

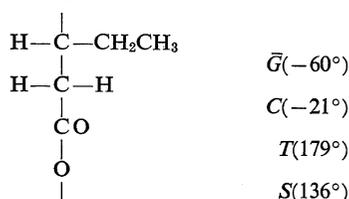
Structural Studies of Polyesters. VII. Molecular and Crystal Structures of Racemic Poly(β -ethyl- β -propiolactone)

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ABSTRACT: The molecular and crystal structures of the synthesized racemic poly(β -ethyl- β -propiolactone) $[-\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{COO}-]_n$ were studied by X-ray diffraction. The unit cell is orthorhombic, $P2_12_12_1(D_2^4)$, with $a=9.32\text{\AA}$, $b=10.02\text{\AA}$, and $c(\text{fiber axis})=5.56\text{\AA}$; two molecules pass through the unit cell. The molecule has a conformation



shown by the Fischer projection for the case of the rectus polymer, giving a left-handed (2/1) helix: the O—C bond is nearly *skew*, 136° , and the C—C(O) bond is far from the *gauche* form, -21° . The internal rotation angle about the sequence O—CH—CH₂—CH₃ is 64° . From the results of the X-ray analysis, it may be concluded that (1) the crystalline polymer prepared from the racemic monomer, β -ethyl- β -propiolactone, is isotactic and (2) the bulk sample of this racemic polymer consists of two kinds of crystallites, one composed only of left-handed helices of rectus polymer chains, the other only of right-handed helices of sinister polymer chains.

KEY WORDS Structure of Poly(β -ethyl- β -propiolactone) / X-ray Diffraction / Energy Calculation / Constrained Least-Squares Method / Isotactic Polymer /

In a previous paper,¹ the crystal structure of poly(β -hydroxybutyrate) $[-\text{CH}(\text{CH}_3)\text{CH}_2\text{COO}-]_n$ has been reported as an extension of the structural studies of aliphatic polyesters. In the present paper, the crystal structure of racemic poly(β -ethyl- β -propiolactone) $[-\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{COO}-]_n$ is reported. On the basis of X-ray analysis, several models of molecular conformation were selected by utilizing the calculations of the intramolecular interaction energies.

EXPERIMENTAL

Sample

Monomer, DL- β -ethyl- β -propiolactone, was obtained by reacting propionaldehyde with ketene; the preparative separation was carried out by using a Silicone DC-500 (Dow Chemical Co.) column.

Racemic polymer was prepared by polymerizing DL- β -ethyl- β -propiolactone with $\text{AlEt}_3\text{—H}_2\text{O—epichlorohydrine}$ catalyst. The melting point of the crystalline polymer is $105\text{—}108^\circ\text{C}$.² The samples for X-ray measurements were prepared by quick drawing of the molten sample during the cooling process to room temperature, followed by further elongation giving necking, and heat-treatment at 92°C under tension *in vacuo* for one day.

X-Ray Measurements

Throughout the present study, X-ray photographs were taken by using nickel-filtered Cu— $K\alpha$ radiation. An X-ray photograph of racemic poly(β -ethyl- β -propiolactone) taken with a cylindrical camera is given in Figure 1. The meridional reflection data were taken from the

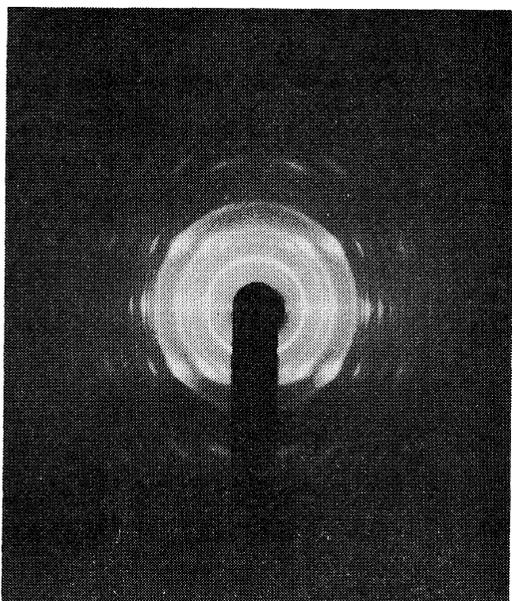


Figure 1. X-ray fiber photograph of racemic poly(β -ethyl- β -propiolactone).

photograph using a Weissenberg camera, where the sample was oscillated about an axis normal to the fiber axis. From the photograph in Figure 1, sixty-one independent reflections were observed. The camera radius was corrected with the spacings of the reflections of aluminum powder. The reflection intensities of the fiber diagram obtained by the multiple-film method were measured by visual comparison with a standard intensity scale. The corrections using Lorentz-polarization factors and the obliquity effect in the fiber diagram were made.

ANALYSIS AND RESULTS

Unit Cell and Space Group

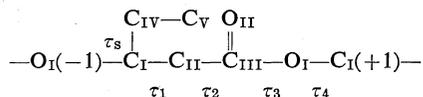
The reflections observed on the photograph could be indexed by an orthorhombic cell: $a=9.32\text{\AA}$, $b=10.02\text{\AA}$, and c (fiber identity period) $=5.56\text{\AA}$. Assuming four monomeric units in the cell, the calculated density is 1.28 g/ml , and this value is in agreement with the observed density measured by the flotation method, 1.20 g/ml . The space group is $P2_12_1(D_2^4)$ from the following systematic absences: $h00$ when h is odd, $0k0$ when k is odd, and $00l$ when l is odd. This space group is the same as that of poly(β -hydroxybutyrate).¹ It was assumed from these experi-

mental data that this polymer molecule has a two-fold helical symmetry relating two monomeric units, and that two molecules pass through the unit cell.

Molecular Models

According to the conformational energy calculations reported so far, the conformations of polymers predicted from the calculated energies were in agreement with the reported crystallographic results.³ Polypivalolactone [$-\text{CH}_2\text{C}(\text{CH}_3)_2\text{COO}-$]_{*n*},⁴ poly(β -hydroxybutyrate), and poly(β -ethyl- β -propiolactone) have the same main chain chemical structures, but have different kinds and positions of substituent groups. From the results of the energy calculations of polypivalolactone and poly(β -hydroxybutyrate),⁵ the parameters for the energy calculation of the isolated polyester chain seemed to be reliable. Therefore, we tried an application of the energy calculation to the structure analysis of poly(β -ethyl- β -propiolactone).

The conformational energies were calculated for all the possible rectus polymer chain models with two-fold helical symmetry, by fixing the fiber identity period of 5.56\AA . The energies were computed by taking into account the internal rotation barriers, the nonbonded interactions, and the dipole-dipole interactions, where the bond lengths and the bond angles were fixed. The parameters for the energy calculation in the present paper were the same as those used in ref 5, and the following bond lengths and bond angles were assumed: $\text{C}-\text{C}=1.54\text{\AA}$, $\text{C}-\text{H}=1.09\text{\AA}$, $\text{C}-\text{O}=1.43\text{\AA}$, $\text{C}-\text{C}(\text{O})=1.52\text{\AA}$, $\text{C}(\text{O})-\text{O}=1.36\text{\AA}$, $\text{C}(\text{O})=\text{O}=1.23\text{\AA}$, $\angle\text{C}-\text{C}(\text{O})-\text{O}=115^\circ$, $\angle\text{C}-\text{C}(\text{O})=\text{O}=\angle\text{O}=\text{C}(\text{O})-\text{O}=122.5^\circ$, and $\angle\text{C}(\text{O})-\text{O}-\text{C}=112^\circ$, while all the other bond angles were regular tetrahedral [$\text{C}(\text{O})$ is the carbon atom of the carbonyl group]. The numbering of the atoms and the internal rotation angles are as follows:



The internal rotation angle about the sequence $\text{O}_{\text{I}}(-1)-\text{C}_{\text{I}}-\text{C}_{\text{IV}}-\text{C}_{\text{V}}$ is expressed as τ_8 . From the results of the structure analyses of polyesters,¹ the internal rotation angle τ_8 was reasonably fixed at 180° . By fixing τ_8 at 180° and

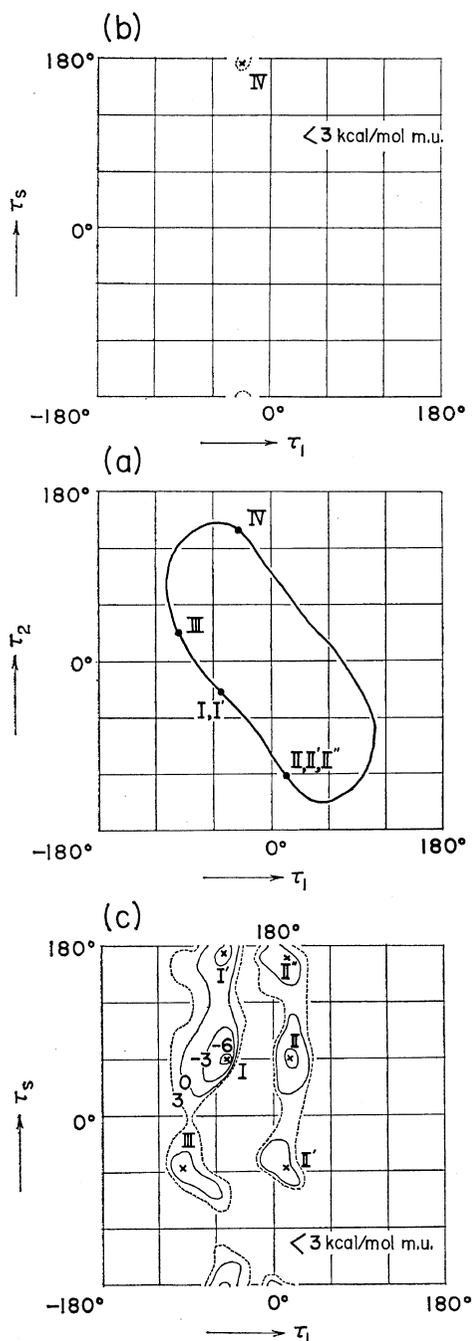


Figure 2. (a) Three-dimensional closed curve showing the relationship between τ_1 , τ_2 , and τ_4 for a possible conformation of the main chain of poly(β -ethyl- β -propiolactone); (b) the energy contour map of the rectus polymer chain on the τ_1 - τ_s plane for the upper part of the closed curve shown in (a); (c) the energy contour map for the lower part of the closed curve.

Table I. Energetically stable molecular models

Model	$\tau_1, ^\circ$	$\tau_2, ^\circ$	$\tau_3, ^\circ$	$\tau_4, ^\circ$	$\tau_s, ^\circ$	E^a	$R, \%$
I	-51	-34	180	138	61	-6.0	26.7
I'	-51	-34	180	138	171	-3.8	40.5 ^b
II	15	-122	180	71	62	-3.9	42.8
II'	15	-122	180	71	-54	-2.6	43.4 ^b
II''	15	-122	180	71	166	-2.2	49.2 ^b
III	-94	31	180	113	54	-0.8	34.8
IV	-31	141	180	-55	175	2.3	36.8

^a kcal/mol m.u.

^b Only the equatorial reflections.

varying τ_1 and τ_2 from -180° to 180° , the values of τ_4 for all possible molecular models were obtained, which satisfy the two-fold helical symmetry and the fiber identity period of 5.56\AA . The possible sets of the internal rotation angles are on one closed curve in a cube defined by the three-dimensional Cartesian coordinates, τ_1 , τ_2 , and τ_4 , each covering from -180° to 180° . In Figure 2a, the projection of the closed curve on the τ_1 - τ_2 plane is shown. Since the rotation of the side group (ethyl group) is independent of the conformation of the main chain, there is another degree of freedom: τ_s can vary from -180° to 180° on the closed curve. The energy contour maps in the τ_1 - τ_s planes of the upper part and the lower part of the closed curve are shown in Figures 2b and c, respectively, where the methyl group was assumed to be in the staggered form. From these calculations, seven potential minima were found. The internal rotation angles and the conformational energies, E , are listed in Table I. A prime and double prime indicate a difference in the conformation of the side chain. In Figure 3, models I, II, III, and IV of the seven rectus polymer models are shown. Thus, we succeeded in selecting seven models from an infinitely large number of molecular models, but we could not conclude which was the most acceptable one from the results of the energy calculation alone.

Structure Factor Calculations

The crystal structure factors were calculated for these seven molecular models. There remain two variable parameters for the space group $P2_12_12_1(D_2^4)$, *i.e.*, the azimuthal angle about the helix axis and the translation along the c axis (fiber axis). At first, the azimuthal angle was

Crystal Structure of Poly(β -ethyl- β -propiolactone)

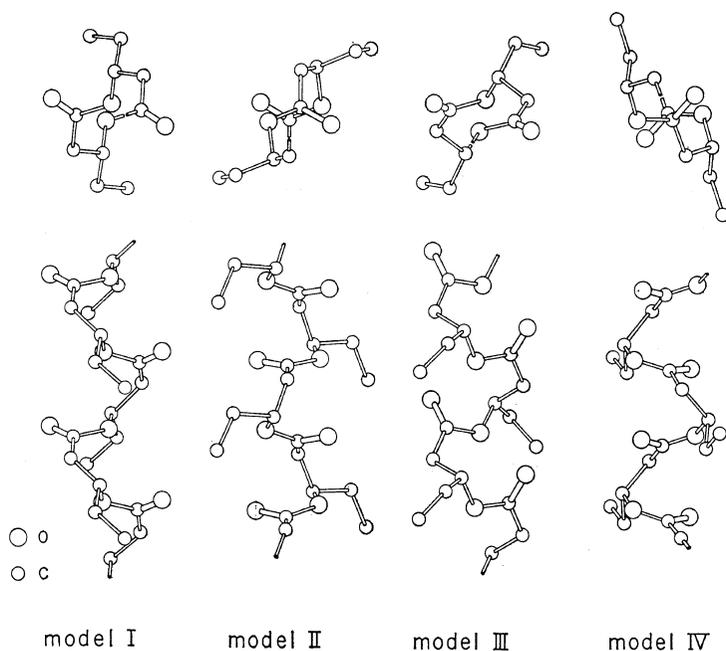


Figure 3. Four energetically stable molecular models for the rectus polymer.

determined for each molecular model so that close agreement between the observed and calculated structure factors for the equatorial reflections could be obtained. Fixing the azimuthal angle thus obtained for each molecular model, the translational parameter was determined by the use of the 1st- and 2nd-layer reflection data. The values of the discrepancy factor

$$R = \frac{\sum |(I_o)^{1/2} - (I_c)^{1/2}|}{\sum (I_o)^{1/2}}$$

of the molecular models for all the observed reflections are listed in Table I. From the values of the R factor and the conformational energy, model I was considered to be the most probable. Then, the atomic coordinates and the thermal coefficients in the crystal were refined by the

constrained least-squares method^{6,7} by using model I as a starting model. The discrepancy factor R was reduced to 19.5%. Table II lists the atomic coordinates and the thermal coefficients. The crystal structure of the rectus polymer chains is shown in Figure 4 with its symmetry elements. The comparison between the observed and calculated intensities is given in Table III. For all the computations, the NEAC-2200 model-700 electronic computer in this University was used.

DISCUSSION

It was found from the X-ray analysis of racemic poly(β -ethyl- β -propiolactone) that each crystallite is composed of only rectus polymer chains or only sinister polymer chains, of which one is the mirror image of the other. Therefore, in the bulk sample of this racemic polymer, two kinds of crystallites compensate for the optical activity of each other. The same kind of optical compensation has been already reported for the cases of poly(propylene sulfide)⁸ and poly(β -hydroxybutyrate).¹ This also implies that the synthesized crystalline poly(β -ethyl- β -propiolactone) prepared from the racemic monomer is

Table II. Atomic coordinates and thermal coefficients

	x	y	z	$B, \text{\AA}^2$
C _I	0.398	-0.049	0.575	4.2
C _{II}	0.358	-0.161	0.745	6.7
C _{III}	0.240	-0.121	0.900	3.8
C _{IV}	0.527	-0.092	0.416	7.8
C _V	0.578	0.026	0.268	6.3
O _I	0.282	-0.013	0.426	5.0
O _{II}	0.160	-0.201	1.004	5.2

Table III. Comparison of observed and calculated structure factors for racemic poly(β -ethyl- β -propiolactone)

h	k	l	$(I_o)^{1/2 a}$	$(I_c)^{1/2 b}$	h	k	l	$(I_o)^{1/2 a}$	$(I_c)^{1/2 b}$
1	1	0	121.6	114.9	4	8	0	—	18.5
0	2	0	68.3	60.6	8	3	0	—	—
2	0	0	29.6	29.7	8	4	0	—	—
1	2	0	66.7	47.1	6	7	0	18.6	20.7
2	1	0	—	6.6	3	9	0	—	—
2	2	0	19.7	8.8	7	6	0	—	—
1	3	0	33.6	32.3	0	1	1	26.1	28.3
3	1	0	54.7	57.8	1	0	1	—	—
2	3	0	38.4	42.9	1	1	1	72.6	84.7
3	2	0	17.7	18.7	0	2	1	37.8	36.3
0	4	0	28.3	16.9	2	0	1	39.3	52.6
1	4	0	20.8	21.9	1	2	1	79.3	86.1
4	0	0	—	4.6	2	1	1	—	—
3	3	0	—	—	2	2	1	40.4	46.7
4	1	0	30.1	32.6	0	3	1	—	—
2	4	0	19.6	12.8	1	3	1	23.6	23.5
4	2	0	14.1	25.4	3	0	1	—	—
1	5	0	—	—	3	1	1	29.0	29.4
3	4	0	38.8	43.0	2	3	1	37.0	22.5
4	3	0	—	9.1	3	2	1	37.7	18.8
2	5	0	—	—	0	4	1	45.2	44.7
5	1	0	13.8	15.5	1	4	1	—	—
5	2	0	14.2	5.8	4	0	1	47.3	52.6
4	4	0	16.5	10.2	3	3	1	—	—
3	5	0	—	—	4	1	1	24.6	28.0
0	6	0	18.5	20.1	2	4	1	24.6	28.0
1	6	0	—	—	4	2	1	—	14.7
5	3	0	18.9	24.5	0	5	1	—	23.2
2	6	0	—	—	1	5	1	44.3	27.7
6	0	0	19.7	24.3	3	4	1	—	—
6	1	0	—	8.1	4	3	1	37.0	29.4
4	5	0	—	—	5	0	1	26.5	12.4
5	4	0	26.2	37.9	2	5	1	16.6	18.4
6	2	0	—	—	5	1	1	—	—
3	6	0	—	4.8	5	2	1	—	7.4
1	7	0	—	—	4	4	1	—	—
6	3	0	—	15.3	3	5	1	41.9	35.8
2	7	0	—	—	0	6	1	—	—
5	5	0	15.1	22.2	1	6	1	—	11.6
4	6	0	—	—	5	3	1	—	3.4
6	4	0	—	3.5	2	6	1	—	—
7	1	0	—	16.4	6	0	1	22.8	25.8
3	7	0	—	—	6	1	1	—	—
7	2	0	20.0	19.2	4	5	1	23.3	17.2
0	8	0	—	1.7	5	4	1	—	—
5	6	0	—	—	6	2	1	—	12.6
1	8	0	—	6.5	3	6	1	—	5.8
7	3	0	—	—	0	7	1	—	5.7
6	5	0	—	—	1	7	1	17.3	15.7
4	7	0	—	8.7	6	3	1	—	—
2	8	0	—	13.5	2	7	1	—	—
7	4	0	15.6	2.6	5	5	1	27.3	18.9
8	0	0	—	—	4	6	1	—	—
3	8	0	16.5	19.9	1	1	2	32.1	42.9
8	1	0	—	—	0	2	2	24.2	26.6
6	6	0	—	—	2	0	2	—	—
5	7	0	—	12.0	1	2	2	50.3	58.7
8	2	0	—	—	2	1	2	—	—
7	5	0	—	—	2	2	2	18.4	15.6
1	9	0	18.7	13.7	0	3	2	—	—
					1	3	2	58.9	47.3
					3	0	2	—	—

Crystal Structure of Poly(β -ethyl- β -propiolactone)

Table III. (Continued)

h	k	l	$(I_o)^{1/2 a}$	$(I_c)^{1/2 b}$	h	k	l	$(I_o)^{1/2 a}$	$(I_c)^{1/2 b}$
2	3	2)	65.0	51.5	2	4	2	26.9	22.3
3	2	2)			4	2	2		
1	4	2	39.0	38.5	0	5	2)	56.3	37.5
4	0	2)	40.5	48.1	1	5	2)		
3	3	2)			3	4	2)		

^a The observed structure factors $(I_o)^{1/2}$'s were put on the same scale as the $(I_c)^{1/2}$'s by setting $\sum k(I_o)^{1/2} = \sum (mF_c^2)^{1/2}$, where k is the scale factor and m is the multiplicity.

^b $(I_o)^{1/2}$'s of the reflections which overlap on the X-ray fiber photograph are $[\sum (mF_c^2)]^{1/2}$.

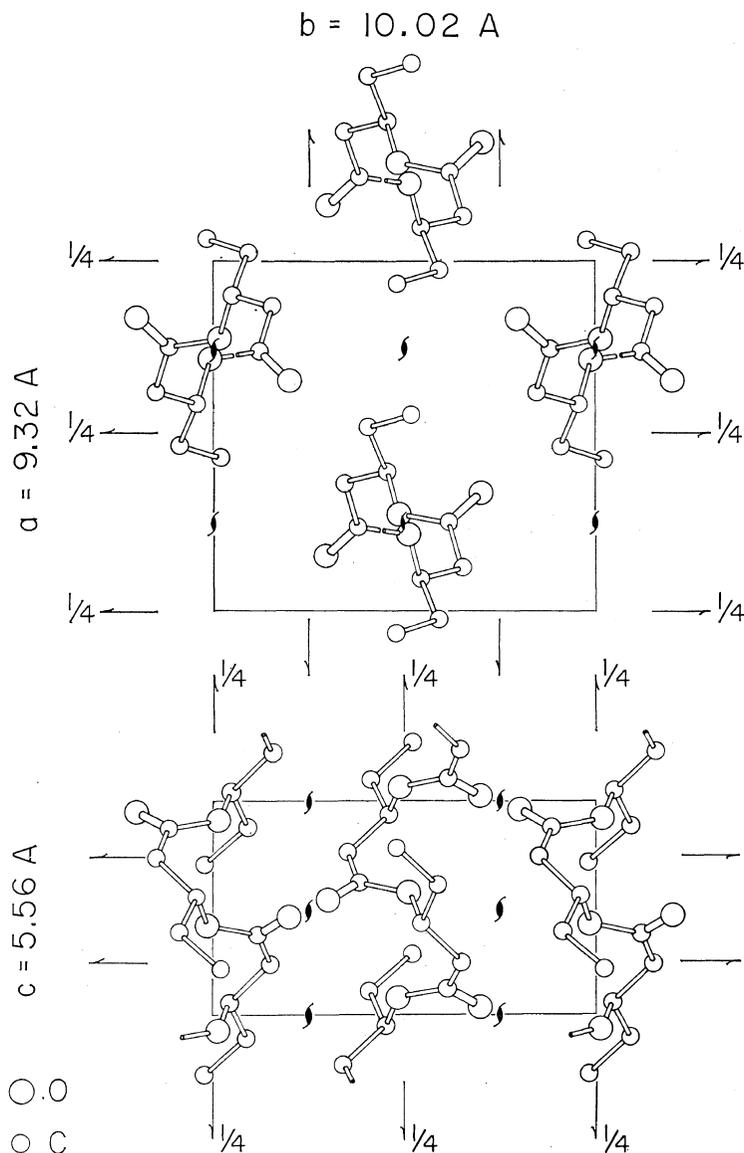


Figure 4. Crystal structure of the rectus polymer chains of poly(β -ethyl- β -propiolactone).

Crystal Structure of Poly(β -ethyl- β -propiolactone)

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