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# The conformation of crystalline poly(phenylene sulphide)

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**Abstract**

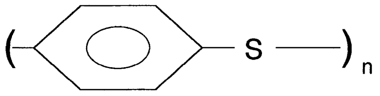
The crystallographic structure of crystalline poly(phenylene sulphide) has been calculated from wide-angle X-ray diffraction pattern of a range of materials with different degrees of crystallinity. The orthorhombic unit cell has parameters refined by a least-squares method: $a = 0.868 \pm 0.002$ nm, $b = 0.566 \pm 0.002$ nm, and $c = 1.026 \pm 0.005$ nm. The crystalline density was determined to be 1.43 g cm$^{-3}$ and the enthalpy of fusion of crystalline PPS, $\Delta H_f^0$, 76.5 J g$^{-1}$ at the mp.

Using computer modelling and potential energy minimisation, the torsional angle of the C–S–C bond was determined to be 108° and the phenylene groups arranged at 45° to the plane of the molecular chain. These results have been confirmed by comparison of computed and measured X-ray diffraction intensities. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Poly(phenylene sulphide); Amorphous; Crystalline

## 1. Introduction

Polyphenylene sulphide, PPS,



has attracted considerable interest as an engineering polymer because of its high modulus, tensile strength and good dimensional stability. Its high deflection temperature of about 500 K, flame retardancy and resistance to organic fluids determine many of its applications. These properties make it particularly useful in the electronics and automotive industries. It can be quenched from above the melting point to an amorphous sheet or crystallised to a high degree of crystallinity.

Central to a study of the morphology of PPS is the establishment of the degree of crystallinity and the unit cell dimensions. Unit cell dimensions were first reported by Tabor et al. [1] from which the crystalline density was calculated to be 1.43 g cm$^{-3}$ with four chain segments per unit cell. The amorphous density was measured as 1.32 g cm$^{-3}$. The dimensions of the unit cell were consistent with

1. a planar zig-zag structure for the chain;
2. the phenylene rings inclined at 45° to the plane of the zig-zag;
3. a S–S separation along the chain of 0.627 nm;
4. a C–S–C bond angle of 110°.

Garbarczyk [2] has questioned this structure on the basis that it could not account for the high electrical conductivity of PPS for which a planar alignment of the rings was preferred [3] and lower torsional angle would allow conjugation of the phenylene $\pi$ with the sulphur p-electrons. Using a series of oligomers as models, Garbarcyk suggested, from an NMR spectroscopic study of dimers and trimers, that the C–S–C bond angle was in the range 103–107°. Reducing the bond angle allowed the angle of rotation of the phenylene ring to be reduced with alternate pairs being nearly coplanar with the plane of the zig-zag while the other rings were inclined at 60°. This was consistent with structure of PPS oligomers. He also suggested that Tabor et al.'s fibre samples had been distorted by heat treatment or by stretching of the sample that opened the C–S–C bond to 110°. Lovinger et al. [3,4] have subsequently confirmed the crystallographic structure of PPS outlined by Tabor et al. on fibre samples.

There is some discrepancy in the precise conformation of the PPS chains in the crystalline phase and we have used X-ray diffraction studies on crystalline samples and molecular modelling to resolve this. Un-stretched stress-relieved bulk specimens were used in this study to eliminate any possibility of chain distortion.

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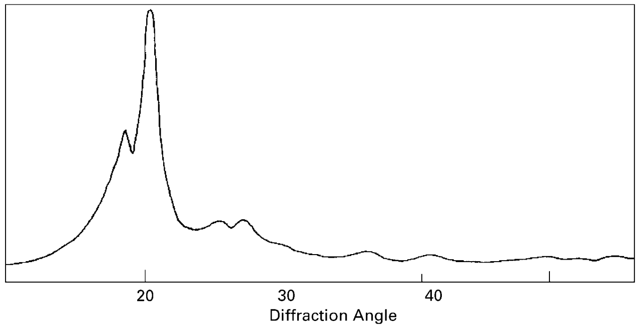

Fig. 1. WAX diffraction pattern of partially crystalline PPS.

## 2. Experimental

PPS was obtained from Phillips Petroleum as Ryton, grade GR04, in the form of beige coloured pellets. The pellets were dried for 4 h at 150°C prior to moulding. Plaques, 100 × 100 mm of different thickness, 0.1–3.00 mm, were made by compression moulding of the dried pellets between aluminium plates for 7 min at 220°C. Amorphous material was produced by quenching plaques, less than 1 mm thick, directly into ice/water. Crystalline material was produced either by slow cooling in the press or annealing the amorphous plaques at preset temperatures.

X-ray diffraction studies were carried out on a Picker high-resolution automated powder diffractometer using Cu Kα radiation with a step scan interval of 0.10° in $2\theta$. It was calibrated for position using a quartz standard and the diffraction pattern analysed as described elsewhere [5,6].

A Perkin–Elmer differential scanning calorimeter, DSC-2c, interfaced to a PC was used to determine the thermal characteristics of crystalline and amorphous PPS, using procedures detailed elsewhere [7].

## 3. Results and discussion

### 3.1. Crystallographic structure

X-ray diffraction patterns were measured for amorphous and semi-crystalline PPS samples as scattered intensities as a function of Bragg angle, $2\theta$, see Fig. 1. The scattered intensities from an amorphous sample was scaled for the amorphous content and subtracted from that of the crystalline sample to leave the pattern for the crystalline PPS. The program PROFIT was used to determine the positions, width and intensities of all peaks in the patterns. The cell dimensions were determined by using Cohen's least-squares method [8] to minimise $\Delta\sin^2\theta$ and so $\Delta\theta = (\theta_{obs} - \theta_{calc})$. The least-square cell parameters are listed in Table 1, along with the assignments of the reflections and a comparison made with those listed by Tabor et al. [1] and Lovinger et al. [3]. There was an excellent agreement within the standard errors between all three determinations. The space group was *Pbcn*.

The intensities of these reflections were corrected from

Table 1

*(a) Unit cell dimensions*

| | | $a \pm 0.002$ (nm) | $b \pm 0.001$ (nm) | $c \pm 0.002$ (nm) | Crystalline density ± 0.010 (g cm$^{-3)}$ |
|---|---|---|---|---|---|
| Reference | Tabor et al. | 0.867 | 0.561 | 1.026 | 1.439 |
| | Lovinger | 0.868 | 0.566 | 1.026 | 1.425 |
| | Reflectance | 0.862 | 0.563 | 1.032 | 1.434 |
| | Transmittance | 0.868 | 0.566 | 1.026 | 1.425 |
| | | | | | 1.430 (average) |

*(b) WAX diffraction assignments*

| *hkl* | *d* (nm) | $2\theta$ | Relative intensity (peak height) | | | |
|---|---|---|---|---|---|---|
| | | | Observed | 45° | 90° | 180° |
| 110 | 0.470 | 18.8 | 27 | 26 | 74 | 5 |
| 111[a] | 0.428 | 20.6 | 100 | 100 | 100 | 100 |
| 200[a] | 0.434 | 20.4 | | | | |
| 201 | 0.400 | 22.2 | 10 | 15 | 20 | 10 |
| 112[a] | 0.348 | 25.6 | 10 | 16 | 16 | 0 |
| 210[a] | 0.344 | 25.8 | | | | |
| 211 | 0.324 | 27.7 | 17 | 18 | 0 | 0 |
| 020 | 0.285 | 31.3 | 4 | 8 | 16 | 10 |
| 021 | 0.271 | 32.9 | 2 | 8 | 16 | 10 |
| 311 | 0.248 | 36.1 | 9 | 16 | 18 | 5 |
| 114 | 0.226 | 39.8 | 6 | 8 | 5 | 10 |

[a] Not resolved.

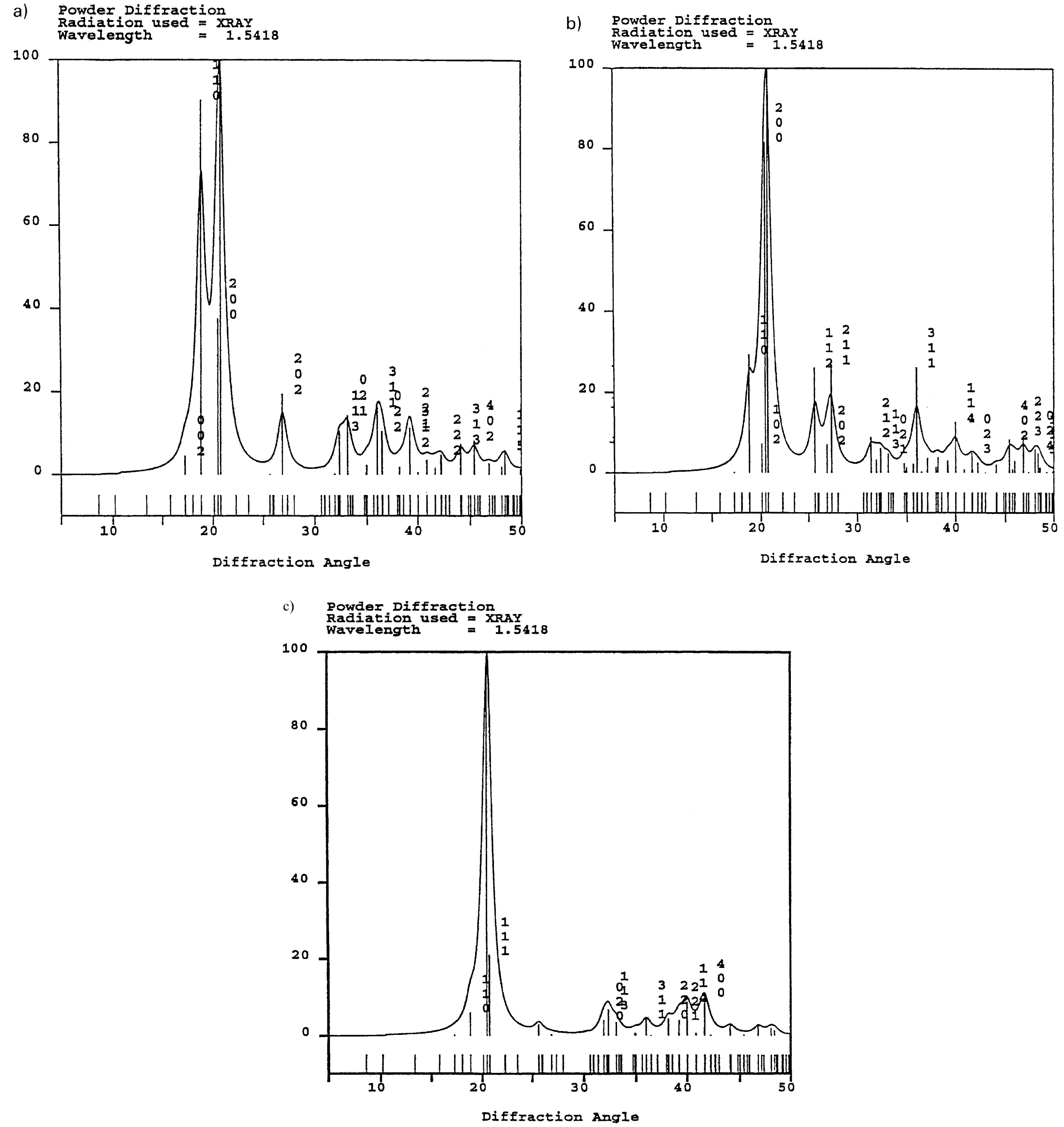

Fig. 2. Computer generated WAX diffraction patterns of PPS: (a) phenylene rings inclined at ±45°; (b) phenylene rings inclined at ±90°; (c) phenylene rings inclined at ±180°.

the measured absorption coefficient, $\mu$, of the sample used, since

$$I = I_0 \exp(-\mu t) \quad (1)$$

$I_0$ and $I$ are the intensities of the incident and detected beams, and $t$ the sample thickness. The shape of the line profile was also considered from the parameter, $\phi = \alpha/\beta$, where $\alpha$ is the width at half maximum intensity and $\beta$ the integral breadth. For all the samples, $\phi$ was constant and close to 0.84. This value is intermediate between the Lorentzian and Gaussian limits. Crystallite size was the dominant cause of line broadening.

Further studies were carried out to determine if the unit cell dimensions were dependent on crystallisation conditions as has been observed with the aromatic polymer PEEK [9]. Samples were heated to above the melting temperature, and crystallised at 373 and 473 K; no changes were observed in the WAX diffraction pattern and there were no systematic variations, within the standard deviations, in the unit cell dimensions. Transmitted and reflectance studies were also carried out in order to see

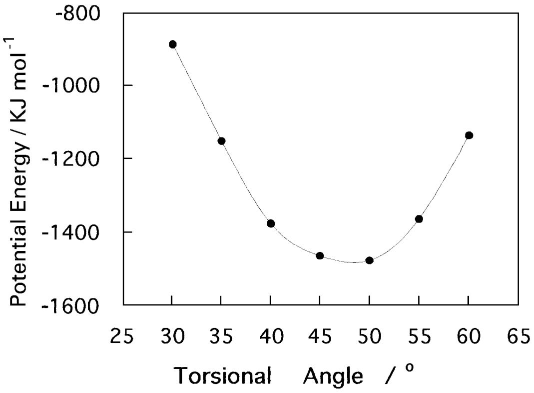

Fig. 3. The effect of the torsional angle on the molecular potential energy.

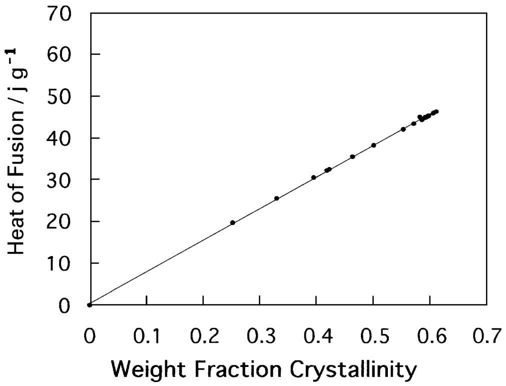

Fig. 4. The variation of the enthalpy of fusion with weight fraction degree of crystallinity.

what effect the method of measuring the WAX scattering effected the dimensions of the unit cell. No systematic variations were observed within the standard deviations in measuring the unit cell dimensions. The effect of these variations on the crystalline density of PPS is listed in Table 1.

Molecular modelling was carried out to investigate changes in chain configuration on the diffraction pattern and determine the angle of the phenyl ring to the plane of the zig-zag using Cerius software [10]. Energy minimisation calculations were also carried out on the chain conformation. The molecular structure of crystalline PPS proposed by Tabor et al. [1] was initially assumed and the angle of the rings to the plane of the zig-zag altered systematically from 45 to 180° since these represented the two extremes postulated by Tabor et al., i.e. 45° and co-planarity the zig-zag. The changes in the X-ray diffraction patterns were then calculated using Cerius for each of these structures and in particular the 110, 112 and 202 reflections showed the greater changes in intensity as the rotational angle increased. The closest fit to the experimental X-ray diffraction pattern of PPS was that with the plane of the rings at 45° to the planar zig-zag, as can be seen in Fig. 2 where the computed powder diffraction pattern for the PPS structures with the phenylene rings making an angle of ±45, 90 and 180° to the plane of the molecular chain are shown for comparison. The diffraction patterns are clearly sensitive to this angle. The relative intensities of the diffraction lines are shown in Table 1 and compared with the observed values. The ratio of the intensities were found for the group of the most intense lines centred close to 20.6° and assigned to the 200, and 111 reflections. It can be seen that the 45° pattern most closely fits the observed intensities of the diffraction lines for PPS, particularly the changes in the 110 line, and the other assigned angles cannot account for the observed powder diffraction pattern.

The same range of structures was used to calculate the total potential energy [11] of each crystalline structure by building up the monomer units into a polymer chain. Conventional bond angles and lengths were adopted for the structure of PPS in the crystal. Each structure was energy minimised using a steepest descent iteration procedure. After 50 iterations, the lowest potential energy corresponded to the structures with the rings at 47 ± 5° to the plane of the zig-zag (Fig. 3) and the minimised C–S–C angle was 107.8°.

Both the planar zig-zag structure with the phenylene rings alternating 45° to this plane and the C–S–C bond angle of 107.8° are entirely consistent with the structure proposed by Tabor et al. [1] for crystalline PPS.

### 3.2. The degree of crystallinity

The volume fraction degree of crystallinity of PPS samples, $X_c$, were determined from the WAXD pattern from the ratio of the areas under the crystalline and amorphous diffraction pattern. The samples were crystallised isothermally over a range of temperature and for various periods of time. The WAXD pattern of amorphous was scaled for the amorphous content and subtracted from the overall diffraction pattern. The two areas were then separately determined. Averaged over several determinations on the same sample the degree of crystallinity was reproducible to ±2%.

The weight fraction degree of crystallinity, $X_w$, is conventionally from the enthalpy of fusion, $\Delta H_f$, of the samples and the corresponding value for the completely crystalline sample, $\Delta H_f^0$, i.e.

$$X_w = \Delta H_f / \Delta H_f^0 \tag{2}$$

The enthalpy of fusion of the samples was determined from the area under the melting endotherm for all the samples using DSC as outlined elsewhere.

Since

$$X_w = X_v \rho_c / \rho_{obs} \tag{3}$$

where $\rho_c$ is the crystalline density, and $\rho_{obs}$ the sample density. The weight fraction degree of crystallinity was determined from the calculated crystalline and the measured density of the samples. The weight fraction crystallinity is plotted against the enthalpy of fusion in Fig. 4 from which it was deduced that the enthalpy of fusion of crystalline PPS at the mp, $\Delta H_f^0$ was 76.5 J $g^{-1}$.

## 4. Conclusions

The unit cell dimensions of PPS have been confirmed by X-ray diffraction as $a = 0.862$ nm, $b = 0.561$ nm, and $c = 1.026$ nm, confirming the original work of Tabor et al. The cell symmetry was *Pbcn* with four molecules per unit cell. No change in the dimensions was observed on annealing or with increasing crystallisation temperature ruling out the possibility that these values could be attributed to a distorted structure from internal strain or heat distortion on rapid cooling. Computer calculated WAX diffraction patterns confirmed that the phenylene groups were inclined at 45 ± 3° to the plane of the zig-zag. From molecular calculations optimising the interaction energy the angle between the C–S–C bonds was between 108 and 109° close to value of 110° determined from X-ray diffraction studies and at odds with the concept that there is conjugation between adjacent pairs of phenylene rings and the p-electrons on the sulphur atom.

The enthalpy of fusion of crystalline PPS, $\Delta H_f^0$, was determined from the weight fraction degree of crystallinity as 76.5 J $g^{-1}$ at the $T_m$.

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