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Synthesis and Characterization of Ordered Poly(amide−ester)s from Isophthaloyl Chloride and 4-(2-Aminoethyl)phenol

Li Li, Hiroshi Seino, Koichiro Yonetake, and Mitsuru Ueda*

Department of Human Sensing and Functional Sensor Engineering, Graduate School of Engineering, Yonezawa, Yamagata 992-8510, Japan

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ABSTRACT: The ordered [head-to-head (H−H) or tail-to-tail (T−T)] poly(amide−ester) was prepared by polycondensation of a symmetric monomer, isophthaloyl chloride **(1),** with 4-(2-aminoethyl)phenol **(2)** as a nonsymmetric monomer. The polymerization was conducted in NMP in the presence of triethylamine (TEA) at −20 °C by slow addition of **1** to **2**, giving the ordered H−H or T−T poly(amide−ester) with an inherent viscosity of 0.27 dL/g, measured at a concentration of 0.5 g/dL at 30 °C in NMP. The authentic H−H or T−T, H−T ordered and random poly(amide−ester)s were prepared to verify the structure of ordered polymers. The microstructure of polymers obtained was investigated by ^{1}H and ^{13}C NMR spectroscopy, and it was found that the polymer obtained by polycondensation had the expected H−H or T−T ordered structure. Furthermore, the model reactions were studied in detail to demonstrate the feasibility of polymer formation. The constitutional regularity of polymers influenced the solubility, thermal properties, and crystallinity.

Introduction

Condensation polymers are prepared by the reaction between two different bifunctional symmetric monomers (XaaX and YccY), yielding the −aacc− repeating units. However, when nonsymmetric monomer (XabX) in place of symmetric monomer (XaaX) is used, polymers with different constitutional isomerisms, that is, a head-to-head or tail-to-tail (H−H or T−T) ordered polymer, a head-to-tail (H−T) ordered polymer, and a random polymer, are formed. Here, −ab− and −cc− represent the nonsymmetric and symmetric monomeric units in the chain, respectively, and X is the leaving group in the polymerization reaction. YccY represents a bifunctional symmetric monomer and XabX a similar but nonsymmetric monomer. Y is again a leaving group.

Structure−property relationships arising from constitutional isomerism are not well-known for condensation polymers. Therefore, it is very 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.

Several reports have been published on the synthesis of condensation polymers with different regularities from XabX and YccY.[1] However, the clear difference in physical properties has not been observed because of a strong interaction between polymers, such as interchain amide NH···OC bonds. We also reported a series of ordered polymer syntheses by direct polycondensation.[2] But, no difference in the solubility, thermal properties, and crystallinity due to isomerism could be detected.

Using the greater reactivity of aromatic amino groups relative to phenol groups, the synthesis of ordered aromatic poly(amide−ester)s was examined by interfacial and solution polycondensation of *m*- and *p*-aminophenols or 4-(4-amino-α,α-dimethylbenzyl)phenol with diacid chlorides.[3] The detailed characterization of polymers, however, was not reported.

For the studies of the influence of constitutional isomers on the physical properties of polycondensates, the strong interactions between polymers are not favorable because this strong effects may mask subtle effects due to isomerism. Thus, we were interested in a poly(amide−ester) containing aliphatic linkages as a candidate to study the theme described above.

In this article, we report the synthesis and properties of ordered poly(amide−ester)s by the polycondensation of isophthaloyl chloride with 4-(2-aminoethyl)phenol.

Experimental Section

Materials. *N*-Methyl-2-pyrrolidinone (NMP) and pyridine were purified by vacuum distillation and stored over 4 Å molecular sieves. Isophthaloyl chloride **(1)** and 4-(2-aminoethyl)phenol **(2)** were purified by recrystallization. Benzoyl chloride was purified by vacuum distillation (69 °C/6 mmHg). Triethylamine (TEA) was purified by a usual method. Other reagents and solvents were obtained commercially and used as received.

The condensing agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) was prepared according to the reported procedure.[4]

Competitive Reaction of Phenethylamine and Phenol with Benzoyl Chloride. Phenethylamine (0.13 mL, 1.0 mmol), phenol (0.094 g, 1.0 mmol), and TEA (0.15 mL, 1.1 mmol) were dissolved in NMP (1 mL) at 0 °C. To this solution was added benzoyl chloride (0.12 mL, 1.0 mmol) in NMP (1 mL). After stirring for 5 min in air, the products ratio was determined by HPLC (acetanilide as the internal standard). The reaction yielded a single product, *N*-phenethylbenzamide. The yield was 100%, mp 116−117 °C (lit. mp 116 °C [5]). IR (KBr, cm^{-1}): ν 1645 (C═O), 3285 (NH). ^{1}H NMR (δ, ppm, DMSO-d_6): 8.52 (t, 1H, NH), 3.42 (m, 2H, −CH_2−NH−), 2.79 (t, 2H, −CH_2−CH_2−NH).

Authentic Ordered (H−H or T−T) Poly(amide−ester) (3a). *N,N*′-Bis(4-hydroxyphenethyl)isophthaldiamide (4). To a solution of **2** (1.509 g, 11.0 mmol) and TEA (1.40 mL, 10.0 mmol) in NMP (20 mL) at −20 °C was slowly added **1** (1.015 g, 5.0 mmol) grain by grain. After stirring for 2 h, the reaction mixture was poured into water. The precipitate was filtered off, washed, and dried. The yield was 1.984 g (98%). Recrystallization from acetic acid/water afforded white needles, mp 200−202 °C. IR (KBr, cm^{-1}): ν 3410 (OH), 3295 (NH), 1650 (C═O). ^{1}H NMR (δ, ppm, DMSO-d_6): 9.23 (s, 2H, OH), 8.68 (t, 2H, NH). Anal. Calcd for $C_{24}H_{24}N_2O_4$: C, 71.26; H, 5.98; N, 6.93. Found: C, 71.46; H, 6.18; N, 6.74.

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Poly(amide−ester) 3a. Compound **4** (0.405 g,1.0 mmol) and TEA (0.35 mL, 2.5 mmol) were dissoved in NMP (2 mL) at 0 °C. To this cooled solution was added solid **1** (0.212 g, 1.05 mmol) in one portion. Then the solution was stirred at this temperature for 6 h in air. The resulting polymer was precipitated by pouring the solution into methanol and dried. Yield 0.539 g (100%). The inherent viscosity of the polymer in NMP was 0.32 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (KBr, cm^{-1}): ν 3320 (NH), 1735 (C=O, ester), 1650 (C=O, amide). ^{13}C NMR (ppm, DMSO-d_6): 166.13 (C=O, amide), 164.06 (C=O, ester). Anal. Calcd for $(C_{32}H_{26}N_2O_6\cdot0.6H_2O)_n$: C, 70.74; H, 4.88; N, 5.13. Found: C, 70.84; H, 4.99; N, 5.04.

Ordered (H−T) Poly(amide−ester) (3b). 3-Methoxycarbonyl-*N*-(4-hydroxyphenethyl)benzamide (5). The condensing agent DBOP (0.422 g, 1.1 mmol) was added to a solution of methyl hydrogen isophthalate (0.180 g, 1.0 mmol) and TEA (0.14 mL, 1.0 mmol) in NMP (1 mL). After stirring for 30 min at room temperature, **2** (0.137 g, 1.0 mmol) was added. The solution was stirred for 2 h and poured into 1% aqueous sodium hydrogen carbonate. The precipitate was filtered off, washed with water, and dried. The yield was 0.299 g (87%). Recrystallization from methanol/water yielded white crystals, mp 114−115 °C. IR (KBr, cm^{-1}): ν 3400 (NH), 1705 (C=O, ester), 1645 (C=O, amide). ^{1}H NMR (δ, ppm, DMSO-d_6): 9.20 (s, 1H, OH), 8.74 (t, 1H, NH), 3.88 (s, 3H, CH_3). Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.22; H, 5.72; N, 4.68. Found: C, 68.04; H, 5.92; N, 4.81.

3-Carboxy-*N*-(4-hydroxyphenethyl)benzamide (6). Compound **5** (0.450 g, 1.5 mmol) was dissolved in ethanol (15 mL). To this solution was added potassium hydroxide (0.256 g, 4.5 mmol) and stirred at 80 °C for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in water. The solution was made to pH 4 with aqueous HCl solution. The precipitate was filtered off, washed with water, and dried. The yield was 0.417 g (98%). Recrystallization from methanol gave white powder, mp 267−269 °C. IR (KBr, cm^{-1}): ν 3300 (NH), 1690 (COOH), 1630 (C=O, amide). ^{1}H NMR (δ, ppm, DMSO-d_6): 9.21 (s, 1H, OH), 8.77 (t, 1H, NH). Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.56; H, 5.31; N, 4.86.

Poly(amide−ester) 3b. To thionyl chloride (0.16 mL, 2.2 mmol) cooled with an ice−water bath was slowly added pyridine (0.62 mL, 8.0 mmol) for 10 min to keep the reaction temperature low. After stirring for 30 min, the solution of **6** (0.285 g, 1.0 mmol) in NMP (1 mL) was added slowly for 10−20 min to control the reaction temperature, and then the cooling bath was removed. The reaction mixture was stirred at room temperature for 20 min and at 80 °C for 15 h in air. The resulting viscous solution was diluted with NMP and poured into methanol to precipitate the polymer, yield 0.267 g (100%). The inherent viscosity of the polymer in NMP was 0.51 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (KBr, cm^{-1}): ν 3285 (NH), 1735 (C=O, ester), 1635 (C=O, amide).^{13}C NMR (ppm, DMSO-d_6): 165.76 (C=O, amide), 164.80 (C=O, ester). Anal. Calcd for $(C_{16}H_{13}NO_3\cdot1.4H_2O)_n$: C, 65.70; H, 5.41; N, 4.79. Found: C, 65.85; H, 5.58; N, 4.67.

Poly(amide−ester) (3c) from 1 and 2 by One-Pot Polymerization. Compound **2** (0.274 g, 2.0 mmol) and TEA (0.28 mL, 2.0 mmol) were dissolved in NMP (4 mL) at −20 °C. To this solution was added **1** (0.426 g, 2.1 mmol) slowly for 30 min, and then TEA (0.42 mL, 3.0 mmol) was added to the solution. The mixture was stirred for 1 h at −20 °C and then for 5 h at room temperature in air. The resulting polymer was isolated as described above, yield 0.528 g (99%). The inherent viscosity of the polymer in NMP was 0.27 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (KBr, cm^{-1}): ν 3320 (NH), 1735 (C=O, ester), 1650 (C=O, amide). ^{13}C NMR (ppm, DMSO-d_6): 166.13 (C=O, amide), 164.06 (C=O, ester). Anal. Calcd for $(C_{32}H_{26}N_2O_6\cdot0.6H_2O)_n$: C, 70.74; H, 4.88; N, 5.13. Found: C, 70.58; H, 5.05; N, 5.11.

Random Poly(amide−ester) (3d). Compound **1** (0.426 g, 2.1 mmol) was added in one portion to a solution of **2** (0.274 g, 2.0 mmol) and TEA (0.70 mL, 5.0 mmol) in NMP (4 mL) at room temperature in air. After stirring for 6 h, the polymer was isolated as described above, yield 0.536 g (100%). The inherent viscosity of the polymer in NMP was 0.37 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (KBr, cm^{-1}): ν 3310 (NH), 1735 (C=O, ester), 1645 (C=O, amide). ^{13}C NMR (ppm, DMSO-d_6): 166.13, 165.76, 164.80, 164.06. Anal. Calcd for $(C_{32}H_{26}N_2O_6\cdot0.6H_2O)_n$: C, 70.74; H, 4.88; N, 5.13. Found: C, 70.88; H, 5.04; N, 5.13.

Model Compounds. The following model compounds were prepared from the corresponding acyl chloride and amine or phenol.

***N,N′*-Di(2-phenylethyl)isophthalamide (7).** Compound **7** was prepared from phenethylamine and **1** in the presence of TEA in THF. The yield was 93%, mp 172−174 °C (from ethanol). ^{13}C NMR (ppm, DMSO-d_6): 166.17 (C=O). Anal. Calcd for $C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.49; N, 7.52. Found: C, 77.36; H, 6.61; N, 7.52.

***N,N′*-Di(4-methylphenyl)isophalate (8).** Compound **8** was prepared from *p*-cresol and **1** in the presence of TEA in THF. The yield was 88%, mp 169−171 °C (from ethanol). ^{13}C NMR (ppm, $CDCl_3$): 165.07 (C=O). Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.47; H, 5.28.

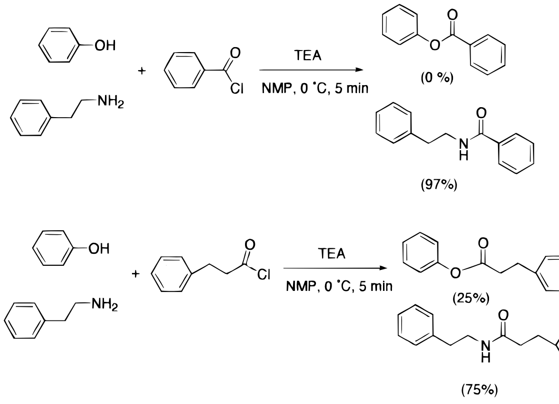
4-Methylphenyl *N*-(2-Phenylethyl)-3-carbamoylbenzoate (9). Compound **9** was prepared from phenethylamine with (4-methylphenyl) hydrogen isophthalate, which was obtained from the equimolar reaction of *p*-cresol with **1**. The yield was 88%, mp 118−121 °C (from ethanol). ^{13}C NMR (ppm, DMSO-d_6): 165.69, 164.83 (C=O). Anal. Calcd for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.89; N, 3.90. Found: C, 76.74; H, 5.99; N, 3.94.

Measurements. The infrared spectra were recorded on a Hitachi I-5020-FT-IR spectrophotometer and the NMR spectra on a JEOL EX270 (270 MHz) spectrometer. Viscosity measurements were carried out at a concentration of 0.5 g/dL in NMP at 30 °C by using an Ostwald viscometer. Gel permeation chromatography (GPC) analyses were carried out by Tosoh HLC-8120 system (LiBr (1 g/ L) in DMF as eluant) on the basis of standard polystyrene samples. The measurement of solubility was conducted at about 0.1 g of polymer in l mL of solvent. The thermal analyses were performed on a Seiko SSC 5200 TG/DTA 220 thermal analyzer at a heating rate of 10 °C min^{-1} and a SSC 5200 DSC 220 at a heating rate of 20 °C min^{-1}. X-ray diffraction studies of the polymers were performed by the powder method using nickel-filtered Cu Kα radiation.

Results and Discussion

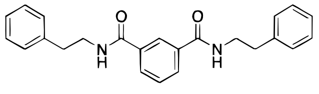
Suter et al. reported a series of theories on the structural regularity of condensation polymers obtained from nonsymmetric monomers.[6] The following conclusion was deduced for the synthesis of head-to-head or tail-to-tail (H−H or T−T) polymers from the symmetric (YccY) and nonsymmetric (XabX) monomers. A sufficient difference in the reactivity of functional groups in a nonsymmetric monomer is necessary to produce condensation polymers with an ordered structure; that is, the ratio of rate constants for the reaction of functional groups of nonsymmetric monomer XabX to symmetric monomer YccY, r = kbx/kax, should be small. Furthermore, the feed speed of a symmetric monomer to the nonsymmetric monomer in polymerization is another important factor to achieve ordered polymers.

Before the synthesis of the ordered polymer, the following model compound work was performed to determine whether the model compounds were formed in quantitative yields to constitute an ordered polymer forming reaction. The competitive reaction between acyl chlorides with phenethylamine and phenol in the presence of TEA was carried out in NMP at 0 °C for 5 min (eq 1). The selective acylation of phenethylamine with benzoyl chloride was observed, and the desired product, *N*-phenethylbenzamide, was obtained in quantitative yield. On the other hand, more reactive aliphatic acyl chloride toward nucleophiles, 3-phenylpropionyl chloride, produced the mixture of ester and amide in the mole ratio of 0.25/0.75.



(1)

On the basis of this model reaction and the availability of reagents, we decided to use isophthaloyl chloride **(1)** and 4-(2-aminoethyl)phenol **(2)** as the symmetric and nonsymmetric monomer, respectively. The model compounds **(7**, **8**, **9)** depicted in eq 2 were prepared in order to clarify the structure of polymers obtained.



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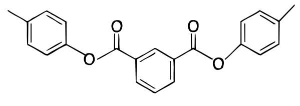

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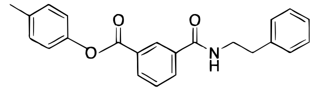

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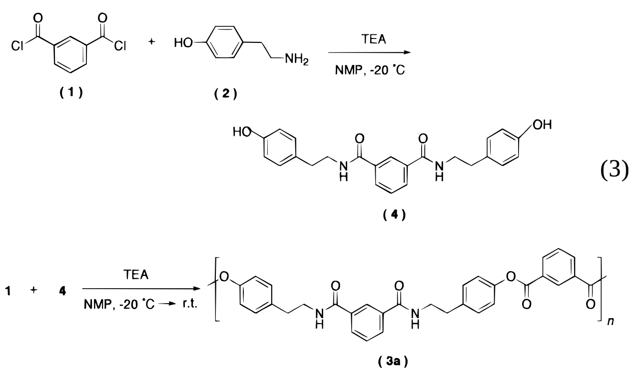
Polymer Synthesis. Synthesis of Authentic H−H or T−T Poly(amide−ester) 3a. The authentic poly(amide−ester)s, such as H−H or T−T and H−T polymers, were synthesized for characterization of the structure of ordered poly(amide−ester) by one-pot polycondensation. The H−H or T−T poly(amide−ester) **(3a)** was prepared by condensation of isophthaloyl chloride **(1)** with *N*,*N*′-bis(4-hydroxyphenethyl)isophthaldiamide **(4)**, which was prepared from **1** and **2** (eq 3). The polycondensation proceeded smoothly, giving polymer **3a** with an inherent viscosity of 0.32 dL/g.



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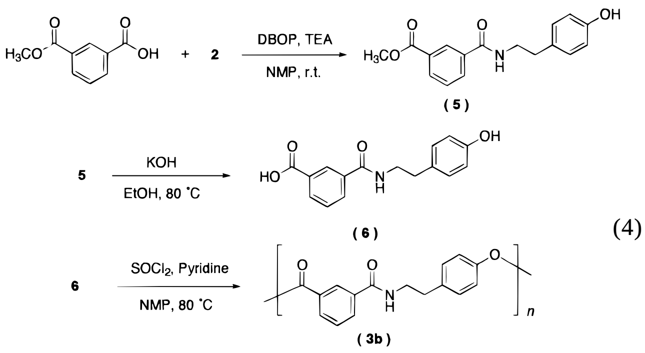
Synthesis of Authentic H−T Poly(amide−ester) 3b. The authentic H−T poly(amide−ester) **(3b)** was prepared as shown in eq 4. The condensation of methyl hydrogen isophthalate with **2** in the presence of DBOP as a condensing agent gave 3-methoxycarbonyl-*N*-(4-hydroxyphenethyl)benzamide **(5)**, which was treated with an alkaline solution to afford 3-carboxy-*N*-(4-hydroxyphenethyl)benzamide **(6)**. The direct self-polycondensation of monomer **6** was carried out with thionyl chloride/pyridine in NMP at 80 °C[7] and produced H−T poly(amide−ester) **3b** in quantitative yield with an inherent viscosity of 0.51 dL/g.



(4)

Synthesis of Poly(amide−ester) 3c. As briefly described in the Introduction, to obtain the H−H or T−T polymer, YccY should be added slowly to XabX, that is, if YccY is added slowly to XabX so that there will never be any unreacted −cY groups. After half of the YccY is added, the only XbaccabX will be produced. Upon addtion of the rest of YccY, only −bccb− structures will be formed. Accordingly, the resulting polymer will contain −acca− and −bccb− arrangements only; thus, H−H or T−T polymer is formed. Polycondensation of **1** and **2** was carried out in the presence of TEA at −20 °C to room temperature by slow addition of **1** to **2**, giving poly(amide−ester) **3c** with an inherent viscosity of 0.27 dL/g.

$$\mathbf{1} + \mathbf{2} \xrightarrow[\text{NMP, -20 °C} \rightarrow \text{r.t.}]{\text{TEA}} \textbf{Polymer 3c} \qquad (5)$$

Synthesis of Random Poly(amide−ester) 3d. If XabX monomer is mixed all at once with YccY monomer, where we have arbitrarily chosen the −aX monomer to be the faster reacting group ($r \ll 1$),[6] only a random polymer can be obtained. Thus, the random poly(amide−ester) **3d** was prepared from **1** and **2** by mixing both monomers all at once (eq 6), with an inherent viscosity of 0.37 dL/g.

$$\mathbf{1} + \mathbf{2} \xrightarrow[\text{NMP, 0°C} \rightarrow \text{r.t.}]{\text{TEA}} \textbf{Polymer 3d} \qquad (6)$$

Polymer Characterization. The IR spectra of all polymers prepared showed characteristic NH, amide, and ester carbonyl bands in the range 3280−3320, 1630−1650, and 1735 cm^{-1}, respectively. Elemental analyses also supported the formation of the expected polymers.

The microstructure of the polymers was determined by ^{1}H and ^{13}C NMR, taken in DMSO-d_6 using TMS as

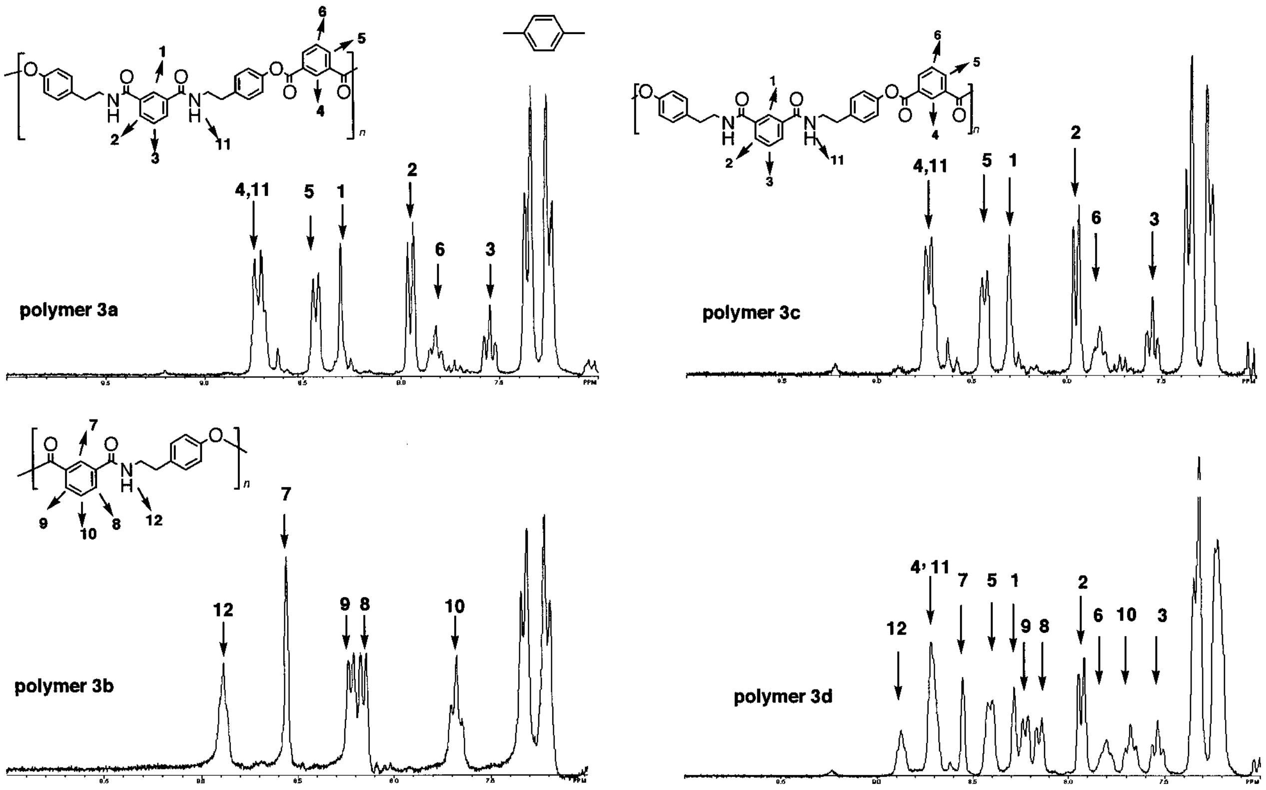
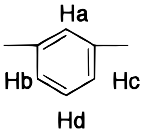


Figure 1. ^{1}H NMR spectra of polymers **3a**, **3b**, **3c**, and **3d** in DMSO-d_6 measured at room temperature (see Chart 1).

internal reference. According to the chemical shifts of model compounds, the signals of proton nuclei on the benzene ring derived from isophthaloyl chloride provide sensitive probes for the substitution patterns in the polymer backbone.



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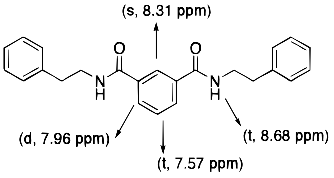
Meta-disubstituted aromatic ring with amide or ester bonds can be expected to exhibit three signals: a singlet (Ha), a doublet (Hb and Hc), and a triplet (Hd) (eq 7).[8] Furthermore, corresponding peaks for aromatic protons substituted by ester groups will be observed downfield from those for aromatic protons substituted by amide groups, based on the chemical shifts of model compounds **7**, **8**, and **9** (eq 8). Thus, six signals (two pairs of Ha, Hb, and Hd) will be observed for the H−H or T−T ordered polymer, and the H−T ordered polymer will exhibit four signals due to the Ha, Hb, Hc, and Hd protons.



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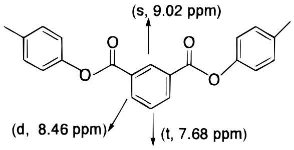

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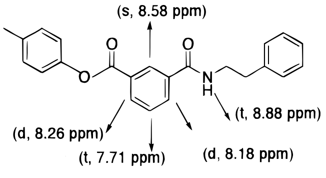

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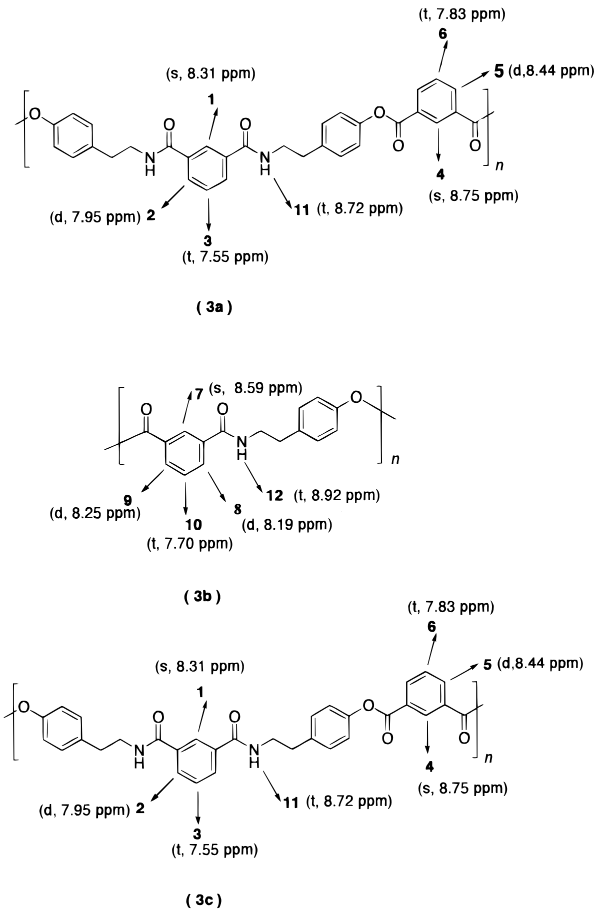
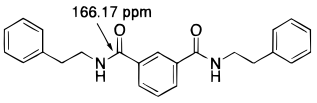
The expanded ^{1}H NMR spectra in the aromatic proton region and assignment of polymers were presented in Figure 1. The six signals of aromatic protons for the authentic polymer **3a** appeared at 7.55 ppm (1H, t), 7.83 ppm (1H, t), 7.95 ppm (2H, d), 8.31 ppm (1H, s), 8.44 ppm (2H, d), and 8.75 ppm ppm (1H, s). These peaks are assigned, as shown in the inset of Figure 1. On the other hand, the H−T ordered polymer **3b** showed four signals at 7.70 ppm (1H, t), 8.19 ppm (1H, d), 8.25 ppm (1H, d), and 8.59 ppm (1H, s). For the random polymer **3d**, the 10 signals would be expected from its random structure. In fact, the 10 signals for polymer **3d** appeared. Furthermore, the spectrum of polymer **3a** was identical to that of polymer **3c** prepared by polycondensation. The other spectral evidence was provided by the signals of amide protons. The resonances for polymer **3b** and **3a** appeared at 8.92 and 8.72 ppm, which overlapped with one of the signal of aromatic protons. These amide protons were assigned with weakening of the above peaks in the presence of D_2O.

The most conclusive spectral evidence for the microstuctures of polymers was provided by ^{13}C NMR spectroscopy. The ^{13}C NMR chemical shifts of amide or

Chart 1



ester carbonyl carbons for model compounds were as follows:



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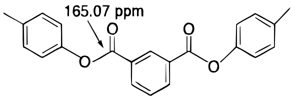

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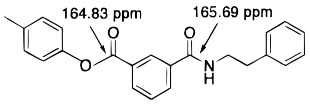

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The expanded ^{13}C NMR spectra in the carbonyl region of polymers are presented in Figure 2. The signals of carbon nuclei in amide and ester carbonyl groups for polymer **3a** appeared at 166.13 and 164.06 ppm. On the other hand, they were observed at 165.76 and 164.80 ppm for polymer **3b**. In contrast, the four peaks of carbon nuclei for polymer **3d** appeared as expected from its random structure. Moreover, the spectrum of polymer **3c** was identical to that of authentic H−H or T−T ordered polymer **3a**, and no peaks derived from the H−T unit were found. These findings indicate that the polycondensation of **1** and **2** can produce the desired H−H or T−T ordered poly(amide−ester).

Chart 2

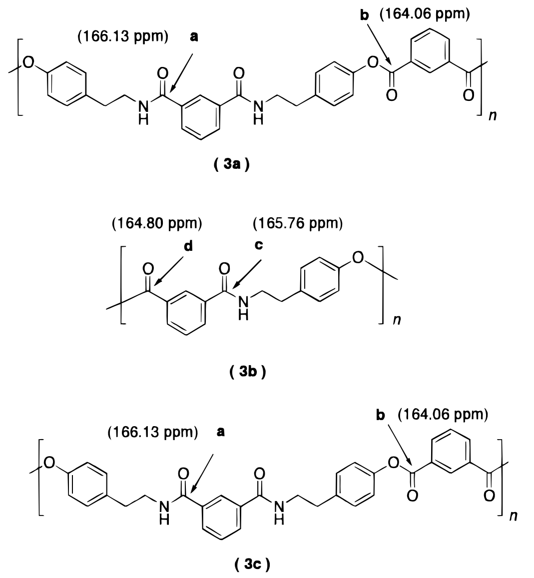

Table 1. Molecular Weight Analyses of Obtained Poly(amide−ester)s

polymer	$[\eta]^a$ (dL/g)	$M_w{}^b \times 10^{-4}$	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$
H−H or T−T polymer **3a**	0.32	1.90	1.07	1.77
H−T polymer **3b**	0.51	6.18	2.10	2.94
one-pot polymer **3c**	0.27	1.09	0.70	1.55
random polymer **3d**	0.37	3.27	1.44	2.27

[a] Measured at a concentration of 0.5 g/dL at 30 °C, NMP. [b] Estimated by GPC (DMF with LiBr (1 g/L), Pst. standard).

The polymers obtained were white powders. All of the polymers were readily soluble in sulfuric acid, dipolar aprotic solvents, such as NMP, DMF, *m*-cresol, and DMSO, and completely insoluble in methanol, THF and H_2O. The solubility difference between ordered polymers **3a**, **3b**, and **3c** and random polymer **3d** was observed toward pyridine. The latter polymer was soluble at room temperature, but the former polymers were partially soluble even on heating, owing to their higher regularity.

The molecular weight of the polymers was estimated (relative to polystyrene standard) by GPC in DMF containing LiBr, which is summarized in Table 1. The chromatograms of polymers were unimodel distribution and indicated that M_n and M_w values were 7000−21 000 and 10 900−61 800, respectively. The ratios of M_w/M_n were around 2−3.

Thermal Properties of Polymers 3a, 3b, and 3d. The thermal properties of polymers were examined by thermogravimetry (TG) and differencential scanning calorimetry (DSC). These results are summarized in Table 2. The polymers exhibited comparatively high thermal stability. The rapid weight loss of all polymers started at approximately 400 °C. The thermal degradation behaviors were almost same despite the different chain regularities.

The DSC traces of the first-heating process for the polymers are illustrated in Figure 3. Endothermic peaks were clearly observed at 279 and 287 °C in the DSC traces of polymer **3a** and **3b**, respectively. Thus, they were expected to be semicrystalline polymers. On the other hand, the DSC trace of polymer **3d** showed only a baseline shift at 150 °C corresponding to glass transition temperature (T_g); there is no endothermic peak. Polymer **3d** is considered to be amorphous due to the random sequence.

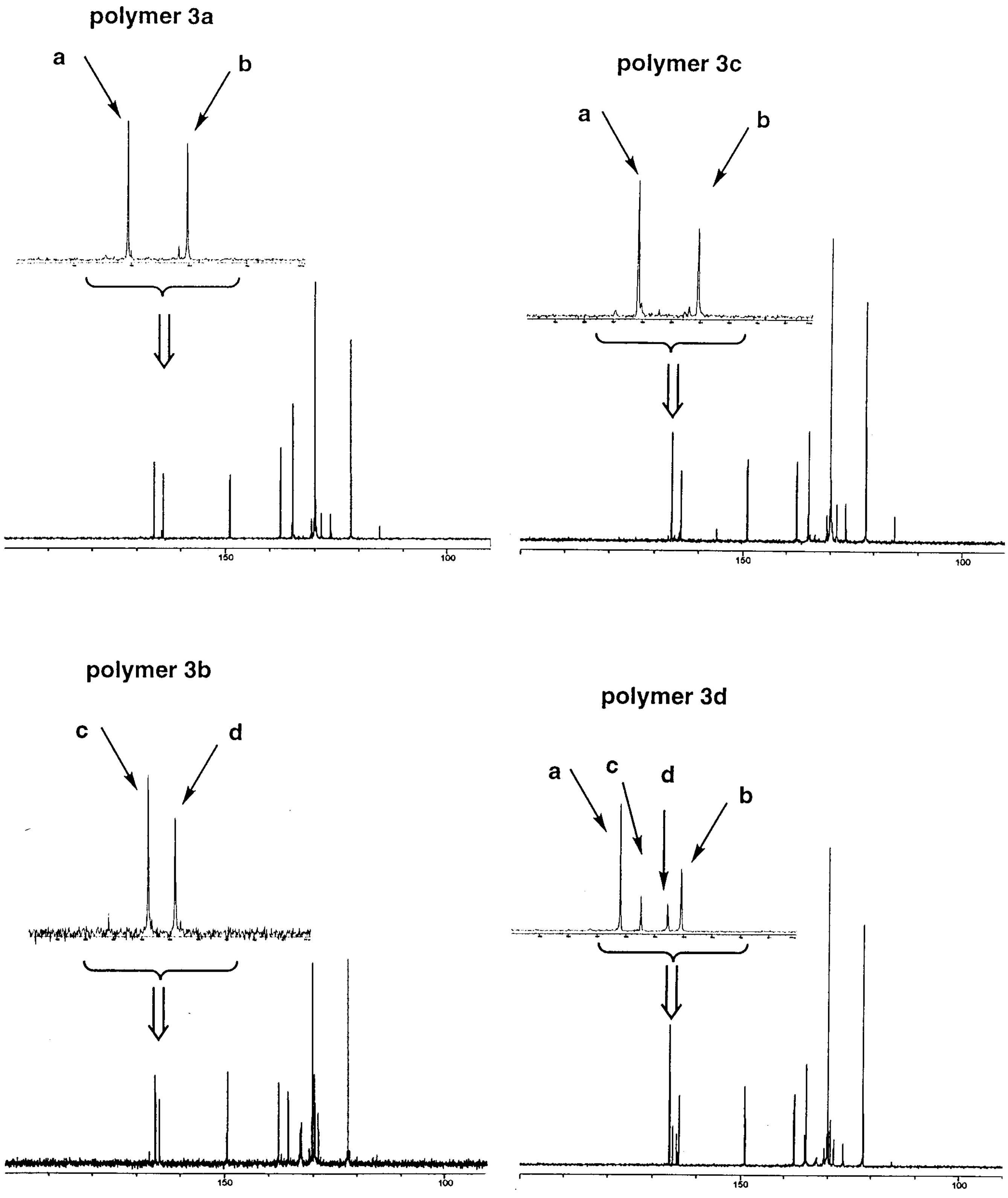

Figure 2. ^{13}C NMR spectra of polymers **3a**, **3b**, **3c**, and **3d** in DMSO-d_6 measured at room temperature (see Chart 2).

As shown in Figure 4, no endothermic peak was observed in the second-heating DSC traces of polymer **3a** and **3b**, indicating only typical glass transition profiles. The T_g's were 147 and 152 °C, which is close to that of polymer **3d**. Once the as-synthesized polymers were melt, no crystalline could be formed on the cooling process. The chain mobility seemed to be restricted by hydrogen bonds between the intermolecular or intramolecular amide bonds. The hydrogen bonds occurring in the process of cooling from the melt would restrict the chain movement and hinder the formation of regular chain conformations.

Fine Structures of Polymers. The WAXD intensity curves of the as-synthesized polymers **3a** and **3b** represented several reflections indicating semicrystalline nature, as shown in Figure 5. The findings support that the endothermic peaks in the DSC curves of polymer **3a** and **3b** correspond to T_m. Thus, the polymer

Table 2. Thermal Analyses of Poly(amide−ester)s

polymer	T_m (°C)[a] 1st heating	ΔH (mJ/mg)	T_g (°C)[a] 2nd heating	T_{10} (°C)[b] in N_2	T_{10} (°C)[b] in air
H−H or T−T polymer **3a**	279	31.9	147	408	408
H−T polymer **3b**	287	16.9	152	406	402
one-pot polymer **3c**	279	32.1	147	406	405
random polymer **3d**	no		152	404	404

[a] Obtained by DSC under nitrogen atomosphere with heating rate of 20 °C min^{-1}. [b] The 10% weight loss temperature by TGA measurement with heating rate of 10 °C min^{-1}.

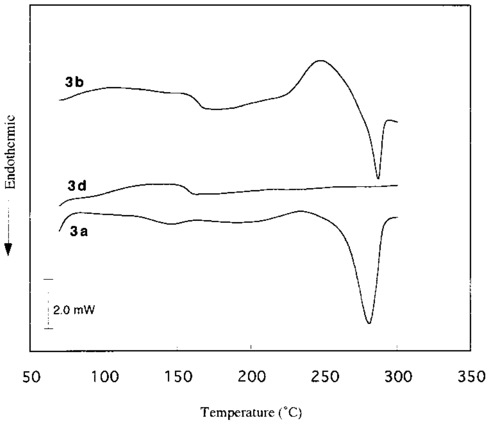

Figure 3. DSC traces of the first-heating process for polymers **3a**, **3b**, and **3d**.

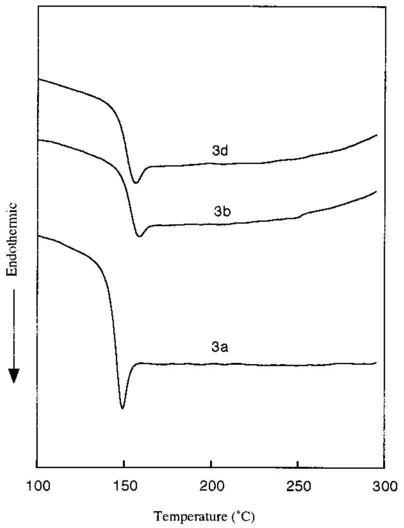

Figure 4. DSC traces of the second-heating process for polymers **3a**, **3b**, and **3d**.

chains were aggregated and the crystallites were formed during the polymerization processes. The WAXD profiles of polymers **3a** and **3b** are quite different from each other. It suggests the different chain packing modes in the crystal unit cells, that is, the head−tail and head−head sequences, require different chain conformations and structures. Thus, it is possible to alter the physical properties of the polymers using same monomers. Polymer **3d**, on the other hand, showed an amorphous profile due to the random chain sequence.

When the as-synthesized polymers **3a** and **3b** were annealed for 2 h at 250 °C close to the melting temperatures, the endothermic peaks became larger as shown in Figure 6, and the values of the enthalpy change (ΔH) at melting points increased. WAXD profiles of the annealed polymers **3a** and **3b** are illustrated in Figures 7 and 8. The reflections became sharp, and the intensity of the reflections remarkably increased. The degrees of crystallinity of polymers **3a** and **3b**, as shown in Table 3, estimated using the X-ray method were increased by the annealing treatment. The results agree with those of DSC. These findings suggest that the partical melt

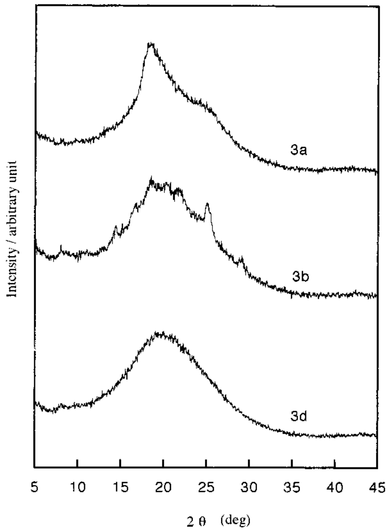

Figure 5. WAXD intensity curves of the as-synthesized samples for polymers **3a**, **3b**, and **3d**.

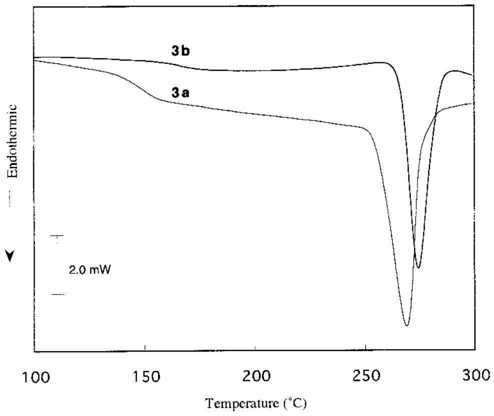

Figure 6. DSC traces of polymers **3a** and **3b** annealed at 250 °C for 2 h.

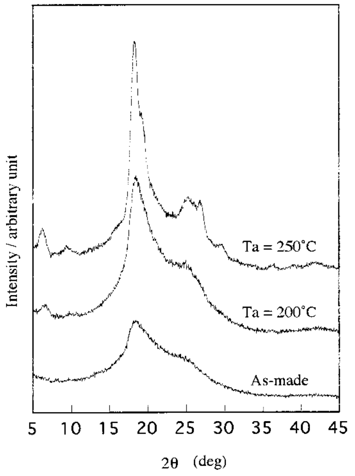

Figure 7. WAXD intensity curves of Head−head polymer **3a**: as-synthesized sample and samples annealed at 200 °C and 250 °C for 2 h.

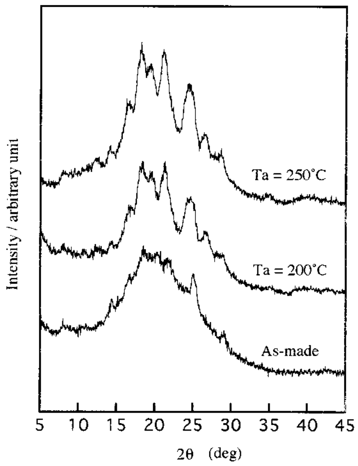

Figure 8. WAXD intensity curves of Head–tail polymer **3b**: as-synthesized sample and samples annealed at 200 °C and 250 °C for 2 h.

Table 3. Degree of Crystallinity of Polymers 3a and 3b after Annealing Treatment

sample	degree of crystallinity (%)
3a, as-synthesized	32.4
3a, T_a = 200 °C	39.6
3a, T_a = 250 °C	47.2
3b, as-synthesized	19.4
3b, T_a = 200 °C	32.9
3b, T_a = 250 °C	40.4

and recrystallization occurred during annealing at the high temperature close to T_m.

Molecular models of polymers **3a** and **3b** were built with the Cerius^2 program, using standard bond distance and bond angles. Each molecule could be regularly hydrogen-bonded to its neighbors. Thus, the crystalline nature of these polymers came from suitable packing of the molecular chains due to the intermolecular hydrogen bonds. It might be hard to form regular hydrogen bonds among the extended chains composed of a random sequence.

Conclusions

In summary, we have demonstrated that the synthesis of ordered H–H or T–T poly(amide–ester) **3c** can be achieved by polycondensation of symmetric monomer **1** with nonsymmetric monomer **2**. The structure of polymer **3c** was characterized by comparison with the ^{1}H and ^{13}C NMR spectra of authentic polymer **3a**. Furthermore, the authentic H–T ordered and random poly(amide–ester)s were prepared to verify the structure of ordered polymers. Constitutional regularity of these polymers strongly influenced the physical properties of polymers, such as solubility, thermal property, and crystallinity.

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