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Synthesis of Ordered Polymer by Direct Polycondensation. 7. Ordered Poly(acylhydrazide−amide)

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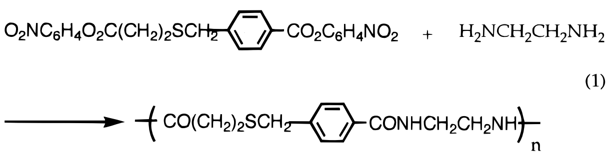
ABSTRACT: An ordered (−aadcbbcd−) poly(acylhydrazide−amide) was prepared by the direct polycondensation of a pair of symmetric monomers (XabX), 2,5-dimethylterephthalic acid (XaaX) and 4,4′-(oxydi-*p*-phenylene)dibutanoic acid (XbbX), with a nonsymmetric monomer (YcdY), 4-aminobenzhydrazide, using the condensing agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (**1**). The polymerization was carried out by mixing the dicarboxylic acids, condensing agent **1,** and triethylamine (TEA) in NMP for 2 h at room temperature, followed by adding 4-aminobenzhydrazide, yielding the ordered poly(acylhydrazide−amide) with an inherent viscosity of 0.40 dL/g. The authentic ordered polymer was prepared to verify the structure of the ordered polymer. The microstructures of polymers obtained were investigated by ^{13}C-NMR spectroscopy, and it was found that the polymer had the expected ordered structure. Furthermore, the model reactions were studied in detail to demonstrate the feasibility of polymer formation.

Introduction

As part of our research programs on the synthesis of condensation polymers by direct polycondensation using condensing agents, we have been interested in a synthesis of ordered polymer from nonsymmetric monomers by direct polycondensation. In previous papers, we reported a successful synthesis of ordered polyamides (head-to-head or tail-to-tail) from a symmetric monomer and a nonsymmetric monomer,[1,2] and ordered polyamides (head-to-tail) from a symmetric monomer and a nonsymmetric monomer or a pair of two symmetric monomers.[3]

Recently, we succeeded in synthesizing an ordered (−aadcbbcd−) poly(acylhydrazide−amide) by the direct polycondensation of a pair of two symmetric monomers with a nonsymmetric monomer, where a carboxylic acid and a carboxylic acid derivative were used as a nonsymmetric monomer,[4] because the selective amidation of carboxylic acids would be difficult using condensing agent **1**, due to the small difference of pK_a values between carboxylic acids. However, head-to head and tail-to-tail polyamides have been prepared by the slow addition of a symmetric monomer, ethylenediamine, to a nonsymmetric monomer, aliphatic and aromatic bis(*p*-nitrophenyl) ester (eq 1).[5]



(1)

This result prompted us to investigate the synthesis of ordered polymers from two dicarboxylic acids and a nonsymmetric monomer. We found that the selective amidation was possible by using the active amides derived from carboxylic acids and condensing agent **1**.

We now report a successful synthesis of ordered (−aadcbbcd−) poly(acylhydrazide−amide) by the direct polycondensation of a pair of symmetric monomers (XabX), 2,5-dimethylterephthalic acid (XaaX) and 4,4′-(oxydi-*p*-phenylene)dibutanoic acid (XbbX), with a nonsymmetric monomer (YcdY), 4-aminobenzhydrazide, using the condensing agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (**1**). Here −aa− and −cd− represent the symmetric and nonsymmetric monomeric units in the chain, respectively, and X the leaving group in the polymerization reaction. XaaX represents a homobifunctional symmetric monomer and YcdY a similar but nonsymmetric monomer. Y is again a leaving group.

Experimental Section

Materials. *N*,*N*-Dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) were stirred over powdered calcium hydride overnight, distilled under reduced pressure, and then stored over 4A molecular sieves. 4-Aminobenzhydrazide (**12**) was prepared from methyl 4-aminobenzoate and hydrazine monohydrate according to the reported procedure.[6] 3-Benzoylbenzoxazoline-2-thione (**5b**) was prepared by the reaction of benzoyl chloride and 2-mercaptobenzoxazole (**4**). 2,5-Dimethylterephthalic acid (**10**) was purified by recrystallization. Triethylamine (TEA) and tetrahydrofuran (THF) were purified by the 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 (**1**) was prepared according to the reported procedure.[8]

3-Lauroylbenzoxazoline-2-thione (**5a**) and 3-(*o*-toluoyl)benzoxazoline-2-thione (**5c**) were prepared from the corresponding acid chlorides and **4** in the presence of TEA in THF.

5a: Recrystallization from ethanol gave white needles: yield 83%; mp 73−74 °C; IR (KBr) ν 1720 cm^{-1} (C=O); ^{13}C-NMR (CDCl$_3$) 178.7 (C=S), 174.2 ppm (C=O). Anal. Calcd for $C_{19}H_{27}NO_2S$: C, 68.43; H, 8.16; N, 4.20. Found: C, 68.58; H, 8.13; N, 4.16.

5c: Recrystallization from *n*-hexane gave yellow needles: yield 87%; mp 88−91 °C; IR (KBr) ν 1700 cm^{-1} (C=O); ^{13}C-NMR (CDCl$_3$) 178.6 (C=S), 168.9 ppm (C=O). Anal. Calcd for $C_{15}H_{11}NO_2S$: C, 66.90; H, 4.12; N, 5.20. Found: C, 67.12; H, 4.19; N, 5.35.

4,4′-(Oxydi-*p*-phenylene)dibutanoic Acid (11). 4,4′-Oxybis(3-benzoylpropionic acid) was synthesized by the method of Higgins et al.[7] in 82% yield by the reaction between diphenyl ether and succinic anhydride in nitrobenzene using aluminum chloride.

To a solution of potassium hydroxide (6.73 g, 0.1 mol) in diethylene glycol (22 mL) were added 4,4′-oxybis(3-benzoylpropionic acid) (7.41 g, 20 mmol) and 85% hydrazine hydrate

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(5 mL). The mixture was heated for 1 h under reflux, and then water and excess hydrazine were removed at 150 °C. After stirring at 195 °C for 5 h, the mixture was cooled and acidified with dilute hydrochloric acid. The precipitate was crystallized from ethanol to give faint yellow crystals: yield 3.58 g (52%); mp 168−170 °C; IR(KBr) ν 1700 cm^{-1} (C=O); ^{13}C-NMR (DMSO-d_6) 174.2 ppm (C=O). Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.40; H, 6.50.

Model Compounds. 4,4′-(Oxydi-*p*-phenylene)bis(*N*′-benzoylbutanohydrazide). Condensing agent **1** was added to a solution of **11** (0.171 g, 0.5 mmol) and benzhydrazide **(8)** (0.136 g, 1.0 mmol) in NMP (2 mL) at room temperature. The solution was stirred for 3 h and poured into 10% aqueous sodium hydrogen carbonate. The precipitate was filtered out, washed with water, and dried. Recrystallization from acetic acid−water afforded white crystals: yield 0.272 g (94%); mp 165−168 °C; IR (KBr): ν 1650 cm^{-1} (C=O); ^{13}C-NMR (DMSO-d_6) 165.5, 171.4 ppm (C=O). Anal. Calcd for $C_{34}H_{34}N_4O_5$; C, 70.57; H, 5.92; N, 9.68. Found: C, 70.53; H, 5.99; N, 9.47.

4,4′-(Oxydi-*p*-phenylene)bis(*N*′-benzoylbutanoanilide). This compound was prepared from **11** and aniline **(6)** as described above. The yield was 90%. Recrystallization from toluene gave white needles: mp 145−147 °C; IR (KBr) ν 1670 cm^{-1} (C=O); ^{13}C-NMR (CDCl$_3$) 171.5 ppm (C=O). Anal. Calcd for $C_{32}H_{32}N_2O_3$: C, 78.02; H, 6.55; N, 5.69. Found: C, 78.13; H, 6.72; N, 5.48.

***N*′-Benzoyl-*o*-toluohydrazide.** Recrystallization from benzene yielded white needles: mp 173−174 °C: IR (KBr) ν 1700, 1640 cm^{-1} (C=O); ^{13}C-NMR (CDCl$_3$) 165.6, 168.5 ppm (C=O). Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.51; H, 5.53; N, 10.76.

Competitive Reaction of 8 and 6 with 5a. Compounds **8** (0.136 g, 1.0 mmol) and **6** (0.091 mL, 1.0 mmol) were added to a solution of **5a** (0.334 g, 1.0 mmol) and TEA (0.14 mL, 1.0 mmol) in THF at room temperature. The solution was stirred for 1 h and was poured into 1 M aqueous sodium hydroxide. The precipitate was filtered, washed with water, and dried. The product was identified as *N*′-benzoyllaurohydrazide (**9**). The yield was 0.315 g (99%). Recrystallization from *n*-hexane gave white needles: mp 105−107 °C; IR (KBr) ν 1670 cm^{-1} (C=O); ^{13}C-NMR (CDCl$_3$) 165.2, 172.1 ppm (C=O). Anal. Calcd for $C_{32}H_{32}N_2O_3$: C, 71.66; H, 9.50; N, 8.80. Found: C, 71.65; H, 9.48; N, 8.70.

Competitive Reaction between 5a and 5c with 8. Compound **8** (0.136 g, 1.0 mmol) was added to a solution of **5c** (0.269 g, 1.0 mmol), **5a** (0.334 g, 1.0 mmol), and TEA (0.28 mL, 2.0 mmol) in NMP (10 mL) at room temperature. The solution was stirred for 1 h and was poured into 1 M aqueous sodium hydroxide. The precipitate was filtered, washed with water, and dried. The product was **9**. The yield was 0.312 g (99%).

Authentic Ordered Poly(acylhydrazide−amide) (15). 4,4′-(Oxydi-*p*-phenylene)bis(*N*′-(4-aminobenzoyl)butanohydrazide] (13). Condensing agent **1** (0.843 g, 2.2 mmol) was added to a solution of **11** (0.342 g, 1.0 mmol), **12** (0.302 g, 2.0 mmol), and TEA (0.28 mL, 2.0 mmol) in NMP (4 mL) at room temperature. The solution was stirred for 2 h and poured into 10% aqueous sodium carbonate. The precipitate was filtered out, dried, and refluxed in acetone. The insoluble material was 0.553 g (91%): mp 179−181 °C; IR (KBr) ν 1685 cm^{-1} (C=O); ^{1}H-NMR (DMSO-d_6) 9.7, 9.8 ppm (s, 2H, NHNH); ^{13}C-NMR (DMSO-d_6) 166.0, 171.9 ppm (C=O). Anal. Calcd for $C_{34}H_{36}N_6O_5$: C, 67.09; H, 5.96; N, 13.81. Found: C, 66.70; H, 5.95; N, 13.26.

Compound **13** (0.304 g, 0.5 mmol) was dissolved in NMP (2.0 mL) at room temperature. The solution was cooled in a dry ice−acetone bath, to which was added 2,5-dimethylterephthaloyl chloride (0.116 g, 0.5 mmol) in one portion, and the cooling bath was changed to ice water. The mixture was stirred for 30 min at 0 °C and then for 3 h at room temperature. The resulting polymer solution was diluted with NMP (2 mL) and precipitated by pouring the solution into methanol. After through washing with methanol and drying, the polymer weighed 0.388 g (100%). The inherent viscosity of polymer in NMP was 0.62 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (KBr) ν 3270 (N−H), 1660 cm^{-1} (C=O); ^{13}C-NMR (DMSO-d_6) 167.1 (C=O, amide), 164.8, 170.9 ppm (C=O, acylhydrazide). Anal. Calcd for $(C_{44}H_{42}N_6O_7\cdot 0.8\ H_2O)_n$: C, 67.60; H, 5.42 N, 10.75. Found: C, 67.71; H, 5.57; N, 10.29.

Poly(acylhydrazide−amide) (16) Prepared by Direct Polycondensation. Condensing agent **1** (0.843 g, 2.2 mmol) was added to a solution of dimethylterephthalic acid (**10**) (0.0971 g, 0.5 mmol), 4,4′-(oxydi-*p*-phenylene)dibutanoic acid (**11**) (0.171 g, 0.5 mmol), and TEA (0.28 mL, 2.0 mmol) in NMP−HMPA (3:1) (2 mL). The solution was stirred at room temperature for 2 h. To the resulting solution was added **12** (0.151 g, 1.0 mmol). Then the solution was stirred at room temperature for 24 h and 80 °C for 12 h and poured into methanol. After thorough washing with water and drying, the polymer weighed 0.364 g (95%). The inherent viscosity of polymer in NMP was 0.40 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (KBr) ν 3270 (N−H), 1660 cm^{-1} (C=O); ^{13}C-NMR (DMSO-d_6) 167.1 (C=O, amide), 164.8, 170.9 ppm (C=O, acylhydrazide). Anal. Calcd for $(C_{44}H_{42}N_6O_7\cdot 1.2\ H_2O)_n$: C, 66.96; H, 5.36; N, 10.65. Found: C, 66.96; H, 5.56; N, 10.61.

Random Poly(acylhydrazide−amide) (18). To a solution of **10** (0.0971 g, 0.5 mmol), **11** (0.171 g, 0.5 mmol), **12** (0.151 g, 1.0 mmol), and TEA (0.28 mL, 2.0 mmol) in NMP (2 mL) was added condensing agent **1** (0.843 g, 2.2 mmol). The mixture was stirred at 80 °C for 10 h. The resulting solution was diluted with NMP (2 mL) and poured into methanol (100 mL). The polymer was collected and dried in vacuo at 80 °C. The yield was 0.340 g (89 %). The inherent viscosity of the polymer in NMP was 0.48 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (KBr) ν 3260 (N−H), 1660 cm^{-1} (C=O); ^{13}C-NMR (DMSO-d_6) 167.2, 167.4, 164.9, 165.0, 170.8, 170.9 ppm (C=O, amide and acylhydrazide). Anal. Calcd for $(C_{44}H_{42}N_6O_7\cdot H_2O)_n$: C, 67.33; H, 5.39; N, 10.71. Found: C, 67.28; H, 5.50; N, 10.64.

Kinetic Measurement. Equimolar amounts of the active amide **5** and **6** were reacted in the presence of TEA in NMP at 25 °C for a specified time. Rates of the aminolysis reaction were followed by measuring the weights of the isolated products. The overall second-order rate constants were calculated from the slopes of the reciprocal plots of $(a - x)$ versus time (t), where a and x are the initial concentration of benzoic acid and the concentration of product at any time.

Measurements. The infrared spectra were recorded on a Horiba FT-210 IR spectrophotometer, and the NMR spectra on a JEOL EX270 (270 MHz) spectrometer. Viscosity measurements were carried out with an Ostwald viscometer at 30 °C. Thermal analyses were performed on a Seiko SSS 5000 TG/DTA 220 thermal analyzer at a heating rate of 10 °C/min for thermogravimetric analysis.

Results and Discussion

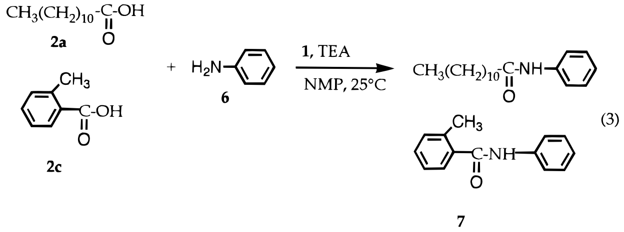
The elementary reactions and the relative reactivities of functional groups of two nonsymmetric monomers for the polymerization are shown as follows (eq 2):[9]

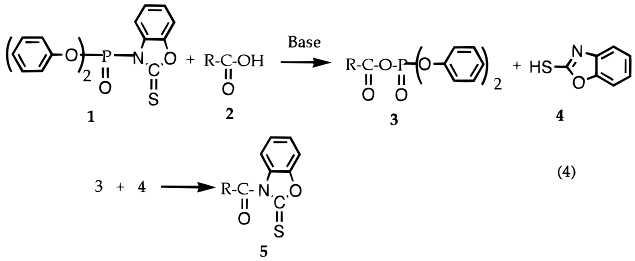
$$\begin{array}{llll}
\text{-aX} + \text{Yc-} \xrightarrow{k_{ac}} \text{-ac-} + \text{XY}, & r_1 = k_{ad}/k_{ac}, & 0 < r_1 < 1 & \\
\text{-aX} + \text{Yd-} \xrightarrow{k_{ad}} \text{-ad-} + \text{XY}, & r_2 = k_{bc}/k_{ac}, & 0 < r_2 < 1 & \qquad (2) \\
\text{-bX} + \text{Yc-} \xrightarrow{k_{bc}} \text{-bc-} + \text{XY}, & r3 = k_{bd}/k_{ac}, & 0 < r_3 < 1 & \\
\text{-bX} + \text{Yd-} \xrightarrow{k_{bd}} \text{-bd-} + \text{XY} & & &
\end{array}$$

The polymer with −bacd− order is obtained when the relative reactivity ratios of r_1 and r_2 are both smaller than unity (<0.01). In this case, the first intermediate is XbacdY, which will later polymerize stoichiometrically to the fully ordered (−bacd−) polymer.

The choice of nonsymmetric dicarboxylic acids and diamines is most important in the preparation of the ordered polyamides from two nonsymmetric monomers by direct polycondensation using condensing agent **1**.

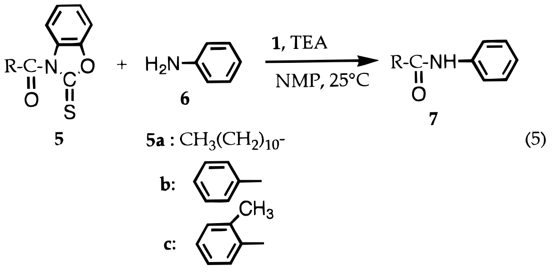
Selection of Nonsymmetric Dicarboxylic Acid. The reactivity difference between aromatic and aliphatic acid derivatives toward aniline was studied. In aromatic acid derivatives, the positive charge on the carbonyl carbon can be delocalized into the aromatic ring, while such delocalization is not possible in aliphatic acid derivatives. For this reason, aromatic acid derivatives are generally less reactive toward nucleophiles than aliphatic acid derivatives. Therefore, the competitive reaction of carboxylic acids **(2)** such as lauric acid **(2a)**, benzoic acid **(2b)**, and *o*-toluic acid **(2c)** with aniline **(6)** was carried out in NMP in the presence of **1** at 25 °C for 1 h. However, selective amidations were not observed in all cases. Even in the case of **2a** and **2c** with **6**, *N*-phenyllauramide and *N*-phenyl-*o*-toluamide were obtained in the mole ratio of 5:1. In these reactions, the active intermediates are mixed carboxylic-phosphoric anhydride [RCOO−PO(OAr)$_2$] **(3)**, which reacts rapidly with available nucleophiles such as amines and alcohols to give the condensing products (eqs 3 and 4).[10]





The reactivity difference of the active intermediates **3** with **6** was not enough to prepare the ordered polymer. If there are no such nucleophiles, the intermediate, mixed carboxylic−phosphoric anhydrides **3** react with the leaving group (**4**) of condensing agent **1** to yield the active amides (**5**).

The reactivity of active amides **5** toward nucleophiles is lower than that of mixed anhydrides **3**. Thus, a selective amidation was expected. Active amides **5**, 3-lauroylbenzoxazoline-2-thione (**5a**), 3-benzoylbenzoxazoline-2-thione (**5b**), and 3-(*o*-toluoyl)benzoxazoline-2-thione (**5c**) were prepared by the reaction of corresponding acid chlorides with **4** in the presence of TEA. The overall second order rate constants of **5** with **6** are summarized in Table 1 (eq 5).



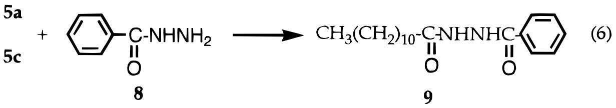
The rate constants changed almost 200 times when the active amide was varied from **5a** to **5c**.

Table 1. Overall Second-Order Rate Constants for the Reaction of 5 with 6[a]

active amide 5	rate constant (mol/L·min)
5a	5.73
5b	0.63
5c	0.025

[a] Reaction was carried out with 1 mmol of each reactant at 25 °C in NMP.

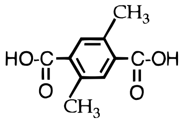
The competitive reaction between **5a** and **5c** with benzhydrazide **8** was carried out at room temperature for 1 h. Selective amidation was observed and *N*′-benzoyllaurohydrazide (**9**) was obtained in quantitative yield (eq 6).



Selection of Nonsymmetric Amines. There is a linear relationship with a slope of 1 between log *k* (second-order constant) and pK_a of aniline derivatives for the reaction of **2b** with various anilines in NMP in the presence of **1**.[11] Therefore, a similar relationship would be expected for the reaction of active amides **5** with amines. The competitive reaction between **5a** with **8** (pK_a = 7) and **6** (pK_a = 4) was carried out in NMP at room temperature for 1 h and gave compound **9** in quantitative yield (eq 7).

$$\mathbf{5a} + \begin{matrix}\mathbf{6}\\ \mathbf{8}\end{matrix} \longrightarrow \mathbf{9} \qquad (7)$$

On the basis of these model reactions and the availability of reagents, we decided to use a pair of dicarboxylic acids, 2,5-dimethylterephthalic acid (**10**) and 4,4′-(oxydi-*p*-phenylene)dibutanoic acid (**11**), as a nonsymmetric monomer (XabX) and 4-aminobenzhydrazide (**12**) as a nonsymmetric monomer (YcdY). Compound **11** was used as an aliphatic dicarboxylic acid, because active amides derived from aliphatic dicarboxylic acids, such as adipic acid and sebacic acid, were precipitated from the polymerization solvents.



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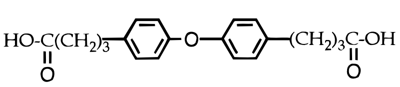

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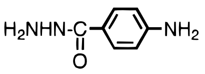

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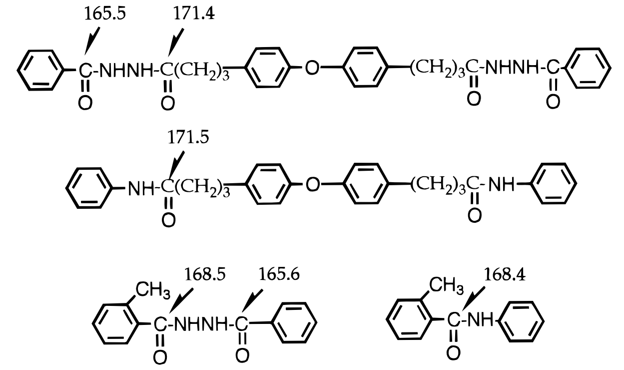
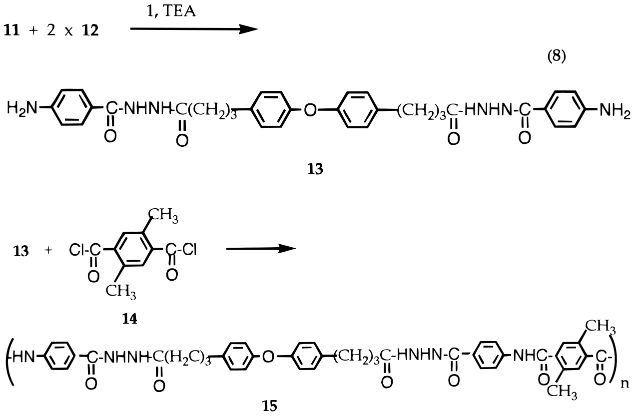
To clarify the structure of polymers obtained, the following model compounds were prepared from the corresponding caboxylic acids and amines in the presence of **1**.



Polymer Synthesis. Synthesis of Ordered Poly(acylhydrazide−amide) (15). The authentic ordered polymer **15** was synthesized for the characterization of the structure of ordered polymer obtained by direct polycondensation. Authentic polymer **15** was prepared as shown in eq 8.



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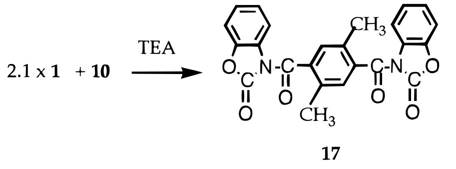
The reaction of **11** with **12** in the presence of **1** yielded 4,4′-(oxydi-*p*-phenylene)bis[*N*′-(4-aminobenzoyl)butanohydrazide] (**13**). The low-temperature solution polycondensation of 2,5-dimethylterephthaloyl chloride (**14**) with **13** was carried out, giving poly(acylhydrazide−amide) **15** with an inherent viscosity of 0.62 dL/g.

Synthesis of Ordered Poly(acylhydrazide−amide) (16). The synthesis of the ordered polymer **16** was carried out by using a two-step procedure involving two separate steps: (i) activation of the carboxylic acid component, i.e., generation of the active amide from **1** and carboxylic acid, and (ii) condensation of this intermediate with the amine. The reaction of **10** with **1** was performed to determine if the method gave the desired active amide in high enough yield to give promise as a polymer-forming reaction. The desired active diamide (**17**) was obtained in quantitative yield (eq 9).



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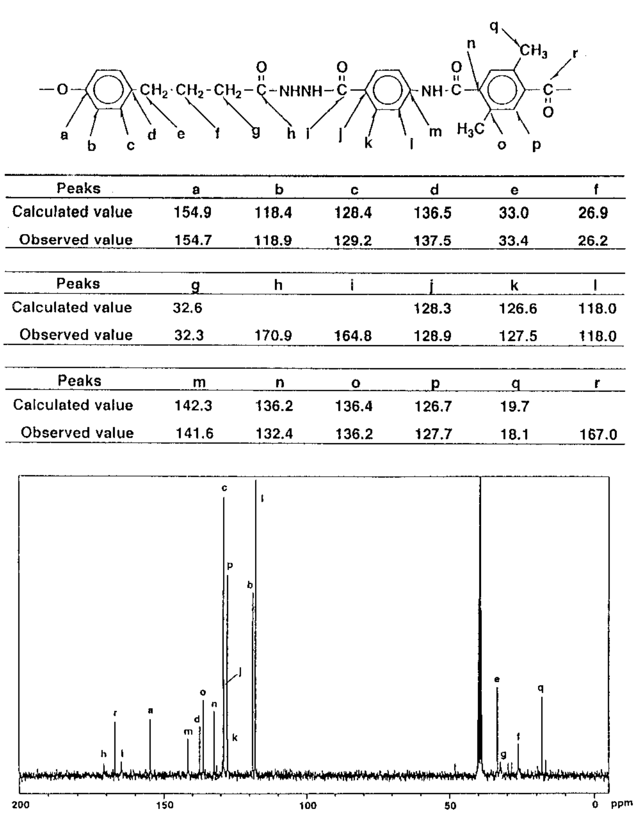
The direct polycondensation was performed by mixing condensing agent **1** with dicarboxylic acids **10** and **11** in NMP−HMPA (3:1) for 2 h at room temperature followed by adding **12**. The polycondensation proceeded slowly and gave polymer **16** with an inherent viscosity of 0.40 dL/g (eq 10).



Peaks	a	b	c	d	e	f
Calculated value	154.9	118.4	128.4	136.5	33.0	26.9
Observed value	154.7	118.9	129.2	137.5	33.4	26.2

Peaks	g	h	i	j	k	l
Calculated value	32.6			128.3	126.6	118.0
Observed value	32.3	170.9	164.8	128.9	127.5	118.0

Peaks	m	n	o	p	q	r
Calculated value	142.3	136.2	136.4	126.7	19.7	
Observed value	141.6	132.4	136.2	127.7	18.1	167.0

Figure 1. ^{13}C-NMR spectrum of polymer **15** in DMSO-d_6.

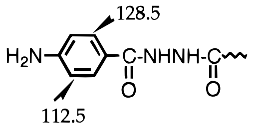
$$\mathbf{10} + \mathbf{11} \xrightarrow[\text{step 1}]{\text{1, TEA}} \xrightarrow[\text{step 2}]{2 \times \mathbf{12}} \textbf{Poly(acylhydrazide-amide) 16} \qquad (10)$$

Synthesis of Random Poly(acylhydrazide−amide) (18). Random poly(acylhydrazide−amide) **18** with an inherent viscosity of 0.48 dL/g was synthesized from **10**, **11**, and **12** in the presence of **1** by mixing the three monomers at once at 80 °C.

Polymer Characterization

The IR spectra of the poly(acylhydrazide−amide)s **15** and **16** were identical and consistent with those of model compounds and known analogues. Both polymers **15** and **16** showed characteristic NH, amide I, and amide II bands in the ranges 3260−3270, 1650−1660, and 1520−1540 cm^{-1}, respectively. Elemental analyses also supported the formation of the expected polymers.

The microstructure of the polymers was determined by means of ^{13}C-NMR spectroscopy. The ^{13}C-NMR spectra of authentic ordered polymer **15** and polymer **16** prepared by direct polycondensation are presented in Figures 1 and 2. The signals of carbon nuclei in amide carbonyl groups for polymers **15** and **16** appeared at 164.8, 167.0, and 170.9 ppm. These peaks are assigned, as shown in the inset of Figure 1, on the basis of chemical shifts for model compounds. Two small extra peaks for polymer **16** were observed at 112.5 and 128.5 ppm, which would be derived from the end amino benzoyl groups as shown in eq 11.



(11)

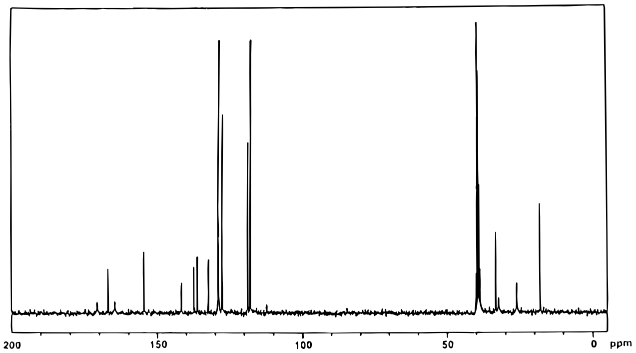


Figure 2. ^{13}C-NMR spectrum of polymer **16** in DMSO-d_6.

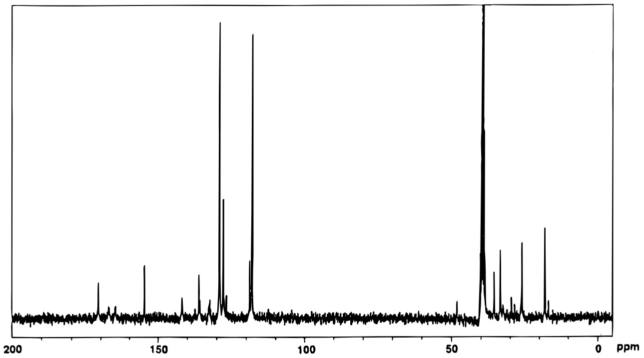


Figure 3. ^{13}C-NMR spectrum of polymer **18** in DMSO-d_6.

On the other hand, the six peaks of carbon nuclei in the amide carbonyl groups for the random polymer would be expected from its random structure. In facts, the six signals for random polymer **18** appeared at 164.9, 165.0, 167.2, 167.4, 170.8, and 170.9 ppm (Figure 3). Furthermore, the spectrum of polymer **15** is identical to that of polymer **16** prepared by direct condensation. These findings indicate that polymer **16** prepared by direct polycondensation was the desired ordered poly(acylhydrazide−amide).

The polymers were light yellow solids, soluble in sulfuric acid and dipolar aprotic solvents such as NMP, DMF, DMSO, and pyridine and insoluble in other common organic solvents.

The thermal stability of the polymers was examined by thermogravimetry (TG) and differential thermal analysis (DTA) (Figure 4). The rapid weight loss for all polymers, observed at 300−390 °C in the TG trace, amounted to 5.5% of the weight of polymer. This value is in good agreement with the value of weight loss (4.7%) calculated from the elimination of water due to the 1,3,4-oxadiazole ring formation.

We expected differences in their properties owing to different regularity. However, no difference in the solubility and thermal stability among these poly(acylhydrazide−amide)s can be detected because extensive interchain NH−OC bonds might mask subtle effects due to isomerism.[12]

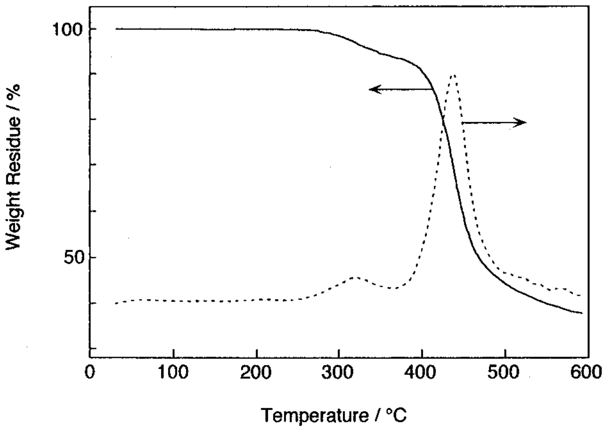


Figure 4. TG and DTA traces of polymers **16** in nitrogen.

In summary, we have demonstrated that the synthesis of ordered poly(acylhydrazide−amide) can be achieved by the direct polycondensation of a pair of symmetric monomers, **10** and **11,** as a nonsymmetric monomer, with a nonsymmetric monomer, **12**, using condensing agent **1**.

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