Optically Active Polyamides Having (−)-Anti Head-to-Head Coumarin Dimer Component. 2. Chiroptical Property in the Film State

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The chiroptical property of optically active polyamides (**3a—i**), derived from (−)-anti head-to-head coumarin dimer (**1**), was investigated by comparing their UV and circular dichroism (CD) spectra with those of the corresponding model diamides (**8a—i**) in the film state. The result suggests that the polyamides (**3a—c,g**) derived from acyclic aliphatic diamines, exist in a random conformation due to the flexibility of the diamine components. The polyamides (**3d,h**), consisting of piperazine, are assumed to be in a rod-like conformation, resulting from their rigid and fixed main chains. The polyamides (**3e,f,i**), prepared from aromatic diamines, show reversed and split Cotton effects at 270—300 nm in comparison with those of model diamides. This phenomenon is interpreted by the formation of an ordered conformation of macromolecular asymmetry.

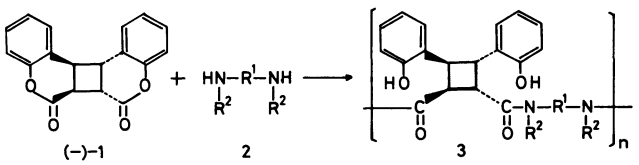
Recently, we have synthesized a series of optically active polyamides by the ring-opening polyaddition reaction of (—)-anti head-to-head coumarin dimer with diamines,[1,2] and have shown that these polyamides exist in a random or ordered conformation in solution depending on the medium and/or on the structure of diamine components.[1,2] For example, the polyamide, consisting of (—)-anti head-to-head coumarin dimer and 1,4-phenylenediamine components, exists in a random coil in *N,N*-dimethylacetamide solution, while in basic media it exists in an ordered conformation due to the electronic repulsion of the phenolate anions formed by the base. It is well-known that CD spectral study is very effective to investigate the chiroptical property of polypeptides in the film-state.[3,4] These observation and fact prompted us to disclose the conformations of the optically active polyamides in the film state, since it is considered to be possible that these polyamides form an ordered conformaion even in film state depending on the rigidity of the diamine component.

In this paper, we wish to report the chiroptical property of the optically active polyamides, derived from (—)-anti head-to-head coumarin dimer, in the film state on the basis of the comparison of their UV and CD spectra with those of the corresponding model diamides.

Results and Discussion

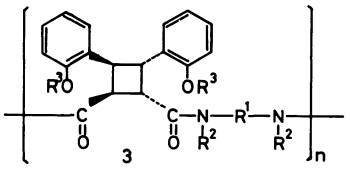
Synthesis of Optically Active Polyamides and Model Diamides. Optically active polyamides **3a—f** were synthesized by the ring-opening polyaddition reaction of (−)-anti head-to-head coumarin dimer **1** as described in detail in the literature.[2]

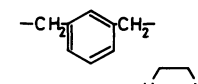
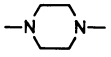
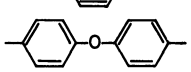
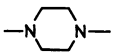
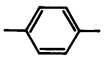
Optically active *O*-methylated polyamides **3g—i** were prepared by the interfacial polycondensation reaction of bis(acid chloride) **6** with diamines using benzyltriethylammonium chloride as a phase-transfer catalyst. The starting material **6** could be obtained from **1** by three steps as shown in the following Scheme 2.

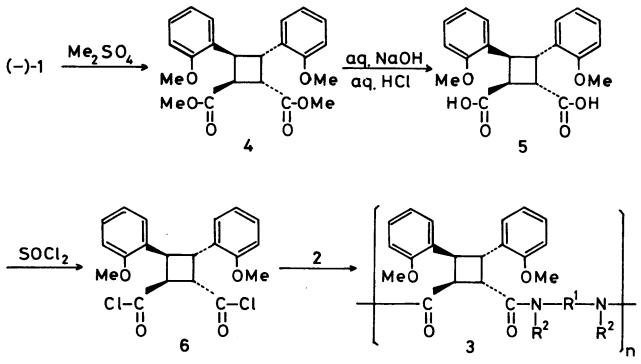


Scheme 1.

The notations for the optically active polyamides are as follows:



Polyamide	R^1	R^2	R^3	η_{inh}
3a	$-(CH_2)_6-$	H	H	0.88
3b	$-(CH_2)_6-$	CH_3	H	0.35
3c		H	H	0.63
3d			H	0.51
3e		H	H	0.36
3f		H	H	0.31
3g	$-(CH_2)_6-$	H	CH_3	1.01
3h			CH_3	1.00
3i		H	CH_3	0.50



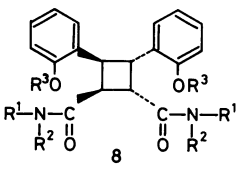
Scheme 2.

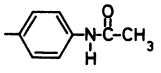
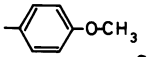
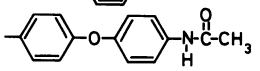
Similar to the ring-opening polyaddition reaction, the interfacial polycondensation also gave high-molecular-weight polyamides (η_{inh}=0.50—1.01 dl g^{-1}). These *O*-methylated polyamides showed no solubility in common organic solvents, but could dissolve in *m*-cresol, *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), and acetic acid very slowly.

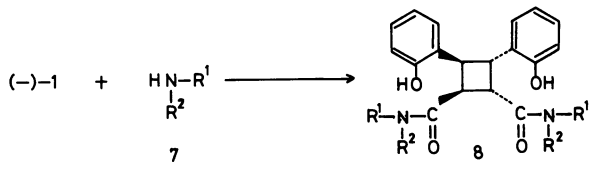
Model diamides **8a—f** were synthesized by ring-opening addition reaction as reported in the literature.[2] In order to study the influence of the extension of resonance on UV and CD spectra, model diamides **8e′, f′** were synthesized in a similar manner.

O-Methylated model diamides **8g—i** were synthesized by interfacial condensation without the phase-transfer catalyst.

The notations for the model diamides are as follows:



Diamide	R^1	R^2	R^3
8a	$-(CH_2)_5CH_3$	H	H
8b	$-(CH_2)_5CH_3$	CH_3	H
8c	$-CH_2-C_6H_4-CH_3$	H	H
8d			H
8e		H	H
8e′		H	H
8f		H	H
8f′		H	H
8g	$-(CH_2)_5CH_3$	H	CH_3
8h			CH_3
8i		H	CH_3



Scheme 3.

Scheme 4.

Chiroptical Property in the Film State. Polyamide **3** was cast on the outside surface of a quartz cell and dried to give a clear and homogeneous thin film. In the case of model diamide **8**, a clear and homogeneous thin deposit could also be obtained with the exception of **8b**. The cast sample was found to be isotropic on the basis of the fact that UV and CD spectra, obtained by rotating the sample around the axis of the incident beam, were identical to each other.

It is known that the chiroptical property of synthetic polyamides can be investigated by comparing their CD spectra with those of the corresponding model diamides.[5] In general, the random conformation of the polymer results in weaker Cotton effect at about the same wavelength than that of the corresponding model diamide. In this study, we compared mainly the Cotton effects of the amide carbonyl and aromatic chromophores in polyamide **3** with those of model diamide **8**, respectively.

As listed in Table 1, model diamides **8a, c, d, g, h**, derived from aliphatic amines, show maximum absorption(s) at about 275 nm in their UV spectra, which apparently corresponds to the π-π^* transition of hydroxyphenyl group. In CD spectra, all of the model diamides show *negative* Cotton effects at about 235 and 275 nm. The former negative CD band may be assigned to a component of the split π-π^* transition due to an exciton coupling of amide carbonyl chromophore,[6] although a short-wavelength component of this split cannot be observed because of the limit of measurement. Moreover, the latter can be assigned to the π-π^* transition of the aromatic[2] chromophore.

In the case of model diamides **8e, f, i** derived from aromatic amines, their molar extinction coefficients are much larger than those of the model diamides derived from aliphatic amines. Negative CD bands of the amide carbonyl and aromatic chromophores in **8, f, i** appear at about 240 and 280 cm, respectively, namely, the CD bands red-shifted about 5 nm in

Table 1. Optical Properties of Model Diamides in the Film State

Diamide	UV spectra		CD spectra	
	ε	λ_{max}	$\Delta\varepsilon$	λ_{max}
8a	4780	273.2	−2.60	270.8
	4500	280.0	−7.92	236.0
8c	5150	275.0	−3.50	275.0
	4700	281.0	−9.02	235.0
8d	3820	280.0	−3.42	277.0
			−4.36	236.5
8g	3880	273.1	−1.93	270.0
	3780	280.0	−1.59	230.0
8h	4318	276.0	−3.79	274.0
			−11.14	235.5
8e	21700	249.0	−7.95	279.0
			−13.63	241.0
8e'	39000	272.0	−6.00	282.5
			−7.80	238.5
8f	24900	257.5	−10.33	279.0
			−19.25	238.5
8f'	59300	262.0	−7.25	282.5
			−9.08	241.0
8i	19700	251.3	−11.00	279.0
			−10.82	243.0

comparison with those of the aliphatic counterparts. These phenomena would be attributable to the resonance effect of the amide carbonyl chromophore with the aromatic amine residue and to the effect of the aromatic amine residue as an aromatic chromophore. Moreover, **8e'** and **8f'**, synthesized to clarify the influence of the extension of the resonance on CD spectra in the film state, show also only a little decrease and shift in CD bands, although they show an enhanced molar extinction coefficient in UV spectra.

From these facts, it is clear that the negative CD bands of model diamide **8** result simply from the chiral carbons of cyclobutane ring and that the extension of the resonance in the aromatic amine residue results only in a little decrease and shift of the CD bands.

The UV and CD spectra of polyamide **3a** and model diamide **8a** in the dry film state are shown in Fig. 1. The negative CD bands of **3a** at 230—240 and 260—280 nm are, as mentioned for model diamides, assigned to a component of the split π–π^* transition of the amide carbonyl chromophore and to the π–π^* transition of the hydroxyphenyl chromophore, respectively. Comparing the bands with those of **8a**, the former band shows enhanced intensity with a blue shift although the latter exhibits weaker intensity.

Similar enhanced intensity and blue shift of the CD band of polyamide at 230—240 nm in comparison with that of the corresponding model diamide were also

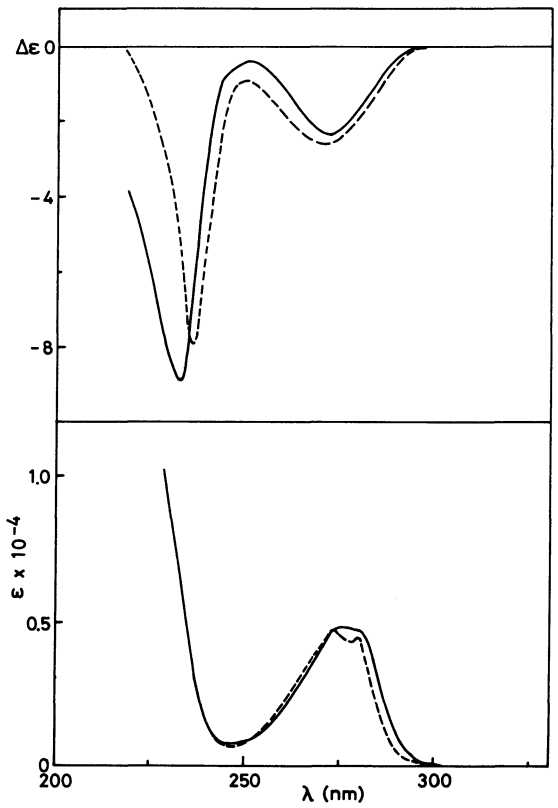


Fig. 1. CD and UV spectra of polyamde **3a** (——) and model diamide **8a** (------) in the film state.

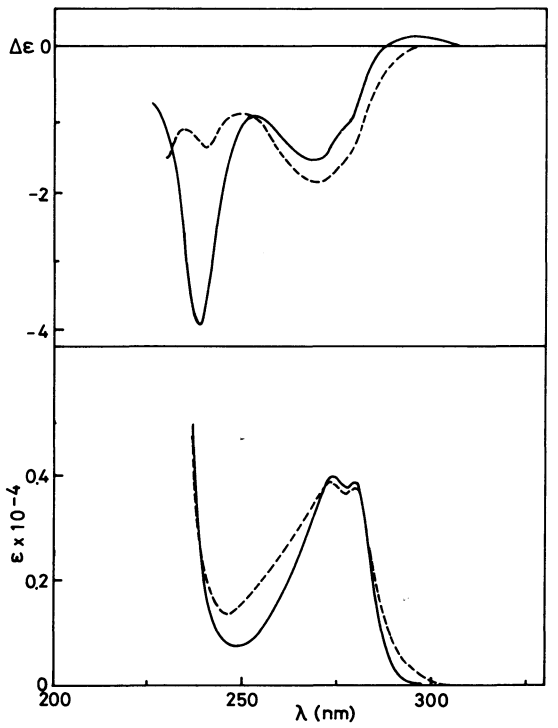


Fig. 2. CD and UV spectra of polyamide **3g** (——) and model diamide **8g** (------) in the film state.

observed for **3g**. Namely, *O*-methylated polyamide **3g** shows stronger CD band at ca. 240 nm than that of model diamide **8g**, while the band at 270 nm is weaker than that of **8g** as shown in Fig. 2.

Similarity in the CD shape between **3a** and **8a**, and between **3g** and **8g**, suggests that they possess similar conformational preference, resulting from the asymmetric cyclobutane ring. But the enhancement of the band at 230—240 nm indicates that **3a** and **3g** aggregate by the interaction between the amide groups, respectively, although **3a** and **3g** exist essentially in a random conformation.

In the case of polyamide **3c**, both negative CD bands are weaker in intensity than those of model diamide **8c** (Fig. 3). This is a typical phenomenon for a completely random conformation.[5] Then, **3c** would exist in a random conformation in the film state.

The preparation of the thin film of **8b** was not successful since it precipitated out and became opaque on drying. Then, the chiroptical study of polyamide **3b** could not be conducted by comparing directly the CD spectrum of **3b** with that of **8b**. But the CD spectrum is very similar to that of **3c**, indicating that **3b** exists in a random conformation in the film state. The random conformation would result from the flexibility of the diamine component and the lack of amide hydrogen.

Considering the structural difference between **3a**, **3b**, and **3g**, it would be concluded that the amide hydrogen plays an important role for macromolecular aggregation but the phenolic hydroxyl does not. The lack of aggregation in polyamide **3c** would be attributed to the steric crowd near by the amide group.

The CD bands of polyamides **3d** and **3h** at the wavelength shorter than 250 nm degenerate significantly in comparison with those of **8d** and **8h**, respectively, as shown in Figs. 4 and 5. The much smaller mean residue rotation and molecular circular dichroism of **3h** in DMAc than those of **8h**, similar to that observed between **3d** and **8d**,[1,2] indicate the existence of a rigid conformation of **3h** in DMAc. The Corey-Pauling-Koltun space-filling molecular models of **3d** and **3h** show that the diacid component is in a very tight conformation and that neither polymer main chain nor hydroxyphenyl (or methoxyphenyl) group in the side chain can rotate. On the basis of these observations, it seems possible to say that polyamides **3d** and **3h**, derived from piperazine, have a fixed rod-like conformation in the film state as well as in solution.

The film-state UV and CD spectra of polyamide **3e** and model diamides **8e, e'** are shown in Fig. 6. Model diamide **8e** shows normal negative CD bands at 235—245 and 270—285 nm, which can be assigned to a component of the split π-π^* transition of the amide carbonyl chromophore and the π-π^* transition of the

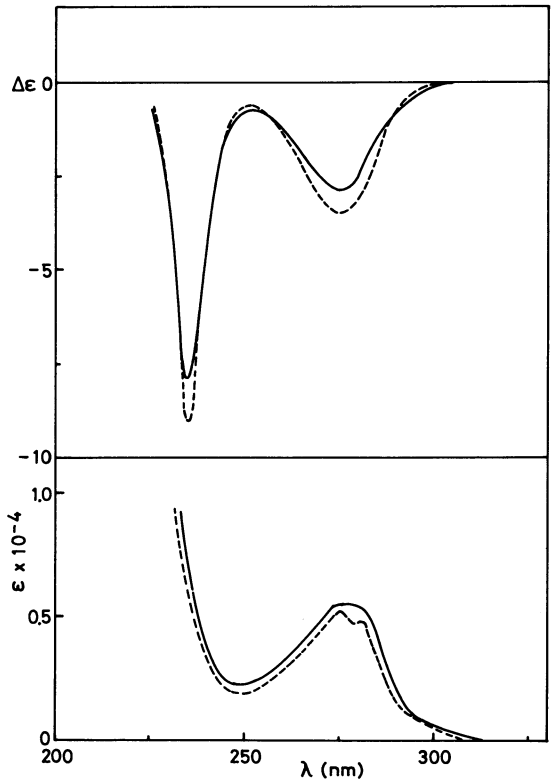


Fig. 3. CD and UV spectra of polyamide **3c** (——) and model diamide **8c** (------) in the film state.

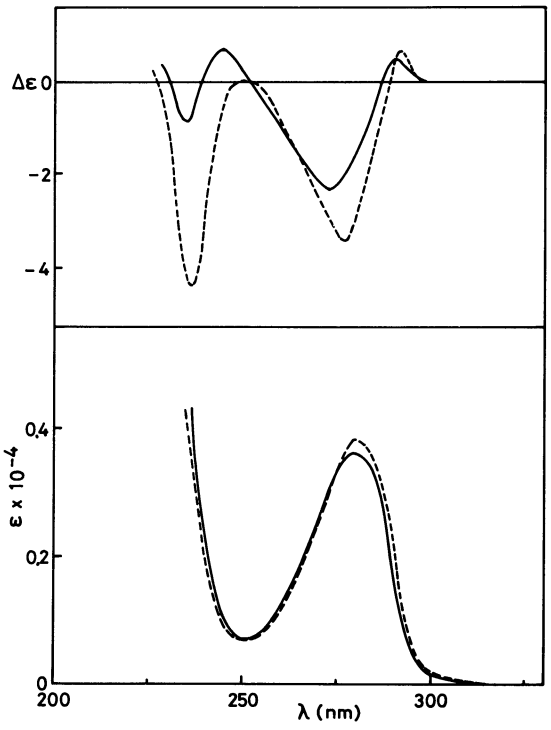


Fig. 4. CD and UV spectra of polyamide **3d** (——) and model diamide **8d** (------) in the film state.

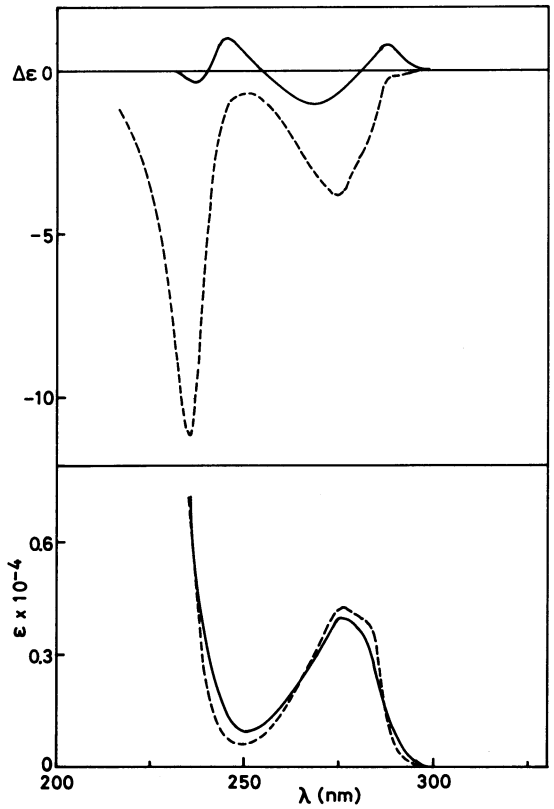


Fig. 5. CD and UV spectra of polyamide **3h** (——) and model diamide **8h** (------) in the film state.

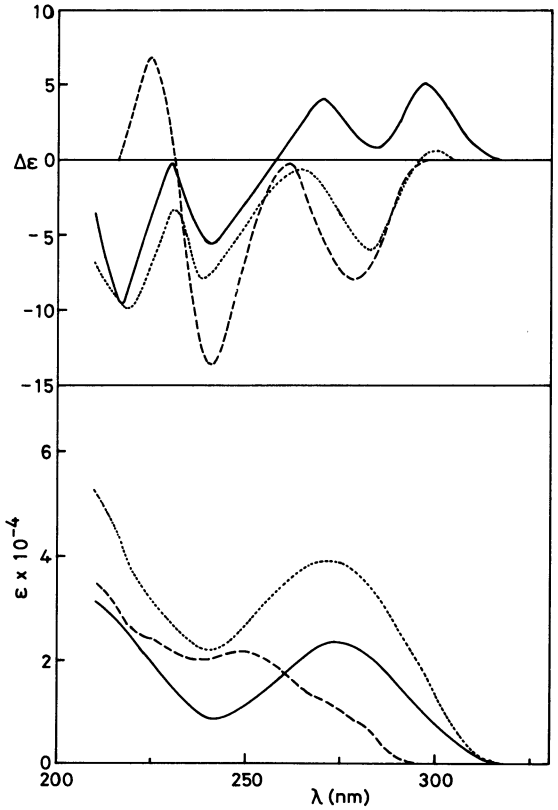


Fig. 6. CD and UV spectra of polyamide **3e** (——) and model diamide **8e** (------), **8e′** (·····) in the film state.

aromatic chromophore, respectively. The red shift and increased intensity of the UV absorption of **8e′** in comparison with that of **8e** would be attributed to the extension of its mesomeric region. But, this extension in **8e′** results only in a little decrease and shift of the CD bands at 235—245 and 270—285 nm. However, in the CD spectrum of **3e**, two *positive* CD bands appear at 265—275 and 290—302 nm in contrast to the *negative* bands of **8e** and **8e′** at 270—285 nm. These two positive CD bands would be attributed to the π–π^* transitions of 2-hydroxyphenyl group in the side chain and 1,4-phenylenediamine residue in the main chain. Then, the drastic difference is considered to result from a second ordered conformation, for which the aromatic residues in the main and side chains probably play an important role. Similar CD spectral change was observed for **3e** in DMAc on addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The CD spectrum of **3e** in the film state is quite similar to that of **3e** in DMAc when DBU/hydroxyphenyl in the side chain is 2.[2] But, it is not so developed as observed in 0.2 M (1 M=1 mol dm^{-3}) NaOH, in which **3e** exists in a fully developed ordered conformaion.[2] This means that in the dry film state **3e** exists in an ordered conformation of macromolecular asymmetry though it is incomplete.

As shown in Fig. 7, *O*-methylated polyamide **3i**

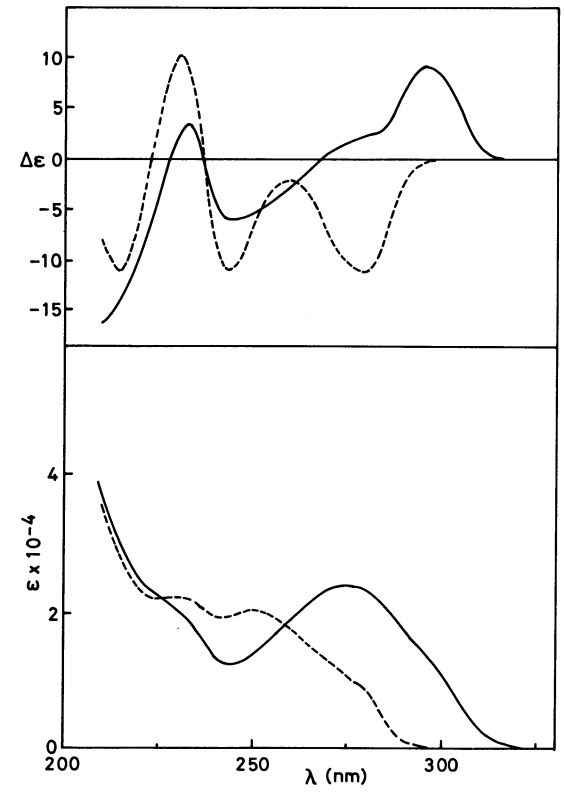


Fig. 7. CD and UV spectra of polyamide **3i** (——) and model diamide **8i** (------) in the film state.

shows CD bands similar to that of **3e**, i.e. the *positive* band at 290—300 nm with shoulder at 270—285 nm. This means that **3i** forms an ordered conformation similar to that of **3e** in spite of its lack of phenolic hydroxyl group in the side chain.

From these results, it is considered that the ordered conformation of **3e** and **3i** in the film state would be attributed to the hydrogen bonding of amide residue, which renders the polymer main chain taking a macromolecular asymmetry to release the strain.[7,8] To ascertain the contribution of the amide hydrogen to the ordered conformation, the preparation of the polyamide, consising of **1** and *N,N'*-dimethyl-1,4-phenylenediamine, was tried. But, the reaction gave only low-molecular-weight polyamide. Then, the contribution could not be demonstrated directly.

As shown in Fig. 8, the CD bands of **3f** at 255—300 nm tends to appear in *positive* region in contrast to those of negative bands of **8f** and **8f'**. This means that **3f** is also in an ordered conformation of macromolecular asymmetry, although this ordered conformation is less developed than that of **3e** due to the flexibility of the diphenyl ether linkage.

On the basis of these CD spectral studies, the following chiroptical property in the dry film state is concluded for polyamide **3**: Polyamides **3a**—**c** and **3g**, derived from acyclic aliphatic diamines, exist essentially in a random conformation due to the flexibility of the diamine components, but **3a** and **3g** show an aggregation phenomenon, for which the amide hydrogen is important. Polyamides **3d** and **3h**, derived from piperazine, have a fixed rod-like conformation due to their very rigid and tight main chain. Polyamides **3e**, **3f**, and **3i** exist in an ordered conformation of macromolecular asymmetry though it is incomplete. In the formation of the ordered conformation, the structure of the diamine component and the amide hydrogen play an important role. At present, these ordered conformations of **3e**, **3f**, and **3i** cannot be specified, but they possess the possibility to form a sheet and/or helical conformation in the dry film state. The chiroptical property of the polyamides in the film state is summarized in Table 2 with that in solution.[2]

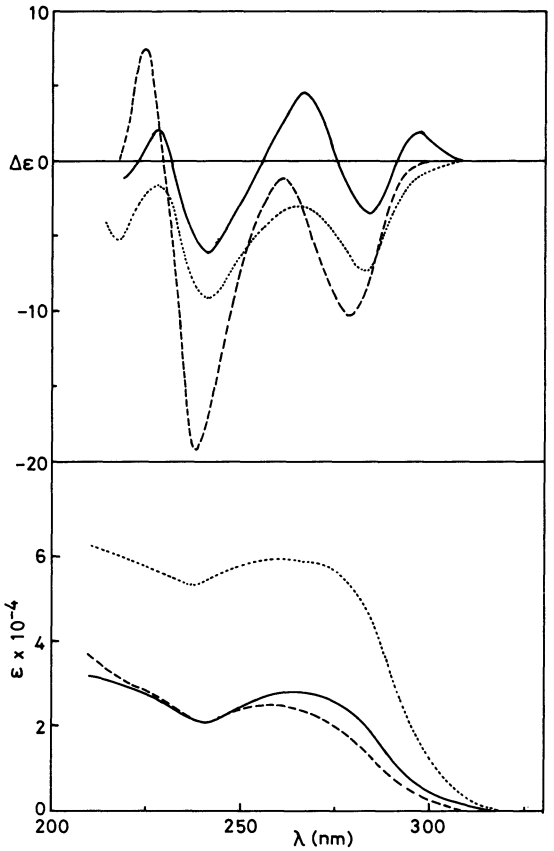


Fig. 8. CD and UV spectra of polyamide **3f** (——) and model diamide **8f** (------), **8f'** (·····) in the film state.

Table 2. Conformation of Polyamides **3a**—**i** in the Film State with that in Solution

Polyamide	In solution		Film state
	DMAc	Basic media	
3a	random	random	aggregation
3b	random	—[a]	random
3c	random	random	random
3g	random[b]	—[a]	aggregation
3d	ordered (rigid)	ordered (rigid)	ordered (rigid)
3h	ordered[b] (rigid)	—[a]	ordered (rigid)
3e	random	ordered	ordered
3f	random	ordered	ordered
3i	ordered[b]	—[a]	ordered

a) Insoluble. b) The chiroptical property of *O*-methylated polyamides in DMAc was investigated in this work.

Experimental

Measurement. Melting points were determined on a Laboratory Devices Mel-Temp and are uncorrected. The IR spectra were obtained on a Jasco IR-810 spectrophotometer. ^{1}H NMR spectra were recorded with a Hitachi R-40 (90 MHz) spectrometer. The optical rotations were measured with a Jasco DIP-360 digital polarimeter at 20 °C in a 1.0 dm cell. The inherent viscosities of the polyamides were measured at 30 °C with an Ostwald viscometer at the concentration of 0.30 g dl^{-1}. The circular dichroism and UV spectra were measured on a Jasco J-500 spectropolarimeter and on a Shimadzu UV-260 spectrophotometer, respectively, at room temperature.

Materials. (−)-Anti head-to-head coumarin dimer (**1**) was obtained from the racemate by the diasteriomeric resolution method as reported in the previous paper.[9] Before use, **1** was recrystallized from benzene and dried at 60 °C in vacuo (ca. 2 mmHg) for 24 h: $[\alpha]_D$ −9.0° (*c* 1.00, benzene), almost 100% enantiomeric excess on the basis of

HPLC analysis of its diamide derivative with *S*-(−)-1-phenylethylamine.[10]

3,4-Bis(2-methoxyphenyl)-1,2-cyclobutanedicarbonyl Dichloride (6). To a solution of **1** (7.31 g, 25.0 mmol) in acetone/2.0 M NaOH (73 ml/150 ml) was added dropwise dimethyl sulfate (99.21 g, 786 mmol) in a period of one hour at room temperature. After stirring for 4 h at the temperature, acetone was evaporated, and the mixture was extracted with carbon tetrachloride (150 ml×3). The evaporation of the solvent to dryness gave an oily product. The purification of the crude product by silica-gel chromatography (eluent: hexane/ethyl acetate=60/40 (v/v)), followed by recrystallization from hexane/acetone, gave 6.00 g (63%) of dimethyl 3,4-bis(2-methoxyphenyl)-1,2-cyclobutanedicarboxylate (**4**): Mp 85.5—86.5 °C; $[\alpha]_D$ −169.8° (*c* 0.5, chloroform); IR (KBr) 1720, 1240, 1020, and 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.25 (6H, s), 3.77 (8H, s with shoulder), 4.75 (2H, pseudo d, *J*=8.0 Hz), and 6.5—7.2 (8H, m).

Found: C, 68.93; H, 6.40%. Calcd for $C_{22}H_{24}O_6$: C, 68,74; H, 6.29%.

Diester **4** (4.61 g, 12.0 mmol) was hydrolyzed in a solution of 1.0 M NaOH/MeOH (50 ml/25 ml) at 50 °C for 5 h, and then the solution was acidified with 1.0 M HCl after evaporation of methanol. The precipitates appeared were collected by filtration and recrystallized from water/ethanol to give 3.65 g (85%) of 3,4-bis(2-methoxyphenyl)-1,2-cyclobutanedicarboxylic acid (**5**): Mp 268.0—269.5 °C: $[\alpha]_D$ −121.2° (*c* 0.5, MeOH); IR (KBr) 2600, 1700, 1246, 1030, and 757 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ=3.5 (2H, pseudo d, *J*=8.0 Hz), 4.6 (1H, pseudo d, *J*=8.0 Hz), 3.75 (6H, s), 6.4—7.2 (8H, m), and 11.75 (2H, s).

Found: C, 67.37; H, 5.65%. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66%.

Dicarboxylic acid **5** (3.65 g, 10.2 mmol) was refluxed in a mixture of thionyl chloride/benzene (75 ml/90 ml) for 2 h until the solution became clear. After evaporation of thionyl chloride and benzene, the residue was recrystallized from hexane to give 3.70 g (92%) of 3,4-bis(2-methoxyphenyl)-1,2-cyclobutanedicarbonyl dichloride (**6**): ^1H NMR ($CDCl_3$) δ=3.78 (6H, s), 4.2—4.7 (4H, m), and 6.5—7.3 (8H, m). Bis(acid chloride) **6** was immediately used in the interfacial synthesis of polyamides and model diamides without further purification

General Procedure for Synthesis of Polyamides 3. The synthesis of optically active polyamides **3a—f** by ring-opening polyaddition reaction has been described in the previous paper.[2]

O-Methylated polyamides **3g—i** were synthesized by the interfacial polycondensation reaction of **6** with the corresponding diamines as follows: To a solution of diamine (2.78 mmol) in 12 ml of 1.0 M NaOH was added 0.63 g of benzyltriethylammonium chloride (2.78 mmol) as a phase-transfer catalyst. Then, a chloroform solution (11 ml) of **6** (1.09 g, 2.78 mmol) was added to the aqueous solution at once under vigorous stirring at room temperature. The precipitates appeared were collected by filtration, washed successively with methanol and hot water, and dried in vacuo at 80 °C for 48 h.

Polyamide 3g: Yield 84%; η_{inh}=1.01 dl g^{-1} (*m*-cresol); $[\alpha]_D$ −70.3° (*c* 0.3, *m*-cresol); IR (KBr) 3500—3300, 3000—2800, 1645, 1525, 1247, 1024, and 755 cm^{-1}.

Found: C, 68.47; H, 6.97; N, 5.85%. Calcd for $(C_{26}H_{32}N_2O_4 \cdot H_2O)_n$:C, 68.70; H, 7.54; N, 6.16%.

Polyamide 3h: Yield 86%; η_{inh}=1.00 dl g^{-1} (DMAc); $[\alpha]_D$ −40.7° (*c* 0.3, DMAc); IR (KBr) 3600—3300, 3100—2800, 1630, 1243, 1028, and 755 cm^{-1}.

Found: C, 67.25; H, 6.25; N, 6.36%. Calcd for $(C_{24}H_{26}N_2O_4 \cdot H_2O)_n$: C, 67.90; H, 6.65; N, 6.60%.

Polyamide 3i: Yield 99%; η_{inh}=0.50 dl g^{-1} (DMAc); $[\alpha]_D$ +5.7° (*c* 0.3, DMAc); IR (KBr) 3600—3200, 3100—2800, 1668, 1545, 1245, 1026, and 755 cm^{-1}.

Found: C, 69.82; H,5.24; N, 6.07%. Calcd for $(C_{26}H_{24}N_2O_4 \cdot H_2O)_n$: C, 69.94; H, 5.87; N, 6.27%.

General Procedure for the Synthesis of Model Diamides 8. The synthesis of optically actically active diamides (**8a—f**) by ring-opening addition reaction has been reported in the previous paper.[2] Model diamides **8e′**, **8f′** were also synthesized by this method.

The general procedure for the synthesis of *O*-methylated model diamides **8g—i** by interfacial condensation reaction is described as follows: To a solution of amine (4.00 mmol) in 2.0 ml of 1.0 M NaOH was added dropwise a chloroform solution (2.0 ml) of **6** (0.16 g, 0.40 mmol) in a period of 5 min under vigorous stirring at room temperature. After stirring for additional 10 min, chloroform was evaporated, and the remaining solid mass was collected by filtration. The recrystallization gave the corresponding 3,4-bis(2-methoxyphenyl)-1,2-cyclobutanedicarboxamide (**8g—i**).

***N,N′*-Bis(4-acetylaminophenyl)-3,4-bis(2-hydroxyphenyl)-1,2-cyclobutanedicarboxamide (8e′)**: Light brown prism (EtOH-H_2O); yield 79%; mp 198 °C (decomp); $[\alpha]_D$ −131.4° (*c* 0.3, DMAc), −109.9° (*c* 0.3, 0.37 M NaOH); IR (KBr) 3600—2800, 1660, 1610, 1255, 1020, 940, 840, and 760 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ=1.90 (6H, s), 3.81 (2H, pseudo d, *J*=8.0 Hz), 4.73 (2H, pseudo d, *J*=8.0 Hz), 6.4—7.5 (16H, m), 9.2—9.5 (4H, 2 peaks), and 9.61 (2H, s).

Found: C, 66.92; H, 5.40; N, 9.07%. Calcd for $C_{34}H_{32}N_4O_6 \cdot H_2O$: C, 66.87; H, 5.61; N, 9.18%.

***N,N′*-Bis[4-(4-acetylaminophenoxy)phenyl]-3,4-bis(2-hydroxyphenyl)-1,2-cyclobutanedicarboxamide (8f′)**: Light yellow needle (dioxane-EtOH); yield 48%; mp 184.0—185.5°C; $[\alpha]_D$ −69.6° (*c* 0.3, DMAc); IR (KBr) 3600—3000, 1660, 1610, 1220, 1020, 830, and 755 cm^{-1}: ^1H NMR (Me_2SO-d_6) δ=2.00 (6H, s), 3.87 (2H, pseudo d, *J*=8.0 Hz), 4.80 (2H, pseudo d, *J*=8.0 Hz), 7.3—8.6 (24H, m), 9.43 (4H, s), and 9.80 (2H, s).

Found: C, 69.63; H, 5.29; H,7.30%. Calcd for $C_{46}H_{40}N_4O_8 \cdot H_2O$: C, 69.51; H, 5.33; N, 7.05%.

***N,N′*-Dihexyl-3,4-bis(2-methoxyphenyl)-1,2-cyclobutanedicarboxamide (8g)**: Colorless prism (EtOH-H_2O); yield 66%; mp 131.5—132.0 °C; $[\alpha]_D$ −81.0 ° (*c* 0.3, *m*-cresol); IR (KBr) 3330, 3000—2800, 1645, 1250, 1030, and 750 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ=0.5—1.4 (22H, m), 3.42 (2H, pseudo d, *J*=8.0 Hz), 3.75 (6H, s), 4.57 (2H, pseudo d, *J*=8.0 Hz), and 6.3—7.3 (8H, m).

Found: C, 73.26; H, 8.84; N, 5.06%. Calcd for $C_{32}H_{46}N_2O_4$: C, 73.53; H, 8.87; N, 5.36%.

***N,N′*-[3,4-Bis(2-methoxyphenyl)-1,2-cyclobutanedicarbonyl] bis[piperidine] (8h)**: Colorless prism (EtOH-H_2O); yield 80%; mp 212.5—214.0 °C; $[\alpha]_D$ −83.0 ° (*c* 0.3, DMAc); IR (KBr) 3450, 3100—2800, 1622, 1245, 1030, and 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.4—1.5 (12H, m), 2.6—3.4 (8H, m), 3.7 (6H, s), 4.17 (2H, pseudo d, *J*=8.0 Hz), 4.86 (2H, pseudo d, *J*=8.0 Hz), and 6.5—7.3 (8H, m).

Found: C, 73.17; H, 7.72; N, 5.42%. Calcd for $C_{30}H_{38}N_2O_4$: C, 73.44; H, 7.81; N, 5.71%.

3,4-Bis(2-methoxyphenyl)-1,2-cyclobutanedianilide (8i): Colorless needle (benzene–hexane); yield 73%; mp 221.0—222.0 °C; $[\alpha]_D$ −32.7° (*c* 0.3, DMAc); IR (KBr) 3400, 3100—2800, 1675, 1600, 1245, 1022, and 755 cm^{-1}: ^1H NMR (Me_2SO-d_6) δ=3.73 (8H, s with shoulder), 4.67 (2H, pseudo d, J=8.0 Hz), 6.2—7.5 (18H, m), and 9.37 (2H, s).

Found: C, 75.75; H, 5.90; N, 5.39%. Calcd for $C_{32}H_{30}N_2O_4$: C, 75.87; H, 5.97; N, 5.53%.

Preparation of Thin Films for Chiroptical Study. The thin films of the polyamides and model diamides were prepared by casting their solution (ca. 30 mg ml^{-1} DMAc) on the outside surface of a quartz cell (10×45×10 mm). The coated films were dried at ambient air and then in vacuo for 24 h at room temperature. The obtained thin films were at the concentration of ca. 10^{-4} repeating-unit mmol (or mmol) cm^{-2}. All CD spectra were given in $\Delta\varepsilon$, molecular circular dichroism, with cm^2/repeating-unit-mmol (or mmol) unit, which was calculated by the following equation:

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

where MW is the repeating-unit molecular weight (or molecular weight) of the polyamide (or the model diamide); 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}$).

Thin film were also cast on the outside surface of a cylindrical quartz cell [10×20 (o.d.) mm], and each CD measurement was repeated four times by rotating the sample cell by 45, 90, and 120 degrees from the first position around the axis of the incident light beam to give almost identical spectra.

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