Synthesis of Ordered Polyamides by Direct Polycondensation. 3

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ABSTRACT: Ordered (head-to-tail) polyamides were prepared by the direct polycondensation of a symmetric monomer, succinic anhydride, with a nonsymmetric monomer, 2-(4-aminophenyl)ethylamine, or a pair of two symmetric monomers, 4,4′-oxydianiline and *m*-xylylenediamine, using the activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate. The polycondensation was carried out by mixing the monomers all at once, yielding the sequential (head-to-tail) polyamides with inherent viscosities up to 0.22 dL/g. The authentic ordered and random polyamides were prepared to verify the structures of ordered polyamides. The microstructures of polyamides obtained were investigated by means of ^{13}C NMR spectroscopy, and it has been found that the polyamides obtained had the expected head-to-tail structures. Furthermore, the model reaction was studied in detail to demonstrate the feasibility of ordered polyamidation.

Introduction

Direct polycondensation using activating agents has led to the in situ activation of carboxylic acids, followed by condensation under mild conditions.[1]

In a previous paper,[2] we demonstrated that the highly chemoselective polyamidation of multifunctional dicarboxylic acids and diamines without need to protect the acylation-sensitive groups can be achieved by direct polycondensation using the activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (1).

Our next goal was to establish the method as a synthetic procedure for sequantial polyamides using the activating agents. The synthesis of proteins in the living cell from activated amino acids takes places on the surfaces of ribosomes. The resulting polypeptide molecules have a specific amino acid sequence governed by the m-RNA that was coded by the DNA in the nucleous of the cell. In our procedure, there are no such active templates that direct the sequence of alignment of amino acids. Therefore, the chemical synthesis of polypeptides is carried out step by step with the addition of each amino acid residue.

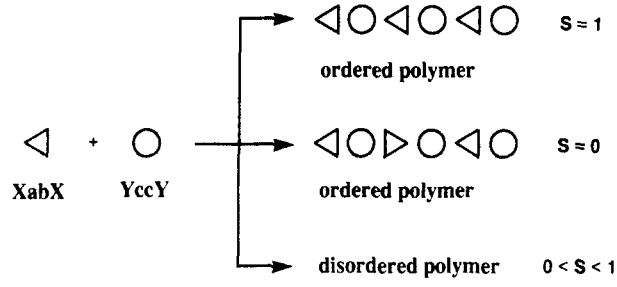
Most condensation polymers are prepared by reactions between two different bifunctional symmetric monomers. However, the synthesis of condensation polymers from a symmetric (YccY) and nonsymmetric (XabX) monomer has been only slightly explored.[3] Pino and co-workers[4] have reported a series of studies of the influence of constitutional isomerism on the physical properties of polycondensates, where theoretical aspects of structural regularity of polycondensation were systematically investigated. They showed that the probability, *s*, of two adjacent nonsymmetric units in a chain pointing in the same directions could be used to quantify structural regularity. When XabX is reacted with YccY, the shortest structural elements in the polymer are –acca–, –accb–, –bcca–, and –bccb–, where the two structures –accb– and –bcca– would be indistinguishable. The probability, *s*, of an –accb– placement is given by

$$s = [\text{accb}]/([\text{acca}] + [\text{accb}] + [\text{bccb}])$$

where [accb] includes –accb– as well as –bcca– arrangements. Three general cases are shown in Scheme I. For a chain where all units point in the same direction, $s = 1$ (head-to-tail); when the orientation of the units is strictly alternating, $s = 0$ (head-to-head or tail-to-tail). If no preference for the different enhancement exists, $s = {}^1/_2$.

On the basis of the detailed kinetics consideration, it was concluded that a difference in the reactivity of functional groups in a nonsymmetric monomer was not sufficient to produce condensation polymers with a ordered structure. If the –aX group of the nonsymmetric monomer is more reactive than the –bX group (the kinetics parameters of interest are the ratio of rate constants for the reactions of functional groups of nonsymmetric monomer XabX, $r = k_{bx}/k_{ax}$), immediate mixing of two monomers gives a random polymer. To obtain a head-to-head or tail-to-tail polymer, YccY should be added slowly to XabX, that is, YccY is added slowly to XabX so that there would never be any unreacted functional group, defined –cY, present in the reaction. After half of the YccY is added, then only XbaccabX will be produced. Upon addition of the remaining YccY units, only –bccb– structure would be formed in the polymer. Accordingly, the resulting polymer would contain –acca– and –bccb– arrangements only, and $s = 0$.

Scheme I
Schematic Representation of Polymers with Different Values of *s*



Suter et al.[4f] studied the polycondensation of terephthaloyl chloride with 2,6-disubstituted diamines by the Schotten–Baumann reaction and found that ordered polymers ($s \simeq 0$) were obtained by slow addition of terephthaloyl chloride to a reaction flask containing the diamines.

In the preceding papers,[5] we reported a method for the synthesis of ordered polyamide (head-to-head or tail-to-tail) by direct polycondensation. These polymers were prepared by the polycondensation of a symmetric monomer, isophthalic acid with a nonsymmetric monomer, 2,6-dimethyl-*p*-phenylenediamine or 2-(4-aminophenyl)-ethylamine using activating agent 1.

To obtain the head-to-tail polymer ($s = 1$), we need to introduce other parameters g_a and g_b.[4] g_a is the ratio of the reaction rate constants of the second reacting functional group on the YccY monomer to that of the first

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reacting functional group, if the first one has reacted with an -aX group. Thus

$$g_a = k_{cY,second}/k_{cY,first}\ (-aX) \quad (0 \le g_a)$$

$$g_b = k_{cY,second}/k_{cY,first}\ (-bX) \quad (0 \le g_b)$$

Deactivating induction means that g_a (or g_b) < 1, while activating induction means g_a (or g_b) > 1. A head-to-tail polymer is obtained when the following requirements are satisfied: (1) r is sufficiently small, (2) the second reacting group on the YccY is strongly deactivated by the reaction of the first, and (3) the monomers are mixed infinitely fast. Therefore, the molecular design of YccY and XabX monomers to meet requirements 1 and 2 is important.

This article describes a successful synthesis of ordered (head-to-tail) polyamides by the direct polycondensation of succinic anhydride (**2b**) with 2-(4-aminophenyl)ethylamine (**4a**) or a pair of two diamines, 4,4'-oxydianiline (**4b**) and *m*-xylylenediamine (**4c**).

Experimental Section

Materials. *N*-Methyl-2-pyrrolidone (NMP), 1,3-dimethyl-2-imidazolidinone (DMI), and hexamethylphosphoric triamide (HMPA) were purified by vacuum distillation and stored over 4-Å molecular sieves. Succinic acid (**2a**), succinic anhydride (**2b**), and 4,4'-oxydianiline (ODA, **4b**) were purified by recrystallization. 2-(4-Aminophenyl)ethylamine (**4a**) and *m*-xylylenediamine (**4c**) were purified by vacuum distillation. Triethylamine (TEA) was purified by the usual method. Other reagents and solvents were obtained commercially and used as received.

The activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (**1**) was prepared according to the reported procedure.[6]

***N,N'*-Bis(2-phenylethyl)succinamide (3a).** 2-Phenylethylamine (0.14 mL, 1.0 mmol) was added to a solution of **2b** (0.100 g, 1 mmol) in NMP (1.0 mL) at room temperature. The solution was stirred for 10 min. To this solution was added activating agent **1** (0.422 g, 1.1 mmol), TEA (0.14 mL, 1 mmol), and 2-phenylethylamine (0.15 mL, 1.1 mmol). The mixture was stirred at room temperature for 1 h. The solution was poured into 10% aqueous sodium carbonate. The precipitate was filtered, washed with water, and dried. The yield was 0.279 g (86%). Recrystallization from a mixture of methanol and water afforded white needles, mp 207 °C. IR (KBr) ν 3300 (N-H) and 1630 cm^{-1} (C=O). ^{13}C NMR (CF_3COOD) 178.3 ppm (C=O). Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.05; H, 7.46; N, 8.63. Found: C, 74.05; H, 7.49; N, 8.44.

***N,N'*-Bis(*p*-ethylphenyl)succinamide (3b).** To a solution of **2b** (0.100 g, 1 mmol) in NMP (1.0 mL) was added *p*-ethylaniline (0.25 mL, 2 mmol), TEA (0.14 mL, 1 mmol), and activating agent **1** (0.422 g, 1.1 mmol) at room temperature. The mixture was stirred for 1 h. The product was isolated as described above. The yield was 0.274 g (84%). Recrystallization from the mixture of methanol and water gave white plates, mp 250–251 °C. IR (KBr) 3290 (N-H), 1660 cm^{-1} (C=O). ^{13}C NMR (CF_3COOD) 176.9 ppm (C=O). Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.05; H, 7.46; N, 8.63. Found: C, 74.27; H, 7.40; N, 8.55.

***N*-(*p*-Ethylphenyl)-*N'*-(2-phenylethyl)succinamide (3c).** *p*-Ethylaniline (0.126 g, 1 mmol) was added to a solution of **2b** (0.100 g, 1 mmol) in NMP (1.0 mL) at room temperature. The solution was stirred for 10 min. To this solution was added activating agent **1** (0.422 g, 1.1 mmol), TEA (0.14 mL, 1 mmol). After 10 min of stirring, 2-phenylethylamine was added and stirred for 1 h. The product was isolated as described above. The yield was 0.258 (82%). Recrystallization from methanol yielded white needles, mp 211–213 °C. IR (KBr) 3300 (N-H), 1640 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.05; H, 7.46; N, 8.63. Found: C, 74.10; H, 7.41; N, 8.58.

Authentic Ordered Polyamide 6a. *N*-[2-(*p*-Aminophenyl)ethyl]succinamic acid (5): A solution of **2b** (5.00 g, 5 mmol) in NMP (5 mL) was added dropwise at room temperature with stirring to a solution of 2-(4-aminophenyl)ethylamine **4a** (0.681 g, 5 mmol) in NMP (5 mL). The addition was completed in 10 min, and the stirring was continued for an additional 10 min. The solution was poured into ether (200 mL). The precipitate was filtered, washed with ether, and dried. The yield was 0.963 g (79%). Recrystallization from ethanol afforded faint yellow needles, mp 152 °C (by DTA). IR (KBr) ν 3370, 3320, (N-H), 1710 (COOH), 1645 cm^{-1} (C=O). ^{13}C NMR (CF_3COOD): 180.6, 178.3 ppm (C=O). Anal. Calcd for $C_{12}H_{16}N_2O_3$: C, 61.00; H, 6.83; N, 11.86. Found: C, 60.68; H, 6.95; N, 11.58.

The activating agent **1** (0.422 g, 1.1 mmol) was added to a solution of **5** (0.236 g, 1 mmol), and TEA (0.28 mL, 2 mmol) in the mixture of DMI (1.8 mL) and HMPA (0.2 mL). The mixture was stirred at room temperature for 24 h. The resulting solution was poured into methanol (200 mL). The polymer that precipitated was filtered and washed with methanol. The polymer was collected and dried in vacuo at 100 °C. The yield was 0.221 g (99%). The inherent viscosity of the polymer in concentrated sulfuric acid was 0.25 dL/g at a concentration of 0.5 g/dL at 30 °C. IR (KBr) ν 3300 (N-H), 1640 cm^{-1} (C=O). ^{13}C NMR (CF_3COOD) 179.1, 176.9 ppm (C=O). Anal. Calcd for $(C_{12}H_{14}N_2O_2 \cdot {}^1/_4H_2O)_n$: C, 64.70; H, 6.56; N, 12.58. Found: C, 64.93; H, 6.35; N, 11.99.

Random Polyamide 6b from 2a and 4a. The activating agent **1** (0.843 g, 2.2 mmol) was added to a solution of **2a** (0.118 g, 1 mmol) and TEA (0.28 mL, 2 mmol) in DMI (0.5 mL). The mixture was stirred for 10 min at room temperature. To this solution was added a solution of **4a** (0.136 g, 1.0 mmol) in DMI (1 mL). After 24 h of stirring, the resulting solution was poured into methanol (200 mL). The polymer was isolated as described above. The yield was 0.210 g (96%). The inherent viscosity of the polymer in concentrated sulfuric acid was 0.18 dL/g at a concentration of 0.5 g/dL at 30 °C. IR (KBr) ν 3290 (N-H), 1650 cm^{-1} (C=O). ^{13}C NMR (CF_3COOD) 179.1, 178.5, 177.3, 176.9 ppm (C=O). Anal. Calcd for $(C_{12}H_{14}N_2O_2 \cdot {}^1/_4H_2O)_n$: C, 64.70; H, 6.56; N, 12.58. Found: C, 64.46; H, 6.50; N, 12.38.

Polyamide 6c from 2b and 4a. To a solution of **4a** (0.138 g, 1.02 mmol) in DMI (0.8 mL) and HMPA (0.2 mL) was added a solution of **2b** (0.102 g, 1.02 mmol) in DMI (0.5 mL), **1** (0.429 g, 1.12 mmol), and TEA (0.145 mL, 1.02 mmol). The mixture was stirred for 24 h at room temperature and poured into methanol (200 mL). The polymer was isolated as described above. The inherent viscosity of the polymer in concentrated sulfuric acid was 0.20 dL/g at 30 °C. IR (KBr) ν 3300 (N-H), 1640 cm^{-1} (C=O). ^{13}C NMR (CF_3COOD) 179.1, 176.9 ppm (C=O). Anal. Calcd for $(C_{12}H_{14}N_2O_2 \cdot {}^1/_3H_2O)_n$: C, 64.27; H, 6.59; N, 12.49. Found: C, 64.01; H, 6.38; N, 11.92.

***N,N'*-Dibenzylsuccinamide (7a).** This compound was prepared from **2b** and benzylamine as described above. The yield was 92%. Recrystallization from methanol afforded white plates, mp 211–212 °C (lit.[7] 210–211 °C). IR (KBr) ν 3300 (N-H) and 1640 cm^{-1} (C=O). ^{13}C NMR {$(CD_3)_2SO$} 171.1 ppm (C=O).

***N,N'*-Bis(*p*-methoxyphenyl)succinamide (7b).** This compound was prepared from **2b** and *p*-methoxyaniline as described above. The yield was 85%. Recrystallization from propionic acid gave white needles, mp 256 °C (by DTA; lit.[8] 243 °C). IR (KBr) 3310 (N-H), 1650 cm^{-1} (C=O). ^{13}C NMR {$(CD_3)_2SO$} 169.5 ppm (C=O).

***N*-Benzyl-*N'*-(*p*-methoxyphenyl)succinamide (7c).** This compound was prepared from **2b**, *p*-methoxyaniline, and benzylamine as described above. The yield was 82%. Recrystallization from methanol yielded white needles, mp 194 °C (by DTA). IR (KBr) 3290 (N-H), 1640 cm^{-1} (C=O). ^{13}C NMR {$(CD_3)_2SO$} 171.0, 169.6 ppm (C=O). Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97. Found: C, 68.94; H, 6.45; N, 8.94.

Authentic Ordered Polyamide 9a. *N,N'*-(*m*-Xylylene)disuccinamic acid (8): A solution of *m*-xylylenediamine (**4c**, 0.66 mL, 5 mmol) in THF (10 mL) was added dropwise at room temperature with stirring to a solution of **2a** (1.1 g, 11 mmol) in THF (10 mL). The addition was completed in 10 min, and the stirring was continued for an addition 1 h. The product was obtained after removal of the solvent. The yield was 1.65 g (98%). Recrystallization from dioxane produced white needles, mp 160–161 °C. IR (KBr) ν 3310 (N-H), 1700 (COOH), 1660 cm^{-1} (C=O). Anal. Calcd for $C_{16}H_{20}N_2O_6$: C, 57.14; H, 5.99; N, 8.33. Found: C, 57.04; H, 5.98; N, 8.15.

The activating agent 1 (0.843 g, 2.2 mmol) was added to a solution of 8 (0.336 g, 1 mmol), 4,4′-oxydianiline (**4b**, 0.200 g, 1 mmol), and TEA (0.28 mL, 2 mmol) in the mixture of NMP (1 mL) and HMPA (1 mL). The mixture was stirred at room temperature for 24 h. The resulting solution was poured into methanol (200 mL). The polymer that precipitated was filtered and washed with methanol. The polymer was collected and dried in vacuo at 100 °C. The yield was 0.497 g, 99%). The inherent viscosity of the polymer in NMP (containing 3% LiCl) was 0.23 dL/g at a concentration of 0.5 g/dL at 30 °C. IR (KBr) ν 3290 (N–H), 1660 cm^{-1} (C=O). ^{13}C NMR {$(CD_3)_2SO$} 172.0, 170.8 ppm (C=O). Anal. Calcd for $(C_{28}H_{28}N_4O_5 \cdot {}^1/_2H_2O)_n$: C, 66.00; H, 5.74; N, 10.99. Found: C, 66.33; H, 5.62; N, 10.71.

Random Polyamide 9b from 2a, 4b, and 4c. The activating agent 1 (0.843 g, 2.2 mmol) was added to a solution of **2a** (0.118 g, 1 mmol) and TEA (0.28 mL, 2 mmol) in NMP (0.5 mL). The mixture was stirred for 10 min at room temperature. To this solution was added a solution of **4b** (0.100 g, 0.5 mmol) and **4c** (0.0681 g, 0.5 mmol) in NMP (1 mL). After 24 h of stirring, the resulting solution was poured into methanol (200 mL). The polymer was isolated as described above. The inherent viscosity of the polymer in NMP was 0.18 dL/g at a concentration of 0.5 g/dL at 30 °C. IR (KBr) ν 3290 (N–H), 1650 cm^{-1} (C=O). ^{13}C NMR {$(CD_3)_2SO$} 171.8, 171.9, 170.7, 170,8 ppm (C=O). Anal. Calcd for $(C_{28}H_{28}N_4O_5 \cdot {}^1/_2H_2O)_n$: C, 66.00; H, 5.74; N, 10.99. Found: C, 66.22; H, 5.58; N, 10.60.

Polyamide 9c from 2b, 4b, and 4c. To a solution of **4b** (0.205 g, 1.025 mmol) and **4c** (0.140 g, 1.025 mmol) was added a solution of **2b** (0.205 g, 2.05 mmol) in NMP (0.5 mL), 1 (0.805 g, 2.1 mmol), and TEA (0.29 mL, 2.05 mmol). The mixture was stirred for 24 h at room temperature and poured into methanol (200 mL). The polymer was isolated as described above. The inherent viscosity of the polymer in NMP was 0.22 dL/g at 30 °C. IR (KBr) ν 3290 (N–H), 1650 cm^{-1} (C=O). ^{13}C NMR {$(CD_3)_2SO$} 172.0, 170.8 ppm (C=O). Anal. Calcd for $(C_{28}H_{28}N_4O_5 \cdot {}^1/_2H_2O)_n$: C, 6.00; H, 5.74; N, 10.99. Found: C, 65.53; H, 5.60; N, 10.48.

Measurements. The infrared spectra were recorded on a I-5020-FT-IR spectrometer, and the NMR spectra on a Hitachi R-24B (60 MHz) and Hitachi R-22 (90 MHz). Viscosity measurements were carried out by using an Ostwald viscometer at 30 °C. Thermal analyses were performed on a Selko SSS 5000 thermal analyzer at a heating rate of 5 °C min^{-1} for thermogravimetric analysis (TG).

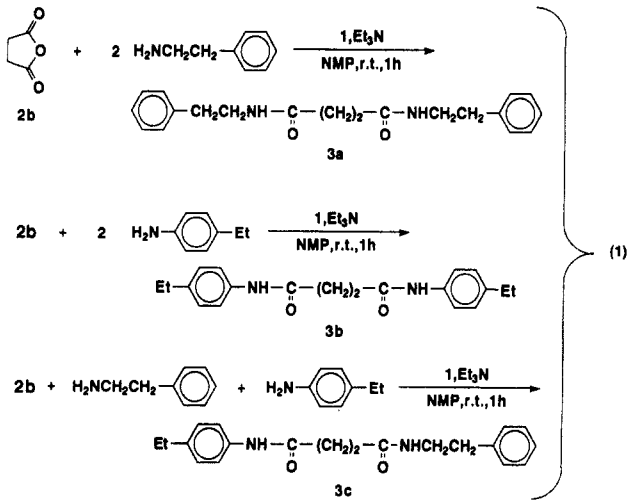
Results and Discussion

The synthesis of head-to-tail polyamides from XabX and YccY monomers requires that the ratios of rate constants for the reactions of functional groups of nonsymmetric monomer XabX, r and g, should be smaller than 1.

Suter et al.[4c] measured the reaction rate constants relevant in the aminolysis of bis(4-nitrophenyl)carbonate with 2-phenylethylamine and p-ethylaniline and found that the ratio of rate constants r is 1.0×10^{-5}, and g_a and g_b are 3.6×10^{-3} and 1, respectively. On the basis of these findings, they prepared the sequential polyurea with substantially head-to-tail order by mixing two monomers, bis(4-nitrophenyl)carbonate and 2-(4-aminophenyl)ethylamine (**3a**).

In the previous paper,[5a] we measured the overall second-order rate constant (k) for the reaction of benzoic acid with various anilines in NMP in the presence of the activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (**1**) and found that there is a linear relationship with a slope of 1 between log k and pK_a of aniline derivatives. The difference of pK_a values between an aliphatic amine and an aromatic amine is about 6. Thus, the rate constants for the aminolysis of the active intermediate will be changed by more than 10^6 when the amine is varied from the aliphatic amine to the aromatic amine. Thus, 2-(4-aminophenyl)ethylamine was chosen as the XabX monomer to meet condition 1. On the other hand, succinic anhydride (**2b**) was chosen as the YccY monomer, which was expected to have a deactivating induction.

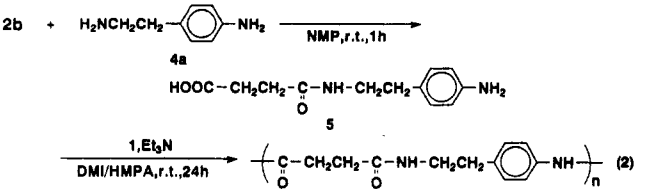
Prior to the synthesis of ordered polyamides, the following model compound work was performed by the direct procedure to determine if the model compounds were formed in quantitative yields to constitute a polymer-forming reaction. This procedure consists of adding **1** to a solution of carboxylic acid and amine in NMP that contains a tertiary organic base to form a carboxylate anion. The reaction of **2b** with 2-phenylethylamine or p-ethylaniline and that of **2b** with 2-phenylethylamine and p-ethylaniline were studied (eq 1).



These reactions afforded the model compounds *N,N′*-bis(2-phenylethyl)succinamide (**3a**), *N,N′*-bis(*p*-ethylphenyl)succinamide (**3b**), and *N*-(*p*-ethylphenyl)-*N′*-(2-phenylethyl)succinamide (**3c**) in high yields. The synthesis of **3c** was carried out by the two methods. Method 1 is a two-step reaction. *N*-(*p*-Ethylphenyl)succinamic acid is formed by the reaction of **2b** with p-ethylaniline, followed by immediate treatment with 2-phenylethylamine in the presence of **1**. Method 2 is a one-step reaction. A solution of activating agent **1** and **2b** is added to a solution of p-ethylaniline and 2-phenylethylamine all at once. Both methods gave the nonsymmetric amide **3c** without the formation of the symmetric amides **3a** and **3b**. This means that **2b** reacts preferentially with 2-phenylethylamine.

Polymer Synthesis. Synthesis of Authentic Ordered Polyamide. The authentic ordered polyamide **6a** (head-to-tail) and random polyamide **6c** were synthesized for characterization of the structure of ordered polyamides obtained by the direct polycondensation.

The authentic head-to-tail polyamide (**6a**) was prepared as shown in eq 2. The ring-opening addition of **2b** with



2-(4-aminophenyl)ethylamine **4a**, gave *N*-[2-(*p*-aminophenyl)ethyl]succinamic acid (**5**). The direct self-polycondensation of **5** was carried out with the activating agent **1** in DMI and HMPA at room temperature, producing polyamide **6a** in quantitative yield with an inherent viscosity of 0.25 dL/g. Random polyamide **6b** synthesized

from succinic acid **2a** with **4a** in the presence of 1 by mixing both monomers at once (eq 3).

$$\underset{\textbf{2a}}{HOOC(CH_2)_2COOH} + \textbf{4a} \xrightarrow[DMI/HMPA,\ room\ temp]{1,\ Et_3N} \text{random polyamide } \textbf{6b} \quad (3)$$

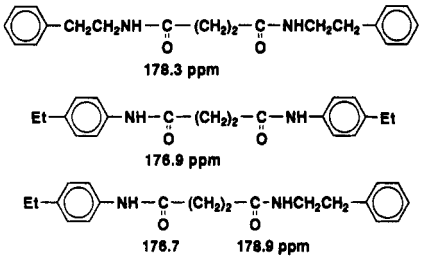
Synthesis of Ordered Polyamide (Head-to-Tail) 6c. As briefly described in the Introduction, the head-to-tail polymer is obtained when the monomers are mixed infinitely fast. Therefore, the synthesis of the ordered polyamide was carried out by mixing two monomers, **2b** and **4a**, all at once in the presence of 1 in DMI/HMPA at room temperature. The polycondensation proceeded smoothly and gave the polyamide **6c** with inherent viscosity of 0.20 dL/g (eq 4).

$$\textbf{2a} + \textbf{4a} \xrightarrow[DMI/HMPA,\ room\ temp]{1,\ Et_3N} [\text{–CO–}(CH_2)_2CONHCH_2CH_2\text{–}C_6H_4\text{–NH–}]_n \quad (4)$$

6c

Polymer Characterization. The IR spectra of the polyamides **6a–c** were consistent with model compounds and known analogues. All polyamides prepared showed characteristic N–H, amide I, amide II bands in the range 3220–3320, 1630–1640, and 1520–1540 cm^{-1}, respectively. Elemental analyses also supported the formation of the expected polymers.

The microstructure of polymers was determined by means of ^{13}C NMR spectroscopy. ^{13}C NMR chemical shifts of amide carbonyl groups for model compounds **3** in CF_3COOD are as follows:



The ^{13}C NMR spectra of authentic ordered head-to-tail polyamide **6a** and random polyamide **6b** are presented in Figure 1.

The signals of carbon nuclei in amide carbonyl groups for polyamide **6a** appeared at 179.1 and 176.9 ppm, and that for random polyamide **6b** were observed at 179.1, 178.5, 177.3, and 176.9 ppm. These peaks were assigned, as shown in the inset in Figure 1, on the basis of assignments for model compounds. Furthermore, the spectrum of authentic ordered polyamide **6a** is identical to that of polyamide **6c** (Figure 1). These findings clearly indicate that the direct polycondensation of **2b** and **4a** produced the desired head-to-tail polyamide **6c**.

The polyamides were white solids, soluble in sulfuric acid and methanesulfonic acid and insoluble in dipolar aprotic solvents, such as NMP, DMF, and DMSO.

The thermal stability of the polymer was examined by thermogravimetry (TG) and differential thermal analysis (DTA). Typical traces of polymers **6b** and **6c** in a nitrogen atmosphere are shown in Figure 2. These polymers showed the different thermal behavior. The DTA trace of polymer **6b** exhibited an endotherm at 310 °C, which correlated

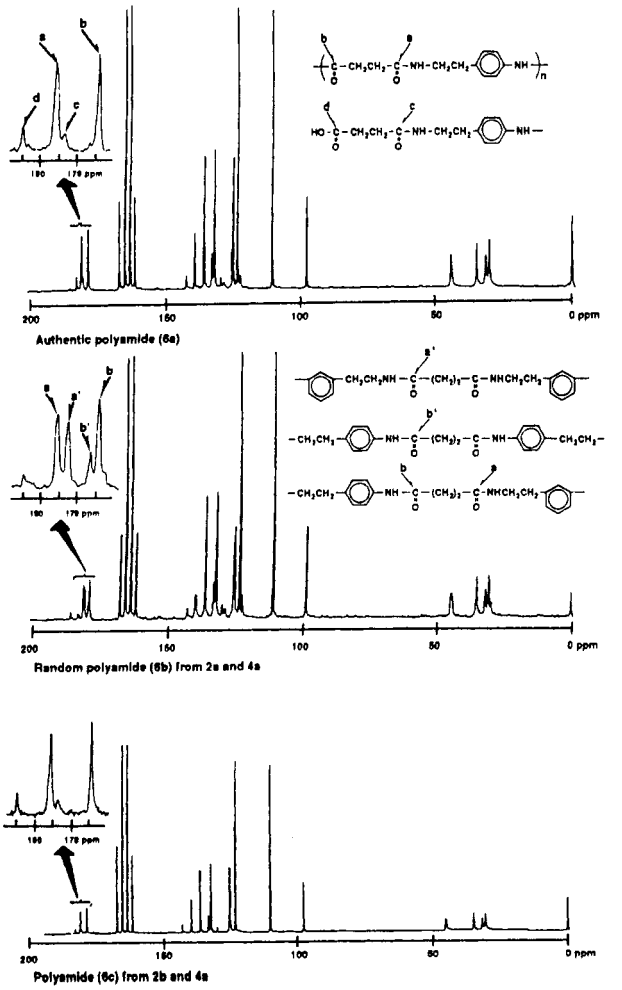


Figure 1. ^{13}C NMR spectra of polyamides **6a**, **6b**, and **6c** in CF_3COOD at 25 °C.

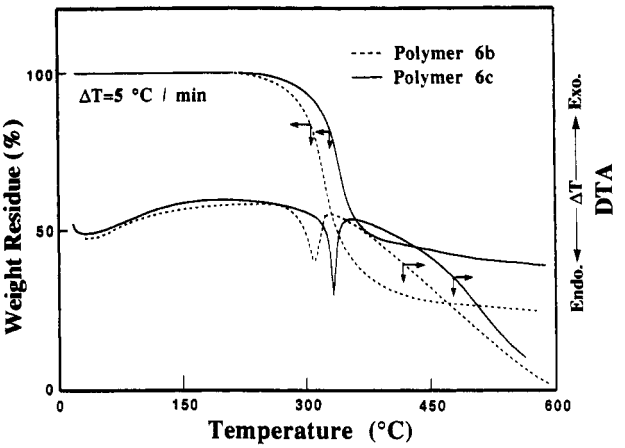
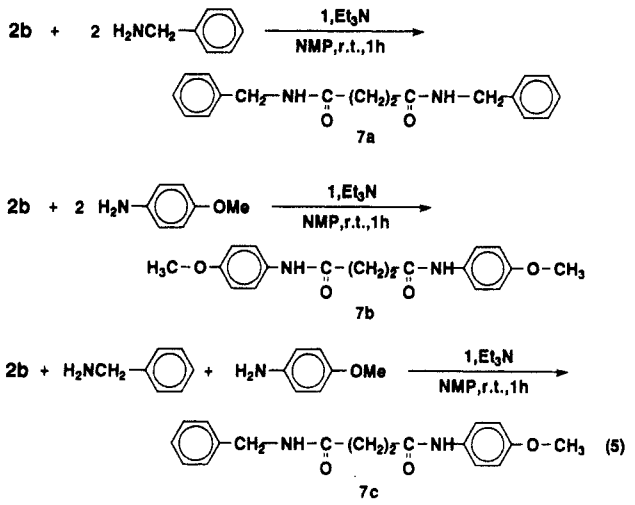


Figure 2. TG and DTA traces of polyamides **6b** and **6c** in nitrogen.

well with the weight loss temperature in the TG trace. This rapid weight loss is presumably due to the random intramolecular imidization of polymer **6b**, followed by the volatilization of small molecules cleavaged. In the IR spectrum of polymer **6b** which was heated to 310 °C under nitrogen, characteristic absorptions assigned to imide carbonyl bands were observed at 1773 and 1710 cm^{-1}, while amide absorptions were reduced in intensities. On the other hand, the sharp endotherm peak in DTA was observed at 330 °C in both polymer **6a** and **6c**. This difference in the temperature of imidization can be rationalized by assuming better packing of the ordered chains in the solid state.

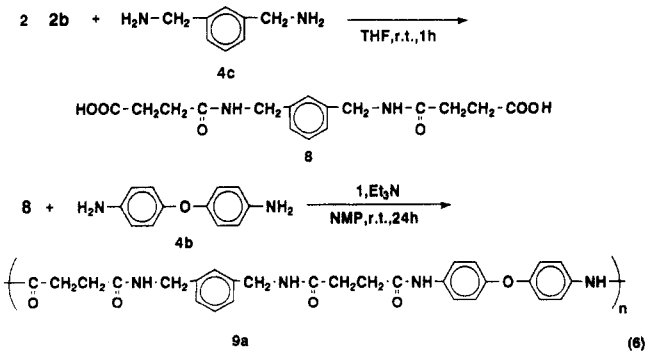
Synthesis of Ordered Polyamide from 2b, 4b and 4c. On the basis of the success of the synthesis of ordered polyamides from two monomers, **2b** and **4a**, we performed the synthesis of sequential polyamides using three monomers, where 4,4′-oxydianiline (**4b**) and *m*-xylylenediamine (**4c**) were used as aromatic and aliphatic diamines, respectively.

The model compounds **7a–c** were prepared in order to clarify the structure of polymers obtained (eq 5). Symmetric diamides *N,N′*-dibenzylsuccinamide (**7a**) and *N,N′*-bis(*p*-methoxyphenyl)succinamide (**7b**) were prepared by the reaction of **2b** with benzylamine and *p*-methoxyaniline, respectively. A nonsymmetric diamide, *N*-benzyl-*N′*-(*p*-methoxyphenyl)succinamide (**7c**), was also prepared from **2b**, benzylamine, and *p*-methoxyaniline.



Polymer Synthesis. The authentic ordered polyamide **9a** (head-to-tail) and random polyamide **9b** were synthesized for the characterization of the structure of sequential polyamides obtained by the direct polycondensation.

The authentic head-to-tail polyamide **9a** was prepared by the direct polycondensation of **4b** with *N,N′*-(*m*-xylylene)disuccinamic acid 8 which was obtained from **2b** and **4c** (eq 6). The polycondensation proceeded smoothly, giving the polyamide with an inherent viscosity of 0.23 dL/g.



The random polyamide **9b** was synthesized from **2a**, **4b**, and **4c** in the presence of 1 at room temperature. Polycondensation was carried out by the rapid mixing of two solutions of **2a** and of **4b** and **4c** in NMP all at once (eq 7).

$$\mathbf{2a} + \mathbf{4b} + \mathbf{4c} \xrightarrow[\text{NMP, room temp, 24 h}]{\text{1, Et}_3\text{N}} \text{random polyamide } \mathbf{9b} \quad (7)$$

The direct polycondensation of **2b**, **4b**, and **4c** in the presence of 1 was carried out at room temperature by mixing three monomers all at once and gave polyamide with the inherent viscosity of 0.22 dL/g (eq 8).

$$\mathbf{2b} + \mathbf{4b} + \mathbf{4c} \xrightarrow[\text{NMP, room temp}]{\text{1, Et}_3\text{N}} \text{polyamide } \mathbf{9c} \quad (8)$$

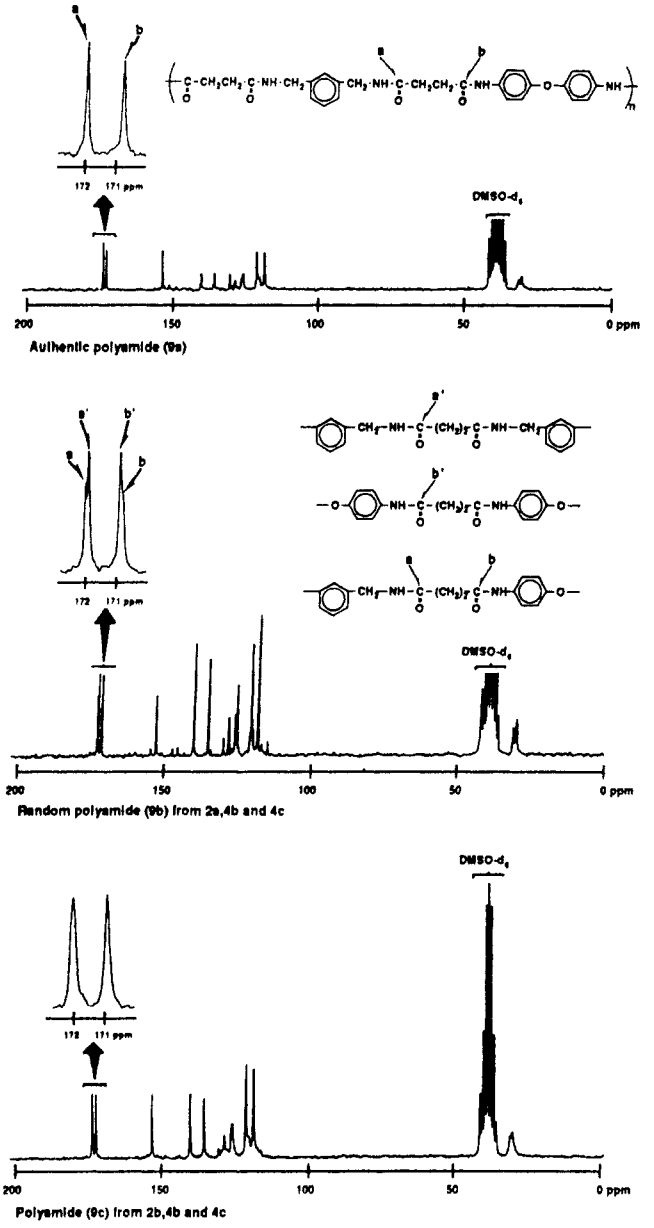


Figure 3. ^{13}C NMR spectra of polyamides **9a**, **9b**, and **9c** in $[(CD_3)_2SO]$ at 25 °C.

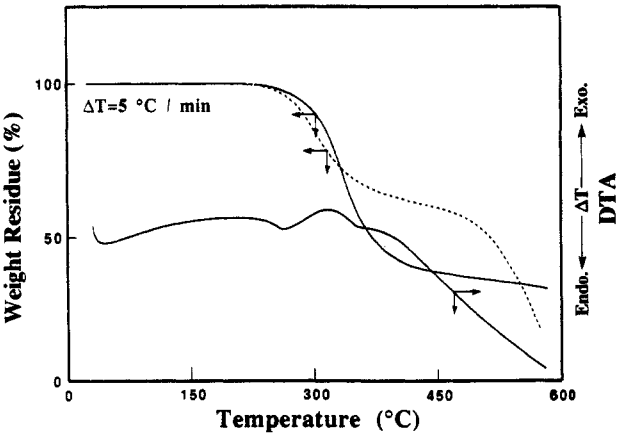
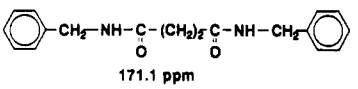
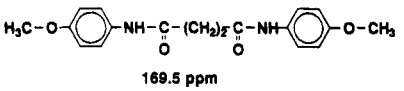


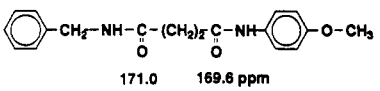
Figure 4. TG and DTA traces of polyamide **9c** in nitrogen (—) and air (– – –).

Polymer Characterization. All polyamides **9a–c** prepared showed characteristic N–H, amide I, and amide II bands in the ranges 3220–3320, 1630–1640, and 1520–1540 cm^{-1}, respectively. Elemental analyses also supported the formation of the expected polymers.

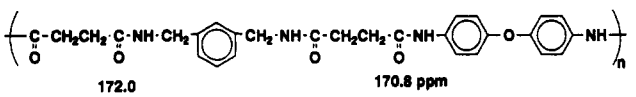
The most conclusive spectral evidence for the proposed polyamide structures and especially for the ordered polyamidation, was provided by ^{13}C NMR. The ^{13}C chemical shifts of amide carbonyl groups for the model compounds are as follows:







The ^{13}C NMR spectra of polyamide **9c** and authentic ordered polyamide **9a** are presented in Figure 3. The spectrum of polyamide **9c** is identical to that of polyamide **9a**. The ^{13}C chemical shifts of amide bonds for authentic ordered polyamide are as follows:



On the other hand, the four peaks of carbon nuclei in amide carbonyl groups for random polyamide were observed at 171.8, 171.9, 170.7, and 170.8 ppm (Figure 3) as expected from its random structure. These findings indicate that the direct polycondensation of **2a**, **4b**, and **4c** produced the desired head-to-tail polyamide.

The polyamides were white solids, soluble in sulfuric acid, methanesulfonic acid, and in dipolar aprotic solvents, such as NMP, DMF, and DMSO.

The thermal stability of the polymer was examined by thermogravimetry (TG). A typical trace of polymer **9c** is shown in Figure 4. The polymer showed a 10% weight loss in air and nitrogen at 300 and 320 °C, respectively.

We expected differences in their properties owing to different regularity. However, no difference in the solubility and thermal stability among these polyamides can be detected. Pino et al.[4d] observed a similar behavior for the studies of the influence of constitutional isomerism on the physical properties of polycondensates and reported that unsubstituted polyamides might not be very suitable because strong effects brought about extensive interchain NH···OC bonds might mask subtle effects due to isomerism.

In summary, we have demonstrated that the synthesis of ordered (head-to-tail) polyamide can be achieved by the direct polycondensation of symmetric monomer **2b** with nonsymmetric monomer **4a** or symmetric monomers **4b** and **4c** using activating agent **1**.

Acknowledgment. We thank S. Kato for technical assistance and T. Takahashi for performing the elemental analyses. Financial support for this study by Tokuyama Science Foundation is gratefully acknowledged.

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Registry No. 1, 111160-56-6; **2b**, 108-30-5; **3a**, 143969-98-6; **3b**, 143969-97-5; **3c**, 143969-99-7; **5**, 143970-00-7; **6a** (copolymer), 143970-06-3; **6b** (copolymer), 143970-07-4; **7a**, 71067-27-1; **7b**, 143970-01-8; **7c**, 143970-02-9; **8**, 143970-03-0; **9b** (copolymer), 143970-08-5; **9c** (copolymer), 143970-09-6; *p*-ethylaniline, 589-16-2; benzylamine, 100-46-9; *p*-methoxyaniline, 104-94-9; 2-phenylethylamine, 64-04-0.