

The Crystal Structures of Polyethylene Adipate and Polyethylene Sebacate

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(Received 15 May 1961)

The structures of the crystalline regions of cold-drawn fibres and highly oriented, stretched rubber-like specimens of polyethylene adipate (PEA) and polyethylene sebacate (PES) have been determined. The unit cells are monoclinic with one chemical unit per fibre repeat and two chains per cell. The cell dimensions are:

$$\begin{aligned} \text{PEA, } a &= 5.47, b = 7.23, c \text{ (fibre axis)} = 11.72 \text{ \AA}, \beta = 113^\circ 30'; \\ \text{PES, } a &= 5.51, b = 7.25, c \text{ (fibre axis)} = 14.28 \text{ \AA}, \beta = 114^\circ 30'. \end{aligned}$$

Space group $P2_1/a$. The c projection of the cell has dimensions similar to those found in polyethylene. Atomic positions were deduced by trial and error. The chain configurations are very similar in the two polymers; there is considerable deviation from the planar configuration in the glycol part of the chain. The packing of the chains and the angle β seem to be determined by the interaction between C=O dipoles of neighbouring chains. Other crystalline forms of PEA and PES have been observed.

Introduction

The earliest X-ray diffraction work on the crystal structures of aliphatic polyesters was done by C. S. Fuller and his collaborators at Bell Telephone Laboratories (Fuller & Erickson, 1937; Fuller & Frosch, 1939*a, b*; Fuller, 1940); they investigated a series of polyesters of ethylene glycol with different dibasic acids, and reported chain-repeat distances and unit-cell dimensions. The chain-repeat distances showed that the chains are not plane zigzags. A detailed investigation of the structure of polyethylene adipate (PEA), $(-\text{CO}(\text{CH}_2)_4\text{CO}.\text{O}(\text{CH}_2)_2\text{O}-)_p$, was first undertaken by the present authors in the laboratories of Imperial Chemical Industries Limited, Alkali Division, at Northwich, Cheshire, in 1943, and the main features of the structure were then worked out. Subsequently some preliminary work on the closely related polyethylene sebacate (PES), $(-\text{CO}(\text{CH}_2)_6\text{CO}.\text{O}(\text{CH}_2)_2\text{O}-)_p$, was done by Miss D. J. Smith in Plastics Division laboratories at Welwyn Garden City. The refinement of both structures has now been carried out.

Fuller and his collaborators used cold-drawn specimens of moderate molecular weight. In the present work it was found possible to obtain more detailed fibre patterns by using specimens in which the molecular weight was increased by treatment of the initial polymer with 1-8% of hexamethylene diisocyanate, which links the molecules end-to-end by reaction with both hydroxyl and carboxyl end groups, forming carbamate and amide groups respectively, and also makes occasional cross-links to give either fibre-forming or rubber-like polymers, according to the method of preparation. These, on cold-drawing, or stretching above the melting point, gave X-ray

patterns showing a higher degree of crystal orientation than in specimens of the pure ester. The rubber-like polymers gave very highly oriented specimens, but of rather smaller crystallite size than in cold-drawn specimens, as might be expected.

No significant differences between the relative intensities of the reflections of the pure ester and those of the isocyanate-treated polymer, or between the unit-cell dimensions, were observed. It appears that only the pure ester parts of the chains form the crystalline regions, the carbamate and amide portions being in the amorphous regions, so that the use of the highly oriented isocyanate-treated specimens for structure determination is justified.

Experimental data: unit cell and space group

X-ray fibre photographs were taken with a cylindrical camera and Cu $K\alpha$ radiation. The diffraction data fit monoclinic cells of the type proposed by Fuller. The dimensions of the unit cells in Ångström units are:

$$\begin{aligned} \text{PEA } a &= 5.47 \pm 0.03, b = 7.23 \pm 0.02, c = 11.72 \pm 0.04 \text{ \AA} \\ &\text{(fibre axis); } \beta = 113^\circ 30', a \sin \beta = 5.02 \pm 0.02 \text{ \AA}. \\ \text{PES } a &= 5.51 \pm 0.03, b = 7.25 \pm 0.02, c = 14.28 \pm 0.04 \text{ \AA} \\ &\text{(fibre axis); } \beta = 114^\circ 30', a \sin \beta = 5.01 \pm 0.02 \text{ \AA}. \end{aligned}$$

The chains pack side-by-side in an orthogonal arrangement of closely similar dimensions in the two polymers.

Unsuccessful attempts were made to produce doubly oriented specimens of the PEA rubber in order to confirm the unit cell by the method used for nylon (Bunn & Garner, 1947), but only very slight indica

tions of double orientation were obtained. Confirmation was, however, obtained in another way for PEA, as the X-ray diagram showed definite signs of the tilted-crystal effect. The displacements of the reflections could be satisfactorily accounted for by the suggested unit cell, if it is assumed that the crystallites are tilted at a very small angle to the fibre axis with the axis of tilt parallel to the *b*-axis. The effect was too small, however, to permit unambiguous indexing of all the reflections, as was carried out for polyethylene terephthalate (Daubeny, Bunn & Brown, 1954).

The density of a drawn fibre of PEA was 1.26 g.cm.⁻³ which is consistent with a unit cell containing two repeating units, giving a crystalline density of 1.34 g.cm.⁻³.

Except for a weak $10\bar{1}$ reflection on the PEA photographs the diffraction data for both polymers are consistent with the space group $P2_1/a$, and this space group has been accepted for the main α -form of both polymers. The presence of the $10\bar{1}$ reflection is attributed to the presence in small proportion of a second (β) crystalline form in PEA, possessing the same unit cell but different space group. The principal evidence that this $10\bar{1}$ reflection is due to the presence of a second crystalline species is provided by the variation in its intensity relative to the rest of the reflections in different specimens; it is strongest in photographs of the cold-drawn pure ester and weakest in those of the rubber-like materials. Theoretically, it may be observed that if $10\bar{1}$ were an α species reflection, the space group would be $P2_1$, and this would mean that the natural centre of symmetry of the molecule would not be utilized in the structure; packing considerations suggest that this is unlikely. Moreover, if the space group were $P2_1$, more $h0l$ reflections with *h* odd would probably be seen; actually, of the 12 such reflections potentially observable, 10 are unequivocally absent because their spacings are such that they would not overlap with other reflections on the same layer. Lastly the PES photographs are entirely consistent with the space group $P2_1/a$, and the very close similarity between the diffraction patterns of PES and PEA suggests that the two polymers have closely similar structures, with chains of similar chain configuration packed in much the same way. The structure of the β form of PEA is discussed later in this paper.

The intensities of the reflections were measured by visual comparison with calibration spots of known relative exposure. Careful corrections were made for area, estimated visually, although these necessarily are not very accurate on the upper layer lines where the spots are very drawn out. For PES the multiple-film method was used, and corrections were made for the loss in intensity in the upper layer lines in successive films due to the oblique incidence of the diffracted beam (Grenville-Wells, 1955).

The observed intensities for PEA and PES listed in

Table 1 have been corrected for Lorentz and polarization factors and multiplicity.

Since it is estimated that only one-twentieth of the crystalline material is in the β -form in the rubber-like PEA specimens, and since only minor variations have been observed in the relative intensities on photographs showing different proportions of the two forms, the effect of the β -structure on the PEA intensities has been ignored.

Structure determination

The calculated identity periods of one chemical repeating unit of PEA and PES, based on a planar zig-zag chain configuration and the generally accepted bond lengths and angles, are 12.2 and 14.72 Å respectively, showing that the fibre repeat comprises one chemical unit of the chain. Based on the space group $P2_1/a$ the structures are fully described by a determination of the atomic co-ordinates of one asymmetric unit, half the chain repeat. The difference between the observed and calculated repeats indicates a shortening of the chain which must occur by distortion from the planar chain configuration. Fuller & Erickson (1937) found that in the series of polyesters of ethylene glycol with different dibasic acids, the shortening, based on one chemical unit, is practically constant, 0.5 Å for all members, with the exception of the succinate; this suggests that the shortening occurs in the only part of the chain which remains constant throughout the series, the glycol part. The great similarity between the PEA and PES photographs also lends support to this hypothesis, since this indicates that the distortions are very similar in both polymers, and the addition of the extra CH₂ group in PES to the $-\text{CO}(\text{CH}_2)_n\text{CO}-$ portion of the chain does not upset the spatial configuration of the chain in the neighbourhood of the distortion. The constant difference in fibre-repeat distance between successive members of the series 2.5 Å is also consistent with the idea of a planar carbon-carbon chain running nearly parallel to the fibre axis in the $-\text{CO}(\text{CH}_2)_n\text{CO}-$ region of the chain. The shortening of 0.5 Å can only be effected by large rotations around bonds leading to a markedly non-planar chain configuration.

Polyethylene adipate

The space group and the unit-cell dimensions suggest that the chains are arranged side by side in much the same way as in polythene; if we accept this, there are two ways of arranging the chains in the unit cell which appear identical when viewed along the *c* axis; these are shown in Figs. 1(a) and 1(b). The latter form may be considered to be derived from the former by rotation of each chain through 180°. Both forms were taken into account in considering distortions. In seeking by trial and error the atomic positions which gave the best agreement between calculated and observed intensities, the bond

lengths and bond angles were assumed to have their normal values:

Bond lengths		Bond angles	
C—C	1.53 Å	C—C—C	112°
C—O	1.43	C—C—O(ether)	109
C=O	1.25	C—O(ether)—C	111

Various distortions were considered which gave the correct chain repeat, 11.72 Å. The $-\text{CO}(\text{CH}_2)_4\text{CO}-$ part of the chain was initially assumed planar. Later, distortions of this section were brought into consideration, but the evidence is that the original assumption is correct, and all the distortion is in the glycol portion.

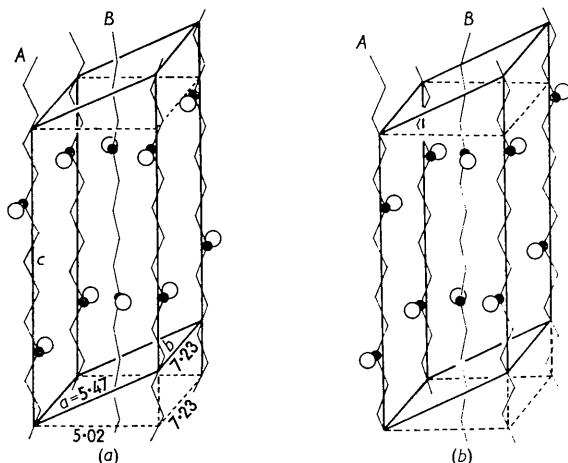


Fig. 1(a) and 1(b). Unit cell of PEA and the two possible orientations of the chain.

Promising agreement between observed and calculated intensities was obtained for one chain configuration based on that shown in Fig. 1(a), and this structure was partially refined by trial-and-error methods. Later, three-dimensional Fourier summations were carried out along lines parallel to the a , b , and c directions passing through the approximate position of each atom as already determined, in an attempt to obtain more accurate co-ordinates. The positions of the maxima confirmed strongly the essential correctness of the atomic positions already assumed, but the amount of diffraction information was not sufficient to refine the structure beyond the stage already reached. The Fourier summation carried out through a line parallel to c at $x = -0.073$, $y = 0.025$, showed four clear maxima in one repeat (see Fig. 2), indicating that the centres of four chain atoms lay close to this line. If the chain were a planar zig-zag then there would be five maxima, but there was only a faint peak at the z co-ordinate of the glycol CH_2 , showing that this atom was correctly placed well away from the mean plane of the chain.

Structure-factor calculations had so far been carried out using the Viervoll & Øgrim (1949) atomic scat-

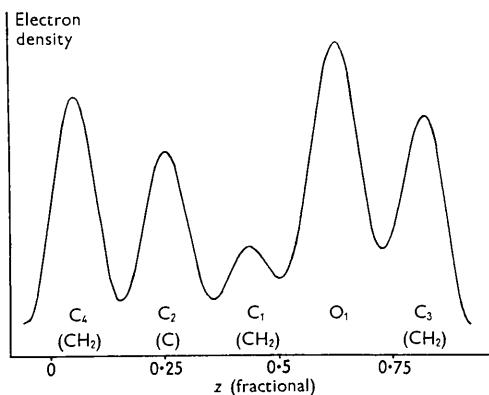


Fig. 2. Fourier summation through $x = -0.073$, $y = 0.025$ parallel to the c -axis.

tering curves for f_H , f_C , and f_O ; that for f_{CH_2} being taken as $2f_H + f_C$. Appreciable improvement in intensity agreement was effected by calculating the contributions of hydrogen atoms separately instead of treating CH_2 as a separate scattering unit. The co-ordinates of the H-atoms were found by assuming C—H bonds of 1.09 Å and the normal tetrahedral angles. Further refinement was carried out by trial and error following the introduction of the hydrogen atoms, and the final calculation of F 's was carried out on the electronic computer of Messrs. Elliott Brothers, Boreham Wood. The temperature factor used in the final intensity calculations, $\exp -B(\sin \theta/\lambda)^2$ where $B = 17 \times 10^{-16}$ cm. was calculated from the observed and calculated intensities by the usual method, (compare with polyethylene terephthalate where a B value of 18×10^{-16} cm. was used).

A comparison of observed and calculated intensities, (I_o and I_c) is given in Table 1. The I_o values have been placed as far as possible on an absolute scale by reference to the calculated values. So that undue weight should not be given to the strong reflections 110 and 020, which contribute more than one half of ΣI_o , the scaling factor has been obtained by excluding them. The I_o figures given in brackets in Table 1 denote half the minimum intensity potentially observable for all reflections which are absent from the photographs, and have been used in calculating ΣI_o and ΔI . These figures increase with θ and the number of the layer line because of the increasing diffuseness of the reflections. Reliability factors, calculated on both I values and F values from the expressions

$$R_I = \frac{\Sigma |I_o - I_c|}{\Sigma |I_o|} \quad \text{and} \quad R_F = \frac{\Sigma |F_o - F_c|}{\Sigma |F_o|}$$

are given in Table 2, including and excluding the two very strong reflections 110 and 020, and are considered quite satisfactory for a polymer structure. In evaluating R_F overlapping reflections were considered by dividing I_o in the ratio of the I_c values. R_F is better than R_I as a measure of the correctness of the structure and gives less weight to the few strong reflections

Table 1. *Observed and calculated intensities for PEA and PES*(Units-electrons² × 10⁻¹: figures in brackets denote half the minimum observable intensity)

PES			PEA			PES			PEA		
<i>hkl</i>	<i>I_o</i>	<i>I_c</i>	<i>hkl</i>	<i>I_o</i>	<i>I_c</i>	<i>hkl</i>	<i>I_o</i>	<i>I_c</i>	<i>hkl</i>	<i>I_o</i>	<i>I_c</i>
110	997	762	110	608	480	32 $\bar{2}$	(2)	—	32 $\bar{2}$	} 5	5
020	840	717	020	608	474	14 $\bar{2}$	} 3	5	14 $\bar{2}$		
120	62	78	120	56	61	23 $\bar{2}$			} 8	7	23 $\bar{2}$
200	39	39	200	18	18	24 $\bar{2}$	} (2)	2			24 $\bar{2}$
210	4	4	210	1	1	33 $\bar{2}$			} (2)	1	003
130	82	66	130	71	48	31 $\bar{2}$	} 4	3			
220	20	19	220	13	14	05 $\bar{2}$			} (2)	1	01 $\bar{3}$
040	28	10	040	16	4	15 $\bar{2}$	} (1)	—			20 $\bar{3}$
230	7	5	230	} 5	10	32 $\bar{2}$			} 41	52	21 $\bar{3}$
140	8	11	140			310	5	003			} 11
310	7	8	310	320	(1)	013	} 12	19	12 $\bar{3}$	} (1)	
320	(1)	—	320	240	5	13 $\bar{3}$			} 18		13
240	9	9	240	330	7	12 $\bar{3}$	} 16	16		23 $\bar{3}$	
150	8	3	330	} 2	2	20 $\bar{3}$			} (2)	1	20 $\bar{3}$
330	(1)	—	150			001	4	32 $\bar{3}$			} (2)
400	} 7	5	001	011	10	04 $\bar{3}$	} 6	6	14 $\bar{3}$	} 5	
250			4	4	011	(10 $\bar{1}$)			(1.5)		14 $\bar{3}$
340	} 4	4	11 $\bar{1}$	11 $\bar{1}$	18	22 $\bar{3}$	} 16	16	22 $\bar{3}$	} (>2)	2
410			(2)	—	111	111			—		
060	(2)	—	021	021	1	004	} 24	23	004	} 33	32
160	(2)	1	12 $\bar{1}$	12 $\bar{1}$	4	11 $\bar{4}$			} 30		
001	32	21	20 $\bar{1}$	20 $\bar{1}$	33	014	} (1)	2		204	} 35
011	12	14	12 $\bar{1}$	12 $\bar{1}$	—	124			} (1)	1	
11 $\bar{1}$	17	28	20 $\bar{1}$	20 $\bar{1}$	33	214	} 9	22			214
111	—	—	121	121	1	024			} 11	7	024
021	—	4	21 $\bar{1}$	21 $\bar{1}$	5	114	} 11	12			114
12 $\bar{1}$	(1)	3	031	031	9	224			} 15	13	224
121	} 34	40	201	201	22	134	} 14	16			134
20 $\bar{1}$			3	4	13 $\bar{1}$	13 $\bar{1}$			—	034	} 14
21 $\bar{1}$	} 13	17	211	211	18	314	} 14	16	314	} 14	
031			13	17	221	221			18		234
201	} 27	16	131	131	4	134	} (2)	—	134	} (2)	—
131			6	11	221	221			(1)		
221	(2)	4	041	041	(1)	324	} (3)	—	324	} (3)	—
231	} (2)	3	231	231	(1)	144			} (3)		
041			19	13	141	141	20	044		} (3)	8
141	} 19	13	311	311	14	224	} (3)	2	224		
311			} 11	10	231	231			12	244	} (>3)
231	11	10			141	141	9	334	} (>3)	2	
141	} 36	27	321	321	(2)	144	} (>3)	—			144
002			36	27	311	311			4	234	} 14
012	3	2	241	241	2	204	} (2)	—	204	} (2)	
11 $\bar{2}$	6	—	002	002	41	134			} (2)		—
022	1	1	012	012	—	134	} (2)	—		134	
11 $\bar{2}$	} 53	55	112	112	10	214			} 5	5	214
12 $\bar{2}$			73	81	122	122	—	324			} (3)
20 $\bar{2}$	(2)	—	112	112	7	144	} (3)	—	144	} (3)	
21 $\bar{2}$	(1)	1	202	202	7	044			} (3)		8
122	21	38	212	212	5	224	} (3)	2		224	
032	(1)	—	122	122	19	244			} (>3)	—	244
222	} 15	14	032	032	(1)	334	} (>3)	2			334
132			15	14	222	222			20	144	} (>3)
202	24	46	132	132	15	404	} (>3)	—	404	} (>3)	
212	(2)	—	202	202	—	234			} (>3)		—
132	4	2	212	212	29	414	} (>3)	—		414	
232	(2)	—	132	132	36	115			} (1)	—	004
222	} 21	26	232	232	(2)	005	} 33	29			114
312			21	26	312	312			8	015	} (1)
042	} (2)	1	222	222	15	205	} 54	82	204	} 58	
142			(2)	1	222	222			8		215
			142	142	12	125	} 3	4	124	} (1)	1
						025					

Table 1 (cont.)

PES			PEA		
<i>hkl</i>	<i>I_o</i>	<i>I_c</i>	<i>hkl</i>	<i>I_o</i>	<i>I_c</i>
225̄	6	9	224̄	9	7
115̄	7	—	114̄		
135̄	2	8	134̄	(2)	3
035̄	(2)	—	124̄	(2)	—
125̄	5	5	034̄		
315̄			314̄	5	2
235̄	(2)	—	234̄	7	8
325̄	5	7	324̄		
135̄	13	10	134̄	(4)	2
145̄			214̄	11	5
205̄	144̄	204̄	(5)		
215̄	(2)	4		044̄	
045̄			224̄	(5)	4
245̄	(3)	1	244̄		
335̄	8	4	334̄		
225̄			(3)	—	
405̄	(3)	—			
415̄	(3)	—			
116̄	14	15	115̄	18	20
006̄	40	49	005̄	19	35
206̄	104	52	205̄	78	61
016̄	18	27	015̄		
216̄	(4)	4	215̄	1	2
126̄	52	57	125̄	32	47
026̄	20	12	025̄	2	7
226̄	37	18	225̄	36	13
136̄	28	31	135̄	14	21
116̄			115̄		
316̄	36	11	315̄	33	31
036̄	30	32	035̄		
236̄	(3)	8	235̄	19	40
126̄	6	7	125̄		
326̄			325̄	6	3
146̄	23	23	145̄	16	16
136̄	27	19	135̄		
336̄			205̄	16	12
046̄	045̄				
206̄	18	15	335̄		
246̄			245̄		
406̄			215̄		

which in polymer diffraction patterns tend to contain a large proportion of the total diffracted intensity.

Polyethylene suberate

Evidence has already been given for the similarity of the structures of PEA and PES and the reasons for assuming that the distortions take the same form in both polymers. The first trial co-ordinates were therefore obtained by assuming exactly the same spatial configuration for the PES chain and its position in the *c*-projection. The extra CH₂ group was added in so that the -CO(CH₂)₆CO- part of the chain remained planar; in other words, the atomic co-ordinates (in Å) referred to rectangular axes perpendicular to the *c*-axis were kept identical with those in PEA and the *c* co-ordinates adjusted to accommodate the extra C atom in the lengthened *c* cell dimension, except that slight adjustments were made to co-ordinates to keep the suberate part of the chain substantially planar and the bond lengths in this part of the chain correct. The intensities, calculated using *f_o* and *f_c* only and

excluding hydrogen atoms were then inserted as before and the intensities recalculated on the computer. As the agreement was as good as for PEA no further refinement was carried out. The comparison between observed and calculated intensities is given in Table 1. The *R*-factor data are given in Table 2 for comparison with that for PEA.

Table 2. *R*-factor data

	PEA		PES	
	<i>R_I</i> %	<i>R_F</i> %	<i>R_I</i> %	<i>R_F</i> %
All reflections	27	19	25	19
Excluding 110, 020	32	21	32	20

Description of structure and interatomic distances

The atomic co-ordinates expressed in fractions of unit-cell edges for PEA and PES are given in Table 3. Since Fourier methods have not played any part in the refinement of this structure it is not possible to give any numerical estimate of the errors in the atomic positions.

The numbering of the atoms of one asymmetric unit of PEA is shown in Figs. 3 and 4. C₅, H₇ and H₈

Table 3. Atomic co-ordinates expressed in fractions of unit cell edges

Polyethylene suberate			
	<i>x</i>	<i>y</i>	<i>z</i>
C ₁	+0.059	+0.069	+0.474
O ₁	+0.101	-0.035	+0.398
C ₂	-0.060	+0.025	+0.301
C ₃	+0.068	-0.050	+0.232
C ₄	-0.063	+0.035	+0.125
C ₅	+0.064	-0.039	+0.055
	<i>x</i>	<i>y</i>	<i>z</i>
H ₁	+0.246	+0.125	+0.530
H ₂	-0.081	+0.182	+0.438
O ₂ (CO)	-0.278	+0.105	+0.276
H ₃	+0.279	-0.014	+0.268
H ₄	+0.044	-0.201	+0.227
H ₅	-0.043	+0.185	+0.131
H ₆	-0.275	0	+0.091
H ₇	+0.277	-0.002	+0.089
H ₈	+0.041	-0.189	+0.051
Polyethylene adipate			
	<i>x</i>	<i>y</i>	<i>z</i>
C ₁	+0.059	+0.069	+0.468
O ₁	+0.102	-0.035	+0.374
C ₂	-0.060	+0.025	+0.258
C ₃	+0.068	-0.050	+0.173
C ₄	-0.063	+0.035	+0.044
	<i>x</i>	<i>y</i>	<i>z</i>
H ₁	+0.248	+0.125	+0.535
H ₂	-0.081	+0.182	+0.426
O ₂ (CO)	-0.280	+0.105	+0.230
H ₃	+0.281	-0.014	+0.214
H ₄	+0.044	-0.202	+0.167
H ₅	-0.043	+0.186	+0.051
H ₆	-0.276	0	+0.004

constitute the extra CH_2 group in the PES asymmetric unit. Figs. 3-6 all represent the PEA structure, but the following remarks regarding interatomic distances and packing apply equally well to PES. Fig. 3 shows the configuration of a single molecule viewed roughly perpendicular and parallel to the planar chain of the adipate portion, Fig. 4 the arrangement of the molecules viewed down the fibre axis, and Fig. 5 the b -projection of the structure with hydrogen atoms omitted. In Fig. 5 the unit cell of PES is shown dotted and the extra C_5 atoms inserted. The planar hydrocarbon chain lies at a mean angle of 40° to the ac plane and is tilted by a very small angle to the c -axis. The C_2-O_1 bond of the chain is rotated by 10° round the C_2-C_3 bond, the O_1-C_1 bond by 18° round C_2-O_1 , and C_1-C_1 by 66° round O_1-C_1 ; the $\text{C}_2=\text{O}_2$ bond is 6° out of the plane $\text{C}_3-\text{C}_2-\text{O}_1$ (ether). The result is a considerable spread of the chain atoms in the c -projection. The bond lengths and angles are given in Table 4. Those for PES involving C_5 are included.

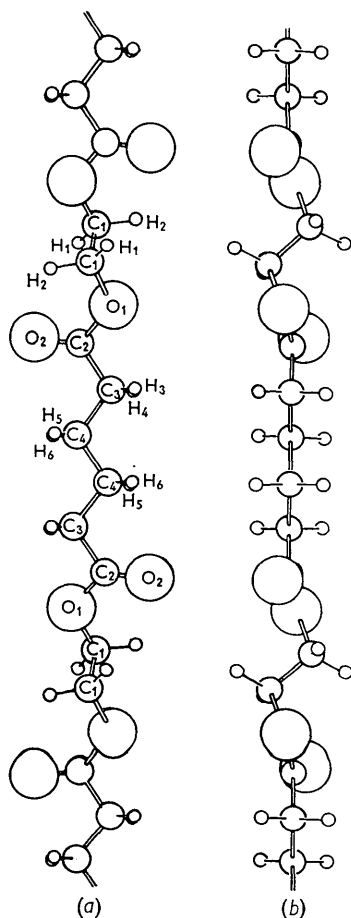


Fig. 3. PEA chain configuration viewed (a) perpendicular, (b) parallel to the plane of the adipate chain.

While, as stated previously, the bond lengths and angles were, as far as possible, kept to their accepted

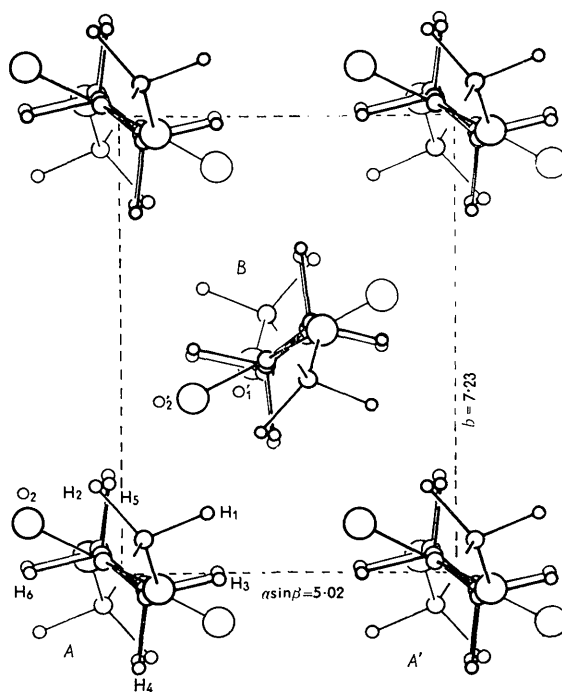


Fig. 4. Arrangement of PEA molecules in the c -projection.

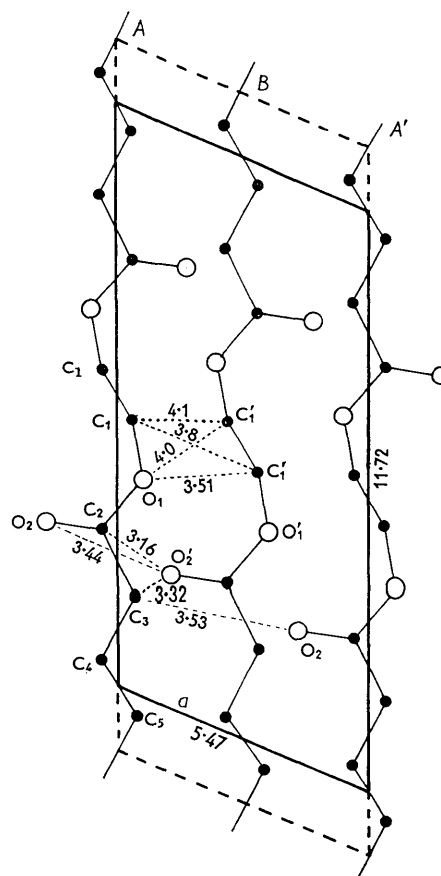


Fig. 5. Arrangement of PEA molecules in the b -projection.

values, all the shortening of the glycol portion of the chain to account for the observed chain repeat of 11.72 Å could not be attributed to rotation around chain bonds alone as the resultant distortions from the planar configuration were too great for good agreement between calculated and observed intensities. Some of the observed shortening therefore has been attributed to a reduction in the O₁-C₂ bond length to 1.37 Å. The X-ray data are not sufficiently detailed to determine the precise location of the shortening but this is justified by evidence for the shortening of the CO-O bonds of ester groups in other structures. Electron-diffraction results summarized by Allen & Sutton (1950) are given in Table 5.

Table 4. Bond lengths and angles in PEA and PES

PEA	C ₁ -C ₁ '	1.53 Å	C ₁ '-C ₁ -O ₁	106°
	C ₁ -O ₁	1.43	C ₁ -O ₁ -C ₂	111°
	O ₁ -C ₂	1.37	O ₁ -C ₂ -C ₃	106°
	C ₂ =O ₂	1.24	O ₁ -C ₂ =O ₂	125° 30'
Adipate chain	C ₂ -C ₃	1.53	C ₃ -C ₂ =O ₂	124° 30'
	C ₃ -C ₄	1.53	C ₂ -C ₃ -C ₄	111°
	C ₄ -C ₄ '	1.53	C ₃ -C ₄ -C ₄ '	112°
	PES	C ₄ -C ₅	1.53	C ₃ -C ₄ -C ₅
	C ₅ -C ₅ '	1.54	C ₄ -C ₅ -C ₅ '	113°

Table 5. C-O bond length

	CO-O	CH ₃ -O
Methyl formate	1.36 Å	1.46 Å
Methyl acetate	1.36	1.46
Methyl chloroformate	1.35	1.46

Jeffrey & Dougill (1953) found that the CO-O bond in dimethyl oxalate was shortened to 1.31 Å, which they ascribed to resonance and partial double bond character of this bond. A corresponding type of shortening in the CO-N bonds of amides from 1.46 Å to 1.33 Å has been observed (Carpenter & Donohue, 1950; Brown & Corbridge, 1954).

Packing of the molecules

As suggested by Fuller (1937), the arrangement of the chains side by side is very similar to that found in polyethylene and the straight chain monomeric hydrocarbons; note the similarity in the dimensions of the *c*-projection of the unit cell, (polyethylene $a=7.40$, $b=4.93$ Å; PEA $b=7.23$, $a \sin \beta=5.02$ Å) and the angle of approximately 40° made by the planar adipate portion of the chain with the *a* axis compared with the corresponding angle with the *b* axis in polythene of 41.2°. The distances between chain atoms of neighbouring molecules, Fig. 5, are those characteristic of Van der Waals forces; the shortest are given in Table 6. The carbonyl O₂ atoms of neighbouring *A* and *B* chains whose positions are related by operation of the *a* glide plane and therefore lie in a plane parallel to the *ab* plane are 3.44 Å apart, and are not true contact distances. The cell dimensions are evidently determined by the hydrocarbon

part of the chain and the carbonyl oxygen and the chain distortion do not distort the unit cell appreciably.

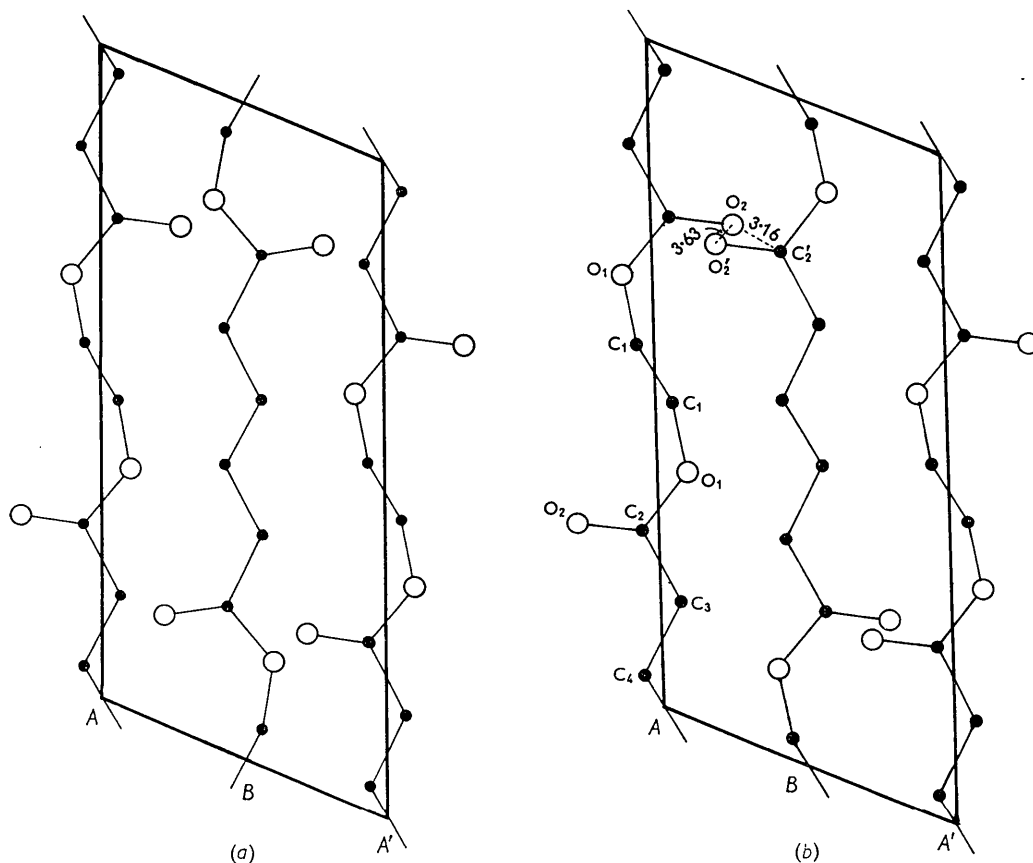
Table 6. Some intermolecular distances in PEA and PES

O ₂ '-C ₂	3.16 Å	O ₁ -C ₁ '	3.51, 4.0 Å
O ₂ '-C ₃	3.32	O ₂ -O ₂ '	3.44
O ₂ '-C ₄	3.35	C ₃ -O ₂ (A')	3.53
C ₁ -C ₁ '	3.80, 4.10	O ₁ -O ₂ '	3.7

It is significant that the shortest approach, 3.16 Å, is that between the positively charged carbon atom C₂ and the negatively charged oxygen atom O₂' of the C=O dipoles and although this approach is not unduly short, assuming the radii of carbon and oxygen to be 1.7 and 1.35 Å respectively, it does indicate some dipole attraction. The O₂'-C₃ and O₂'-C₄ distances correspond to a close packed arrangement if the radius of a CH₂ group is taken as 2.0 Å.

Fuller (1937) showed that the polyesters of this series of esters containing an odd number of chain atoms per chemical repeating unit fit orthorhombic cells, indicating that the C=O groups of neighbouring molecules align themselves in horizontal planes. In the case of the even esters PEA and PES, a chain at the edge of the cell is displaced with respect to its neighbour along *a* by 2.2 Å parallel to its length. This is made clear in Fig. 1. This is an example of Schoon's suggestion (1938) put forward to account for the polymorphism exhibited by the monomeric hydrocarbons where the side-by-side packing of the chains will be the same if adjacent chains are displaced by whole-number multiples of the zig-zag period 2.5 Å. The displacement of one zig-zag only in PEA and PES would appear to be accounted for by the dipole interaction; larger shifts would result in a greater distance than 3.16 Å between oppositely charged dipole atoms of neighbouring chains. The reason why there is any shift at all and the even esters do not also crystallize in the orthorhombic form is more difficult to understand from a consideration of the structure. When the CO groups of the odd polyesters lie in planes perpendicular to the *c* axis both of the CO groups in the asymmetric unit have identical environments, but if the chains are displaced by one zig-zag, as in the even esters, then this is no longer true. It would also lead to a rather short O(CO)···O (ether) van der Waals distance. This may explain why the old esters crystallize in the orthorhombic and not the monoclinic form. However, in both the monoclinic and the orthorhombic arrangements of the even esters all the CO groups of each form have the same environment. Presumably the free energy of the monoclinic form is the smaller, and this is therefore the more stable form.

The rotation of 66° of the C₁-C₁ bond around the C₁-O₁ bond does not correspond to the staggered position, and indicates either that this is a potential minimum for the isolated molecule or that the potential barrier to rotation around the C₁-O₁ bond is low



Figs. 6(a) and 6(b). Alternative structures suggested for the β -form shown in b -projection.

enough to permit distortions from the minimum by intermolecular forces. The difference in the rotation around this bond in polyethylene terephthalate (Daubeny *et al.*, 1954) and PEA (20° and 66° respectively) indicates that the potential barrier is low (for it is unlikely that there would be two minima only 46° apart). The packing of the molecules, and not the hindrance to rotation around this bond, apparently is the over-riding feature in determining the configuration of the chain in this region, the small size of the oxygen atom, compared with a CH_2 group, permitting the chain to collapse on itself to give closer packing. Beyond this the reason for the precise configuration in the glycol part is not clear.

The existence somewhere in the polyester molecule of a point of ready flexibility is demanded by the fact that the melting points of PEA and PES, 52° and 65° , and of aliphatic polyesters generally, are low—lower than that of polyethylene in spite of the existence in the polyester molecule of $\text{C}=\text{O}$ dipoles which by themselves would increase the melting point. The evidence provided by the structures of PEA and PES is that the bond around which rotation is comparatively easy is the $\text{C}_1\text{—O}_1$ bond ($\text{CH}_2\text{—O}$) and to a lesser extent the $\text{O}_1\text{—C}_2$ (O—CO) bond and not the $\text{C}_2\text{—C}_3$ (CO—CH_2) bond.

The melting points of PEA and PES relative to polyethylene terephthalate, polymethylene, and nylon, and in relation to the flexibilities of the molecules and the cohesive forces between them, have already been discussed by Daubeny, Bunn & Brown (1954), and will not be further discussed here.

Other crystalline forms of PEA and PES

The existence of a β -crystalline structure of PEA, which must possess the same unit cell as the α -structure, is suggested to account for the extra $10\bar{1}$ spot. Two possible structures for the β -form are discussed below.

(1) The distance between consecutive carbonyl oxygens of the same chain is practically equal to half the fibre period corresponding to the two sections of the chemical repeating unit, $\text{—CO}(\text{CH}_2)_4\text{CO—}$ and $\text{—CO O}(\text{CH}_2)_2\text{O.CO—}$. On drawing, a measure of stability may be attained when the adipate and glycol sections of some chains are interchanged, since the $\text{C}=\text{O}$ dipole interaction and the packing will be similar. This corresponds to rotating the B molecule of the α -structure through 180° and displacing by $c/2$ (Fig. 6(a); compare Fig. 5). The cell would be triclinic, pseudo monoclinic, possessing only a centre of symmetry.

(2) The β -structure possesses the space group $P2_1/n$ (Fig. 6(b)).

$10\bar{1}$ is not a space-group absence on either of these arrangements. Intensity calculations, on the basis of the same chain configuration as in the α -structure, show that in structure (1) $10\bar{1}$ has a low calculated intensity requiring more than one quarter of the total crystallites to have the β -structure in the rubbery specimens, and more than one half in the cold drawn specimens. This is not acceptable because such a large proportion would affect the relative intensities of other reflections as between the rubbery and the cold drawn specimens, whereas in fact only $10\bar{1}$ has been observed to change intensity appreciably. In structure (2), $10\bar{1}$ has a large calculated intensity, requiring only 1/20 of the crystallites to have the β -form; this would not affect the other intensities appreciably: in this proportion no other $h0l$ (h odd) reflections would be strong enough to be visible on the photographs. On theoretical grounds the $P2_1/n$ space group is as likely as $P2_1/a$ since the A and B molecules have identical environments. The C=O dipole distance is 3.16 Å, the same as in the α -structure, 3.17 Å, so that the packing of the chains is similar in this respect and the $P2_1/n$ structure would be expected to have some measure of stability. It has therefore been accepted as the most likely for the β -form.

Specimens of pure PEA of moderate molecular weight and of PEA lightly linked with hexamethylene diisocyanate contain a third crystalline form (γ) in the unstretched state which, on cold drawing to give an oriented fibre, is converted into the α -structure. The γ -form shows three very strong equatorial reflec-

tions of combined intensity equal to the two strong reflections, 110 and 020, of the α -structure. Two of these reflections have the same spacings as 110 and 020, the third slightly greater than 110, as if the 110 reflection were split into two reflections of roughly equal intensity. PES can also occur in a second crystalline form in the unoriented state.

The authors wish to express their thanks to Drs D. R. Holmes and E. R. Howells, and Mr R. P. Palmer, of these laboratories, for many helpful discussions.

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Experimental Determination of Order Phenomena in Liquids and Amorphous Solids

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(Received 20 March 1961)

A study has been made to determine with what accuracy information can be obtained about order phenomena in liquids and amorphous solids by means of X-ray diffraction. It is shown that with proper experimental conditions and a suitable evaluation of the X-ray intensities, dispensing with sharpening of intensities and with the concept of point atoms, very reliable distribution curves can be obtained, showing no spurious effects near the origin. This method has been tested with good results for cyclohexane, benzene and vitreous silica.

Introduction

It was first shown by Debye (1915) and Ehrenfest (1915), that a regular crystalline arrangement is not

essential for the production of diffraction effects. Debye (1925, 1927) later, in a paper on the diffraction of X-rays by gases, introduced the idea of a probability function, expressing the probability of the occurrence of any given interatomic distance. Similar ideas were put forward by Zernike & Prins (1927) in a very

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