Variations in the crystal lattice of PEEK and related *para*-substituted aromatic polymers: 2. Effect of sequence and proportion of ether and ketone links

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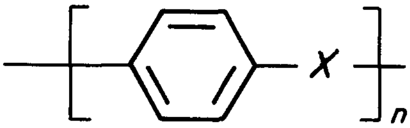
The crystal lattice constants have been measured for PEEK and the related aromatic polymers PEEKEK, PEK, PEEKK, PEKEKK and PEKK. Measurements were made on uniaxially oriented film samples using the 110, 200 and 020 reflections from X-ray equatorial scans to determine the *a* and *b* parameters and using the 006 and 008 from meridional scans to determine *c*. All polymers are able to crystallize with a PEEK type cell, although the *b* and *c* parameters increase with the proportion of ketone links. At higher ketone content a new crystal form is able to occur alongside the normal PEEK cell. The new cell was the dominant form in the PEKK sample. The new cell in PEKK is orthorhombic with parameters $a = 4.17 \pm 0.02$ Å, $b = 11.34 \pm 0.04$ Å, $c = 10.08 \pm 0.01$ Å and density 1.395 ± 0.008 g ml^{-1}. It is proposed that the new cell has the same symmetry, chain conformation and relative chain packing as the normal PEEK cell, but with *a* reduced and *b* enlarged.

(Keywords: *para*-substituted aromatic polymers; PEEK; PEKK; crystal lattice constants)

INTRODUCTION

Part 1[1] of this series dealt with the dimensional changes in the crystal lattice of the aromatic polymer PEEK resulting from thermal expansion. This second part is concerned with the variation in the lattice resulting from changing the sequence and proportion of the ether and ketone links in the chain. The general formula of the polymers in question can be represented by the repeating para-substituted aromatic motive:



where *X* can be either –O– for an ether link or carbonyl for a ketone link. Homopolymers of this type will comprise a regular repeating group sequence of these motives. Following the generally accepted nomenclature for PEEK, such a group sequence can be described by using E for the motive where *X* is an ether and K for the motive where *X* is a ketone. Using this scheme, *Table 1* lists the polymers that have been examined in the present study, together with their melting points. It should be emphasized that all these polymers have been synthesized to make all-*para* linked phenyl rings. In particular one should note that the polymer referred to as PEKK should not be confused with the polymer referred to by Chang[2]; this is described as PEKK but contains a proportion of *meta* linked phenyls and accordingly has a lower melting point (338°C) than the polymer examined in this present paper.

Early studies of the two polymers PEEK and PEK have shown that their basic crystal structures are almost identical[3]. The substitution of an ether by a ketone would appear to have a minimal effect on the positions and relative intensities of the dominant X-ray reflections. This has led to the adoption of a spatial sub-cell to describe the basic symmetry of the crystal[3–7]. The sub-cell contains two side by side chains, where the *c*-axis periodic repeat along each chain consists of average two phenyl motives. However more detailed examination does reveal differences in the diffraction from the polymers[4,5]. Apart from differences in the relative intensities of the main reflections, synchrotron radiation has been used to detect very weak reflections which can be indexed on the true spatial chemical repeat[8] (i.e. comprising six phenyl motives for PEEK). There are also differences in the position of the reflections due to small changes in the dimension of the lattice[3–5]. The present paper explores these small dimensional changes but also shows that in polymers containing a higher ketone content, there can be a more drastic change to an entirely different unit cell.

As with Part 1, the polymers have been examined in the form of unidirectional oriented tapes. This allows the unit cell parameters to be measured fairly directly by monitoring the strong *hk0* reflections (i.e. 110, 200, 020) using equatorial X-ray scans and the strong 00*l* reflections (i.e. 002, 006, 008) using meridional scans.

EXPERIMENTAL

Materials

Table 1 lists the polymers used in the study and also gives observed d.s.c. melting points obtained from reheat scans at 20°C min^{-1}.

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Table 1 List of polymers examined and their measured lattice parameters

Polymer	T_m (°C)	a (Å)	b (Å)	c (Å)	Cell volume (Å^3)	Density (g ml^{-1})
PEEK	335	7.76 ± 0.15	5.89 ± 0.1	9.95 ± 0.1	454.3	1.404 ± 0.005
PEEKEK	340	7.79	5.94	9.96	460.8	1.396
PEK	365	7.76	6.00	10.01	466.0	1.398
PEEKK	360	7.80	6.01	10.01	469.1	1.388
PEKEKK	370	7.74	6.04	10.05	469.9	1.403
PEKK	385	4.17	11.34	10.08	476.4	1.395

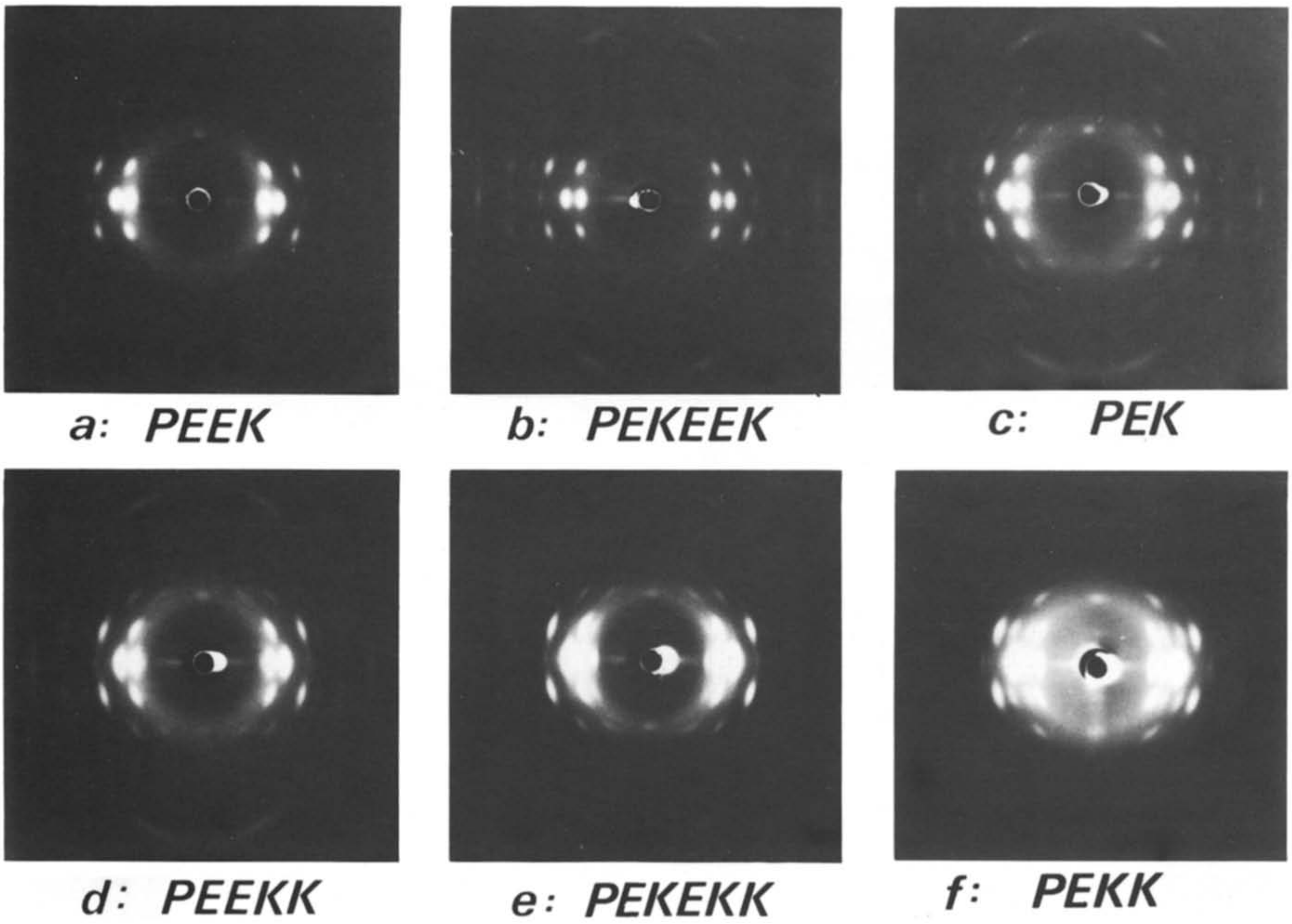
a: PEEK b: PEKEEK c: PEK
d: PEEKK e: PEKEKK f: PEKK

Figure 1 X-ray fibre pattern photographs of (a) PEEK; (b) PEEKEK; (c) PEK; (d) PEEKK; (e) PEKEKK; (f) PEKK

The oriented PEEK sample was prepared as in Part 1[1] from ICI's Victrex PEEK. The remaining polymers were available in smaller quantities. These were compression moulded at about 50°C above their melting points and then quenched into water to give amorphous films. Strips of these films were then oriented in a drawing frame where the drawing force was provided by a brass weight whose movement was damped by an oil dashpot. The temperature was gradually raised. At the glass transition of each polymer, the film sample necked and was drawn in a controlled way to a draw ratio of about 3:1. The films were then cooled and subsequently post annealed under uniaxial restraint in a steel jig.

X-ray measurements

The oriented films were examined in a Philips vertical goniometer in the symmetrical transmission mode using a slit configuration of 1/6°, 4°, 4°. Each sample was examined in turn with the draw axis parallel and then perpendicular to the goniometer axis in order to obtain the equatorial and then the meridional diffraction scans. The 2θ scale of the goniometer was calibrated using silicon powder dusted on adhesive film. X-ray fibre patterns were taken with a Unicam S25 circular camera.

Diffraction simulation

Use was made of the chain modelling software OSCA (developed by Dr A. H. Windle's group at Cambridge) to define the crystal structure of the new crystal cell. The software enables chains and crystals to be built and for the predicted fibre or powder X-ray patterns to be simulated.

RESULTS

X-ray photographs are illustrated in *Figures 1a–f*. *Figures 1a–e* are virtually indistinguishable and demon-

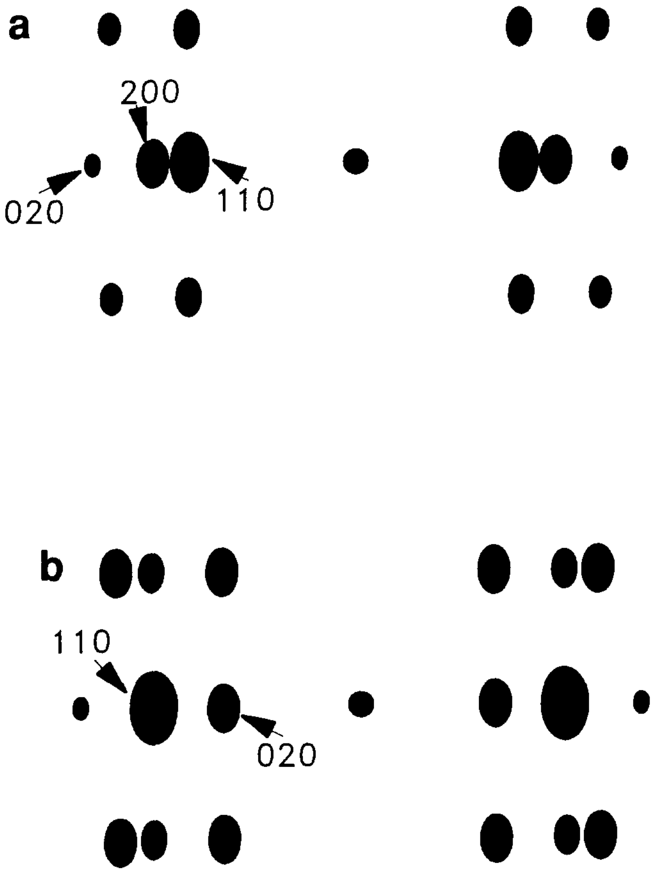

Figure 2 Schematic key to main reflections of fibre patterns. (a) PEEK; (b) new PEKK cell

strate the well established fact that from the viewpoint of the main diffraction spots the crystal structures are essentially identical; the ketone and ether groups can be effectively interchanged without affecting the main features of the cell and the pattern. The reflections in the photos can be indexed according to the sub-cell[2–6] as in the sketch in *Figure 2a*.

In the pattern for PEKEKK shown in *Figure 1e*, additional reflections occur that cannot be indexed with this standard sub-cell. The most notable extra reflection is on the equator inside the 110 spots. Higher exposure revealed that the extra spots are also present in the pattern of PEEKK. In the pattern for PEKK in *Figure 1f* the extra reflections become very pronounced. Their increase in intensity is accompanied by a corresponding decrease in the reflections associated with the normal PEEK cell. This suggests that they are in fact originating from an entirely NEW cell structure. The layer lines of the new reflections coincide with those of the normal cell and show that the fibre repeats and possibly the chain conformation are almost identical. Analysis of the new reflections suggests an orthorhombic cell with approximate parameters $a = 4.2$ $b = 11.0$ $c = 10$ Å, where the reflections can be indexed as in *Figure 2b*; the strong inner reflection being indexed as a 020.

Figures 3 and *4* respectively show the equatorial and meridional scans for the PEEK sample; they are typical of the scans obtained from the other polymers apart from PEKK.

These scans show respectively the dominant *hk0* and 001 reflections. As will be discussed below they can be used to obtain more accurate values for the lattice parameters than those measured from the X-ray photos.

Figure 5 illustrates the equatorial scan from the PEKK sample and shows the 020 and 110 reflections from the proposed new unit cell at around 15° and 22° respectively. There is also an 'impurity' reflection from the 110 reflection of the normal unit cell at around 19°. This scan and the (008) reflection from the corresponding meridional scan provide the following more refined estimates of the parameters for the new cell: $a = 4.17 \pm 0.02$ Å; $b = 11.34 \pm 0.04$ Å; $c = 10.08 \pm 0.01$ Å.

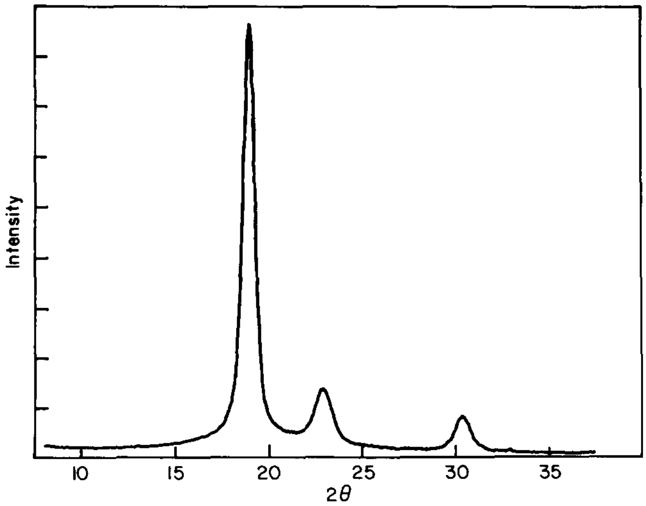

Figure 3 Equatorial scan for PEEK

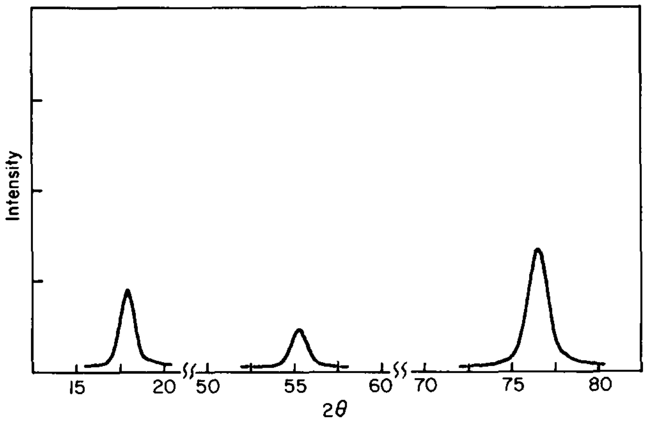

Figure 4 Meridional scan for PEEK

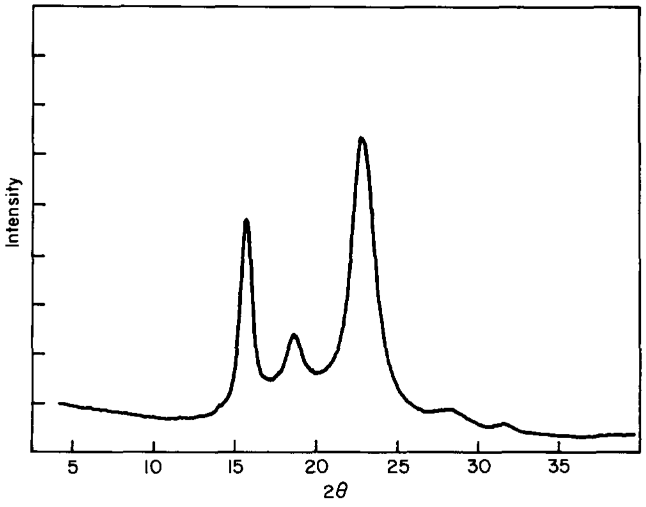

Figure 5 Equatorial scan for PEKK

DISCUSSION

New PEKK cell

Attempts have been made using the OSCA modelling software to determine the crystal structure of the new unit cell formed in the PEKK sample. Because the normal crystal cell is also present as a minority 'impurity', it is only feasible to propose the main features of the cell. The software was used to build chains into the above unit cell and then to predict diffraction patterns to compare with experimental information. Two experimental data were used for the comparison with the predictions; the oriented fibre pattern of the X-ray photo of *Figure 1* and the unoriented powder diffraction scan obtained from a melt crystallized sample shown in *Figure 6*.

Excellent agreement with the experimental data was obtained by using a trial unit cell based on the chain conformation that has already been established for the normal PEEK cell. Previous workers[4,6,7] who have studied the PEEK and PEK cells all agree that the chain confirmation is a planar zig-zag between the ether oxygen and ketone carbons, with the intervening phenyl groups torsionally rotated out of the zig-zag planes by alternate torsion angles of $\pm\Phi$. The consensus so far is that Φ is about 37°.

The projection of the normal PEEK cell looking along the *c*-axis is illustrated in *Figure 7*. The crystal structure we propose for the new PEKK cell is shown in projection in *Figure 8*. It has the same basic chain conformation as for PEEK, the same crystal symmetry and the same relative arrangement of the chains. The difference is that the *a*-axis has been considerably reduced and the *b*-axis expanded. The predicted fibre pattern is shown diagrammatically in *Figure 9*. The predicted powder pattern with simulated broadening is shown in *Figure 10*. The best match with the powder pattern was obtained with a smaller torsional angle of $\Phi = 25°$. Such a reduction in Φ could be the consequence of conformational adjustment to accommodate the close packing in the *a*-direction.

Effect of ketone/ether ratio on crystal lattice

The *a* and *b* dimensions of the normal PEEK cell in the polymer series have been deduced directly from the positions in the equatorial scans of the 200 and 020 diffraction peaks and are listed in *Table 1*. These values are totally consistent within experimental error with the observed positions of the corresponding 110 peaks, based on the assumption of an orthorhombic cell.

With the *c*-dimension of the sub-cells there is a problem in that the 002 meridional peak infers a value that is about 1% lower than the values deduced from the

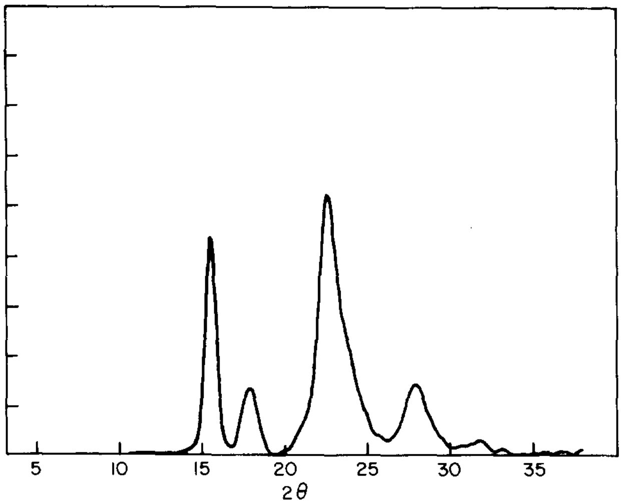

Figure 6 Diffraction scan for unoriented, melt crystallized PEEK, after subtraction of fitted amorphous curve

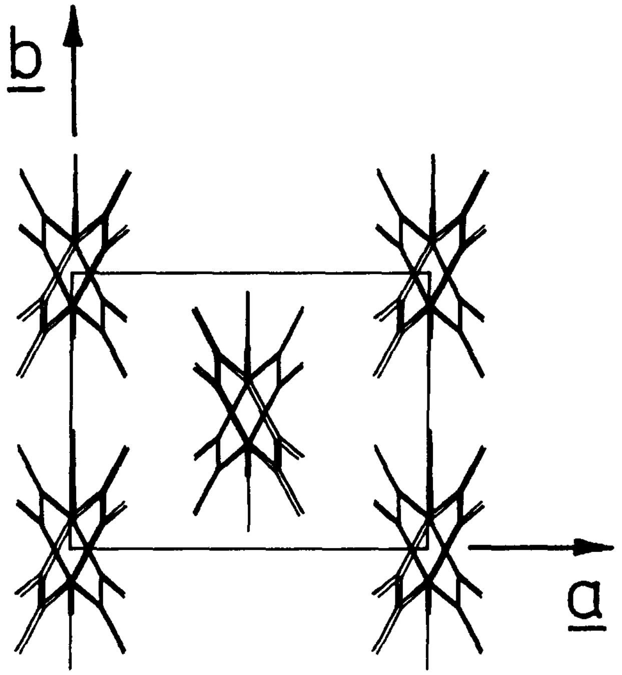

Figure 7 Projection along chain axis of the normal PEEK cell

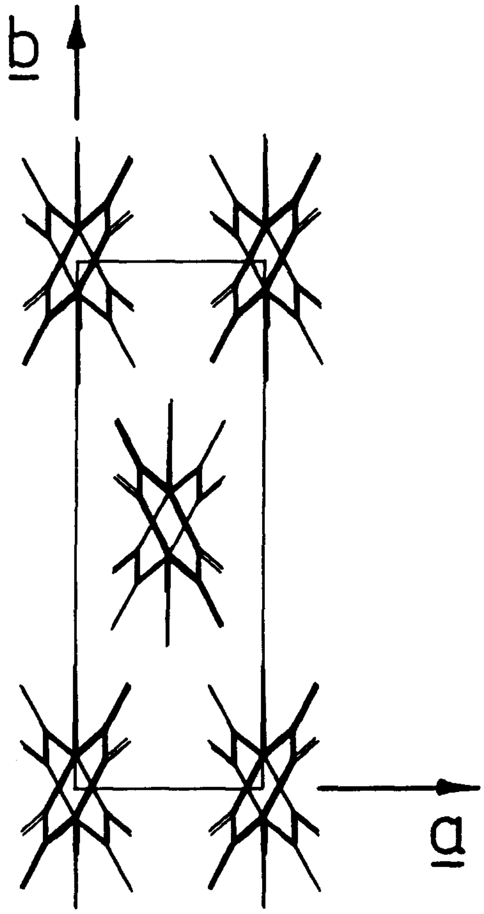

Figure 8 Projection along chain axis of the new PEKK cell

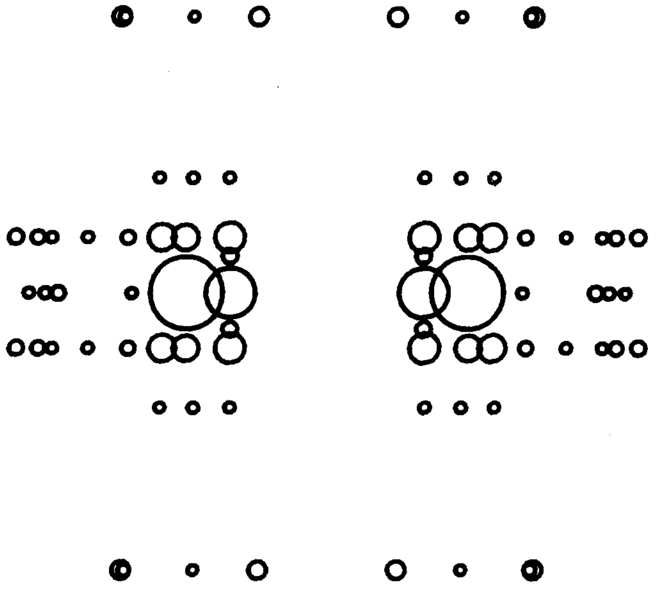

Figure 9 Predicted fibre pattern from proposed PEKK cell

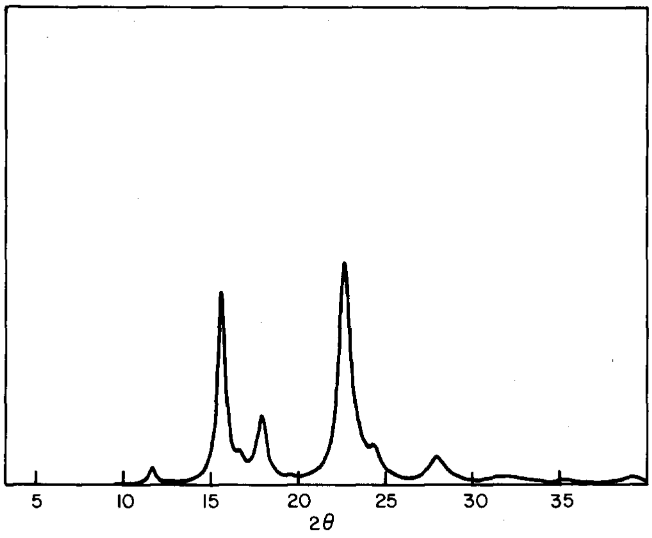

Figure 10 Predicted powder diffraction scan from proposed PEKK cell

position of the 006 and 008 reflections. For example, in the case of PEEK, our data give *c* dimensions of 9.85, 9.95 and 9.95 from the 002, 006 and 008, respectively. The discrepancy has also been noted for PEEK by Nakamae *et al.*[9] as part of their study of crystal elastic moduli. They also noted a discrepancy in the apparent crystal moduli and concluded the 008 value was more reliable. We have used the 006 and 008 peak positions to deduce the *c*-parameter in *Table 1*.

Before discussing these results, we should note the recent published data showing that the crystal cell of PEEK in its own right can vary according to the conditions of prior crystallization. Hay *et al.*[10] and Wakelyn[11] show that PEEK crystallized at high temperature (~320°C) can have a 2% smaller *a* parameter and a 1% smaller *b* parameter than when crystallized at low temperatures (~190°C). Thus, in order to achieve a valid comparison between different polymers, one must try to crystallize under comparable conditions. All the drawn samples in this present study were crystallized by annealing in the range 280–300°C except for the PEEK sample that was crystallized at 325°C. There may therefore be some influence from this effect in our results, particularly along the *a* direction.

The results for the *a* and *b* parameters, which are plotted in *Figures 11a* and *b* show a systematic 2.5% increase in *b* as the ketone/ether is raised whereas the *a* shows an uncorrelated overall scatter of about 1%. Although some of the fluctuation in *a* can be attributed to the small variations in crystallization conditions, the *b* variation is clearly closely related to the ketone content and is much larger than the effect of the crystallization conditions.

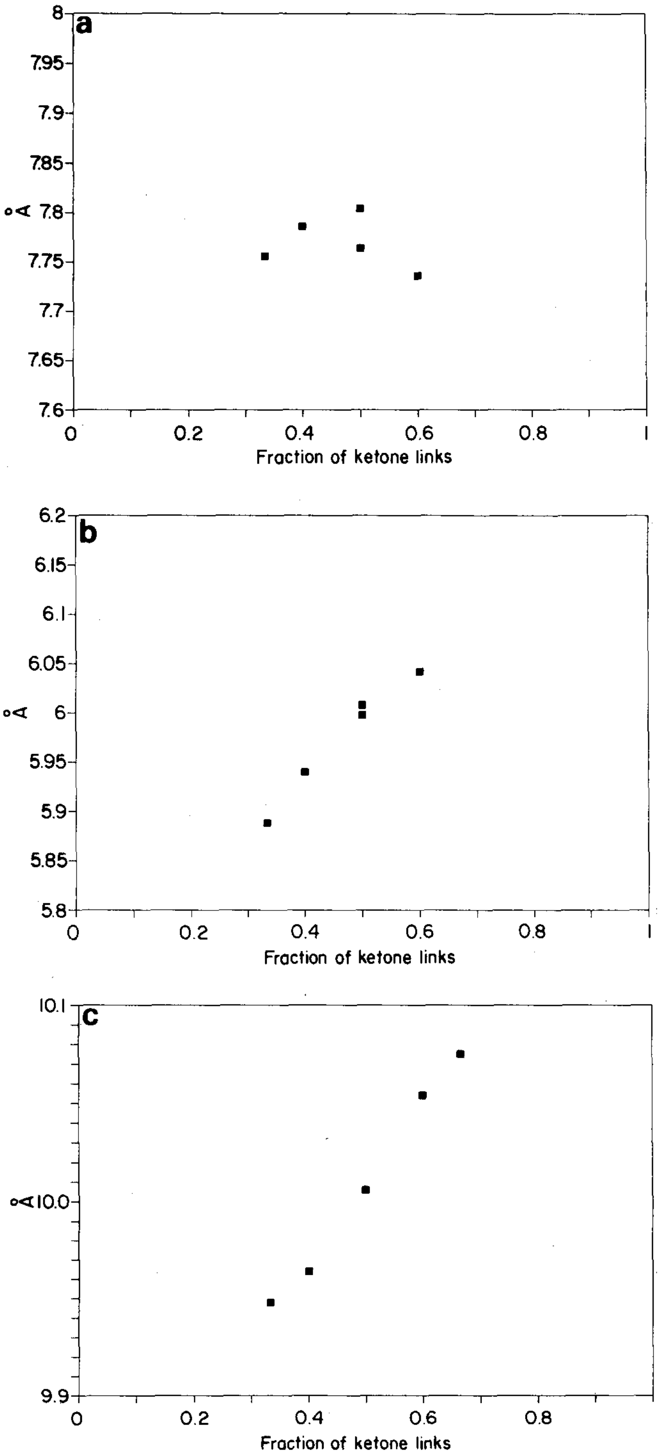

Figure 11 Variation of lattice parameters with ratio of ketone/ether links. (a) *a* Parameter; (b) *b* parameter; (c) *c* parameter

The picture that therefore emerges is that an increase in the proportion of ketone group causes neighbouring chains to be pushed further apart in the *b* direction whilst maintaining a similar spacing in the *a* direction. When the ketone/ether ratio reaches about two, as in the polymer PEKK, the *b*-parameter has expanded to a distance such that it becomes energetically more favourable for the chains to flip into an alternate packing regime of the above new cell. The change to a new cell is achieved without any significant change in the chain conformation, so that a transformation between cell structures could possibly be achieved with some ease. The close similarity of the cells of PEK and PEEKK shows that the sequence of ether and ketone links has little effect on the chain packing.

Figure 11c shows that there is also a systematic increase in the *c* parameter, which smoothly carries over to PEKK in the new cell configuration. This is directly relatable to the larger bond length for the ketone link. There is an increase in the cell volume which is predominantly due to the increase in *b* and *c* cell parameters. Interestingly however, the deduced crystal cell density remains almost unchanged. The mean density of all seven polymers in *Table 1* is 1.400 with a standard deviation of 0.006; this deviation could easily be accounted for by experimental errors and the small fluctuations brought about by differences in crystallization conditions of the sample.

It should be noted that the above change in shape of the main PEEK cell is predominantly along the *b* axis direction. This contrasts with the variation with crystallization conditions[10,11] and with the variation on thermal expansion[1] which occur predominantly along the *a*-axis direction.

CONCLUSIONS

Increasing the proportion of ketone links causes the basic PEEK cell to systematically expand in the *b* direction. The variation in the *a* direction is smaller and less systematic and is probably mainly a consequence of differences in crystallization conditions. The increase in the *c* chain repeat is quantitatively consistent with the longer bond lengths in the ketone link. The overall cell volume increases directly in relation to the increased mass associated with the ketone links and results in a minimal variation in the crystal density.

In the polymer PEKK which has the highest ketone content of the polymers examined, there is a preferential switch to a totally new cell which has the same relative arrangement of chains but with a much expanded *b* parameter and a much reduced *a* parameter.

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