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# Crystal and molecular structure of the thioether-analogue of PEEK from X-ray powder data and diffraction-modelling

Howard M. Colquhoun [a,*], Peter L. Aldred [a], Allan S. Hay [b], Antisar Rih Hlil [b], Kenji Miyatake [b], David J. Williams [c]

[a] School of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK
[b] Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Canada H3A 2K6
[c] Department of Chemistry, Imperial College, South Kensington, London SW7 2AZ, UK

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## Abstract

Analysis of X-ray powder data for the melt-crystallisable aromatic poly(thioether thioether ketone) $[–S–Ar–S–Ar–CO–Ar]_n$, ('PTTK', Ar = 1,4-phenylene), reveals that it adopts a crystal structure very different from that established for its ether-analogue PEEK. Molecular modelling and diffraction-simulation studies of PTTK show that the structure of this polymer is analogous to that of melt-crystallised poly(thioetherketone) $[–S–Ar–CO–Ar]_n$ in which the carbonyl linkages in symmetry-related chains are aligned anti-parallel to one another, and that these bridging units are crystallographically interchangeable. The final model for the crystal structure of PTTK is thus disordered, in the monoclinic space group *I*2/*a* (two chains per unit cell), with cell dimensions $a = 7.83$, $b = 6.06$, $c = 10.35$ Å, $\beta = 93.47°$.

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

## 1. Introduction

A more detailed understanding of high-performance polymer structure, especially the relationship between molecular structure and crystal structure, will prove invaluable for the development of rational design strategies in high-performance polymer chemistry. However, crystallographic analyses of aromatic polymers are often difficult because of limitations on the diffraction data available—for example, thermal intractability and insolubility can prevent access to fibre data, and very small crystallite sizes lead to broad and overlapping reflections. Thus for example, even the crystal structure of an aromatic polymer as long-established and industrially-significant as poly(1,4-phenylene terephthalamide) (e.g. Kevlar) has only been clarified very recently by neutron fibre-diffraction studies of partly deuterated materials [1]. In the present work a combination of X-ray powder diffraction and computational simulation is used to explore, for the first time, the structure of a thioether analogue of the important industrial thermoplastic known as PEEK.

Semi-crystalline aromatic poly(ether ketones), especially PEEK (**1**) and PEK (**2**), have a very wide range of industrial applications [2], and as a result their synthetic and structural chemistry has been intensively investigated over the past two decades [3,4]. The melt-crystallisable polyarylene-thioether known as polyphenylenesulfide, PPS (**3**), is also manufactured as an engineering polymer [5], and on a substantially larger scale than the poly(ether ketone)s. Extensive crystallographic studies of polymers **1**, **2** and **3** by X-ray fibre and powder methods have shown them to have very similar structures (orthorhombic, space group *Pbcn*, two chains per unit cell) [4h,4i,6], and indeed electron diffraction studies suggest that **1** and **3** even form a compatible blend in which the two types of chain co-crystallise [7]. However, despite the structural similarity between aromatic poly(thioether)s and poly(ether ketone)s, crystallographic analysis of poly(thioetherketone) $[–SArCOAr]_n$ (**4**, Ar = 1,4-phenylene) [8], crystallised from the melt or from solution, has shown that the presence of alternating thioether and ketone units in the same polymer chain leads to a new and entirely different type of crystal structure (body-centred monoclinic, space group *I*2/*a*) in which the carbonyl groups in adjacent, symmetry-related chains are

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* Corresponding author. Tel.: +44 118 378 8454; fax: +44 118 378 8450.
*E-mail address:* h.m.colquhoun@reading.ac.uk (H.M. Colquhoun).

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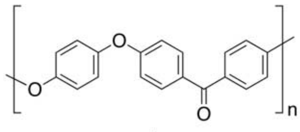
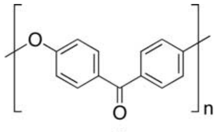
aligned anti-parallel to one another [9].



**1**



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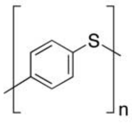

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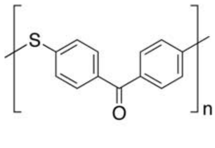

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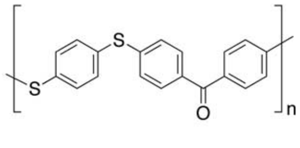

**5**

The thioether-analogue of PEEK, [–SArSArCOAr–]$_n$, (Ar = 1,4-phenylene) **5**, ('PTTK') was recently synthesised at high molecular weight by polycondensation of benzene-1,4-dithiol—generated in situ—with 4,4′-difluorobenzophenone [10]. Polymer **5** was found to crystallise very readily from the melt, and preliminary inspection of its X-ray powder pattern (shown here as Fig. 1, with background scattering subtracted) led to the suggestion [10] that the crystal structure of this polymer could well be analogous to that of PEEK [11]. However, in view of the profound differences between the crystal structure of PEK (**2**) and that of its thioether anlogue **4** [9], we have undertaken a detailed analysis of the structure of crystalline PTTK (**5**) using computational modelling and diffraction-simulation techniques. We now report that PTTK in fact adopts a very different crystal structure from that of PEEK.

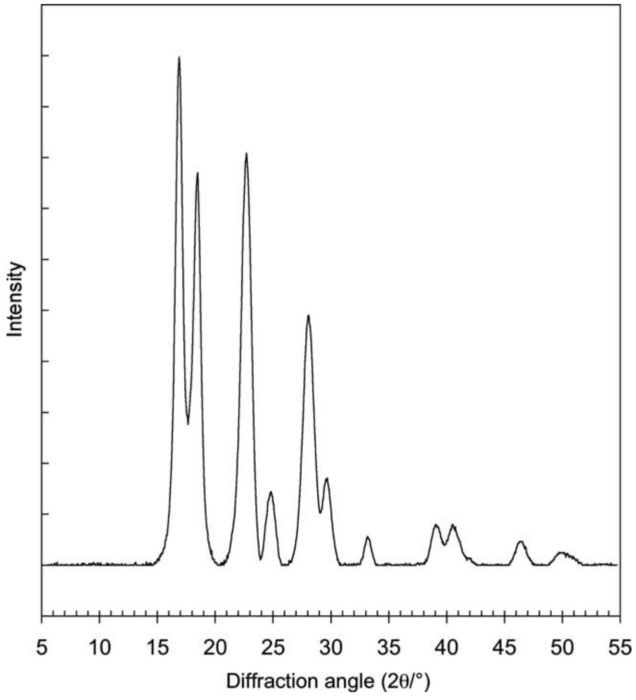

Fig. 1. X-ray powder pattern (background-subtracted) for polymer **5** (PTTK).

## 2. Experimental

The poly(thioether thioether ketone) **5** (PTTK) was synthesised by polycondensation of benzene-1,4-dithiol—generated in situ from the *O*-dimethylthiocarbamate of hydroquinone by rearrangement and base cleavage—with 4,4′-difluorobenzophenone, in the presence of caesium carbonate and calcium carbonate [10]. The as-made polymer was purified by exhaustive extractions with dilute hydrochloric acid and with methanol to remove any residual salts and low molecular weight organic materials. Polymer X-ray powder data were obtained using a Siemens D5000 powder diffractometer (Cu $K_\alpha$ radiation, Bragg-Brentano geometry) externally calibrated with quartz powder. Molecular modelling, diffraction simulation, and Rietveld refinement were carried out using Cerius2, v. 3.5, and Materials Studio v. 1.2, both from Accelrys Inc., San Diego.

### 2.1. Crystal structure of polymer **5**

$[C_{19}H_{12}OS_2]_n$, $M=(320.43)_n$, monoclinic, space group $I2/a$, $a=7.83$, $b=6.06$, $c=10.35$ Å, $\alpha=93.47°$, $V=490.35$ Å$^3$, $Z=2$, $T=298$ K, $D_c=1.47$ g cm$^{-3}$. Powder data collection range, $2\theta=5.0$–$55.0°$, step size 0.02°, Cu $K_\alpha$, $\lambda=1.542$ Å. Peak profile function: Thompson-Cox-Hastings, $U=-0.4370$, $V=4.5035$, $W=-0.5853$, $X=-1.7309$, $Y=0.1447$, $Z=0.0000$. Peak asymmetry correction: Berar-Baldinozzi, $P1=-0.3103$, $P2=-0.2914$, $P3=0.5503$, $P4=0.5595$. Zero point correction 0.182°. Polymer crystallite dimensions: $a=75$, $b=122$, $c=70$ Å. Lattice strain: $a=0.89$, $b=1.72$, $c=0\%$. Global anisotropic temperature factors (U): $a=0.29$, $b=0.17$, $c=0.17$ Å$^2$. Final agreement factors: $R_{wp}=0.082$, $R_p=0.133$.

## 3. Results and discussion

An initial model for PTTK (Fig. 2) was constructed in an orthorhombic unit cell analogous to that of PEEK ($a=7.78$ Å, $b=5.92$ Å, [4i]) and with the same symmetry relationship between the two chains in the cell (a $b$ glide in space group *Pbcn*). The $c$-dimension of the unit cell (30.67 Å) was required by symmetry to be twice the length of the chemical repeat unit. The bond lengths, bond angles and initial torsion angles used in this model were as previously obtained from a single crystal X-ray study of the model thioether-ketone oligomer PhCOArSArCOPh (Ar = 1,4-phenylene) [12].

The Cerius$^2$ Universal force field, re-optimised so as to reproduce these molecular parameters, was then used to minimise the overall energy of the model in a unit cell with the dimensions fixed at the above values. Comparison of a powder pattern simulated from the resulting model with the experimental data for PTTK showed very large discrepancies indeed (Fig. 3), and all attempts to refine the unit cell parameters in an orthorhombic or monoclinic cell failed to improve the fit significantly. It was concluded that no structure

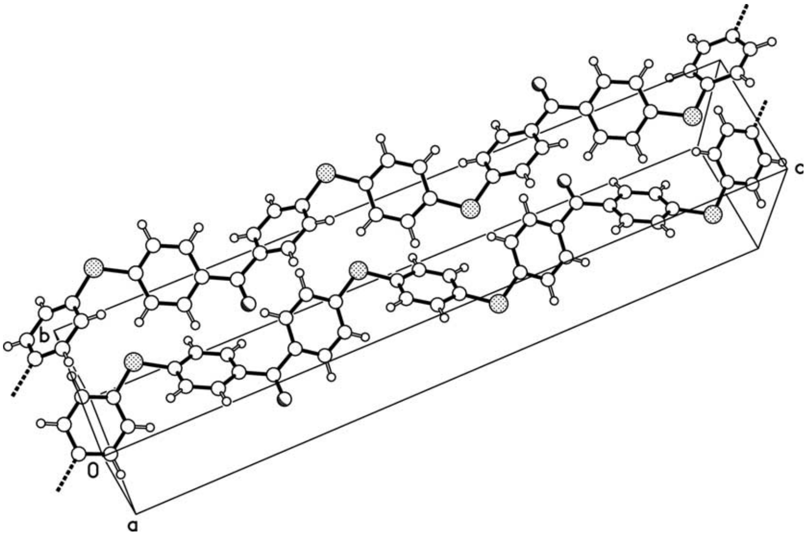

Fig. 2. Initial model for the structure of PTTK (**5**), based on an orthorhombic PEEK-type lattice in space group *Pbcn*.

for PTTK, which is directly analogous to that of poly(ether ether ketone) is likely to be compatible with the experimental X-ray powder data.

A new model was, therefore, constructed, analogous to that of melt-crystallised **4** [9] in which the two chains are related to each other by body-centering within a monoclinic unit cell (Fig. 4). The lateral cell dimensions initially used for the new model ($a = 7.58$ Å, $b = 6.09$ Å) were those found for polymer **4** [9], but although the powder pattern simulated from this structure was obviously a great improvement over that from the PEEK-type model, noticeable discrepancies in peak positions still remained. Unit cell dimensions, including the $\beta$-angle, were, therefore, refined against the experimental data, so greatly improving the fit, and the potential energy of the model was then re-minimised in the refined unit cell, giving a structure in space group *I*2/*a* with cell parameters $a = 7.85$ Å, $b = 6.06$ Å, $c = 31.0$ Å, and $\beta = 86.3°$.

Rietveld refinement of peak-profiles and instrumental/sample peak-broadening effects gave a final agreement factor, $R_{\text{wp}}$, for this structure of 12.9%. Nearly all the peaks observed in the experimental diffraction pattern were represented in the simulated data, but an additional predicted medium-intensity reflection at $2\theta = 14.90°$ (011) was absent from the experimental pattern (Fig. 5). Moreover, rigid-body positional refinement of the thioether and phenylene units failed to resolve this discrepancy, with the intensity of the predicted 011 reflection remaining undiminished for all structurally reasonable models.

However, it is well established that the geometrically-similar aromatic ether and ketone units are crystallographically interchangeable [11], and that this generally leads to poly(ether-ketone)s adopting disordered structures in which the linking groups in adjacent polymer chains are randomly positioned instead of being in register [13]. It has also been proposed that the high thermal parameters observed in the final, ordered model for melt-crystallised PTK might be accounted for on the basis of crystallographic disorder between the thioether and ketone groups [9], even though the difference in bridge–bond angles (119 − 122° at ketone, cf. 106–109° at the thioether sulfur) would require a much higher degree of positional disorder than in analogous ether-ketone polymers. Thus, to explore the possibility that thioether and ketone linkages might be crystallographically interchangeable, a third model for PTTK was constructed, with weighted substitutional disorder of the thioether and carbonyl groups. The new unit cell was built to represent a disordered version of the previous body-centred model, with all inter-ring bridging groups becoming equivalent. The linking atoms (one carbon and two sulfurs) were thus averaged to create a single type of pseudo-atom, X, with atomic number 13. The occupancy of the carbonyl oxygen at each linkage was set to 1/3, and the

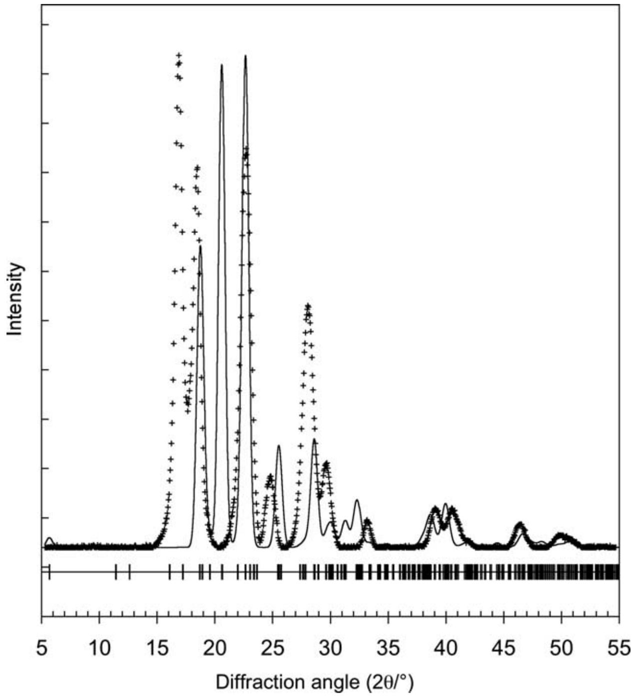

Fig. 3. Experimental X-ray powder data (+) for PTTK (**5**) compared to a pattern (−) simulated from the PEEK-type structure shown in Fig. 2.

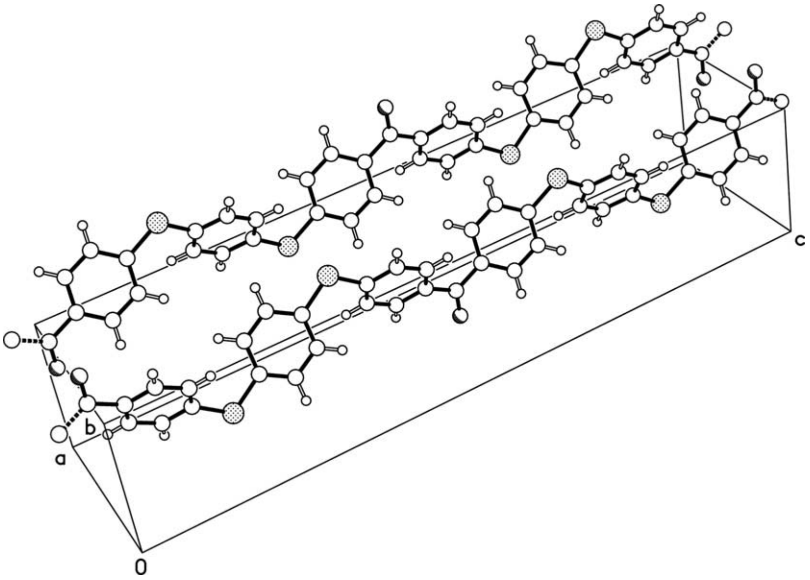

Fig. 4. Body-centred unit cell for PTTK (**5**), analogous to that of polymer **4**.

increased symmetry of the chain now reduced the crystal-repeat in *c* to only two arylene rings. The force field was revised, so that the bond lengths between arylene carbon atoms and linking group atoms were optimised at 1.679 Å (the weighted average bond length for 2×C–S and 1×C–CO). Similarly, the force field was modified to optimise the bond angle for C–X–C (disordered linking group) at a value of 112.4°, representing the weighted average of 'standard' bond angles for 2×C–S–C and 1×C–CO–C. The unit cell dimensions of the initial disordered model (assuming a monoclinic cell) were then manually adjusted to give a reasonably close match between simulated peak positions and the experimental values, and the model was energy-minimised in this cell. Analysis of the symmetry elements for the resulting model showed that the space group *I*2/*a* was retained.

The disordered model (Fig. 6) gave a simulated X-ray powder pattern, which showed no evidence of the 011 reflection, predicted by the corresponding ordered model but absent from the experimental data, and overall was in very good agreement with the observed pattern. This disordered model was submitted to Rietveld refinement of unit cell dimensions, crystallite size/strain, peak asymmetry and thermal and other parameters (Section 2 for details), giving a final agreement factor $R_{\mathrm{wp}}$ of 8.2%—a substantial improvement over the value for the fully-ordered structure shown in Fig. 4. The final unit cell parameters were $a=7.83$ Å, $b=6.06$ Å, $c=10.35$ Å, and $\beta=93.47°$. Simulated and difference powder diffraction patterns for the disordered model are shown in Fig. 7 superimposed on the experimental data. Some slight discrepancies do still remain, including a very weak predicted reflection at $2\theta=37.5°$ (220), which is absent from the experimental pattern but, in view of the approximations involved in constructing a model for the disordered structure, the overall agreement is excellent. As with polymer **4** [9], the apparent thermal parameters (0.17–0.29 Å$^2$) are relatively high, but this is to be expected in a disordered structure where the model can only describe averaged atomic positions and identities.

The final model for PTTK (body-centred monoclinic; space group *I*2/*a*) is shown in Fig. 7. Planes of aromatic ring-systems in adjacent chains are inclined to one another by ca. 50°, such that the hydrogens of one molecule are directed towards the π-systems of its neighbour with the $\mathrm{H}\cdots\pi_{\mathrm{centroid}}$ separation of 3.03 Å and a $\mathrm{C{-}H}\cdots\pi_{\mathrm{centroid}}$ angle of 134°. Atomic co-ordinates for the model are given in Table 1. This structure corresponds very closely to the disordered model previously

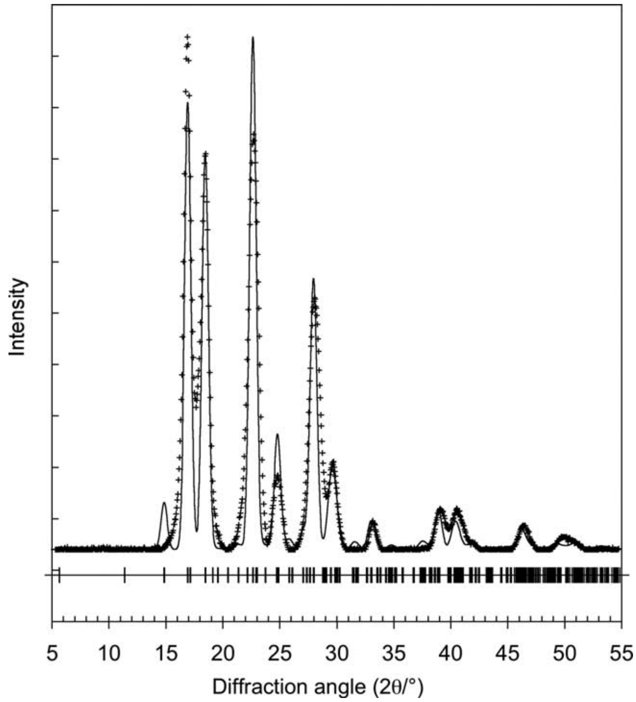

Fig. 5. Experimental X-ray powder data (+) for PTTK (**5**) compared to a pattern (−) simulated from the body-centred structure shown in Fig. 4.

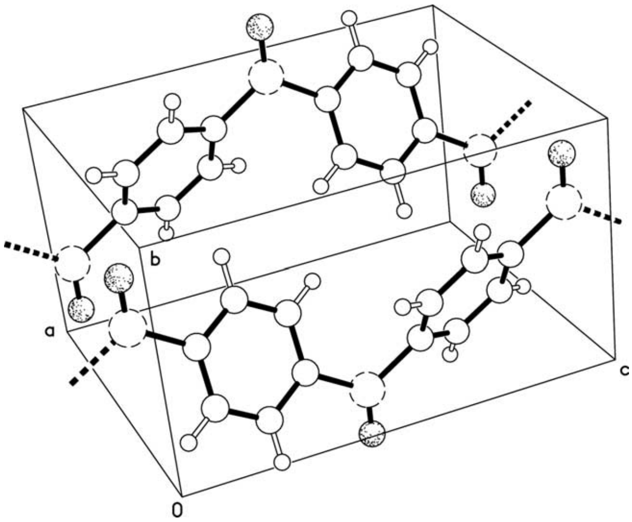

Fig. 6. The final, disordered model for PTTK (**5**). The bridging unit represents a weighted geometric average of carbon and sulfur atoms (dashed circle) bonded to a one-third-occupancy carbonyl oxygen atom (shaded circle).

suggested [9] for the simple, alternating poly(thioether-ketone) **4** (space group *I*2/*a*; cell dimensions: $a=7.58$ Å, $b=6.09$ Å, $c=10.25$ Å, $\beta=93.70°$), and indeed differs from it only in the relative weightings and occupancies given to thioether and carbonyl linkages, and in the consequent but minor changes in molecular geometry and cell dimensions.

The final unit cell parameters obtained in this work for PTTK ($a=7.83$ Å, $b=6.06$ Å, $c=10.35$ Å, and $\beta=93.47°$) are in fact also very close to those proposed initially by Hay and co-workers for an orthorhombic (*Pbcn*) PEEK-type structure ($a=7.84$ Å, $b=5.99$ Å, $c=10.30$ Å), where disordering of the thioether and ketone linkages would also be required [10].

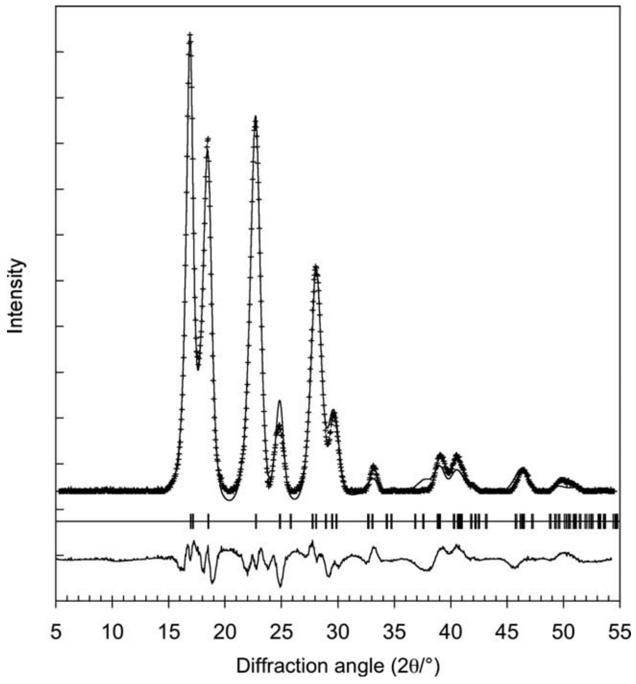

Fig. 7. Experimental (+), simulated (−) and difference patterns for the final, disordered model for PTTK.

Table 1
Fractional atomic co-ordinates for the disordered model of PTTK (**5**) in space group *I*2/*a*

| | *x* | *y* | *z* |
|---|---|---|---|
| X[a] | 0.75000 | 0.97402 | 0.50000 |
| C(1) | 0.74990 | 0.12928 | 0.63582 |
| C(2) | 0.82857 | 0.16507 | 0.86313 |
| C(3) | 0.82623 | 0.04324 | 0.74978 |
| H(1) | 0.88256 | 0.10459 | 0.94290 |
| H(2) | 0.88135 | 0.89880 | 0.74929 |
| O(1)[b] | 0.75000 | 0.72774 | 0.00000 |

[a] Pseudo-atom comprising the weighted average of two sulfurs and one carbon.

[b] One-third occupancy carbonyl oxygen atom.

Using the model for a disordered PTTK chain developed in the present work, we were able to construct exactly the proposed structure in space group *Pbcn* and to check its predicted X-ray powder pattern. This proved virtually indistinguishable from that generated by the ordered PEEK-type structure shown in Fig. 2, which was clearly incompatible with the experimental X-ray data (Fig. 3).

## 4. Conclusions

Thioether analogues of both PEEK and PEK adopt crystal structures in which the two chains of a monoclinic unit cell are related by body-centering rather than by the *b*-glide found in the polyetherketones. Despite the significant difference in bridge-bond angles between aromatic thioether (ca. 108°) and ketone (ca. 121°) units, crystallographic interchangeability of these linkages is required to account for the observed X-ray powder pattern of PTTK, and also for the high apparent temperature factors in the structures of both poly(thioether ketone)s.

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