Refinement of the structure of PEEK fibre in an orthorhombic unit cell

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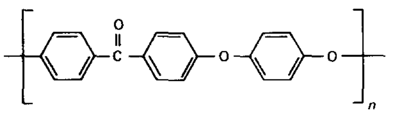
The crystalline structure of oriented fibres of poly(ether-ether-ketone) (PEEK) has been analysed by X-ray diffraction and refined by the 'linked-atom least-squares' procedure. The conformation of chains, consisting of a six-aryl ring unit, is approximated by the refinement of a two-aryl ring unit within the orthorhombic unit subcell with dimensions: $a = 7.83 \pm 0.02$ Å, $b = 5.94 \pm 0.01$ Å and $c = 9.86 \pm 0.04$ Å. Certain constraints imposed by Pbcn space group symmetry are relaxed during refinement. The results of the two-ring refinement indicate that a single torsion angle can be used to describe the conformation of the six-ring unit. The torsion angle corresponds to the average tilt of the phenylene rings out of the (100) face, and the best fit is obtained with an angle of 37°. The simulated powder diffraction pattern based on the atomic coordinates of the six-ring unit matches very closely previously reported patterns for a variety of PEEK specimens. The analysis supports and extends to oriented fibres the previously reported finding that space group Pbcn is a valid representation for the structure of PEEK.

(Keywords: poly(ether-ether-ketone); X-ray diffraction; fibre patterns; structural refinement; powder pattern)

INTRODUCTION

Crystalline and amorphous poly(aryl-ether-ether-ketone) (PEEK), having the following chemical composition



is a promising engineering thermoplastic polymer with important structural applications. Recent papers have reported the unit cell structure of various PEEK specimens, including oriented heat treated fibres$^{1-5}$. These papers point to the similarity of the unit cell dimensions and chain conformation as confirming evidence that the Pbcn space group and unit cell structure for poly(phenylene oxide) (PPO) is a good model for PEEK^{6}. The manner in which the chains pack in the crystallite regions is, however, an aspect of the PEEK structure that has been somewhat more difficult to characterize. As depicted in *Figure 1*, the c-axis fibre repeat extends over two aryl units, while the chemical repeat encompasses three aryl units, suggesting a disordered structure in which the ether and ketone groups are crystallographically equivalent. The disorder might be viewed in terms of an irregular sequence of ketone and ether linkage groups along the polymer chain. Additional axial chain stacking irregularity would further complicate the disorder picture. Another viewpoint assumes no inherent irregularity in the sequence of linkage groups, but is based on an irregular packing of neighbouring chains. Depending on factors such as the degree of crystallinity and density, the arrangement of neighbouring chains could range from one of random stacking of adjacent ketone and ether groups to one in which the stacking is more perfect.

The paper reports the refinement of the structure of crystalline PEEK fibre in an orthorhombic unit cell using the 'linked-atom least-squares' (LALS) technique^{7}. Where possible, the symmetry constraints of space group Pbcn have been maintained. The conformation and packing of chains are approximated by refinement of the two-ring unit within a unit subcell. The volume of the subcell is one-third the volume of the Pbcn unit cell. It is concluded from the results of the refinement of the two-ring unit that a single torsion angle can be used to describe the conformation of the six-ring unit.

EXPERIMENTAL

Materials

Heat treated monofilament of diameter 0.2 mm was obtained from Albany International, Homer, New York. The density of the fibre was measured by flotation in a toluene–carbon tetrachloride mixture, and also by the buoyancy method by immersing the sample in toluene.

X-ray photography

X-ray diffraction photographs were obtained from precession and 28.6 mm radius single crystal cylindrical

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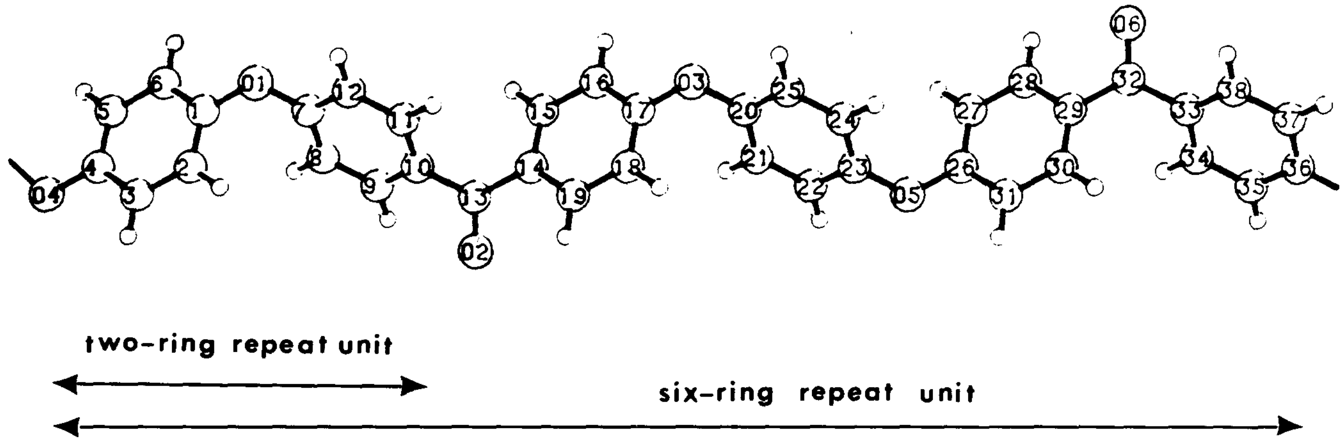

Figure 1 Atom numbering scheme of carbon atoms for the two- and six-ring repeat units. Hydrogen atoms are numbered according to the carbon atoms to which they are attached

cameras employing Ni-filtered CuKα radiation. A bundle of 3 monofilaments furnished sufficient sample mass to provide reasonable exposure times. Photographs were recorded with various exposure times in order to bring all reflections into the correct range of optical density.

The diffraction patterns were indexed in terms of an orthorhombic unit cell. Accurate unit cell dimensions were obtained by a least-squares refinement of the *d*-spacings of 15 diffraction peaks on precession photographs.

Intensity measurements

Fibre rotation photographs were scanned on an Optronics Photoscan P1000 microdensitometer. The instrument records the optical density (*OD*) at each point on the film as a binary integer on magnetic tape. The digitized patterns were then processed by the computer program PHOTO[8]. The peak volume option gave a number representing the integrated intensity of each peak. A background correction was made for each peak by averaging the *OD* at the four corners of a box enclosing the peak. The peak volume versus exposure time plot was found to be linear to approximately $OD = 1.5$. However, to ensure that the measurements corresponded to the linear portion of the plot, only peak volume measurements on peaks with $OD = 1.0$ or less were used. Reflections which could not be resolved were treated as an overlapping group. Lorentz and polarization corrections were applied directly to the peak volume data. Structure factors were derived from $F_{\mathrm{obs}} = (I/LP)^{1/2}$.

RESULTS

X-ray analysis and density measurement

The fibre rotation and precession photographs are shown in *Figure 2*. The unit cell parameters $a = 7.83 \pm 0.02$ Å, $b = 5.94 \pm 0.01$ Å and $c = 9.86 \pm 0.04$ Å are in good agreement with previously reported values[2,3]. They refer to the subcell, which contains the two-ring unit of *Figure 1*. The dimensions deduced for the complete Pbcn unit cell are identical to those of the subcell, except that the *c* dimension is tripled (29.58 Å). The *c*-axis is 1 Å less than the value (30.50 Å) reported by Wakelyn for various powder specimens[5].

The crystal density based on the subcell dimensions and an average molecular weight of 192.2 daltons is 1.392 g cm^{-3}. The calculated crystal density based on the

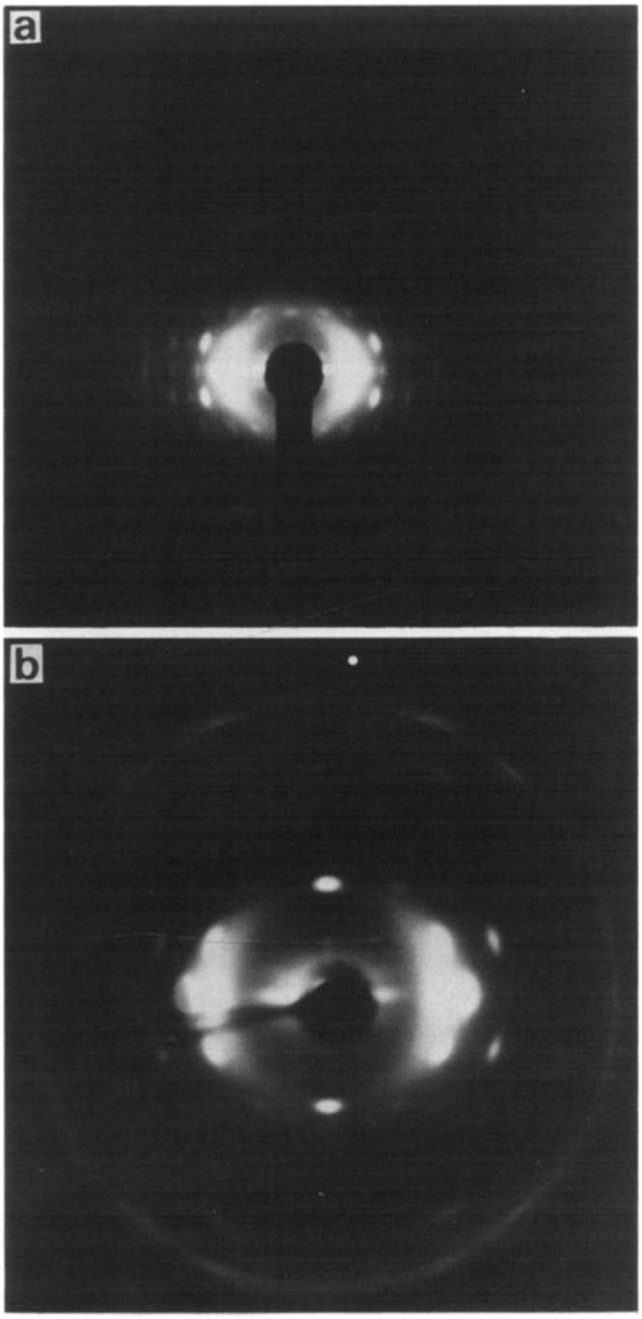

Figure 2 (a) Fibre rotation photograph, CuKα radiation, camera radius 28.6 mm; (b) precession photograph, zero layer screen, $\mu = 25°$, CuKα radiation, sample to film distance 6.0 cm. The fibre direction is vertical in both photographs

unit cell parameters of Rueda *et al.*[2] is 1.415 g cm^{-3}, and 1.400 g cm^{-3} for the cell of Dawson and Blundell[1]. The monofilament fibre density measured 1.298 ± 0.005 g cm^{-3} by the flotation method and 1.296 ± 0.005 g cm^{-3} by the buoyancy method. Experimental densities are reported to vary from 1.264 g cm^{-3} for quenched amorphous specimens to 1.314 g cm^{-3} for oriented samples[1,2]. A linear extrapolation has yielded 1.378 g cm^{-3} for the crystal density[3].

Refinement of the two-ring unit

The small quantity of diffraction data (20 observed peaks) coupled with the rather large number of chain conformational torsion angles precluded the refinement of the six-ring unit (*Figure 1*). The strategy adopted to obtain the initial orientation of the phenylene rings involved the refinement of the two-ring unit, positioned within the unit subcell described above. Two phenylene rings connected by alternating ether and carbonyl links comprise the two-ring unit. The ratio of the respective site-occupancy factors (s.o.f.) for these linkage groups was held fixed at either 1:1 or 2:1. The latter ratio served to represent a disordered chain in which the composition of the crystallographic repeat matched the known chemical repeat of the polymer. The initial trial model for the LALS method was constructed using the following literature values for bond distances and angles:[3,9]

C——O	1.36 Å	C——O——C	125°
C══O	1.23 Å	C——CO——C	125°
C——CO	1.47 Å		
C┄┄C	1.395 Å		

Two chains, related by a 2/1 screw axis and aligned along the *c*-axis, were placed in the subcell with the centre of the phenylene ring of one chain at the origin. Refinement was effected by varying the chain conformation angles t_1–t_5 and the orientation of the chain within the subcell. Angles t_3 and t_5 were constrained so that their initial difference was always zero degrees in order to maintain 2-fold rotational symmetry along the carbonyl bond. Refinement was terminated when the *R*-index, $R=\frac{\sum|F_0-F_c|}{\sum|F_0|}$, did not change on successive cycles. The results are summarized in *Table 1*. The function minimized in the least-squares procedure contained terms which represented the deviations of the calculated interatomic distances from the desired values. The coincidence constraints between pairs of atoms related by translational symmetry along *c* were also included. Throughout the refinement the isotropic temperature factor remained fixed at $B=6.0$ Å^2. The angle *t* is defined as follows: If the section of chain C2–C1–O1–C7 is viewed from C7 down the O1–C1 bond, then t_1 is positive if clockwise rotation of the front bond (C7–O1) brings it into eclipsed configuration with the back bond (C1–C2).

Table 1 Results of the refinement of the two-ring unit

	t (degrees) S.o.f. ratio (ether/ketone)	
Torsion angle	1:1	2:1
t_1 C7–O1–C1–C2	45.3	44.3
t_2 C8–C7–O1–C1	37.5	43.9
t_3 O2–C13–C10–C9	−38.6	−37.7
t_4 C14–C13–C10–C9	138.6	132.5
t_5 C15–C14–C13–C10	−38.6	−37.7
R-index (%)	27.0	24.6

The refinement of the disordered chain gave the expected improvement in the *R*-index; however, the average of the magnitudes of t_1, t_2 and t_3 changed only slightly. The shortest intermolecular contact for the 1:1 calculation was 2.52 Å between atoms O2 and H8 on chains related by the 2/1 screw axis. The contacts for the disordered calculation were normal, except for one very short contact (1.64 Å) involving the disordered carbonyl oxygen atom. With standard deviations as large as 3° for *t*, the differences between the magnitudes of t_1, t_2 and t_3 were hardly significant at this level of refinement. For the 1:1 calculation the average tilt of the phenylene rings out of the (100) face was 40°. Hay *et al.*[3] arrived at the same value for crystalline PEEK by employing a procedure adopted by Rietveld of fitting the wide-angle diffraction pattern[10]. The sum of the magnitudes of t_3 and t_4 for the 1:1 calculation approaches 180°, which strongly suggested that the ring carbon atoms attached to the ketone and ether oxygen atoms do not deviate significantly from the (100) face. Such deviations would still be consistent with Pbcn symmetry. A similar conclusion may be drawn for the 2:1 calculation even though the sum of t_3 and t_4 of 170° makes the argument less convincing. Thus the planar zig-zag geometry of C–O–C and C–OC–C links is restricted to the (100) face. This arrangement is now carried over to the refinement of the six-ring unit.

Conformation of the six-ring unit

Based on the results of the two-ring refinement a single torsion angle *t* was used to describe the conformation of the six-ring unit (*Figure 1*). The initial placement of the chains followed the description of Wakelyn[5]. The *R*-index was computed for a range of fixed *t* values. The variables which remained to be refined were the angles defining the inclination of the molecule within the unit cell, and a scale

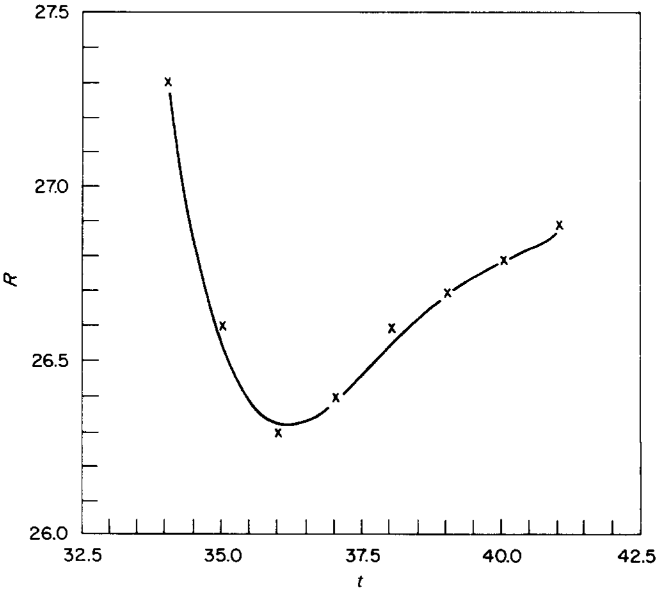

Figure 3 Plot of *R*-index *versus t*

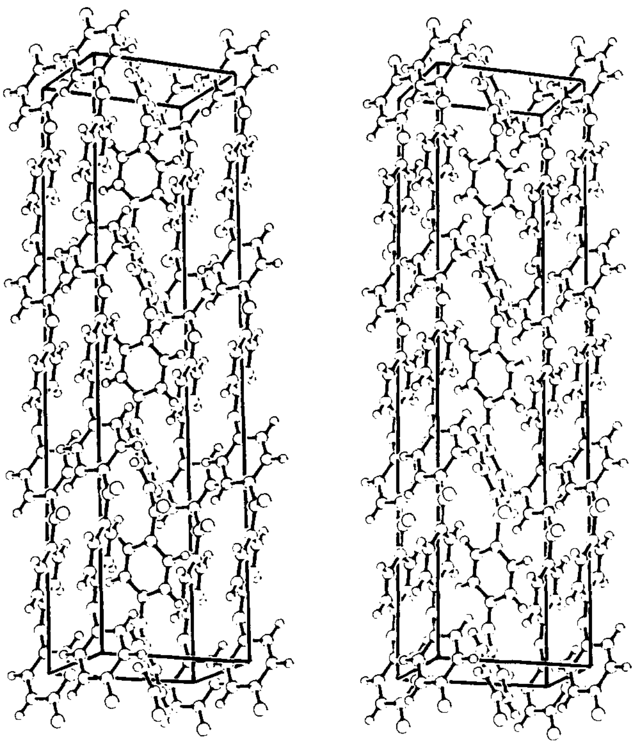

Figure 4 Stereodiagram of unit cell viewed down the negative *b*-axis

Table 2 Observed and calculated *d*-spacings and structure amplitudes (×10)

h	*k*	*l*	d_0^* (Å)	d_c (Å)	F_0	F_c
1	1	0	4.75	4.72	2707	2153
1	1	3	4.29	4.26	1430	1042
1	0	6	4.17	4.17	583	483
2	0	0	3.96	3.93	2248	2528
1	1	6	3.42	3.41	496	356
2	1	3	3.09	3.10	1075	563
0	2	0	2.98	2.98	912	557
1	1	9	2.73	2.72	434	352
2	1	6	2.72	2.72	633	592
1	2	3	2.66	2.67	542	659
3	1	0	2.39	2.39	482	430
2	2	0		2.36		
3	1	3	2.31	2.32	868	913
2	2	3		2.30		
2	1	9	–	2.32	231	357
3	0	6	–	2.31	201	450
1	1	12	–	2.18	971	601
1	3	0	–	1.92	799	668
0	2	12	–	1.90	949	800
1	3	3	–	1.88	1051	634
3	2	3	–	1.92		
1	3	6	–	1.79	245	27
2	2	12	–	1.70	556	417
3	1	12	–	1.72		

* d_0 values were measured from precession photographs

factor. Even though space group symmetry requires the carbonyl function to coincide with the 2-fold rotation axis at (0,*y*,1/4), the restriction was relaxed and the molecule was allowed to rotate freely about the *c*-axis. As measured by the difference of the *x* coordinates of atoms C13 and O2, no significant deviation (approximately 0.1 Å) of the carbonyl bond from the rotation axis was observed. The smallest deviations were observed when *t* was in the range 37°–40°. The variation of the *R*-index with *t* is illustrated in *Figure 3*. The minimum is fairly broad and *t* of 37° was considered the best fit based on the minimum in the *R*-index and the extent of deviation of the carbonyl bond from the 2-fold axis. The uncertainty in *t* was estimated to be about 3°. A stereodiagram of the unit cell is shown in *Figure 4*. Observed and calculated *d*-spacings and

Table 3 Fractional atomic coordinates of the six-ring unit for the case where $t = 37°$

Atom	*x*	*y*	*z*
O1	0.021	−0.212	0.082
O2	−0.042	0.426	0.251
O3	0.021	−0.212	0.419
O4	−0.021	0.212	−0.082
O5	−0.021	0.212	0.584
O6	0.042	−0.426	0.752
C1	0.011	−0.107	0.042
C2	0.083	0.104	0.036
C3	0.072	0.211	−0.006
C4	−0.011	0.107	−0.042
C5	−0.083	−0.104	−0.036
C6	−0.072	−0.211	0.006
C7	0.011	−0.107	0.123
C8	−0.100	0.073	0.129
C9	−0.111	0.180	0.171
C10	−0.011	0.107	0.207
C11	0.100	−0.073	0.201
C12	0.111	−0.180	0.159
C13	−0.022	0.220	0.251
C14	−0.011	0.107	0.295
C15	−0.083	−0.104	0.301
C16	−0.072	−0.211	0.342
C17	0.011	−0.107	0.378
C18	0.083	0.140	0.372
C19	0.072	0.211	0.331
C20	0.011	−0.107	0.460
C21	−0.100	0.073	0.465
C22	−0.111	0.180	0.507
C23	−0.011	0.107	0.543
C24	0.100	−0.073	0.537
C25	0.111	−0.180	0.495
C26	−0.011	0.107	0.624
C27	−0.083	−0.104	0.630
C28	−0.072	−0.211	0.672
C29	0.011	−0.107	0.708
C30	0.083	0.104	0.702
C31	0.072	0.211	0.660
C32	0.022	−0.220	0.752
C33	0.011	−0.107	0.796
C34	−0.100	0.073	0.802
C35	−0.111	0.180	0.843
C36	−0.011	0.107	0.879
C37	0.100	−0.073	0.873
C38	0.111	−0.180	0.832
H2	0.143	0.180	0.062
H3	0.125	0.364	−0.010
H5	−0.143	−0.180	−0.062
H6	−0.125	−0.364	0.010
H8	−0.173	0.126	0.103
H9	−0.191	0.310	0.175
H11	0.173	−0.126	0.226
H12	0.191	−0.310	0.155
H15	−0.143	−0.180	0.275
H16	−0.125	−0.364	0.346
H18	0.143	0.180	0.398
H19	0.125	0.364	0.326
H21	−0.173	0.126	0.440
H22	−0.191	0.310	0.511
H24	0.173	−0.126	0.563
H25	0.191	−0.310	0.491
H27	−0.143	−0.180	0.604
H28	−0.125	−0.364	0.676
H30	0.143	0.180	0.728
H31	0.125	0.364	0.656
H34	−0.173	0.126	0.776
H35	−0.191	0.310	0.848
H37	0.173	−0.126	0.899
H38	0.191	−0.310	0.828

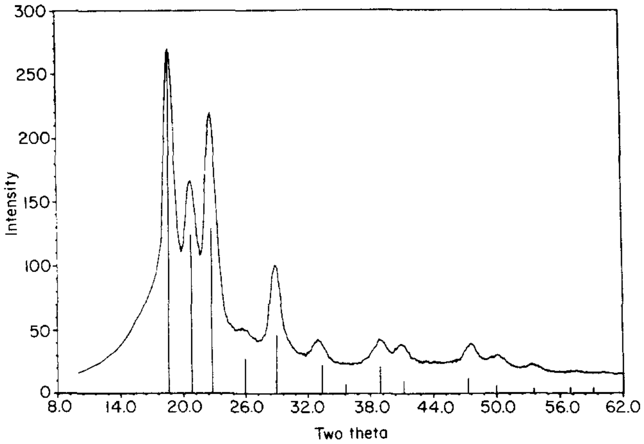

Figure 5 Comparison of the simulated powder pattern (peaks displayed as vertical lines) with the X-ray diffractogram of an unoriented PEEK specimen. The simulated powder pattern was calculated using the POWD7 program and the coordinates of the six-ring unit in *Table 3*

structure factors for the case of $t = 37°$ are compared in *Table 2*, and the corresponding atomic fractional coordinates are presented in *Table 3*. With the suspicion that the space group was not Pbcn, another symmetry operation relating the two-chains was tried; namely, a 2-fold rotation axis replaced the 2/1 screw axis. The resulting intermolecular contacts were unsatisfactory and the R-index was considerably higher.

Simulated powder pattern

The computer program POWD7[11] was utilized to calculate the theoretical powder diffractogram of PEEK. The calculation assumes Laue symmetry mmm and is based on the coordinates of the six-ring unit of *Table 3*. The half-width of a diffraction profile was taken to be 1.0° at $2\theta = 20°$. The theoretical peak positions (displayed as vertical lines) are compared in *Figure 5* with the experimental X-ray diffractogram of an unoriented specimen prepared by melt-quenching (400°C) a sample of PEEK resin. The four major calculated peaks (18.76°, 20.82°, 22.72° and 28.78°) are indexed 110, 113, 200 and 213, respectively. Weaker peaks (with indices) are also found at 32.88° (216), 33.52° (123) and 38.78° (313). The results are in good agreement with published X-ray diffractograms for various PEEK samples[5].

CONCLUSIONS

The structure of crystalline PEEK fibre has been analysed using accurate diffraction intensities from fibre rotation patterns. The analysis supports and extends to monofilaments the previously reported finding for other PEEK specimens that space group Pbcn is a valid representation of the structure. Atomic coordinates are derived for the six-aryl ring unit and are used as input parameters in the calculation of a theoretical powder pattern. A comparison of the experimental and theoretical patterns provides additional support for the Pbcn space group assignment.

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