polymer reports

X-ray data for poly(aryl ether ketones)

P. C. Dawson and D. J. Blundell

ICI Plastics Division, Welwyn Garden City, Herts, UK

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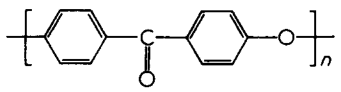
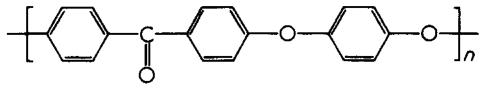
INTRODUCTION

This report reports observations on the crystalline unit cell of a family of poly(aryl ether ketones) and in particular focusses on the following two members:

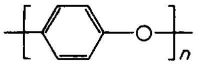


Polymer I



Polymer II

Details of the preparation of these polymers will be published separately[1]. The present crystallographic results are of particular interest because of the i.r. similarity to the structure reported by Boon *et al.*[2] for poly(phenylene oxide):



EXPERIMENTAL

Samples of both fibres and highly annealed, unoriented plaques were made from the polymers. The best values for the lattice spacings of the crystallographic reflections were obtained from annealed isotropic samples using a 114.6 mm Philips powder camera. The reflections were indexed by referring to the oriented pattern from a fibre sample taken with a 60 mm Unicam camera. In both cases Ni filtered $CuK\alpha$ radiation was used. The thermal transitions of the polymers were obtained with a Perkin–Elmer DSC-1 using 10 mg samples heated at 16°C min^{-1}.

RESULTS

For most practical purposes, the diffraction patterns from polymers I and II were found to be identical. Examples for polymer II are shown in *Figure 1*. Other polymers from the family which were essentially copolymers of I and II also gave the same pattern.

The reflections could be indexed, assuming orthorhombic cells of the dimensions listed in *Table 1*. The indexing of

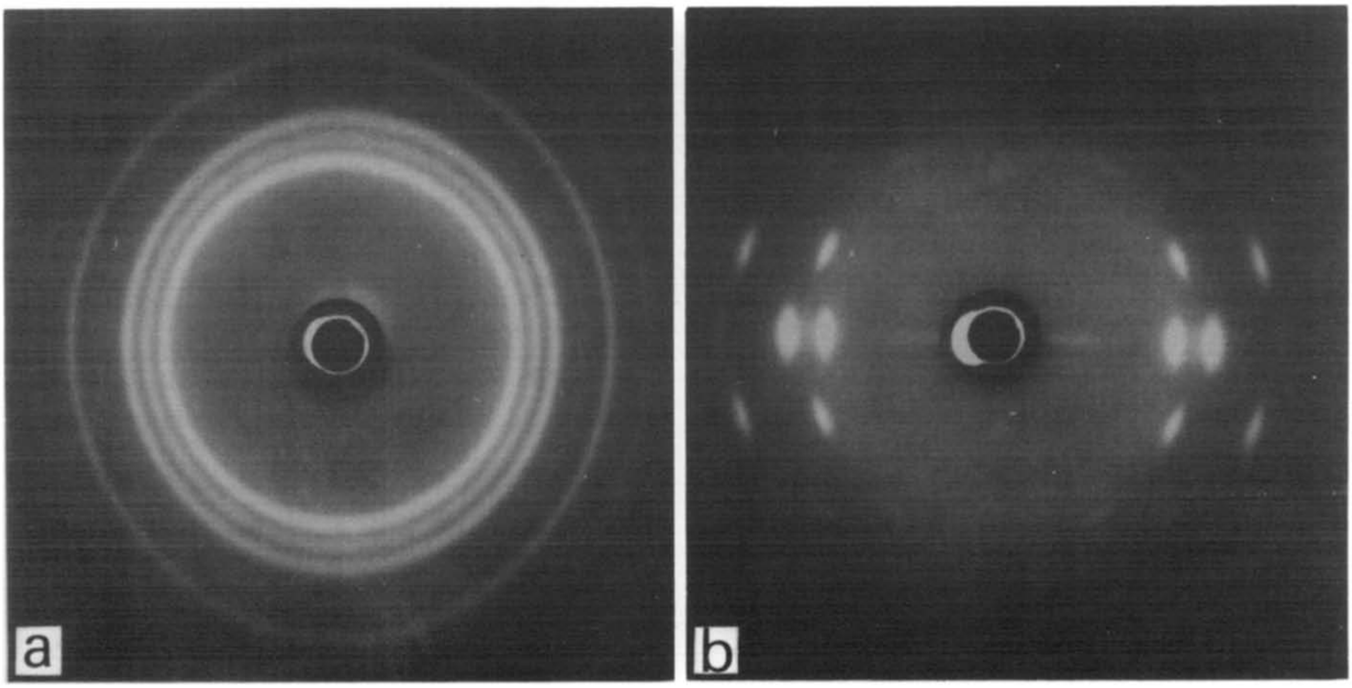


Figure 1 X-ray photographs: (a) isotropic moulding; (b) drawn fibre

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Table 1

	Polymer I	Polymer II	Poly (phenylene oxide)	Poly (phenylene sulphide)
Lattice parameters (Å)				
a	7.63	7.75	8.07	8.67
b	5.96	5.86	5.54	5.61
c	10.0	10.0	9.72	10.26
Crystal density	1430	1400	1410	1430
Measured amorphous density (kg m^{-3}	1272	1265	1270	1320
Main chain bond angle	123°	125°	124°	110°
T_g (°C)	154	144	85	92
Crystal melting point (°C)	367	335	285	295

the main reflections are shown in *Table 2*. The degree of accuracy in all these results is limited by the relatively low crystallinity of these polymers which is usually less than 50%.

Also shown in *Table 1* is the data of Boon *et al.* for poly(phenylene oxide)[2] and poly(phenylene sulphide)[3]. The similarity of the unit cell and of the chain conformations of these polymers strongly suggest that the crystal structure of Boon *et al.* for poly(phenylene oxide) is also a good model for the present aryl ether ketone polymers.

The *c*-axis fibre repeat of the unit cell extends over the equivalent of two aryl units and corresponds to the chemical repeat of polymer I. However, for polymer II, the chemical repeat covers three aryl units so that the cell quoted in *Table 1* can only be considered as the effective subcell. The hypothetical complete cell of II must be at least six aryl units in the *c*-direction, and the *a*- and *b*-directions may also be larger, dependeng on the arrangement of neighbouring chains. The striking similarity of the unit cells for the series shows that from the viewpoint of chain packing in the crystalline regions, the ketone and ether linkages can be interchanged with only the minimum of distortion. Thus it will be difficult, even in the case of the simplest polymer I, for perfect packing to occur where the ketone and ether links of neighbouring chains are in strict register with each other. In practice one can envisage that there will be a range in the regularity of the stacking of neighbouring ketone and ether groups, from near randomness for samples crystallized at high undercooling to the more perfect stacking for low undercooling. The trend towards random stacking is likely to be greater in polymer II than in polymer I. This is reflected by the maximum attainable degree of crystallinity which is about 10% higher for I than for II.

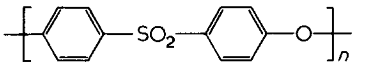
The crystalline densities shown in *Table 1* have been calculated from the unit subcell assuming the 'average' molecular composition. These values lead to a reasonable consistency between observed densities and the crystallinities deduced by X-rays.

Table 2 Principle X-ray reflections

Index	Intensity	I (Å)	II (Å)
110	vs	4.70	4.67
111, 102	m	4.26	4.23
200	s	3.82	3.87
112	w	3.44	3.43
211, 202	m	3.07	3.08

The 'average' molecular compositions have also been combined with the deduced *c*-axis repeat in order to estimate the average bond angle of the ketone and ether linkages. For this it was assumed that O–C is 1.36 Å, C=C is 1.39 Å and C–C is 1.54 Å. Both polymers gave values close to the value of 124° obtained by Boon *et al.* for poly(phenylene oxide). This again demonstrates the similarity of ketone and ether linkages in the unit cell.

Table 1 also enables the thermal transitions to be compared with those of related polyaryls. The effect of replacing ether links by the more rigid ketone links is to increase both the T_g and the crystalline melting point. The replacement of ether links by the sulphide link as in poly(phenylene sulphide) does not have such a marked effect as that of ketone links on the thermal transitions. In this context it is worth noting that the introduction of sulphone groups as in the poly(ether sulphone)



markedly increases T_g to 225°C. However, the sulphone grou destroys crystallinity, presumably because the bond angle of the sulphone linkage is only 105° compared with the apparen 124° of the other links[4].

ACKNOWLEDGEMENT

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3 Tabor, B. J., Magré, E. P. and Boon, J. *Eur. Polym. J.* 1971, 7, 1127
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