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Polymer 40 (1999) 607–612

polymer

Chain-conformation and chain-folding in 'PK99': evidence from single-crystal X-ray studies of linear and cyclic oligomers

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Received 17 March 1998; revised 7 April 1998

Abstract

The structure of a seven-ring model for the crystalline polyetherketone known as 'PK99', has been determined by single crystal X-ray methods. The central benzene-1,3-dicarbonyl group in this oligomer adopts an 'open' conformation, approximately in agreement with that proposed earlier for PK99 on the basis of X-ray powder and fibre diffraction data. The present oligomer structure (and a polymer structure simulated by extrapolation from the oligomer) do not, however, require the benzene-1,3-dicarbonyl group to adopt the previously assumed coplanar conformation. A single crystal X-ray study of a cyclic ether–ketone oligomer, also based on the benzene-1,3-dicarbonyl unit, demonstrates the potential of this group to act as a site for sharply re-entrant chain-folding. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polyetherketone; Oligomer; X-ray structure

1. Introduction

The aromatic polyetherketone **1** (Fig. 1) known as 'PK99' [1], is reported to show unusual crystallisation and melting behaviour in that: (i) it shows a double maximum in the crystal growth-rate versus temperature curve; (ii) its melting point (306°C) is low relative to the value expected from its glass transition temperature (158°); and (iii) the lamellar thickness of this polymer shows 'quantisation' on crystallisation at progressively higher temperatures, with *l*-values (~35 and 55 Å) corresponding to relatively small numbers of aromatic rings (~7 and 12, respectively) [2,3].

Since thermal crystallisability in polyetherketones is more generally associated with an all-1,4-substitution pattern, it seems likely that the unusual characteristics of PK99 reflect the 1,3-substitution which occurs at every fifth ring in the polymer chain. It will be noted that the latter can give rise to two very different chain-conformations (Fig. 2).

Conformation **A** clearly leads to an extended-chain structure for PK99, as originally proposed from X-ray fibre and powder diffraction studies [2,3], whereas the alternative conformation **B** leads to a 180° reversal of the chain-direction, i.e. to a sharply re-entrant chain-fold. Although a number of X-ray crystallographic and morphological investigations of PK99 have been reported [2–6], and the existence of chain-folded crystalline lamellae clearly demonstrated [6], the possibility that the anomalous properties of this polymer might result from specific, re-entrant chain-folding at the benzene-1,3-dicarbonyl linkage does not appear to have been previously considered. Moreover, although the crystal structure of this polymer has been analysed by a number of independent workers, there is as yet no direct crystallographic evidence for the high-energy, coplanar conformation assumed for the benzene-1,3-dicarbonyl unit in these studies [2–6], and also proposed in studies of other polyketones containing this group [7,8].

In an attempt to clarify the conformational characteristics of polyketones containing the benzene-1,3-dicarbonyl group, and to evaluate its potential to act as a site for re-entrant chain-folding, we now report the synthesis and structural characterisation by single-crystal X-ray methods of both linear and cyclic ether–ketone oligomers containing this sub-unit.

2. Experimental

2.1. Oligomer syntheses

2.1.1. Linear oligomer 2

In a 1 l flask, equipped with a condenser and Dean-Stark

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0032-3861/98/$ - see front matter
PII S0032-3861(98)00290-0

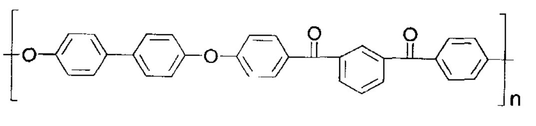

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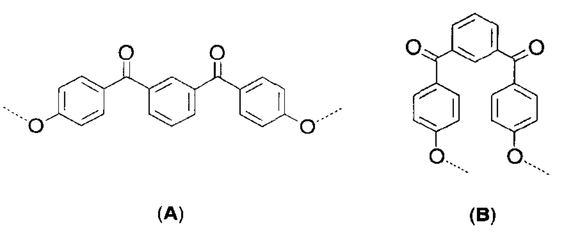
Fig. 1. Molecular formula of PK99 (**1**).

trap, a nitrogen inlet, a thermometer and a magnetic stirrer, were placed 1,3-bis(4-fluorobenzoyl)benzene (10.73 g, 0.033 mmol), potassium carbonate (4.83 g, 0.035 mmol), 4-hydroxybiphenyl (11.90 g, 0.070 mmol), toluene (150 cm^3) and dimethylacetamide (200 cm^3). The mixture was stirred at 130°C for 2 h, with removal of water, and then the temperature was raised to 160°C by removal of toluene and held at that temperature for a further 6 h. The solution was cooled, poured into water (1000 cm^3), and the precipitated solid filtered off, washed with water and methanol, dried, and recrystallised from dimethylacetamide to give 12.80 g (62% yield) of oligomer **2** as a white crystalline solid, m.p. 228–229°C. Found: C, 84.93; H, 4.77%. Calculated for $C_{44}H_{30}O_4$: C, 84.88; H, 4.82%. Single crystals in the form of very thin plates were grown by slow cooling of a solution in DMF.

2.1.2. Cyclic oligomer 3

In a 500 cm^3 flask, equipped with a condenser and Dean-Stark trap, a nitrogen inlet, a thermometer and a magnetic stirrer, were placed resorcinol (0.77 g, 7.0 mmol), potassium carbonate (1.50 g, 11 mmol), benzene (50 cm^3) and dimethylacetamide (250 cm^3). The mixture was stirred at 130°C for 2 h, with removal of water, and then the temperature was raised to 160°C by removal of benzene. The flask was then cooled to room temperature and 1,3-bis(4-fluorobenzoyl)-benzene (2.26 g, 7.0 mmol) was added. The temperature was raised to 160°C and the mixture stirred under nitrogen at that temperature for a further 16 h. The solution was cooled, poured into water/methanol (1/1, 1500 cm^3), and the precipitated solid filtered off, washed with water and methanol, dried, and recrystallised from chloroform/hexane to give 0.25 g of cream crystals, m.p. 283–284°C. Accurate mass (electron ionisation). Found: 302.104. Calculated for $C_{28}H_{16}O_4$, 302.105. Single crystals suitable for X-ray analysis were grown from dichloromethane/heptane.



(A) (B)

Fig. 2. Alternative conformations of the benzene-1,3-dicarbonyl unit in a polyetherketone, leading to either chain-extension (**A**) or to chain-folding (**B**).

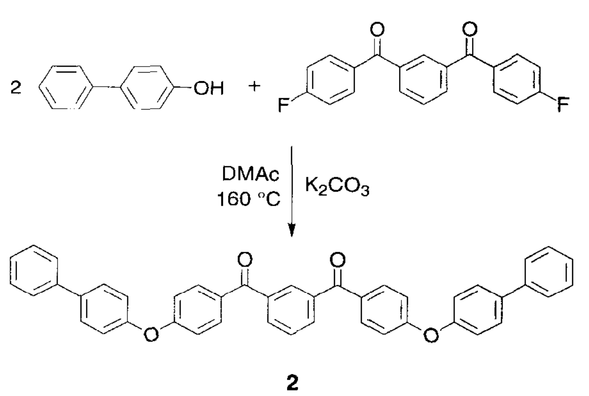


Fig. 3. Synthesis of the linear oligomer **2**.

2.2. X-ray structures

2.2.1. Crystal data for 2

$C_{44}H_{30}O_4$, M = 622.68, monoclinic, space group $P2_1/n, a = 7.502(1)$, b = 6.077(1), c = 66.933(8) Å, β = 91.175(9)°, U = 3050.6(6) $Å^3$, Z = 4, T = 173 K, D_c = 1.356 g cm^{-3}, μ(Cu-Kα) = 6.81 cm^{-1}, F(000) = 1304.

2.2.2. Crystal data for 3

$C_{26}H_{16}O_4$, M = 392.39, orthorhombic, space group $Pnma$, a = 18.980(1), b = 15.447(1), c = 6.538(1) Å, U = 1916.9(2) $Å^3$, Z = 4, T = 293 K, D_c = 1.360 g cm^{-3}, μ(Cu-Kα) = 7.44 cm^{-1}, F(000) = 816.

Data for both compounds were measured on a Siemens P4/RA diffractometer with graphite-monochromated Cu-Kα radiation using ω-scans. For **2**, 4523 independent reflections ($2\theta < 120°$) and for **3**, 4171 independent reflections ($2\theta < 124°$) were collected, of which 2078 and 1293 reflections, respectively, had $I > 2\sigma(I)$, and were considered to be observed. The data were corrected for Lorentz and polarisation factors but not for absorption. The structures were solved by direct methods and the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters $U = 1.2\ U_{eq}(C)$ and allowed to ride on their parent carbons. Refinement was by full-matrix least squares based on F^2, to give for **2** $R_1 = 0.1313$, $wR_2 = 0.3161$, and for **3** $R_1 = 0.0496$, $wR_2 = 0.1301$. Computations were carried out using the SHELXTL program package [9]. Tables of fractional atomic coordinates, bond lengths, bond angles and thermal parameters for both **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre; reference CCDC 101-069. Copies can be obtained by application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ. E-mail: deposit@chemcrys.cam.ac.uk.

2.3. Molecular modelling

Molecular simulation and diffraction modelling studies were carried out using the Cerius-2 program (Molecular

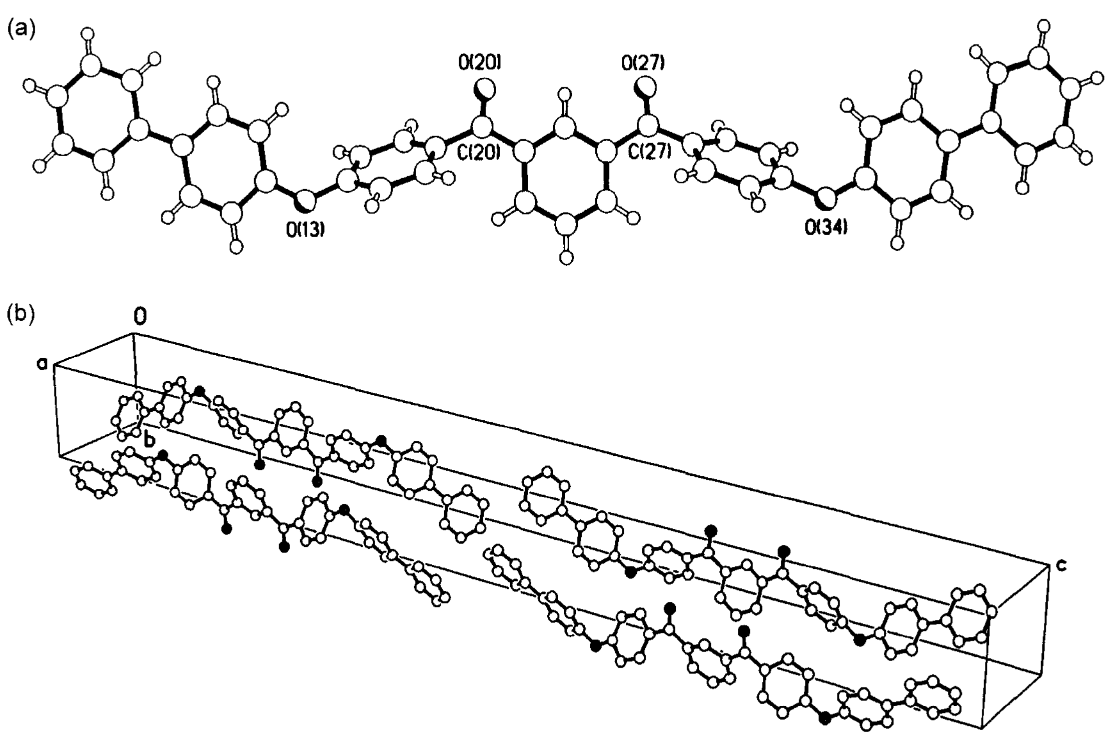


Fig. 4. (a) Molecular structure of oligomer **2**; and (b) crystal packing of oligomer **2**.

Simulations Inc.) on an Silicon Graphics O2 workstation. Molecular mechanics and crystal energy minimisations were performed using a modified version of the Dreiding II force field [10]. Final optimised peak broadening parameters used in the calculated powder diffraction pattern for PK99 were as follows. Crystallite dimensions, $a = 180$, $b = 400$, $c = 180$ Å; crystallite strain, $a = 0.5$, $b = 0.1$, $c = 0.05\%$; anisotropic temperature factors, $x = 0.05$, $y = 0.05$, $z = 0.02$ Å^2; pseudo-Voigt peak shape, mixing parameter 0.6.

3. Results and discussion

The open-chain oligomer **2** was synthesised as shown in Fig. 3. Single crystals invariably adopted a very thin, paper-like morphology, but a crystal suitable for X-ray analysis was eventually obtained by very slow cooling (ca. 48 h) of a solution of the oligomer in dimethylformamaide. The X-ray structure (Fig. 4(a)) shows the molecule to adopt a fully extended conformation, with the planes of the 'etherketone' rings steeply inclined (by ca. 55°) to those of the biphenyl and 1,3-substituted ring systems.

The biphenyl units are also tilted slightly with respect to the central 1,3-substituted ring, producing an overall bowing of the oligomer chain. The axes of the two biphenyl units subtend a dihedral angle of 156°.

As postulated in crystallographic studies of PK99 and related polymers [2–8], the carbonyl groups of the central benzene-1,3-dicarbonyl unit lie very close to the mean plane of the oligomer 'backbone' (defined by the linking atoms C_{Ar}–O–C_{Ar} and C_{Ar}–C_{Ar}). However, as is evident from the packing diagram shown in Fig. 4(b), the central ring does not lie in this plane but subtends a ca. 20° dihedral angle to it, in contrast to the coplanar conformation previously suggested [2–8].

The distance between the centres of the two biphenyl units, corresponding to the 'chemical-repeat' for PK99, is 24.1 Å—a value in excellent agreement with the experimental c-axis length of 48.2 Å obtained from X-ray fibre data and from electron-diffraction studies of the polymer, in which the crystallographic repeat comprises two chemical-repeat units [6]. The conformation of oligomer **2** thus appears to be a valid representation of that present in the polymer, unlike that of a closely-related but smaller oligomer in which the terminal biphenyl residues are replaced by phenyl groups. The latter was shown to adopt a 'loosely folded' structure in the crystal; a conformation more closely related to **B** than to **A** (Fig. 2) [11].

A further significant feature of oligomer structure **2** as a model for the polymer PK99 is the observation of lamellar packing in the solid state (Fig. 4(b)). Adjacent, glide-related chains within the unit cell are aligned with negligible displacement in the chain direction. We have found that a provisional structure for PK99 can in fact be generated directly from that of oligomer **2** simply by placing a crystallographic inversion centre at the centre of each biphenyl unit and discarding the terminal phenyl groups. In this initial model (Fig. 5) the glide relationship between adjacent chains is unchanged, as are two of the crystallographic

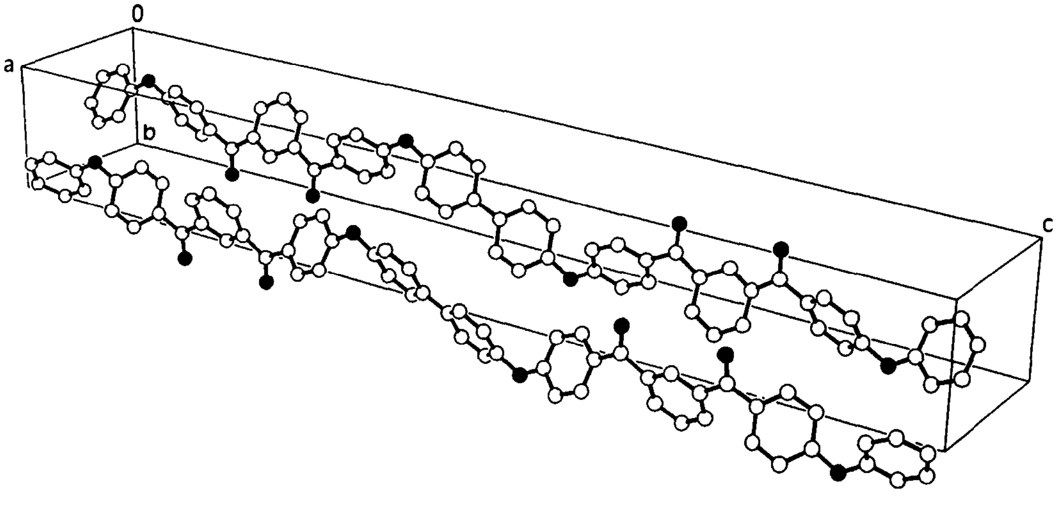


Fig. 5. Oligomer-derived model for the crystal structure of PK99.

axes (*a* and *b*). The crystal lattice is redefined so that the newly-introduced inversion centre coincides with the cell origin, generating an orthorhombic unit cell. This process for constructing the polymer crystal produces inversion centres at 0 and 1/2 in *c* and mirror planes at 1/4 and 3/4 parallel to *ab*. The resulting space group, taking account of molecular inversion and mirror symmetries, and of the glide relationship between adjacent chains, is *Pbnm*.

The *c*-axis length of the initial structure, at 48.11 Å, corresponds very closely to the experimental value of 48.20 Å, reported recently by Hill and co-workers [6], as indeed does the *b*-axis length (6.08 Å, compared with the reported experimental value of 6.09 Å). There is however a noticeable discrepancy between the length of the *a* axis in the simulated structure (7.53 Å) and an experimental value for the polymer of 7.88 Å. Similar discrepancies have in fact been observed for a number of polyetherketone systems (the polymer *a*-axis always being greater than that of the oligomer by some 0.1–0.3 Å) [12,13], and are accounted for by the fact that polymer lamellae (unlike oligomer-analogues) must accommodate folds or other amorphous structures (loops, cilia, etc.) associated with chains entering and leaving the crystallite. Expansion of the lattice is thus favoured [14], especially when, as in PK99, lamellar thicknesses are small.

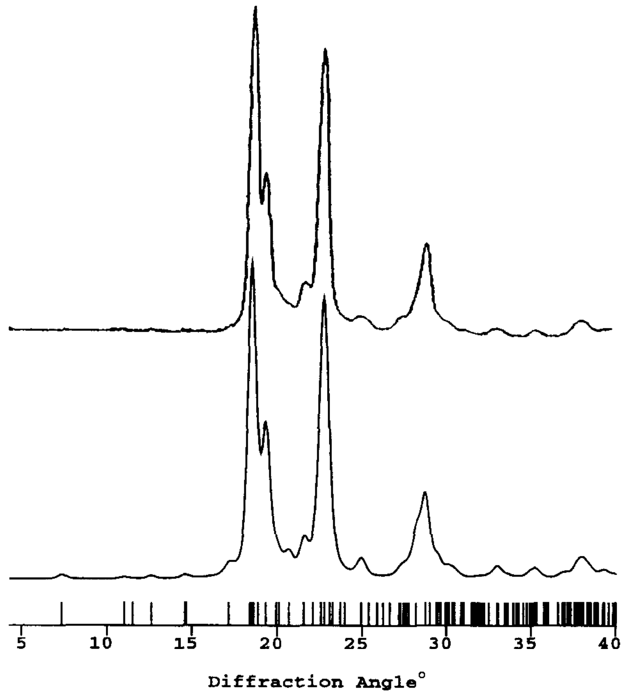


Fig. 6. Experimental (upper trace) and simulated (lower trace) X-ray powder diffraction patterns (Cu-Kα) for PK99 and the currently optimised model for this polymer, based on the conformation and packing found for oligomer **2**.

Optimisation of the initial polymer structure was carried out using the molecular modelling/diffraction simulation package Cerius-2. Adjustment of the unit cell parameters, modification of the crystallite dimensions and thermal parameters to realistic values, and minimisation of the crystal packing energy (without changes to the oligomer-derived chain-conformation) produced an excellent match in both peak positions and relative intensities between a simulated X-ray powder pattern and the experimental pattern reported by Blundell and co-workers for PK99 (Fig. 6) [2,3]. Moreover, a flat-plate fibre pattern calculated for the present

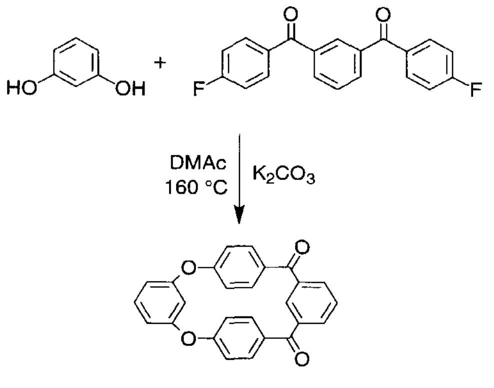


Fig. 7. Synthesis of the cyclic oligomer **3**.

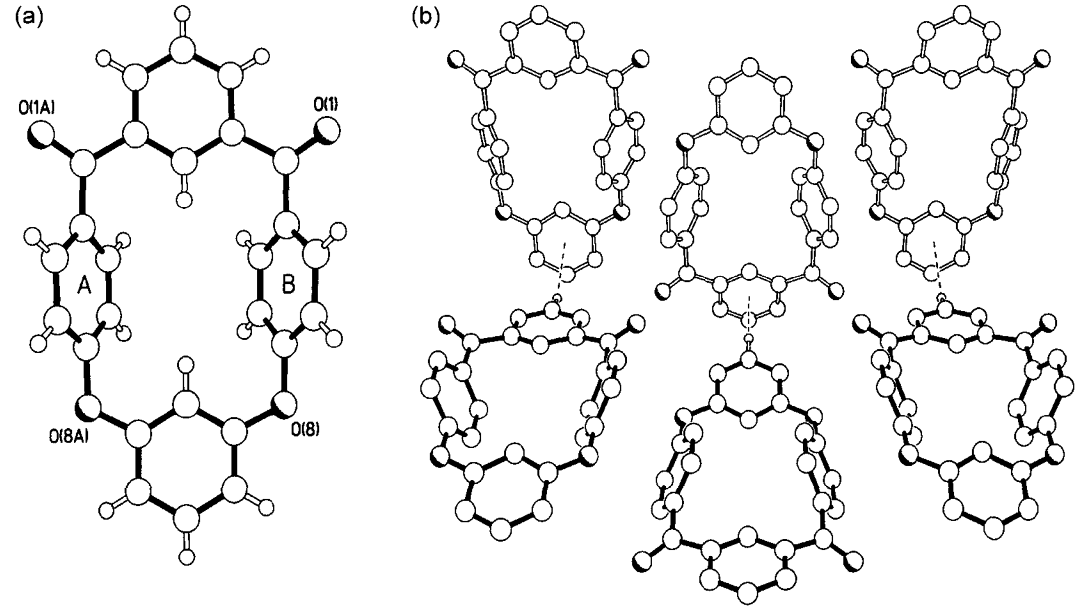


Fig. 8. (a) Molecular structure of the cyclic oligomer **3**; and (b) crystal packing of oligomer **3**, showing the strong intermolecular C–H· · ·π interaction.

structure exhibits all the features (specifically the 116, 215, and the high-angle 1119 reflections) reported recently by Hill and co-workers for PK99 [6]. The final dimensions of the optimised unit cell ($a = 7.88$, $b = 6.07$, and $c = 48.11$ Å) match experimental values very closely indeed.

Comparing the present chain-conformation with that originally proposed for PK99 [2,3], the biphenyl rings are coplanar in both structures, and the C–C–O–C torsion angles at the ether linkages are in very good agreement at 34 ± 1°. The C_{Ar}–O–C_{Ar} planes, defining the plane of the polymer backbone, lie parallel to the crystallographic *bc* plane in both structures. In the present structure, however, the 1,3-substituted rings are inclined by ca. 20° to this plane, rather than being in the plane of the backbone. As in oligomer **2**, the carbonyl groups subtend an angle of some 17° to their associated ring-plane, but lie close to the *bc* plane (Fig. 5(b)).

The problem next to be addressed is whether the benzene-1,3-dicarbonyl unit can, as postulated in Fig. 2, act as a site for re-entrant chain-folding. To this end, we have synthesised and structurally characterised a cyclic ether–ketone oligomer (**3**) based on this unit (Fig. 7).

The crystal structure of oligomer **3** is shown in Fig. 8. The macrocycle has crystallographic mirror symmetry about a plane passing through the 2 and 5 positions of the 1,3-substituted aromatic rings. The 1,4-substituted rings are inclined by 56° to one other, forming a distinct cleft, whereas the two 1,3-substituted rings fold in the opposite sense, subtending a dihedral angle of 160°.

The molecules pack end-to-end, with the *para*-substituted A and B rings in a parallel π-stacking arrangement (mean interplanar separation of 3.44 Å) with their centrosymmetrically related counterparts. Adjacent π-stacked arrays are oriented approximately orthogonally, with the hydrogen atoms at the 5-positions of the resorcinol-derived units in one stack being directed into the centres of the benzene-1,3-dicarbonyl rings of the next (Fig. 8). The H· · ·π distance is 2.50 Å, with an associated C–H· · ·π angle of 178°, both consistent with a strong C–H· · ·π hydrogen-bonding interaction [15].

In this compound the benzene-1,3-dicarbonyl unit quite clearly adopts the conformation **B**, proposed in Fig. 2 as being appropriate for chain-folding. The separation of the

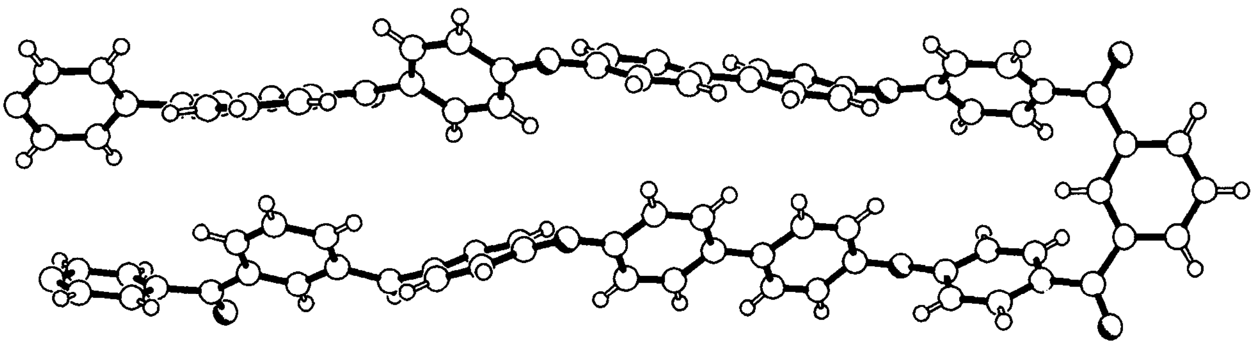


Fig. 9. A simulated chain-fold in PK99, produced by linking two glide-related (nearest-neighbour) chains in the crystal structure of oligomer **2** by a benzene-1,3-dicarbonyl unit and minimising the conformational energy of the fold.

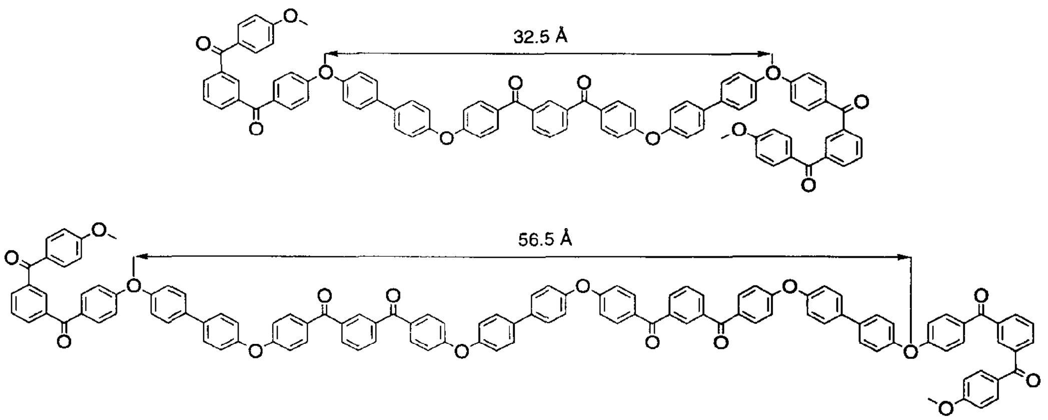


Fig. 10. Lamellar thickness values obtained by folding the PK99 chain at every second and every third benzene-1,3-dicarbonyl unit.

two ether oxygen atoms O(8) and O(8A) is 4.85 Å. This distance is in excellent agreement with the separation of the corresponding oxygen atoms of adjacent glide-related molecules in the crystal structure of the linear oligomer **2** (average 4.83 Å)—a structure which, as we have shown, leads to a reliable model for the polymer. Fig. 9 shows a simulated chain-fold obtained by linking two glide-related chains in the crystal structure of oligomer **2** by a benzene-1,3-dicarbonyl unit and then minimising the conformational energy of the fold (i.e. of the benzene-1,3-dicarbonyl group and its two adjacent rings). We see from Fig. 9 that the geometry adopted by the benzene-1,3-dicarbonyl unit in this minimised chain-fold matches closely that found in the crystal structure of the cyclic oligomer **3**.

Finally, as shown in Fig. 10, the SAXS-derived lamellar thickness values in PK99 [2,3], at ca. 35 and 56 Å, correlate reasonably well with crystallite thicknesses (32.5 and 56.5 Å) obtained by introducing a sharply re-entrant chain-fold at every second and every third benzene-1,3-dicarbonyl unit, respectively. (It is assumed that the three rings comprising the chain-fold lie outside the lamella crystal lattice.) A parallel could be drawn with the specific chain folding observed in monodisperse long-chain paraffins [16], which also leads both to quantisation of lamellar thickness and to a double maximum in the crystal growth-rate versus temperature curve.

4. Conclusions

Single crystal X-ray studies of a seven-ring linear ether-ketone oligomer based on the isophthaloyl unit, together with computer modelling and diffraction-simulation, afford a model for the crystal and molecular structure of 'PK99' (space group *Pbnm*) which is in good agreement with experimental X-ray powder and fibre data. Unlike earlier models, this structure does not require the benzene-1,3-dicarbonyl group to be coplanar, nor to lie parallel to the plane of the polymer backbone. Extension of these studies to the crystal structure of a cyclic oligomer reveals a mechanism for chain-folding at the benzene-1,3-dicarbonyl unit which offers a possible explanation for the previously observed 'quantisation' of lamella thickness in PK99.

Acknowledgements

This work was supported by the Royal Society, the Wolfson Foundation, and the Engineering and Physical Sciences Research Council of the United Kingdom (grant no. GR/K/73442).

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