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Synthesis and Chiroptical Properties of Optically Active Polyamides Having *anti* Head-to-Head Umbelliferone Dimer as a Component

Yutaka ADEGAWA, Lan FANG, Masataka NAKAMURA, Masaki HASEGAWA,[†] and Kazuhiko SAIGO*
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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Optically active polyamides having 2,4-dihydroxyphenyl groups in the side chain were synthesized by the ring-opening polyaddition reaction of (−)-*anti* head-to-head umbelliferone dimer with diamines, such as 1, 6-hexanediamine, 1,4-phenylenediamine, *m*-xylene-α,α'-diamine, and piperazine. Chiroptical properties of the polyamides were elucidated on the basis of their circular dichroism (CD) spectra in solution and in the film state. The polyamide having a 1,4-phenylene moiety in the diamine component existed in an ordered conformation even in a neutral DMAc solution. Moreover, the polyamides having 1,4-phenylenediamine or piperazine as a component existed in an ordered conformation in the film state. The steric repulsion and/or hydrogen bonding of the *para*-hydroxyl group on the phenyl group in the side chain was found to play a significant role to reveal the ordered conformations.

Anti head-to-head coumarin dimer (**1**) has a six-four-six-membered fused ring system with high strain, which accumulates in the course of photodimerization of coumarin[1)] and, subsequently, is susceptible to nucleophilic ring opening with alcohols and amines to give the corresponding diesters and diamides, respectively.[2)] Furthermore, **1** is a chiral molecule having a C_2 axis and is resolved into a pair of optically active forms by a diastereomeric method.[3)] Optically active dimer **1** can be used as an optically active derivatizing reagent with high reactivity[4)] and as an optically active diacid component in polymer synthesis.[5—8)] Some of optically active polyamides **4**, derived from optically active **1**, are found to exist in an ordered conformation[6,7)] and to have a chiral recongnition ability;[7,8)] the phenolic hydroxyl group in the side chain is considered to play an important role to reveal these properties.

On the other hand, racemic *anti* head-to-head umbelliferone (7-hydroxycoumarin) dimer (**2**), which can be easily prepared from umbelliferone via 7-acetoxycoumarin, has the same skeleton as **1** with C_2 symmetry and is useful as a diacid component in polymer synthesis.[10)] Therefore, optically active polyamides **5** would be easily derived from optically active **2** and are expected to reveal different properties from those of polyamides **4** derived from optically active **1**, since polyamides **5** have phenolic hydroxyl groups in the side chain larger in number than the corresponding polyamides **4**.

In the present paper, we describe the synthesis of optically active polyamides **5** having *anti* head-to-head umbelliferone dimer (**2**) as a diacid component and their structures determined on the basis of circular dichroism (CD) spectra.

Results and Discussion

Ring-Opening Polyaddition Reaction of (−)-2 with Diamines 3a—d. Optically active polyamides **5a**—**d** having a 2,4-dihydroxyphenyl moiety in theside-chain were synthesized by the ring-opening polyaddition reaction of (−)-**2** with diamines **3a**—**d**, such as 1,6-hexanediamine, 1,4-phenylenediamine, *m*-xylene-α,α'-diamine, and piperazine (Scheme 1). Since (−)-**2**, which was optically resolved by a diastereomeric method, followed by recrystallization from 2-propanol or purification with short silica-gel column chromatography, contained 0.5 equimolar amount of water,[11)] it was dehydrated by heating just before use. In the light of the optimized conditions for the polymerization of (±)-**2** with diamines,[10)] the polymerization of (−)-**2** was carried out. The purification of the polyamides was performed by adding solutions of the polyamides to a poor solvent, ethyl acetate or chloroform.

The lactone ring-opening polyaddition reaction of (−)-**2** with diamines proceeded smoothly to give high-molecular-weight polyamides, except for the reaction with 1,4-phenylenediamine (Table 1).

The ^{1}H NMR spectrum of **5b** showed a pair of doublets of 1,4-phenylene protons and a slightly broad singlet of amino protons, which were assigned to be the protons of the 1,4-phenylenediamine terminus. Moreover, no detectable 2,4-dihydroxycinnamoyl moiety, arising from the thermal symmetric scission of the cyclobutane rings in the main chain, was observed in its ^{1}H NMR spectrum. In the IR spectrum of **5b**, a carbonyl absorption attributable to a carboxylic acid was not detected at all. These results indicate that polyamide **5b** has diamine-termini. On the basis of the integration of the protons in the ^{1}H NMR, the average degree of polymerization of polyamide **5b** was estimated to be 10. The reason why the molecular weight of polyamide **5b** was relatively lower than those of the other optically active polyamides may be attributed not only to the lower nucleophilicity of the aromatic amine than

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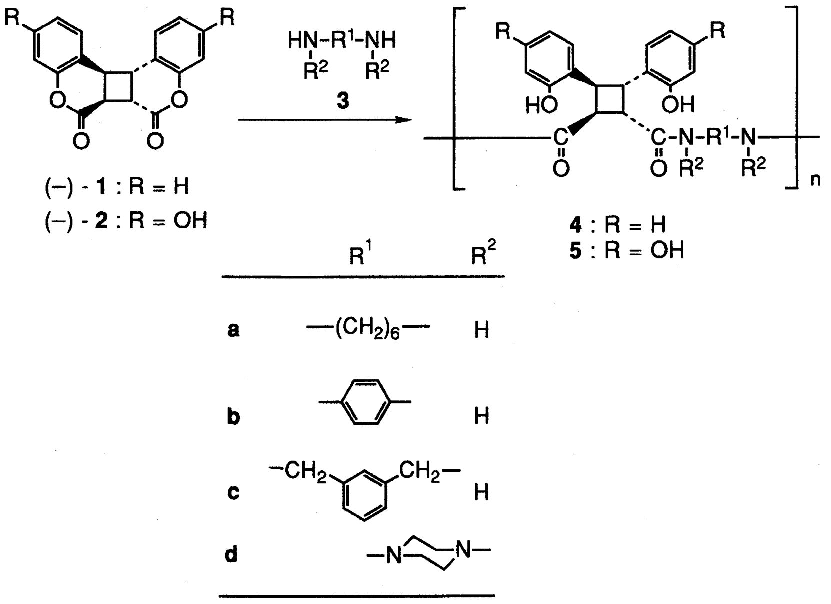
[†] Present address: Department of Materials Science and Technology, Faculty of Engineering, Toin University of Yokohama, Kurogane-cho, Midori-ku, Yokohama 225.



Scheme 1.

Table 1. Ring-Opening Polyaddition Reaction of (−)-**2** with **3**[a)]

Polyamide 5	Concn mol dm^{-3}	Temp °C	Time h	Yield[b,d)] %	η_{inh}[c,d)] dl g^{-1}
a	0.5	R.T.	24	90[e)] (quant.)	0.81 (0.81)
b	1	50	36	91 (95)	0.15 (0.41)
c	1	50	36	72 (90)	0.79 (0.52)
d	1	50	36	quant. (91)	1.42 (0.96)

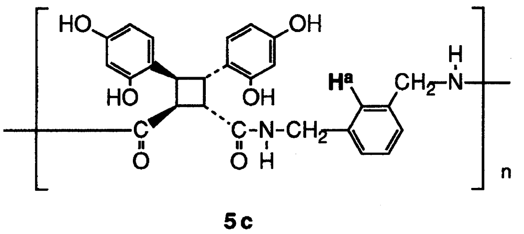
a) In DMAc. b) Chloroform-insoluble part. c) 0.3 g dl^{-1}. d) The yields and inherent visconsities in parentheses are those of the corresponding racemic polyamides **5′**. e) Ethyl acetate-insoluble part.

those of the other aliphatic amines, but also to the difference in reactivity between two amino groups on the same 1,4-phenylene moiety; the reaction of one of the amino groups in 1,4-phenylenediamine with the lactone ring of (−)-**2** results in lowering the nucleophilicity of the other amino group of the diamine due to the electron-withdrawing character of the acyl moiety. Thus, the rate of the polyaddition reaction of (−)-**2** with 1, 4-phenylenediamine would be made slower than those with the other diamines.

All of the polyamides, even **5b** with a low inherent viscosity, were able to form a transparent and flexible film by casting their *N*,*N*-dimethylacetamide (DMAc) solutions on a glass plate.

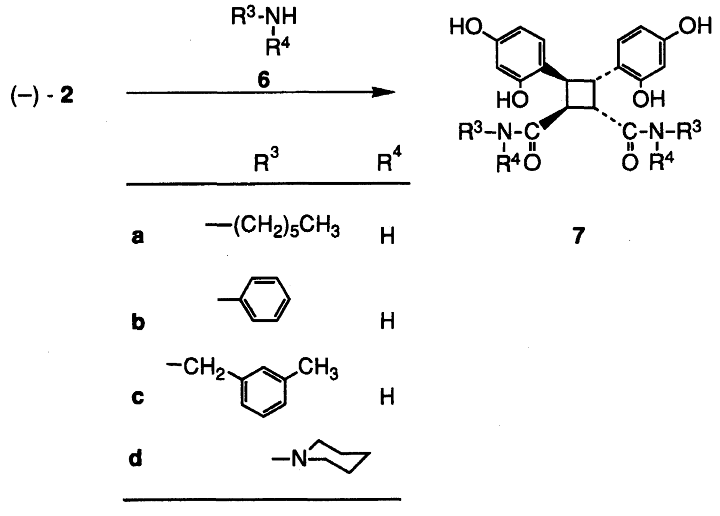
Comparison of the ^{1}H NMR spectrum of polyamides **5** with that of the corresponding racemic polyamides **5′** gave a valuable information concerning the tacticity of racemic polyamides **5′**. The aromatic proton (**H**^{a}) of optically active polyamide **5c** (Chart 1) showed one singlet ($\delta = 6.61$), whereas that of the corresponding racemic polyamide **5′c** split into two singlet ($\delta = 6.54$ and 6.62); the singlet peak at lower magnetic field was attributed to the proton existing between two cyclobutanes of the same absolute configuration, since its chemical shift was almost identical with that observed for optically active polyamide **5c**, whereas the other might arise from the proton existing between two cyclobutanes of opposite absolute configuration. Moreover, the area ratio of the two peaks of racemic polyamide **5′c** was 1 : 1. These results indicate that *meso*-diads, the cyclobutane sequences of (*S*,*S*,*S*,*S*)-(*S*,*S*,*S*,*S*) and (*R*,*R*,*R*,*R*)-(*R*,*R*,*R*,*R*), appeared in the same frequency as *racemo*-diads, the cyclobutane sequences of (*S*,*S*,*S*,*S*)-(*R*,*R*,*R*,*R*) and (*R*,*R*,*R*,*R*)-(*S*,*S*,*S*,*S*). A similar correlation was clearly observed between optically active polyamide **5d** and its corresponding racemic polyamide **5′d**. On the basis of these observation, it is concluded that racemic polyamides **5′** are atactic.

In order to investigate the properties of optically active polyamides **5a**—**d**, model diamides **7a**—**d** were synthesized by the ring-opening addition reaction of (−)-**2**·0.5H$_2$O with amines **6a**—**d**, such as hexylamine, aniline, 3-methylbenzylamine, and piperidine



5c

Chart 1.



Scheme 2.

Table 2. Ring-Opening Addition Reaction of (−)-**2** with **6**

Diamide **7**	Recryst. solvent	Yield %	Mp(decomp) °C
a	—a)	69	(ca. 204)
b	Ethyl acetate/dichloromethane	30	191—193
c	Ethanol/water	28	190—192
d	*N*,*N*-Dimethylacetamide/tetrahydrofuran	54	199—202

a) Purified only by silica-gel column chromatography.

(Scheme 2). The yields of model diamides **7a**—**d** are listed in Table 2.

Chiroptical Property in Solution. As summarized in Table 3, all of model diamides **7a**—**d**, derived from (−)-**2**, were levorotatory at 589 nm in DMAc. Although polyamides **5a**—**c** were also levorotatory with a similar absolute rotation value to that of the corresponding model diamide, the optical rotation of polyamide **5d** was quite different from that of model diamide **7d**. This anomalous optical behavior prompted us to study the chiroptical properties of the polyamides in detail.

Overberger and his co-workers have shown that the chiroptical property of a synthetic polyamide could be elucidated by comparing its CD spectrum with that of the corresponding model diamide; in general, the random conformation of a polymer results in weaker Cotton effect at almost the same wavelength as that of the corresponding model diamide, whereas a polymer in an ordered conformation gave much enhanced Cotton effect and/or different profile of CD spectrum from that of the corresponding model compound.[12)] According to this guideline, the CD spectra of polyamides **5a**—**d** were measured in DMAc at wavelengths longer than 260 nm and compared with those of model diamides **7a**—**d**, especially concerning the Cotton effects of the amide carbonyl and aromatic chromophores.

Table 3. Optical Rotation of **5** and **7**

Polyamide **5**	$[m]_D$ a) deg cm^2 dmol^{-1}	Diamide **7**	$[M]_D$ a) deg cm^2 dmol^{-1}
a	−347	**a**	−284
b	−709	**b**	−556
c	−115	**c**	−91
d	+357	**d**	−524

a) 0.15 g dl^{-1} in DMAc.

The UV and CD data of polyamides **5a**—**d** in DMAc are listed in Table 4 with those of model diamides **7a**—**d**. Polyamides **5a** and **5c** showed essentially the same CD spectra as those of model diamides **7a** and **7c**, respectively; the polyamides exhibited a medium negative Cotton effect at 280—285 nm, which may be attributable to the π–π^* transition of the 2,4-dihydroxyphenyl chromophore. On the basis of their CD spectral behavior as well as their optical rotation behavior mentioned above, it is concluded that polyamides **5a** and **5c** exist in a random conformation in a DMAc solution.

In a similar manner, the CD spectrum of polyamide **5d** was almost identical to that of model diamide **7d**, indicating that polyamide **5d** possessed similar conformational preference to model diamide **7d**; the observation is in contrast to its anomalous behavior in optical rotation. Then, we examined the structure of polyamide **5d** by using the Corey–Pauling–Koltun (CPK) space-filling molecular models. As a result, it was revealed that neither polymer main chain nor dihydroxyphenyl

Table 4. UV and CD data of **5** and **7** in DMAc

Polyamide **5**	UV λ_{max}/nm(ε)	CD λ_{ext}/nm($\Delta\varepsilon$)	Diamide **7**	UV λ_{max}/nm (ε)	CD λ_{ext}/nm ($\Delta\varepsilon$)
a	283 (5460)	284 (−4.45)	**a**	283 (5940)	285 (−4.91)
b	282 (28900)	300 (+4.20) 273 (−34.3)	**b**	283 (shoulder)	288 (−10.3)
c	283 (5430)	281 (−1.67)	**c**	283 (6030)	283 (−1.26)
d	285 (5710)	281 (−4.47)	**d**	285 (6990)	281 (−3.59)

group could easily rotate due to its very rigid structure. Accordingly, it seems likely that **5d** has an extended rod-like structure. This structural feature is strongly supported by the following observations. The inherent viscosity of polyamide **5d** was obviously higher than that of the corresponding racemic polyamide **5′d**, which was prepared under the same conditions as those for **5d**. This result can be consistently explained by considering that in the case of racemic polyamide **5′d**, the polymer main chain can fold due to its atactic structure, resulting in relatively low inherent viscosity. Moreover, in the ^{1}H NMR spectra, optically active polyamide **5d** showed rather broad peaks, while the other optically active polyamides **5a**—**c** showed sharp peaks (for example, the half widths of two peaks of **5d**, which were assigned to the protons of the phenolic hydroxyl groups in the side chain, were 60 and 24 Hz, whereas those of polyamides **5a**—**c** were 4—15 Hz). This observation indicates that the thermal motion of **5d** in solution is much inferior to those of the other polyamides, which might be caused by the rigid structure of **5d**.

On the other hand, the CD spectrum of polyamide **5b**, having a rigid 1,4-phenylene moiety in the diamine component, was quite different from that of the corresponding model diamide **7b** (Fig. 1). This evidence clearly demonstrates that polyamide **5b** exists in an ordered conformation. Similar CD spectral distinction between polyamides and their model diamides in solution has been observed for *O*-methylated and *O*-carbamoylated polyamides of **4b**, which existed in an ordered conformation in solution due to a steric repulsion,9) although HO-free mother polyamide **4b** has been reported to exist in a random conformation.6) On the basis of the similarity in CD spectral behavior between polyamide **5b** and the *O*-methylated and *O*-carbamoylated polyamides of **4b**, the ordered conformation of polyamide **5b** might arise from the steric repulsion and/or hydrogen bonding of the *para*-hydroxyl group on the phenyl group in the side chain.

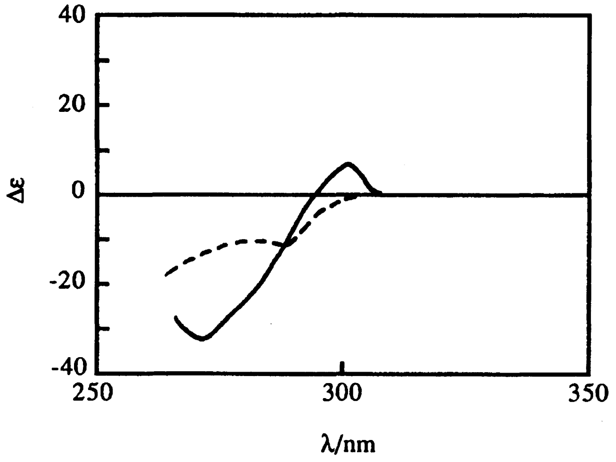


Fig. 1. CD spectra of **5b** (——) and **7b** (- - -) in DMAc.

Chiroptical Property in the Film State. When polyamides **5a**—**d** and model diamides **7a**—**d** were cast from their DMAc solutions on the outside surface of a quartz cell and were dried, clear homogeneous thin films and deposits were obtained, respectively. Each cast sample was found to be isotropic on the basis of the fact that CD spectra, obtained by rotating the sample around the axis of the incident beam, were identical to each other. The CD spectra of polyamides **5a**—**d** and model diamides **7a**—**d** in the film state or in the solid state are shown in Fig. 2. The deposits of model diamides **7a**—**d**, showed maximum absorption peaks at around 280 and 235 nm in their UV spectra, which apparently correspond to the π–π* transition of the 2,4-dihydroxyphenyl group and the n–π* transition of the amide carbonyl, respectively. Therefore, the Cotton effect at longer wavelength can be assigned to the π–π* transition of the aromatic chromophore, whereas that at shorter wavelength is attributed to the n–π* transition of amide chromophore.

Polyamide **5c** showed essentially the same CD spectrum as that of model diamide **7c** (Fig. 2c). Thus, it is obvious that polyamide **5c** exists in a random conformation.

Similarity in CD spectral shape between polyamide **5a** and model diamide **7a** suggests that they possess similar conformational preference (Fig. 2a). However, large enhancement of the band at 239 nm indicated that polyamide **5a** would aggregate with each other by the interaction between the amide moieties. This consideration is supported by the following observation; a solution of polyamide **5a** at a concentration of 0.1 g ml^{-1} (corresponding 0.24 mol dm^{-3}) in DMAc brought about gelation, while the other polyamides **5b**—**d** did not set to gel at all.

The CD patterns of polyamides **5b** and **5d** (Figs. 2b and 2d) at the wavelength longer than 260 nm were drastically different from those of the corresponding

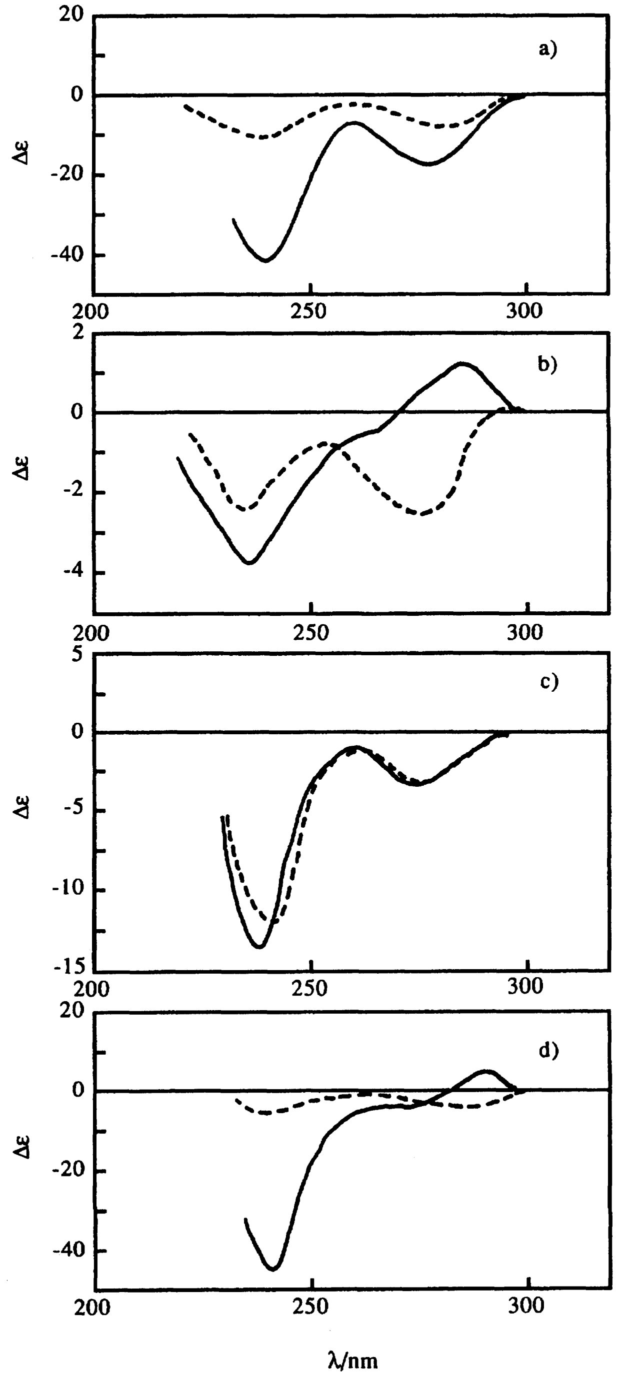


Fig. 2. CD spectra of **5a**—**d** (——) and **7a**—**d** (- - -) in the film state.

model diamides, **7b** and **7d**, respectively. These observations suggest that **5b** and **5d** exist in an ordered conformation in the film state.

Table 5 shows the conformation of polyamides **5** with that of polyamides **4**,[6,7)] derived from optically active *anti* head-to-head coumarin dimer (**1**) for comparison. Polyamide **5b** formed an ordered conformation even in a neutral DMAc solution in contrast to polyamide **4b**, which existed in a random conformation in neutral DMAc. Although polyamide **5a** set to gel in a solution, the gelation was not observed for solution of polyamide **4a** at the same concentration. Moreover, the CD spectrum of polyamide **5c** in the film state is almost identical to that of polyamide **4c**, but the molecular circular dichroism (Δε) of polyamide **5d** at 240 nm was more than 10 times larger than that of polyamide **4d**. These observations indicate that the *para*-hydroxyl group on the phenyl group in the side chain plays a significant role to manifest the characteristic properties of polyamide **5**.

Table 5. Conformation of Polyamides **5** Compared with That of Polyamides **4**

	In DMAc		Film state	
	Polyamide **5**	Polyamide **4**	Plyamide **5**	Polyamide **4**
a	Random	Random	Aggregation (stronger)	Aggregation (weaker)
b	Ordered	Random	Ordered	Ordered
c	Random	Random	Random	Random
d	Ordered (Rod-like)	Ordered (Rod-like)	Ordered (Rod-like)	Ordered (Rod-like)
Ref.	This work	6)	This work	7)

On the basis of the structural difference between polyamides **5a**—**d**, their difference in chiroptical property may be explained as follows: The hexamethylene moiety of polyamide **5a** is too flexible to form an ordered conformation in solution. In the film state, however, **5a** can aggregate due to its flexibility. In contrast, the *m*-xylene-α,α′-diyl moiety of **5c** is still too flexible to form an ordered conformation in solution, but too rigid to aggregate in the film state. The 1,4-phenylene moiety of **5b** is rather rigid and, subsequently, forms an ordered conformation both in solution and in the film state. Polyamide **5d** has an extremely rigid main chain, so that it is forced to exist in an extended rod-like structure.

Experimental

General. Melting points were determined using a Laboratory Devices Mel-Temp and are uncorrected. Decomposition points were determined on the basis of differential scanning calorimetric (DSC) curves recorded on a Shimadzu DSC-50 instrument under a nitrogen stream at a heating rate of 10°C min^{-1}. Inherent viscosities (0.30 g dl^{-1} in DMAc) were measured at 30°C with an Ostwald viscometer. ^{1}H and ^{13}C NMR spectra were measured at 22—25°C using a JEOL GX-400 spectrometer (399.8 MHz for ^{1}H and 100.5 MHz for ^{13}C). Infrared spectra (KBr pellets) were recorded on a JASCO IR-810 infrared spectrophotometer. Specific rotations were measured using a JASCO DIP-360 digital polarimeter at about 20°C in a 1-dm cell at a sample concentration of ca. 0.15 g dl^{-1} in DMAc. The circular dichroism (CD) and UV spectra were measured in a 1.0-cm cell at room temperature on a JASCO-500A spectropolarimeter and on a Shimadzu UV-260 spectrometer, respectively, at a concentration of ca. 10^{-4} repeating-unit-mol dm^{-3} (or mol dm^{-3}) in DMAc. The measurements were carried out just after the sample was dissolved completely.

Material. (−)-*anti* Head-to-head umbelliferone dimer, (−)-**2**·0.5H_2O, was obtained from racemic 7-acetoxycoumarin dimer by a diastereomeric resolution method reported previously.[11] Just before use, (−)-**2**·0.5H_2O was dehydrated as described in the procedure for polymerization. All of the diamines and amines are of commercial origin. 1,6-Hexanediamine, *m*-xylene-α,α'-diamine, and all of the amines were purified by distillation just before use. 1,4-Phenylenediamine and piperazine were recrystallized twice from benzene, followed by drying at room temperature in vacuo for 24 h. DMAc was pre-dried with 4A molecular sieves and then distilled under reduced pressure just before use.

Ring-Opening Polyaddition Reaction of (−)-2. A typical procedure of polymerization of (−)-**2** is as follows: Dimer (−)-**2**·0.5H_2O was placed in a flask and dried in vacuo over P_2O_5 at 150°C; upon being heated for 24 h, (−)-**2**·0.5H_2O was completely dehydrated to afford (−)-**2**. A freshly distilled 1,6-hexanediamine (247 mg, 2.13 mmol) and an equimolar amount of (−)-**2** were placed in a 30-ml two-necked flask which was evacuated and then filled with argon three times, and DMAc (4.26 ml) was added to the flask with a syringe to give a clear solution of a ca. 0.5 mol dm^{-3} concentration. After being stirred for 24 h at room temperature under an argon atmosphere, the reaction mixture was diluted with DMAc (20 ml). The solution was added drop by drop into ethyl acetate (900 ml), and the precipitate which appeared was collected by filtration. The precipitate was dried over P_2O_5 in vacuo at room temperature for 24 h to give polyamide **5a** (994 mg, 90%). The polyamide was hygroscopic.

Pollyamide 5a: DSC 54.7°C (*endo*), 243.9°C (*exo*), and 263.6°C (*endo*); ^{1}H NMR (DMSO-d_6) δ=0.8—0.9 (4H, br), 0.9—1.0 (4H, br), 2.6—2.7 (2H, br), 2.8—2.9 (2H, br), 3.42 (2H, d, J=6 Hz), 4.44 (2H, d, J=6 Hz), 6.03 (2H, dd, J=2 and 8 Hz), 6.20 (2H, d, J=2 Hz), 6.74 (2H, d, J=8 Hz), 7.08 (2H, s), 8.90 (2H, s), and 9.18 (2H,s); ^{13}C NMR (DMSO-d_6) δ=26.06, 28.95, 38.12, 38.52, 43.76, 101.84, 105.51, 117.08, 128.26, 155.72, 156.50, 171.53; IR (KBr) 3650—3000, 2930, 1620, 1520, 1460, 974, and 840 cm^{-1}.

Found: C, 60.26; H, 6.80; N, 6.51%. Calcd for $(C_{24}H_{28}N_2O_6\cdot0.5DMAc\cdot2H_2O)_n$: C, 60.04; H, 7.07; N, 6.73%.

Polyamide 5b: DSC 80.0°C (*endo*), 182.6°C (*endo*), and 248.2°C (*exo*); ^{1}H NMR (DMSO-d_6) δ=3.71 (2H, m), 4.56 (2H, m), 4.75 (0.2×2H, s, terminal N$\underline{H}_2$), 6.03 (2H, d, J=8 Hz), 6.19 (2H, s), 6.46 (0.2×2H, d, J=8 Hz, terminal $C_6\underline{H}_4$), 6.82 (2H, d, J=8 Hz), 6.92 (0.2×2H, J=8 Hz, terminal $C_6\underline{H}_4$), 7.14 (4H, s), 8.88 (2H, s), and 9.30 (4H+0.2×1H, s); ^{13}C NMR (DMSO-d_6) δ=38.52, 44.82, 101.89, 105.60, 113.60, 117.03, 119.65, 121.52, 128.26, 134.34, 144.60, 151.95, 155.74, 156.49, 170.54; IR (KBr) 3650—3000, 1610, 1512, 1460, 1404, 972, and 836 cm^{-1}.

Found: C, 60.81; H, 5.66; N, 7.22%. Calcd for $H_2NC_6H_4NH(C_{24}H_{20}N_2O_6)_{10}H\cdot5DMAc\cdot21H_2O$: C, 60.90; H, 5.67; N, 7.21%.

Polyamide 5c: DSC 70.4°C (*endo*), 193.9°C (*endo*), and 254.7°C (*exo*); ^{1}H NMR (DMSO-d_6) δ=3.55 (2H, m), 3.84 (2H, d, J=12 Hz), 4.17 (2H, d, J=12 Hz), 4.58 (2H, m), 6.07 (2H, d, J=6 Hz), 6.24 (2H, s), 6.41 (2H, d, J=6 Hz), 6.61 (1H, s), 6.81 (2H, d, J=7 Hz), 6.91 (1H, t, J=5 Hz), 7.69 (2H, s), 8.96 (2H, s), and 9.20 (2H, s); ^{13}C NMR (DMSO-d_6) δ=38.01, 41.97, 44.31, 102.00, 105.62, 117.13, 124.96, 125.33, 128.01, 128.41, 138.82, 155.92, 156.61, 171.90; IR (KBr) 3650—3000, 1620, 1520, 1456, 970, and 920 cm^{-1}.

Found: C, 61.63; H, 5.70; N, 6.18%. Calcd for $(C_{26}H_{24}N_2O_6\cdot0.3DMAc\cdot2.5H_2O)_n$: C, 61.45 H, 6.01; N, 6.06%.

Polyamide 5d: DSC 68.5°C (*endo*), 175.4°C (*endo*), and 271.7°C (*exo*); ^{1}H NMR (DMSO-d_6) δ=1.7—1.9 (4H, br), 3.0—3.2 (2H, br), 3.6—3.8 (2H, br), 3.8—4.0 (2H, br), 4.4—4.6 (2H, br), 6.0—6.2 (2H, br), 6.2—6.4 (2H, br), 6.7—6.9 (2H, br), 8.8—9.2 (2H, br), and 9.4—9.6 (2H, br); ^{13}C NMR (DMSO-d_6) δ=36.36, 40.56, 43.47, 101.84, 106.12, 115.99, 128.64, 155.88, 157.01, 169.62; IR (KBr) 3650—3000, 2930, 1610, 1520, 1460, 1436, 974, and 840 cm^{-1}.

Found: C, 60.70; H, 6.69; N, 8.39%. Calcd for $(C_{22}H_{22}N_2O_6\cdot DMAc\cdot H_2O)_n$: C, 60.57; H, 6.45; N, 8.15%.

Synthesis of Model Diamides 7. A typical procedure of the ring-opening addition reaction of (−)-**2** is as follows: To a solution of (−)-**2**·0.5H_2O (82 mg, 0.25 mmol) in tetrahydrofuran (THF) (2 ml) was added hexylamine (250 mg, 2.5 mmol) in excess. After being stirred for 3 h at room temperature under argon atmosphere, the reaction mixture was added drop by drop into hexane (500 ml). The precipitate which appeared was collected by filtration and purified by silica gel column chromatography (eluent: ethyl acetate). Drying in vacuo over P_2O_5 at room temperature for 24 h afforded **7a** (90 mg, 69%). The diamide was hygroscopic.

Diamide 7a: ^{1}H NMR (DMSO-d_6) δ=0.83 (6H, t, J=7 Hz), 0.98 (8H, m), 1.08 (4H, m), 1.18 (4H, m), 2.66 (2H, m), 2.89 (2H, m), 3.40 (2H, dd, J=2 and 9 Hz), 4.42 (2H, dd, J=2 and 7 Hz), 6.02 (2H, dd, J=2 and 7 Hz), 6.20 (2H, d, J=2 Hz), 6.73 (2H, d, J=9 Hz), 7.08 (2H, t, J=5 Hz), 8.86 (2H, s), and 9.19 (2H, s); ^{13}C NMR (DMSO-d_6) δ=14.04, 22.05, 26.06, 29.06, 31.13, 38.21, 38.49, 43.85, 101.90, 105.51, 117.16, 128.27, 155.77, 156.61, and 171.55; IR (KBr) 3700—3000, 2940, 2850, 1620, 1540, 1520, 1460, 1370, 1300, 1260, 1220, 1200, 1165, 1130, 1115, 1095, 970, 840, 790, 720, 630, and 580 cm^{-1}.

Found: C, 67.02; H, 8.23; N, 5.56%. Calcd for $C_{30}H_{42}N_2O_6\cdot0.5H_2O$: C, 67.27; H, 8.09; N, 5.23%.

Diamide 7b: ^{1}H NMR (DMSO-d_6) δ=3.79 (2H, dd, J=2 and 7 Hz), 4.61 (2H, dd, J=2 and 8 Hz), 6.02 (2H, dd, J=2 and 9 Hz), 6.20 (2H, d, J=2 Hz), 6.84 (2H, d, J=9 Hz), 6.95 (2H, t, J=7 Hz), 7.19 (4H, t, J=7 Hz), 7.36 (4H, d, J=8 Hz), 8.90 (2H, s), 9.38 (2H, s), and 9.46 (2H, s); ^{13}C NMR (DMSO-d_6) δ=38.64, 44.93, 101.97, 105.68, 117.00, 119.52, 123.01, 128.32, 128.51, 139.17, 155.87, 156.61, and 170.93; IR (KBr) 3700—3000, 3150, 3030, 1660, 1620, 1600, 1555, 1540, 1520, 1500, 1445, 1350, 1320, 1300, 1275, 1250, 1230, 1190, 1160, 1120, 1110, 970, 840, 760, and 690 cm^{-1}.

Found: C, 66.95; H, 5.50; N, 5.39%. Calcd for $C_{30}H_{26}N_2O_6\cdot1.5H_2O$: C, 67.03; H, 5.44; N, 5.21%.

Diamide 7c: ^{1}H NMR (DMSO-d_6) δ=2.21 (6H, s), 3.54 (2H, dd, J=2 and 6 Hz), 3.86 (2H, dd, J=5 and 15 Hz), 4.23 (2H, dd, J=7 and 15 Hz), 4.60 (2H, dd, J=2 an 7 Hz), 6.07 (2H, dd, J=2 and 8 Hz), 6.25 (2H, d, J=2 Hz), 6.49 (2H, d, J=8 Hz), 6.73 (2H, s), 6.83 (2H, d, J=9 Hz), 6.94 (2H, d, J=7 Hz), 7.02 (2H, t, J=8 Hz), 7.74 (2H, t, J=6 Hz), 8.96 (2H, s), and 9.19 (2H, s); ^{13}C NMR (DMSO-d_6) δ=21.07, 38.13, 42.06, 44.45, 102.12, 105.73, 117.22, 124.08, 127.07, 127.44, 128.07, 128.51, 137.07, 139.24, 156.04, 156.72, and 172.02; IR (KBr) 3600—3300, 2920, 1620, 1520, 1460, 1300, 1220, 1165, 1130, 1030, 970, 840, 790, 740, and 700 cm^{-1}.

Found: C, 68.76; H, 6.41; N, 4.47%. Calcd for $C_{34}H_{34}N_2O_6 \cdot 1.5H_2O$: C, 68.79; H, 6.28; N, 4.72%.

Diamide 7d: ^{1}H NMR (DMSO-d_6) δ=0.7—0.8 (2H, br), 1.0—1.1 (2H, br), 1.1—1.4 (8H, br), 1.83 (1H, m), 2.82 (2H, m), 3.12 (4H, m), 3.60 (1H, m), 3.94 (2H, d, J=9 Hz), 4.42 (2H, d, J=9 Hz), 6.11 (2H, dd, J=2 and 8 Hz), 6.19 (2H, d, J=2 Hz), 6.86 (2H, d, J=8 Hz), 9.00 (2H, s), and 9.23 (2H, s); ^{13}C NMR (DMSO-d_6) δ=23.88, 25.01, 25.16, 37.31. 40.95, 41.63, 45.12, 101.77, 105.86, 116.95, 128.68, 155.82, 156.67, and 169.31; Ir (KBr) 3700—3000, 2940, 2855, 1590, 1520, 1460, 1450, 1400, 1250, 1220, 1170, 1140, 1095, 1020, 975, 850, and 600 cm^{-1}.

Found: C, 65.17; H, 7.27; N, 6.55%. Calcd for $C_{28}H_{34}N_2O_6 \cdot 0.5\text{DMAc}$: C, 65.02; H, 7.00; N, 6.31%.

CD Measurement. All of CD data of the polyamides and model diamides in DMAc were given in molecular circular dichroism ($\Delta\varepsilon$), with cm^2 repeating-unit-mmol^{-1} (or $\text{cm}^2\ \text{mmol}^{-1}$) unit, which was calculated by the following equations;

$$\Delta\varepsilon = [\theta]/3300 \quad \text{and} \quad \theta = [\theta] \times C \times l,$$

where C is the concentration (repeating-unit-mol dl^{-1} or mol dl^{-1}), l is the length of the cell (dm), θ is the measured ellipticity (deg), and $[\theta]$ is the molecular ellipticity (deg cm^2 dmol^{-1}).

The thin films of the polyamides were prepared by casting their solutions (ca. 30 mg ml^{-1} in DMAc) on the outside surface of a quartz cell (10×45×10 mm). The coated films were dried in a desiccator over P_2O_5 at atmospheric pressure for 24 h and then in vacuo for 48 h at room temperature. CD measurement were carried out at a concentration of ca. 10^{-7} repeating-unit-mmol cm^{-2}. The amorphous deposits of the model diamides were also carried out by a similar method (ca. 30 mg ml^{-1} in acetone for **7a**—**c**, in DMAc for **7d**). All of the CD data were given in $\Delta\varepsilon$ with cm^2 repeating-unit-mmol^{-1} (or $\text{cm}^2\ \text{mmol}^{-1}$) unit, which was calculated by the following equations;

$$\Delta\varepsilon = [\theta]/3300 \quad \text{and} \quad \theta = 0.1 \times [\theta] \times m/MW,$$

where MW is the repeating-unit molecular weight of the polyamides (or molecular weight of the model diamides), m is the sample weight per unit area (g cm^{-2}), θ is the measured ellipticity (deg), and $[\theta]$ is the molecular ellipticity (deg cm^2 dmol^{-1}).

The thin films were also cast on the outside surface of a cylindrical quartz cell (10×20 (o.d.) mm), and CD measurements were repeated for six times by rotating the sample cell by −30°, 30°, 60°, 90°, and 120° from the first position around the axis of the incident light beam to give almost identical spectra.

References

1) C. H. Krauch, S. Farid, and G. O. Schenck, *Chem. Ber.*, **99**, 625 (1966).

2) M. Hasegawa, Y. Suzuki, and N. Kita, *Chem. Lett.*, **1972**, 317; Y. Suzuki, M. Hasegawa, and N. Nishikawa, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 173 (1973); M. Hasegawa, N. Yonezawa, T. Kanoe, and Y. Ikebe, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 309 (1982); M. Hasegawa, K. Saigo, H. Katsuki, N. Yonezawa, and T. Kanoe, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2345 (1983); N. Yonezawa and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, **56**, 367 (1983); N. Yonezawa, Y. Ikebe, T. Yoshida, T. Hirai, K. Saigo, and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, **57**, 1608 (1984).

3) K. Saigo, K. Sekimoto, N. Yonezawa, and M. Hasegawa, *Tetrahedron Lett.*, **24**, 5381 (1983); K. Saigo, N. Yonezawa, K. Sekimoto, M. Hasegawa, K. Ueno, and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, **58**, 1000 (1985); Corrections: *Bull. Chem. Soc. Jpn.*, **60**, 2704 (1987).

4) K. Saigo, K. Sekimoto, N. Yonezawa, F. Ishii, and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, **58**, 1006 (1985).

5) N. Yonezawa, T. Kanoe, K. Saigo, Y. Chen, K. Tachibana, and M. Hasegawa, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 617 (1985).

6) K. Saigo, Y. Chen, N. Yonezawa, T. Kanoe, K. Tachibana, and M. Hasegawa, *Macromolecules*, **19**, 1552 (1986).

7) Y. Chen, K. Saigo, N. Yonezawa, and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, **60**, 1895 (1987).

8) K. Saigo, Y. Chen, K. Fujioka, N. Yonezawa, and M. Hasegawa, *Chem. Lett.*, **1988**, 647; K. Saigo, M. Nakamura, Y. Adegawa, S. Noguchi, and M. Hasegawa, *Chem. Lett.*, **1989**, 337; K. Saigo, T. Shiwaku, K. Hayashi, K. Fujioka, M. Sukegawa, Y. Chen, N. Yonezawa, M. Hasegawa, and T. Hashimoto, *Macromolecules*, **23**, 2830 (1990).

9) K. Saigo, *Prog. Polym. Sci.*, **17**, 35 (1992).

10) K. Saigo, M. Nakamura, Y. Suzuki, L. Fang, and M. Hasegawa, *Macromolecules*, **23**, 3722 (1990).

11) Y. Adegawa, Y. Hashimoto, L. Fang, M. Nakamura, K. Kinbara, M. Hasegawa, and K. Saigo, *Bull. Chem. Soc. Jpn.*, **66**, 900 (1993).

12) C. G. Overberger, and Y. Shimokawa, *Macromolecules*, **4**, 718 (1971); C. G. Overberger and T. Nishiyama, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 331 (1981); C. G. Overberger and D. W. Wang, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1153 (1984).