Crystal and Molecular Structures of Poly(1,4-phenylenesulfone) and Its Trisulfone and Tetrasulfone Oligomers

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ABSTRACT: The structures of poly(1,4-phenylenesulfone), $[1,4\text{-}ArSO_2]_n$ (Ar = 1,4-phenylene), and its tetrasulfone oligomer $ArSO_2ArSO_2ArSO_2ArSO_2Ar$ (Ar = phenyl or 1,4-phenylene) have been determined from X-ray powder diffraction data interfaced to molecular simulation and diffraction modeling. An initial model for the tetrasulfone oligomer was developed using conformational and packing information obtained from a single-crystal X-ray determination of the structure of the trisulfone $ArSO_2ArSO_2ArSO_2Ar$, in which the aromatic ring planes lie essentially orthogonal to a plane defined by the bridging C−S−C groups. Energy-minimization and crystallographic refinement of the tetrasulfone structure by Pawley and Rietveld methods yielded an agreement factor (R_{wp}) of 15.3%., and an analogous approach led to solution of the crystal structure of poly(1,4-phenylenesulfone) (R_{wp} = 5.5%). In all three structures, the diaryl sulfone units adopt near-perfect open-book conformations and the molecules crystallize with the aromatic rings of laterally adjacent chains essentially parallel. The polymer unit cell is *C*-centered orthorhombic (two chains per cell), space group *Cmcm*, with $a = 10.79$, $b = 5.05$, and $c = 9.97$ Å. The polymer chain adopts 2_1 helical geometry, and crystal packing is dominated by S═O···H−C interactions (O···H = 2.68 Å).

Introduction

Aromatic polyethersulfones are among the most important of all commercial high-performance polymers,[1] but structural characterization of these materials has been severely restricted by their essentially amorphous character.[2] As a result, little is known about the conformational and chain-packing characteristics of sulfone-based aromatic polymers, although efforts have recently been made to develop computational approaches to this problem.[3,4]

Unlike the vast majority of poly*ether*sulfones, the "parent" polysulfone **1** is highly crystalline, very high melting (T_m > 500 °C) and extremely insoluble.[5] Efforts were made some years ago to determine its structure from X-ray fiber data,[6] but the samples used in that study were obtained by peroxide oxidation of oriented, amorphous poly(1,4-phenylenesulfide), and doubts have recently been expressed as to whether such procedures actually afford poly(1,4-phenylenesulfone).[7] The reported unit cell parameters and calculated density (on a basis of two chains per cell) were entirely consistent with the oxidized material consisting of poly(1,4-phenylenesulfone), but the very limited X-ray fiber data available precluded a more conclusive structural analysis at that time.

However, recent developments in computational diffraction-simulation and structural refinement techniques mean that the detemination of polymer structure from limited diffraction data is now a more feasible proposition. Here we report a detailed study of the poly(1,4-phenylenesulfone) system, including a single-crystal X-ray analysis of the model trisulfone oligomer **2**, determination of the structure of its tetrasulfone homologue **4** from X-ray powder data and diffraction modeling, and finally solution and refinement of the crystal and molecular structure of the polymer itself, also from X-ray powder data. Preliminary molecular simulation studies of polymer **1** have been described in an earlier communication.[8]

Experimental Section

Synthesis of Polymer 1 and Its Oligomers. Poly(1,4-phenylenesulfone) (**1**) and the trisulfone oligomer (**2**) were synthesized as described by Robello et al.[7] The previously unreported tetrasulfone oligomer (**4**) was obtained as shown in Scheme 1. A mixture of 1,4-benzenedithiol (5.90 g, 41.5 mmol), 4-chlorophenyl phenyl sulfone (23.07 g, 91.3 mmol), and potassium carbonate (26.4 g, 191 mmol) in dimethylformamide (DMF, 130 mL) was heated to 150 °C and stirred under nitrogen for 24 h before cooling to room temperature and adding to water (2 L). The solid was filtered off, washed with water, and dried. Recrystallization from 1,2-dichlorobenzene, with charcoal treatment and hot filtration, gave white crystals of the disulfide-disulfone **3**, (19.80 g) which were filtered off, washed with diethyl ether, and dried under vacuum. Mp: 237−239 °C. A solution of compound **3** (1.00 g) in chloroform (20 mL) and trifluoroacetic acid (20 mL) was treated with 50% hydrogen peroxide (3.20 g) and heated with stirring to 70 °C. After 1 h, additional 50% hydrogen peroxide (2.00 g) was added and stirring was continued at 70 °C for a further 6 h. The suspension was then cooled to room temperature, poured into water (500 mL), and the white solid was filtered off, dried, extracted with hot 1,2,4-trichlorobenzene (400 mL), refiltered, and finally washed with acetone and dried under vacuum to

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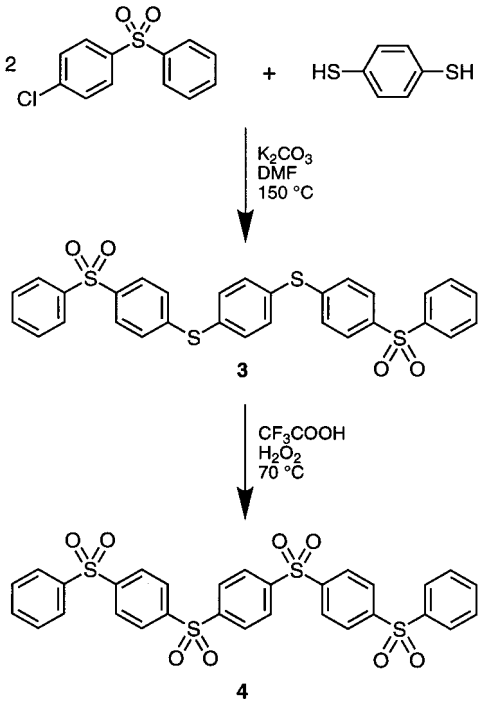
Scheme 1. Synthesis of Oligomer 4



afford the tetrasulfone **4** (1.02 g, 92% yield), mp 397−399 °C. $[M + Na]^+$ = 661 Da (MALDI−TOF). Anal. Calcd. for $C_{30}H_{22}O_8S_4$: C, 56.41; H, 3.47. Found: C, 57.10; H, 3.38.

Crystallographic Methods. Crystals of oligomer **2** were grown by very slow cooling of a dilute solution in dimethylformamide. Single-crystal X-ray data for **2** were measured on a Siemens P4/RA diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) using ω-scans, and the structure was solved using the SHELXTL-PC program system. X-ray powder data for oligomer **4** and for polymer **1** were measured at the CLRC-Daresbury Synchrotron Radiation Source, at a wavelength of 1.400 Å. The finely powdered samples were held in Lindemann tubes, cooled to −100 °C. During data collection the sample tube was continuously rotated about its long axis, perpendicular to the X-ray beam. Computational model-building, diffraction-simulation and crystallographic refinement from powder data were carried out using the program systems Cerius2, (v. 3.5) and Materials Studio (v. 1.2), both from Accelrys Inc., San Diego, CA.

Crystal Data for Oligomer 2 (Single-Crystal Diffraction). $C_{24}H_{18}O_6S_3$, M = 498.56, monoclinic, space group $C2$, a = 10.880(2) Å, b = 5.014(1) Å, c = 20.198(4) Å, β = 101.65(3)°, U = 1079.1(4) Å^3, Z = 2, T = 293 K, D_c = 1.534 g cm^{-3}, μ(Cu Kα) = 35.03 cm^{-1}, $F(000)$ = 516. R_1 = 0.0742, wR_2 = 0.1998 for 830 independent observed and absorption-corrected reflections [2θ < 126°; $I > 2\sigma(I)$]. Full crystallographic details are available as Supporting Information.

Crystal Data and Structure Determination for Oligomer 4 (Powder Diffraction). $C_{30}H_{22}O_8S_4$, M = 638.76, monoclinic, space group $C2/c$, a = 10.841 Å, b = 4.952 Å, c = 49.441 Å, β = 92.39°, U = 2652.4 Å^3, Z = 4, T = 173 K, D_c = 1.60 g cm^{-3}. Data collection range, 2θ = 4.98−48°, synchrotron, λ = 1.400 Å. Peak profile function: Thompson−Cox−Hastings, U = 0.1191, V = −0.5133, W = 0.0116, X = −0.0513, Y = −0.2388, Z = 0.00059. Peak asymmetry correction: Besar−Baldinozzi, P1 = 0.1333, P2 = −0.0374, P3 = −0.2336, P4 = −0.0655. Crystallite dimensions: a = 208, b = 169, c = 166 Å. Lattice strain: a = 0.984, b = 1.201, c = 1.111%. Zero point correction, −0.0268°. Agreement factors: R_{wp} = 0.153; R_p = 0.110. Atomic coordinates are given as Supporting Information.

Crystal Data and Structure Determination for Polymer 1 (Powder Diffraction). $[C_{12}H_8O_4S_2]_n$, M = $(280.33)_n$, orthorhombic, space group $Cmcm$, a = 10.790 Å, b = 5.050 Å, c = 9.975 Å, U = 543.6 Å^3, Z = 2, T = 173 K, D_c = 1.71 g cm^{-3}. Data collection range, 2θ = 6.04−49.48°, synchrotron, λ = 1.400 Å. Peak profile function: Thompson−Cox−Hastings, U = 5.0707, V = 14.388, W = −1.9639, X = 0.14216, Y = 0.11384, Z = 0.00154. Peak asymmetry correction: Besar−Baldinozzi, P1 = 3.7721, P2 = 0.04535, P3 = −7.6357, P4 = −0.93191. Polymer crystallite dimensions: a = 1584, b = 610, c = 106 Å. Lattice strain: a = 0.151, b = 2.544, c = 0.134%. Zero point correction, −0.0226°. Agreement factors: R_{wp} = 0.055; R_p = 0.123.

Results and Discussion

Preliminary diffraction-modeling studies of poly(1,4-phenylenesulfone) (**1**) using laboratory X-ray powder data had suggested a *C*-face centered crystal structure in which the aromatic rings within each polymer chain are oriented orthogonally to the C−S−C plane of the linking sulfone groups.[8] To confirm (or otherwise) the correctness of such a structure, we first investigated the structure of a model trisulfone oligomer (**2**) by single-

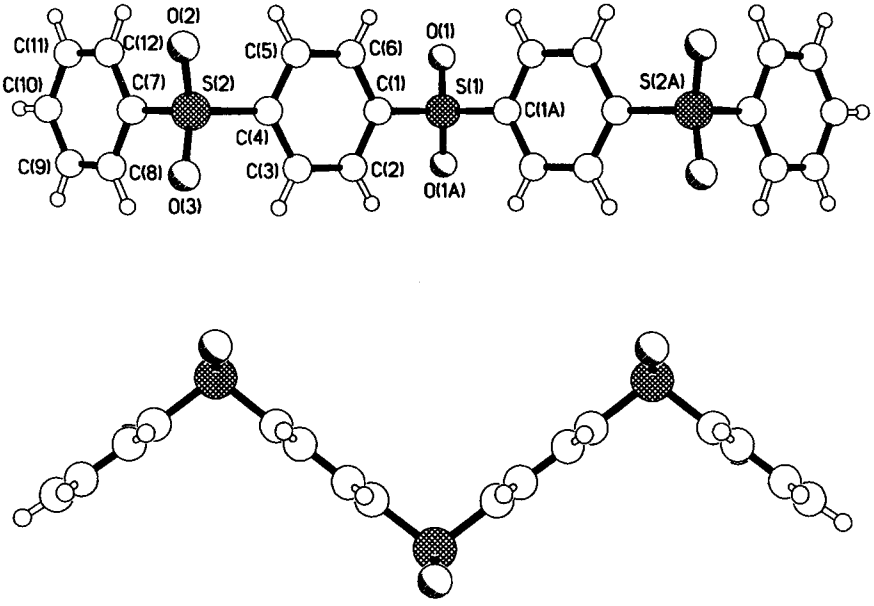


Figure 1. Molecular structure of the trisulfone oligomer **2**, projected (a) parallel and (b) perpendicular to the plane defined by C(1)−S(1)−C(1A).

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Oligomer 2

bond	length (Å)	bonds	angle (deg)
S(1)−C(1)	1.776(9)	C(1)−S(1)−C(1A)	103.7(6)
C(4)−S(2)	1.762(8)	C(4)−S(2)−C(7)	104.7(5)
S(2)−C(7)	1.758(9)		
S(1)−O(1)	1.442(7)	O(1)−S(1)−O(1a)	119.9(6)
S(2)−O(2)	1.440(6)	O(2)−S(2)−O(3)	120.0(5)
S(2)−O(3)	1.441(7)		
C(1)−C(2)	1.390(10)	C(1A)−S(1)−O(1)	108.1(3)
C(2)−C(3)	1.400(20)	C(1)−S(1)−O(1)	108.0(4)
C(3)−C(4)	1.400(11)	C(4)−S(2)−O(2)	107.8(3)
C(4)−C(5)	1.391(11)	C(4)−S(2)−O(3)	107.8(4)
C(5)−C(6)	1.358(14)	C(7)−S(2)−O(2)	107.7(4)
C(7)−C(8)	1.402(12)	C(7)−S(2)−O(3)	107.9(4)
C(8)−C(9)	1.350(20)		
C(9)−C(10)	1.380(20)	C(1A)−S(1)−C(1)−C(2)	89.0(6)
C(10)−C(11)	1.360(20)	C(1A)−S(1)−C(1)−C(6)	90.1(6)
C(11)−C(12)	1.370(20)	C(3)−C(4)-S(2)−C(7)	88.7(6)
		C(5)−C(4)-S(2)−C(7)	89.3(6)
		C(4)−S(2)-C(7)−C(8)	89.5(6)
C−H (defined)	0.976	C(4)−S(2)-C(7)−C(12)	88.7(6)

crystal X-ray methods, thereby affording the first unambiguous geometric, conformational, and packing data for this type of polysulfone.

The molecular structure of **2** is shown in Figure 1, projected both perpendicular and parallel to the O−O vector of the central sulfone unit. Key bond lengths, bond angles, and torsion angles are given in Table 1. The distance between atoms S(2) and S(2A), which are related by a crystallographic 2-fold axis through S(1), is 9.92 Å. This separation represents the structural repeat-distance for polymer **1** and, by the convention which aligns the polymer chain with the crystallographic *c* axis, gives a provisional value for the *c*-dimension of the polymer unit cell. The aromatic rings are essentially orthogonal to the plane of the three sulfur atoms, with independent C−C−S−C torsion angles of 88.7, 89.5, 88.7, 89.3, 89.0, and 90.1° leading to a sequence of three almost perfect "open-book" geometries at the sulfone bridges. This type of conformation is generally believed to represent the torsional-energy minimum for a diaryl sulfone unit,[9,10] but although a simple orbital overlap model involving $C_{p\pi}-S_{d\pi}$ interactions has been proposed to account for this preference,[11] no more rigorous quantum-mechanical explanation has yet been reported.

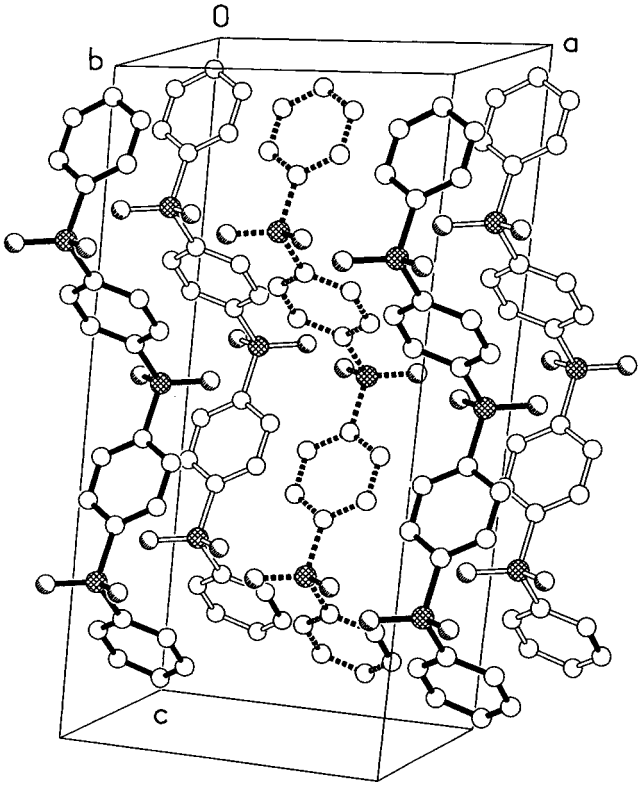


Figure 2. Unit cell of oligomer **2**, containing two molecules per cell.

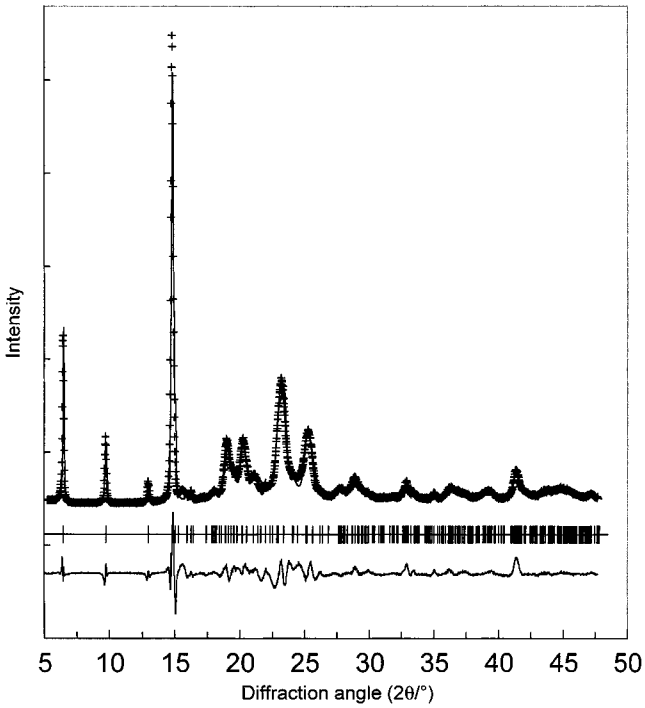


Figure 3. Rietveld difference plot (lower line) for oligomer **4**, based on the final structure containing four molecules per unit cell. Experimental data (background-subtracted) are shown as + marks, calculated data as a solid line, and calculated peak positions as tick marks.

The two molecules of oligomer **2** within the unit cell are related by *C*-face centering and are thus aligned parallel with one another. The oligomer chains are however not aligned precisely along the *c* axis of the unit cell, but lie perpendicular to the *ab* plane (Figure 2) and thus make an angle of 11.65° to the *c* direction, so presumably optimizing end-to-end packing interactions. The only significant intermolecular contacts are of the type C−H···O═S, where the O···H distances and C−H···O angles are 2.68 Å and 148° respectively. Given the polarity of these contacts ($H^{\delta+}\cdots O^{\delta-}$) they may be viewed as weak but cooperative hydrogen bonding interactions. With a well-defined oligomer structure available, the Dreiding II force field [12] within Cerius2 was reparametrized so that it reproduced the structure of oligomer **2** to a good degree of accuracy, and this modified force field was used in further analyses of the poly(1,4-phenylenesulfone) system.

The previously unreported tetrasulfone oligomer **4** (an even more realistic model for polymer **1** than the trisulfone homologue **2**) was synthesized as shown in Scheme 1, but efforts to grow X-ray quality single crystals were frustrated by its extreme insolublity. However, since oligomer **4** gave a reasonably well-resolved X-ray powder pattern, it seemed possible that extrapolation from the crystal structure of **2** might enable the structure of **4** to be determined by diffraction modeling.

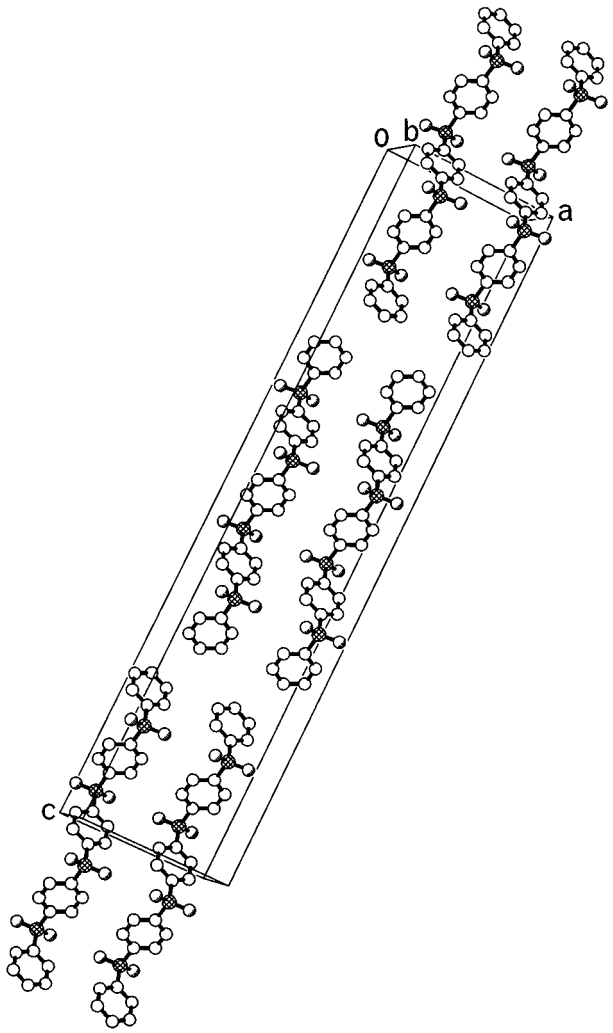


Figure 4. Unit cell of oligomer **4**, containing four molecules per cell.

A preliminary model for the tetrasulfone **4**, containing two molecules per unit cell, was thus constructed using geometric, conformational and symmetry data derived from the crystal structure of **2**, and this model was energy-minimized using the modified Dreiding II force field described above. However, although the powder pattern predicted for this preliminary structure showed close similarities to the experimental pattern for oligomer **4** (notably in the positions and intensities of the 001, 002, 003, 004, and 200 reflections), a number of serious discrepancies remained. It thus seemed that a structure for oligomer **4** directly analogous to that of oligomer **2** could not be correct.

In fact, reexamination of the *end-to-end* packing of oligomer molecules in the crystal of **2** showed that the same arrangement could not be present in a structure for **4** which has only two molecules per unit cell, because of the now-odd number of aromatic rings in the oligomer chain. However, the same type of end-to-end packing *could* be present in crystalline oligomer **4** if the unit cell contained *four* molecules rather than two, the two additional molecules being generated by the introduction of a 2-fold axis parallel to *b*. Construction and minimization of such a model for **4,** using the force-field developed from the structure of **2**, led to a structure in space group *C*2/*c* whose simulated powder pattern gave very good qualitative agreement with the observed pattern. Further refinement of this structure by Pawley and Rietveld methods (Figure 3) led to the final structure shown in Figure 4, having a weighted-profile *R* value (R_{wp}) of 15.3%. Oligomer **4** has four molecules per unit cell with crystallographic inversion symmetry about the center of each molecule, but otherwise the structure is similar to that of **2**, with the same conformation and the same symmetry relationship (*C*-face-centering) between laterally adjacent chains. In oligomer **4** however, the longer oligomer chains are aligned more closely to the *c* direction, resulting in a much smaller β-angle for the unit cell.

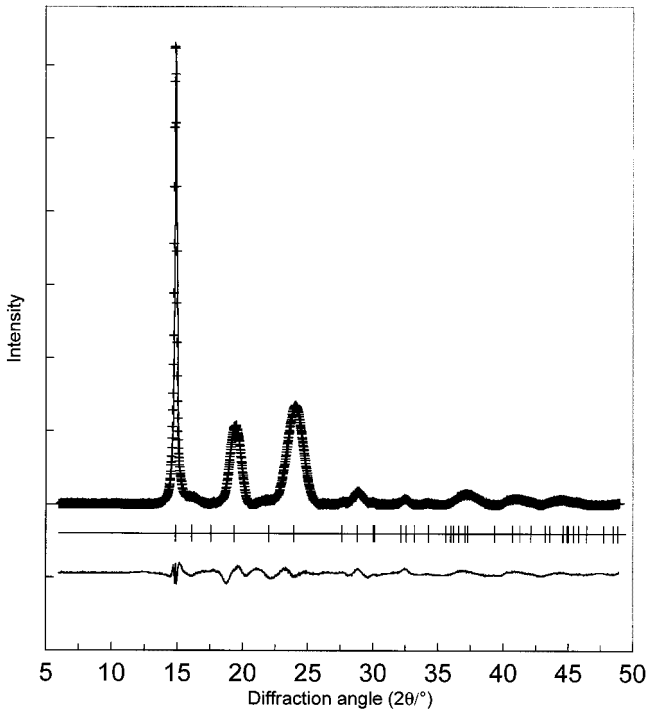


Figure 5. Rietveld difference plot (lower line) for the final structure of polymer **1**. Experimental data (background-subtracted) are shown as + marks, calculated data as a solid line, and calculated peak positions as tick marks.

The chain conformations determined for oligomers **2** and **4** clearly suggest that an orthogonal torsional relationship between the aromatic rings and the bridging sulfone units should also occur in the corresponding polymer chain. Similarly, the *C*-centered relationship between laterally adjacent oligomer chains in the structures of both **2** and **4** provides strong support for this type of packing in poly(1,4-phenylenesulfone) itself. Interestingly, the crystal structure of oligomer **2** could be used directly to generate a preliminary model for the unit cell of polymer **1**, since the two molecules in the oligomer unit cell are related by simple *C*-centering and pack strictly in register to give a well-defined lamellar-type structure. By connecting the sulfur atoms S(2) and S(2A) of four translationally related oligomer molecules, a provisional *C*-centered polymer unit cell with a = 10.89, b = 5.01, and c = 9.92 Å and with α = 90.0, β = 90.0, and γ = 90.0° could be generated.

The experimental X-ray powder pattern for polymer **1** (Figure 6) was indexed in terms of a just such a *C*-face-centered orthorhombic unit cell. From this pattern, the cell dimensions were determined as a = 10.79, b = 5.05, and c = 9.96 Å, in reasonably good agreement with both the above, oligomer-derived unit cell and with the polymer unit cell obtained by Tsvankin et al. from X-ray fiber data (a = 11.00, b = 5.05, c = 9.75 Å).[6] A model

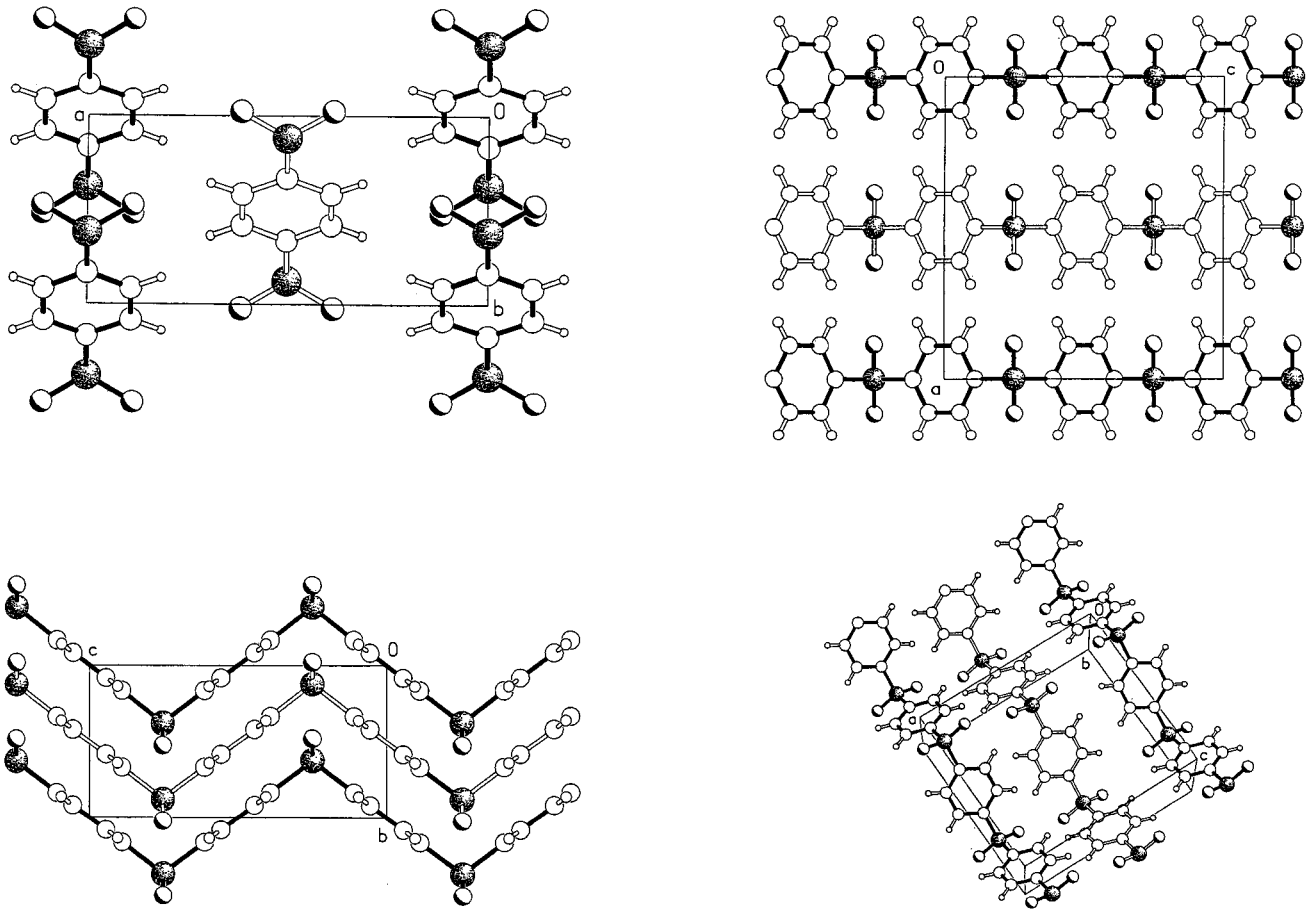


Figure 6. Crystal structure of polymer **1** shown projected on the three faces of the unit cell and also shown in perspective.

Table 2. Fractional Atomic Coordinates and Isotropic Temperature Factors (Å^2) for the Asymmetric Unit of Polymer 1, in Space Group *Cmcm*

atom	*x*	*y*	*z*	U_i
S	0.00000	−0.38008	0.25000	0.1838
O	0.11559	−0.52354	0.25000	0.1417
C(1)	0.00000	0.16711	−0.10984	0.0002
C(2)	−0.11133	0.08389	−0.05485	0.0461
H	−0.18966	0.14298	−0.09359	0.1360

for the polymer crystal, having two chains per unit cell, was constructed in Cerius2 using bond lengths, bond angles, and torsion angles derived from oligomer **2**, although the symmetry relationship between the two chains was not specified at this stage. Minimization of this structure using the modified Dreiding II force field described above, within the experimentally derived unit cell, led quite unambiguously to a *C*-centered arrangement of the chains, and analysis of the symmetry elements in the present in the model provisionally identified the space group as *Cmcm*. The final space group assignment is however dependent on whether 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 the C_2 axis through sulfur and the inversion center at the center of the aromatic ring are retained, a nonorthogonal torsion angle would be permitted within the monoclinic space group *C*2/*c*. In practice, reducing the energy-barrier associated with the originally imposed 90° torsional preference led to *no* significant change of the C−C−S−C torsion angle, and it is therefore concluded that *Cmcm* remains quite the most probable space group for poly(1,4-phenylenesulfone).

A simulated powder-diffraction pattern for this structure gave excellent agreement between observed and calculated peak positions, and refinement of the structure by Pawley and Rietveld methods eventually gave a weighted-profile agreement factor (R_{wp}) of 5.5% (Figure 5).

The final structure, with atom labeling, is shown in Figure 6 projected along the *a*, *b*, and *c* directions, together with a perspective view of the unit cell. Atomic coordinates and isotropic atomic thermal parameters 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] interactions (O···H = 2.68 Å, C−H···O = 150°) analogous to those observed in the structure of oligomer **2**; there are no other intermolecular contacts at or below van der Waals distances.

The unit cell reported here for polymer **1**, although derived from the powder pattern of material formed by self-polycondensation of [1,4-$FC_6H_4SO_2$]$^-$, is nevertheless in reasonably good agreement with the cell derived from the fiber pattern of material produced by peroxide oxidation of amorphous poly(1,4-phenylenesulfide) (orthorhombic, two chains per cell, a = 11.00, b = 5.05, and c = 9.75 Å, and D_c = 1.73 g cm^{-3}).[6] A simulated X-ray fiber pattern for polymer **1** (contour plot, based on the unit cell reported here) is shown in Figure 7, together with the experimental fiber pattern from ref 6. The very close agreement between these two patterns strongly suggests that oxidation of amorphous poly(1,4-phenylenesulfide) does in fact produce a material in

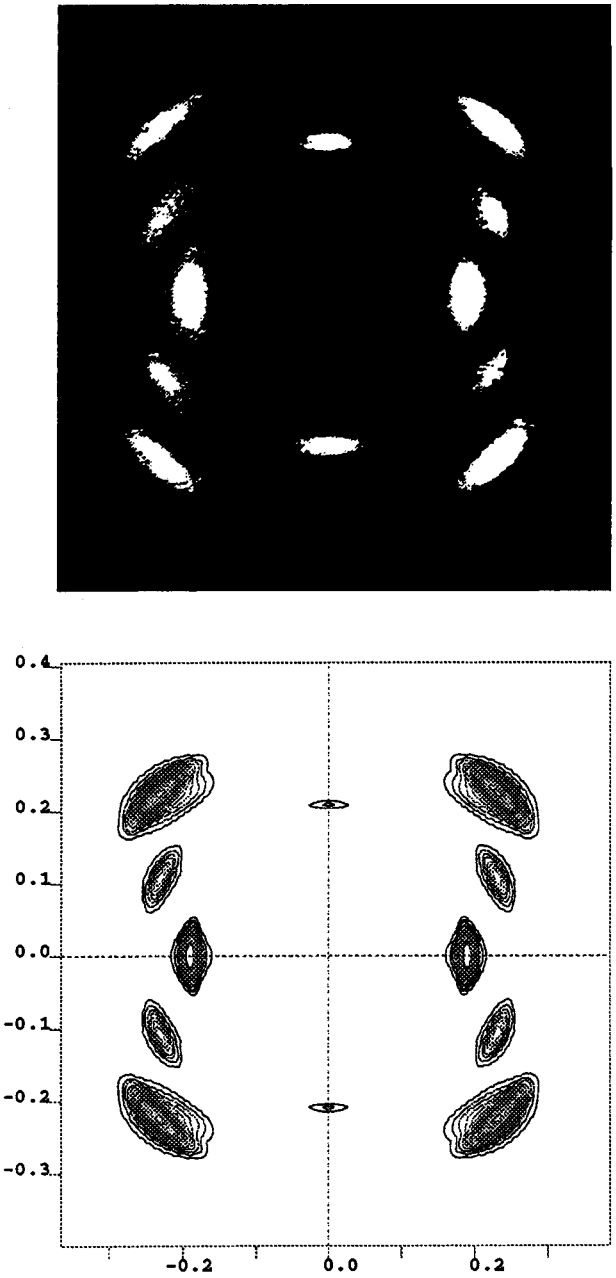


Figure 7. Experimental X-ray fiber pattern (flat plate, Cu Kα radiation) from ref 6, together with a fiber pattern simulated from the crystal structure reported here for polymer **1**.

which poly(1,4-phenylenesulfone) comprises at least the crystalline phase.

The differences in unit cell dimensions between the powder and fiber samples undoubtedly reflect the relative molecular weights of these materials. It is well established that semicrystalline polymers of high molar mass generally adopt unit cells with significantly greater lateral dimensions (*a* and/or *b*) than their oligomeric analogues,[13] and it is thought that this effect results from the presence of amorphous or chain-folding regions, present in high molar mass polymers but absent from low molar mass or oligomeric material. Chains entering a thin, lamellar crystallite from an amorphous and/or chain-folded region are laterally stressed by the transition from a low-density to a high-density phase and thus adopt a more expanded crystal lattice than would occur in low molar mass material, where the chains are contained entirely within the crystallite.[14] In the present work, the observed expansion of the *a*-dimension from 10.79 Å in our low molar mass powder-sample to 11.00 Å in the fiber-sample previously obtained by oxidation of oriented, high molar mass poly-(1,4-phenylene sulfide),[6] is clearly quite consistent with this explanation.

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Supporting Information Available: Tables of full crystallographic data for the single-crystal structure of oligomer **2** and atomic coordinates for oligomer **4** and a figure showing the structure for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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