

## Structural Studies of Polyesters. III. Crystal Structure of Poly- $\epsilon$ -caprolactone

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**ABSTRACT:** In the course of structural studies of aliphatic polyesters, the crystal structure of poly- $\epsilon$ -caprolactone,  $[-(\text{CH}_2)_5-\text{CO}-\text{O}-]_n$ , was determined by interpretation of X-ray diffraction patterns. The crystallographic data are:  $a = 7.47\text{\AA}$ ,  $b = 4.98\text{\AA}$ ,  $c$ (fiber axis) =  $17.05\text{\AA}$ , the orthorhombic space group  $P2_12_12_1-D_2^4$ , two molecular chains in the unit cell. The chain conformation of poly- $\epsilon$ -caprolactone is almost planar zigzag, but evidently deviates from the fully extended form, i.e., the  $\text{CH}_2$  sequences are planar but the plane of atoms of the ester group tilts slightly to the fiber axis. The molecular chains are arranged side by side in the same way as in polyethylene, but the carbonyl groups of the two chains in the unit cell are separated by an amount of  $3/14c$  along the fiber axis.

**KEY WORD** X-ray Diffraction/Crystal Structure/Poly- $\epsilon$ -caprolactone/  
Disordered Phase / Conformations / Polyesters /

Among laborious X-ray studies of polyesters by Fuller and his coworkers,<sup>1-5</sup> aliphatic polyesters of the type  $[-(\text{CH}_2)_z-\text{CO}-\text{O}-]_n$  received somewhat less attention than polyesters of the type  $[-\text{O}-(\text{CH}_2)_z-\text{O}-\text{CO}-(\text{CH}_2)_y-\text{CO}-]_n$ . They reported, however, that poly- $\omega$ -hydroxydecanoate ( $z = 9$ ) had a zigzag-planar chain and the chains were packed side-by-side in the same way as in polyethylene.<sup>2</sup> They also suggested that in general the higher members of polyesters of the type  $[-(\text{CH}_2)_z-\text{CO}-\text{O}-]_n$  had polyethylene-like crystal structures; that the molecular arrangements were quite similar to that of polyethylene, but even members of  $z$  belonged to the monoclinic system while the odd members occurred in orthorhombic form. Their studies, however, were performed over thirty years ago, and they did not carry out the structure analysis in detail.

In a previous paper,<sup>6</sup> the crystal structure of polyglycolide ( $z = 1$ ), the simplest polyester of the type  $[-(\text{CH}_2)_z-\text{CO}-\text{O}-]_n$ , was reported. The chain conformation of polyglycolide is planar zigzag and the molecular arrangement is quite different from that of polyethylene, and

the abnormally high melting point of polyglycolide in the homologous series was considered to be due to the crystal structure. Referring to the variation of the melting points of this polymer series against the number of the methylene groups,  $z$ ,<sup>6</sup> it seems to be that poly- $\epsilon$ -caprolactone ( $z = 5$ ) has a polyethylene-like crystal structure as well as poly- $\omega$ -hydroxydecanoate. Therefore in the present paper, poly- $\epsilon$ -caprolactone will be examined by X-ray diffraction, to provide a detailed study of the molecular and crystal structures of these odd members of polyesters, since poly- $\epsilon$ -caprolactone is more suitable than poly- $\omega$ -hydroxydecanoate, owing to its simpler chemical composition.

### EXPERIMENTAL

#### Samples

Samples of poly- $\epsilon$ -caprolactone were prepared by polymerization of  $\epsilon$ -caprolactone by using  $\text{Al(O-}t\text{-Bu)}_3$  catalyst.<sup>7</sup> The intrinsic viscosity  $[\eta]$  of the sample was 0.9, and the melting point measured by the polarizing microscopic method was  $63^\circ\text{C}$ .

Uniaxially oriented samples for the X-ray measurements were prepared by quick quenching of molten samples in ice water, followed by

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drawing at room temperature with elongation of about 700%. The crystallinities, however, were significantly effected by the conditions under which the samples were prepared. This point will be discussed later. The highest crystalline sample was used in the crystal structure analysis.

#### *Unit Cell, Space Group and Intensity Measurement*

Throughout the present X-ray study, nickel-filtered CuK $\alpha$  radiation (wavelength 1.542 Å) was used. An X-ray fiber photograph of poly- $\epsilon$ -caprolactone is shown in Figure 1. The spacings and relative intensities of the reflections on the equatorial line are very similar to the case of polyethylene. The unit cell was thus easily determined. An orthorhombic unit cell with  $a = 7.47 \pm 0.03$  Å,  $b = 4.98 \pm 0.03$  Å,  $c$  (fiber axis) =  $17.05 \pm 0.04$  Å, having four chemical repeating units was determined by comparison of the calculated density of  $1.20$  g/cm $^3$  with the observed one of  $1.13$  g/cm $^3$  obtained by the flotation method. These cell dimensions were obtained by using sodium chloride powder lines as a calibrating standard. The  $a$  and  $b$  dimensions differ slightly from the dimensions of  $a(7.40$  Å) and  $b(4.93$  Å) in polyethylene.<sup>8</sup> Systematic extinctions of reflections are  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd, and  $00l$  with  $l$  odd. Therefore the possible space group is P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>-D<sub>2</sub><sup>4</sup>.

The procedures of intensity measurement and conversion to observed structure factors were similar to a previous work. On the fiber photograph, 95-independent reflections were observed. The intensities of  $00l$  reflections were measured

by using a Weissenberg photograph taken with the perpendicular direction to the fiber axis as the rotation axis. In addition to the film method by visual comparison, a single crystal diffractometer of the Rigaku Denki Company was used to measure the intensities of the  $00l$  and comparatively strong  $hkl$  reflections.

## STRUCTURE ANALYSIS

#### *Molecular model*

The identity period of the fully extended zigzag model of poly- $\epsilon$ -caprolactone is calculated to be 17.16 Å, in which two chemical repeating units are contained (Figure 3a). Therefore the observed fiber period of 17.05 Å suggests that the conformation of this polymer is fully extended or almost planar zigzag.

In the polyesters of ethylene glycol with dibasic acids,  $[-O-(CH_2)_2-O-CO-(CH_2)_y-CO-]_n$ , the shortening of the observed fiber period from the calculated one based on the fully extended form is about 0.5 Å for polyethylene adipate ( $y = 4$ ), suberate ( $y = 6$ ),<sup>9</sup> and sebacate ( $y = 8$ ).<sup>10</sup> In these polyesters, the CH<sub>2</sub> sequences have plane carbon chains, but the distortion occurs in the ester groups, as already studied in detail by Turner-Jones and Bunn.<sup>9</sup> The shortening of the observed fiber period in poly- $\epsilon$ -caprolactone is much smaller than the shortening in these ethylene glycolic polyesters. Therefore the fully extended model was adopted at the initial stage of our analysis.

#### *Structure of ab Projection*

The space group of P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>-D<sub>2</sub><sup>4</sup> contains only twofold screw axes as its symmetry element along each crystal axis. As already mentioned, however, at first glance of the X-ray fiber photograph we could confirm that the molecular arrangement of the *ab* projection must be quite similar to that of polyethylene. Actually both the plane groups of the *ab* plane of polyethylene and poly- $\epsilon$ -caprolactone are pgg. Accordingly it might be most plausible to suppose that the chain axis of poly- $\epsilon$ -caprolactone coincides with the twofold screw axis along the *c* axis as shown in Figure 2a. Some trial and error procedures in structure factor calculations were adopted by changing the angle ( $\phi$ ) between the molecular plane and the *b* axis. At this stage the molec-

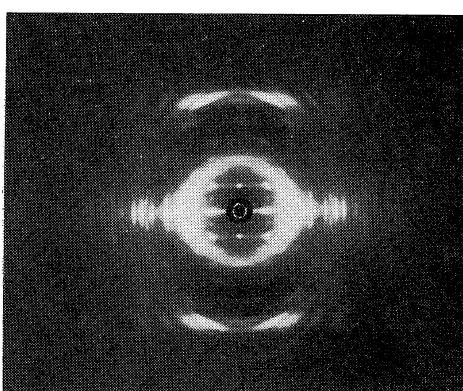
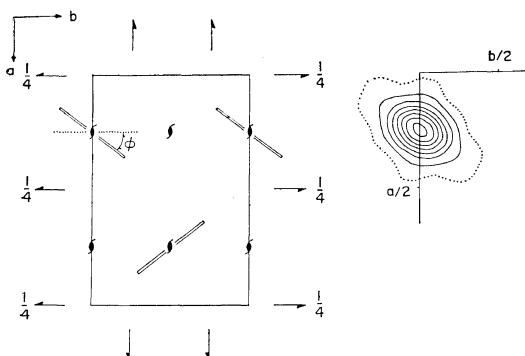


Figure 1. X-ray fiber photograph of poly- $\epsilon$ -caprolactone.



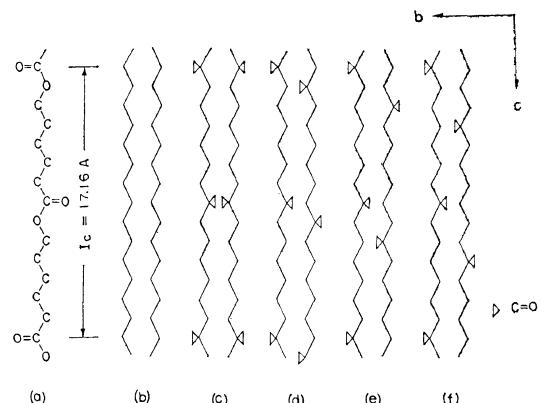
**Figure 2.** (a) Molecular arrangement of poly- $\epsilon$ -caprolactone in the unit cell of the space group  $P2_12_12_1$  and (b) Fourier projection on the  $ab$  plane.

ular model was fixed at the fully extended form. The most plausible  $\phi$  value was found to be  $40^\circ$  (*cf.*  $41^\circ$  in polyethylene). A Fourier synthesis of the  $hk0$  was also tried. Although the resolution of the electron density map was poor owing to overlapping of many atoms as shown in Figure 2b, the angle  $\phi$  agreed well with the value obtained by the trial and error procedures.

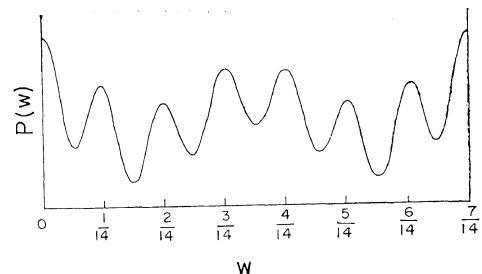
#### Three Dimensional Structure

Among the observed layer lines, apart from the equatorial line, the 7th layer line is the most intense and the intensity distribution resembles that of the 1st layer line of polyethylene, though owing to difference of the space groups of the two substances,  $Pnam$  for polyethylene and  $P2_12_12_1$  for poly- $\epsilon$ -caprolactone, the  $h0l$  with odd  $h$  is absent in the case of polyethylene. This indicates that there is a division of the fiber period by relatively strong planes spaced about  $2.5\text{\AA}$  apart. Therefore two chains in the unit cell of poly- $\epsilon$ -caprolactone must be arranged so that each atom in one chain has the same height as one of the atoms of the other chain, as in the case of polyethylene (Figure 3b). Concerning the  $C=O$  groups, however, four different types of chain arrangement can be obtained, as shown in Figures 3c, d, e, and f.

In order to determine the relative height of the two chains in the unit cell, one-dimensional Patterson synthesis using the  $00l$  with  $l = 2$  to 14 was carried out. This is shown in Figure 4. The result excluded the three models of Figures 3c, d and e, since the strongest peaks at  $3/14c$



**Figure 3.** Relative heights of poly- $\epsilon$ -caprolactone molecules in the unit cell.



**Figure 4.** One-dimensional Patterson synthesis along the fiber axis.

and  $4/14c$  mean that the  $C=O$  groups of the two chains in the unit cell are separated by an amount of  $3/14c$  or  $4/14c$  along the fiber axis. For example, model 3d must give the strongest peaks at  $1/14c$  and  $6/14c$ . Only model 3f, therefore, remains plausible. Next, by studying the difference in the  $CH_2$  group and the oxygen atom in the skeletal chain, two molecular arrangements are possible from model 3f. These are shown in Figures 5a and b. Both models were refined by changing the  $\phi$  value and  $z$  parameter of each atom. But the reliability factor  $R (= \sum |F_o| - |F_c|) / \sum |F_o|$ ) was not improved below 25% as long as the fully extended model was used.

Further refinement was then undertaken by using a least squares method. A diagonal approximation least squares program was used on an NEAC 2200 electronic computer at Osaka University. The most apparent variations of the molecular conformation revealed by the least squares refinement are (1) the skeletal atoms do

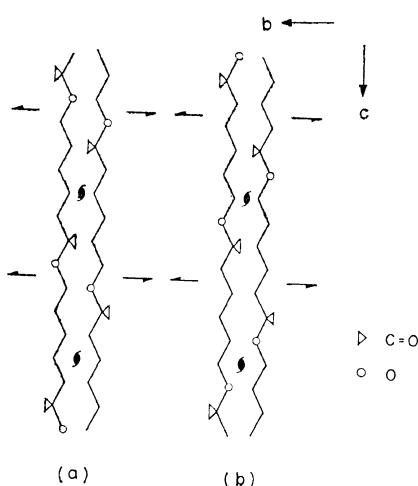


Figure 5. Two possible arrangements of molecules in the unit cell.

not form a planar zigzag in either models 5a or b, (2) the thermal coefficient of the oxygen atom of the carbonyl group is about twice as large as that of any other atoms. However, according to the result of the least squares refinement, some of the bond lengths and bond angles obtained are more or less different from the usually accepted values, *e.g.*, the  $C(H_2)$ — $C(H_2)$  bond lengths are in the range 1.45 Å and 1.60 Å, and the  $C=O$  bond length is 1.31 Å. The standard deviations of the atomic coordinates,  $\sigma(x)$ ,  $\sigma(y)$  and  $\sigma(z)$ , are about 0.035 Å, and that of thermal coefficient,  $\sigma(B)$ , is about 1.1 Å<sup>2</sup>. But it seems likely that the  $CH_2$  sequences are almost planar and the plane of the carboxyl group does tilt slightly toward the fiber axis. The reliability factors for both models 5a and b are 14% and 15%, respectively. The difference in the reliability factors for both models is too small to decide which model is the more plausible. Such an unfortunate situation arises from the fact that the only difference in the two models is replacement of an oxygen atom and a methylene group attached to the carbonyl group, and the oxygen atom and the methylene group have very similar X-ray scattering powers. But model 5a seemed to be more reasonable from a consideration of bond lengths and thermal coefficients.

After slight modification of the molecular model resulting from the least squares refinement in order to obtain reasonable bond lengths and

Table I. Atomic coordinates and thermal coefficients

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å <sup>2</sup>
C(1)	0.721	0.566	0.366	8.0
C(2)	0.732	0.615	0.228	8.0
C(3)	0.810	0.471	0.156	8.0
C(4)	0.733	0.604	0.082	8.0
C(5)	0.813	0.459	0.011	8.0
C(6)	0.761	0.408	0.437	8.0
O(1)	0.621	0.755	0.366	15.0
O(2)	0.786	0.481	0.298	8.0

angles, the final atomic coordinates with the thermal coefficients were determined as tabulated in Table I for model 5a. In Table II, the calculated structure factors based on the final atomic coordinates are compared with the observed ones. In the calculation, the contribution of the hydrogen atoms is included, assuming the  $C-H$  bond length of 1.09 Å and the tetrahedral angle of the carbon atom. The reliability factor was 15% for all observed reflections.

#### Disordered Phase

In addition to the sharp Bragg reflections, the continuous scatterings appear on several layer lines. On the sample stretched quickly soon after quenching, in particular, these streaks are more intense, as shown in Figure 6. These streaks on the layer lines (except on the equator) still exist in a photograph taken with monochromatized  $CuK\alpha$  radiation using an LiF crystal. These streaks suggest the existence of a type of disordered molecular arrangement along the fiber axis, *i.e.*, if regions having irregu-

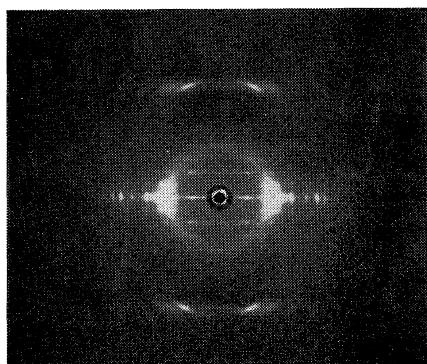


Figure 6. X-ray fiber photograph of a sample stretched quickly soon after quenching.

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Table II. Comparison of observed and calculated structure factors

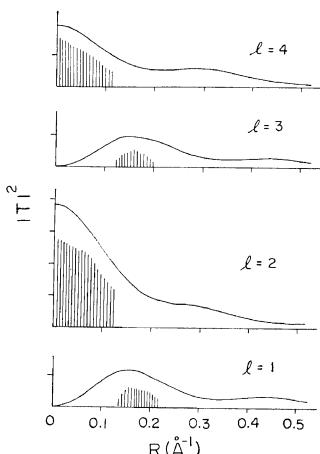
$h k l$	$ F_o $	$ F_c $	$h k l$	$ F_o $	$ F_c $	$h k l$	$ F_o $	$ F_c $
1 1 0	120	113.4	1 0 3	8	9.2	1 1 6	8	9.6
2 0 0	106	109.3	0 1 3	11	17.8	2 0 6	4.5	4.6
2 1 0	29	29.5	1 1 3	3.5	2.5	2 1 6	6	6.0
0 2 0	34	36.2	2 0 3	8	9.9	3 0 6 }	5.5	6.7
1 2 0	6	11.0	2 1 3	3.5	1.6	0 2 6 }	7	8.6
3 1 0	37	40.8	3 0 3 }	5.5	7.7	1 2 6	8	10.0
2 2 0	28	27.8	2 0 3 }	2.5	3.6	3 1 6	4	5.0
4 0 0	23	24.1	1 2 3	5	3.5	2 2 6	6	5.1
3 2 0 }*	8	12.5	3 1 3	5.4	6.7	4 0 6	5.5	7.4
4 1 0 }*	4.5	6.7	2 2 3	5	7.7	3 2 6 }		1.2
1 3 0	13	10.8	4 0 3		3.6	4 1 6 }		1.4
2 3 0	3.5	5.4	3 2 3 }		1.6	0 3 6	3	4.8
4 2 0	12	10.5	4 1 3 }		4.1	1 3 6	8	8.2
5 1 0	10.5	9.2	0 3 3		2.1	2 3 6		3.6
3 3 0	4.5	3.7						
5 2 0	7	7.2	1 0 4	7	7.7	1 0 7	12	12.2
			0 1 4	5.5	7.1	0 1 7	36.5	35.3
1 0 1	7.5	7.3	1 1 4	4	2.9	1 1 7	18	19.3
0 1 1	8	2.8	2 0 4	2	2.2	2 0 7	26.5	28.8
1 1 1	29	25.5	2 1 4	9	13.0	2 1 7	14	19.0
2 0 1	28	26.7	3 0 4 }	2.5	3.0	3 0 7 }	9	11.8
2 1 1	13	13.2	0 2 4 }	6.8	8.9	0 2 7 }	9	12.2
3 0 1 }*	4	4.1	1 2 4	5	6.5	1 2 7	18	21.1
0 2 1 }*	9.2	9.3	3 1 4		1.8	3 1 7	12.5	16.5
1 2 1	11.5	13.8	2 2 4	2.5	0.8	2 2 7	8.8	10.2
3 1 1	7	7.1	4 0 4	3.5	4.2	4 0 7	14	14.7
2 2 1	7.5	6.8	3 2 4 }	4.5	5.0	3 2 7 }	11	11.9
4 0 1	7	6.8	4 1 4 }	2.4	2.5	4 1 7 }	8	8.3
3 2 1 }*	8.7	10.9	0 3 4		4.8	0 3 7	14	12.5
4 1 1 }*	8.1	10.0	1 3 4		0.4	1 3 7	7	6.6
0 3 1	3	5.1	2 3 4		4.4	2 3 7	10	10.4
1 3 1	3	3.0						
2 3 1		5.4	1 0 5	8	7.6	1 0 8	1	0.5
5 0 1		5.7	0 1 5		1.9	0 1 8	4	6.3
			1 1 5	6	6.7	1 1 8	5	4.3
1 0 2	15	18.5	2 0 5		4.8	2 0 8	7	5.1
0 1 2	2	2.7	2 1 5		3.7	2 1 8	6	5.7
1 1 1	12	14.7	3 0 5 }		2.5	3 0 8 }		0.8
2 0 2	4	7.4	0 2 5 }		0.0	0 2 8 }		4.7
2 1 2	5	9.5	1 2 5	6	5.8	1 2 8	7	8.8
3 0 2 }*		1.7	3 1 5	5	4.9			
0 2 2 }*		4.2	2 2 5	3	2.6	0 0 2	3	4.7
1 2 2		1.2	4 0 5		1.5	0 0 4	14	16.0
3 1 2	5	7.9	3 2 5 }		2.5	0 0 6	10	5.9
2 2 2		5.6	4 1 5 }		2.2	0 0 8	3	2.8
4 0 2		3.2	0 3 5		2.6	0 0 10	3	0.5
3 2 2 }*	8.4	9.2	1 3 5		0.1	0 0 12		0.7
4 1 2 }*	4.9	5.1	2 3 5		0.5	0 0 14	9	9.2
0 3 2	5	3.0						
1 3 2		4.0	1 0 6	6	4.3			
2 3 2		3.1	0 1 6	6	7.2			

\*  $|F_o|$ 's of overlapping reflections were obtained by dividing  $I_o$  in the ratio of the  $I_c$  values.

larities about the mutual heights of chains exist, such streaks on the layer lines can be expected. But the fact that there is no streak on the equatorial line implies that the lateral arrangement of molecular chains in such a disordered region is the same as in the regular crystalline part. In order to examine this possibility, a simple calculation was undertaken for the intensity distributions of these streaks. As a simplified model having no interrelation between the heights of molecular chains along the fiber axis, a cylindrically averaged intensity of one molecular chain (squares of molecular transform  $T$ ) was calculated on each layer line, using the following equation:

$$\langle I(R, l/c) \rangle_\phi = |T|^2 = \sum_j \sum_{j'} f_j f_{j'} J_0(2\pi R r_{jj'}) \exp(2\pi i l z_{jj'}/c),$$

where  $R, \phi, l/c$  are the cylindrical coordinates of the reciprocal space;  $f_j$  is the atomic scattering factor of the  $j$ -th atom including the thermal factor;  $J_0$  is the Bessel function of zero order;  $r_{jj'}$  and  $z_{jj'}$  are the radial component and axial component of the interatomic distance of the  $j$  and  $j'$ -th atoms, respectively. The summation is taken for the atoms in the identity period. In Figure 7 are shown the calculated intensities with the thermal coefficient  $B$  of  $8\text{\AA}^2$ . The calculated intensity distributions are found to agree qualitatively with the ones observed as shown by the solid vertical lines. Such a

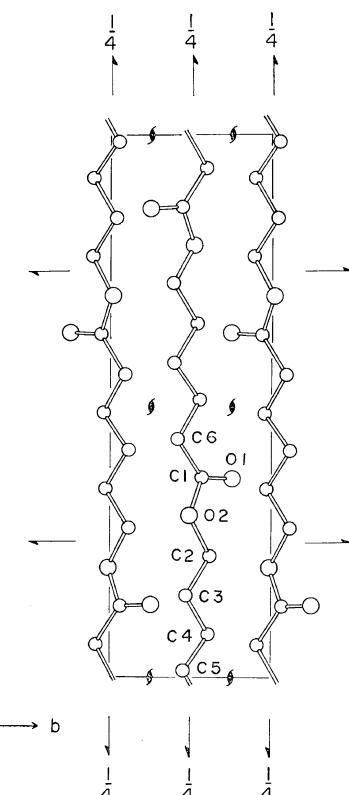


**Figure 7.** Plots of  $|T|^2$  for the layer lines of  $l = 1-4$ . The solid vertical lines indicate qualitatively observed streak intensities.

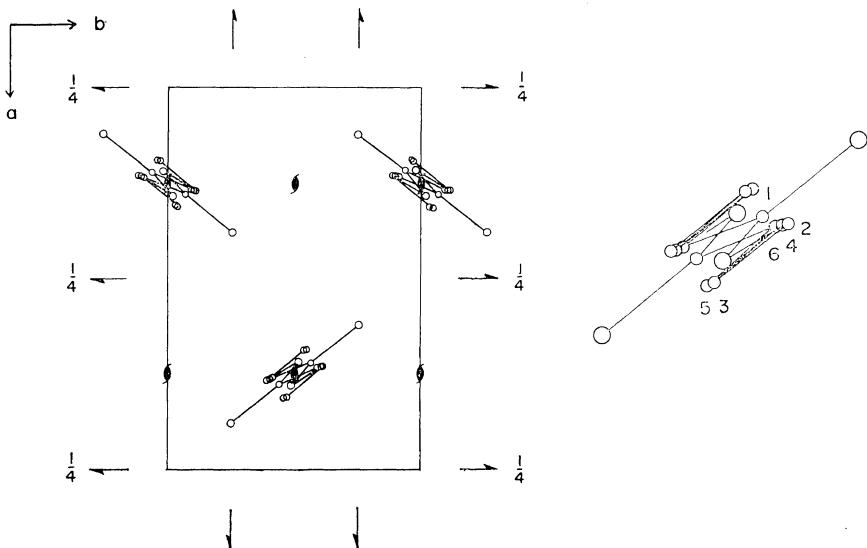
disordering of molecular arrangement might be due to the similarity of the size and symmetry of the methylene group and the carbonyl group and the coexistence of the molecular arrangement of the up and down directions.

## RESULTS AND DISCUSSION

The crystal structure of poly- $\epsilon$ -caprolactone is shown in Figures 8 and 9. The  $ab$  projection of the molecular arrangement is quite similar to that of polyethylene. It is worthwhile, however, to discuss the deformation of the molecular conformation from the fully extended form. As already mentioned, the slightly deformed conformation was obtained by the least squares refinement. Compared with a refinement of single crystal analysis of a compound of low molecular-weight, there is, admittedly, a low degree of accuracy due to poor data. But from the standard deviations of the atomic coordinates,



**Figure 8.** A projection of the crystal structure of poly- $\epsilon$ -caprolactone viewed along the  $a$  axis.

Figure 9. A projection of the structure of poly- $\epsilon$ -caprolactone viewed along the  $c$  axis.

it may be confirmed that the departure from the fully extended form is significant. The slight shortening of the observed fiber period compared with the calculated one based on the fully extended form is thus explained by the twisting of the skeletal chain: the sequences of the methylene groups take a planar zigzag conformation but the ester group tilts to the fiber axis. The C(1)—O(2) bond and C(5)—C(6) bond rotate 7° and 11°, respectively, from the trans form. The bond lengths, bond angles and internal rotation angles calculated from the final atomic coordinates are shown in Table III.

Interchain atomic distances were also evaluated, and no abnormal distances are found. Some close contacts are listed in Table IV. The closest contact is 3.29 Å for O.....C and 3.99 Å for C.....C. From the intermolecular contacts, it is recognized that if the fully extended molecule is assumed to be arranged at an angle  $\phi$  of 40° as polyethylene, the intermolecular C(4).....O(1) distance is too short, about 3.0 Å, while on the resultant structure, the shortest C(4).....O(1) distance is 3.29 Å owing to the molecular twist. An interesting fact associated with this problem is that the crystal structure of polyketone ( $-\text{CH}_2-\text{CH}_2-\text{CO}-)_n$  is isomorphous to that of polyethylene: the cell dimensions of which are  $a = 7.97 \text{ \AA}$ ,  $b = 4.76 \text{ \AA}$ ,  $c(\text{fiber axis}) = 7.57 \text{ \AA}$ ,

Table III. Bond lengths, bond angles, and internal rotation angles

Bond lengths	
C(1)—O(1)	1.20 Å
C(1)—O(2)	1.33
C(1)—C(6)	1.47
C(2)—O(2)	1.43
C(2)—C(3)	1.54
C(3)—C(4)	1.54
C(4)—C(5)	1.53
C(5)—C(6)	1.53
Bond angles	
C(6)—C(1)—O(1)	123°
C(6)—C(1)—O(2)	118
O(1)—C(1)—O(2)	119
C(1)—O(2)—C(2)	118
O(2)—C(2)—C(3)	118
C(2)—C(3)—C(4)	110
C(3)—C(4)—C(5)	108
C(4)—C(5)—C(6)	108
C(5)—C(6)—C(1)	112
Internal rotation angles	
C(5)—C(6)—C(1)—O(2)	176°
C(6)—C(1)—O(2)—C(2)	173
C(1)—O(2)—C(2)—C(3)	185
O(2)—C(2)—C(3)—C(4)	174
C(2)—C(3)—C(4)—C(5)	180
C(3)—C(4)—C(5)—C(6)	179
C(4)—C(5)—C(6)—C(1)	191

**Table IV.** Interchain atomic distances

O(1).....C(4)	3.29 Å	<i>a</i> ..... <i>d</i>
O(1).....C(3)	3.42	<i>a</i> ..... <i>d</i>
O(1).....C(6)	3.62	<i>b'</i> ..... <i>b</i>
C(5).....C(6)	3.99	<i>c</i> ..... <i>b</i>
C(4).....C(6)	4.00	<i>a</i> ..... <i>d</i>
C(4).....C(6)	4.08	<i>c</i> ..... <i>b</i>
<i>a</i> :	<i>x, y, z</i>	
<i>b</i> :	$1/2 - x, -y, 1/2 + z$	
<i>b'</i> :	$1/2 - x, 1 - y, 1/2 + z$	
<i>c</i> :	$1/2 + x, 1/2 - y, -z$	
<i>d</i> :	$-x, 1/2 + y, 1/2 - z$	

and the C=O groups of two chains in the unit cell locate at the same height of  $z = 1/4c$  and  $3/4c$ .<sup>11</sup> In the polyketone, however, the *a* dimension is 0.5 Å larger than that of polyethylene whereas the *b* dimension is smaller than that of polyethylene. Thus reasonable intermolecular distances are maintained by decreasing the angle  $\phi$  to 39°. On the other hand, in respect of poly-ε-caprolactone, it seems likely that reasonable molecular contacts result from the slight twisting of the chain from the fully extended form without significant alternation of the cell dimensions from those of polyethylene. Three factors could account for this: (a) larger concentration of methylene groups than the polyketone; (b) the flexibility of the ester group, and (c) the differing heights of carbonyl groups of the two chains in the unit cell.

In conclusion the crystal structure of poly-ε-caprolactone is described as polyethylene-like in structure, but the molecule is slightly twisted and the carbonyl groups of the two chains in

the unit cell are not located at the same level but rather different levels. The diffused streaks on the layer lines are attributed to the existence of the disordered phase caused by the disordering of longitudinal direction, *i.e.*, disorder due to the irregularly located carbonyl groups along the chain direction or disorder about up-and-down sense of molecules. It appears that the crystal structures of polyesters of the type  $[-(\text{CH}_2)_z-\text{CO}-\text{O}-]_n$  with odd numbers of *z* higher than 5 are analogous to each other.

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