S0032-3861(96)00779-3

Polymer Vol. 38 No. 4, pp. 991–994, 1997

0032-3861/97/\$17.00 + 0.00

Crystal and molecular simulation of poly(1,4-phenylenesulfone)

Howard M. Colquhoun
Department of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK
(Received 31 July 1996)

Knowledge-based molecular modelling, crystal packing calculations and diffraction-simulation techniques are combined with existing X-ray powder and fibre diffraction data to investigate the crystal and molecular structure of poly(1,4-phenylenesulfone). The unit cell thus obtained has C-centred orthorhombic symmetry (two chains per cell), space group *Cmcm*, with dimensions $a = 10.79$, $b = 5.05$, $c = 9.97$ Å and density 1.71 g cm^{-3}. The polymer chain adopts 2_1 helical geometry, with aromatic ring planes orthogonal to a plane defined by the bridging C–S–C groups. Crystal packing is dominated by S=O...H–C van der Waals' contacts (O...H = 2.68 Å). The final model is consistent with X-ray data for poly(1,4-phenylenesulfone) produced not only by self-polycondensation of $[1,4\text{-}FC_6H_4SO_2]^-$, but also by peroxide oxidation of poly(1,4-phenylenesulfide). © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(1,4-phenylenesulfone); molecular simulation; crystal structure)

Introduction

Structural analysis of aromatic polysulfones has always been restricted by the generally amorphous character of poly*ether*sulfones and by the extreme intractability of crystalline materials such as poly(1,4-phenylenesulfone), for which the melting point exceeds 500°C[1]. Although a unit cell for poly(1,4-phenylenesulfone) based on X-ray fibre data was reported in 1980[2], doubt has been cast even on this result by recent suggestions that the oxidation of poly(1,4-phenylenesulfide) films, used to produce oriented polymer for the X-ray fibre diffraction study, may in fact lead to cross-linking rather than conversion into poly(1,4-phenylenesulfone)[3]. In the present work, published X-ray powder data for material produced in an unambiguous synthesis of poly(1,4-phenylenesulfone)[3] are combined with molecular modelling, crystal packing calculations and diffraction-simulation techniques to investigate the structure of this material.

Experimental and theoretical knowledge

Bond lengths and bond angles used in the present simulation are shown in *Table 1*. These are averaged experimental values derived from six single crystal studies of diaryl sulfones, weighted according to the *R*-factor of each crystal structure[4–6]. In these structures, the torsion angles relating the aromatic ring-planes to the plane of the C–S–C bridge are close to 90° (the average modulus for C–C–S–C torsion angles is in fact 91° with standard deviation 7°) so that the diaryl sulfone unit is frequently described as adopting an 'open book' conformation. There are no obvious *steric* reasons why this conformation should be so strongly preferred, but a reasonable orbital-symmetry explanation, put forward many years ago by Koch and Moffit[7], involves the overlap of filled aromatic-carbon p–π orbitals with a vacant d–π (or d/p–π hybrid) orbital on sulfur (*Figure 1*).

This explanation is entirely consistent with chemical evidence for the sulfone unit possessing strong π-acceptor character, as for example, in its powerfully activating effect on nucleophilic aromatic substitution at the *ortho* and *para* positions[8]. Both experimental and theoretical evidence thus tend to suggest that the diaryl sulfone unit is constrained by π-overlap to adopt a relatively narrow range of torsion angles, close to 90°. Such torsional rigidity is of course in keeping with the very high glass transition temperatures of aromatic polysulfones. The T_g of polyether sulfone, $(1,4\text{-}C_6H_4O\text{-}1,4\text{-}C_6H_4SO_2)_n$, for example, is 225°C, some 135°C higher than that of its all-ether analogue, $(1,4\text{-}C_6H_4O)_n$[9,10].

Simulation

Molecular mechanics and diffraction-simulation calculations were carried out using the materials modelling package 'Cerius2' (Biosym Molecular Simulations Inc.). The Cerius2 Open Force Field was constrained to generate not only the crystallographically derived bond lengths and bond angles shown in *Table 1*, but also a 90° C–C–S–C torsion angle. Because of the high confidence levels placed on bond lengths and angles, these values remained tightly constrained throughout subsequent calculations. Although the initially constrained C–C–S–C torsion angle was subsequently allowed to relax, no significant deviation from orthogonality was in fact observed.

A poly(1,4-phenylenesulfone) crystal lattice was first generated from the 'monomer' $(1,4\text{-}C_6H_4\text{-}SO_2\text{-}1,4\text{-}C_6H_4\text{-}SO_2)$ within an arbitrary unit cell ($a = b = 20$ Å; $\alpha = \beta = \gamma = 90°$). This procedure led to a c-dimension (aligned to the polymer chain-axis) of 9.97 Å. Minimization of crystal packing energy for the resulting polymer chain led to a near-monoclinic structure (one chain per cell) with unit cell parameters $a = 4.95$, $b = 6.31$, $c = 9.97$ Å, $\alpha = 90.3$, $\beta = 90.7$ and $\gamma = 113°$. The lattice was then *set* to monoclinic-C symmetry, and a simulated X-ray powder pattern (CuK_α) was generated from the resulting structure. A strong similarity in peak positions

Table 1 Crystallographically derived bond lengths and angles[4–6] used to construct the model for poly(1,4-phenylenesulfone)

Bond	Length (Å)	Bonds	Angle (°)
		C–C–C	120.0
		C–C–H	120.1
C–S	1.763	C–C–S	119.6
S–O	1.441	C–S–C	104.9
C–H	0.976	C–S–O	107.9
C–C	1.383	O–S–O	119.6

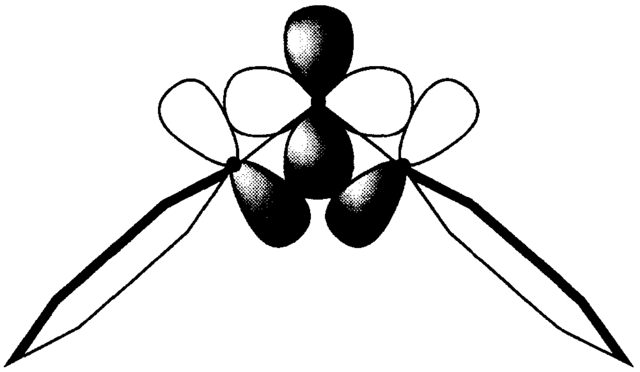

Figure 1 Overlap between a vacant sulfur d–π orbital and filled carbon p–π orbitals as a possible explanation for the 'open-book' conformation observed in diaryl sulfones[7]

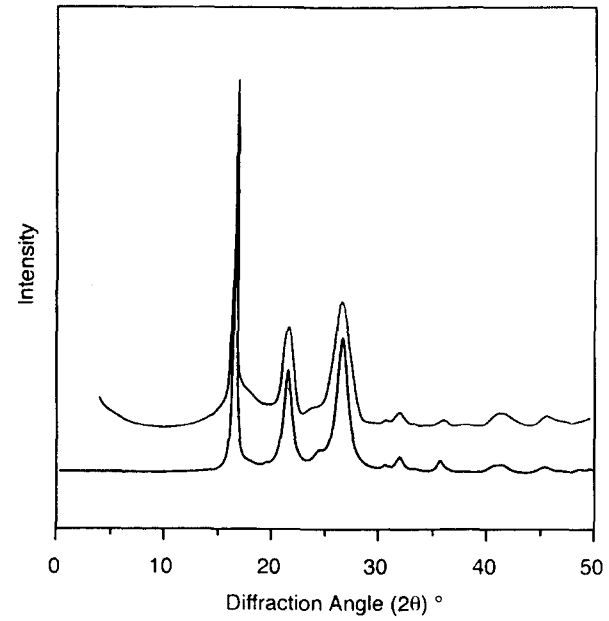

Figure 2 Experimental (upper trace) and simulated (lower trace) X-ray powder patterns for poly(1,4-phenylenesulfone) and the current model, respectively. The upper trace is reproduced from ref. 3 by permission of the American Chemical Society

Table 2 Crystal data and fractional atomic coordinates for poly(1,4-phenylenesulfone)

Atom	*x*	*y*	*z*
S	0.00000	0.12150	0.25000
O	0.11542	−0.02204	0.25000
C(1)	0.00000	0.33404	0.11025
C(2)	0.11136	0.41755	0.05556
H	0.18962	0.36035	0.09522

Crystal data: $[C_6H_4SO_2]_n$, orthorhombic, $a = 10.79$, $b = 5.05$, $c = 9.97$ Å, $U = 543$ Å^3, space group *Cmcm*, $Z = 4$, $D_c = 1.71$ g cm^{-3}

and relative intensities between the simulated pattern and the experimental powder pattern reported by Robello *et al.*[3] indicated that this structure was at least a reasonable starting point for further work. The fit between simulated and experimental peak positions was subsequently improved by manual optimization of the unit cell parameters to $a = 5.05$, $b = 5.95$, $c = 9.97$ Å and $\gamma = 115°$.

At this point it became apparent that the optimized primitive lattice was transformable *without modification* to C-centred orthorhombic symmetry (two chains per cell), with cell dimensions $a = 10.79$, $b = 5.05$ and $c = 9.97$ Å. Optimization of the various peak-broadening parameters gave an extremely good overall match between the simulated and experimental powder patterns (*Figure 2*) for polymer crystallite dimensions $a = 2000$, $b = 300$ and $c = 50$ Å, lattice strain values $a = 0.8$, $b = 0.5$ and $c = 0.1\%$, and anisotropic thermal parameters $a = 0.15$, $b = 0$ and $c = 0.20$ Å^2. The rather high thermal parameter in the chain-direction is perhaps a little difficult to understand, but as noted in the pioneering diffraction-modelling studies of Hanna *et al.*[11], too much physical significance should not be attached to individual peak-broadening parameters in this type of simulation.

Evaluation of the symmetry elements present in the model led to provisional identification of the space group as *Cmcm*. The final space group assignment is, however, dependent on whether or not the C–C–S–C torsion angle remains at exactly 90°. Any deviation from this value would destroy the axial mirror symmetry of the chain and would thus be inconsistent with the orthorhombic space group. However, provided that the C_2 axis through sulfur and the inversion centre at the centre of the aromatic ring are retained, a non-orthogonal torsion angle would be permitted within the monoclinic space group *C*2/*c*. In practice, relaxation of the 90° torsional constraint led to *no* significant change of torsion angle on reminimizing the structure within an unconstrained unit cell, and it is therefore concluded that *Cmcm* remains much the most probable space group for poly(1,4-phenylenesulfone).

The final structure, with atom labelling, is shown in *Figure 3* projected on the *ab* plane, and a perspective view of the unit cell is shown in *Figure 4*. Crystal data and atomic coordinates for the asymmetric unit ($C_{1.5}HS_{0.25}O_{0.5}$) in space group *Cmcm* are given in *Table 2*. Crystal packing appears to be dominated by [S=O...H–C] van der Waals' contacts (O...H = 2.68 Å); there are no other intermolecular contacts at or below van der Waals' distances.

The unit cell reported here is based on the powder pattern from polymer formed[3] by self-condensation of $[1,4\text{-}FC_6H_4SO_2]^-$. It is nevertheless in good agreement with the cell derived from the fibre pattern of a material produced by peroxide oxidation of amorphous poly(1,4-phenylenesulfide) (orthorhombic, two chains per cell, $a = 11.00$, $b = 5.05$, $c = 9.75$ Å, $D_c = 1.73$ g cm^{-3})[2]. Indexed reflections predicted by the present model for poly(1,4-phenylenesulfone) are given in *Table 3*, together with the experimental fibre and powder data. Although some slight inconsistencies

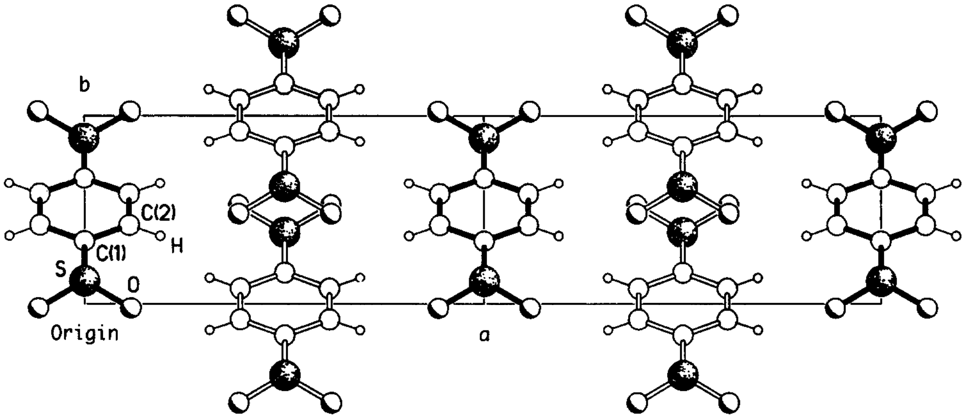

Figure 3 Crystal structure (two unit cells) of poly(1,4-phenylenesulfone) projected on the *ab* plane. Atom labels indicate the asymmetric unit [$C_{1.5}HS_{0.25}O_{0.5}$]

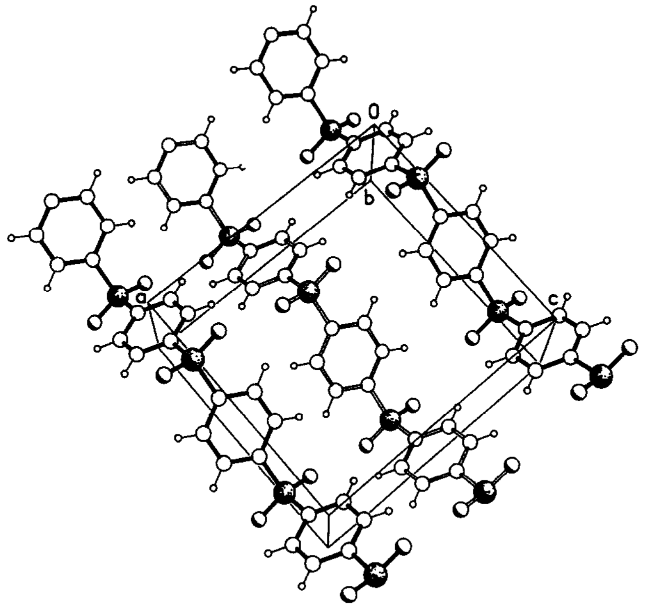

Figure 4 Perspective view of the crystal structure of poly(1,4-phenylenesulfone). Symmetry-related chains are indicated by the use of filled and open bonds

Table 3 Principal reflections for poly(1,4-phenylenesulfone) from fibre data[2], powder data[3] and diffraction simulation

hkl	d_{fibre} (Å)	d_{powder} (Å)	$d_{\text{sim.}}$ (Å)
200	5.50	5.40	5.40
002	4.87		4.98
111	4.16	4.13	4.16
112	3.32	3.37	3.37
310	2.95	2.92	2.93
311	2.86	2.81	2.81
113	2.63		2.69
020	2.53		2.52
004	2.47		2.49
402	2.41		2.37
022	2.20		2.25
114	2.16	2.20	2.19
023	2.00		2.01
223	1.85	1.85	1.88

remain (notably in the exact lengths of the *a* and *c* axes), these data tend to confirm not only that the model is substantially correct, but also that the oxidation of poly(1,4-phenylenesulfide)[2] produces a material in which poly(1,4-phenylenesulfone) comprises at least the crystalline phase.

Acknowledgements

The author thanks the Royal Society for the award of an Industry Fellowship, and the Engineering and Physical Sciences Research Council of the United Kingdom for support of this research. The author is especially grateful to Professor D. J. Williams of Imperial College, London, for much crystallographic advice and encouragement.

References

1 Gabler, R. and Studinka, J. *Chimia* 1974, **28**, 567
2 Tsvankin, D. Y., Papkov, V. S., Dubovik, I. I., Sergeev, V. A. and Nedel'kin, V. I. *Vysokomol. Soedin., Ser. B* 1980, **22**, 366
3 Robello, D. R., Ulman, A. and Urankar, E. J. *Macromolecules* 1993, **26**, 6718
4 Sime, J. G. and Woodhouse, D. I. *J. Cryst. Mol. Struct.* 1974, **4**, 269

5 Sime, J. G. and Woodhouse, D. I. *J. Cryst. Mol. Struct.* 1974, **4**, 287
6 Colquhoun, H. M. and Williams, D. J. *Macromolecules* 1996 **29**, 3311
7 Koch, H. P. and Moffitt, W. E. *J. Chem. Soc.* 1951, 7
8 Miller, J. 'Aromatic Nucleophilic Substitution', Elsevier, London, 1968, p. 77
9 Attwood, T. E., King, T., Leslie, V. J. and Rose, J. B. *Polymer* 1977, **18**, 369
10 Wrasidlo, W. *J. Polym. Sci. A-2* 1972, **10**, 1719
11 Hanna, S., Coulter, P. D. and Windle, A. H. *J. Chem. Soc., Faraday Trans.* 1995, **91**, 2615