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Crystal and molecular structure of poly(thioether-ketone) from single crystal oligomer data and diffraction-modelling: 1. Polymer crystallised by orientation

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Abstract

The aromatic poly(thioether-ketone) $[ArSArCO]_n$ (Ar = 1,4-phenylene) is known to exist in two different crystalline forms, one produced by orientation of the amorphous polymer and the other by heat treatment or crystallisation from the melt. In the present work, single crystal X-ray data for the oligomer [ArCOArSArCOAr] reveal that bond angles at the thioether and carbonyl linkages are substantially different, at 108° and 121° respectively, and that the linear chain-conformation required for polymer crystallisation is achieved by a series of bond-angle distortions elsewhere in the molecule—in particular by pyramidalisation of the carbon atoms adjacent to the thioether bridge. Crystal and molecular simulation of orientation-crystallised poly(thioether-ketone) shows that the unit cell is analogous to the "Form II" cell known for poly(etherketone)s. The polymer crystal structure thus has orthorhombic symmetry (two chains per cell), space group *Pb2n*, $a = 4.12$, $b = 11.30$, $c = 10.44$ Å, and density 1.45 g cm^{-3}. The previously reported monoclinic unit cell is shown to be based on a modification of the present orthorhombic lattice.

Keywords: Poly(thioether-ketone); Crystal structure; X-ray

1. Introduction

The semi-crystalline aromatic poly(thioether-ketone) $[ArSArCO]_n$ (Ar = 1,4-phenylene) was first described in 1972 [1], but preliminary studies of the crystal structure and morphology of this material have only recently been reported. Takahashi and co-workers found that the polymer exists in two different crystalline forms, one produced by orientation of the amorphous material and the other by thermal treatment or crystallisation from the melt [2]. The crystal form produced by orientation was reported to be monoclinic ($a = 8.36$, $b = 6.06$, $c = 10.44$ Å, $\gamma = 68.5°$), and the melt-crystallised form (based on a very weak X-ray powder pattern) was indexed in terms of an orthorhombic unit cell analogous to that commonly observed for aromatic poly (*ether*-ketone)s [3].

The ability of poly(ether-ketone)s to crystallise rapidly from the melt is generally ascribed to the geometrical and conformational equivalence of aromatic ether and carbonyl linkages, Bond angles (C–O–C and C–C–C) at both these linkages are close to 121° and the average torsion angle relating the plane of the aromatic ring to the C–X–C plane (X = O or C) is around 31° [4]. Consequently, the linear chain-geometry required for polymer crystallisation is readily achieved. The aromatic thioether unit however is far from geometrically equivalent to a carbonyl group, crystallographic studies having established that the C_{Ar}–S–C_{Ar} bond angle tends to lie in the range 105°–108° [5]. It is thus not obvious how a series of alternating, para-linked thioether and ketone linkages can give rise to a linear chain-geometry; a curved (or extended-helical) structure would be predicted (Fig. 1).

In order to establish the actual chain configuration of poly(thioether-ketone) (PTEK) we have carried out a single crystal X-ray study of the model oligomer [ArCOArSArCOAr] (Ar = phenyl or 1,4-phenylene). Here we report that the data so obtained not only provide an explanation for the crystallisability of PTEK, but also enable the determination (by diffraction-modelling) of the crystal and molecular structure of this polymer in its orientation-crystallised form.

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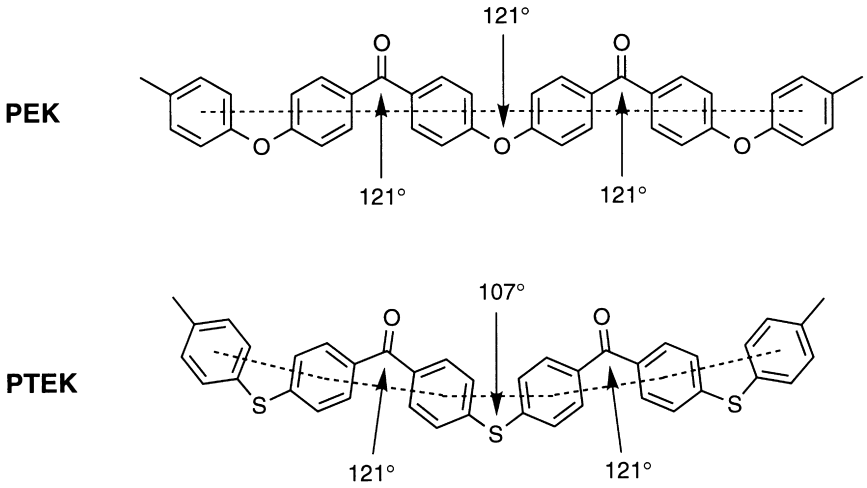


Fig. 1. Predicted bond angles and chain geometries in poly(ether-ketone) (PEK) and poly(thioether-ketone) (PTEK).

2. Experimental

The oligomer [ArCOArSArCOAr] (Ar = 1,4-phenylene) was synthesised by reaction of 4-mercaptobenzophenone with 4-chlorobenzophenone [6], and single crystals suitable for X-ray analysis were grown by slow evaporation of a chloroform solution. Molecular modelling and diffraction simulation studies were carried out using *Cerius*2, version 3.5 (Molecular Simulations Ltd, Cambridge, UK) running on a Silicon Graphics *02* workstation. Optimised parameters for simulation of polymer fibre-diffraction patterns (Cu–K_α radiation) were: Orientation half-width, 4°; crystallite dimensions, $a = 200$, $b = 800$, $c = 100$ Å; isotropic temperature factors, $U = 0.1$ Å^2.

2.1. Single crystal oligomer structure:

$C_{26}H_{18}O_2S$, $M = 394.46$, monoclinic, space group $P2_1/n$, $a = 6.051(1)$, $b = 41.826(1)$, $c = 7.589(1)$ Å, $\beta = 90.04(1)°$, $U = 1920.6(5)$ Å^3, $Z = 4$, $T = 173$ K, $D_c = 1.36$ g cm^{-3}, μ(Cu–K_α) = 16.5 cm^{-1}, $F(000) = 824$. Data were measured on a Siemens P4/RA diffractometer with graphite-monochromated Cu–K_α radiation using ω–scans. A total of 3055 independent reflections ($2\theta < 126°$) were collected, of which 2335 had $I > 2\sigma(I)$, and were considered to be observed. The data were corrected for Lorentz and polarisation factors, and also for absorption. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters $U = 1.2\ U_{eq}$(C) and allowed to ride on their parent carbons. Refinement was by full-matrix least squares based on F^2, to give $R_1 = 0.0531$, $wR_2 = 0.1386$. Computations were carried out using the SHELXTL program package. Tables of fractional atomic co-ordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre; reference CCDC 103–539. Copies can be obtained by application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@chemcrys.cam.ac.uk.

3. Results and discussion

The molecular structure of the four-ring oligomer [ArCOArSArCOAr] (Ar = phenyl or 1,4-phenylene) with selected bond lengths and bond angles is shown in Fig. 2,

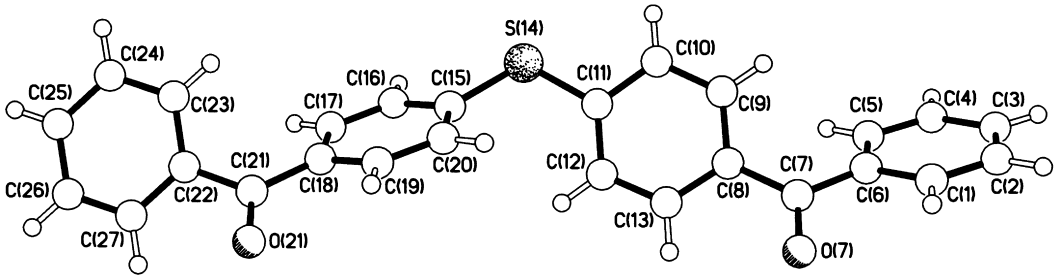


Fig. 2. Molecular structure of [ArCOArSArCOAr] (Ar = phenyl or 1,4-phenylene). Selected bond lengths and bond angles: C(6)– C(7), 1.499(5); C(7)– (8), 1.490(5); C(11)– S(14), 1.769(3); S(14)– C(15), 1.771(4); C(18)– C(21), 1.486(5); C(21)– (22), 1.489(5) Å; C(6)– C(7)– C(8), 121.3(3); C(10)– C(11)– S(14), 115.4(3); C(12)– C(11)– S(14), 124.7(3); C(11)– S(14)– C(15), 107.7(2); S(14)– C(15)– C(16), 115.5(3); S(14)– C(15)– C(20), 124.0(3); C(18)– C(21)– C(22), 121.5(3)°.

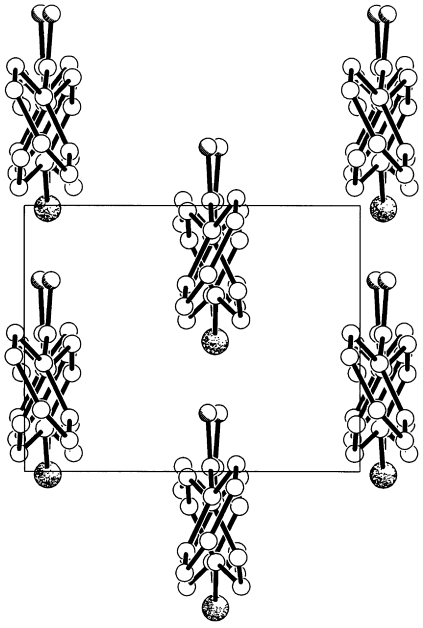


Fig. 3. Crystal structure of [ArCOArSArCOAr] (Ar = phenyl or 1,4-phenylene) viewed down the *b*-axis, showing only laterally adjacent molecules (H-atoms omitted).

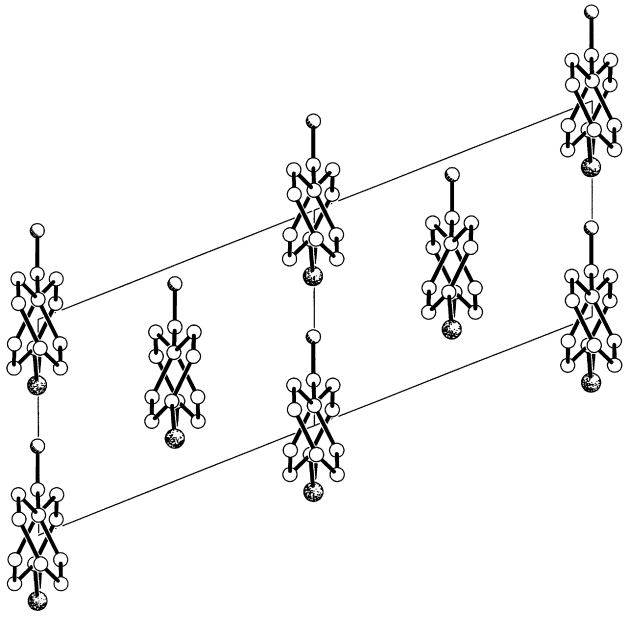


Fig. 5. Two-chain monoclinic structure for PTEK, based on the unit cell proposed in Ref. [2]. Two unit cells shown.

and the crystal packing of laterally-adjacent molecules is illustrated in Fig. 3. Although the unit cell is monoclinic, the β-angle of 90.04° indicates that there is negligible offset between laterally adjacent molecules. As in an analogous ether-ketone oligomer [4], and indeed in poly (ether-ketone) itself, the symmetry relationship between such molecules is an *n*-glide.

Despite the difference in bond angle between the thioether and carbonyl linkages (107.8° and 121.1° respectively), the oligomer attains near-linear geometry as a consequence of bond angle distortions at the arene carbons adjacent to sulfur (C–C–S averaging 124.3° and 115.4°, Fig. 2) and an unprecedented 0.21 Å out-of-plane displacement of the sulfur atom, which together open up the "effective" bond angle at sulfur very significantly (Fig. 4). The two carbonyl-group carbons in fact subtend an angle of ca. 116° at the central sulfur atom, a value at least approaching the 121° required for a linear chain-geometry, but suggesting that an even greater out-of-plane distortion might be required to generate a truly linear PTEK chain. The torsion angles of the aromatic rings in the oligomer, relative to C–S–C and C–CO–C planes, each average 29°.

A preliminary model for the polymer was constructed in an orthorhombic unit cell having the same lateral dimensions as those found for the oligomer ($a = 7.59$, $b = 6.05$ Å) and with the same symmetry relationship between adjacent chains in the unit cell. The *c*-dimension was based on the oligomer carbonyl-carbonyl (C…C) distance (10.25 Å). The *Cerius2* Open Force Field was edited to reproduce the bond lengths and bond angles (but not necessarily the torsion angles or out-of-plane distortions) found in the oligomer, and the energy of the polymer model was then minimised in a fixed unit cell. The minimisation, for which the chain-geometry is *required* to be linear, indeed generated a greater out-of-plane displacement at the arene-sulfur linkage than that observed in the oligomer structure, the sulfur atom now lying some 0.24 Å from the plane of the adjacent aromatic ring. This result confirms the requirement for a significant out-of-plane distortion at the C–S linkage if PTEK is to achieve a linear chain-geometry in the solid state.

This preliminary cell was then transformed, maintaining

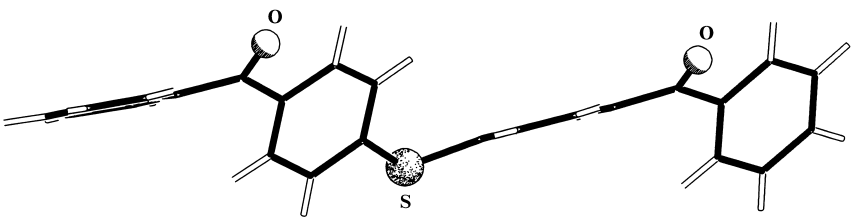
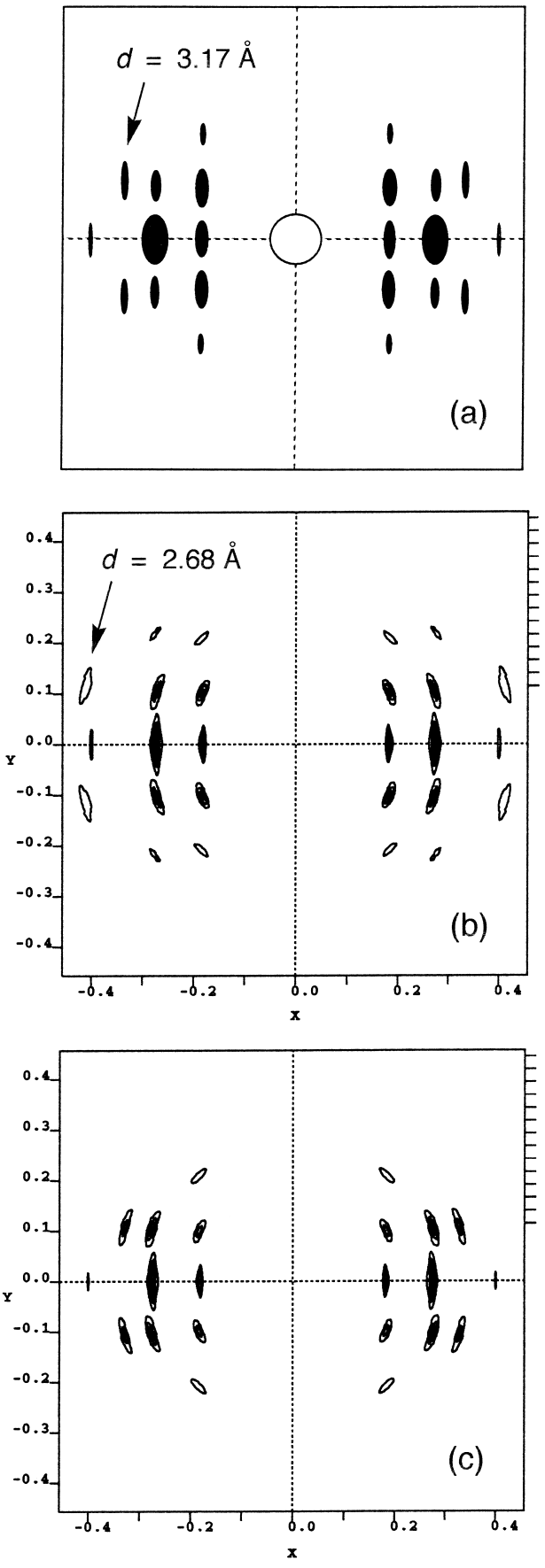


Fig. 4. Molecular structure of [ArCOArSArCOAr] (Ar = phenyl or 1,4-phenylene). Pyramidalisation of one arene carbon linked to sulfur, resulting in a 0.21 Å out-of-ring-plane displacement of the sulfur atom, is clearly evident. A similar displacement also occurs at the other S-connected ring.



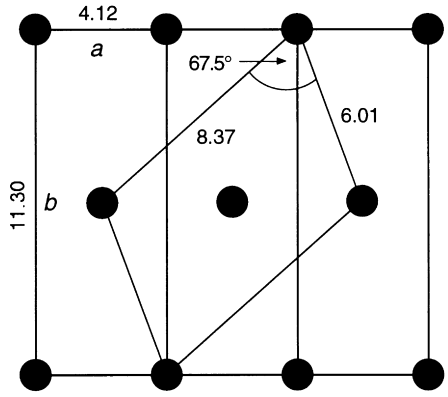


Fig. 7. Two-chain, Orthorhombic, " Form II" PTEK lattice viewed along the *c*-direction, showing also the apparent monoclinic unit cell (spacings in Å).

the glide relationship between the two polymer chains, to give the monoclinic cell (*c* unique, Fig. 5) proposed by Takahashi for PTEK which has been crystallised by orientation of the amorphous polymer ($a = 8.36$, $b = 6.06$, $c = 10.44$ Å, $\gamma = 68.5°$) [2]. A simulated fibre pattern for this structure (Fig. 6b) showed definite similarities to the experimental pattern represented schematically in Fig. 6a, notably in the *d*-spacings and relative intensities of the equatorial reflections, but there were also a number of significant discrepancies. In particular, a prominent reflection, present, on the first layer line of the experimental fibre pattern at $d = 3.17$ Å, was absent from the pattern simulated for the structure shown in Fig. 4. Moreover, the simulation (Fig. 6b) contains a strong reflection on the first layer line at $d = 2.68$ Å which is not observed in the experimental pattern (Fig. 6a) [2].

At this point the lattice was examined for possible higher symmetry. The monoclinic structure in fact proved to be transformable with only minor changes in cell parameters to an orthorhombic lattice ($a = 4.12$, $b = 11.30$ Å), corresponding very closely indeed to the metastable "Form II" structure found in poly(ether-ketone)s with a high carbonyl to ether ratio [7]. In PEKK for example this crystal form has unit cell dimensions $a = 4.17$ and $b = 11.34$ Å.[8] The relationship between these two alternative lattices is shown in Fig. 7. There is however a very significant difference between this orthorhombic unit cell and the original monoclinic cell shown in Fig. 5, in that the two polymer chains which were related by a glide plane in the original cell are now related by a simple lattice translation, a difference which must clearly affect the diffraction pattern.

Our preliminary, oligomer-derived cell was therefore converted to the orthorhombic "Form II" unit cell shown

Fig. 6. Graphical representations of (a) the experimental fibre data for orientation-crystallised PTEK (adapted from Ref. [2]), (b) simulated fibre pattern (flat plate contour plot) for the monoclinic structure shown in Fig. 5 and (c) simulated fibre pattern for the orthorhombic "Form II" type structure shown in Fig. 7.

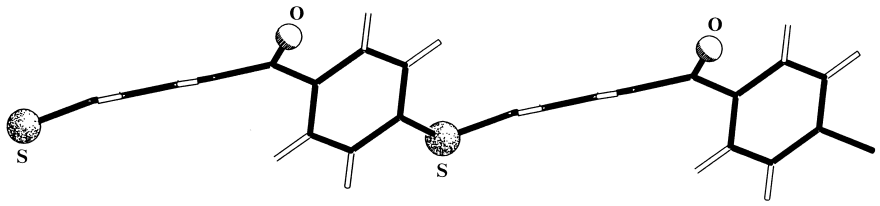


Fig. 8. Molecular structure of PTEK, showing the 0.24 Å out-of-ring-plane displacement of the sulfur atom which enables the polymer chain to achieve a linear geometry.

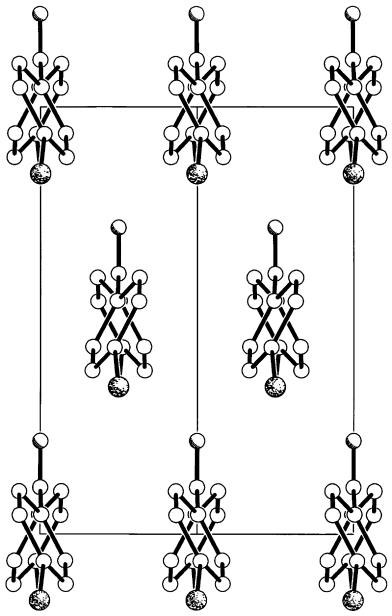


Fig. 9. Crystal packing of PTEK in the "Form II" type orthorhombic cell.

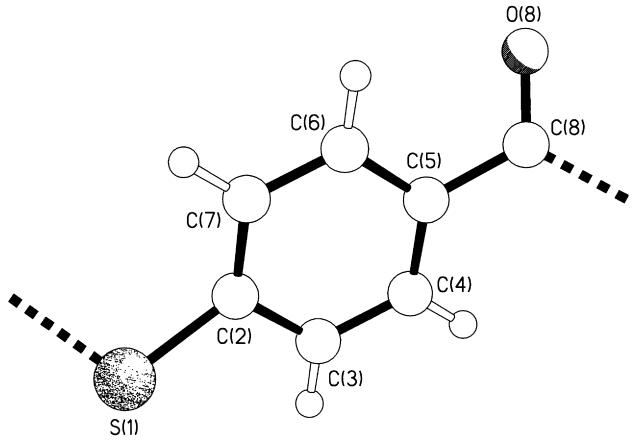


Fig. 10. The asymmetric unit of PTEK ($C_{6.5}H_4O_{0.5}S_{0.5}$) in space group *Pb2n*. Selected bond lengths and bond angles: S(1)– C(2), 1.77; C(5)– C(8), 1.49; C_{Ar}–C_{Ar}, 1.39 Å; C(2)– S(1)– C(2'), 108; C(5)– C(8)– C(5'), 122; S(1)– C(2)– C(3), 114; S(1)– C(2)– C(7), 125°. The "long-range" angles within the polymer chain, represented by S(1)– C(8)– S(1') and C(8)– S(1)– C(8'), are both 120°.

Table 1
Principal X-ray reflections and *d*-spacings (Å) for PTEK in the orientation-crystallised form, from experimental fibre data [2] and from the final diffraction-simulation

h k l	d_{expt}	I_{expt}	d_{simuln}	I_{simuln}(%)
020	5.64	S	5.65	32
110	3.88	VS	3.87	100
040	2.83	W	2.83	3
021	4.98	S	4.97	23
111	3.62	M	3.63	25
121	3.17	M	3.17	15
022	3.85	M	3.83	13

Table 2
Fractional atomic co-ordinates for PTEK in space group *Pb2n*

	X	*Y*	*z*
S(1)	0.5000	0.3424	0.0000
C(2)	0.5226	0.4347	0.1371
C(3)	0.6664	0.3814	0.2434
C(4)	0.6626	0.4384	0.3619
C(5)	0.5064	0.5471	0.3751
C(6)	0.3632	0.6007	0.2687
C(7)	0.3666	0.5436	0.1502
C(8)	0.5000	0.6115	0.5000
O(8)	0.5000	0.7196	0.5000
H(3A)	0.7753	0.3051	0.2344
H(4A)	0.7633	0.4010	0.4361
H(6A)	0.2538	0.6768	0.2779
H(7A)	0.2654	0.5809	0.0760

in Fig. 7, and a simulated fibre diffraction pattern was generated. The reflection on the first line at $d = 3.17$ Å, which was absent from the original monoclinic simulation, was now very evident (relative intensity 18%, indexed as 121), and the "rogue" reflection at $d = 2.68$ Å had disappeared, confirming the validity of the orthorhombic cell shown in Fig. 7. Finally, the *c*-axis length was adjusted to the experimental value (10.44 Å) obtained by Takahashi and co-workers [2], and the energy of the model was re-minimised in this orthorhombic unit cell, with all cell parameters fixed.

The resulting polymer structure is depicted in Figs. 8 and 9, and the fibre pattern simulated from this structure is shown in Fig. 6c. Reflections observed in the experimental fibre-pattern [2], re-indexed in terms of the orthorhombic cell, are given in Table 1, together with *d*-values calculated for the current structure. Evaluation of the symmetry elements present in the model led to identification of the space group as *Pb2n*, resulting in an asymmetric unit

(Fig. 10) of formula $[C_{6.5}H_4O_{0.5}S_{0.5}]$. The final crystal data for poly(thioether-ketone) in its orientation-crystallised form are thus: $[C_{13}H_8OS]_n$, orthorhombic, space group *Pb*2*n*, $a = 4.12$, $b = 11.30$, $c = 10.44$ Å, $\rho = 1.45$ g cm^{-1}, $V = 486.1$ Å^3. Atomic co-ordinates for the asymmetric unit are listed in Table 2. Crystal packing in the polymer appears to be dominated by C–H…O contacts (2.37 Å) between H(4A) and the carbonyl oxygen atom O(8) which are at less than 90% of their normal van der Waals separation.

It should be appreciated that there still exists the possibility that thioether and carbonyl groups may be crystallographically interchangeable, as is generally believed to be the case for aromatic *ether* and carbonyl linkages [3]. In the present structure, crystallographic randomisation of the bridging units would place an inversion centre at the centre of each aromatic ring, resulting in a change of space group, from *Pb*2*n* to *Pbcn*. However, in view of the differences of bond lengths and bond angles at the thioether and carbonyl units, such randomisation is perhaps less likely in poly(*thioether*-ketone)s than in conventional poly(ether-ketone)s, although it cannot be ruled out altogether.

The alternative crystal structure of PTEK, produced by crystallisation from the melt, is currently under investigation and will be discussed in a future paper.

Acknowledgements

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