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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

* 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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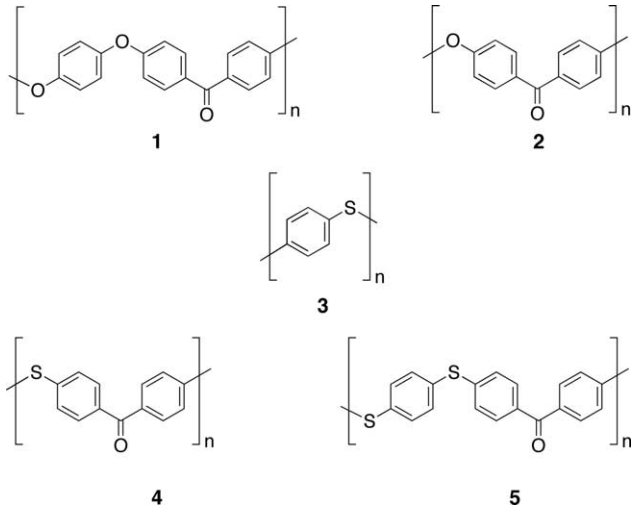
aligned anti-parallel to one another [9].



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.

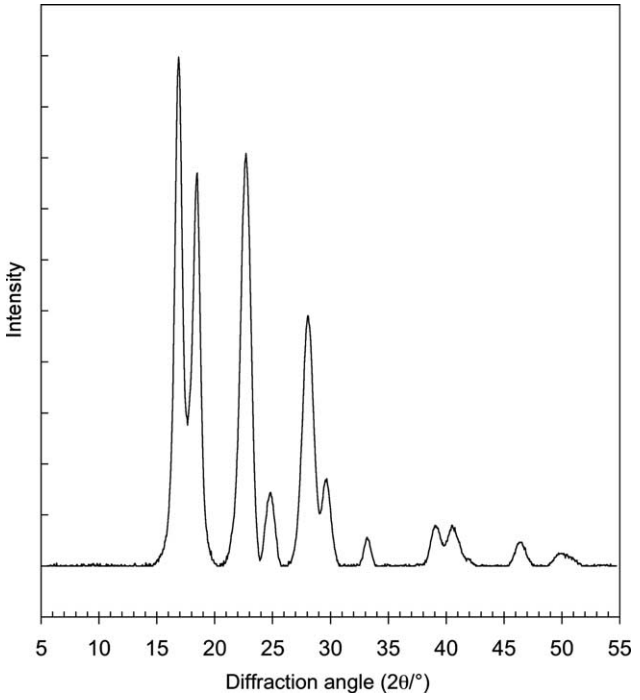


Fig. 1. X-ray powder pattern (background-subtracted) for polymer **5** (PTTK).

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_α 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 *I*2/*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_α, $\lambda = 1.542$ 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 PhCOAr-SArCOPh (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