Crystal and molecular structure of poly(aryl ether ether diketone)

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The crystal and molecular structure of poly(aryl ether ether diketone) has been determined through wide-angle X-ray diffraction methods and conformational analysis. The unit cell, corresponding to a statistical structure, is orthorhombic, with cell dimensions $a = 9.96 \pm 0.10$ Å, $b = 4.78 \pm 0.05$ Å and $c = 10.7 \pm 0.10$ Å. The space group is *Pbcn*. The statistical subperiodicity along the chain axis $c = 10.7$ Å is slightly larger than in the case of poly(aryl ether ketone) and poly(aryl ether ether ketone), which also have statistical structures. In addition, in the fibre spectra, weak haloes in layers are observed, which correspond to a periodicity three times larger, in agreement with the chemical constitution. While the phenylenic groups take approximately ordered positions in the crystals, this is not so for the constitutional units –CO–CO– and –O– of neighbouring chains.

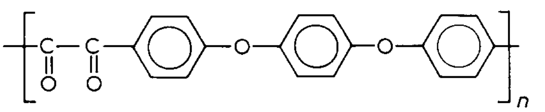
(Keywords: poly(aryl ether ether diketone); X-ray diffraction; conformational analysis; crystal structure)

INTRODUCTION

Poly(aryl ether ketones), containing only ether and carbonyl linkages between the phenylic groups, show virtually identical X-ray diffraction patterns, indicating that all these polymers have very similar crystal structures[1].

Detailed X-ray diffraction analyses have been made for poly(aryl ether ether ketone) (PEEK)[2–5] and for poly(aryl ether ketone) (PEK)[6], and the similarity of their structures to the structure of poly(p-phenylene oxide) (PPO)[7] has been pointed out. In particular, these polymers show a chain axis periodicity $c = 10.0$–10.1 Å, which is very near to the value of 9.7 Å found for the c axis in the crystal structure of PPO[7]. For both polymers, the diaryl ether and the diaryl carbonyl groups are interchangeable in a statistical way along the crystallographic c axis. Accordingly these polymers maintain the same space group *Pbcn* of PPO, with very similar unit-cell parameters.

In this paper, we perform an X-ray and conformational analysis of the crystal and molecular structure of a new polymer of this class, prepared in the laboratories of Istituto 'G. Donegani' of Montedison, poly(aryl ether ether diketone) (PEEDK), whose constitution is:



This polymer differs from PEEK in having a dicarbonyl group instead of a carbonyl group linking two phenylic rings.

As will be shown in the present paper, also in this case the fibre spectrum of the polymer presents well defined layers corresponding to a statistical subperiodicity; the statistical subperiodicity $c = 10.7$ Å is slightly larger than in the case of PEK and PEEK, and, in addition, weak haloes in layers are observed, which correspond to a periodicity three times larger, in agreement with the chemical constitution.

EXPERIMENTAL

X-ray diffraction patterns, using Ni-filtered Cu Kα radiation, were made on unoriented as well as oriented crystalline samples. A powder spectrum is shown in *Figure 1*. To obtain uniaxially oriented crystalline samples the powder was compression moulded, drawn at 155°C up to a draw ratio of about 2.5 and then annealed at 240°C, under tension, for 15 min. A fibre spectrum, using a cylindrical camera, is shown in *Figure 2*. The diffracted intensities were qualitatively estimated from the fibre spectrum, with the exception of the four most intense reflections. For these reflections, the relative intensities were evaluated in a quantitative way from the height of the peaks in the Geiger spectrum.

METHODS OF ENERGY CALCULATION

The internal energy, referred to the asymmetric unit, has been calculated as a function of the relevant conformational parameters as the sum of two energy terms:

$$E = E_{\mathrm{tor}} + E_{\mathrm{nb}}$$

where E_{tor} is the sum of torsional potential energy contributions around single bonds, calculated according to the general formula:

$$(k_t/2)[1 \pm \cos(n\theta)]$$

and E_{nb} is the sum of energy contributions due to the interactions between non-bonded atoms (separated by

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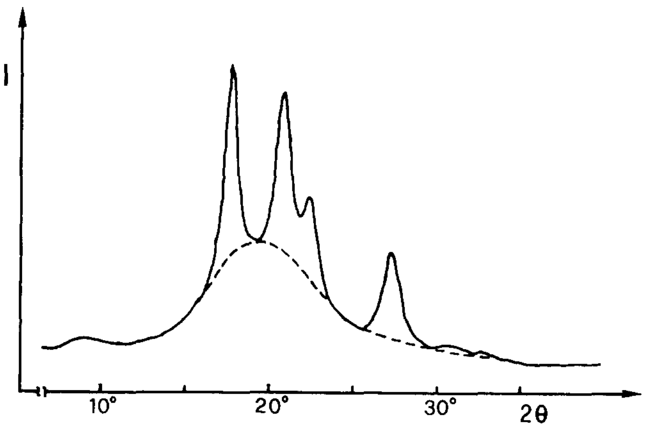

Figure 1 X-ray diffractogram (Cu Kα) of a compression-moulded sample of PEEDK

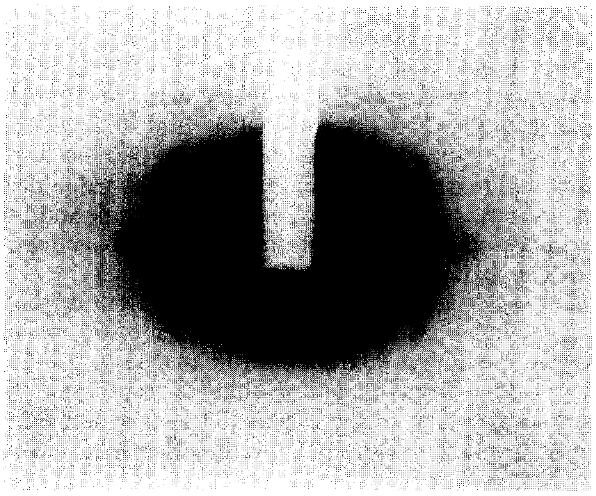

Figure 2 X-ray fibre spectrum of a drawn sample of PEEDK

more than two bonds if the atoms belong to the same molecule) at a distance r, calculated according to the general formula:

$$Ar^{-12} - Br^{-6}$$

The non-bonded interactions were calculated between the atoms of one asymmetric unit and the atoms of the same and of the surrounding molecules (if the packing energy was considered) within spheres having radii twice the van der Waals distance for each pair of atoms.

In all our energy calculations the values of the bond lengths and the bond angles have been left fixed at the values reported in *Table 1*.

The non-bonded energy parameters are from Flory *et al.*[8,9]. The torsional potential barrier around the C_{ar}–O bond was assumed as six-fold, and it has been considered equal to that reported by Hopfinger[10] for the C_{ar}–C_{sp^3} bond. The torsional potential barrier around the C_{ar}–CO bond is two-fold, and it has been considered equal to that reported for benzaldehyde and obtained from far-infra-red spectroscopy[11–13].

All the values of the energy parameters used are reported in *Table 2*.

ANALYSIS OF THE FIBRE SPECTRUM

The fibre spectrum of PEEDK shows well defined layer lines, consisting of sharp reflections and haloes. The sharp reflections can be indexed on the basis of an orthorhombic unit cell with constants:

$$a = 9.96 \pm 0.10\ \text{Å} \quad b = 4.78 \pm 0.05\ \text{Å} \quad c = 10.7 \pm 0.10\ \text{Å}$$

Assuming the presence of two chains per unit cell, the calculated density is 1.37 g cm^{-3}, in good agreement with the experimental density (1.32 g cm^{-3}).

On the basis of the systematic extinction of the reflections ($h\ k\ 0$) with $h + k = 2n + 1$, ($0\ k\ l$) with $k = 2n + 1$ and ($h\ 0\ l$) with $l = 2n + 1$, we assumed the space group *Pbcn*.

The length of the fibre axis c corresponds to a periodicity that is statistical. Accordingly, we note that, in addition to sharp spots on layers with l integer, weak haloes are present in the spectrum, on layers l having orders equal or near to 2/3, 4/3, 7/3, 8/3 and 10/3. This observation is indicative of a periodicity three times larger (32.1 ± 0.3 Å) within each chain, consistent with the chemical constitution. In fact, the relative positions of the diketone (–CO–CO–) and oxo (–O–) groups are ordered within each chain. They are not ordered among different chains, however, as indicated by the occurrence of sharp spots only on layers corresponding to the statistical periodicity c = 10.7 Å. In the crystal structure, the diaryl dicarbonylic group appears to be interchangeable more or less at random with the diaryl ether group, as was found for the diaryl carbonylic and diaryl ether groups in PEEK[4,5] and PEK[6]. The weak haloes observed should thus correspond to the Fourier transform of the

Table 1 Bond lengths and bond angles used

Bond lengths (Å)		Bond angles (deg)	
C–C	1.52	C–C–C_{ar}	119
C–C_{ar}	1.48	C_{ar}–C=O	122
C_{ar}–C_{ar}	1.39	C–C=O	119
C=O	1.21	C–C_{ar}–C_{ar}	120
C_{ar}–H	1.09	C_{ar}–C_{ar}–O	120
		C_{ar}–O–C_{ar}	125
		C_{ar}–C_{ar}–C_{ar}	120
		C_{ar}–C_{ar}–H	120

Table 2 Parameters used in the energy calculations

Torsion angle		K_t (kJ mol^{-1})	n	Sign
C_{ar}–C_{ar}–C=O		20.9	2	–
C_{ar}–C_{ar}–O–C_{ar}		2.4	6	+
Interacting pair		$A \times 10^{-3}$ (kJ mol^{-1} Å^{12})	B (kJ mol^{-1} Å^{6})	
C	C	2515	2310	
C	C_{ar}	3212	2310	
C	O_{eth}	1240	1606	
C	O_{carb}	1345	1858	
C	H	295	665	
C_{ar}	C_{ar}	4066	2310	
C_{ar}	O_{eth}	1607	1606	
C_{ar}	O_{carb}	1859	1858	
C_{ar}	H	394	665	
O_{eth}	O_{eth}	630	1174	
O_{eth}	O_{carb}	722	1344	
O_{eth}	H	133	446	
O_{carb}	O_{carb}	828	1543	
O_{carb}	H	394	666	
H	H	30	196	

single chains and will not be considered any further in this paper.

The following considerations will apply, according to context, to the statistical structure ($c = 10.7$ Å) or to a hypothetical completely ordered structure ($c' = 3c$).

DETERMINATION OF THE CHAIN CONFORMATION AND PACKING ANALYSIS

On the basis of the 'statistical' space group ($c = 10.7$ Å), if the polymeric chain had hypothetically the complete *tic* symmetry[14] imposed by the space group, the phenylene groups should be centrosymmetric and adjacent groups should be symmetry-related by two-fold axes. This 'statistical' chain is shown schematically in *Figure 3a*.

We have assumed that the overall shape and as many symmetry elements as possible are maintained in the real chain, having the regular constitution depicted in *Figure 3b* (and hence having a triple identity period ($c' = 3c$)). Therefore, we have assumed for the 'real' chain a *tic* line repetition group, as shown in the figure, with inversion centres on the phenylene groups bonded to the oxygen atoms and two-fold axes perpendicular to the chain axis, passing through the middle of the CO–CO bonds.

The bond lengths and the bond angles used in the following analysis are those reported in *Table 1*. In particular for the chain portion in brackets in *Figure 3b*, the values reported were taken from the crystal structure of the low-molecular-weight compound dibenzoyl[15], while for the bond angles at the oxygen atoms between the phenylene groups, we assumed a value of 125°, which represents a mean value between 124° given for PPO[7] and 124.6° and 126.5° suggested for PEEK[4] and PEK[6], respectively.

Having fixed the chain symmetry, the bond lengths and the bond angles, we have to define the four torsion angles θ_1, θ_2, θ_3 and θ_4 (*Figure 3b*), in order to get the complete chain conformation in the crystals on the basis of further geometrical and energetic considerations.

We note first that the torsion angles θ_1 and θ_2 are analogous to those which define the conformation of dibenzoyl in the crystalline state; also this molecule presents a two-fold axis of symmetry perpendicular to the bond between the two carbonyl groups. The values assumed in this compound are 115° for the torsion angle corresponding to θ_1 and $-9°$ for the torsion angle corresponding to θ_2 (ref. 15).

Secondly, we note that the identity period of PEEDK does not depend on all four torsion angles θ_1, θ_2, θ_3 and θ_4, but only on θ_1 and $\theta_v = \theta_2 + \theta_3$. This is easily seen if we introduce the virtual bonds C(3)–O(1) and O(1)–O(2), as shown in *Figure 3c*, and we observe that the torsion angle around the virtual bond O(1)–O(2) is fixed at 180° by the presence of the inversion centre on this bond. The torsion angle $\theta_v = \theta(\mathrm{C(2)}\text{–}\mathrm{C(3)}\text{–}\mathrm{O(1)}\text{–}\mathrm{O(2)})$ corresponds to the sum of $\theta_2 + \theta_3$, where $\theta_2 = \theta(\mathrm{C(2)}\text{–}\mathrm{C(3)}\text{–}\mathrm{C(4)}\text{–}\mathrm{C(5)})$ and $\theta_3 = \theta(\mathrm{C(6)}\text{–}\mathrm{C(7)}\text{–}\mathrm{O(1)}\text{–}\mathrm{C(8)})$ (see *Figures 3b* and *3c*), because of the assumed planarity of the benzene ring. The value of θ_4 does not have any influence on the identity period and determines only the orientation of the centrosymmetric phenylene group around the O(1)–O(2) axis.

In *Figure 4* we report the calculated length of the c' axis as a function of θ_v for some values of θ_1, having fixed the remaining internal coordinates as in *Table 1*. It is evident from *Figure 4* that to reproduce the experimental value of the c' axis (32.1 Å) within 0.3 Å, θ_1 must be greater than 110°. On the other hand, values

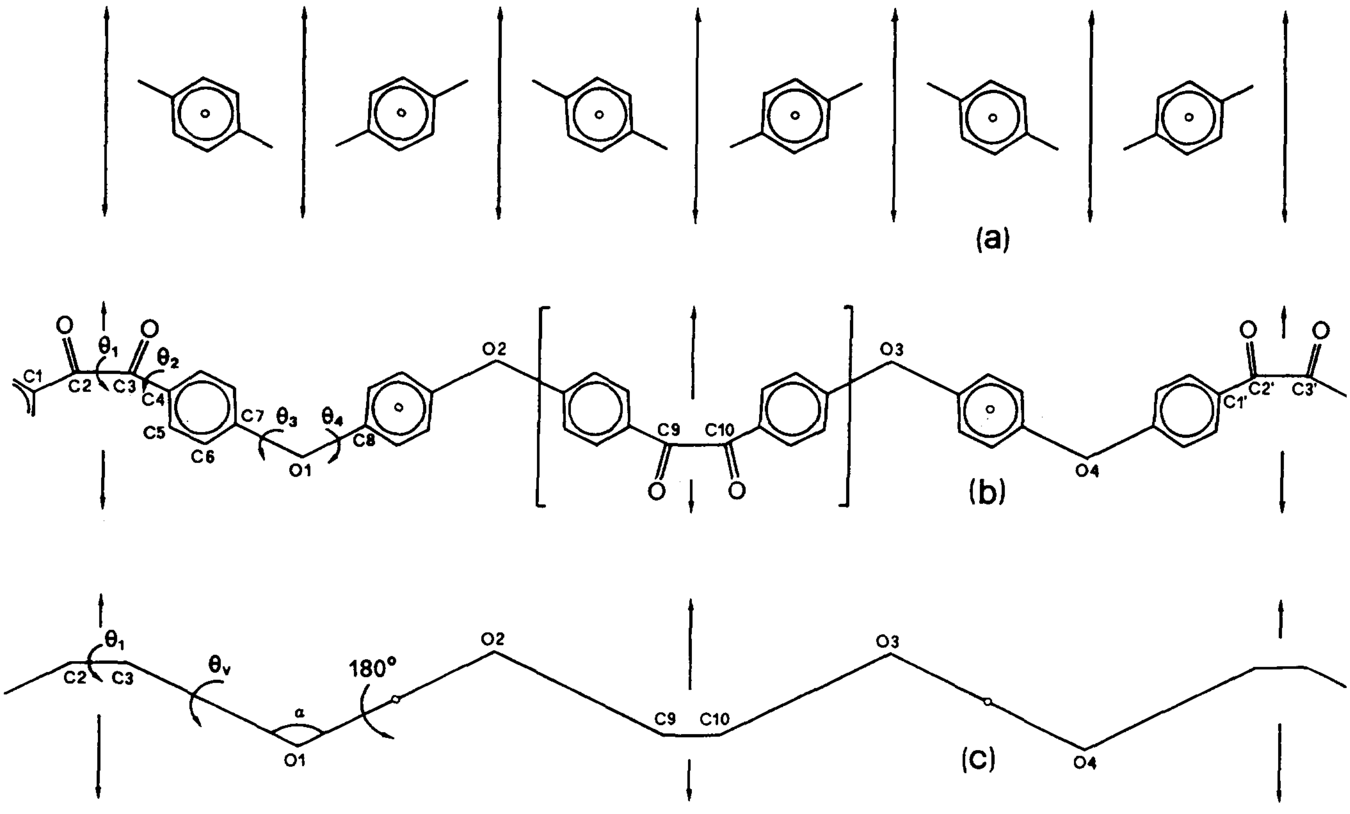

Figure 3 Schematic views of a chain of PEEDK having a *tic* symmetry: (a) hypothetical chain with statistical subperiodicity $c = 10.7$ Å; (b) real chain with periodicity $c' = 3c$; (c) backbone of the real chain using virtual bonds instead of the phenylene groups. The inversion centres (open circles) and the binary axes (double arrows) are indicated

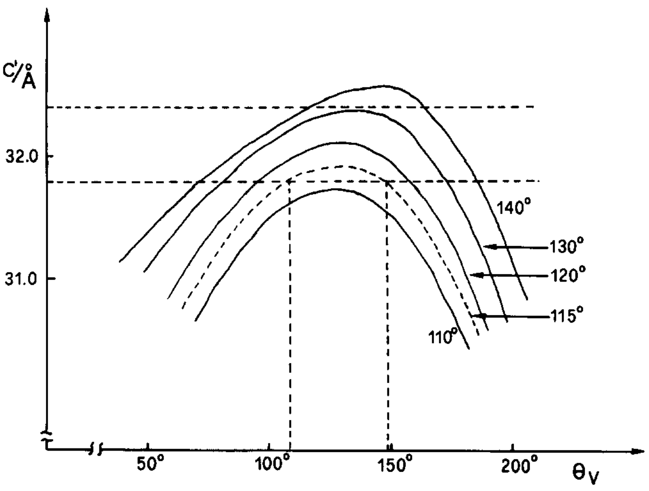

Figure 4 Calculated lengths of the c' axis as a function of θ_v for some values of θ_1 (see *Figure 3c*). The experimental interval of c' (32.1 ± 0.3 Å) is indicated. The allowed interval of θ_v for $\theta_1 = 115°$ is also indicated

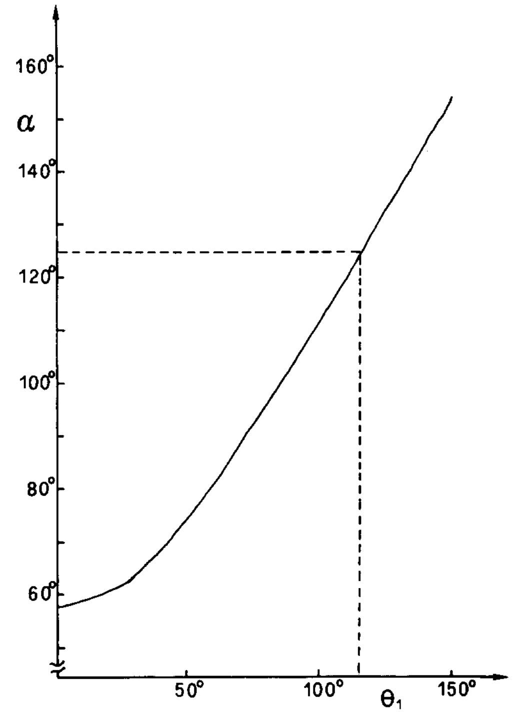

Figure 5 Values of the angle α between the virtual bonds O(2)–C(9) and O(3)–C(10) of *Figure 3c* as a function of θ_1

of $\theta_1 \gg 110°$ are hardly reconcilable with the experimental evidence in favour of the statistical interchangeability (and hence similar shape) of the diphenyl ether and the dibenzoyl groups in the crystals. Values of $\theta_1 \gg 110°$ give to the benzoyl group a shape that may differ strongly from that of the diaryl ether group. To show this point, the angle α between the O(2)–C(9) and O(3)–C(10) axes (see *Figure 3c*) is reported in *Figure 5* as a function of θ_1. It may be seen from *Figure 5* that to have a value for α equal to 125° (corresponding to the bond angle at the oxygen between phenylene groups and therefore to the angle between the virtual bonds C(3)–O(1) and O(1)–O(2) of *Figure 3c*), θ_1 must be equal to 115°. On the basis of all these considerations we assumed for θ_1 the value 115° observed for the analogous torsion angle in the crystalline structure of dibenzoyl.

If $\theta_1 = 115°$, it is seen from *Figure 4* that the value of $\theta_v = \theta_2 + \theta_3$ should then be between 110° and 150°. To fix the value of θ_2, we did a conformational analysis study of dibenzoyl as a model compound. We computed the conformational energy of this molecule (imposing a two-fold axis symmetry) as a function of θ_2 for $\theta_1 = 115°$. The results are reported in *Figure 6*. The minimum is sharp, and very near to the experimental value of −9° found for the dibenzoyl molecule[15]. Henceforth, we assumed this value for θ_2 also in the polymer.

If we go back now to the analysis of *Figure 4* and we assume $\theta_2 = -9°$, then θ_3 $(= \theta_v - \theta_2) = \theta_v + 9°$ must be in the interval 120–160°.

To determine the best value for θ_3, we have performed a parallel analysis of the packing energy and of the agreement between the observed and the calculated intensities (only for the most intense reflections) for a non-statistical structure and for the space group *Pbcn*, on varying θ_3. In this phase of our study, we also allowed the θ_4 torsion angle to vary.

A map of the packing energy as a function of θ_3 and θ_4 is reported in *Figure 7*. It may be of interest to note that the value assumed by θ_3 in the region of minimum

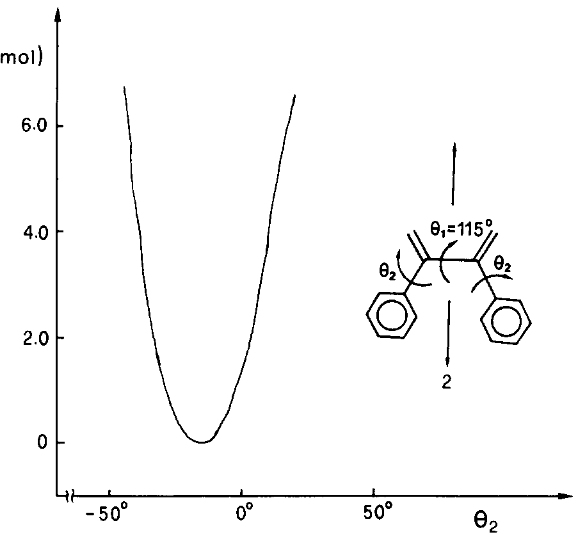

Figure 6 Conformational energy E of the model compound dibenzoyl (sketched in the figure) as a function of θ_2 for $\theta_1 = 115°$

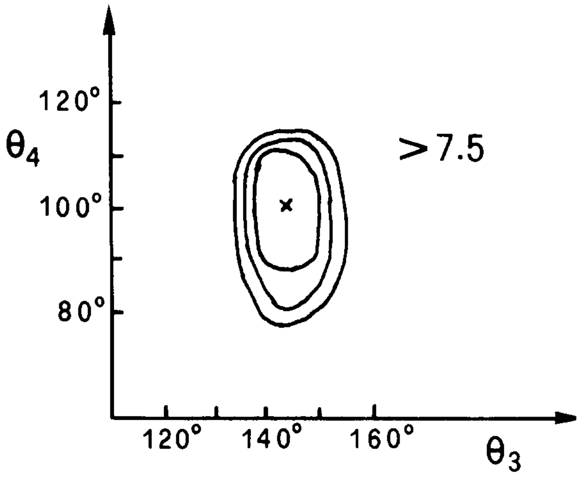

Figure 7 Map of the packing energy as a function of the internal rotation angles θ_3 and θ_4 of chains of PEEDK with periodicity $c' = 32.1$ Å for the space group *Pbcn*. The curves are reported at intervals of 2.5 kJ/(mole of asymmetric units)

Table 3 Series of calculated X-ray intensities, for the non-statistical structure of PEEDK in the space group *Pbcn*, as a function of θ_3 and θ_4, for the most intense reflections. The temperature factor used is $B = 4$ Å^2. The corresponding observed intensities estimated from both the fibre spectrum and the powder spectrum are indicated

	Calculated intensities, I_{calc}								I_{obs}	
θ_4	$\theta_3 = 120°$	130°	140°	150°	160°	*h*	*k*	*l*	Powder	Fibre
90°	648	713	785	923	1442					
100°	687	788	921	1190	1931	2	0	0	895	vs
110°	766	935	1145	1547	2639					
90°										
100°	1000	1000	1000	1000	1000	1	1	0	1000	vs
110°										
90°	818	708	583	406	256					
100°	816	715	599	455	274	1	1	3	296	s
110°	804	721	616	472	279					
90°	176	234	282	280	279					
100°	239	309	362	380	342	2	1	3	493	s
110°	316	383	435	434	377					
90°	194	158	135	91	70					
100°	184	151	132	99	68	1	1	6		mw
110°	177	143	123	94	49					
90°	61	76	92	91	128					
100°	80	103	125	140	165	2	1	6		m
110°	101	130	152	170	197					

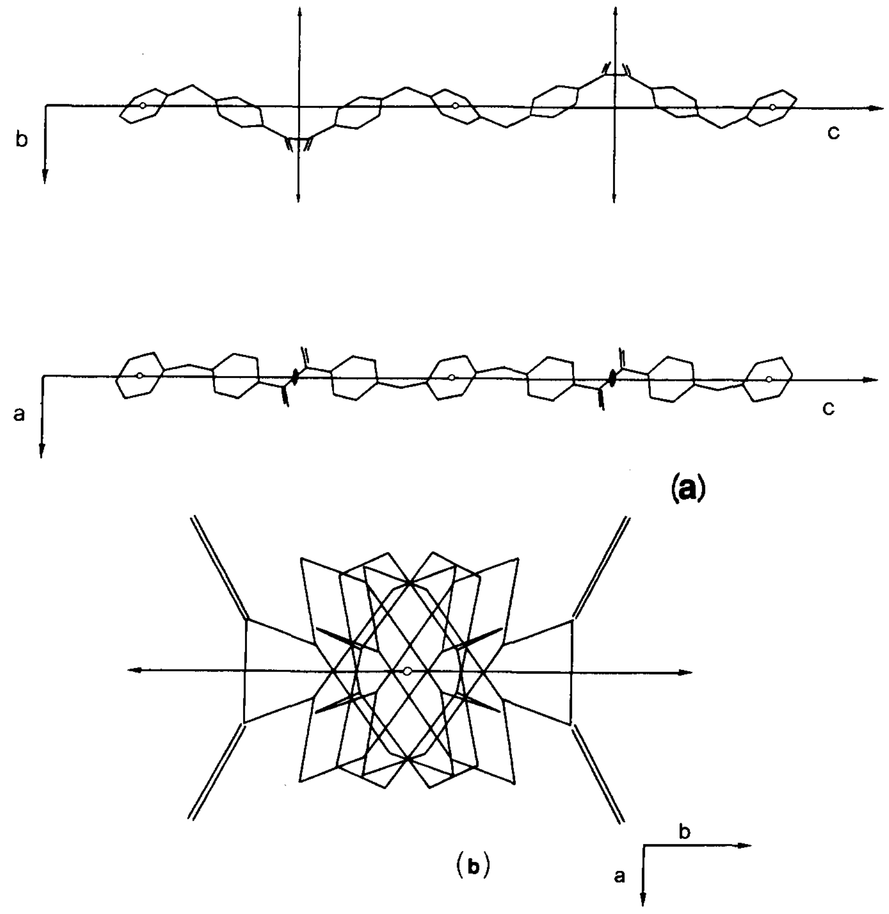

Figure 8 Orthogonal projections along the crystallographic axes of a chain of PEEDK having a conformation ($\theta_1 = 115°, \theta_2 = -9°, \theta_3 = 145°, \theta_4 = 100°$) near to that of the minimum packing energy. The inversion centres (open circles) and the binary axes perpendicular (black ellipses) and parallel to the plane of the paper (double arrows) are indicated. The views along the *a* and *b* axes (a) and the view along the *c* axis (b) are on different scales

Table 4 Comparison between the observed and calculated intensities ($B = 4$ Å^2) for a non-statistical structure of PEEDK and for the space group *Pbcn*, in which the chain conformation is near to that of the minimum packing energy shown in *Figure 8*. Only layers with $l = 3n$, for which the calculated intensities would be the same in the hypothesis of a statistical structure, are reported

h	k	l	$\sin\theta/\lambda$	I_{calc}	I_{obs}
1	0	0	0.0502	0	
2	0	0	0.1004	1036	vs
1	1	0	0.1160	1000	vs
3	1	0	0.1834	54	w
4	0	0	0.2008	54	mw
0	2	0	0.2092	0	vw
2	2	0	0.2321	19	
5	1	0	0.2719	26	vvw
4	2	0	0.2900	7	vvw
1	3	0	0.3178	12	
1	1	3	0.1251	535	s
2	1	3	0.1523	377	s
3	1	3	0.1892	59	
0	2	3	0.2144	0	
1	2	3	0.2202	18	vvw
4	1	3	0.2312	20	w
2	2	3	0.2367	15	
3	2	3	0.2620	23	w
5	1	3	0.2759	1	
4	2	3	0.2937	9	
0	0	6	0.0935	68	mw
1	0	6	0.1061	4	
2	0	6	0.1372	0	
1	1	6	0.1490	117	mw
2	1	6	0.1725	134	m
3	0	6	0.1772	6	
3	1	6	0.2058	49	
4	0	6	0.2215	21	
0	2	6	0.2291	3	
1	2	6	0.2346	1	
4	1	6	0.2449	3	
2	2	6	0.2502	10	
5	0	6	0.2678	0	
3	2	6	0.2742	9	
5	1	6	0.2875	8	
1	1	9	0.1820	0	w
2	1	9	0.2017	20	vvw
3	1	9	0.2308	4	vw
0	2	9	0.2518	16	
1	2	9	0.2568	6	
4	1	9	0.2663	0	
2	2	9	0.2711	8	
3	2	9	0.2934	5	
0	0	12	0.1869	22	
1	0	12	0.1935	10	
2	0	12	0.2122	28	
1	1	12	0.2200	131	vw
2	1	12	0.2366	8	vw
3	0	12	0.2400	4	
3	1	12	0.2618	1	
4	0	12	0.2743	20	
0	2	12	0.2805	13	
1	2	12	0.2850	13	
4	1	12	0.2936	3	

energy ($\theta_3 = 145° \pm 5°$) depends mainly on interchain packing conditions, while the conformation energy of an isolated chain would be less sensitive to the variation of that angle.

In *Table 3*, we report a series of calculated X-ray intensities as a function of θ_3 and θ_4 in the region of the minimum packing energy, together with the observed intensities. It is fairly evident that the values of θ_3 and θ_4, that correspond to the best agreement between calculated and observed intensities are also those of minimum packing energy.

In *Figure 8* we report the orthogonal projections of a chain conformation ($\theta_1 = 115°$; $\theta_2 = -9°$; $\theta_3 = 145°$; $\theta_4 = 100°$) near to that of minimum energy along the crystallographic axes. In *Table 4* we report a comparison between the observed intensities obtained from the fibre spectrum and the calculated intensities for a non-statistical structure based on that conformation and the layers with $l = 3n$. For these layers, the calculated intensities are also the same in the hypothesis of a statistical structure.

In fact, for a statistical model, the structure factors $F(hkl)$ can be calculated by adding to the contribution F' of each chain in the non-statistical unit cell, with $c' = 32.1$ Å, the contribution of two other chains, obtained from the first one, by shifting the z fractional coordinates by 1/3 and 2/3 and giving a weight 1/3 to all the atoms. As a result $F(hkl) = 0$ when $l \neq 3n$ and $F(hkl) = F'$ when $l = 3n$.

CONCLUSIONS

We have characterized the crystal and molecular structure of PEEDK. The chain conformation has been examined through minimum energy and structure factor calculations, with results in good accordance between themselves. While the phenylene groups take approximately ordered positions in the crystals, this is not so for the constitutional units –CO–CO– and –O– of neighbouring chains.

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