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Single crystal X-ray diffraction studies of aromatic oligomers: resolution of the bond-angle anomaly in poly(aryletherketone)s

Howard M. Colquhoun*
ICI Chemicals and Polymers Ltd, The Heath, Runcorn, WA7 4QE, UK

and Caroline A. O'Mahoney and David J. Williams*
Department of Chemistry, Imperial College, London SW7 2AY, UK
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To resolve long-standing uncertainties surrounding the bridge-bond angles of crystalline poly(aryletherketone)s, the structure of an oligomeric ether-ketone, ClArCOArOArCOArCl (Ar = 1,4-phenylene), has been determined by single crystal X-ray methods. The average torsion angle ϕ of the two 'ether-ketone' rings, relative to a plane defined by the bridging oxygen and carbonyl-carbon atoms is 31°. The bond angles at carbonyl-carbon and ether-oxygen are 121.9(3)° and 121.2(3)°, respectively, values which are substantially lower than those consistently reported for poly(aryletherketone)s on the basis of X-ray powder- and fibre-diffraction studies. [An average bridge-bond angle of 126.5(6)° has, for example, been proposed to account for the *c*-axis length of 10.09(2) Å in the prototype poly(etherketone) (PEK) (-OArCOAr-)$_n$.] Despite this apparent difference in bridge-bond angles, a PEK *c*-axis distance of 10.11(1) Å, entirely consistent with that of the polymer, is found in the present oligomer structure. More detailed analysis of the oligomer structure reveals a pattern of sterically induced bond angle distortions at the aromatic carbon atom linked to an ether or ketone bridge, a pattern that is repeated in the X-ray structure of a second oligomer ArOArCOArArCOArOAr (Ar = phenyl or 1,4-phenylene). These findings strongly suggest that bridge-bond angles in poly(aryletherketone)s actually lie in the region of 121–122°, and that the range 125–127° consistently reported in the literature is an artifact deriving from the assumption of ideal geometry elsewhere in the polymer chain.

(Keywords: poly(aryletherketone); X-ray; oligomer; crystal structure)

INTRODUCTION

Since the commercial introduction of semicrystalline poly(aryletherketone)s[1] as high-performance engineering thermoplastics (*Figure 1*), numerous X-ray fibre- and powder-diffraction studies have been published, giving details of chain dimensions, molecular conformations, and the nature of crystal packing in these materials[2–10].

In view of the very limited number of X-ray reflections observed in powder and fibre studies, solution of a polymer structure requires most molecular parameters (typically all bond lengths and nearly all bond angles) to be set at 'standard' values, so that refinement of only a very few bond angles and torsional angles is possible. For poly(aryletherketone)s this approach has invariably meant idealizing aromatic rings to be planar, regular and with internal and external bond angles equal to 120°. All bond lengths (aromatic and non-aromatic) are fixed at nominal values. Bridge-bond angles (θ) at ether-oxygen and carbonyl-carbon are assumed to be equal, as are the torsional angles (ϕ) of aromatic rings relative to a plane defined by the carbonyl and ether groups of the backbone (*Figure 2*). Thus the only molecular parameters actually derived from the X-ray data are the values of θ and ϕ, which are reported to lie in the ranges 125–127° and 34–40°, respectively[2–10].

Although this range of torsion angles ϕ is not unreasonable, the bridge angles θ (derived from crystallographic *c*-dimensions) are significantly higher than those obtained crystallographically for small molecules such as 4,4'-dichlorobenzophenone[11] and 3,3',4,4'-tetrachlorodiphenyl ether[12], where values of 120–121° are observed. Only in sterically overcrowded molecules such as 2,2'-dimethoxybenzophenone does the

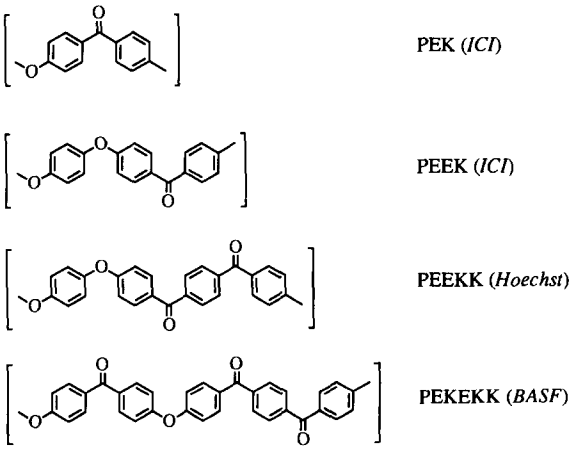

Figure 1 Commercially available poly(aryletherketone)s

*To whom correspondence should be addressed

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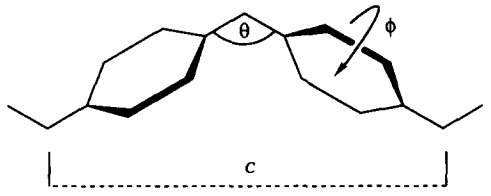


Figure 2 Geometric descriptors for a poly(aryletherketone) chain

bridging angle increase significantly[13]. Theoretical studies have suggested that the anomalously high bridge-bond angles in poly(aryletherketone)s result from the polymer chain adopting a more flattened conformation (i.e. a lower torsion angle ϕ) than is observed for smaller molecules, leading to increased steric repulsion between adjacent aromatic rings (H . . . H and/or H . . . C), with a consequent opening up of the bridge-bond angles[14]. However, more recent calculations have also indicated a lengthening of the bridge-bonds Ar–O and Ar–CO relative to 'standard' values[15], so that it is still unclear whether anomalously high bond angles are in fact required to account for the *c*-axis or polymer-repeat distances derived from X-ray powder and fibre studies.

In order to resolve these uncertainties surrounding the molecular geometry of poly(aryletherketone)s we have determined the structures of two oligomeric aromatic ether-ketones, ClArCOArOArCOArCl (**1**)[16] and ArOArCOArArCOArOAr (**2**)*, by single-crystal X-ray methods. Anomalously high bridge-bond angles are not observed, nor is there a substantial overall increase in bond lengths over previously quoted figures (though individual bond lengths prove significantly different from 'standard' values). However, a consistent pattern of bond angle distortions is found at the *aromatic carbon atom adjacent to an ether or ketone bridge*, which appears to resolve the problem of bond angle anomalies in poly(aryletherketone)s.

RESULTS AND DISCUSSION

Oligomer **1** crystallizes in the orthorhombic space group *Pcan*† with unit cell parameters $a = 6.054(2)$, $b = 7.446(2)$ and $c = 45.556(3)$ Å. The *a* and *b* dimensions compare reasonably, (though not exactly, see below) with the values of $b = 5.97(1)$ and $a = 7.65(1)$ Å reported for unoriented poly(etherketone) (PEK)[6]. Transposition of the *a* and *b* axes of an orthorhombic cell is not significant in this context and, as shown in *Figure 3*, the overall conformation and crystal packing of **1** correspond very closely to those established for the polymer[6].

The structure of oligomer **1** is shown in more detail in *Figure 4*. The molecule has a crystallographic two-fold axis, with bridge-bond angles at ether and carbonyl of 121.2(3)° and 121.9(3)° respectively. The average torsion angle ϕ of the two ether-ketone rings, relative to a plane defined by the bridging oxygen O(14) and carbon atoms C(7), C(7′) is 31°, i.e. a little less than that found for PEK (34°)[6]. The fact that oligomer **1** adopts a slightly more flattened conformation than the polymer is entirely consistent with the minor changes in *a* and *b* dimensions between oligomer and polymer.

The distance between equivalent carbonyl-carbon atoms C(7) and C(7′) in oligomer **1** represents a

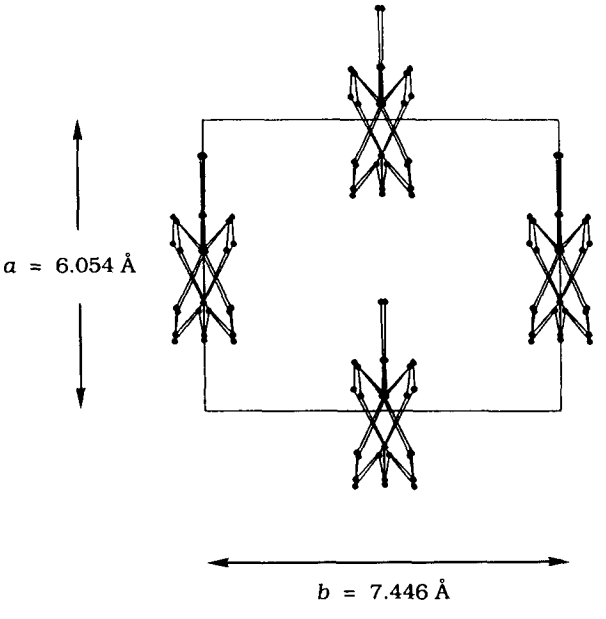


Figure 3 Unit cell of oligomer **1**, viewed along the crystallographic *c*-direction

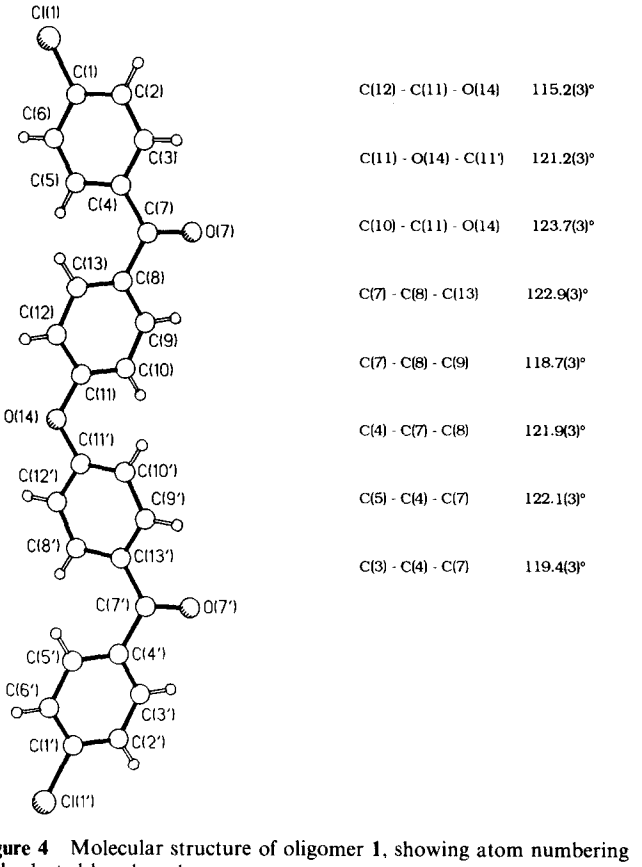


Figure 4 Molecular structure of oligomer **1**, showing atom numbering and selected bond angles

*Oligomer **2**, m.p. 277°C, was synthesized by condensation of excess diphenyl ether with biphenyl-4,4′-dicarboxylic acid in trifluoromethanesulphonic acid; full details will be reported in a forthcoming paper

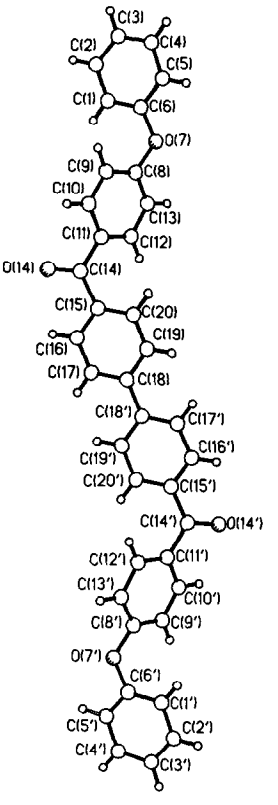
†Crystal data for **1** (single crystals from toluene): $C_{26}H_{16}Cl_2O_3$, $M = 447.3$, orthorhombic, $a = 6.054(2)$, $b = 7.446(2)$, $c = 45.556(3)$ Å, $U = 2054$ Å^3, space group *Pcan*, $Z = 4$ (the molecule is disposed about a twofold axis), $D_c = 1.45$ g cm^{-3}, Cu–Kα radiation, μ(Cu–Kα) = 31 cm^{-1}. The structure was solved by direct methods and refined anisotropically to give $R = 0.053$, $R_w = 0.057$ for 1075 independent observed reflections [$|F_o| > 3\sigma|F_o|$]. Full crystallographic details are available from the authors on request

complete PEK-repeat distance and, at 10.11(1) Å, is identical within error to that determined for the polymer (10.09(2) Å)[6]. Since the average bridge-bond angle in the oligomer at 121.5°, is some 5° lower than that previously thought necessary to account for a PEK-repeat of 10.09 Å there is obviously some flaw in the usual assumption that poly(aryletherketone)s adopt 'standard' bond lengths and/or idealized aromatic ring geometries. The nature of this flaw is immediately apparent in *Figure 4*, where a clear pattern of bond-angle distortions can be identified at the aromatic carbon atoms C(11), C(8) and C(4), i.e. those linked to an ether or ketone bridge. It appears that steric repulsions between adjacent aromatic rings lead not, as was previously suggested[14], to an opening up of the bridge-bond angles, but instead to an *in-plane bending-distortion* at the aromatic ring-carbons attached to the bridge. The average distortion in oligomer **1**, defined as the mean deviation from 120° of the external angles at ring-carbons linked to bridging atoms, as shown in *Figure 4*, is 3.1°. The effect is considerably greater at the ether linkage (4.2° average distortion) than at the carbonyl group (1.5° average), and there are additional, though less significant, distortions within the aromatic rings themselves.

This in-plane bending (the sum of bond angles at the aromatic carbon involved remains at 360°) produces an increase in the polymer-repeat distance C(7)–C(7′), just as would an opening of the bridge-bond angles. Indeed, it is interesting to calculate an average [---C---O---C---O---] bridge-to-bridge angle in oligomer **1** since the assumption of ideal ring geometry in polymer studies means that it is this angle, rather than the bridge-bond angle, which is actually determined from the X-ray data. The 'long-range' C–O–C angle between ether-oxygen O(14) and carbonyl-carbons C(7) and C(7′) is found to be 127.5(3)°, and a corresponding O–C–O half-angle of 62.6° (× 2 = 125.2°) can be calculated at C(7). The average bridge-to-bridge angle in oligomer **1** is therefore (127.5 + 125.2)/2 ≈ 126.4°, in excellent agreement with the value of 126.5° determined for PEK itself[6].

The general occurrence of in-plane bending distortions in aromatic ether-ketone chains was established from a second single-crystal structure analysis, that of the six-ring biphenyl-centred oligomer **2**, ArOArCOArArCOArOAr (Ar = phenyl or 1,4-phenylene)*. The molecular structure of **2**, which has a crystallographic centre of symmetry, is shown in *Figure 5*. Comparison with oligomer **1** (*Figure 3*) reveals an almost identical pattern of bridge-bond angles (averaging 121.5(2)°), and bond-angle distortions (averaging 2.9°) at aromatic carbon atoms linked to the bridging ether and ketone groups. The average ether-ketone ring-torsion angle ϕ is 30°.

As noted in the Introduction, recent theoretical studies have suggested that the discrepancy between expected and observed *c*-axis lengths in poly(aryletherketone)s might be resolved, without resorting to anomalously high bridge-bond angles, if assumptions about the 'standard' bond lengths appropriate to molecules of this type were found to be incorrect[15]. Indeed, as shown in *Table 1*, the oligomer-derived values for Ar–O and Ar–CO are significantly different from those previously assumed for PEK, as indeed is the aromatic C–C distance, but overall the differences are virtually self-cancelling, so that bond-length corrections on their own do not resolve the discrepancy.



C(1) - C(6) - O(7)	123.4(2)°
C(5) - C(6) - O(7)	115.6(2)°
C(6) - O(7) - C(8)	121.7(2)°
O(7) - C(8) - C(9)	123.1(2)°
O(7) - C(8) - C(13)	115.5(2)°
C(10) - C(11) - C(14)	118.4(2)°
C(12) - C(11) - C(14)	122.6(2)°
C(11) - C(14) - C(15)	121.3(2)°
C(14) - C(15) - C(16)	119.0(2)°
C(14) - C(15) - C(20)	122.8(2)°

Figure 5 Molecular structure of oligomer **2**, showing atom numbering and selected bond angles

Table 1 Average bond lengths (Å) for oligomers **1** and **2**, together with 'standard' values used in earlier polymer studies

Bond	1	2	Ref. 3	Ref. 4	Ref. 6	Ref. 8
Ar–CO	1.486(4)	1.490(3)	1.47	1.47	1.50	1.47
Ar–O	1.386(4)	1.388(3)	1.36	1.36	1.36	1.36
C–C (Ar)	1.384(4)	1.383(3)			1.395	1.395
C=O	1.223(4)	1.223(2)			1.29	1.23

CONCLUSIONS

The bridge-bond angles in oligomeric ether-ketones lie in the range 121–122°, and ring torsion angles relative to the plane of the backbone are 30–31°. For both the oligomers studied here, a sterically induced in-plane bending distortion (averaging 3°) occurs at each ring carbon linked to a bridging oxygen or carbon atom, leading to an oligomer-derived *c*-axis for PEK which is entirely consistent with that determined for the polymer. These results strongly suggest that bridge-bond angles in poly(aryletherketone)s also lie in the region of 121–122°, and that the range 125–127° consistently reported in the literature is an artifact arising from the assumption of ideal geometry elsewhere in the polymer chain.

*Crystal data for **2** (single crystals from dimethylformamide): $C_{38}H_{26}O_4$, $M = 546.6$, monoclinic, $a = 6.101(1)$, $b = 7.536(1)$, $c = 29.389(5)$ Å, $\beta = 92.33(1)°$, $U = 1350$ Å^3, space group $P2_1/a$, $Z = 2$ (the molecule is disposed about a centre of symmetry), $D_c = 1.45$ g cm^{-3}, Cu–Kα radiation, μ(Cu–Kα) = 7 cm^{-1}. The structure was solved by direct methods and refined anisotropically to give $R = 0.037$, $R_w = 0.040$ for 1320 independent observed reflections [$|F_o| > 3\sigma|F_o|$]. Full crystallographic details are available from the authors on request

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