Structure of poly(*p*-phenylene sulphide)

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We have examined the unit-cell structure of the important high-temperature and high-strength polymer, poly(*p*-phenylene sulphide) (PPS); this has recently been in dispute, with two different models proposed from oriented and unoriented polycrystalline specimens, respectively. Having obtained single crystals of PPS from solution and from thin films of the melt (the latter in both flat-on and edge-on orientations), we determined the lattice dimensions of the orthorhombic unit cell using electron diffraction. These are $a = 8.68$ Å, $b = 5.66$ Å and $c = 10.26$ Å, in agreement with the original model based upon alternating $\pm 45°$ inclinations of the phenyl rings to the plane of the sulphur bonds. We have also determined the rate of expansion of the intermolecular lattice as a function of electron dose, and found PPS to be one of the most radiation-stable polymers, preserving its crystallinity to 3100 C m^{-2} (i.e. more than 30 times that of polyethylene).

(Keywords: crystallization; morphology; high-performance polymers)

INTRODUCTION

Poly(*p*-phenylene sulphide) (PPS) is a high-performance polymer that is receiving increasing attention for its high-temperature and high-strength properties[1], its processability and chemical resistance[2], as well as its electrical conductivity upon doping[3,4]. Its crystalline structure, reported in 1971 by Tabor *et al.*[5], has recently been questioned by Garbarczyk[6]. In the original model[5], the molecular chains adopt an all-*trans* conformation defined by the plane of their C–S–C linkages, while the phenyl rings are successively inclined at ±45° with respect to this plane (see *Figure 1a*). The alternative model[6], albeit not based on a full structural analysis, differs from the original one both *intra*- and *inter*molecularly. In terms of chain structure, it proposes[6] smaller C–S–C– bond angles of 103–107° (compared with 110° of the earlier model[5]), leading to significant shortening of the molecular repeat. As a result of this reduction in bond angle, the rotation of phenyl rings is supposed[6] to be diminished, leading to the suggestion that alternate rings are nearly coplanar with the zigzag plane, while the remaining ones are inclined by ~60°. This alternative conformation is based upon structural analyses of quasi-dimeric and quasi-trimeric analogues[7,8] where the alternating angles are 4–15° and 59–62°, respectively, and is seen schematically in *Figure 1b*. Such a conformational difference is expected to affect the *inter*molecular dimensions, as well: in fact, Garbarczyk[6] reports significantly reduced interplanar spacings for the interchain reflections of PPS.

The differences in the two models are attributed in ref. 6 to variations in sample treatment. The study of Tabor *et al.*[5] was performed on lightly crosslinked, heated and stretched PPS, while that of Garbarczyk[6] utilized PPS powder and low-molecular-weight analogues. Reference 6 suggests that the earlier study[5] may reflect molecular distortions resulting from sample extension; however, it is clear that the second study[6] has also been performed on a less-than-ideal specimen (as-received, commercial, polycrystalline powder).

To resolve these differences, we have investigated specimens that are either single crystals or have a single-crystalline orientation. Such specimens were grown as we described in the first reports of the morphology of PPS crystallized from both solution[9] and the melt[10]. The unit cell obtained in this manner should provide an independent means of evaluating the two previous models using much more suitable (i.e. single-crystal-like) morphologies than hitherto examined.

EXPERIMENTAL

Single crystals of PPS (Ryton V-1 powder from Phillips Petroleum Co., i.e. the same material used in refs. 5 and 6)

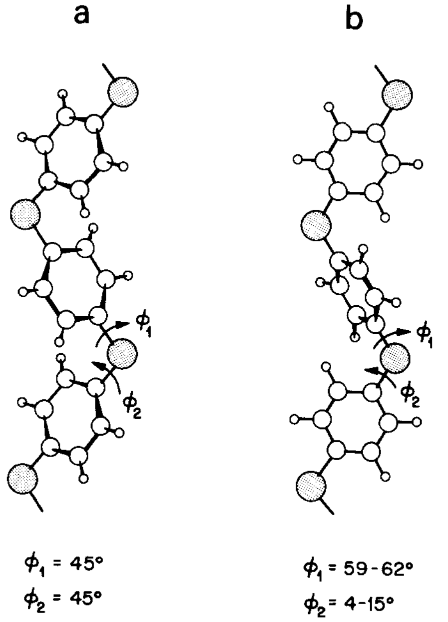

Figure 1 Molecular models of the conformation of PPS according to (a) ref. 5 and (b) ref. 6. The three types of circle represent S, C and H atoms (in decreasing order of size)

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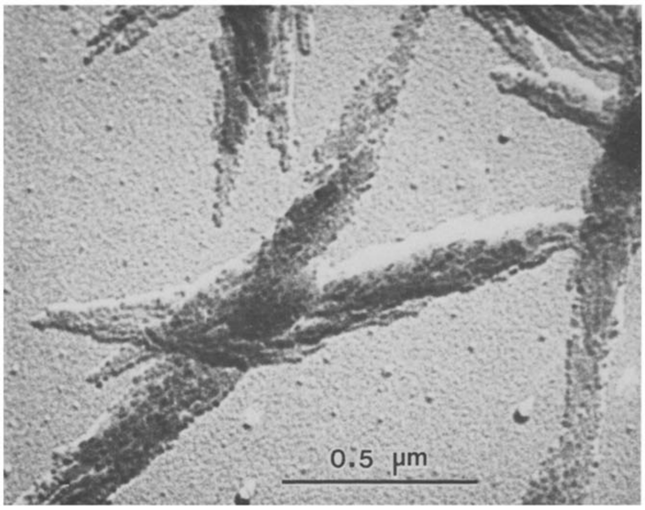

Figure 2 Typical morphology of PPS single crystals grown at 160°C for 3 days from a 0.005% solution in α-chloronaphthalene

were grown from 0.005% solutions in α-chloronaphthalene held at 160°C for 3 days. Single crystals and single-crystal-like aggregates were also obtained from the melt by isothermal crystallization of very thin films (10–30 nm) at high temperatures (260–265°C) on freshly cleaved mica. After the usual Pt/C shadowing, carbon coating, flotation from their substrates and deposition onto electron-microscope grids, many of these films were coated with evaporated TlCl serving as an internal calibration standard. They were then examined in a transmission electron microscope at 100 keV and under low-dose conditions to minimize the effects of electron irradiation.

RESULTS

Single crystals of PPS grown even from very dilute solutions are small, acicular, very irregular, devoid of macroscopic crystallographic faceting and replete with overgrowths. Their characteristic morphology is seen in *Figure 2*. Such solution-grown crystals are extremely similar to those previously reported[11,12] for another high-performance polymer of similar chain conformation and packing, poly(ether ether ketone) (PEEK). It is obvious from *Figure 2* that solution-grown PPS crystals would not be suitable for precise unit-cell structural determination.

For this reason, we have attempted to obtain crystals of greater perfection by growth from the melt at significantly higher temperatures. We have shown[10] that spherulites of PPS, crystallized from the melt in thin films, consist of very fine fibrils (which are simply lamellae on edge) in all regions except at the spherulitic 'eyes' adjacent to the central sheaf. In this location, crystals from the nucleus grow outwards in a flat-on orientation with little competition, and can therefore attain substantial lateral dimensions. This situation is illustrated in *Figure 3a*, where a few crystals exhibiting sharp faceting and much greater perfection than those grown from solution can be discerned. A typical electron diffraction pattern from such melt-grown single crystals is seen in *Figure 3b*.

From multiple measurements of seven such diffraction patterns, utilizing the internal TlCl calibration, taking into account the curvature of the Ewald sphere, and correcting for very slight azimuthal distortions due to inhomogeneities in the magnetic fields of the electron lenses, we obtained averaged values for the major *inter*molecular spacings shown in *Table 1*. In this table, although the last decimal digit is not significant, it is included to demonstrate the extremely small standard deviation of our data. It is clear from *Table 1* that our values for the *inter*molecular lattice of PPS from relatively perfect single crystals are in close agreement with those of ref. 5 and in significant disagreement with their counterparts from ref. 6.

According to ref. 6, the *inter*molecular differences between the two models are directly attributable to *intra*molecular causes, i.e. the C–S–C valence angle. The valence angle consistent with the 10.26 Å chain repeat reported in ref. 5 is 110°. This is considered too large by Garbarczyk[6], who proposed values between 103 and 107°; in the latter case, the chain repeat would lie between 9.80 and 10.07 Å. Since the only experimental value[5] for the *c*-axis repeat originates from uniaxially stretched (and possibly distorted[6]) specimens, we decided to obtain this measurement in single crystals. The type of crystal used for our intermolecular data is not suitable since the reflections are $h\,k\,0$, thus not containing any contribution from the *c*-axis. Tilting of such crystals during electron diffraction would allow probing of 1 1 1 and other reflections with $l \neq 0$ (in fact, such reflections are also seen in *Figure 3b* from parts of crystals that happened to be inclined to the substrate). However, calculation of the molecular repeat from such data would be indirect, and would incorporate cumulative errors from our values for the *a*- and *b*-axes.

A much better approach is to be able to probe crystals that have grown with an $0\,k\,l$ orientation. Such crystals are profusely available in our thins films in the form of lamellae grown on edge[10], similarly to the situation also described in PEEK[13]. However, because of their spherulitic growth, they have an overall cylindrical symmetry about the *a*-axis, which is normal to the film plane. Nevertheless, in regions far from the spherulitic centre, these lamellae will be effectively parallel, yielding a local single-crystalline orientation extending over regions sufficiently large for electron diffraction. Such a case is depicted in *Figure 4*, with the edge-on lamellae of the bright-field image giving rise to the accompanying diffraction pattern. The latter is seen clearly to correspond to the $0\,k\,l$ reciprocal-lattice plane, with the b^*- and c^*-axes parallel respectively to the longitudinal and transverse directions of these crystals. The 0 0 2 and 0 0 8 reflections are identified in *Figure 4* (both are much more clearly resolved in the orignal negative, which shows also the 0 0 4 and 0 0 6 reflections). From eight measurements of $0\,0\,l$ reflections, our value for the molecular repeat is $10.26_4 \pm 0.02_8$. We conclude that this direct measure of the *intra*molecular repeat in unstressed single crystals (just as our values for the *inter*molecular dimensions) is in agreement with the structure of Tabor *et al.*[5] and not with that of ref. 6. Of course, our results do not allow resolution of the difference regarding phenyl ring rotation about the S–S axes; they do, however, imply that the correct model must be consistent with our determined unit-cell parameters, namely $a = 8.68$ Å, $b = 5.66$ Å, $c = 10.26$ Å.

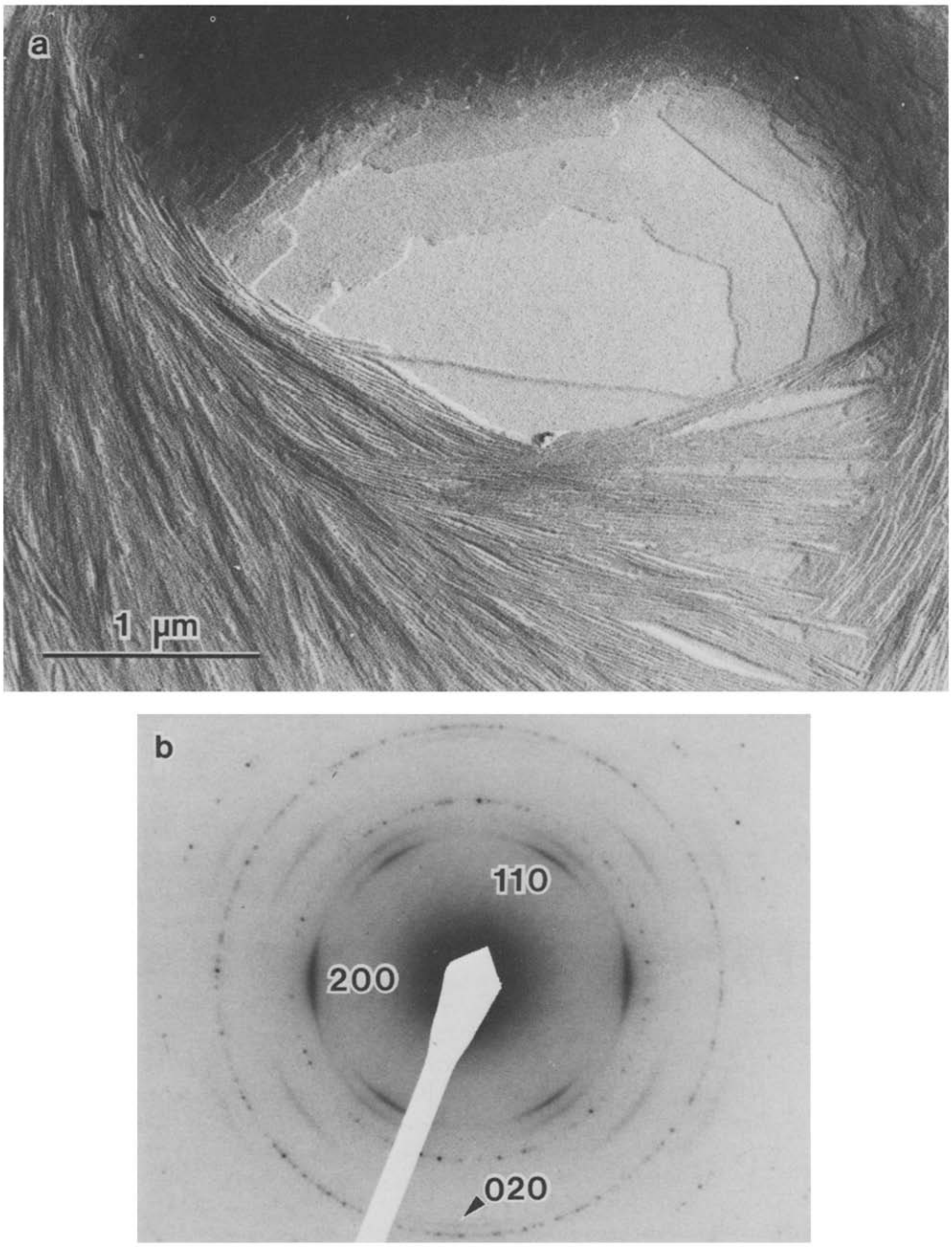

Figure 3 (a) Morphology of PPS melt-crystallized in thin films at 260°C, showing fine fibrosity due to lamellar orientation on edge, as well as large single crystals in a flat-on orientation. (b) Typical electron diffraction pattern from such flat-on crystals. The spotty rings arise from TlCl, evaporated on the specimen for internal calibration

Table 1 Comparison of intermolecular spacings for PPS

	Interplanar spacing (Å)		
Relfection	Ref. 5	Ref. 6	This work
200	4.36	4.28	$4.34_0 \pm 0.00_9$
110	4.73	4.68	$4.73_9 \pm 0.00_3$
020	2.81	2.79 (calc.)	$2.83_0 \pm 0.00_4$

DISCUSSION

Our direct electron diffraction determination of lattice spacings in PPS is unequivocal in terms of its relationship to the two previous reports[5,6]. However, such determination could not be attempted for most polymers because of the highly distorting effects of electron irradiation on their crystalline lattice[14,15]. Not only is crystallinity very rapidly lost due to free-radical formation and consequent crosslinking (although a few polymers undergo chain scission), but major, inhomogeneous, irreversible unit-cell expansion is commonly obtained *en route* to such amorphization. The best-studied case is that of polyethylene[14,15], where significant expansion of the *a*-axis (leading to hexagonal symmetry) is seen already at $\sim 30\,\mathrm{C\,m^{-2}}$, with full amorphization at $\sim 100\,\mathrm{C\,m^{-2}}$. If this were also the case for PPS, our values would not be reliable since they would reflect ongoing intermolecular expansion during electron microscopic observation and recording.

For this reason, we examined quantitatively the effects of electron dose on the crystallinithy and unit-cell structure of PPS. As expected from its aromatic nature, PPS is exceptionally stable to the effects of electron

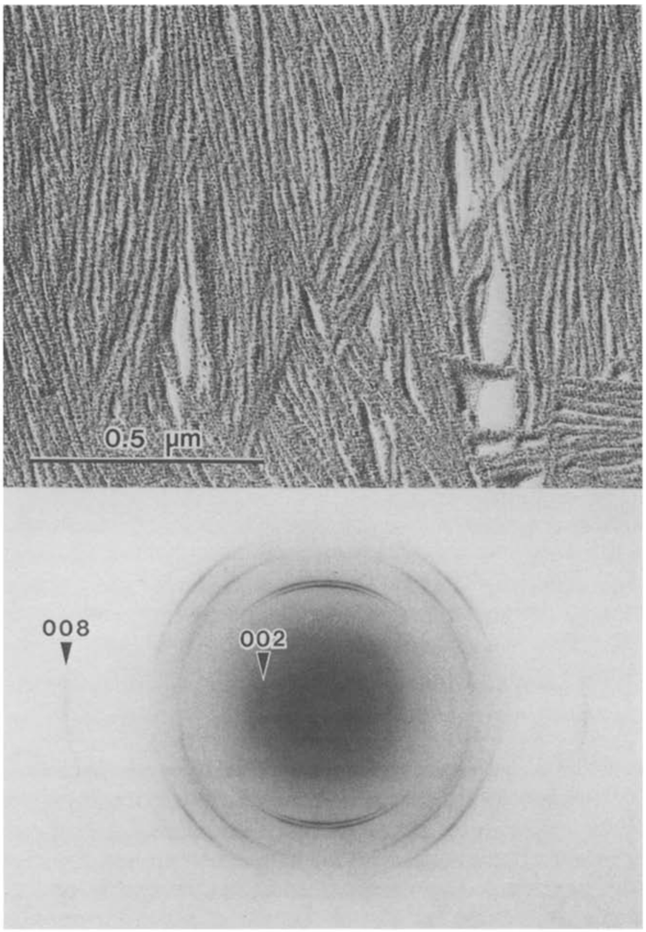

Figure 4 Electron micrograph and corresponding diffraction pattern from PPS lamellae grown on edge from the melt in a thin film at 265°C and exhibiting a combined single-crystal-like orientation

irradiation, maintaining its crystallinity to a dose of $3100\,\mathrm{C\,m^{-2}}$, i.e. over 30 times greater than that of polyethylene. In terms of dimensional changes of the PPS lattice during irradiation, our findings are summarized in *Figure 5*. The length of the b-axis is seen to remain essentially unchanged, while that of the a-axis exhibits a very small expansion. The d-spacing of the (1 1 0) planes shows intermediate behaviour, quantitatively consistent with that of the a- and b-axes, as seen by the near coincidence of the experimental and calculated lines in *Figure 5*. The largest effect of electron irradiation is thus seen to amount to a 0.01 Å expansion of the a-axis for every $170\,\mathrm{C\,m^{-2}}$. If we now take into account that all our diffraction patterns used for d-spacing measurements were recorded at electron doses of $\leqslant 20\,\mathrm{C\,m^{-2}}$, it becomes evident that our results are totally immune from the effects of irradiation.

CONCLUSIONS

The outstanding radiation stability of PPS has allowed us to obtain precise and accurate lattice dimensions from electron diffraction patterns. Single crystals and single-crystal-like aggregates were utilized for this purpose, allowing us to circumvent any conceivable problems related to bond distortion as a result of mechanical drawing. The axial dimensions calculated in this manner are $a = 8.68$ Å, $b = 5.66$ Å and $c = 10.26$ Å. Of the two different unit cells previously proposed[5,6], our results are in close agreement with that of Tabor and coworkers[5].

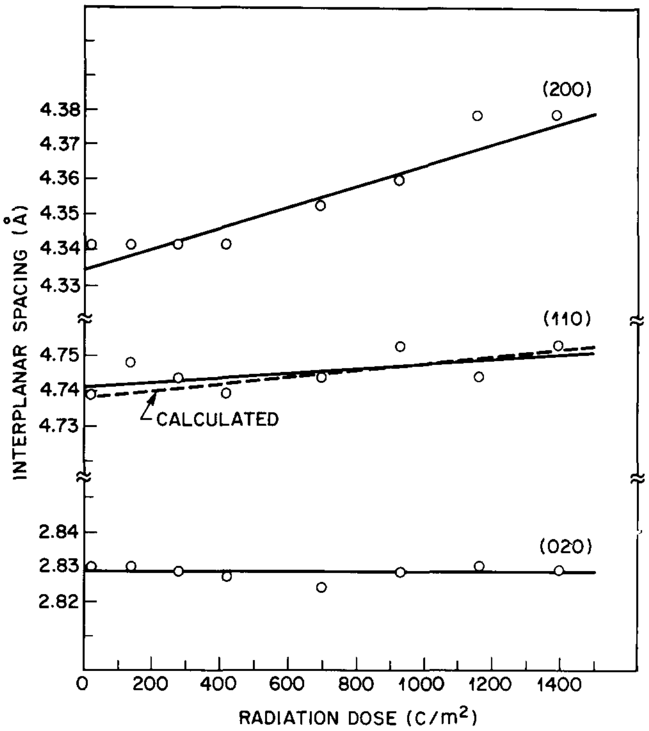

Figure 5 Variation of interplanar spacings of PPS with electron dose, showing the rates of lattice expansion during irradiation. The lines represent least-squares fits of the data. The broken line for (1 1 0) is calculated from the experimental lines for the (0 2 0) and (2 0 0) reflections

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