Chromatographic Optical Resolution of Enantiomers on Polyamides Containing 1,2-Disubstituted Cyclohexane Moiety as a Chiral Residue

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ABSTRACT: Optically active polyamides having (–)-1,2-*trans*-diaminocyclohexane [(–)-DA] or (+)-1,2-*trans*-cyclohexane dicarboxylic acid [(+)-CDA] residue in main chain were synthesized by polycondensation. Polyamides with a *p*-phenylene group in main chain showed better resolution for several racemic compounds than the polyamides with a polymethylene group [(CH₂)_{*n*} (*n* = 2–7)] in main chain. Among the polyamides with a polymethylene group in main chain, the polyamides with a shorter polymethylene group showed better chiral recognition abilities than the polyamides with a longer polymethylene group. Polyamides derived from (–)-*trans*-3,6-endomethylene-1,2,3,6-tetrahydrophthalic acid [(–)-ETHF] showed low chiral recognition ability. CD spectra of these polyamides showed characteristic patterns. Odd-even effect was observed in CD spectra of the polyamides having a series of a polymethylene group.

KEY WORDS Chromatography / Optical Resolution / 1,2-Diaminocyclohexane / 1,2-Cyclohexane Dicarboxylic Acid / Optically Active Polyamide / Chiral Stationary Phase /

Optical resolution by high-performance liquid chromatography (HPLC) has already become an important, practically useful method for the separation of optical isomers, and various optically active polymers have been tested as chiral stationary phases (CSP).^{1,2} The polymers include several synthetic ones such as polyacrylamides,³ polymethacrylamides,⁴ polymethacrylates,⁵ poly(α-amino acid),⁶ polysulfoxide,⁷ poly(crown ether),⁸ and polyamides^{9–11} in addition to naturally occurring macromolecules, proteins and polysaccharides. Saigo, Hasegawa, and coworkers reported that polyamides containing a cyclobutane ring^{9,10} and a polyamide derived from 1,2-diphenylethylenediamine¹¹ show characteristic optical resolving abilities. On the other hand, Over-

berger *et al.* investigated extensively on the syntheses and conformation of optically active polyamides containing cyclic moieties such as cyclohexane,¹² cyclobutane, and cyclopropane in main chains.^{13,14} However, no data are available on the optical resolving abilities of these polyamides.

In this paper, we wish to report the chiral recognition abilities as CSP and CD spectra of a series of optical active polyamides having a cyclohexane moiety in main chain.

EXPERIMENTAL

Materials

(1*R*,2*R*)-(–)-1,2-*trans*-Diaminocyclohexane [(–)-DA] ([α]_D²⁰ –33.4° (*c* = 1.0 g dl^{–1} in

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H₂O)), which was kindly supplied by Toray, was purified by distillation under reduced pressure before polymerization. (1*S*,2*S*)-(+)-And (1*R*,2*R*)-(-)-*trans*-1,2-cyclohexanedicarboxylic acids [(+)- and (-)-CDA] were obtained by optical resolution of racemic acid (Nakarai tesque) with quinine.¹⁵ Quinine salt was recrystallized from 95% ethanol. Free (+)-diacid isolated from the quinine salt was recrystallized from water again (mp 180—180.5°C (lit.,¹⁶ mp 179.5—181.5°C), $[\alpha]_D^{20} + 19.4^\circ$ ($c = 1.0 \text{ g dl}^{-1}$ in acetone)). Enantiomeric excess of the acid was found to be greater than 99.5% by HPLC analysis using a cellulose tris(3,5-dimethylphenylcarbamate) column.¹⁷ The (-)-diacid recovered from the mother liquor of the recrystallization of the quinine salt was also recrystallized from water (mp 176—178°C (lit.,¹⁶ mp 175—180°C), $[\alpha]_D^{20} - 18.6^\circ$ ($c = 1.0 \text{ g dl}^{-1}$ in acetone)).

(±)-*trans*-3,6-Endomethylene-1,2,3,6-tetrahydrophthaloyl diphenyl ester was prepared by esterification of (±)-*trans*-3,6-endomethylene-1,2,3,6-tetrahydrophthaloyl dichloride (Aldrich). Racemic diester was preparatively resolved on an HPLC column (50 × 2 (i.d.) cm) packed with amylose tris(3,5-dimethylphenylcarbamate) using hexane-2-propanol (80:20) as an eluent.¹⁷ About 50 mg of the racemic diester was completely resolved in one injection. (-)-Diester isolated as the first fraction was hydrolyzed to give (-)-diacid ((-)-ETHF). Its optical purity was nearly 100% by chiral HPLC analysis.

Diacid chlorides of (+)- and (-)-CDA, α,ω-alkanedicarboxylic acid [HO₂C-(CH₂)_{*n*}CO₂H, *n* = 3, 5], and (-)-ETHF were prepared by treating the acids with an excess of purified thionyl chloride and were purified by distillation. Terephthaloyl acid dichloride and α,ω-alkanedicarboxylic acid dichlorides (*n* = 2, 4, 7, and 8) (Nakarai and Wako) were purified by distillation under reduced pressure. Suberoyl chloride (*n* = 6, Aldrich) was used without further purification.

α,ω-Alkanediamines [H₂N-(CH₂)_{*n*}NH₂, *n* =

2—6] (Nakarai tesque) were purified by distillation under reduced pressure just before polymerization. *p*-Phenylenediamine was recrystallized from ethyl acetate.

Triethylamine (Et₃N) was distilled and then stored on NaOH pellets. *N,N*-Dimethylacetamide (DMA) was distilled under reduced pressure and then stored on Molecular Sieves 4A.

Synthesis of Polyamides 1—14

Polyamides 1—14 were synthesized by polycondensation in solution. Under nitrogen atmosphere, a diamine (*ca.* 1 g) and lithium chloride (2 g) were placed in a 50 ml two-necked flask, and then DMA (40 ml) and Et₃N (2 ml) were added with syringes. To the above mixture cooled to 0°C, a diacid chloride was added dropwise under vigorous stirring. After 1—20 h, the reaction mixture was poured into 400 ml of water to precipitate a polyamide which was collected by centrifugation. The

Table I. Syntheses of polyamides 1—14

Polyamide	Yield	$[\alpha]_D^{20}$	$[\eta]^b$
	%	deg	10 ² cm ³ g ⁻¹
1	90	-211	0.21
2	46	+65.4	—
3	64	+73.6	0.10
4	89	+66.1	0.17
5	100	+64.1	0.20
6	94	+51.0	0.14
7	79	+53.0	0.14
8	97	+239	0.16
9	57	+56.5	0.12
10	67 (82) ^c	+57.5 (-67.1) ^c	0.13
11	70	+68.5	0.15
12	81 (83) ^c	+30.6 (-32.7) ^c	0.13
13	100	+45.4	0.13
14	72	-220 ^d	0.17 ^d

^a In dichloroacetic acid, 1.0 g dl⁻¹ at 25°C.

^b In dichloroacetic acid at 30°C.

^c Values in parentheses are the yields of polyamides obtained from (-)-CDA.

^d In dimethyl sulfoxide.

Optical Resolution on Polyamides

Polyamide	R ¹	Polyamide	R ²	Polyamide	R ³
1		8		14
2	$\text{---}(\text{CH}_2)_3\text{---}$	9	$\text{---}(\text{CH}_2)_2\text{---}$		
3	$\text{---}(\text{CH}_2)_4\text{---}$	10	$\text{---}(\text{CH}_2)_3\text{---}$		
4	$\text{---}(\text{CH}_2)_5\text{---}$	11	$\text{---}(\text{CH}_2)_4\text{---}$		
5	$\text{---}(\text{CH}_2)_6\text{---}$	12	$\text{---}(\text{CH}_2)_5\text{---}$		
6	$\text{---}(\text{CH}_2)_7\text{---}$	13	$\text{---}(\text{CH}_2)_6\text{---}$		
7	$\text{---}(\text{CH}_2)_8\text{---}$				

Scheme 1.

Scheme 2.

polyamide was washed with water and methanol. The polyamide thus obtained was dried *in vacuo* at 50°C for 3 h.

Table I shows the results of the syntheses of polyamides **1**—**14**.

Synthesis of Model Compounds **25**, **26**, and **27**

Model compounds **25**, **26**, and **27** were synthesized in a similar manner as described in the polymerization procedure.

An acid chloride was added to a benzene solution of an amine. Precipitated amide was separated by filtration, washed with water, ethanol, and ether, and then dried *in vacuo*. All model compounds showed reasonable IR and ¹H NMR spectra. Model Compound **25**: Yield, 52%; mp 254—255°C. *Anal.* Calcd for C₂₀H₂₂O₂N₂: C, 74.51%; H, 6.88%; N, 8.69%. Found: C, 74.42%; H, 6.90%; N, 8.62%. IR (Nujol): ν 1635 cm⁻¹ (C=O). Model Compound **26**: Yield, 17%; mp 245.5—256.5°C. *Anal.* Calcd for C₁₂H₂₀O₂N₂: C, 63.69%; H, 9.80%; N, 12.38%. Found: C, 63.57%; H, 9.76%; N, 12.27%. IR (Nujol): ν 1638 cm⁻¹ (C=O). Model Compound **27**: Yield, 98%; mp 301—302°C. *Anal.* Calcd for C₂₁H₂₀O₂N₂: C, 75.88%; H, 6.60%; N, 8.43%. Found: C, 75.83%; H, 6.10%; N, 8.56%. IR (Nujol): ν 1651 cm⁻¹ (C=O).

Preparation of Chiral Stationary Phase

Macroporous silica gel (Macherey–Nagel, NUCLEOSIL 4000-7) was treated with 3-aminopropyltriethoxysilane in benzene at 80°C. Analysis for the silanized silica gel: C, 0.43%; H, 0.15%. A polyamide (0.68 g) was dissolved in 8 ml of a solvent (1,1,1,3,3,3-hexafluoro-2-propanol or trifluoroacetic acid (TFA)). The solution (*ca.* 4 ml) was added to the above silanized macroporous silica gel (3 g), and the wetted silica gel was dried under vacuum. This coating process was repeated with the remaining solution. The packing materials thus obtained were packed in a stainless steel tube (250 × 4.6 (i.d.) mm) at 380 kg cm⁻² by a slurry method. The plate

numbers of these columns were 2500—3500 for 1,3,5-tri-*tert*-butylbenzene with hexane (0.5 ml min⁻¹) as an eluent at 25°C. Dead time (*t*₀) of the column was also estimated with 1,3,5-tri-*tert*-butylbenzene.¹⁸

Measurement

A JASCO TRIROTAR-II chromatograph equipped with UV (JASCO UVIDEC-100-III) and polarimetric (JASCO DIP-181C) detectors were used. Optical rotation was monitored in a flow cell (50 × 2 (i.d.) mm) at full lamp (mercury) intensity without a filter. Resolution on an analytical column (25 × 0.46 (i.d.) cm) was carried out with a hexane–2-propanol (90:10 or 95:5) mixture at a flow-rate of 0.5 ml min⁻¹ at 25°C unless otherwise stated. IR spectra were taken on a JASCO IR-810 spectrophotometer in Nujol. CD and UV spectra were measured on a JASCO J-500 spectropolarimeter and on a JASCO UVIDEC-610C spectrophotometer, respectively, at room temperature. CD and UV spectra of films were measured in the same manner as reported by Chen *et al.*¹⁰ The films were prepared by casting their solution (20—30 mg ml⁻¹ in TFA) on the surface of a quartz plate. Each CD spectrum was measured four times by rotating the sample quartz plate by 45, 90, and 120° from the first position around the axis of the incident light beam. Every spectrum gave almost identical patterns. The CD spectra were calibrated to the same molecular concentration on the basis of the data of UV measurement.

RESULTS AND DISCUSSION

The resolution of racemic Tröger base **15** on optical active polyamide **1** is shown in Figure 1. The enantiomers were completely separated eluting at *t*₁ and *t*₂. Capacity factors *k*'₁ and *k*'₂, which are estimated as (*t*₁ − *t*₀)/*t*₀ and (*t*₂ − *t*₀)/*t*₀, are 0.33 and 1.28, respectively. Separation factor, $\alpha = k'_2/k'_1$, and resolution factor, $R_s = 2(t_2 - t_1)/(w_1 + w_2)$, are found to be

Figure 1. Chromatographic resolution of Tröger base **15** on polyamide **1**.

3.94 and 5.12, respectively.

Table II shows the results of optical resolution of **15**, cobalt(III) tris(acetylacetonate) **16**, flavanone **17**, *trans*-cyclopropanedicarboxylic acid dianilide **18**, 2,2'-dihydroxy-6,6'-dimethylbiphenyl **19**, 1-(9-anthryl)-2,2,2-trifluoroethanol **20**, 1,2,2,2-tetraphenylethanol **21**, and benzoin **22** on polyamides **1**, **3**, **8**, **11**, and **14**. Each polyamide has characteristic chiral recognition ability for the racemic compounds. Among the polyamides having cyclohexane ring, **1** and **8** with *p*-phenylene groups showed noticeable chiral recognition abilities. Tröger base **15** was efficiently resolved only by polyamide **1**, and **16** was resolved by polyamide **8** with a very high separation factor ($\alpha=9.27$). Racemates **19** and **20** were better resolved on polyamides **3** and **11** with tetramethylene groups. These results indicate

Scheme 3.

Table II. Resolution of enantiomers **15**–**21** on polyamides **1**, **3**, **8**, **11**, and **14**^a

Polyamide	15			16			17		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
1	0.33 (+)	3.94	5.12	1.15 (+)	2.29 ^b		0.82 (+)	1.49	2.19
3	0.12	1.00		0.21 (+)	1		0.25	1.00	
8	0.72 (+)	1		1.14 (–)	9.27	2.38 ^b	0.72 (+)	1.09	
11	0.10 (+)	1		0.20 (+)	1		0.18	1.00	
14	0.84 (+)	1.12		2.92	1.00		2.46	1.00	

Polyamide	18			19			20		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
1	0.67	1.00		2.80 (–)	1.08		1.74 (–)	1.07	
3	1.33 (+)	1.46	0.85	3.81 (–)	1.27	1.03	2.65 (+)	1.23	1.23
8	1.81 (+)	1.32	0.64	4.05 (–)	1.05 ^b		2.22 (+)	1	
11	1.32 (+)	1.14		2.82 (–)	1.41		2.01 (+)	1.15	0.63
14	4.19	1.00		2.87 (+)	1.20	0.47	2.70 (–)	1	

Polyamide	21			22 ^c		
	k'_1	α	R_s	k'_1	α	R_s
1	1.80 (+)	1.11		1.47	1.00	
3	0.82 (+)	1		0.88 (+)	1	
8	1.32 (–)	1.22	0.73	1.16 (–)	1.12 ^b	
11	0.63 (–)	1		0.73 (+)	1	
14	1.53 (+)	1		4.74 (+)	1	

^a Eluent: hexane–2-propanol (90:10).^b Eluent: hexane–2-propanol–CHCl₃ (85:5:10).^c The optical rotation was measured at 435 nm.

that achiral units in the polyamides greatly influence optical resolving abilities. Polyamide **14** with bicyclo ring showed low chiral recognition ability, although it strongly retained several compounds, for instance **18** and **22**.

Tables III and IV show the results of optical resolution of **18**, **19**, **20**, 2,2'-dihydroxy-1,1'-binaphthyl **23**, and 1,2-*trans*-cyclobutane dicarboxylic acid dianilide **24** on polyamides **2**–**7** and **9**–**13** having different number of methylene groups in main chains. Racemates **15**–**17**, **21**, and **22** were not resolved on these polyamides. The chiral recognition abilities of these polyamides depended on the methylene number. For instance, diamide **18** was best

resolved on polyamides **5** with a hexamethylene group among the polyamide derived from (–)-DA (Table III). Polyamide **7** bearing an octamethylene group showed almost no chiral recognition ability. In the polyamides derived from (+)-CDA, **13** exhibited exceptionally high chiral discrimination for **24** (Table IV). In the present chromatographic separation, hydrogen bond may be the main interaction between the amide groups of the polyamides and the solutes. This interaction seems to play the most important role for chiral discrimination. Therefore, the compounds bearing a polar group such as hydroxy, amide, and carbonyl groups which can interact through hydrogen bond with the amide groups appear to be

Optical Resolution on Polyamides

Table III. Resolution of enantiomers **18**–**20**, **23**, and **24** on polyamides **2**–**7**^a

Polyamide	18			19			20		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
2	2.27 (+)	1.26	0.60	4.63 (–)	1.36	0.95	1.10	1.00	
3	2.83 (+)	1.39	0.85	8.84 (–)	1.27		4.31 (+)	1.21	
4	1.80 (+)	1.38	1.28	2.58 (–)	2.13	2.13	3.15	1.06	
5	2.20	1.60		3.31 (–)	1.29		2.60 (+)	1	
6	1.35 (+)	1.21		1.38 (–)	1.17		2.37	1.00	
7	0.67	1.00		0.67 (–)	1		1.43	1.00	

Polyamide	23			24					
	k'_1	α	R_s	k'_1	α	R_s			
2	11.38 (–)	1.42	1.40	1.05 (+)	1.14	0.60			
3	21.97 (–)	1.38	1.08	1.59 (+)	1.21	0.60			
4	16.89 (–)	1.57	1.89	3.09 (+)	1				
5	6.91 (–)	1.47		1.36 (+)	1.10				
6	7.07 (–)	1.32	1.26	1.14 (+)	1.18	0.63			
7	7.05 (–)	1		0.99 (+)	1				

^a Eluent: hexane–2-propanol (95:5).**Table IV.** Resolution of enantiomers **18**–**20**, **23**, and **24** on polyamides **9**–**13**^a

Polyamide	18			19			20		
	k'_1	α	R_s	k'_1	α	R_s	k'_1	α	R_s
9	0.88	1.29		2.01 (–)	1.30	0.93	2.02 (+)	1	
10^b	0.67 (–)	1.17		1.47 (+)	1.92	1.04	1.39	1.00	
11	1.32 (+)	1.14		2.82 (–)	1.41	1.82	2.01	1.15	
12^b	0.70 (–)	1.00		1.32 (+)	1.43	1.03	1.66	1.00	
13	1.48 (–)	1.16		2.42 (–)	1.16	0.89	2.36 (+)	1	

Polyamide	23			24					
	k'_1	α	R_s	k'_1	α	R_s			
9	3.23 (–)	2.02	1.07	0.31	1				
10^b	2.62 (+)	2.01	1.04	0.41 (+)	1				
11	5.40 (–)	1.52		0.79	1.00				
12^b	2.56 (+)	1.73	1.27	0.39 (+)	1				
13	6.29 (–)	1.32	1.28	0.46 (–)	1.74	1.58			

^a Eluent: hexane–2-propanol (90:10).^b (–)-Diacid was used.

suitable for efficient optical resolution.

Since the polyamides used here were insoluble in a hexane–2-propanol (90:10) mixture, the chiral HPLC columns were quite

stable as far as the mixture was used as an eluent.

The fact that chiral discrimination of CSP depended on the number of the methylene units

Fig. 2. CD and UV spectra of polyamide **1** (—) and model compound **25** (---) in film.

Figure 3. CD and UV spectra of polyamide **2** (—) and model compound **26** (---) in film.

of the polyamides suggests that steric structure around amide bonds may be different depending on the number of the methylene units. To attain efficient chromatographic separation of optical isomers, it is preferable that the polyamides take an order structure because the efficient separation can be achieved as a result of the accumulation of a small chiral discrimination step on CSP. If the polyamides are in a disorder structure, such a regular accumulation seems to be difficult. Therefore, higher-order structure of the polyamides may play an important role for chiral recognition. In order to obtain the information on the structure, CD and UV spectra of the polyamides were measured in the solid state and in solutions. Figures 2, 3 and 4 show CD and UV spectra of polyamides **1**, **2**, and **14** and the corresponding model compounds **25**, **26**,

Figure 4. CD and UV spectra of polyamide **14** (—) and model compound **27** (---) in film.

and **27** on solid film, respectively. The UV spectra of the films showed strong absorption assigned to the π - π^* transition of amide chromophore at about 200 nm. The CD spectrum of polyamide **1** showed negative peaks due to amide and aromatic chromophores at about 210 nm and 260 nm, respectively (Figure 2). The CD spectra of polyamide **1** and corresponding model compound **25** in the solid state showed almost opposite patterns, although the CD band of phenylene group of **1** red shifted *ca.* 20 nm. A positive CD peak was observed at about 210 nm in the spectrum of polyamide **2**, and model compound **26** showed almost opposite CD pattern (Figure 3). These differences of the CD spectra between the polyamides and model compounds may be ascribed mainly to two factors, conformational factor and molecular orientation of the polyamide chain. However, the influence of the orientation of the polymer chain seems to be negligible because the

rotation of the sample in the measurement of CD spectra did not greatly varied the spectral pattern. Therefore, it is most likely that the conformation of polyamides **1** and **2** may be different from that of their corresponding model compounds. Since the solid film of the polyamides cast from a TFA solution showed high crystallinity under a polarized microscope, the polyamides seem to take regular conformation, which may result in strong interaction between the adjacent chromophores.

CD spectrum of polyamide **14** was rather similar to that of its model compound **27** (Figure 4). The polymer and model compound appear to have similar conformation in the solid state. This polyamide may not take a regular conformation. Low chiral recognition ability of polyamide **14** may be associated with the lack of regularity of the polymer chain.

Figure 5. CD and UV spectra of polyamides **3** (-----), **5** (-·-·-), and **7** (—) in film.

Figure 6. CD and UV spectra of polyamides **2** (-----), **4** (-·-·-), and **6** (—) in film.

Figure 7. CD and UV spectra of polyamides **10** (---) and **12** (—) in film.

Among polyamides **2**–**7** and **9**–**13**, the CD spectra of the films of the polyamides with odd methylene units were different from those of the polyamides with even methylene units. The CD spectra of the polyamides with even methylene units derived from (–)-DA are presented in Figure 5. These spectra exhibited a weak trough at 220 nm probably corresponding to $n\text{--}\pi^*$ transition of imino chromophore in amide group. However, those of the polyamides with odd methylene units exhibited no trough (Figure 6).

On the other hand, in the polyamides derived from (+)-CDA, the polyamides having odd carbon units showed their CD band in longer wavelength region by about 10 nm than those of the polyamides having even carbon units (Figures 7 and 8). Odd-even effect of the number of methylene units was observed in the CD spectra. This effect may be correlated with higher-order structure of the polyamides. In solid film, polar amide groups may be associated through hydrogen bond. This

Figure 8. CD and UV spectra of polyamides **9** (---), **11** (—), and **13** (....) in film.

association may differ depending on the odd or even number of the methylene units. Saigo *et al.*⁹ showed clear odd-even effect on the optical resolving power of the polyamides derived from coumarin derivatives and α,ω -alkanediamines. However, in our systems such effects did not obviously appear in optical resolution although the effects were observed in CD spectra. In our systems, the small conformational difference which is observed in CD spectra may not clearly influence the chiral recognition ability of the polyamides.

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