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Crystal Structure of Poly-ε-caprolactone

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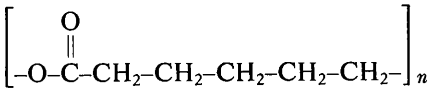
The unit cell of poly-ε-caprolactone was found to be orthorhombic with dimensions $a=7{\cdot}496\pm0{\cdot}002$, $b=4{\cdot}974\pm0{\cdot}001$, $c=17{\cdot}297\pm0{\cdot}023$ Å (fiber axis). The space group is $P2_12_12_1$. This unit cell is only compatible with an extended planar chain conformation of the molecule involving two monomer residues related by a twofold screw axis in the chain direction. The $P2_12_12_1$ space group and the density of 1·146 g.cm^{-3} indicate that the unit cell contains two chains with opposite orientation ('up' and 'down'). Intensity measurements and structure factor calculations require the rotation of the plane of the chains about their axis to an angle of 28° with respect to the a axis; longitudinal chain shift places the ester groups in planes perpendicular to the c axis. Folded chain single crystals with a lancet-like structure were observed by electron microscopy.

Introduction

Polyesters prepared by ring opening polymerization of lactones are coming into prominence as a result of new polymerization catalysts (Chujo, Kobayashi, Suzuki, Tokyhara & Tanabe, 1967; Asahara & Katayama, 1964; Alderson, 1956; Okamura, Higashimore & Tanaka, 1962). Such macromolecules are intrinsically different from conventional polyesters (Fuller & Frosch, 1939; Fuller & Erikson, 1957) in that the chain has a sense of direction by the uniform orientation of the ester groups within the chains. Depending on the distance between the ester groups in the chains and their interactions one can find different intra- or intermolecular arrangements of the chains. For example, it has been found that polypropiolactone can exist in two different polymorphs with an extended and helical conformation respectively (Wasai, Saegusa & Furakawa, 1964). Of particular interest in recent years have been polyesters with side groups attached to the main chain such as poly-β-hydroxybutyrate (Okamura & Marchessault, 1967) which occurs as an optically active natural polymer and polypivalolactone (Knobloch & Statton, 1967) which is an interesting synthetic fiber material.

Poly-ε-caprolactone. made by ring opening polymerization of ε-caprolactone has the following structure:



$$\left[-\mathrm{O}-\overset{\overset{\displaystyle\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\right]_n$$

and it therefore possesses one of the larger repeating units so far studied in polyesters. In this work the unit cell and the chain arrangement in the crystalline state were investigated by means of X-ray diffraction.

Experimental

Preparation of the films

Uniform films of 0·1 mm thickness were prepared by evaporation of a 5% solution of poly-ε-caprolactone in toluene on a glass plate. Strips of these films were cold drawn to an elongation of 600–700%. Hot drawing at 60°C did not result in a higher elongation. The strips were annealed for 20 hours at 60°C. The films used in the powder camera work were all compression moulded. Three different polymer samples were studied having reduced viscosities of 0·80, 0·98 and 3·12. The samples were cut from 0·2 mm films, and had a square cross-section. The 0·80 and 0·98 R.V. films were annealed by heating (melting) at 60°C, followed by slow cooling to 56°C where they were held isothermally for 8 hours. The 3·12 R.V. sample was run as received.

X-ray diffraction diagrams

X-ray diffraction diagrams were recorded with Cu $K\alpha_1$ Ni-filtered radiation ($\lambda=1{\cdot}5418$ Å) under vacuum with both flat film and cylindrical cameras. The fiber diagrams were calibrated with two NaF diffraction lines corresponding to spacings of 2·319 and 1·639 Å. For the exact determination of the unit-cell parameters a 114 mm Debye–Scherrer camera was used. This Straumanis loaded camera was calibrated by exposing each film with two pin points of light through holes drilled into the camera approximately 300° apart. The exact angular distance of separation of the fiducial marks was determined by locating the centers of the forward and back reflection regions of a silicon standard, which, of course, are 180° apart. These fiducial marks minimize film shrinkage errors.

Intensity measurements

The intensities of the reflections were determined by visual comparison with a standard scale of intensities.

The latter was prepared by recording a series of exposures of the most intense poly-ε-caprolactone reflections and assigning the corresponding exposure time as a measure of intensity to each spot of the series. For the unobserved reflections 50% of the intensity of the weakest observable spot was assumed.

Calculations

All calculations were performed with an IBM 1620-II computer. The structure factors of the observed reflections were calculated from the measured intensities by applying the Lorenz–polarization factor corrections. The theoretical structure factors for given molecular arrangements of the chains were calculated using structure factor programs. A Fourier synthesis program was also used during the refinement of the crystal structure.*

Single crystals

Polymer 'single crystals' were prepared by dissolving poly-ε-caprolactone in hot toluene at a concentration of 5 g.litre^{-1} and by adding propanol as precipitant to a weight per cent of 66. The crystals were obtained at room temperature after several hours. The solutions containing the crystals were sprayed on carbon coated grids and shadowed with chromium. A JEM 7A electron microscope was used.

Results

General description of the fiber diagram

The fiber diagram (cylindrical camera) shows seven layer lines and about 50 reflections in one quadrant (Fig. 1). Nearly all reflections of the diagram are sharp and clearly defined, except those in the seventh layer line which are slightly arched. When one compares the fiber diagram of poly-ε-caprolactone with that of polyethylene (Bunn, 1939; Geil, 1963) it is apparent that the equatorial reflections and those on the seventh layer-line of poly-ε-caprolactone are nearly identical to those of polyethylene (equator and first layer line).

Unit cell and symmetry

The fiber diagram could be indexed in terms of an orthorhombic cell (Table 1). The most accurate lattice constants at 25°C, based on careful measurements on Debye–Scherrer diagrams are: $a = 7{\cdot}496 \pm 0{\cdot}002$, $b = 4{\cdot}974 \pm 0{\cdot}001$, c (fiber axis) $= 17{\cdot}297 \pm 0{\cdot}023$ Å. According to convention $c < a < b$ in the orthorhombic system. On the other hand in polymer crystals the c axis coincides with the chain axis. We have chosen $a > b$ in agreement with the definitions of Bunn for the polyethylene unit-cell. The errors are 95% confidence limits of precision, and do not necessarily reflect the accuracy. The cell constants determined only from the fiber diagram and used in the calculations differed slightly and are given in Table 1. Only even order reflections of $h00$, $0k0$ and $00l$ type were observed. The systematic absences indicate three twofold screw axes in orthogonal directions. The space group of poly-ε-caprolactone is therefore $P2_12_12_1$. These data are in agreement with the unpublished results of Okita, Chatani, Tadokoro & Yamashita (1967) who found an orthorhombic cell with $a = 7{\cdot}47$, $b = 4{\cdot}98$ and $c = 17{\cdot}05$ Å and space group $P2_12_12_1$. The calculated value of the density is 1·17 g.cm^{-3} which compares favorably with the measured value of 1·146 g.cm^{-3} (*Union Carbide Bulletin*, 1968).

Chain arrangement

A conformational analysis performed by Pfaffenberger (1969) indicates that the fiber repeat distance of 17·297 Å most probably corresponds to a planar 'zig-zag' conformation of the chains; the ester groups are then in a planar *trans* arrangement. The results of the infrared spectroscopy investigations of Tadokoro, Kobayashi, Yoshidome, Tai & Makano (1968) are in agreement with these findings. Possible motions of the chains are, therefore, rotation about the chain axis and a translational shift of the chains in the **c** direction.

The degree of rotation of the chains in the *ab* projection was determined from the relative intensity of the equatorial reflections. A centrosymmetric arrangement in the *ab* projection can be attained by a proper choice of the origin. In this case the phase problem is reduced to the selection of the proper sign of the structure factors, because only the real components (A terms) of the

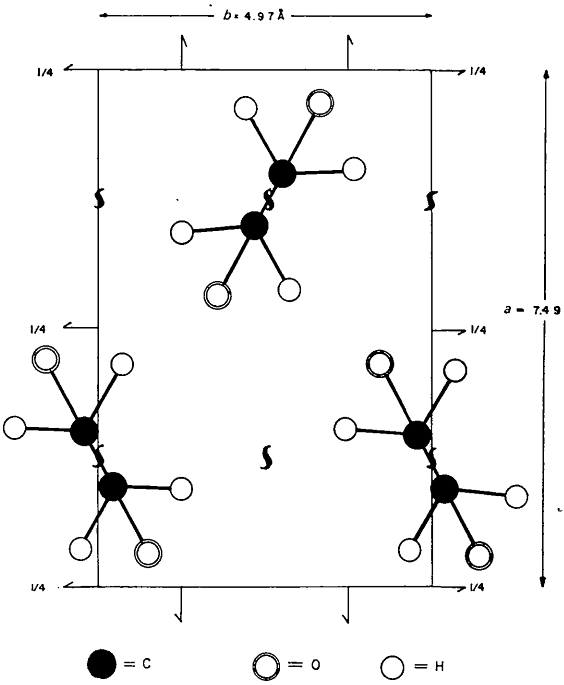


Fig. 2. Unit cell and chain arrangement of poly-ε-caprolactone in the *ab* projection.

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* These programs were originally written by R. Shiono at the Crystallography Laboratory of the University of Pittsburgh and modified by A. Sarko at the State University of New York, College of Forestry, Syracuse, N.Y.

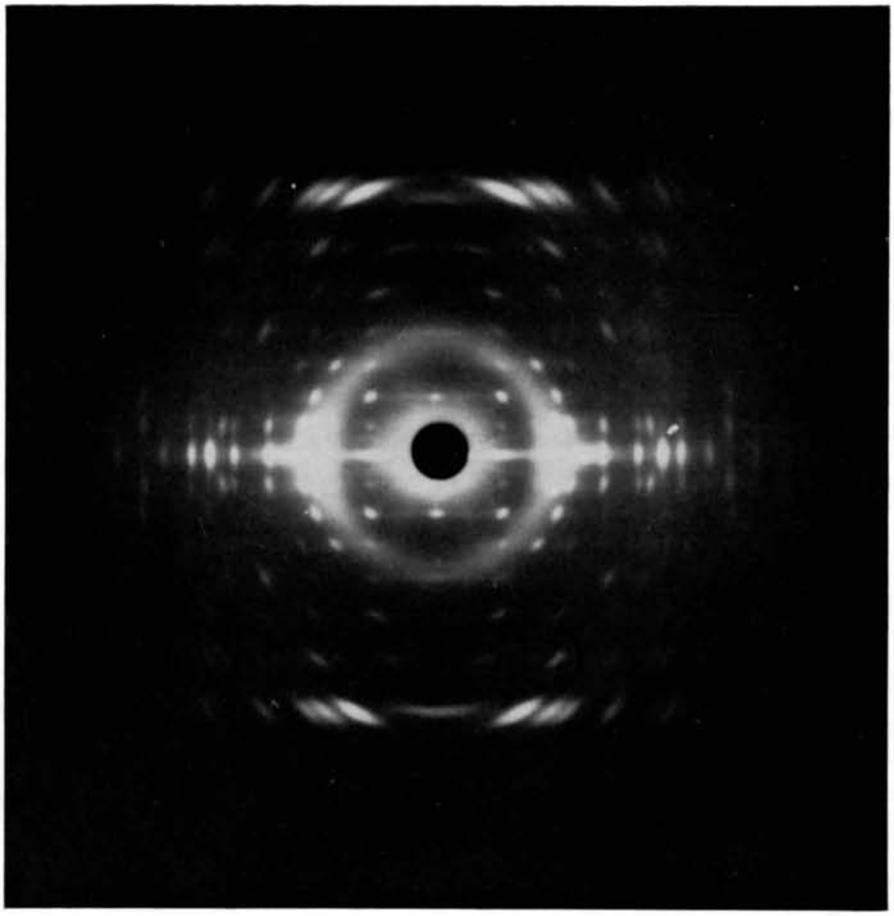

Fig. 1. Fiber diagram of poly-ε-caprolactone, 57·3 mm cylindrical camera, Cu $K\alpha$, Ni-filtered radiation.

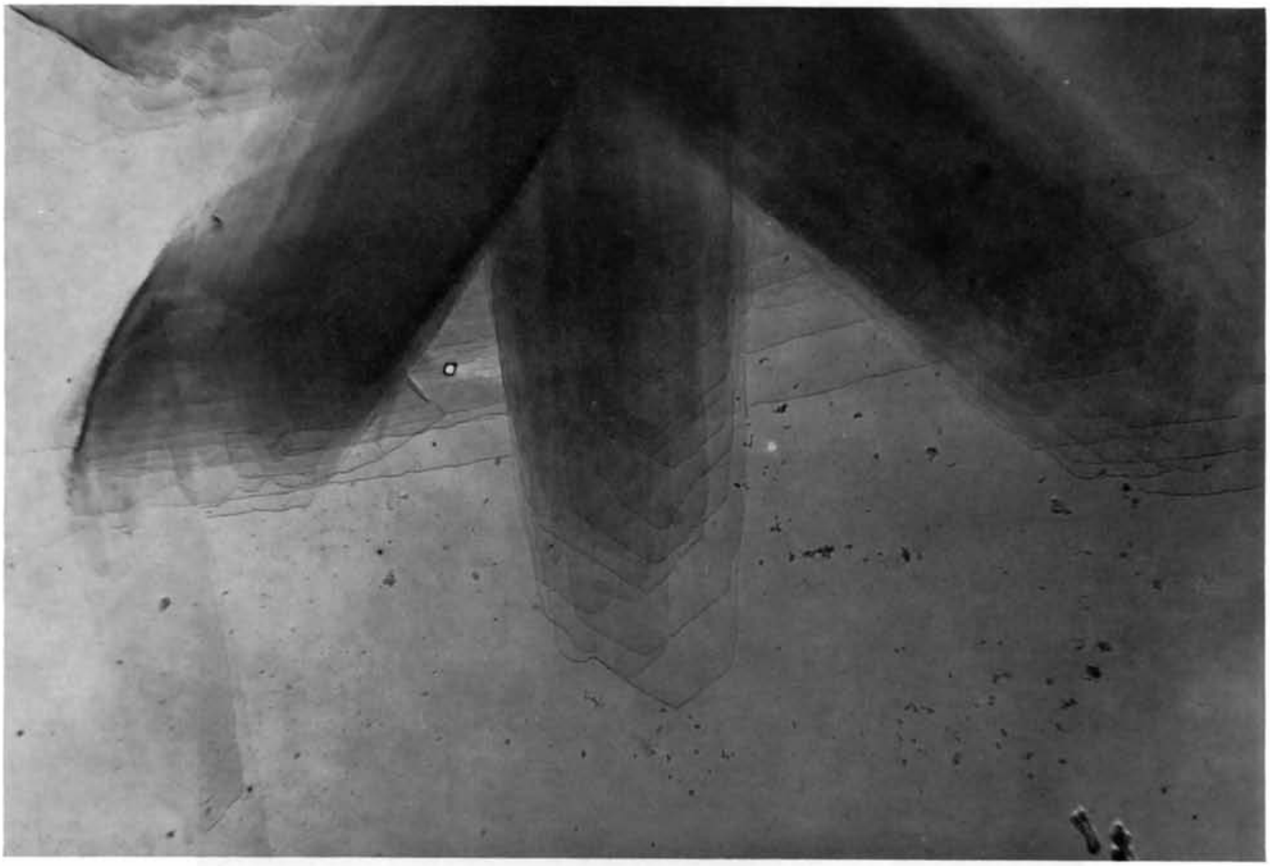

Fig. 4. Single crystals of poly-ε-caprolactone from toluene–66% propanol solution; shadowed with chromium.

structure factors are present. Electron density maps were calculated for a series of combinations of the signs of the structure factors. The most probable map showed a rotation of the plane of the chains of about 30° with respect to the *a* axis. For the exact determination of the rotation angle a computer program was written to rotate the chains in intervals of 1° between 20 and 45°. The best agreement between the observed (F_o) and the calculated structure factors (F_c) was found at 28° with a temperature factor of $B=16$ (Fig. 2; Table 1, columns 5 and 6).

The disagreement index, the so-called '*R* value' $\sum||F_o|-|F_c||/\sum|F_o|$ was 0·15 for the equatorial reflections. It was also found that the hydrogen atoms have a relatively strong influence on the structure factors. This is due to the relatively large number of the hydrogen atoms and their position quite far away from the rotation axis (Fig.2). To fit the structure factors on the higher layer lines, the chains were also shifted along the chain axis. The best agreement was found for a position where the double-bonded oxygen atom was located at $z/c=0{\cdot}4836$ and the second oxygen atom of the ester

Table 1. *Calculated and observed structural parameters*

For an X-ray fiber diagram with unit cell: $a=7{\cdot}496$, $b=4{\cdot}974$, $c=17{\cdot}297$ Å (fiber axis)

Layer line	Miller indices	*d* spacings		Structure factors	
		Observed	Calculated	Observed	Calculated
0	110	4·122 Å	4·145 Å	118·44	112·74
	200	3·710	3·748	66·15	70·96
	210	2·984	2·993	18·27	18·73
	020	2·498	2·487	26·46	45·09
	120	2·365	2·360	5·04	12·47
	310	2·214	2·233	22·05	18·40
	220	2·080	2·072	21·42	25·98
	400	1·859	1·87	11·34	10·39
	410	1·754	1·754	5·67	5·06
1	011*	4·812	4·780	6·93	17·89
	111	4·058	4·030	22·05	11·11
	201	3·700	3·663	20·79	9·30
	211	2·963	2·949	15·12	10·46
	301†	—	2·473	(6·30)	0·15
	021†	—	2·462	(6·30)	2·01
	311†	—	2·214	(5·04)	5·29
	221†	—	2·058	(5·04)	2·39
2	002‡	8·540	8·648	—	—
	102	5·664	5·664	16·38	2·80
	012†	—	4·312	(4·41)	1·97
	112	3·730	3·738	11·97	9·87
	202	3·440	3·439	7·56	9·53
	122	2·280	2·277	6·93	10·72
3	103	4·572	4·570	3·78	3·92
	013	3·730	3·766	13·23	15·45
	113†	—	3·365	(3·15)	9·11
	203	3·141	3·142	5·67	7·88
4	004‡	4·280	4·324	—	—
	104	3·730	3·746	5·04	3·51
	014†	—	3·263	(4·41)	1·91
	114	2·988	2·992	5·04	6·18
	204	2·819	2·832	6·93	9·28
	214	2·461	2·461	5·67	8·43
5	105	3·310	3·141	13·49	4·13
	015†	—	2·840	(4·41)	9·55
	115	2·677	2·656	6·93	5·94
	205†	—	2·542	(5·04)	5·29
6	001‡	2·880	2·883	—	—
	106	2·685	2·691	4·41	1·88
	116	2·349	2·367	5·04	4·39
7	017‡	2·205	2·213	—	—
	117	2·121	2·122	13·23	15·45
	207	2·039	2·063	20·16	18·77
	217	1·894	1·906	9·45	15·33
	307	1·734	1·757	8·82	12·91
	027†	—	1·753	(9·45)	9·09
	127	1·707	1·707	6·93	6·54

* The reflection lies in the amorphous halo.
† Unobserved reflections.
‡ Observed, but not in the sphere of reflection.

group at $z/c=0{\cdot}0504$ (Fig. 3). The ester groups of the chains come to lie in planes perpendicular to the c axis. The final coordinates are given in Table 2. The agreement for the higher layer lines is not as good as for the equatorial reflections. The best value was $R=0{\cdot}271$ for the observed and $R=0{\cdot}296$ for all observed and unobserved reflections in the range considered. Attempts to obtain a better agreement by rotation about the ester bond of the molecule were unsuccessful.

Table 2. *Fractional atomic coordinates of one asymmetric unit of poly-ε-caprolactone*

	x	*y*	*z*
O(1)	0·2048	0·0328	0·0504
C(1)	0·2998	−0·0365	0·1182
H(1*a*)	0·3136	−0·2640	0·1182
H(1*b*)	0·4209	0·0989	0·1182
C(2)	0·2003	0·0365	0·1912
H(2*a*)	0·1965	0·2639	0·1912
H(2*b*)	0·0792	−0·0900	0·1912
C(3)	0·2998	−0·0365	0·2644
H(3*a*)	0·3136	−0·2640	0·2644
H(3*b*)	0·4209	0·0989	0·2644
C(4)	0·2003	0·0365	0·3374
H(4*a*)	0·1965	0·2639	0·3374
H(4*b*)	0·0792	−0·0900	0·3374
C(5)	0·2998	−0·0365	0·4106
H(5*a*)	0·3136	−0·2640	0·4106
H(5*b*)	0·4209	0·0989	0·4106
C(6)	0·2003	0·0365	0·4836
O(2)	0·0523	0·1448	0·4836

Single crystals

The single crystals (Fig. 4) have a lancet-like form; their surfaces are smooth. Associated single crystals are oriented at distinct angles to each other. It was not possible to obtain electron diffraction diagrams, even at very low beam intensities.

Thus, while there is no direct proof of single crystals, the general appearance of the crystals is the same as for all other polymer 'single crystals' with folded chains (Geil, 1963).

Discussion

There is a close similarity between the crystalline structure of poly-ε-caprolactone and that of polyethylene. The a and b dimensions of the unit cells are nearly identical:

polyethylene $a=7{\cdot}40$, $b=4{\cdot}93$ Å ($c=2{\cdot}534$ Å) ;
poly-ε-caprolactone $a=7{\cdot}496, b=4{\cdot}974$ Å ($c=17{\cdot}297$Å).

The chains of both polymers have a planar zigzag conformation, but significant differences seem to exist in the degree of rotation of the planar zigzag chains. Bunn (1939) found for polyethylene a rotation of the chains of 49° with respect to the a axis, whereas we found 28° for poly-ε-caprolactone. He calculated the structure factors without the hydrogen atoms. According to our experience these atoms exert a relatively strong influence. A recalculation of the polyethylene data used by Bunn (that polyethylene was not purely linear, but slightly branched), including the hydrogen atoms, performed by Zugenmeier (1969) gives a rotation of 35° instead of 49°, which is not too different from our value of 28°.

It follows that in the unit cell the chain arrangement in poly-ε-caprolactone and polyethylene is very similar. It seems that the polyethylene lattice can 'accommodate' the ester groups as periodic 'defects' and that they produce all the reflections on the first to sixth layer lines in the diagram of poly-ε-caprolactone. The completely different morphology of the single crystals of polyethylene and poly-ε-caprolactone is, therefore, rather surprising. The single crystals of polyethylene have a nearly isotropic rhombohedric form (Geil, 1963)whereas those of poly-ε-caprolactone are very long and anisotropic (Fig. 4). This may be due to dipole interactions of the ester groups pointing in the **a** direction (Fig. 2).

Apparently these relatively weak interactions of the ester groups do not change the 'polyethylene baseplane lattice'. The same is true for polyketones (ethylene–carbon monoxide copolymers) (Hendus, 1969; Chatani, Tukizawa & Murahashi, 1962). In these copolymers the keto groups are distributed statistically in a 'polyethylene baseplane lattice' without significant disturbance of the fundamental parameters by these groups. The lattice constant a changes from 7·40 to 7·97 Å and b from 4·93 to 4·76 Å for an increase in CO content from 0 to 50%. Between 44 and 50% CO content the fiber repeat distance, c, jumps from 2·54 to 7·57 Å, *i.e.* statistically the copolymer becomes alternating. In spite

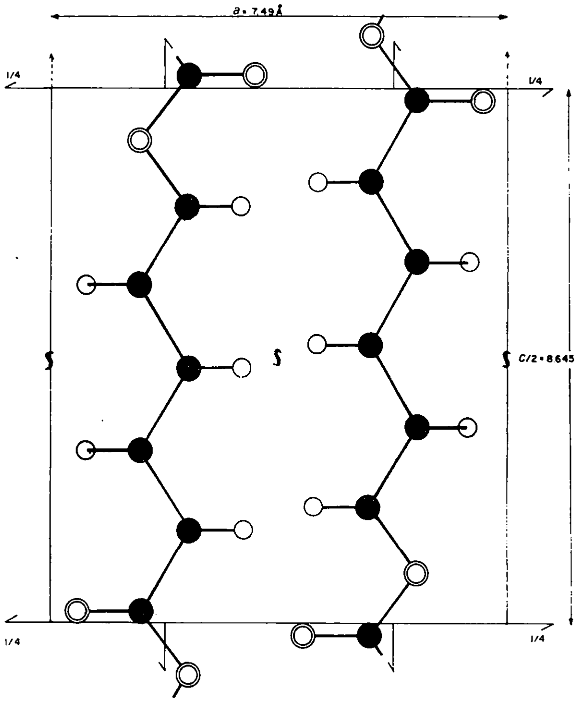

Fig. 3. Unit cell and chain arrangement of poly-ε-caprolactone in the ac projection. Only half ($c/2$) of the unit cell is shown in the c direction.

of these chemical changes the 'polyethylene baseplane lattice' is not significantly modified.

The much stronger interactions (hydrogen bonds) of the amide groups in a comparable polymer, nylon-6, change the 'polyethylene baseplane lattice' to a monoclinic form with $a=9{\cdot}56$, $c=8{\cdot}01$ Å, [b (fiber axis) $=17{\cdot}25$ Å] $\beta=67{\cdot}5°$ (Holmes, Bunn & Smith, 1955; Hendus, Schneider, Schnell, 1960). However, that modification can also be obtained in polyethylene by certain procedures such as pressing or rolling of polyethylene films (Pierce, Tordella & Bryant, 1962; Tanaka, Seto & Hara, 1962). The new lattice has the parameters $a=8{\cdot}09$, $c=4{\cdot}79$ Å, b (fiber axis) $=2{\cdot}53$ Å, $\beta=107{\cdot}9°$. If one doubles the c axis of this unit cell and takes the complement of the angle β, one arrives at the values $a=9{\cdot}58$, $c=8{\cdot}09$ Å, $\beta=72{\cdot}1°$ which are similar to the parameters of the nylon-6 lattice. It seems, therefore, that different modifications of 'polyethylene' are induced depending on the types of defects which may be of a chemical or structural nature.

The influence of the chemical defects on the melting point is quite striking. Thus poly-ε-caprolactone melts at 63°C compared with 136°C for polyethylene. This large drop in melting point, despite the greater polarity of the polyester chains and the nearly identical lattice, is best explained in terms of entropy. Apparently the greater freedom of rotation about the chain backbone leads to a significantly higher entropy of fusion compared with polyethylene. In the case of nylon-6, the hydrogen bonds increase the enthalpy of fusion to such an extent that the melting point rises to 227°C (Niegisch, 1969).

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