtained are shown in Scheme 1. When **5** was used as a nucleophile, the best ratio of the two products was 75:25 at −20 °C in the presence of triethylamine (TEA). The high nucleophilicity of **5** (pK_a = 10) should be responsible for its poor selectivity when it reacts with isocyanates. On the other hand, compound **6** (pK_a = 4.6) having lower nucleophilicity than **5** showed a selective addition to **4** (Scheme 2).

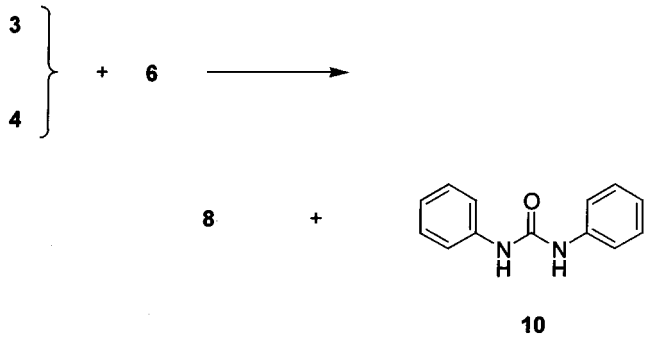
Next, the competitive reaction of **3** with **6** and 2-phenylethanol (**7**) was carried out in THF and formed

Scheme 1



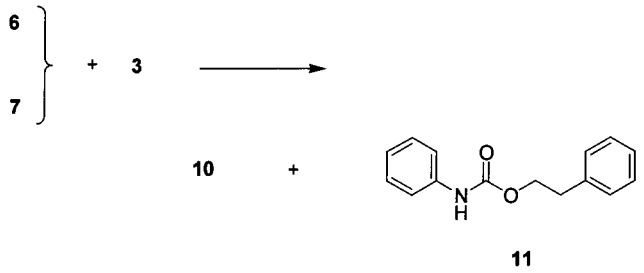
temp.(°C)	catalyst	Product Ratio 8 : 9
25	none	66 : 34
-20	none	63 : 37
-20	TEA (10 mol%)	75 : 25

Scheme 2



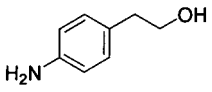
temp.(°C)	catalyst	Product Ratio 8 : 10
25	none	9 : 91
0	none	2 : 98
-20	none	2 : 98

Scheme 3



temp.(°C)	catalyst	Product Ratio **10** : **11**
25	none	99 : 1
0	none	98 : 2
-20	none	98 : 2

Scheme 4



2
(YcdY)

the desired product 1,3-diphenylurea (**10**) quantitatively (Scheme 3).

On the basis of these model reactions, 4-aminophenylethyl alcohol (**2**,YcdY) was chosen as an amino alcohol (Scheme 4). To clarify the structures of the polymers obtained, the model compounds in Scheme 5 were prepared from the corresponding isocyanates and **2**. The data in Scheme 5 show the chemical shifts of methylene and carbonyl groups in ^{13}C NMR spectra. According to the assignment of model compounds, the signals of carbon nuclei for the methylene and the carbonyl groups for the H−H unit were observed at 33.80, 64.35, 152.22, and 153.14 ppm, for the T−T unit 33.93, 64.14, 154.91, and 155.88 ppm, for the H−T unit 33.94, 64.07, 152.19, and 155.86 ppm, and for the T−H unit 33.76, 64.39, 153.15, and 154.92 ppm. Thus, six peaks in the methylene group region and four peaks in the carbonyl group region would appear in the random polymer, considering the overlap of peaks having a similar chemical shift, and the ordered polymer (-bacd-) should exhibit the signals for an H−T unit.

Synthesis of Authentic Ordered Poly(urethane−urea). The authentic ordered polymer was synthesized for characterization of structure for the ordered polymer obtained by the one-step procedure (Scheme 6). Adduct **16** from **1** and **2** was prepared by the slow addition of **2** to excess amount of **1** in toluene at 0 °C. For characterization of **16**, it was converted to the corresponding urea 1-[4-(methoxycarbonylaminomethyl)phenyl]-3-(4-hydroxyethyl)phenylurea **(17)** by treating with methanol (Scheme 6).

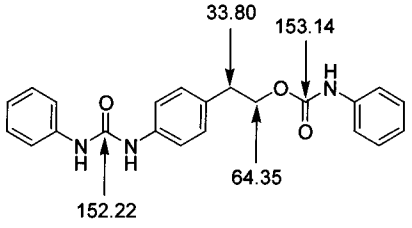
The authentic poly(urethane−urea) **4a** with a molecular weight of M_n= 22 600 was prepared by self-polyaddition of **16** in the presence of DBTL in DMF at room temperature (Scheme 6).

Synthesis of Ordered Poly(urethane−urea). The synthesis of the ordered polymer was carried out using the one-step procedure. A solution of **2** in DMF was added to **1** at 0 °C all at once and stirred for 3 h. This solution was allowed to warm to room temperature. To the resulting solution was added DBTL, and the solution was stirred for 20 h. The polymerization proceeded smoothly, giving polymer **4b** with M_n = 48 800.

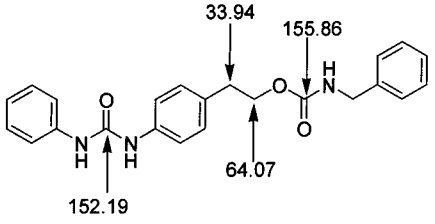
Synthesis of Random Poly(urethane−urea). A random ordered polymer was prepared by a two-step method. A half equivalent of **1** in DMF was fed slowly to a solution **2** at room temperature. After addition was completed, the rest of **1** and DBTL in DMF were added all at once at room temperature, and the solution was stirred for another 20 h. This polymerization produced polymer **4c** with M_n = 50 600.

Polymer Characterization. The IR spectra of the poly(urethane−urea)s were consistent with those of the model compounds and known analogues. All the polymers showed characteristic absorptions at 3300, 1666, and 1694 cm^{-1} due to NH, urea C═O, and urethane C═O stretchings, respectively. Elemental analyses also

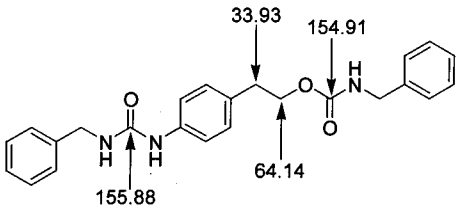
Scheme 5



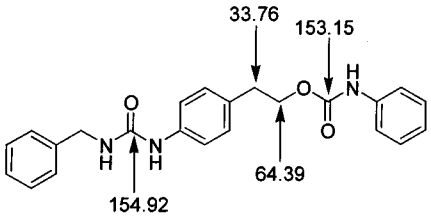
Model compound with head-to-head structure (**12**)



Model compound with head-to-tail structure (**14**)



Model compound with tail-to-tail structure (**13**)



Model compound with tail-to-head structure (**15**)

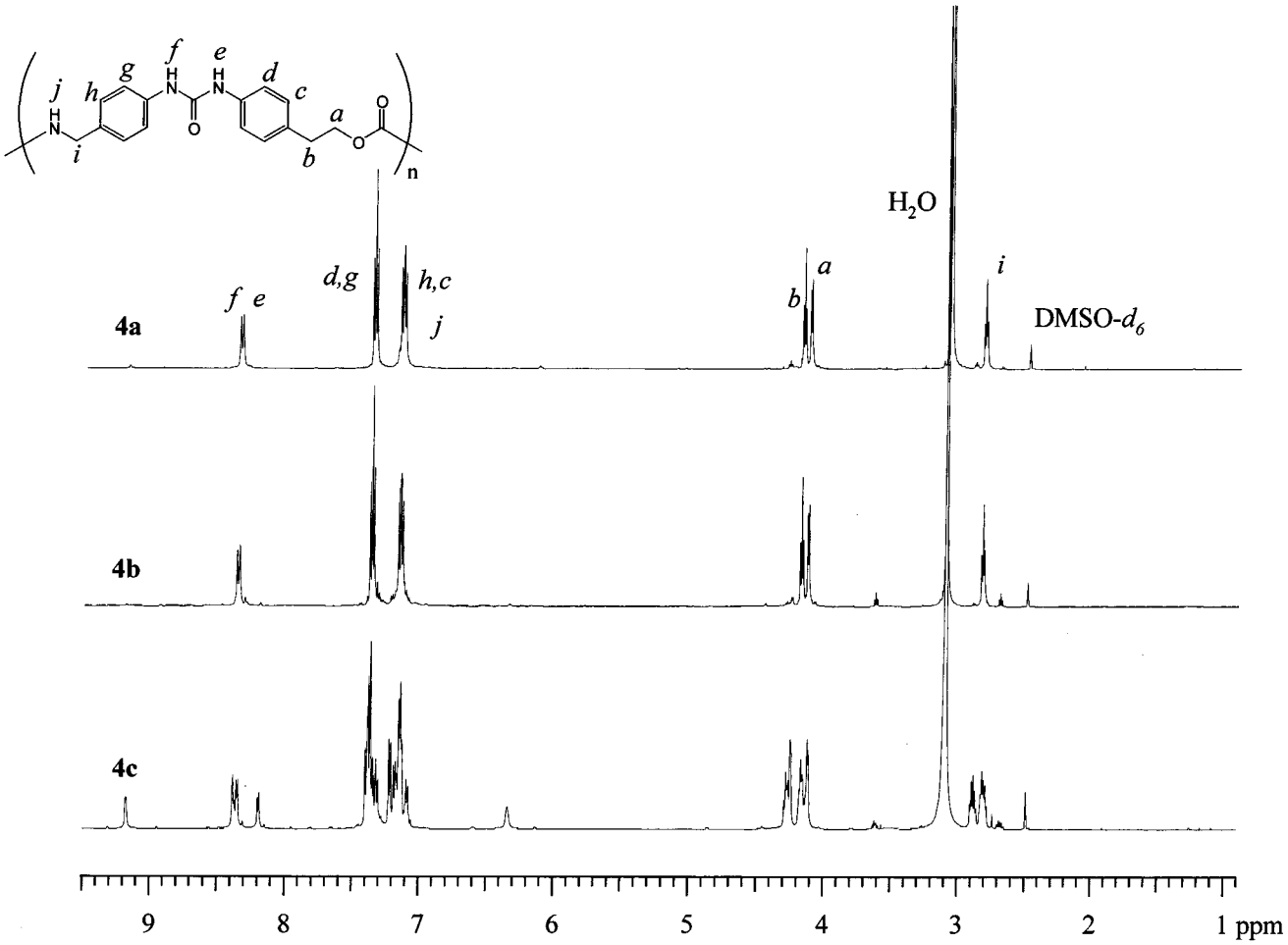
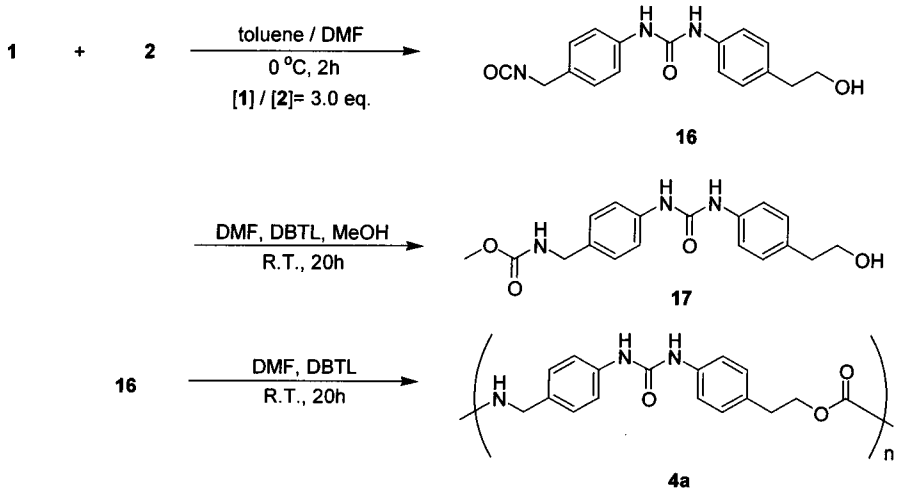


Figure 1. ^{1}H NMR spectra of polymers **4a, 4b**, and **4c** in DMSO-d_6 measured at 100 °C.

Scheme 6



supported the formation of expected polymers. The microstructure of the polymers was determined by ^{1}H and ^{13}C NMR spectroscopy. Figure 1 shows the ^{1}H spectra of authentic ordered polymer **4a**, polymer **4b** prepared by a one-step procedure, and random polymer **4c**. The spectra of polymers **4a** and **4b** are identical, and the peak assignment is shown in the inset of Figure 1 on the basis of chemical shifts for model compounds. On the other hand, random polymer **4c** exhibits many extra peaks, indicating its random structure.

The ^{13}C NMR spectra of polymers **4a**, **4b**, and **4c** are presented in Figure 2. The spectra of polymers **4a** and **4b** are also the same. The signals of the carbon nuclei for the methylene and carbonyl groups for polymers **4a** and **4b** appeared at 34.03, 64.19 ppm and 152.34, 155.94 ppm, respectively. These peaks are attributed to head-to-tail structures on the basis of the assignment of model compounds. On the other hand, six and four peaks of carbon nuclei in the methylene and carbonyl groups for random polymer **4c** would be expected from its random

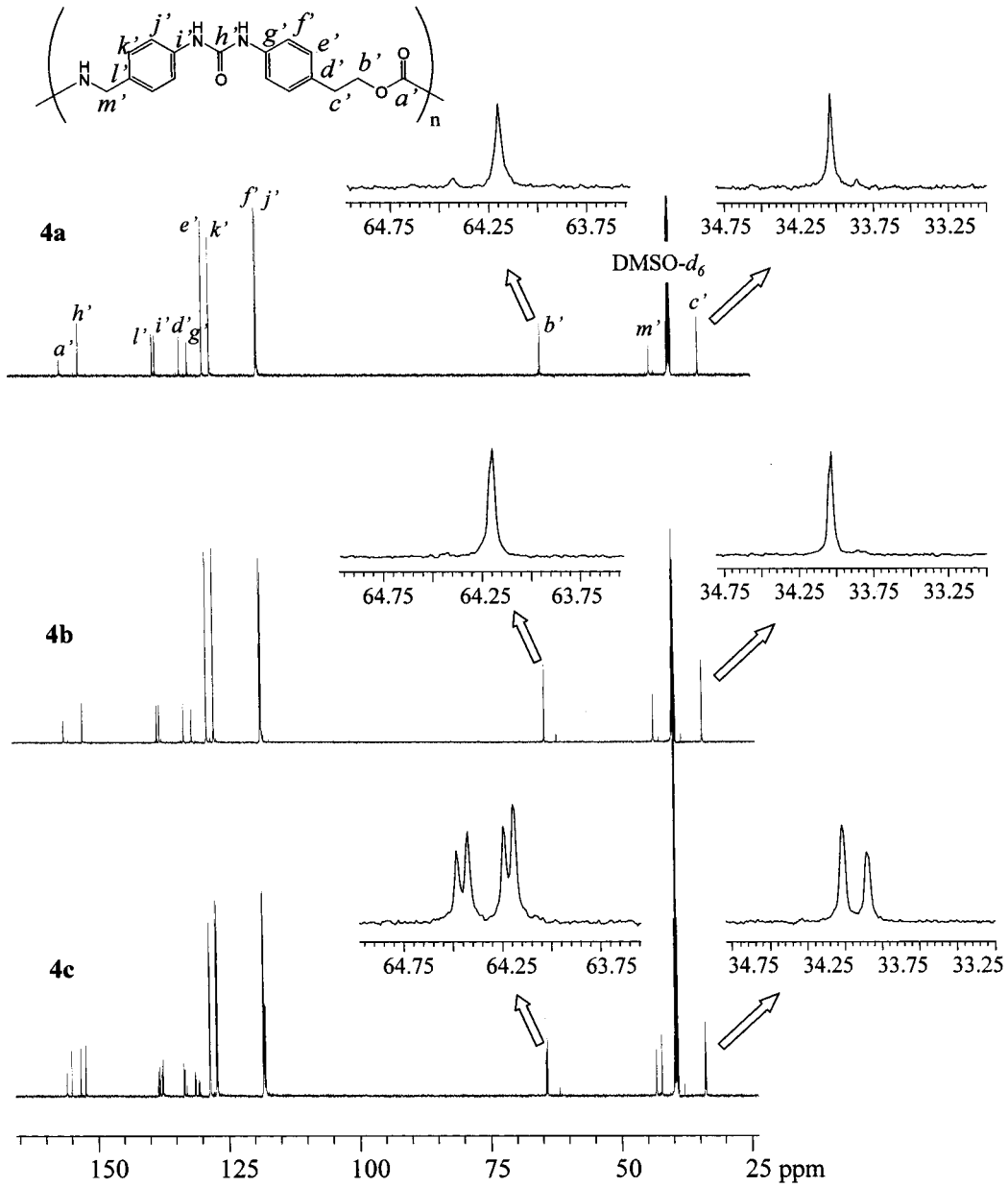


Figure 2. ^{13}C NMR spectra of polymers **4a**, **4b**, and **4c** in DMSO-d_6 measured at 100 °C.

Table 1. Molecular Weight Analyses of Obtained Poly(urethane−urea)s 4

polymer	M_w[a] × 10^{-4}	M_n[a] × 10^{-4}	M_w/M_n[a]
authentic polymer **4a**	6.15	2.26	2.72
one-pot polymer **4b**	12.68	4.88	2.60
random polymer **4c**	14.61	5.06	2.89

[a] Estimated by GPC (DMF with 10 mM LiBr + 10 mM phosphoric acid, Pst standard).

structure. In fact, six signals at 33.85, 34.02, 64.19, 64.24, 64.42, and 64.48 ppm appeared in methylene region (Figure 2) and four signals at 152.34, 153.27, 155.00, and 155.94 ppm in the carbonyl region (Figure 2). These findings indicate that polymer **4b** prepared by a one-step procedure is the desired ordered poly(urethane−urea).

The molecular weights of obtained polymers estimated (relative to polystyrene standard) by GPC in DMF containing LiBr are summarized in Table 1. The chromatograms of polymers were unimodal distributions and indicated that M_n and M_w values were 23 000−51 000 and 62 000−146 000, respectively. The ratio of M_w/M_n was around 2.6−2.9.

Properties of Polymers. (a) Solubility of Polymers. The polymers obtained were white solids. As shown in Table 2, the difference in solubility among polymers **4a**, **4b**, and **4c** toward aprotic solvents is clearly observed. Random polymer **4c** was soluble at room temperature, but ordered polymers **4a** and **4b** were partially soluble owing to their higher regularity.

(b) Thermal Properties of Polymers. Thermal properties of polymers were examined by thermogravimetry (TG) and differential scanning calorimetry (DSC). These results are summarized in Table 3. The TG traces of polymers **4b** and **4c** are illustrated in Figure 3. The rapid weight loss of both polymers started at around 270 °C. Thermal degradation behavior was almost the same despite the different chain regularities.

The DSC traces of first-heating process for polymers **4** are illustrated in Figure 4. Polymers **4a** and **4b** exhibited baseline shifts corresponding to the glass transition temperatures (T_g's) and clear endothermic

Table 2. Solubility of Poly(urethane−urea)s 4[a]

	solvent									
polymer	DMF	DMF + 5% LiCl	DMAc	NMP	DMSO	*m*-cresol	THF	CH_3Cl	MeOH	acetone
authentic polymer **4a**	+−	+	+−	+−	+−	+−	−	−	−	−
one-pot polymer **4b**	+−	+	+−	+−	+−	+−	−	−	−	−
random polymer **4c**	+	+	+	+	+	+	−	−	−	−

Table 3. Thermal Analyses of Poly(urethane−urea)s 4

polymer	T_g[a] (°C)	T_m[a] (°C)	ΔH (mJ/mg)	T_5[b] (°C)
authentic polymer **4a**	171	251	20	276
one-pot polymer **4b**	172	257	31	277
4b cast film	184	267	24	277
random polymer **4c**	170	233	3	276
4c cast film	175	N.D.	N.D.	278

[a] Obtained by DSC under argon atmosphere with heating rate of 10 °C min^{-1}. T_m = melting temperature, T_g = glass transition temperature. [b] The 5% weight loss temperature by TG measurement under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

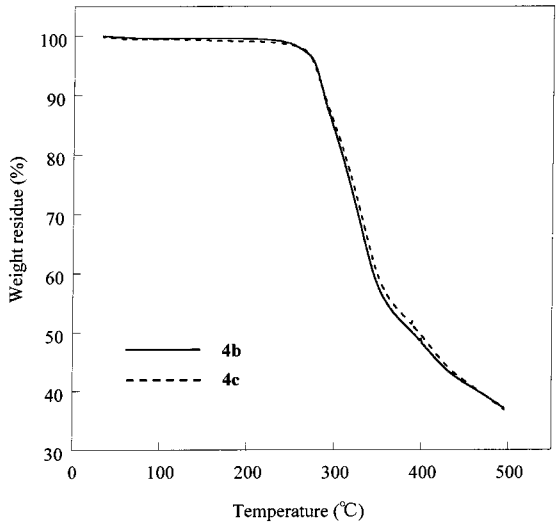


Figure 3. TG traces of polymers **4b** and **4c**.

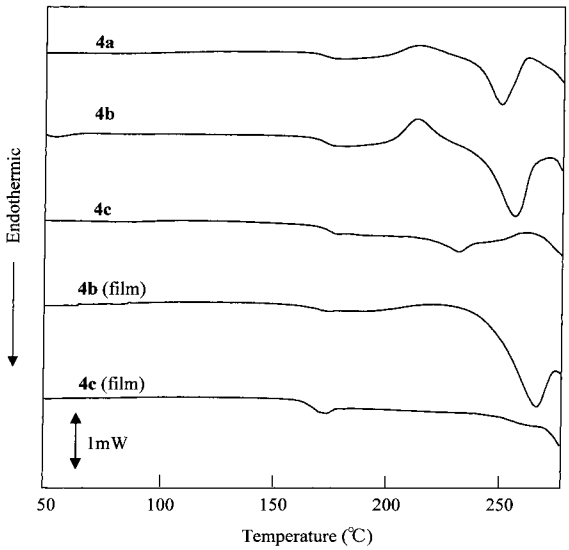


Figure 4. DSC traces of first-heating process for polymers **4a**, **4b**, and **4c**.

peaks due to melting points (T_m's) at 251 and 256 °C. Thus, they were expected to be semicrystalline polymers. On the other hand, the DSC traces of polymer **4c** showed T_g at around 170 °C and a small endothermic peak at 233 °C. The random sequence may prevent the effective hydrogen bondings of urethane or urea moieties between polymer chains. No endothermic peak was observed in the second-heating DSC traces of polymers **4a**, **4b**, and **4c**, indicating only typical glass transitional profiles. Once the as-made polymers have melted, no crystalline region could be formed on the cooling process. The chain mobility seems to be restricted by hydrogen bonds between the intermolecular or intramolecular urethane or urea bonds. The hydrogen bonds formed during the process of cooling from the melting would restrict the chain movement and hinder the formation of regular chain conformations.

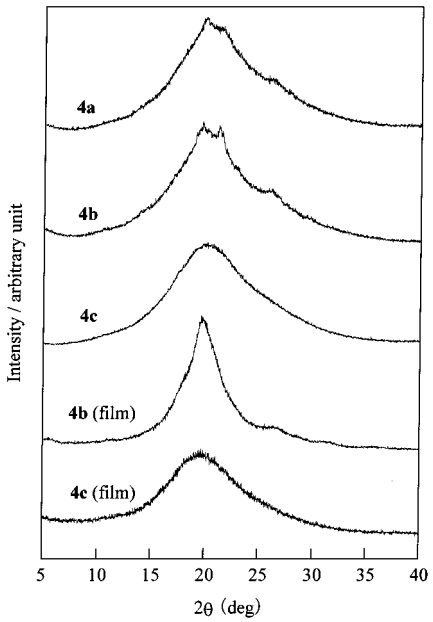


Figure 5. WAXD intensity curves of polymers **4a**, **4b**, and **4c**.

The DSC traces of first-heating process for as-cast films of polymers **4b** and **4c** are illustrated in Figure 4. Polymer **4b** exhibited a slight baseline shift corresponding to T_g (184 °C) and an endothermic peak at 267 °C. Polymer **4b** was considered to retain semicrystalline regions in the film state. The glass transition temperature (T_g) and melting temperature (T_m) of polymer **4b** cast film were higher than those of as-made polymer. This behavior would be explained by the enhanced interaction between polymer chains due to shear stress, compared with as-made sample.

On the other hand, DSC traces of polymer **4c** show only a baseline shift at 175 °C corresponding to the T_g; no endothermic peak was observed. Polymer **4c** is considered to be amorphous due to its random sequence.

(c) Fine Structure of Polymers. The structures of as-made **4a, 4b,** and **4c** and as-cast films **4b** and **4c** were studied by WAXD analyses. WAXD profiles of polymers **4** are shown in Figure 5. Several peaks of reflections indicate that **4a** and **4b** are semicrystalline polymers. On the other hand, polymer **4c** showed an amorphous profile. The WAXD refraction patterns of **4a** and **4b** differed from that of **4c**, showing that the

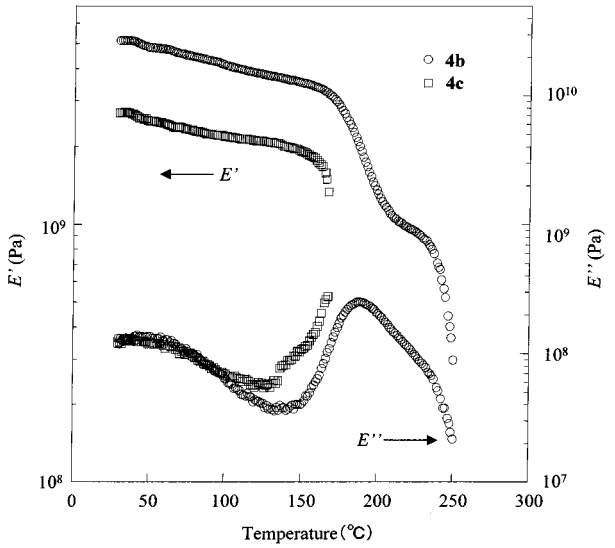


Figure 6. Dynamic mechanical spectroscopy of polymers **4b** and **4c**.

ordered regularity changes the packing structure of the crystalline in poly(urethane−urea). These results agree with DSC data. In the case of as-cast film of polymer **4b**, the WAXD profile became sharp, implying an increase of semicrystalline regions in film state. On the other hand, polymer **4c** showed an amorphous profile of both as-cast film and as-made sample.

(d) Mechanical Properties of Polymers. The temperature dependence of dynamic mechanical storage modulus, E', and the dynamic mechanical loss modulus, E'', of polymers **4b** and **4c** is illustrated in Figure 6. The E' value of polymers **4b** and **4c** exhibited 5.2 and 2.7 GPa at room temperature, respectively. T_g is often designated by the temperature at which the E'' value is at a peak.[9] The E' of polymer **4c** declined rapidly at 160 °C. As a result of large E' change, no significant E'' peak was observed near the T_g observed in the DSC profile. In the case of polymer **4b**, the E' started to decrease rapidly at 170 °C, and the peak of E'' was observed at around 185 °C, corresponding to its T_g. Polymer **4b** maintained 1 GPa of E' up to 200 °C, and its E' decreased around 240 °C, which is near the T_m in the DSC profile.

Figure 7 shows the results of thermal mechanical analysis (TMA) of polymers **4b** and **4c**. For polymer **4c**, both of the thermally treated film and as-cast film were elongated sharply at 175 °C, which is the T_g in the DSC profile. A coefficient of thermal linear expansion (CTE) of as-cast polymer **4c** film in the range 100−150 °C was 62 ppm °C^{-1}. On the other hand, as-cast polymer **4b** film shrank near the T_g and was elongated up to 250 °C, corresponding to the T_m. This behavior was attributed to larger CTE of this film than that of glass plate. As as-cast polymer **4b** film was prepared on glass plate at 150 °C for 4 h, the film was in an elongated state during the cooling process to room temperature. Thus, it is presumed that the stress of this film was released above its T_g. To release the stress from the glass substrate, the film was removed from the glass substrate, and the thermal treatment of this film was performed at 190 °C for 1 h. The thermally treated film showed no shrinkage around 170 °C and a small elongation up to 260 °C. The CTE of this film was 90 ppm °C $^{-1}$ in the range 50−250 °C.

This remarkable different thermal expansion behavior between polymers **4b** and **4c** above T_g comes from

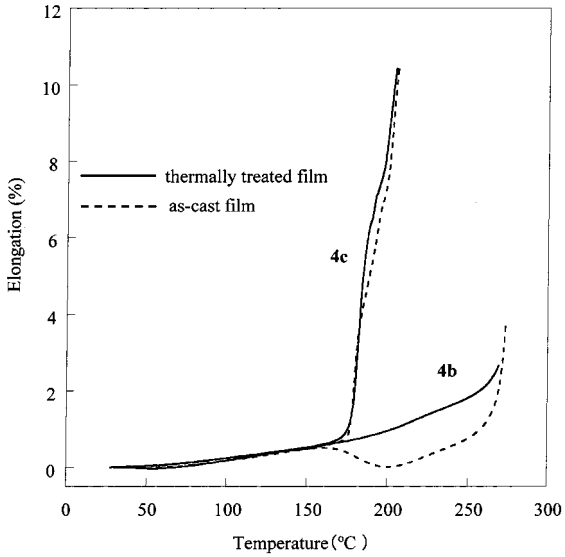


Figure 7. Thermal mechanical spectroscopy of polymers **4b** and **4c**.

the amount of crystalline region in the two polymers. The order chain sequence increases the interaction between poly(urethane−urea)s due to intermolecular hydrogen bonding.

Conclusions

We have successfully prepared the head-to-tail ordered poly(urethane−urea) by polyaddition of **1** with **2** as nonsymmetric monomers. Furthermore, authentic and random poly(urethane−urea)s were prepared to verify ordered polymers. The structure of polymers **4b** and **4c** was determined by comparison with the ^{1}H and ^{13}C NMR spectra of authentic polymer **4a**. Constitutional isomerism has strong effects on the physical properties of polymer, such as solubility, crystallinity, and thermal and mechanical properties.

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