

Synthesis and Characterization of Optically Active Polyesters from Chiral 1,3-Diols and Aromatic Dicarboxylic Acid Chlorides

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ABSTRACT: Optically active polyesters were synthesized from chiral (2*R*,4*R*)-pentane-2,4-diol or its analogues and various aromatic diacid chlorides in refluxing 1,2-dichloroethane in the presence of pyridine. The resulting polyesters had inherent viscosities of 0.22—0.57 dl g⁻¹, and specific rotation from +4° to -421°. The glass transition temperatures of the polymers were in the range from 66°C to 147°C and their initial decomposition temperatures were around 280°C. No remarkable difference in thermal behavior was observed between the optically active polyesters and optically inactive polymers derived from the corresponding racemic diols.

KEY WORDS Optically Active Polyesters / Chiral 1,3-Diols / Dichroic Absorption / Thermal Behavior /

Polyesters having asymmetric carbons in their main chains have been synthesized and characterized by several authors in order to investigate the influence of the chirality to the physical properties of the polymers such as melting point, glass transition temperature, crystallinity, solubility in various solvents, and mechanical properties.¹ Recently much interests have been paid to prepare optically active

polymers having various functionalities and high performances (liquid crystalline polymers,² HPLC chiral stationary phases,³ etc.). In most cases, however, only the derivatives of naturally occurring compounds are sources for optically active units of the polymers. The preparation of optically active monomers by asymmetric synthesis is interesting, because a variety of new types of optically pure

Table I. Properties of chiral diols I

Chiral diols	R ₁	R ₂	Configuration	mp	<i>e.e.</i> ^a	[α] _D ^b
				°C	%	
Ia	CH ₃	CH ₃	2 <i>R</i> ,4 <i>R</i>	46—47	>99	-38.6
Ib	C ₆ H ₅	CH ₃	1 <i>S</i> ,3 <i>R</i>	61—63	94.2	-78.3
Ic	C ₆ H ₅	C ₆ H ₅	1 <i>S</i> ,3 <i>S</i>	152—153	>99	-55.2

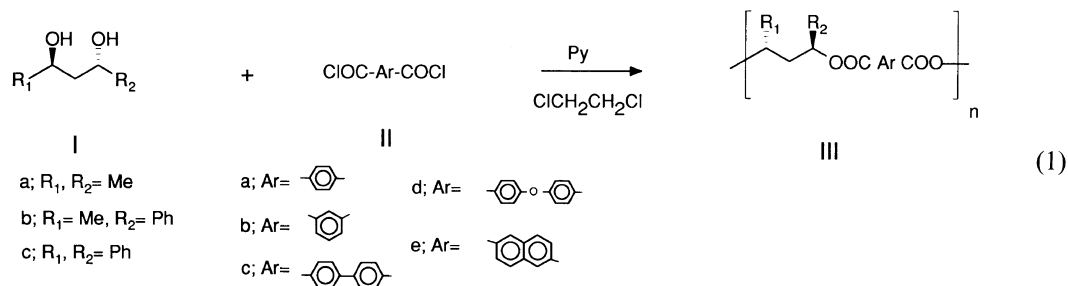
^a Enantiomeric excess determined by HPLC analyses of the corresponding (*R*)-α-trifluoromethylphenylacetyl esters.

^b Measured in chloroform at 25°C.

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monomers could be obtained in both anti-podes. This article deals with the preparation and characterization of optically active polyesters from aromatic dicarboxylic acid chlorides and chiral diols which were derived by the

Ruthenium-BINAP-catalyzed asymmetric hydrogenation of the corresponding β -diketones (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) (eq 1).



EXPERIMENTAL

Measurements

IR spectra were recorded on a JASCO IR-810 spectrophotometer. Both ^1H NMR and ^{13}C NMR spectra were measured on a Bruker AMX 400 spectrometer using tetramethylsilane as an internal standard, and chemical shifts are quoted in ppm. Optical rotation measurements were obtained on a JASCO DIP-360 spectrometer. Circular dichroism (CD) spectra and UV spectra were recorded on a JASCO J-500C spectropolarimeter and a Hitachi 330 spectrophotometer, respectively. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DSC-41M and TGA-40M, respectively, and measurements were run at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen at a flow rate of 50 ml min^{-1} . 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 polystyrene calibration on a Hitachi apparatus (eluent, CHCl_3).

Chiral Diols

Using $\text{Ru}_2\text{Cl}_4[(R)\text{-BINAP}]_2(\text{NEt}_3)$ as the catalyst for the asymmetric hydrogenation, chiral diols **I** were synthesized from the

corresponding β -diketones by the similar procedure reported previously.⁴ (2*R*,4*R*)-Pentane-2,4-diol **Ia** and (1*S*,3*R*)-1-phenylbutane-1,3-diol **Ib** were purified by distillation followed by recrystallization from ether and hexane-ethyl acetate, respectively. (1*S*,3*S*)-1,3-Diphenylpropane-1,3-diol **Ic** was purified by recrystallization from 1,2-dichloroethane. Melting points, configuration, enantiomeric excess (*e.e.*), and specific rotation of purified diols are listed in Table I.

(2*RS*,4*RS*)-Pentane-2,4-diol **IVa** and (1*RS*,3*RS*)-1,3-Diphenylpropane-1,3-diol **IVb**

Equal amount of **Ia** and (2*S*,4*S*)-pentane-2,4-diol (prepared by the asymmetric hydrogenation of 2,4-pentanedione using $\text{Ru}_2\text{Cl}_4[(S)\text{-BINAP}]_2(\text{NEt}_3)$ followed by recrystallization from ether, $>99\%$ *e.e.*, $[\alpha]_D^{25} +41.6^\circ$ (*c* 1.05, CHCl_3) was used as (2*RS*,4*RS*)-pentane-2,4-diol **IVa**.

(1*RS*,3*RS*)-1,3-Diphenylpropane-1,3-diol **IVb** was synthesized as follows: To a solution of 1,3-diphenylpropane-1,3-dione (25.0 g, 0.111 mol) in a mixture of methanol (150 ml) and benzene (150 ml) was added dropwise a solution of sodium borohydride (5.0 g, 0.132 mol) in water (50 ml) upon cooling with an ice bath. The mixture was stirred overnight at room temperature and refluxed for 10 h, and

then poured into water. Extraction with ether, drying on magnesium sulfate, evaporation of the solvents, followed by column chromatography (silica gel, eluent: hexane/ethyl acetate then methanol alone) gave a mixture of (1*RS*,3*RS*)- and (1*RS*,3*SR*)-diols. Recrystallization from a mixture of hexane and chloroform gave 8.4 g (33%) of DL-diol **IVb**. mp 123–125°C.

IR (KBr): 3400, 1455, 1402, 1063, 1036, 1024, 766, 756, 700 cm⁻¹.

¹H NMR (CDCl₃): 2.18 (t, *J* = 5.5 Hz, 2H), 2.75–3.00 (br, 2H), 4.97 (t, *J* = 5.6 Hz, 2H), 7.20–7.38 (m, 10H) ppm.

Anal. Calcd for C₁₅H₁₀O₂: C, 78.92%; H, 7.06%. Found: C, 78.65%; H, 6.95%.

Materials

Reagent-grade dicarboxylic acid chlorides such as terephthaloyl chloride (**IIa**) and isophthaloyl chloride (**IIb**) were purified by distillation under reduced pressure. 4,4'-Biphenyldicarbonyl chloride (**IIc**), 4,4'-oxydi-(benzoyl chloride) (**IId**), and 2,6-naphthalenedicarbonyl chloride (**IIe**) were prepared from the corresponding dicarboxylic acids and thionyl chloride. Compound **IId** was purified by distillation under reduced pressure, while **IIc** and **IIe** were purified by sublimation. 1,2-Dichloroethane and pyridine were distilled over phosphorus pentoxide and calcium hydride, respectively.

Polymerization

A typical example of the polymerization is described below.

Polyester **IIIa**

To a mixture of 1.00 g (9.6 mmol) of **Ia** and 2.00 g (25.3 mmol) of pyridine in 1,2-dichloroethane (20 ml) was added portionwise 1.949 g (9.6 mmol) of terephthaloyl chloride (**IIa**) in a period of 5 min. The reaction mixture was refluxed at 82°C for 10 h under nitrogen, and poured into 200 ml of methanol. The precipitated polymer was collected by filtra-

tion, washed with hot methanol, and dried under vacuum. The polymer weighed 2.20 g (98%) and had an inherent viscosity of 0.56 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ in phenol–1,1,2,2-tetrachloroethane (6:4, v/v) at 30°C. [α]_D²⁵ -295° (*c* 0.20, CHCl₃).

IR (film): 2975, 2925, 1720 (C=O), 1460, 1405, 1378, 1350, 1270, 1100, 1035, 1018, 875, 755, 718 cm⁻¹.

¹H NMR (CDCl₃): 1.54 (d, *J* = 6.3 Hz, 6H), 2.10 (t, *J* = 6.4 Hz, 2H), 5.30 (sextet, *J* = 6.3 Hz, 2H), 8.00 (s, 4H) ppm.

¹³C NMR (CDCl₃): 20.9, 42.5, 69.0, 129.5, 134.3, 165.1 ppm.

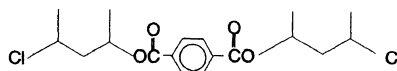
Anal. Calcd for C₁₃H₁₄O₄: C, 66.66%; H, 6.02%. Found: C, 66.29%; H, 6.11%.

Other polyesters were synthesized by the similar procedure.

RESULTS AND DISCUSSION

Polymer Synthesis

The bulk polycondensation of (2*R*,4*R*)-pentane-2,4-diol (**Ia**) with terephthaloyl chloride (**IIa**) by heating at 100°C under reduced pressure gave only low molecular weight polymer. We isolated compound **V** from the resulting mixture by silica gel column chromatography. This result indicated that some of the terminal secondary alcohols were chlorinated by hydrogen chloride generated during the polymerization, and hence this limited molecular weight of the resulting polymer.



V

The polyesters with inherent viscosities of 0.22–0.57 dl g⁻¹ were readily obtained by the solution polycondensation in refluxing 1,2-dichloroethane in the presence of pyridine as a hydrogen chloride acceptor. The results of the synthesis of polyesters are summarized in Table II. The polymers had \bar{M}_n of 7000–56000

Table II. Synthesis of optically active and inactive polyesters

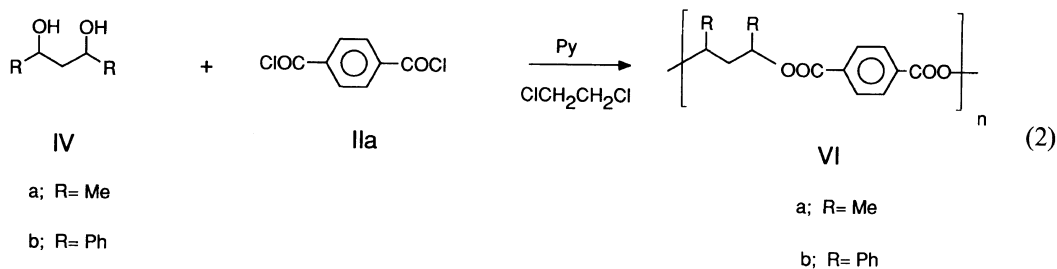
Monomers			Polymer				
Diol	Diacid chloride	Code	Yield	η_{inh}^a	\bar{M}_n^b	\bar{M}_w^b	\bar{M}_w/\bar{M}_n^b
			%	dl g ⁻¹	$\times 10^{-4}$	$\times 10^{-4}$	
Ia	IIa	IIIa	98	0.56	5.0	6.4	1.3
Ia	IIb	IIIb	92	0.47	3.6	5.0	1.4
Ia	IIc	IIIc	89	0.43	1.7	3.5	2.1
Ia	IId	IIId	98	0.57	3.0	5.2	1.7
Ia	IIe	IIIe	86	0.22	0.7	1.4	2.0
Ib	IIa	IIIf	94	0.36	1.4	3.4	2.4
Ic	IIa	IIIg	80	0.41	2.9	4.8	1.7
IVa	IIa	VIa	91	0.48	2.0	4.3	2.1
IVb	IIa	VIb	82	0.37	1.5	3.6	2.4

^a Measured at a concentration of 0.5 g dl⁻¹ in phenol-1,1,2,2-tetrachloroethane (6:4, v/v) at 30°C.

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

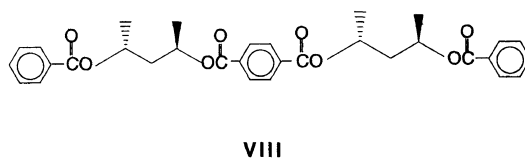
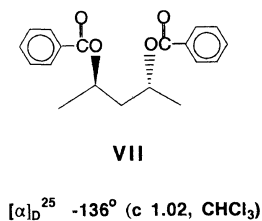
by GPC analyses based on standard polystyrene and the \bar{M}_w/\bar{M}_n values were 1.3–2.4. By the same manner for the syntheses of optically active polymers, we also prepared

optically inactive polyesters **VIa** and **VIb** by the reaction of terephthaloyl chloride with racemic diols **IVa** and **IVb**, respectively (eq 2), and the results are listed in Table II.



Polymer Characterization

The polyesters from chiral diols **I** had negative specific rotation values except for **IIIg** (Table III). We synthesized **VII** and **VIII** as model compounds for polymer **IIIa**.



Model compounds **VII** and **VIII** had specific rotation values of -136° and -180° , respectively, measured in chloroform. As shown in Figure 1, it is noteworthy that the specific rotation of **IIIa** increased with increasing the inherent viscosity, and saturated over around

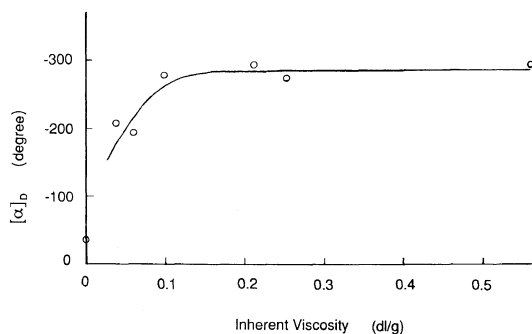


Figure 1. Relationship between inherent viscosity and specific rotation of polymer **IIIa**. Inherent viscosity; measured in phenol–1,2,2-tetrachloroethane (6:4, v/v) at a concentration of 0.5 g dl^{-1} at 30°C . Specific rotation, measured in CHCl_3 at 25°C .

0.1 dl g^{-1} .

Figure 2 shows the CD and UV spectra of optically active polyester **IIIa**. These spectra indicated that the polymers had dichroic absorption from 280 nm to 220 nm, characterized by negative and positive peaks. This suggests that the aromatic nuclei of the polymers are located in a chirally perturbed environment similar to other polyesters reported.⁵

Polymer **IIIc**, **IIIe**, **IIIg**, and **IIIh** whose aromatic rings are linearly bonded in the main chain gave similar CD behavior to that of **IIIa** in the UV absorption region based on $\pi \rightarrow \pi^*$ electronic transitions. The CD spectrum of polymer **IIIh** showed relatively small positive peak compared with negative dichroic band, whereas no maximum peak was obtained for **IIIb** in the region between 220 nm and 300 nm.

Optically active polymers **IIIa**–**IIIh** having methyl side groups were soluble in chloroform, 1,2-dichloroethane, tetrahydrofuran (THF), toluene, and amide solvents, such as *N,N*-dimethylformamide, and *N*-methylpyrrolidone, but insoluble in dimethyl sulfoxide (DMSO) at room temperature. Polymers **IIIi** and **IIIg** having phenyl side groups were more readily soluble in these solvents, even in DMSO at room temperature, while polyester **IIIe** derived from 2,6-naphthalenedicarbonyl chlo-

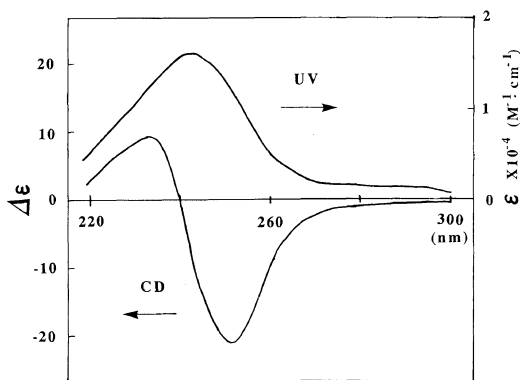


Figure 2. CD and UV spectra of polymer **IIIa** in dioxane dilute solution.

Table III. Optical rotation values and thermal behavior of polyesters

Polymer	$[\alpha]_D^a$	T_g^b	T_d^c	T_{10}^d
	degree	$^\circ\text{C}$	$^\circ\text{C}$	$^\circ\text{C}$
IIIa	-295	84	283	314
IIIb	-183	66	283	311
IIIc	-421	120	285	324
IIIh	-284	100	282	323
IIIe	— ^e	111	277	316
IIIg	-99	113	241	268
IIIi	+4	147	276	307
VIa	0	88	283	319
VIb	0	149	272	294

^a Measured in chloroform at 25°C .

^b Determined by DSC in nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$.

^c T_d is the initial decomposition temperature measured by TG in nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$.

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

^e Only slightly soluble in chloroform.

ride was less soluble in THF, toluene, and DMSO. No remarkable difference of the solubility was observed between the optically active polyesters and the corresponding optically inactive polymers.

The thermal characterization was carried out by means of differential scanning calorimetry (DSC) and thermogravimetry (TG). The thermal behavior of the polyesters are listed in Table III. The glass transition temperatures

(T_g) of the optically active polyesters were observed from 66°C to 147°C by DSC measurements. The results for polymers **IIIa**, **IIIb**, and **IIIg** indicated that the T_g increased with increasing the number of phenyl side groups. This phenomenon is explained in terms of increasing of rigidity caused by the introduction of phenyl group. The thermal decomposition temperature (T_d) of the optically active polymers started at around 280°C under nitrogen. No significant difference in thermal behavior (T_g and T_d) was observed between optically inactive polyesters **VIa** and **VIb** and the corresponding optically active polyesters.

CONCLUSION

We have synthesized optically active polyesters from chiral 2,4-pentanediol or its analogues and aromatic dicarboxylic acid chlorides in the presence of pyridine as a hydrogen chloride acceptor. The CD spectra of some of **III** showed dichroic absorption, characterized by negative and positive peaks. The T_g of the resulting polymers heightened with increasing the number of attached phenyl

groups. The thermal properties and solubility of the optically inactive polyesters **VIa** and **VIb** did not differ significantly from those of the corresponding optically active polyesters.

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