2830 *Macromolecules* **1990,** *23,* 2830–2836

Optically Active Polyamides Consisting of Anti Head-to-Head Coumarin Dimer and α,ω-Alkanediamine. Odd–Even Discrimination in Chiral Recognition Ability Depending on the Methylene Number of the Diamine Component and Correlation between the Ability and Crystallizability[1]

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Received September 12, 1989; Revised Manuscript Received November 28, 1989

ABSTRACT: Optically active polyamides, derived from (–)-anti head-to-head coumarin dimer and α,ω-alkanediamines, possess possible interaction sites for chiral recognition. Their chiral recognition ability was evaluated by using them as chiral stationary phases for high-performance liquid chromatography; they were found to be highly dependent on the methylene number in the diamine components. The polyamides, consisting of a diamine with an even methylene number, showed a sufficient chiral recognition ability, while the polyamides with an odd methylene number did not at all. This odd–even discrimination in chiral recognition was in good agreement with the crystallizability of the polyamides; i.e., only crystallizable polyamides showed a chiral recognition ability. The chiral recognition ability was also closely related to the degree of crystallinity and to the superstructure of the polyamides. The degree of crystallinity of the polyamides coated on the surface of silica gel was significantly influenced by the poor solvent for washing and by the quantity of a residual coating solvent.

Introduction

With the increasing demand for optically active compounds in the medical field, food technology, functional material science, and so on, the development of a new method has been required for the rapid resolution of enantiomers with a high enantiomeric purity. One solution to meet such a requirement is a direct high-performance liquid chromatographic separation upon a chiral stationary phase having a high chiral recognition ability.[3–6] Great effort has been made to develop new macromolecular chiral stationary phases, but only a few of them show a high chiral recognition ability and are practically useful as chiral stationary phases for high-performance liquid chromatography.[7–12] On the other hand, an evaluation of the correlation between the structure of a macromolecule and its chiral recognition ability is very important for developing a new chiral stationary phase having a high chiral recognition ability.

Recently, we have found that optically active polyamides,[13] derived from (–)-anti head-to-head coumarin dimer[14] and diamines, had a high chiral recognition ability and were applicable as chiral stationary phases for the liquid chromatographic resolution of racemates, depending on the structure of the diamine components.[15] The polyamide, derived from 1,6-hexanediamine, showed an excellent chiral recognition ability to racemates containing aromatic group(s).[15] Its chiral recognition was based on simultaneous interactions between the functional groups in the polymer chain and in the racemates, as observed for low molecular weight chiral stationary phases.

In order to elucidate the role of the 1,6-hexanediamine residue in chiral recognition, a series of homologous polyamides were synthesized from (–)-anti head-to-head coumarin dimer and α,ω-alkanediamines ($H_2N(CH_2)_mNH_2$, $m = 2$–10) by a ring-opening polyaddition reaction in solution. In this paper, we report on their chiral recognition ability and discuss the relationship between the resulting distinct odd–even discrimination in the chiral recognition and the structure of the polyamides coated on the surface of silica gel.

Experimental Section

Materials. The (–)-anti head-to-head coumarin dimer (1) employed in this work was prepared from the corresponding racemate by the diastereomeric resolution method, as described in an earlier report.[14] Before use, 1 was recrystallized from benzene and dried at 60 °C in vacuo (ca. 2 mmHg) for 24 h: $[\alpha]^{21}{}_D$ $-9.0°$ (c 1.00, benzene); >99% ee on the basis of high-performance liquid chromatographic analysis of the diamide obtained by the reaction of 1 and (S)-1-phenylethylamine.

α,ω-Alkanedimers (2) (Scheme I) were distilled under atmospheric or reduced pressure, just before use.

1-Methyl-2-pyrrolidone (NMP) was distilled with benzene (v/v = 50/1) under reduced pressure (85–86 °C (10 mmHg)), and water was removed as benzene azeotrope. *N,N*-Dimethylacetamide (DMAc) was predried with molecular sieves (4A) and then distilled under reduced pressure before use (85–88 °C (34 mmHg)).

Measurements. Inherent viscosities were measured at 30 °C with an Ostwald viscometer. The concentrations were 0.30 g/dL in DMAc. ^1H NMR spectra were measured in DMSO-d_6 by using a JEOL GX-400 (400-MHz) spectrometer. Infrared spectra (KBr pellets) were measured with a Jasco IR-810 infrared spectrophotometer. DSC and TGA curves were recorded on Shimadzu DSC-50 and TGA-50 instruments, respectively, under a nitrogen stream with a heating rate of 10 °C/min. TGA mass were recorded on a Shimazu TGAMS-QP1000 instrument.

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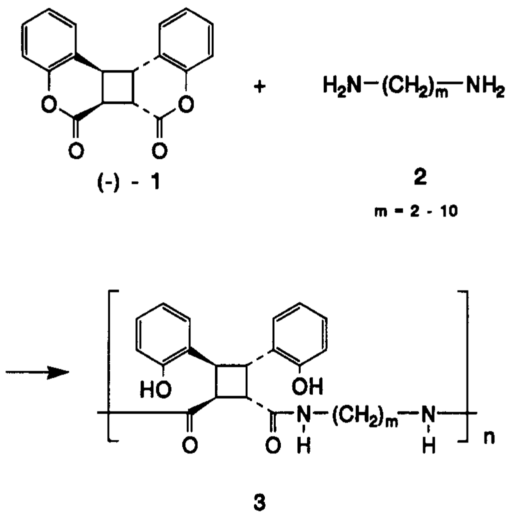
Scheme I



The crystallinity of polyamides was estimated on the basis of wide-angle X-ray diffraction (WAXD) measured by an apparatus with a Rigaku rotating-anode generator (Cu Kα, 50 kV, 200 mA) and with a position-sensitive proportional counter. The WAXD profiles were corrected for the air scattering, the polarization factor, and the absorption factor.

Synthesis of Polyamides. Polyamides 3 were synthesized by a ring-opening polyaddition reaction, as reported in a previous paper.[13] The general procedure for the reaction of (–)-1 with diamines 2 is described as follows: The diamine (ca. 3 mmol) was distilled into a 30-mL two-necked flask, and NMP was added in order to prepare a clear solution of ca. 0.5 mol/L concentration. With gentle stirring, finely powdered (–)-1 (an equimolar amount) was added to the solution, and the mixture was heated at 80 °C for 20 h. All of the operations were carried out under an argon atmosphere. After heating, the reaction mixture was diluted with NMP (10 mL) and was allowed to cool to room temperature. The solution was added drop by drop to methanol (200 mL). The precipitate was collected by filtration and treated with acetone under reflux for 2 h in order to remove residual NMP. The polyamides, thus obtained, were dried at 60 °C in vacuo for 24 h.

The yields and inherent viscosities of polyamides 3 are listed in Table I. The primary structures of polyamides 3 (m = 2–5, 7–10) were confirmed by comparison of their IR and ^{1}H NMR spectra with those of polyamide 3 (m = 6).[13] IR (KBr): 1640 (amide I), 1540 (amide II), 750 (1,2-disubstituted benzene) cm^{-1}. ^{1}H NMR (in DMSO-d_6, TMS, ppm): 9.4 (s, 2 H, phenolic hydroxyl), 7.2 (s, 2 H, amide), 7.0 (d, 2 H, J = 7.9 Hz, phenyl), 6.9 (t, 2 H, J = 8.1 Hz, phenyl), 6.7 (d, 2 H, J = 7.9 Hz, phenyl), 6.6 (t, 2 H, J = 7.5 Hz, phenyl), 4.6 (pseudo d, 2 H, cyclobutane), 3.5 (pseudo d, 2 H, cyclobutane). The signals of the methylene protons in the diamine components were observed in reasonable regions (0.7–3.0 ppm).

Evaluation of Chiral Recognition Ability. Polyamides 3 were coated on silica gel according to a method developed by Okamoto et al.,[7] as described below, and the chiral recognition ability of the polyamides was evaluated by using them as chiral stationary phases for high-performance liquid chromatography.

About a one-fifth portion of a DMAc solution of polyamides 3 (ca. 10 wt %) was added drop by drop onto macroporous silica gel (Nucleosil 1000-7) pretreated with diphenylsilane coupler; the silica gel was heated in vacuo for 2–5 h at each temperature indicated in Table V in order to remove the DMAc. The operations were repeated until all of the solution was added. Then, the silica gel, coated with the polyamide, was washed with methanol or hexane/2-propanol (v/v = 1/1). The silica gel was packed into a stainless steel column (25 × 0.46 (i.d.) cm) by the slurry method.

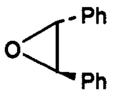
Direct chromatographic separation of racemates was accomplished on a Shimadzu LC-5A HPLC system with a UV detector and an optical rotatory detector at room temperature. A mixture of hexane/2-propanol (v/v = 9/1) was used as an eluent at a flow rate of 0.5 mL/min.

Results and Discussion

Preparation of Optically Active Polyamides. In a similar manner to the method reported in a previous paper,[13] optically active polyamides 3 were easily prepared by the ring-opening polyaddition reaction of (–)-anti head-to-head coumarin dimer 1 and α,ω-alkanediamines 2 (m is the number of methylene groups in α,ω-alkanediamine). As shown in Table I, polyamides 3 were obtained in high yields with a moderate to high inherent viscosity. These polyamides could be easily dissolved in aprotic polar solvents such as DMAc, NMP, and dimethyl sulfoxide (DMSO). Casting their solutions on a glass plate gave a transparent, flexible film, which was isotropic and homogeneous in the optical microscopic scale.

Chiral Recognition Ability of Polyamides 3. It is well-known that one of the driving forces for chiral recognition consists of simultaneous interactions between the functional groups in a chiral stationary phase and in a solute.[4] Optically active polyamides 3 possess possible interaction sites, i.e., phenolic hydroxyl group, aromatic group, and amide linkage. We then prepared silica gel coated with optically active polyamides 3 for high-performance liquid chromatography and chose racemates (4–8) having complementary aromatic group(s) and a hydrogen donating and/or accepting group in order to elucidate the chiral recognition ability of 3. The chiral recognition ability was evaluated by k_1' (capacity factor of less retained enantiomer: k_1' = (retention time of less retained enantiomer – dead time)/dead time), α (separation factor: α = capacity factor of more retained enantiomer/k_1'), and R_s (resolution factor: R_s = 2(difference of retention time of more and less retained enantiomers)/sum of the band width of two enantiomer peaks)).

Polyamides 3 (m = 2–4) showed no chiral recognition ability to all of the racemates examined. In contrast, the chiral recognition ability of polyamides 3 (m = 5–10) was highly dependent on the methylene number in the diamine components. The polyamides with an even methylene number showed a high chiral recognition ability (separation factor α is larger than 1.10) for racemates (4–8), while those with an odd methylene number showed no ability for any of the racemates. Namely, a distinct odd-even discrimination was observed in chiral recognition by these polyamides (Table II).



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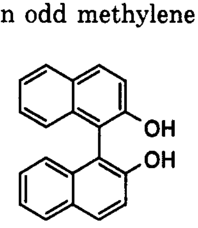

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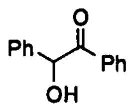

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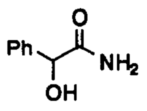

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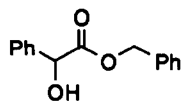

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Table I
Ring-Opening Polyaddition Reaction of 1 with 2[a]

	m								
	2	3	4	5	6	7	8	9	10
yield, %	99	84	85	81	90	85	96	80	94
η_{inh},[b] $dL \cdot g^{-1}$	0.34	0.33	0.42	0.43	0.72	0.40	0.51	0.39	0.44

[a] Concentration: 0.50 mol/L in NMP. Reaction temperature: 80 °C. [b] 0.30 g/dL in DMAc at 30 °C.

Table II
Resolution of Racemates 4–8 on Polyamides 3 (*m* = 5–10) Coated Silica Gel Columns[a]

	racemates														
	4			5			6			7			8		
m	k_1'	α	R_s	k_1'	α	R_s	k_1'	α	R_s	k_1'	α	R_s	k_1'	α	R_s
5	0.71	1		5.00	1		2.96	1		8.12	1		2.12	1	
6	0.40 (–)	1.42	0.92	4.36 (–)	1.17	0.60	1.91 (–)	1.43	1.45	5.59 (–)	1.29	0.88	1.60 (–)	1.10	0.60
7	0.70	1		3.55	1		3.90	1		8.84	1		2.70	1	
8	0.65 (–)	1.19	0.85	7.72 (–)	1	PR[a]	2.26 (–)	1.27	0.96	4.86 (–)	1.19	0.60	1.88 (–)	1.12	0.60
9	0.67	1		5.40	1		2.39	1		4.64	1		1.75	1	
10	0.53	1		7.79 (–)	1.30	0.92	2.38 (–)	2.14	14.70	6.19 (–)	1.36	3.51	2.46 (–)	1.09	0.60

[a] Partial resolution, which could be detected only with an optical rotatory detector.

When a macromolecule is used as a chiral stationary phase for high-performance liquid chromatography, its chiral recognition ability is considered to come from a macromolecular asymmetry of the polymer main chain[7] and/or multiple simultaneous interactions between the functional groups in the polymer and in a solute.[8-12] Polyamides **3** (*m* = 2–10) gave no significant circular dichroism (CD) bands enhanced by a macromolecular asymmetric structure in solutions or in a cast film state. Thus, the chiral discrimination of polyamides **3** might be attributed to a difference in the environment of polyamides **3** on the surface of silica gel (discussed below).

On the basis of the consideration mentioned above, the reason for no chiral recognition by polyamides **3** (*m* = 2–4) would be explained as follows: Upon decreasing the methylene number in the diamine component, the repulsion between the functional groups on the cyclobutane rings in the main chain increases to make the conformation of polyamides **3** on the surface of silica gel disadvantageous for interactions with the racemates. But, the distinct odd–even discrimination of polyamides **3** (*m* = 5–10) is unable to be understood simply by a similar explanation.

In order to clarify the origin of the odd–even discrimination, the structure of polyamide **3** (*m* = 6) coated on silica gel was initially elucidated.

Structure of Polyamide 3 (*m* = 6) on Silica Gel. No valuable information concerning the structure of polyamide **3** (*m* = 6) coated on silica gel could be obtained from its infrared, ultraviolet, and photoacoustic ultraviolet spectra and X-ray diffraction, since the absorptions and diffraction by **3** (*m* = 6) on silica gel were very weak in comparison with the background of silica gel. Differential scanning calorimetry (DSC) using naked silica gel as a reference, however, afforded valuable information concerning the thermal behavior of the polyamide on silica gel.

Figure 1 shows DSC curves of polyamide **3** (*m* = 6) (a) reprecipitated upon the addition of a DMAc solution into methanol ("as-prepared"), (b) cast from a 5 wt % DMAc solution ("as-cast"), and (c) coated on silica gel pretreated with silane coupler ("coated"). All of the samples showed an endothermic peak at about 240 °C and an exothermic peak around 270 °C with an obvious weight loss, which was detected in their thermal gravimetric analysis (TGA) curves. On the basis of these data, it is concluded that these peaks result from the degradation of **3** (*m* = 6). Moreover, a broad endothermic peak at around 80 °C for as-prepared and as-cast samples or at 120 °C for a coated one was ascribed to the vaporization of a small amount of low molecular weight molecules contained in the polyamide, such as H_2O and DMAc, which were detected by TGA mass spectroscopy. Other than these peaks, coated polyamide **3** (*m* = 6) as well as the as-prepared sample showed a sharp endothermic peak at 216 °C. By contrast, as-cast polyamide **3** (*m* = 6) showed no distinct peak up to the temperature of its thermal decomposition. Namely, the thermal behavior of coated polyamide **3** (*m* = 6) is similar to that of the as-prepared polyamide rather than the as-cast polyamide.

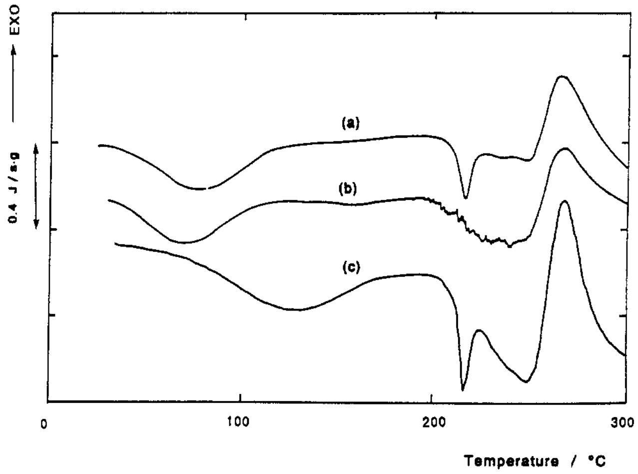

Figure 1. DSC thermograms of **3** (*m* = 6) (a) reprecipitated ("as-prepared"), (b) cast from a DMAc solution ("as-cast"), and (c) coated on silica gel pretreated with silane coupler ("coated"). The thermogram of (c) is magnified by 5 in the vertical axis.

To prepare coated polyamide **3** (*m* = 6), a DMAc solution of **3** (*m* = 6) was added drop by drop to silica gel, and the solvent was removed under reduced pressure, followed by washing with methanol or another solvent. In the stage just after removal of DMAc, a considerable amount of DMAc, however, remained in the polyamide coated on silica gel, which was determined by a ^1H NMR spectrum of the DMSO-d_6-soluble part of the silica gel coated with polyamide **3** (*m* = 6) (see Table V). Then, the washing of coated polyamide **3** (*m* = 6), which still contained DMAc, would result in a similar operation to reprecipitation.

Table III
Peak Decomposition for WAXD Profiles of 3 ($m = 6$) in Semicrystalline (Molded Specimen) and Amorphous (Annealed Specimen) States

	molded specimen[a] for peak no.				annealed specimen[b] for peak no.		
	1	2	3	4	1	2	3
$2\theta_{max}$, deg	7.50	12.97	22.53	28.25	8.57	15.97	22.22
d_{Bragg},[c] Å	11.78	6.82	3.94	3.16	10.31	5.56	4.00
peak intensity[d]	1	0.44	0.93	0.73	0.69	0.48	0.94
half-width, deg	2.18	4.02	3.97	5.84	3.99	9.39	9.37
integral intensity[d]	1	2.4	14.9	15.4	3.7	21.2	63.1
half-width/$2\theta_{max}$[e]	0.29	0.31	0.18	0.21	0.47	0.59	0.42

[a] The excess scattering due to crystalline diffraction (Figure 5c). [b] The amorphous diffraction (Figure 5b). [c] Spacing calculated from Bragg's equation. [d] Relative to the crystalline diffraction numbered 1. [e] Index for the sharpness of each decomposed peak.

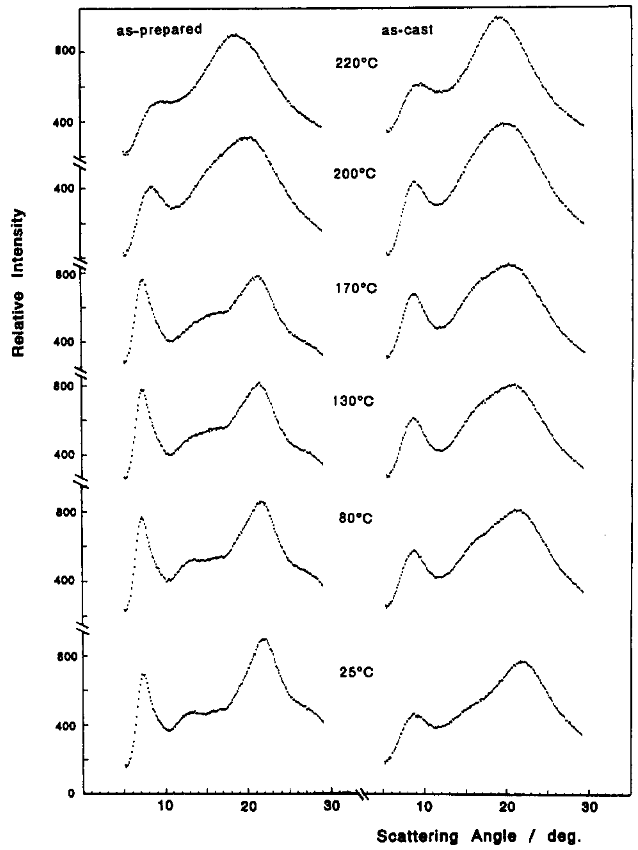

Figure 2. Temperature dependence of WAXD profiles for as-prepared and as-cast 3 ($m = 6$).

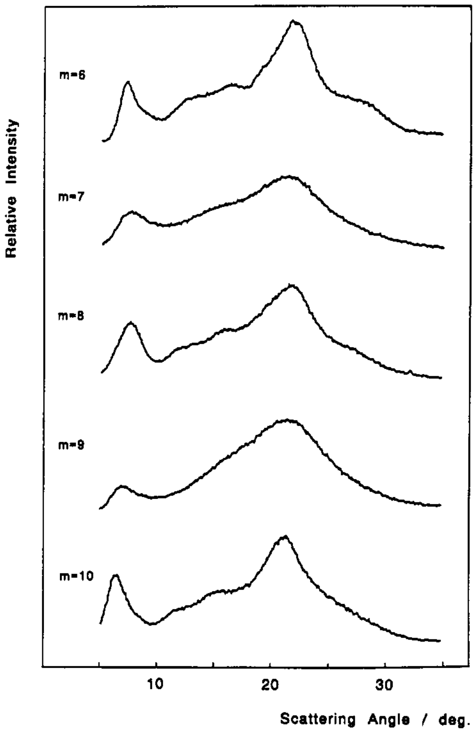

Figure 3. WAXD profiles of as-prepared 3 (m = 6–10) measured at 25 °C.

Table IV
Dependence of Crystallinity of 3 ($m = 6$) on the Solvent Quality Used for Reprecipitation[a]

entry	solvent for reprecipitation	polyamide 3 ($m = 6$) mp, °C	polyamide 3 ($m = 6$) crystallinity, %
1	benzene		0
2	2-propanol/hexane (1/1)	211.2	10
3	2-propanol	216.2	24
4	MeOH	216.7	33
5	H_2O		0

[a] Reprecipitated at 20 °C on addition of 5 mL of 10 wt % DMAc solution in ca. 100 mL of each solvent.

The similarity in the DSC curves of coated and as-prepared polyamides 3 ($m = 6$) indicates that the coated polyamide has the same structure as that of the as-prepared polyamide but different from that of the as-cast polyamide. Subsequently, the structure of coated polyamides 3 would be estimated from that of as-prepared polyamides 3 on the basis of DSC and WAXD analyses, although the structure could not be estimated on the basis of a CD spectral analysis, due to the fact that the as-prepared polyamides 3 were fibrous powders.

Dependence of Odd–Even Discrimination on Crystallizability. The temperature dependence of WAXD profiles of as-prepared and as-cast polyamide 3 ($m = 6$) are shown in Figure 2. The profiles were measured as a function of the temperature in the following way. The WAXD profile for the as-prepared (or as-cast) specimen was first measured at 25 °C. The same specimen was heated up to 80 °C and annealed at this temperature for 30 min, and the WAXD profile was then measured at that temperature. In the same way, annealing was carried out for 30 min at each temperature before each measurement at that temperature. The WAXD profiles of the as-prepared polyamide changed significantly at temperatures between 170 and 200 °C, while those of the as-cast polyamide hardly changed at temperatures from 25 to 220 °C. The profiles of the as-prepared polyamide at temperatures above 200 °C became almost identical with those of the as-cast polyamide at the corresponding temperatures.

For the as-cast specimen, polyamide 3 ($m = 6$) showed no characteristic small-angle X-ray scattering arising from a heterogeneous structure in a spatial scale of a few 10 nm, except for the thermal diffuse scattering. Moreover, the specimen possessed neither optical anisotropy nor heterogeneity in the optical microscopic scale. These observations indicate that the as-cast polyamide is amor-

Table V
Preparation of Silica Gel Columns Coated with 3 ($m = 6$)

run	washing solv	dry-up temp, °C	residual solv,[a] wt %	w_p,[b] %	mp, °C	$-\Delta H_m$, J/g	w_c, %
1	methanol	20	17	16.7	219.4	7.09	23
2		20	55	16.1	219.8	7.18	23
3		60	6	17.1	219.2	7.37	24
4		110	4	13.0	218.2	6.98	23
5	2-PrOH/hexane (1/1)	20	46	20.5	213.1	5.38	18
6		60	22	20.6	196.1	1.97	6
7		110	6	15.0	c	0	0

[a] The ratio of residual DMAc included in the polyamide before washing per polyamide. [b] The ratio of the coated polyamide per the whole polyamide-coated silica gel, which corresponds to the weight loss on treatment of the coated silica gel under oxygen atmosphere at 980 °C for 5 min. [c] The endothermic peak for melting was not observed.

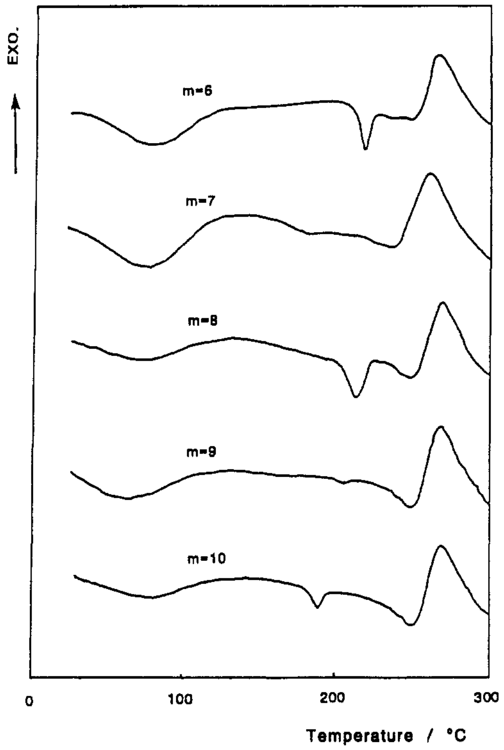

Figure 4. DSC thermograms of as-prepared 3 (m = 6–10).

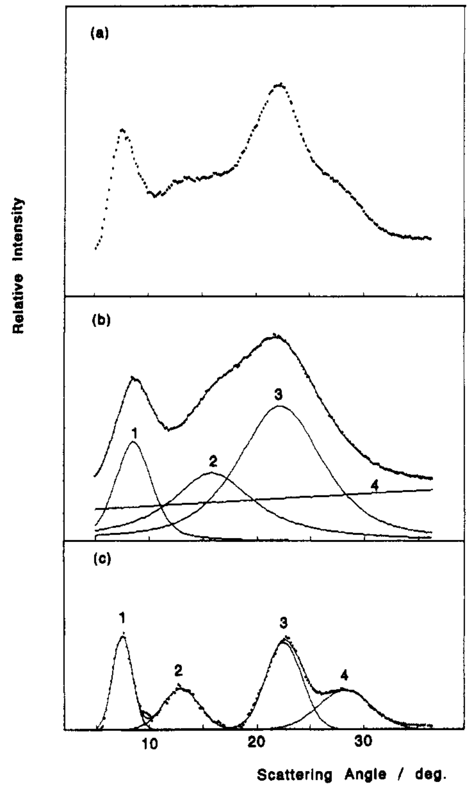

Figure 5. WAXD profiles of (a) as-prepared molded specimen and (b) specimen annealed at 225 °C for 1 min and (c) decomposed diffraction profiles due to crystal parts. Small dots show measured data; solid lines show decomposed peaks, background scattering, and the sum of them (the reconstructed profile).

phous and homogeneous at a micrometer spatial scale.

The temperature at which the WAXD profile of the as-prepared polyamide changes corresponds to that where the sharp endothermic peak starts to develop in its DSC curve. Then, the difference in the WAXD profiles between the as-prepared and as-cast samples would be caused by the crystallinity in the as-prepared polyamide. The melting of the crystallites results in a sharp endothermic peak in the DSC curve of the as-prepared polyamide and in the disappearance of the disparity between the as-prepared and as-cast profiles.

The WAXD patterns and DSC thermograms of as-prepared polyamides 3 (m = 5–10) are shown in Figures 3 and 4, respectively. The polyamides 3 (m = 6, 8, 10) showed the WAXD diffractions arising from the crystalline portion and a DSC endothermic peak corresponding to the melting of the crystalline part. Such WAXD diffractions from the crystalline portion disappeared above the melting temperature. In contrast, the polyamides 3 (m = 5, 7, 9) exhibited neither diffraction nor an endothermic peak associated with the crystalline part. These observations are in good agreement with the odd–even discrimination in the chiral recognition ability of polyamides 3. Consequently, the crystalline portion of polyamides 3 (m = 6, 8, 10) coated on silica gel would play a significant role on chiral recognition.

Dependence of Chiral Recognition Ability on Crystallinity. We estimated the degree of crystallinity of the as-coated sample to make the correlation between the chiral recognition ability and the crystallizability of polyamide 3 (m = 6) clear. As-prepared polyamide 3 (m = 6) was cold-pressed into a sample specimen of about 1-mm thickness. The WAXD pattern of the molded sample measured at 25 °C showed Debye–Scherrer rings, of which the intensity was independent on the azimuthal angle. Figure 5a shows the diffracted intensity at 25 °C as a function of scattering angle. The molded specimen was annealed at 225 °C, which is a little higher than the melting point of polyamide 3 (m = 6), for 1 min and slowly cooled to 25 °C under a nitrogen atmosphere. The annealed specimen was confirmed to be amorphous by DSC. The WAXD profile of the annealed specimen is shown in Figure 5b, and the profile was used as the representative of amorphous scattering.

The WAXD profile of the annealed specimen could be decomposed into three peaks numbered from 1 to 3, each of which was represented by either a Gaussian or Lorent-

Table VI
Resolution of Racemates 6–8 on 3 (m = 6) Coated Silica Gel Columns[a]

	racemates								
	6			7			8		
run	k_1'	α	R_s	k_1'	α	R_s	k_1'	α	R_s
1	1.92	1.65	1.46	8.30	1.35	1.05	1.61	1.18	0.53
2	1.57	1.59	0.93	6.55	1.28	0.61	1.53	1.71	1.13
3	2.05	1.70	1.77	8.02	1.38	1.17	1.76	1.17	0.77
4	2.27	1.62	1.70	8.13	1.37	1.04	1.87	1.14	0.52
5	2.45	1.25	1.12	9.22	1.22	0.69	2.30	1.11	0.30
6	2.61	1		8.12	1		2.19	1	
7	0.89	1		3.04	1		0.77	1	

[a] The run numbers correspond to those in Table V. For columns of runs 1–4, **3** (m = 6) (η_{inh} = 0.40) was used different from that in Table I.

zian distribution, and a background scattering numbered 4 arose from incoherent scattering as shown in Figure 5b. The decomposition was carried out by a least-squares method so as to attain the best fit between the measured profile (shown by small dots) and the reconstructed profile (shown by a solid line). Then, the WAXD profile (Figure 5a) of the semicrystalline as-prepared polyamide was decomposed into the amorphous peaks and the peaks from crystallites by using information obtained from the amorphous sample, i.e., the number of peaks, peak position, peak profile and width. Again the nonlinear least-squares fit method was used for the decomposition. Figure 5c shows, thus decomposed, crystal-diffractions, which comprise four peaks, numbered from 1 to 4. The results for the peak decomposition are summarized in Table III. The weight-average crystallinity (w_c) in the molded specimen was calculated on the basis of the ratio between the integral intensities of the crystalline and amorphous scatterings, and w_c in the molded specimen was found to be 28 wt %. The same molded specimen gave a melting enthalpy (ΔH_m) of −8.5 J/g on the basis of DSC analysis. We can thus determine $\Delta H_m{}^\circ = -8.5/0.28 = -30.4$ J/g for the melting enthalpy of the specimen with 100% crystallinity.

The crystallinity of polyamide **3** (m = 6) was found to depend strongly on the solvent quality for reprecipitation (Table IV). The highest crystallinity was achieved when reprecipitation was carried out at 20 °C by using methanol as a poor solvent. The reprecipitation with 2-propanol at 20 °C also gave polyamide **3** (m = 6) with a rather high crystallinity. In contrast, the crystallinity of the polyamide was low when benzene or water was used as a poor solvent. These results indicate that the balance between hydrophilicity and hydrophobicity of a poor solvent is important for achieving high crystallinity.

Columns consisting of silica gel coated with polyamides **3** (m = 6) with different crystallinity were prepared, and their chiral recognition ability was examined for racemates **6**–**8**. In order to prepare the silica gel, we changed the dry-up temperature from 20 to 110 °C, which influenced the amount of residual DMAc, and used methanol or 2-propanol/hexane (1/1) as a washing solvent. The conditions for the preparation of the silica gel, the amount of residual DMAc before washing, and the crystallinity of the polyamide on the silica gel are shown in Table V. The ΔH_m for polyamide **3** (m = 6) on the silica gel was normalized by the weight fraction of the polyamide (w_p) to whole coated silica gel, which corresponded to the fraction combustible under an oxygen atmosphere at 980 °C for 5 min. The crystallinity w_c of the polyamide coated on the silica gel was calculated from the measured ΔH_m and $\Delta H_m{}^\circ = -30.4$ J/g for a sample with 100% crystallinity; i.e., $w_c = \Delta H_m/\Delta H_m{}^\circ$. The chiral recognition ability of the coated polyamides having different crystallinity is listed in Table VI.

As shown in Table VI, the chiral recognition ability of polyamide **3** (m = 6) was closely related to the crystallinity of the polyamide on silica gel. When washing was carried out with methanol, the crystallinity of the coated polyamide was almost constant, independent of the amount of residual DMAc, and the chiral recognition ability was satisfactory (runs 1–4 in Table VI). In contrast, when 2-propanol/hexane was used as a washing solvent, the amount of residual DMAc strongly influenced the crystallinity of the coated polyamide. A smaller amount of DMAc resulted in lower or no crystallinity (runs 6 and 7, respectively). In both cases, chiral recognition could not be observed. The capacity factors (k_1') for run 6 were larger than those for run 7, indicating the existence of interactions between polyamide **3** (m = 6) and the racemates to some extent. This was probably caused by a low crystallinity of the polyamide on silica gel for run 6. However, in run 6, the degree of perfection of the crystalline portion would be low, since the melting point (196.1 °C) was lower than the ordinary temperature (219 °C, runs 1–4). Then, the chiral recognition ability disappeared not only due to its low crystallinity but also due to its low degree of perfection of the crystalline portion. In the case of run 5, the existence of a large amount of residual DMAc resulted in a considerable degree of crystallinity of the coated polyamide. However, the values of its ΔH_m and melting point were slightly lower than those of methanol-washed polyamides (runs 1–4), suggesting that both the crystallinity and the degree of perfection of crystals were slightly lower. Corresponding to these values, the chiral stationary phase of run 5 showed a slightly low chiral recognition ability in comparison with those of runs 1–4. These observations indicate that the higher crystallinity (as well as degree of crystal perfection) of polyamide **3** (m = 6) results in a higher chiral recognition ability and that the chiral recognition ability of polyamide **3** (m = 6) arises from the superstructure of the polyamides in the crystalline part.

The functional groups of the polyamide would exist in a regular conformation in the crystalline part, resulting in a regular interaction between the polyamide and both enantiomers of a racemate. Under this situation, it is expected that the increased crystallinity improves the chiral recognition ability proportionally. However, a proportional relationship between the crystallinity and the chiral recognition ability cannot be seen. This phenomenon can be explained as follows: In the case of the perfect biphase system consisting of a crystalline part (which will interact regularly with both enantiomers of a racemate) and an amorphous part (which shows random interactions statistically), the chiral recognition ability should be proportional to the crystallinity. However, in the actual polymer there exist some disorder in the crystalline region (which is obvious from the fact that the polyamides **3** of runs 1–6 have different melting temperatures from each other) and some order in the amorphous region nearby the crystalline region. The transition area would influence the separation factor (α), at least in a range of low crystallinity, resulting in a nonproportional relation between the chiral recognition ability and the crystallinity.

Conclusion

Optically active polyamides are easily obtained by the ring-opening polyaddition reaction of (−)-anti head-to-head coumarin dimer with diamines. The polyamides consisting of α,ω-alkanediamine with an even methylene number partially crystallize and show a chiral recognition ability, while the polyamides with an odd methylene number show neither crystallizability nor a chiral recognition ability. The superstructure of the crystalline part has not been clear yet, but the functional groups in the polyamides may exist in a regular conformation in the crystalline part, which play an important role on the chiral recognition ability.

Acknowledgment. The present work was supported by a Grant-in-Aid for Scientific Research (No. 01850200) from the Ministry of Education, Science and Culture, Japan, and by the Asahi Glass Foundation for Industrial Technology, Tokyo.

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7-Phenyl-7,8,8-tricyanoquinodimethane: The First Unsymmetrical Electrophilic Quinodimethane

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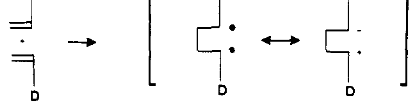
Received June 16, 1989; Revised Manuscript Received October 12, 1989

ABSTRACT: 7-Phenyl-7,8,8-tricyanoquinodimethane (1), the first unsymmetrical electrophilic quinodimethane, was synthesized successfully. The first reduction potential of 1 is −0.11 V by cyclic voltammetry. Title compound 1 can be homopolymerized with an anionic catalyst but does not homopolymerize with radical or cationic initiators. It copolymerized spontaneously and alternatingly with *p*-methylstyrene (MeSt), isobutyl vinyl ether, 2-chloroethyl vinyl ether, and *N*-vinylcarbazole at 60 °C. The propagation mode of the copolymerization for the 1–MeSt system will be discussed.

Introduction

We proposed the "bond-forming initiation theory"[1] to explain the spontaneous polymerizations of electron-rich olefins with electrophilic olefins. The inititating species is proposed to be a tetramethylene intermediate which may be either a zwitterion or a diradical



where A represents electron-accepting substituents such

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