Synthesis and Properties of Stereoregular Poly[D-(2-Methyl-2-hydroxy-ethoxy)-*p*-benzoic Acid]

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ABSTRACT: Stereoregular poly[D-(2-methyl-2-hydroxy-ethoxy)-*p*-benzoic acid] was prepared by polycondensation of D-(2-methyl-2-hydroxy-ethoxy)-*p*-benzoic acid. Polycondensation was carried out with *p*-toluenesulfonic acid as catalyst in a purified nitrogen atmosphere. The polyester with number-average molecular weight of 3870 showed a melting point 147–149°C, a specific rotation $[\alpha]_D^{15} = -61^\circ$ at 589 m μ (in tetrahydrofuran), and was soluble in chloroform, tetrahydrofuran, and other polar solvents. Spherulites were formed by casting the polyester from a chloroform solution. X-ray diffraction proved its crystallinity. The optical rotatory dispersion curves of the polyester in chloroform, tetrahydrofuran and other polar solvents followed a one-term Drude equation. This fact suggests that the polyester does not have any ordered secondary structure in solution.

KEY WORDS Poly[D-(2-Methyl-2-hydroxy-ethoxy)-*p*-benzoic Acid] / Polycondensation / Optically Active Polyester / Crystallinity / ORD / Drude Equation /

Many works¹ on the synthesis and properties of optically active polymers have been reported. However, there have been few studies²⁻⁴ of synthetic optically active polymers other than polypeptides, especially of polyesters.

(Methyl substituted-2-hydroxy-ethoxy)-*p*-benzoic acid (I) has two positional isomers associated with the methyl group. Each of them has two optical isomers corresponding to the molecular structure of I.

or

Three kinds of polyesters with different stereoregularities will be obtained by polycondensation of these four isomers; (A) optically inactive polyester without any regularities in the position of the methyl group along the chain, (B) optically inactive polyester with regularities in the position of the methyl group, and (C) optically active polyester with regularities in the position of the methyl group.

The main purpose of this work is to synthesize the optically active and highly regular polyester (C) and to discuss the effect of the optical activity of the polyester upon some physical properties. Comparison was made between the optically active and inactive polyesters. The conformation of the optically active polyester in several different solutions was studied by measuring the optical rotatory dispersion.

EXPERIMENTAL

Materials

D-1-Bromo-2-propanol was prepared by the method of Levene, *et al.*⁵ The fraction distilled at 45°C (12 mm) showed $[\alpha]_D = -2.7^\circ$ (lit. $[\alpha]_D = -2.87^\circ$).

D-(2-Methyl-2-hydroxy-ethoxy)-*p*-benzoic acid (II) was prepared as follows.

p-Hydroxy benzoic acid (0.1 mol) and sodium hydroxide (0.23 mol) were dissolved in 45 ml of pure water. D-1-Bromo-2-propanol (0.12 mol) was dropped into the solution with vigorous stirring at 80°C. After reaction for two hours, the solution was cooled and acidified by the addition of dilute hydrochloric acid. The pre-

cipitated crystals were recrystallized from pure water and sublimated at 145°C (1 mm) to give pure crystals with mp 157°C and $[\alpha]_D^{15} = -22.5^\circ$ (*c* 0.5, methanol).

Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.12. Found: C, 61.20; H, 6.34.

The racemic monomer (III) was prepared from DL-bromopropanol by the same method. mp 157°C.

Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.12. Found: C, 61.16; H, 6.34.

Polycondensation

Polycondensation was carried out in two steps after the ordinary polycondensation procedure in a molten state in a purified nitrogen atmosphere. The first step was to heat the monomer (II or III) at temperatures between 180 and 195°C under a slow stream of nitrogen through the melt. In the second step, the pressure was reduced to 0.1 mmHg or less and polycondensation was continued at temperatures between 200 and 270°C. The obtained polyester was purified by reprecipitation using chloroform as a solvent and methanol as a precipitant.

Measurements of Physical Properties

The gas chromatography was carried out by using a stainless steel column of 1.5 m in length, 3 mm in diameter, packed with polyethylene glycol on Shimalite. Operation conditions: column temperature, 115°C; flash evaporator, 120°C; carrier gas (helium) speed, 25 ml/min.

Air was employed as an internal standard.

The NMR spectra were recorded on a Varian Model A-60 high resolution spectrometer. Tetramethylsilane was used as an internal standard. A chloroform solution was used.

The infrared spectra were measured on a Perkin-Elmer Model 337 infrared spectrometer and a JASCO Model IR-G spectrometer by the liquid film method with NaCl plates for liquid samples and the KBr tablet method for solid samples, respectively.

The molecular weight of polyester was determined by the vapor pressure method with a chloroform or tetrahydrofuran solution by using a Hitachi-Perkin-Elmer 115 molecular weight apparatus.

The polarizing microphotographs of spherulites of the polyesters under crossed nicols were taken for the films cast from the chloroform solution on a glass plate at room temperature.

The X-ray powder photographs of the monomers and the polymers were taken with a cylindrical camera of 3.5 cm in radius with a Rigaku Denki RU-3 X-ray diffractometer.

The DSC measurements were made with Perkin-Elmer DSC-1 differential scanning calorimeter with a heating rate of 10°C/min.

The optical rotatory dispersion of the polyester in several kinds of solvents was measured at room temperature with a JASCO Model ORD/UV-5 spectropolarimeter, using a quartz cell 1 cm long.

Figure 1. Gas chromatogram of DL-bromopropanol. Operation conditions: column temperature, 115°C; flash evaporator, 120°C; carrier gas (helium) speed, 25 ml/min.

RESULTS AND DISCUSSION

Stereoregularity

Figure 1 shows the gas chromatogram of DL-bromopropanol. DL-Bromopropanol is considered to be composed of two components, which are denoted by A and B in Figure 1. The infrared spectra of the gas chromatography fractions A and B are shown in Figure 2. Stewart, *et al.*,⁶ reported that the infrared spectra of chloropropanol have the characteristic absorption bands of 1-chloro-2-propanol and 2-chloro-1-propanol at 940 cm^{-1} and 980 cm^{-1} , respectively. Comparison of Figure 2 with their spectra⁶ suggests that fraction A is 1-bromo-2-propanol and fraction B is 2-bromo-1-propanol.

Figure 2. IR spectra of DL-bromopropanol.

Figure 3 shows the NMR spectra of fractions A and B. The band caused by the methyl group appears at $\delta = 1.25\text{ ppm}$ in fraction A and $\delta = 1.65\text{ ppm}$ in fraction B. According to Jackman,⁷ the chemical shift of the methyl group for 2-substituent is lowered more in the bromine atom than in the hydroxyl group. It is, therefore, supposed that fraction A has the chemical structure of $\text{CH}_3\text{—CH(OH)—}$ and fraction B has $\text{CH}_3\text{—CH(Br)—}$.

The NMR signal relating to the methylene group is found at $\delta = 3.40\text{ ppm}$ in fraction A and $\delta = 3.68\text{ ppm}$ in fraction B. Their chemical shifts are affected by both 1- and 2-substituents. In the case of the 1-substituent, the chemical shift caused by the hydroxyl group is lowered more than that by the bromine atom. The chemical shift caused by the 2-substituent is lowered more in the bromine atom than in the hydroxyl group. Hence, from Figure 3 it is considered that fraction A has the chemical structure of $\text{CH}_2(\text{Br})\text{—CH(OH)—}$ and that fraction B has $\text{CH}_2(\text{OH})\text{—CH(Br)—}$. Referring to the chemical shifts of the bands relating to the methyl and methylene groups, it is concluded that fraction A is 1-bromo-2-propanol and fraction B is 2-bromo-1-propanol. This conclusion is in accord with the result suggested by the infrared spectra.

Figure 4 shows the gas chromatogram (a), the infrared spectrum (b), and the NMR spectrum (c) of D-bromopropanol. A comparison of Figure 4 with Figures 1, 2, and 3 shows that

Figure 3. NMR spectra of DL-bromopropanol (in CHCl_3).

(a)

(b)

(c)

Figure 4. Gas chromatogram (a), IR spectrum (b), and NMR spectrum (c) of D-bromopropanol.

Synthesis of Stereoregular Polyester

D-bromopropanol contains a large fraction of 1-bromo-2-propanol and a small fraction of 2-bromo-1-propanol.

The compositions of D- and DL-bromopropanol were determined from the peak areas of two fractions in the gas chromatograms (Figures 1 and 4(a)). D-Bromopropanol is composed of 10% 2-bromo-1-propanol and 90% 1-bromo-2-propanol. DL-Bromopropanol is composed of 64% 2-bromo-1-propanol and 36% 1-bromo-2-propanol.

The monomer obtained from D-bromopropanol is, thus, considered to be mainly composed of the isomers, which are optically active and have the methyl group in the 2-carbon atom, although it contains a small amount of the positional isomer having the methyl group in the 1-carbon atom.

On the other hand, the monomer synthesized from DL-bromopropanol is composed of about a 1:2 mixture of two positional isomers.

Polycondensation

Table I lists the reaction conditions employed for examining the effect of catalysts on polycondensation. Zinc and lead acetate hardly increased the viscosity of the product. A product with higher viscosity was obtained by potassium carbonate, but it was highly colored by thermal decomposition. *p*-Toluenesulfonic acid was most effective in giving higher viscosity and a slightly colored product was obtained.

p-Toluenesulfonic acid was adopted thereafter as a catalyst for polycondensation. The reaction conditions are listed in Table II. The crude products were slightly colored and solidified in a glassy state. We called them thereafter the products of no. 6 and 7 DL- and D-polyester, respectively, and inspected the difference in properties between them.

Properties of Polyesters

The purified polyesters were soluble in chloroform, tetrahydrofuran (THF), nitrobenzene,

Table I. Comparison of effectiveness of catalysts in polycondensation of DL-monomer

Catalyst	Concn, mol %	First step		Second step		Products
		Temp, °C	Time, hr	Temp, °C	Time, hr	
Zn(CH ₃ COO) ₂ 2H ₂ O	0.1	200	4	250	3	Grey powder
Pb(CH ₃ COO) ₂ 2H ₂ O	0.1	200	3	240	2	Grey powder
K ₂ CO ₃	0.1	220	4	260	5	Hard block, insoluble
<i>p</i> -Toluenesulfonic acid	0.1	200	3	250	4	Hard block, soluble

Table II. Conditions of Polycondensation of DL- and D-monomers with *p*-toluenesulfonic acid as catalyst

No.	Monomer	Catalyst concn, mol %	First step ^a		Second step ^b		$\bar{M}_n, \times 10^{-3}$
			Temp, °C	Time, hr	Temp, °C	Time, hr	
1	DL-	0.2	195	3	270	2	2.15
2	DL-	0.4	180	2	220	4	—
3	DL-	0.5	185	22	230	22	2.50
4	DL-	1.0	190	5	250	2	—
5	DL-	1.5	180	3	—	—	—
6	DL-	0.2	180	14	200	8	4.00
7	D-	0.2	180	20	200	5	3.87
8	D-	0.2	190	20	200	7	—
9	D-	1.0	190	5	240	4	—

^a Normal pressure and nitrogen atmosphere.

^b Reduced pressure less than 0.1 mmHg.

pyridine, *N,N*-dimethylformamide (DMF), and dichloroacetic acid (DCA), and partially soluble in benzene at room temperature.

Infrared spectra of the monomers and the polyesters measured by the KBr tablet method are shown in Figure 5. The difference in the spectra between the D- (Figure 5a) and the DL-monomer (Figure 5b) may be due to the fact that the DL-monomer includes almost comparable quantities of the two positional isomers, whereas the D-monomer is composed of one of the two positional isomers. On the other hand, such a difference in infrared spectra was not found between the D- and the DL-polyester. The characteristic absorption band of C=O group was observed at 1960 cm^{-1} in the monomers and it shifted to 1720 cm^{-1} in the polyesters. This fact indicates that the COOH group of the monomers was converted into the ester group.

Molecular weights of the products were meas-

ured by the vapor pressure method in chloroform and THF solutions. Table II lists the products that have the number-average molecular weight ranging from 2.15×10^3 to 4.00×10^3 .

D-Polyester film prepared by casting the chloroform solution on a glass plate at room temperature showed spherulites with a double ring extinction pattern under crossed nicols of the polarizing microscope as shown in Figure 6a. This pattern is interpreted by the biaxial birefringence of the polyester crystal. A similar double ring pattern was found in the spherulites of polyethylene adipate.⁸ Figure 6b shows the spherulites of the DL-polyester, which are formed under the same crystallization conditions as in the D-polyester. The extinction pattern of DL-polyester is very much diffused compared with that of D-polyester, which reflects the poor crystallinity of DL-polyester.

X-ray powder photographs of the monomers and the crystallized polyesters are compared in

Figure 5. IR spectra of D-monomer (a), DL-monomer (b), and D-polyester (c).

(a)

(b)

Figure 6. Polarization microphotographs of spherulites of D- (a) and DL-polyester (b) under crossed nicols ($\times 1600$). Spherulites were obtained by solvent-cast at room temperature.

Figure 7. The spacings calculated from the Debye rings in Figure 7 are summarized in Table III. The spacings and the relative intensities of the D-monomer are different from those of the DL-monomer. This fact means that the crystals of DL-monomer are not a simple mixture of D- and L-crystals.

DL-Polyester is crystalline at least, as far as the reflection of $d = 4.26\text{\AA}$ is found, but its crystallinity is very low. The reasons for the low crystallinity of DL-polyester were ascribed to the positional isomerism associated with the methyl group and the optical isomerism of propylene glycol residue. Poly(DL-propylene terephthalate) was reported by Hill, *et al.*,⁹ as amorphous. Their samples were bulk-crystallized ones. In our case the melt-crystallized D- and DL-polyesters were also in an amorphous state. It was necessary to vaporize the solvent from the solution in order to obtain the polyesters in a crystalline state.

(a)

(b)

(c)

(d)

Figure 7. X-ray powder photographs of the monomers and the crystallized polyesters: (a) D-monomer, (b) D-polyester, (c) DL-monomer, and (d) DL-polyester.

The melting points of the crystallized polyesters measured by DSC are listed in Table IV. The thermograms of both the polyesters showed two endothermic peaks. In D-polyester, the higher temperature peak (T_{m_2}') is larger than the lower temperature peak (T_{m_2}''). In DL-polyester, the lower temperature peak (T_{m_2}') is larger than the higher temperature peak (T_{m_2}''). We considered that the temperatures of main peaks correspond with the melting points of polyesters. Thus, the melting point of the D-polyester is taken as 148.0°C and that of the DL-polyester is 114.8°C . The side peaks are considered to be due to the coexistence of the crystals composed of more or less different isomers.

Optical Rotatory Dispersion

Figure 8 shows the ORD curves for D-polyester in various solvents. DL-Polyester was optically inactive. D-Polyester was optically active and showed plain negative dispersion curves in the measured range of wave length

Table III. Spacings of D- and DL-monomers and polyesters

D-monomer <i>d</i> , Å	DL-monomer <i>d</i> , Å	D-polyester <i>d</i> , Å	DL-polyester <i>d</i> , Å
10.48 (w) ^a			
7.90 (m)	6.44 (m)		
	5.95 (m)		
5.53 (v w)	5.57 (s)		
5.03 (s)	4.97 (v w)	5.08 (m)	
	4.69 (s)	4.56 (m)	
	4.18 (w)	4.34 (s)	4.26 (m)
3.94 (s)	3.94 (w)		
3.62 (s)	3.63 (s)	3.62 (m)	
3.36 (w)	3.45 (v w)		
	3.14 (m)		
3.04 (w)	2.97 (v w)		
2.75 (w)	2.82 (v w)		
	2.64 (m)		
2.46 (w)	2.44 (w)		
	2.34 (w)		
2.21 (w)	2.17 (m)		
2.10 (v w)			
2.02 (w)	2.00 (m)		
1.86 (w)	1.82 (m)		

^a Relative intensity: (s), strong; (m), medium; (w), weak; (v w), very weak.

Table IV. Melting points of D- and DL-polyesters by DSC^a

Polyester	<i>T</i> _{m1} ^b , °C	<i>T</i> _{m2} ^c , °C	<i>T</i> _{m2} ^{''} , °C	<i>T</i> _{m3} ^c , °C
D-	117.1	129.7	148.0 ^c	156.4
DL-	87.6	114.8 ^c	135.9	145.2

^a The DSC measurements were made at a heating rate of 10°C/min.

^b *T*_{m1}, starting temperature of fusion; *T*_{m2}['] and *T*_{m2}^{''}, peak temperature of fusion; *T*_{m3}, temperature of end point of fusion.

^c The temperature of main peak which represents melting points of polyesters.

in THF, DMF, and DCA solutions. The ORD curve for the chloroform solution showed the negative single Cotton effect with the trough at 274 mμ ($[\alpha] = -10250^\circ$), intersected the abscissa at the point of 266 mμ and came to a peak at 249 mμ ($[\alpha] = -27500^\circ$). The amplitude of the Cotton effect in chloroform is abnormally large. Such a large Cotton effect has been sometimes observed in the optically active com-

Figure 8. ORD curves for D-polyester in the solvents: chloroform (1 and 6), pyridine, (2), THF (3), DMF (4), and DCA (5).

pounds with an asymmetric center in the vicinity of the aromatic ring and has been explained as due to the enhancement effect of the phenyl group.^{10,11}

In such aromatic compounds, the phenyl group contributes to the total rotation in two ways; (a) by its own rotatory contribution, as found in L-mandelic acid¹² and L-phenylalanine,¹³ and (b) by its vicinal action on the other substituents, as found in 17α-hydroxy-5α-androstane benzoate.¹⁴ Theoretical interpretation has not been given, however, to the enhancement effect of the phenyl group. In the present case, the circular dichroism of D-polyester in a chloroform solution showed a negative peak at 266 mμ, corresponding to the absorption band of the phenyl group. This fact indicates that the phenyl group conjugated with the ester group plays a role of optically active chromophore. Thus the remarkable Cotton effect in D-polyester may be attributed to the enhancement effect of the phenyl group.

The ORD curves of the polyester in chloroform, which is less in polarity, and other polar solvents, followed a one-term Drude equation in the wave length range of 350–600 mμ, as shown in Figure 9. Table V lists the values of optical rotatory dispersion, which are compared with those of D-monomer in various solvents. They give the dispersion constant, λ_0 , of 278—

Figure 9. Lowry plots for D-polyester in the solvents: chloroform (□), pyridine (△), THF (◇), DMF (○), and DCA (▽).

Table V. Specific rotations at 589 mμ and the dispersion constants of ORD curves of D-monomer and D-polyester

Solvent	D-Monomer [α] _D , °	D-Polyester	
		[α] _D , °	λ _c , ^a mμ
Chloroform	—	−150	278
THF	−18	−61	302
DMF	−8	−90	281
Pyridine	—	−50	303
DCA	−38	−84	302
Methanol	−25	—	—

^a 0.1 g/100 ml in chloroform and 0.5 g/100 ml in other solvents at room temperature.

303 mμ, which corresponds to the absorption band of the phenyl group.

It may be considered, therefore, that the D-polyester does not have an ordered secondary structure, but a random conformation in solution. Table V also lists the specific rotations at 589 mμ, [α]_D, for D-polyester in various solutions, which take much larger negative values than those of D-monomer when comparison is made in the same solvents. Because D-polyester does not show the effect of helical structure on its optical rotation, the difference of [α]_D be-

tween D-polyester and D-monomer is considered due to the enhancement effect of the phenyl group on the rotation. Similar effects were found in the comparison of *sec*-butyl alcohol¹⁵ and 17α-hydroxy-5α-androstane¹⁴ with their benzoates, respectively.

In this work, the optically active and stereoregular polyester was synthesized. From the fact that spherulites were formed by casting the polyester from the chloroform solution and that X-ray powder photographs of the crystallized polyesters showed Debye rings, it was proved that the polyester is crystalline. The ORD of D-polyester in several solutions suggested that the D-polyester has a random conformation in the solution similar to the results of several studies²⁻⁴ of optically active polyesters, which have been reported hitherto. D-Polyester has *p*-phenylene rings bonded with ester groups in its chemical structure, which constitute the rigid parts of the main chain. On the other hand, it has flexible ether linkages in its chain at the same time. An ordered secondary structure may be difficult to formulate with such a chain structure.

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