polymer papers

The crystal structures of aryl ether ketone polymers containing *meta*-phenyl links

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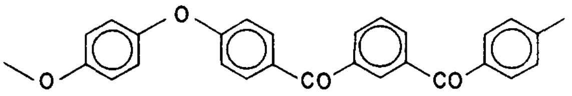
(Received 4 October 1991; accepted 13 January 1992)

The X-ray diffraction patterns have been examined from the crystalline aromatic ketone polymer PEEKmK (aryl ether ether ketone ketone polymer containing *meta*-phenyl links) with the formula:



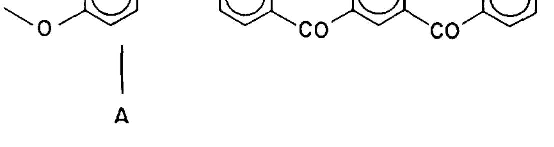
An orthorhombic crystal cell is proposed containing two chains with $a = 7.71$ Å, $b = 6.05$ Å and $c = 39.9$ Å. The lateral dimensions of the cell and the relative arrangement of chains is very close to that of the related all-*para*-phenyl polymer PEEK (poly(aryl ether ether ketone)). The *para*-linked phenyls are torsionally rotated out from the *bc* plane as in PEEK but the *meta*-phenyl ring remains parallel to the *bc* plane. The conformation of the *meta*-phenyl rings imposes an energy penalty, which contributes to the reduced melting point of the polymer.

(Keywords: aryl ketone polymers; *meta*-phenyl links; poly(aryl ether ether ketone); crystal structure)

INTRODUCTION

Aryl ether ketone polymers such as poly(aryl ether ether ketone) (PEEK) and poly(aryl ether ketone) (PEK) have become important as high-performance thermoplastics (e.g. 'Victrex' PEEK from ICI). Most of the polymers available in this class comprise phenyl rings linked via the 1,4 *para* positions. However, some of the reported polymers also contain 1,3 *meta* linked rings, either as a random link or as part of a regular homopolymer sequence. For example, the polymer material poly(aryl ether ketone ketone) (PEKK) from DuPont is reported to contain a minor proportion of EKK sequences where the phenyl between the two ketones is a *meta* link[1,2]. A recent paper by Gardner *et al.* describes a whole series of PEKK polymers ranging from the all-*para* to the all-*meta* polymers[3]. We have also reported observations on a related regular polymer denoted as PK99, which is made up of a sequence containing a biphenyl link as well as a *meta*-phenyl[4]. All of these *meta*-containing polymers, including the homopolymers, are able to develop reasonable levels of crystallinity.

The purpose of this paper is to report information on the conformation and packing of chains in crystals of homopolymers where the *meta*-phenyl occurs at regularly spaced intervals. The paper is focused on one particular polymer with the structure:



Using the same labelling scheme as for PEEK, this polymer will be referred to as PEEKmK (aryl ether ether ketone ketone polymer containing *meta*-phenyl links). PEEKmK has a T_g of 148°C and a melting point of 280°C. It also serves as a model for the previously reported polymer PK99, which has the same formula except that the phenyl ring denoted as A is replaced by a biphenyl link. The polymer has been prepared and crystallized in both the isotropic and uniaxially oriented forms. X-ray diffraction data from these samples have been compared with CERIUS diffraction modelling software (X-ray wavelength 1.5418 Å) in order to elucidate the crystal structures.

EXPERIMENTAL

The polymer PEEKmK was compression moulded and quenched to give an amorphous film 0.5 mm thick. A part of the film was annealed at 240°C for 1 h and then for a further period at 250°C to produce a crystalline isotropic film. The crystallized sample and the amorphous sample were examined with an X-ray diffractometer to obtain wide-angle X-ray scattering (WAXS) scans.

Another part of the amorphous film was drawn and annealed using the method in ref. 5 to produce a crystalline oriented strip. A cylindrical X-ray camera was used to obtain fibre pattern photographs. The oriented sample was also examined on a diffractometer to obtain meridional and equatorial X-ray scans[5].

The CERIUS diffraction modelling software (from Cambridge Molecular Design)* was used to build trial cells of the crystal structures and to produce simulated predictions of the powder and fibre patterns of the crystals.

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* Now renamed Molecular Simulations

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RESULTS

Curve A of *Figure 1* shows the WAXS scan of the isotropic crystalline sample. Curve B is a WAXS profile from the amorphous sample scaled to fit curve A. The difference between these two curves is shown in *Figure 2*; this should be a reasonable representation of the powder pattern from the crystalline part of the sample.

The fibre pattern photograph is shown in *Figure 3*. The main features of the pattern are very similar to that from the all-*para* polymers such as PEEK; the main difference is the greater number of sampled layer lines resulting from the longer repeat of PEEKmK. All the reflections can be indexed in terms of an orthorhombic unit cell. The equatorial diffractometer scan of the reflections on the zero layer line gives more accurate values of the spacings and indicates lateral cell parameters of $a = 7.71$ Å and $b = 6.05$ Å. The meridional diffractometer scan revealed five clear $\{0\,0\,l\}$ diffraction peaks corresponding to even values of $l = 2, 6, 8, 10, 18, 24$ and 32. These spacings give a chain repeat of $c = 39$ Å. It would require two chains per cell to achieve a realistic density for this cell.

These deduced lateral cell dimensions are close to those of the normal crystal cell of PEEK. In this respect it is worth noting that a second crystal form has been identified in aryl ketone polymers of the PEEK family[5]. This alternative crystal gives a distinctly different diffraction pattern from the standard cell and under suitable conditions can become the dominant crystal form in aryl ketone polymers with high ketone content[2,5]. However, it is the standard PEEK cell whose dimensions and patterns are similar to PEEKmK.

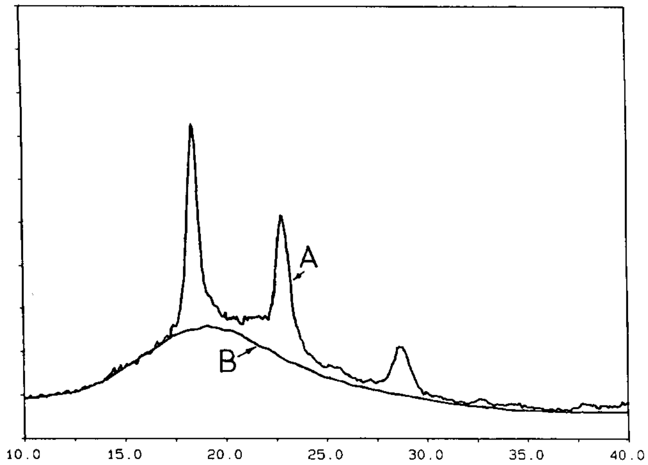

Figure 1 WAXS diffractometer scans of PEEKmK: curve A is from the isotropic, crystallized sample; curve B is a scaled version of the scan from the amorphous sample

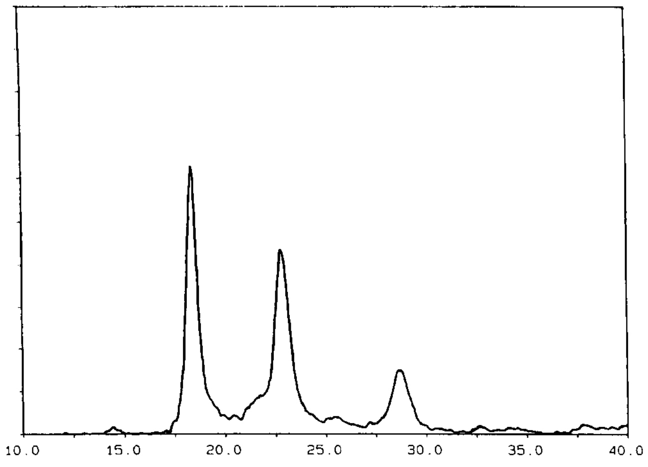

Figure 2 Crystal powder pattern for PEEKmK obtained from *Figure 1* by subtracting curve B from curve A

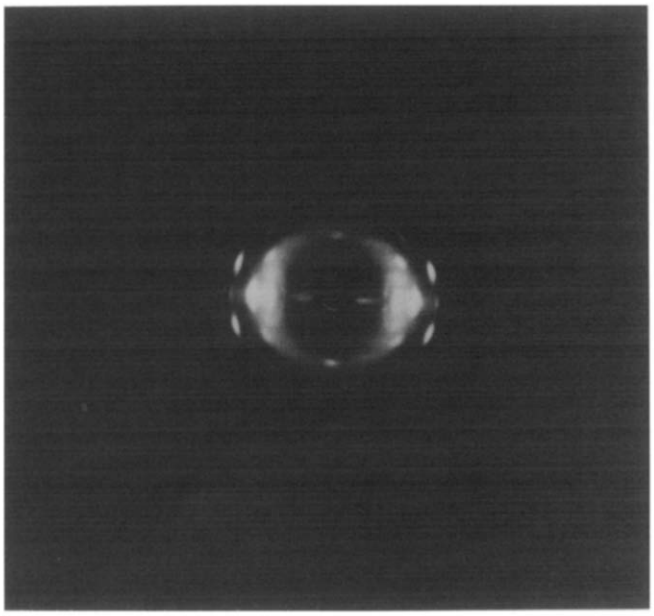

Figure 3 X-ray fibre pattern photo from drawn sample of PEEKmK

DISCUSSION

All of the all-*para*-phenyl polymers related to PEEK appear to be able to crystallize with a cell essentially identical to PEEK itself, there only being minor differences in the cell parameters[5]. The similarity of the diffraction patterns with that of PEEK suggests that the *meta*-phenyl-containing PEEKmK also has a closely related crystal structure. The crystalline chains in PEEK adopt a conformation where the *para* linkages drawn through the phenyl rings form a planar zig-zag parallel to the *bc* plane but where the phenyl rings are torsionally rotated out of the zig-zag plane alternatively by about +35° and −35° (ref. 6). If this torsional rotation were to occur on either side of the *meta*-phenyl rings in PEEKmK as well as for the *para* rings, then the linear simplicity of the chain would be destroyed. The most convenient way of obtaining a regular linear configuration in PEEKmK is for the *meta*-phenyls to remain parallel to the zig-zag plane. This type of chain conformation produces a spatial chain repeat very close to the 39.9 Å crystal repeat deduced from the experimental diffraction patterns.

Figure 4 shows a cell of two chains with this conformation; the second chain in the cell has a mirror symmetry of the first. The cell dimensions are those deduced above from the experimental data. *Figures 5* and *6* show predictions of the powder and fibre patterns for this cell. The agreement with the experimental data in *Figures 2* and *3* is good. The agreement is, however, not perfect. In particular, the observed fibre pattern shows faint $\{1\,0\,l\}$ that are not in the predicted pattern, suggesting further refinement is needed, probably involving a rotation of the chain in the cell.

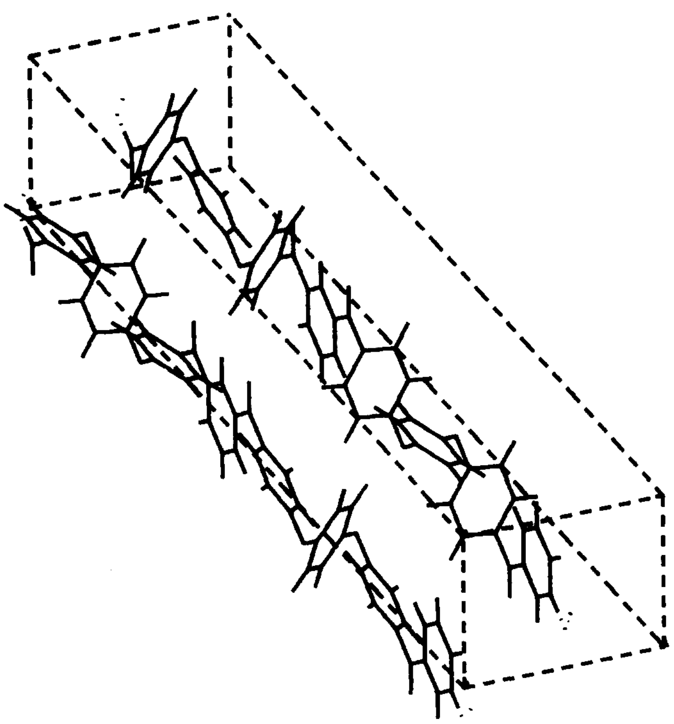

Figure 4 Proposed crystal cell for PEEKmK

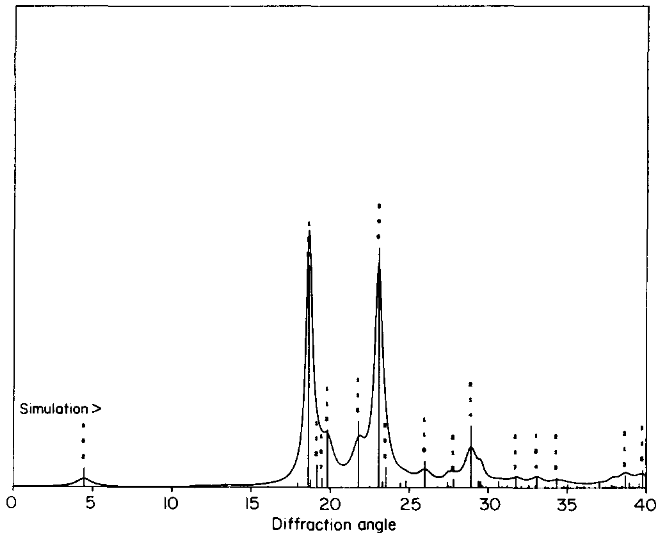

Figure 5 Predicted powder pattern for PEEKmK

The conformation of the chains in this cell involves the two *para*-phenyl rings on each side of the *meta*-phenyl torsionally rotating in the same sense relative to the *meta*-phenyl and gives rise to a mirror plane perpendicular to the *c* axis. There is an alternative related chain conformation shown in the cell in *Figure 7*, where the *para*-phenyls are rotated in the opposite sense and where the mirror reflection is converted into a glide reflection. Both these cells incorporate identical conformations at the ketone links and will therefore be associated with essentially identical torsional bond energies. They also have an identical spatial chain repeat consistent with the observed periodicity of 39 Å. The predicted powder and fibre diffraction patterns for a cell with the alternative conformation are very similar to those of the above cell and are shown in *Figures 8* and *9* respectively. There is, however, an important difference. The first cell shows an intensified {2 1 4} reflection whereas in the second cell this is replaced with an intensification of the {2 1 3} and {2 1 5} reflections. The experimental data from both the fibre and powder patterns more closely resemble the first cell, indicating this to be the better model of the structure of the crystal.

This preferred cell is in fact analogous to that suggested earlier for the polymer PK99 where the phenyl between the ether links is replaced by a biphenyl[4]. It is a further confirmation that the *meta*-phenyl units are incorporated into the crystals with the phenyl plane parallel to the zig-zag plane of the chain backbone. One important

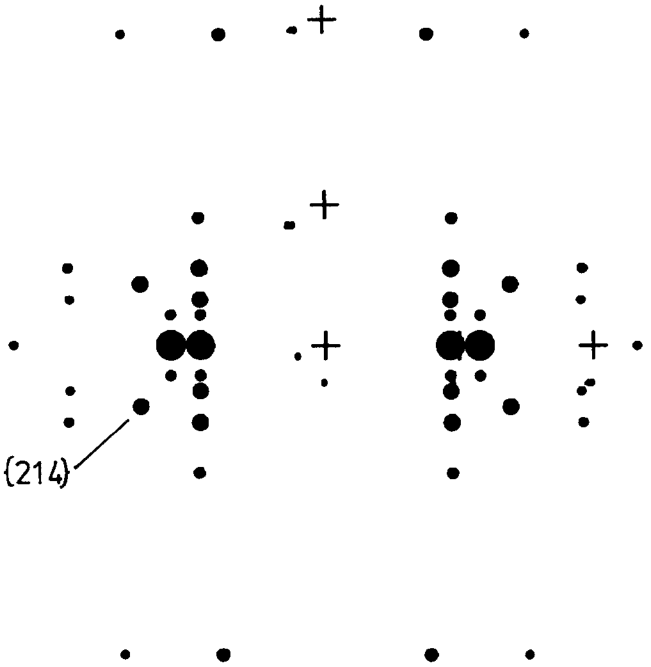

Figure 6 Predicted fibre pattern for PEEKmK

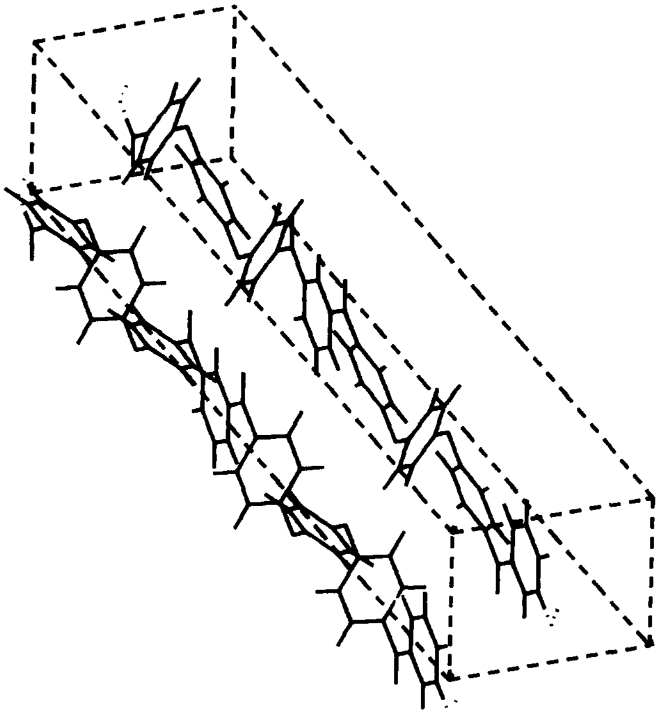

Figure 7 Alternative cell with related chain conformation

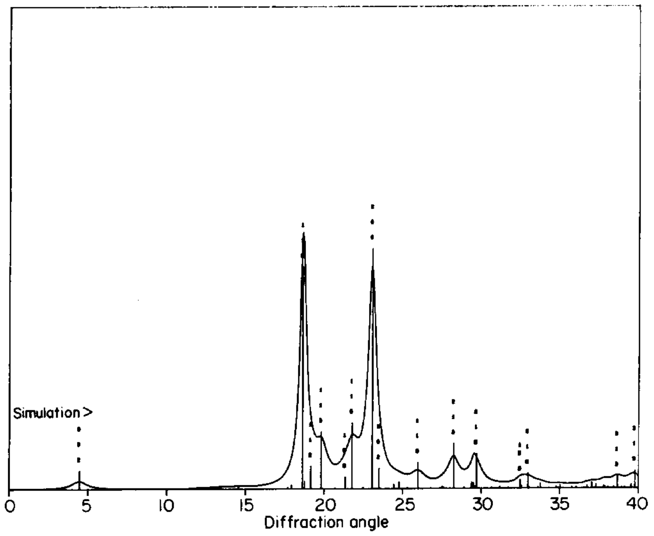

Figure 8 Predicted powder pattern for cell containing chain conformation of *Figure 7*

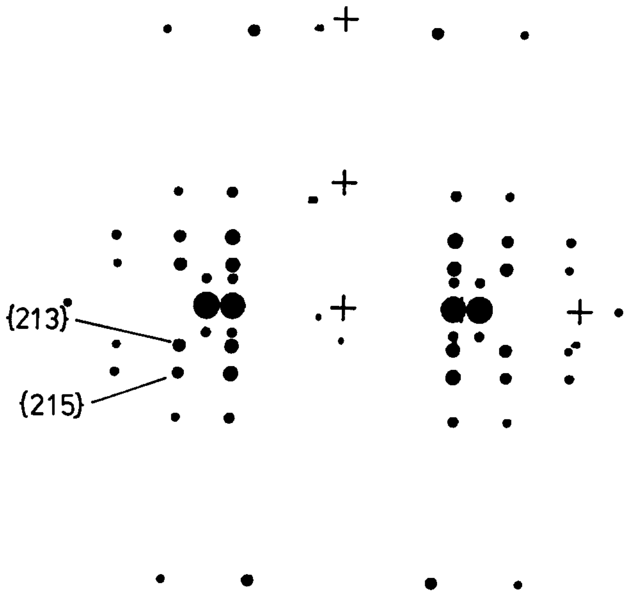

Figure 9 Predicted fibre pattern for cell containing chain conformation of *Figure 7*

consequence of this is that the rings bordering each ketone represent a higher energy conformation than in the corresponding pure *para* polymers. Molecular modelling calculations indicate that the extra energy involved is about 1.7 kcal mol^{-1} for each ketone link. Thus when these *meta*-phenyl-containing polymers crystallize they must incur an energy penalty relative to their all-*para*-phenyl analogues. In the case of PEEKmK this could contribute to a reduction of up to about 35 J g^{-1} in the enthalpy of fusion. This would be expected to be manifested as a reduction in melting point and in the crystallization rate relative to the all-*para*-phenyl polymer. In fact, the analogous polymer PEEKK melts 80°C higher than PEEKmK at 360°C[5].

This energy penalty has already been invoked to explain the unusual melting and crystallization effects in the polymer PK99[4].

CONCLUSIONS

A comparison between the experimental and predicted diffraction patterns of PEEKmK suggests a crystal cell that has a similar chain packing to the cell of PEEK but where the plane of the *meta*-phenyl ring is parallel to the *bc* plane of the backbone zig-zag. This conformation will incur an energy penalty compared with the all-*para*-phenyl analogue polymer and would explain the observed relatively low melting point of PEEKmK.

Two similar chain conformations are feasible for the PEEKmK cell, but the diffraction evidence favours that in *Figure 4*, where the *para*-phenyls bordering the *meta*-phenyl torsionally rotate in the same sense relative to the intervening *meta* ring.

ACKNOWLEDGEMENTS

I wish to thank my many colleagues who have contributed to the work on aromatic ketone polymers, in particular P. A. Staniland for providing the polymer, A. B. Newton for making the oriented sample, and J. Kendrick and M. King for calculations and advice on the energetics of the conformations.

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