

Synthesis and Properties of Optically Active Polyester-amides from Ester-Containing Chiral Dicarboxylic Acid and Aromatic Diamines

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ABSTRACT: The asymmetric hydrogenation of benzyl acetoacetate afforded benzyl (*R*)-3-hydroxybutanoate (**II**). Optically active ester-containing dicarboxylic acid **V** was newly prepared from **II** and terephthaloyl chloride, followed by debenylation. The polycondensation of **V** with aromatic diamines was carried out in the presence of triphenyl phosphite, pyridine, and calcium chloride in *N*-methyl-2-pyrrolidone (NMP). The resulting optically active polyester-amides had inherent viscosities of 0.44—0.79 dl g⁻¹, and specific rotations from -43.6° to -78.5°. The glass transition temperatures of the polymers were in the range from 129°C to 169°C, and their decomposition started at a temperature from 231°C to 249°C to afford biscrotonamide and terephthalic acid. The glass transition temperature of the optically active polymer derived from 4,4'-oxydianiline was 8°C higher than that of the corresponding inactive analogue.

KEY WORDS Optically Active Polyester-amides / Asymmetric Hydrogenation / Polycondensation / Thermal Behavior /

Several examples of optically active polymers obtained by polycondensation have been reported to investigate conformational behavior of the polymers in solution and physical properties such as melting point, glass transition temperature, crystallinity, solubility, and mechanical strength.¹ Recently much interest has been focused on the synthesis of main chain liquid crystalline polymers containing optically active units.² However, general sources of optically active monomers for the polycondensation are derivatives of naturally occurring compounds. Preparation of optically active monomers by asymmetric synthesis is of interest, because a variety of new types of optically pure intermediates could be obtained in both antipodes.

In this paper, we describe the preparation and characterization of optically active

polyester-amides derived from some aromatic diamines and an optically active ester-containing dicarboxylic acid whose chiral centers are produced by the Ruthenium-Binap catalyzed asymmetric hydrogenation (Binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl).

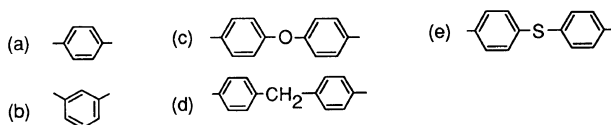
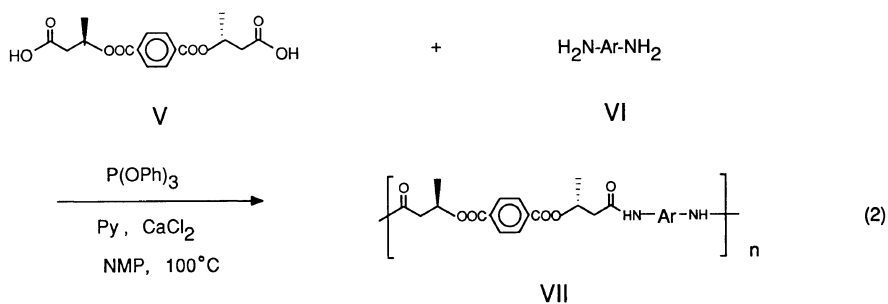
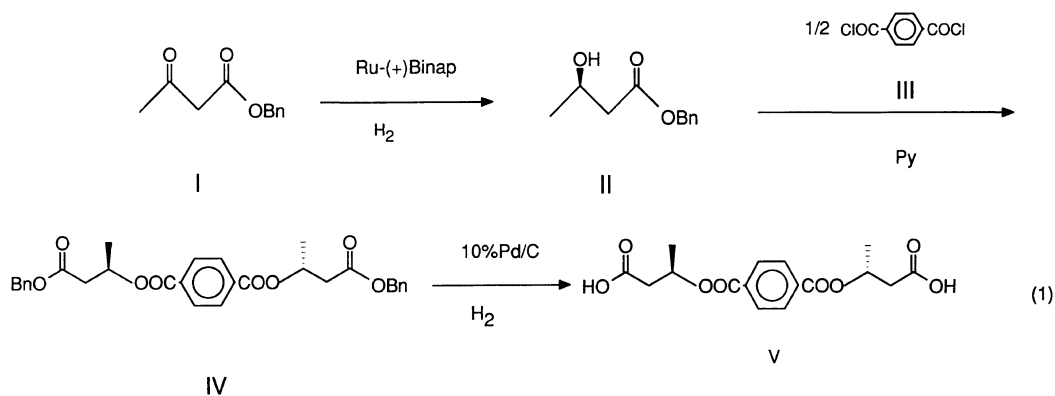
RESULTS AND DISCUSSION

Synthesis of Optically Active Diacid V

Optically active ester-containing dicarboxylic acid **V** was synthesized as shown in eq 1.

The Ruthenium-Binap catalyzed asymmetric hydrogenation³ of benzyl acetoacetate (**I**) gave benzyl (*R*)-3-hydroxybutanoate (**II**) with 94.3% enantiomeric excess in 75% yield. Dibenzyl ester **IV** was prepared by the condensation of **II** with 0.5 molar equivalent of terephthaloyl chloride (**III**) in the presence

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of pyridine in 79% yield. The removal of benzyl groups of **IV** by Pd-C catalyzed hydrogenolysis produced crystals of optically active ester-containing dicarboxylic acid **V** in 65% yield. By using the same procedure, the corresponding optically inactive dicarboxylic acid **VIII** was also prepared from racemic benzyl 3-hydroxybutanoate which was obtained by the sodium borohydride reduction of benzyl acetoacetate (**I**). Dicarboxylic acid **VIII** had higher melting point and showed less solubility in organic solvents than optically active dicarboxylic acid **V**.

Synthesis of Polyester-amides

Optically active dicarboxylic acid **V** was subjected to polycondensation with aromatic diamines **VI** such as *p*-phenylenediamine (**VIa**),

m-phenylenediamine (**VIb**), 4,4'-oxydianiline (**VIc**), 4,4'-methylenedianiline (**VI d**), and 4,4'-thiodianiline (**VIe**) by using a direct polycondensation method in the presence of triphenyl phosphite, pyridine, and calcium chloride in *N*-methyl-2-pyrrolidone (NMP) at 100°C (eq 2).

Dicarboxylic acid **VIII** was further polycondensed with 4,4'-oxydianiline (**VIc**) to give optically inactive polyester-amide **IX** for comparison (eq 3).

The results of the polymerization are summarized in Table I. The yields and inherent viscosities of all the polymers were 85–95%, and higher than 0.44 dl g⁻¹, respectively. The gel permeation chromatography (GPC) indicated that the number-average molecular weight (\bar{M}_n) values were 29000–86000 based

Optically Active Polyester-amides

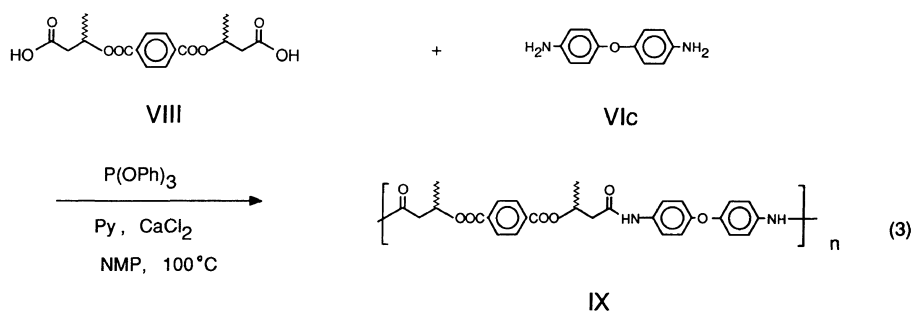


Table I. Synthesis of optically active and inactive polyester-amides

Monomers		Polymer					
Dicarboxylic acid	Diamine	Code	Yield	η_{inh}^a	\bar{M}_n^b	\bar{M}_w^b	\bar{M}_w/\bar{M}_n^b
			%	dl g ⁻¹	($\times 10^{-4}$)	($\times 10^{-4}$)	
V	VIa	VIIa	94	0.71	7.2	10.6	1.5
V	VIb	VIIb	84	0.79	8.6	13.5	1.6
V	VIc	VIIc	85	0.44	2.9	4.1	1.4
V	VIc	VIIc	85	0.59	4.9	7.9	1.6
V	VIe	VIIe	86	0.72	6.7	10.4	1.5
VIII	VIc	IX	90	0.46	3.3	5.0	1.5

^a Measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C.

^b Determined by GPC on the basis of polyoxyethylene calibration.

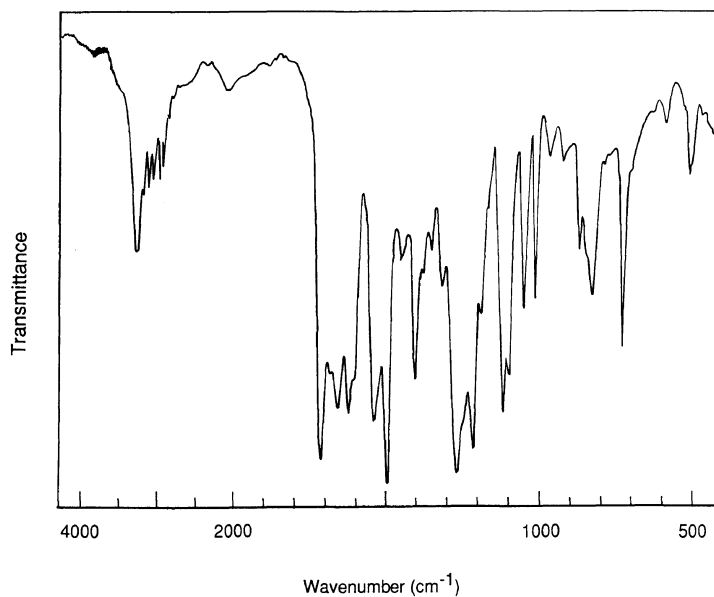


Figure 1. FT-IR spectrum of polymer VIIc (film).

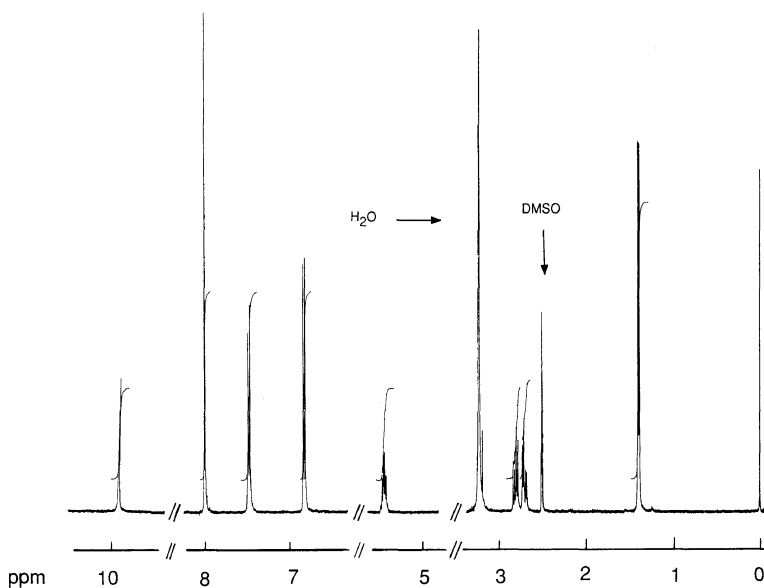


Figure 2. ^1H NMR spectrum measured in CDCl_3 of polymer VIIc.

on standard polyoxyethylene, and the \bar{M}_w/\bar{M}_n values were 1.4–1.6 (\bar{M}_w , weight-average molecular weight).

All the polymers gave satisfactory results for the elemental analyses. The IR and ^1H NMR spectra of polymer VIIc are shown in Figures 1 and 2, respectively. The FT-IR spectra of the polymers exhibited characteristic absorptions of amide group at around 3300 cm^{-1} and $1661\text{--}1671\text{ cm}^{-1}$, and that of ester group at about 1720 cm^{-1} . In the ^1H NMR spectra, the methyl protons gave doublet at about 1.4 ppm, and the non-equivalent geminal protons of methylene group next to the chiral center gave double-doublet at about 2.7 ppm and 2.8 ppm. The methyne proton gave sextet at about 5.5 ppm and the amide proton appeared at about 10 ppm.

Properties of Polymers

The X-ray diffraction studies revealed that all the polymers were amorphous. All the polymers were soluble in pyridine, dimethyl sulfoxide and amide solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and NMP. No difference

Table II. Optical rotation values of polyester-amides^a

	VIa	VIb	VIc	VI d	VIe
$[\alpha]_D$ (degree)	-76.7	-43.6	-64.6	-65.6	-78.5

^a Measured in DMAc at a concentration of $0.64\text{--}0.87\text{ g dl}^{-1}$ at 25°C .

in solubility in various solvents was observed between the optically active and inactive polymers. The polymers obtained from optically active dicarboxylic acid V had negative optical rotation values in the range from -43.6° to -78.5° as shown in Table II.

The thermal characterization of the polymers was carried out by means of dynamic mechanical analysis (DMA), differential thermal analysis (DTA), and thermogravimetry (TG). The glass transition temperatures (T_g) of the optically active polymers were observed in the range from 129°C to 169°C by the DMA measurements of the film samples. As shown in Figure 3, the optically active polymers exhibited a clear endotherm in the range of

233–249°C. The TG measurements showed that all the polymers started to decompose at around 240°C and the 10% weight loss temperatures were in the range from 281 to 292°C.

Figures 4 and 5 show the IR and ^1H NMR spectra, respectively, of thermally decomposed sample of **VIIc** at 240°C for 5 min under nitrogen. The absorption characteristic of ester carbonyl group disappeared and that of carboxylic acid was observed at 1680 cm^{-1} in the IR spectrum. In the ^1H NMR spectrum,

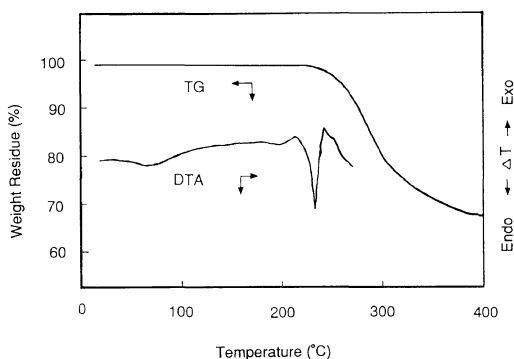


Figure 3. DTA and TG curves of **VIIc** at a heating rate of $10^\circ\text{C min}^{-1}$ in nitrogen.

doublet of the methyl group migrated to 1.85 ppm and double-doublet of the methylene group disappeared. Furthermore, characteristic peaks of the olefinic protons newly appeared in 6.10 ppm and 6.78 ppm.

These spectroscopic data indicated that bis crotonamides **X** and terephthalic acid **XI** were produced by thermal main chain scission (eq 4) just after the endotherm observed by the DTA measurement. The same thermal behavior was reported in the copolyesters of poly(3-hydroxybutanoate), which degraded *via* six-membered ring transition state.⁴ The thermal behavior is summarized in Table III.

There has been several examples that optically active polymers have higher T_g than the corresponding racemic polymers because of stereoregularity of the polymer chain.⁵ In the present case, the difference in T_g between optically active polymer **VIIc** and its optically inactive analogue **IX**, both of which had almost the same inherent viscosities, was 8°C . The little influence of stereoregularity of the optically active polymers on T_g could be explained by the fact that the concentration of asymmetric carbons in the polymer backbone

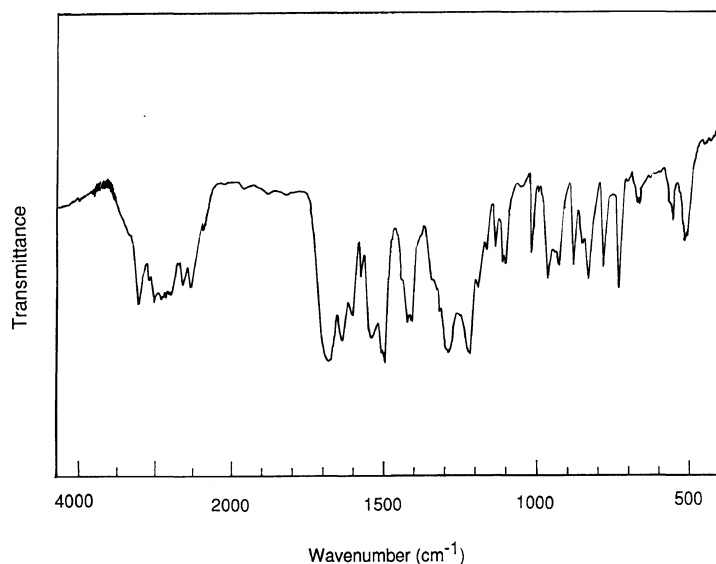


Figure 4. FT-IR spectrum of thermal decomposed sample of **VIIc** at 240°C for 5 min under nitrogen (KBr).

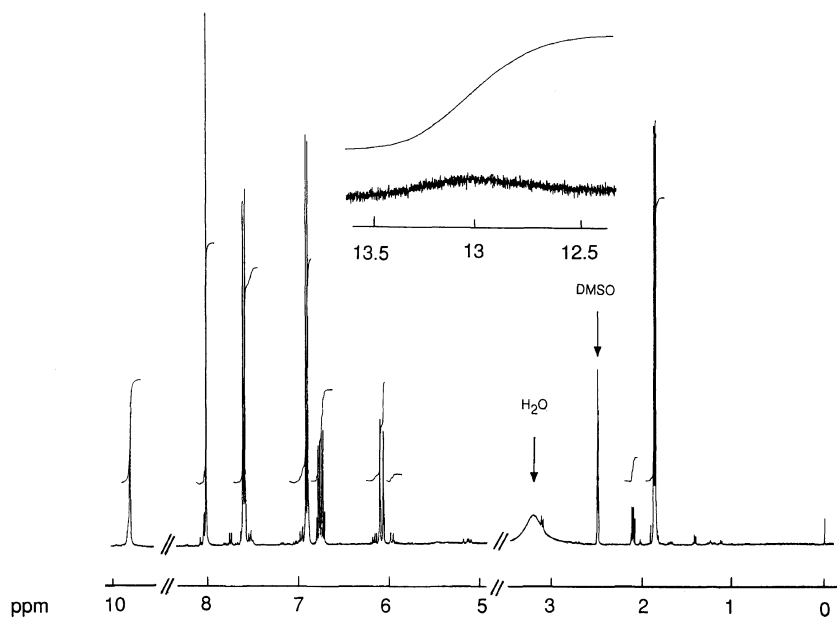


Figure 5. ^1H NMR spectrum measured in CDCl_3 of thermal decomposed sample of VIIc at 240°C for 5 min under nitrogen.

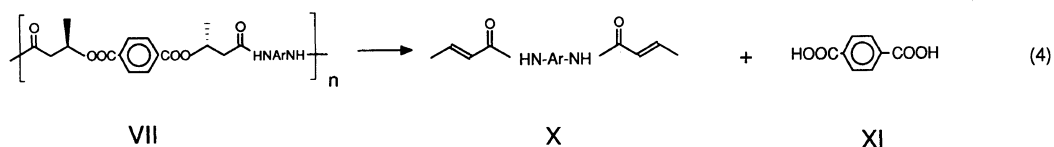


Table III. Thermal behavior of polyester-amides

Polymer	T_g^a	T_d^b	T_{10}^c
	$^\circ\text{C}$	$^\circ\text{C}$	$^\circ\text{C}$
VIIa	160	249	274
VIIb	138	241	284
VIIc	129	233	283
III d	169	231	281
VIIe	132	238	292
IX	121	229	277

^a Determined by DMA at a heating rate of 3°C min^{-1} at 10 Hz.

^b T_d is the decomposition temperature, determined by the peak top of the endotherm obtained by DTA in nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$.

^c T_{10} is the temperature of 10% weight loss, measured by TG in nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$.

is relatively low.

EXPERIMENTAL

Measurements

IR spectra were recorded on a JASCO FT/IR-5000 spectrophotometer. ^1H NMR spectra were measured on a Bruker AMX 400 spectrometer (400 MHz) using tetramethylsilane as an internal standard, and chemical shifts are quoted in ppm. Mass spectra were measured on both Hitachi M-80 and M-200 A spectrometers with relative intensities (%) in parentheses. Optical rotation measurements were obtained on a JASCO DIP-360 spectrometer. Dynamic mechanical analysis (DMA) was performed with a Toyoseiki Rheograph-Solid in tensile mode. Differential thermal

analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DTA-40 and TGA-40M, respectively, and measurements were run at a heating rate $10^{\circ}\text{C min}^{-1}$ under nitrogen at a flow rate of 50 ml min^{-1} . Wide angle X-ray diffraction patterns were obtained at room temperature on a Rigakudenki RU-200 apparatus with nickel-filtered CuK_{α} radiation (50 kV, 180 mA). Weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) were determined by means of gel permeation chromatography (GPC) on the basis of polyoxyethylene calibration on a JASCO apparatus (eluent, DMF).

Materials

m-Phenylenediamine (**VIb**) and 4,4'-methylenedianiline (**VIc**) were distilled under vacuum, and 4,4'-oxydianiline (**VIa**) was recrystallized from tetrahydrofuran. *p*-Phenylenediamine (**VIa**), 4,4'-thiodianiline (**VIe**), and calcium chloride were used as received. NMP, DMAc, and pyridine were purified by distillation over calcium hydride.

Monomer Synthesis

Synthesis of Benzyl (R)-3-hydroxybutanoate (II). A solution of benzyl acetoacetate (**I**) (100 g, 0.52 mol) and $\text{Ru}_2\text{Cl}_4((+)\text{Binap})_2\text{Et}_3\text{N}$ (1.25 g) in methylene chloride (400 ml) and water (1 ml) was stirred at 40°C under hydrogen pressure of 80 kg cm^{-2} . After stirring for 48 h, the mixture was concentrated and the residue was distilled to give 78.3 g (77.6%) of benzyl (*R*)-3-hydroxybutanoate in 94.3% e.e. (determination of enantiomeric excess, see below).

bp $123\text{--}133^{\circ}\text{C}/1\text{ Torr}$, $[\alpha]_{\text{D}}^{25} = -19.1^{\circ}$ ($c = 5.0\text{ g dl}^{-1}$ in CHCl_3). (lit⁶ $[\alpha]_{\text{D}}^{25} = -31.08^{\circ}$, $c = 5.0\text{ g dl}^{-1}$ in CHCl_3).

IR (Neat): 3450 (OH), 2972, 1730 (C=O), 1499, 1456, 1404, and 1293 cm^{-1} .

$^1\text{H NMR}$ (CDCl_3): 1.20 (d, $J = 6.3\text{ Hz}$, 3H), 2.48 (dd, $J = 16.3\text{ Hz}$, $J = 8.0\text{ Hz}$, 1H), 2.50 (dd, $J = 16.4\text{ Hz}$, $J = 4.2\text{ Hz}$, 1H), 2.80—2.95

(br s, 1H), 4.15—4.28 (m, 1H), 5.15 (s, 2H), and 7.20—7.42 (m, 5H) ppm.

Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3$: C, 68.02%; H, 7.26%. Found: C, 68.43%; H, 7.36%.

Determination of Optical Purity

Enantiomeric excess (e.e.) of **II** was determined by high performance liquid chromatography (column, Cosmosil 5SL, $4.6 \times 50\text{ mm}$, flow rate 1.0 ml min^{-1} ; eluent, 9:1 hexane-ether; detection, 254 nm) of its (*R*)-MTPA ester (MTPA = α -methoxy- α -trifluoromethylphenylacetyl). The retention times were 16.17 min (*R* isomer) and 18.68 min (*S* isomer) and the ratio of these peak areas is 34.2/1 (94.3% e.e.).

Synthesis of Dibenzyl Ester IV. To a solution of benzyl (*R*)-3-hydroxybutanoate (**II**) (50.0 g, 0.257 mol) and pyridine (21.0 g, 0.266 mol) in benzene (300 ml) was added portionwise terephthaloyl chloride (**III**) (21.0 g, 0.103 mol) over 10 min. The reaction mixture was stirred overnight at 50°C , and the resulting pyridine salt was separated by filtration. The filtrate was washed with 1 M hydrochloric acid and saturated aqueous sodium chloride, dried over magnesium sulfate, and concentrated. Purification by flash chromatography (silica, eluent; hexane-ethyl acetate = 2:1) gave 42.4 g (79%) of **IV** as an oil.

$[\alpha]_{\text{D}}^{25} = -30.7^{\circ}$ ($c = 0.11\text{ g dl}^{-1}$ in CHCl_3).

IR (Neat): 3034, 2984, 1738 (C=O), 1723 (C=O), 1499, 1456, 1408, 1383, 1358, and 1273 cm^{-1} .

$^1\text{H NMR}$ (CDCl_3): 1.45 (d, $J = 6.3\text{ Hz}$, 6H), 2.70 (dd, $J = 15.5\text{ Hz}$, $J = 5.3\text{ Hz}$, 2H), 2.85 (dd, $J = 15.5\text{ Hz}$, $J = 7.8\text{ Hz}$, 2H), 5.10 (s, 4H), 5.55 (sextet, $J = 6.3\text{ Hz}$, 2H), 7.15—7.30 (m, 10H), and 7.96 (s, 4H) ppm.

MS (*m/e*): 517 (6), 410 (30), 324 (94), 234 (89), 176 (13), 149 (91), 121 (56), 103 (100), 91 (100), 69 (100), 42 (72), and 18 (4).

Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{O}_8$: C, 69.49%; H, 5.83%. Found: C, 69.01%; H, 5.69%.

Synthesis of Ester-Containing Dicarboxylic Acid V. A suspension of **IV** (15.0 g, 0.0289 mol) and 3.2 g of Pd-C (10%) in ethanol (150 ml)

was stirred under hydrogen (ballon) for one day. Filtration of the mixture through celite, followed by evaporation and flash chromatography (silica, eluent, hexane-ethyl acetate = 1:2 then ethyl acetate alone) gave 7.8 g of white crystals. Recrystallization from benzene gave 6.4 g (65%) of dicarboxylic acid **V**.

mp 131–132°C, $[\alpha]_D^{25} = -64.9^\circ$ ($c = 1.07$ g dl⁻¹ in CHCl₃)

IR (KBr): 3000 (OH), 1738 (C=O), 1715 (C=O), 1650, 1505, 1449, 1406, 1352, 1315, and 1204 cm⁻¹.

¹H NMR (DMSO-*d*₆): 1.38 (d, $J = 6.4$ Hz, 6H), 2.60–2.78 (m, 4H), 5.35 (sextet, $J = 6.3$ Hz, 2H), 8.00 (s, 4H), and 11.9–12.4 (brs, 2H) ppm.

MS (*m/e*): 338 (6), 252 (74), 235 (100), 207 (13), 165 (100), 131 (100), 103 (100), 69 (100), and 41 (100).

Anal. Calcd for C₁₆H₁₈O₈: C, 56.80%; H, 5.36%. Found: C, 56.73%; H, 5.62%.

Synthesis of Racemic Dicarboxylic Acid VIII.

To an ice-cold solution of benzyl acetoacetate (**I**) (18.8 g, 0.0978 mol) in 100 ml of benzyl alcohol was added dropwise a solution of sodium borohydride (1.0 g, 0.0264 mol) in 2 ml of water over 15 min. The mixture was stirred for 2 h at room temperature and 200 ml of ether was added. The solution was washed with water, dried over magnesium sulfate, and concentrated. The ether and benzyl alcohol were subsequently removed by evaporation and by distillation (60–80°C/3 Torr). The residue was purified by vacuum distillation to give 16.0 g (54.7%) of racemic benzyl 3-hydroxybutanoate. The ¹H NMR spectrum was the same as that obtained from **II**.

Racemic benzyl 3-hydroxybutanoate was converted into dibenzyl ester (89% yield) by the same procedure as that described for the synthesis of **IV**. Racemic dibenzyl ester was isolated as a white crystal after recrystallization from ethanol.

mp 80–81°C

IR (KBr): 3450, 2985, 1735 (C=O), 1719 (C=O), 1497, 1392, 1300, and 1275 cm⁻¹.

¹H NMR (CDCl₃): 1.45 (d, $J = 6.3$ Hz, 6H), 2.70 (dd, $J = 15.5$ Hz, $J = 5.3$ Hz, 2H), 2.85 (dd, $J = 15.5$ Hz, $J = 7.7$ Hz, 2H), 5.10 (s, 4H), 5.55 (sextet, $J = 6.3$ Hz, 2H), 7.20–7.30 (m, 10H), and 7.96 (s, 4H) ppm.

MS (*m/e*): 519 (23), 411 (88), 384 (5), 343 (20), 321 (100), 298 (18), 271 (20), 235 (100), 181 (57), 149 (98), 91 (100), 69 (100), 42 (72), and 18 (8).

Anal. Calcd for C₃₀H₃₀O₈: C, 69.49%; H, 5.83%. Found: C, 69.30%; H, 5.89%.

Racemic dibenzyl ester was hydrogenolyzed to produce racemic dicarboxylic acid **VIII** in 67% yield.

mp 175–177°C

IR (KBr): 3000 (OH), 1720 (C=O), 1580, 1412, 1383, and 1270 cm⁻¹.

¹H NMR (DMSO-*d*₆): 1.38 (d, $J = 6.4$ Hz, 6H), 2.60–2.78 (m, 4H), 5.35 (sextet, $J = 6.3$ Hz, 2H), 8.00 (s, 4H), and 12.1–12.4 (brs, 2H) ppm.

MS (*m/e*): 339 (6), 253 (50), 235 (96), 166 (85), 149 (100), 132 (86), 86 (99), 69 (70), 43 (70), and 28 (100).

Anal. Calcd for C₁₆H₁₈O₈: C, 56.80%; H, 5.36%. Found: C, 56.63%; H, 5.43%.

Polymerization

A typical example of the polycondensation is described below.

Polyester-amide VIIc. A mixture of dicarboxylic acid **V** (0.846 g, 2.5 mmol), 4,4'-oxydianiline (0.501 g, 2.5 mmol), triphenyl phosphite (1.60 g, 5.2 mmol), pyridine (1.25 ml), and calcium chloride (0.25 g) in 5 ml of NMP was slowly stirred at 100°C under nitrogen. As the polycondensation proceeded, the solution became turbid and viscous. After having stirred for 3 h, the reaction mixture was poured into 180 ml of methanol. The precipitated polymer was isolated, then washed thoroughly with hot methanol. Drying under vacuum gave 1.07 g (85%) of polyester-amide **VIIc** with an inherent viscosity of 0.44 dl g⁻¹ measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C.

IR (Film): 3294 (NH), 3138, 3070, 2984,

2983, 1721 (ester C=O), 1663 (amide C=O), 1638, 1547, 1502, 1408, and 1272 cm^{-1} .

^1H NMR (DMSO- d_6): 1.40 (d, $J=6.3$ Hz, 6H), 2.68 (dd, $J=14.9$ Hz, $J=9.26$ Hz, 2H), 2.78 (dd, $J=14.7$ Hz, $J=7.5$ Hz, 2H), 5.45 (sextet, $J=6.0$ Hz, 2H), 6.90 (d, $J=9.0$ Hz, 4H), 7.52 (d, $J=9.0$ Hz, 4H), 8.00 (s, 4H), and 9.95 (s, 2H) ppm.

Anal. Calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_7$: C, 66.92%; H, 5.21%; N, 5.57%. Found: C, 67.33%; H, 5.22 %; N, 5.51.%.

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