JOURNAL OF
Materials
CHEMISTRY

Macrocyclic oligomers of the aromatic polyetherketone "PK99": synthesis, fractionation, structural characterisation and ring-opening polymerisation

Ian Baxter,[a] Howard M. Colquhoun,*[b] Philip Hodge,*[c] Franz H. Kohnke,*†[c] David F. Lewis[b] and David J. Williams*[a]

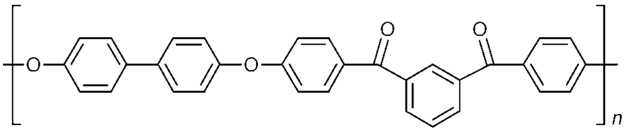
[a]*Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY*
[b]*Department of Chemistry, University of Salford, Salford, UK M5 4WT.*
E-mail: h.m.colquhoun@salford.ac.uk
[c]*Department of Chemistry, University of Manchester, Oxford Road, Manchester, UK*
M13 9PL. E-mail: philip.hodge@man.ac.uk

Received 21st October 1999, Accepted 10th November 1999

Cyclo-condensation of 4,4′-dihydroxybiphenyl with 1,3-bis(4-fluorobenzoyl)benzene under conditions of *pseudo*-high dilution affords a new series of macrocyclic ether-ketone oligomers. A number of these (the cyclic [2+2] dimer, [3+3] trimer, and [5+5] pentamer) have been isolated chromatographically as pure compounds. The odd-numbered macrocycles are readily-soluble, non-crystalline glasses, but the cyclic dimer is crystalline, high-melting (403 °C) and relatively insoluble. Its structure, determined by single-crystal X-ray methods, provides a new model for chain-folding within lamellar crystallites of aromatic polyketones. The [4+4] cyclic tetramer, although detectable by MALDI-TOF MS, appears to be so insoluble that it cannot be extracted from the product mixture. The amorphous cyclic trimer undergoes ring-opening polymerisation at 300 °C in the presence of a fluoride initiator, to give tough, semi-crystalline polymer.

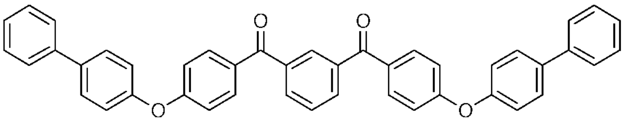
Introduction

The aromatic polyetherketone known as "PK99" (**1**), obtained by polycondensation of 4,4′-dihydroxybiphenyl with 1,3-bis(4-fluorobenzoyl)benzene,[1] exhibits 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 °C) and (iii) there exists an apparent "quantisation" of lamellar crystal thickness, *l*, on crystallisation at progressively higher temperatures, with *l*-values of 35 and 55 Å corresponding to relatively small numbers of aromatic rings (~7 and ~12 respectively).[2] We have proposed that these anomalies may be associated with the 1,3-substitution pattern of the bisketone aromatic unit, which can provide sites for tight chain-folding by switching from an 'extended' conformation (fragment A in Scheme 1) to one that is 'U-shaped' (fragment B).[3]

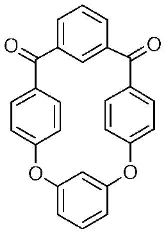


1

Direct evidence for the existence of these two alternative conformations was obtained from single-crystal X-ray structures of firstly the linear oligomer **2**, obtained by condensation of 1,3-bis(4-fluorobenzoyl)benzene with two equivalents of 4-hydroxybiphenyl, and secondly that of the cyclic oligomer **3** obtained by *cyclo*-condensation of 1,3-bis(4-fluorobenzoyl)-benzene with resorcinol.[3] In the same way that single-crystal studies of macrocyclic alkanes provided the first structural models for chain-folding in poly(ethene),[4] the small macrocycle **3** provided a means of investigating structural features of the "U-shaped" aromatic bisketone unit as a possible model for chain-folding within a polymer crystallite.[3] In the present paper we report an extension of this work involving the synthesis, fractionation and characterisation of a novel series of cyclic oligomers based on the repeat unit of PK99 itself, including a single-crystal X-analysis of the [2+2] *cyclo*-dimer and a study of the ring-opening polymerisation of the [3+3] *cyclo*-trimer.[5]



2



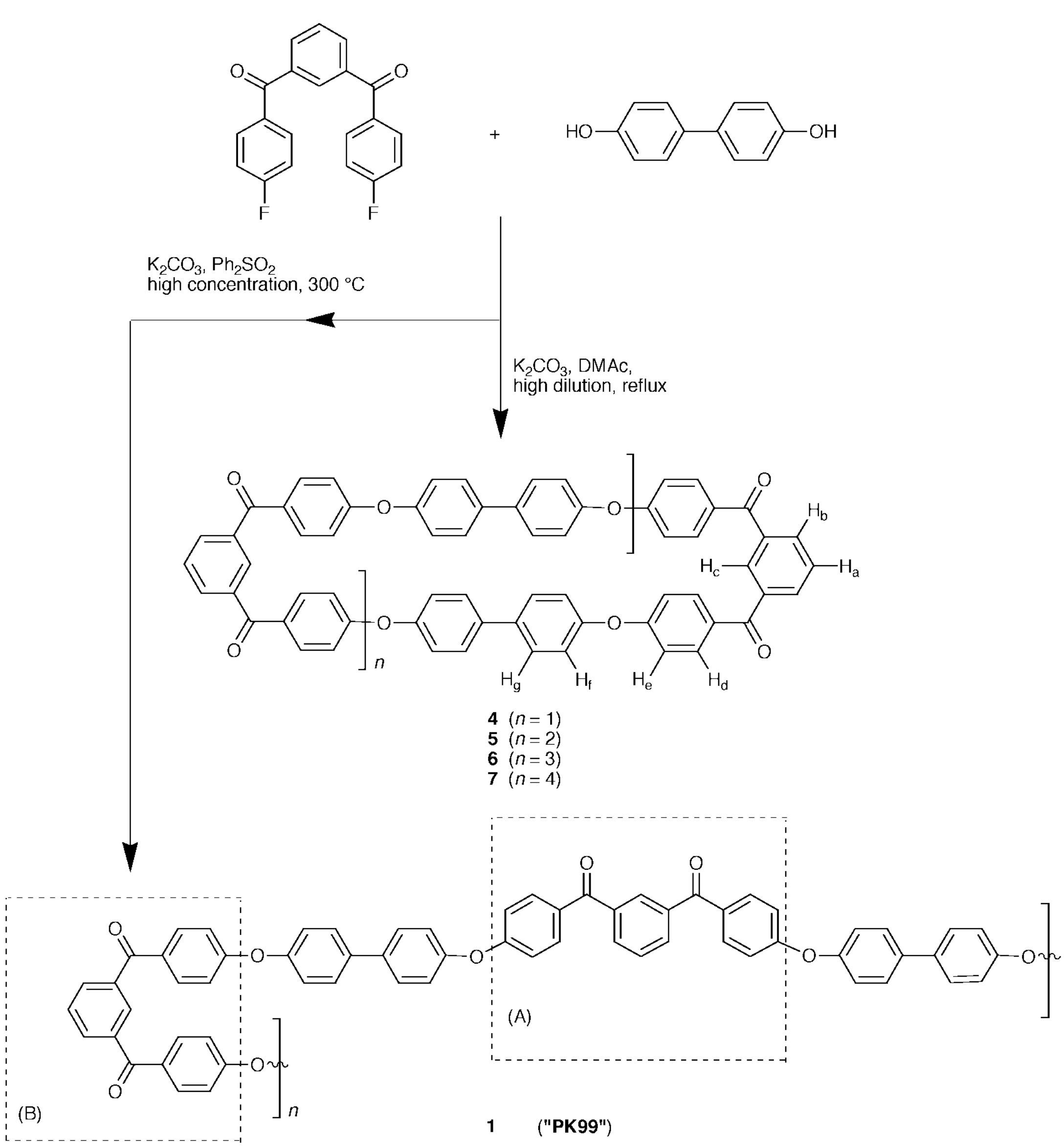
3

Results and discussion

Initially we attempted to synthesise macrocyclic oligomers of PK99 in a simple batchwise reaction. This was conducted by adding 1,3-bis(4-fluorobenzoyl)benzene to a solution of the dipotassium salt of 4,4′-dihydroxybiphenyl (pre-formed by refluxing the bisphenol with K_2CO_3 in a large volume of

---

†On leave from the Dipartimento di Chimica Organica e Biologica, Università di Messina, Salita Sperone 31, 98166 Messina, Italy. E-mail: franz@scirocco.unime.it



Scheme 1 (i) Synthesis of PK99 and (ii) of its cyclic oligomers. The fragments (A) and (B) within the dotted frames represent the 'extended' and 'U-shaped' conformations of the bisketone unit respectively. The hydrogen atoms in the diagram representing the cyclic oligomers are labelled according to the assignments given for their ^{1}H NMR spectra.

dimethylacetamide–toluene, using a Dean–Stark apparatus to remove the water). The mixture was then refluxed for 8 h while the temperature was progressively raised to 165 °C by removal of toluene. This procedure did indeed afford cyclic oligomers, but in only low yield (*ca.* 1.5% for the [2+2] macrocycle) even when operating at very low concentrations (0.04 M in each monomer). The crude products were precipitated from the reaction mixture by addition of water and were filtered off. Small quantities of the cyclic oligomers were obtained by Soxhlet extraction of the precipitate with dichloromethane (DCM), but the bulk of the product remained undissolved. The thermal characteristics of the insoluble material closely resembled those of high molar mass PK99.

When this same reaction was however conducted under *pseudo*-high dilution conditions using a syringe-pump for monomer addition (see Experimental Section), precipitation of the products and extraction with dichloromethane followed by fractional crystallisation and column chromatography afforded the [2+2] *cyclo*-dimer (**4**), [3+3] *cyclo*-trimer (**5**) and [5+5] *cyclo*-pentamer (**7**) as pure compounds, in a total yield of *ca.* 25%. The chromatogram obtained by HPLC analysis of the initial dichloromethane extract is shown in Fig. 1. Three major peaks can be observed which correspond, in order of retention time, to the cyclic dimer, trimer and pentamer respectively. The chemical identity of each peak was confirmed using a purified and characterised sample of each macrocycle as an internal standard. Curiously, there was no evidence of a peak for the expected cyclic tetramer (between the trimer and the pentamer). This is almost certainly a result of its very low solubility, since the presence of [4+4] *cyclo*-tetramer (**6**) in the reaction mixture was confirmed by MALDI-TOF MS—a technique which also showed a series of peaks corresponding to cyclic oligomers up to the [8+8] macrocycle. It is interesting to note at this point that the MALDI-TOF mass spectrum also showed evidence for the [1+1] "cyclo-monomer", a rather strained macrocycle but one which molecular models nevertheless suggest could possibly exist. Indeed, extrapolation of retention times t_R for the higher macrocycles suggests a possible assignment of the very weak HPLC peak at $t_R = 2.2$ min to the cyclic monomer, but we have not yet succeeded in isolating or characterising this compound.

In preparing samples for MALDI-TOF mass spectrometric analysis, intimate mixing between the very insoluble sample and the dithranol matrix was necessary to observe the peaks for the larger cyclics, and such mixing was best achieved in the present system by evaporation of the solvent from a solution of

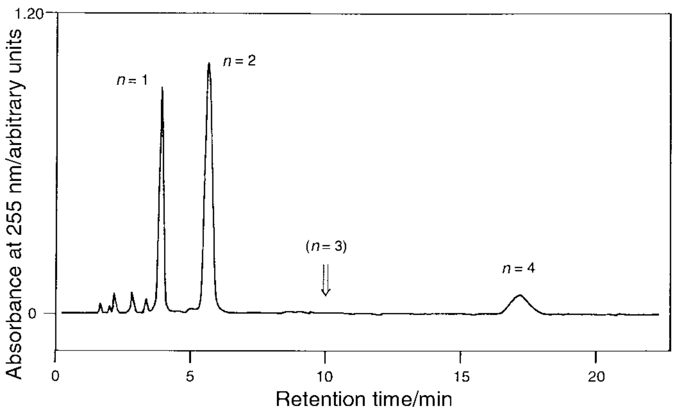


Fig. 1 HPLC trace of the dichloromethane extract from the crude mixture obtained by condensation of 4,4′-dihydroxybiphenyl with 1,3-bis(4-fluorobenzoyl)benzene under *pseudo*-high dilution conditions. The trace shows three well-separated peaks for the cyclic dimer (**4**, $n=1$), trimer (**5**, $n=2$) and pentamer (**7**, $n=4$) in order of retention time. An interpolated retention time for the absent cyclic tetramer (**6**, $n=3$) is also shown.

the sample and matrix in trifluoroacetic acid. Using this approach, the isolated [5+5] *cyclo*-pentamer (**7**) for example showed only a very strong $[M+H]^+$ parent ion at *m/z* 2342 (corresponding to the $^{12}C_{159}{}^{13}C_1$ isotopomer), with no evidence of fragmentation.

The predominant formation of cyclic oligomers when using *pseudo*-high dilution conditions is consistent with dramatic differences in the thermal characteristics of the crude product mixture when compared with those of the mixture from the earlier batchwise reaction. The latter shows only a single endotherm at 305 °C, corresponding to the melting point of PK99, whereas DSC analysis of the *pseudo*-high dilution product shows a complex series of endotherms (associated with the melting of different macrocyclic oligomers) in the temperature range 300–420 °C.

The DSC trace of the isolated and purified [2+2] *cyclo*-dimer **4** contains a sharp but weak endotherm at 360 °C, followed by a strong melting peak at 406 °C. This behaviour is reproducible even when the same sample is subjected to repeated cycles of heating and cooling. Polarising microscopy strongly suggests that the weaker endotherm in fact corresponds to a solid state (crystal–crystal) transition. Macrocycle **4** is sparingly soluble in most organic solvents at room temperature, but can be recrystallised by slow evaporation of a DCM solution, or from hot *N*-methylpyrrolidone (NMP). Addition of strong acids to DCM greatly improves the solubility of **4**. Thus, its ^{13}C NMR spectrum (which contains the expected thirteen resonances) could readily be obtained using a 4 : 1 (v/v) mixture of CD_2Cl_2 with CH_3SO_3H as solvent, and this acid-solubility was also exploited in order to grow single crystals suitable for X-ray analysis. A solution of the macrocycle in DCM–CF_3COOH was placed in a vial with a small opening; this vial was introduced into a larger one containing pellets of potassium hydroxide, and the larger vial was then sealed. Well-formed single crystals of macrocycle **4** were produced over several days, as the volatile acid in the solvent mixture was progressively removed and trapped in the form of its potassium salt by reaction with the solid base.

X-ray analysis of **4** (Fig. 2) shows the molecule to adopt a centrosymmetric conformation in which the biphenyl units have negligible torsion angles (*ca.* 1°) between their aryl rings (as found also in the linear oligomer **2**).[3] As in **2** the planes of the "etherketone" rings are steeply inclined to their adjacent biphenyl units (*ca.* 70°) and to the isophthaloyl ring system (*ca.* 60°). These geometries are, as is usually observed in aromatic etherketones, associated with significant in-plane distortions at the arene carbon atoms linked to ether oxygen.[6] Relevant bond angles and torsion angles characterising the geometry and conformation of macrocycle **4** are given in the caption to Fig. 2. Molecular packing is dominated by π–π and C–H···π interactions, the former between ring C(16)–C(21) and its centrosymmetrically-related counterpart in the $11\bar{1}$ direction, with an interplanar separation of 3.54 Å. The latter involves a pair of interactions in the 110 direction, between C(33)–H and ring C(2)–C(7) and their inversion-related equivalents; the H···π distance is 2.77 Å with a C–H···π angle of 147°. The macrocycles are stacked in a semi-overlapping fashion such that the void within one molecule is occupied by a pair of aromatic ketone units, inserted from opposite directions.

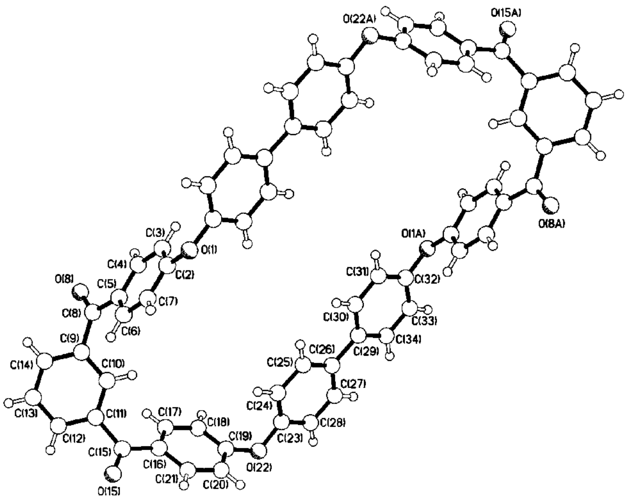


Fig. 2 Molecular structure of the [2+2] *cyclo*-dimer **4**. Selected bond angles: C(32A)–O(1)–C(2), 120.9(2); O(1)–C(2)–C(3), 124.0(3); O(1)–C(2)–C(7), 115.2(3); C(5)–C(8)–C(9), 119.9(2); C(11)–C(15)–C(16), 119.6(2); C(19)–O(22)–C(23), 118.1(2); O(22)–C(23)–C(24), 124.2(3); O(22)–C(23)–C(28), 116.5(3)°. The mean torsional twist angle about C(32A)–O(1) is 64°; about O(1)–C(2) 8°, C(5)–C(8) 22°, C(8)–C(9) 43°, C(11)–C(15) 44°, C(15)–C(16) 21°, C(19)–O(22) 78°, O(22)–C(23) 10°, and C(26)–C(29) 1°.

The potential of the isophthaloyl unit to provide a site for chain-folding is clearly demonstrated in this structure, although here the chain-fold is relatively loose, unlike the situation in the smaller macrocycle **3**, where the isophthaloyl geometry is appropriate to adjacent re-entry. In the present structure the oxygen atoms of the carbonyl groups are directed away from the centre of the macrocycle and towards opposite sides of the plane of the isophthaloyl ring, a geometry in striking contrast to that observed in the small cyclic oligomer **3** and also to that, in the linear oligomer **2**.[3] However, as a consequence of the skewed isophthaloyl conformation, the

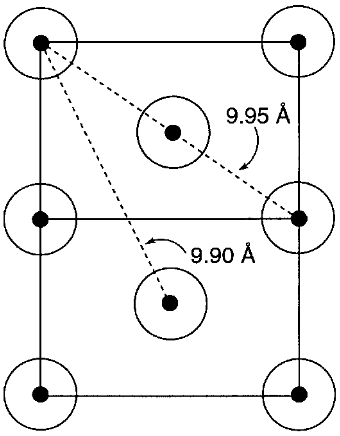


Fig. 3 Lattice projection along the *c*-direction showing interchain distances (ether-oxygen to ether-oxygen) in the crystal structure of PK99: (i) diagonally lattice-translated chains (9.95 Å) and (ii) non-adjacent symmetry-related chains (9.90 Å).

separation of the ether oxygen atoms O(1) and O(22) is 9.82 Å, a value that approaches very closely two independent interchain ($\mathrm{O}_{(\mathrm{ether})}\cdots\mathrm{O}_{(\mathrm{ether})}$) distances (9.95 and 9.90 Å) in the crystal structure of PK99 polymer (Fig. 3).[3]

In the first of these interchain separations a potential chain-fold can link the ether oxygen atoms of diagonally lattice-translated chains, which are separated by 9.95 Å. However, this fold crosses directly over the projection of a glide-related chain so that, unless the latter represents a chain-end, such a fold may not be physically reasonable. On the other hand a chain-fold linking *alternate* glide-related chains spans a similar $\mathrm{O}_{(\mathrm{ether})}\cdots\mathrm{O}_{(\mathrm{ether})}$ distance (9.90 Å) and avoids the problem of chain crossover. Thus, macrocycle **4** appears to provide a further model for chain folding in PK99, again demonstrating the possibility of *specific*, but now *non-adjacent*, chain re-entry into the crystallite. Molecular simulation and energy-minimisation studies confirm that no abnormal bond lengths, angles or torsion angles are required to generate this latter type of chain-fold (Fig. 4).

In contrast to macrocycles with even numbers of repeat units ([2+2] and [4+4]), those with odd numbers ([3+3] and [5+5]) were very soluble in most organic solvents and could not be obtained in crystalline form. The DSC trace of a chromatographically pure sample of the [3+3] macrocycle shows no evidence of a melting endotherm, only a glass transition at 153 °C. This observation encouraged us to attempt the ring-opening polymerisation (ROP) of the amorphous [3+3] cyclic trimer, as there is no requirement in this system to exceed the (often very high) melting point of a crystalline macrocycle before polymerisation can occur. This method of polymer synthesis offers a number of advantages,[5] including the possibility of conducting polymerisation within a mould, or between the fibres of a composite structure, thereby exploiting the low viscosity and good wetting ability of the melt at relatively low temperatures.

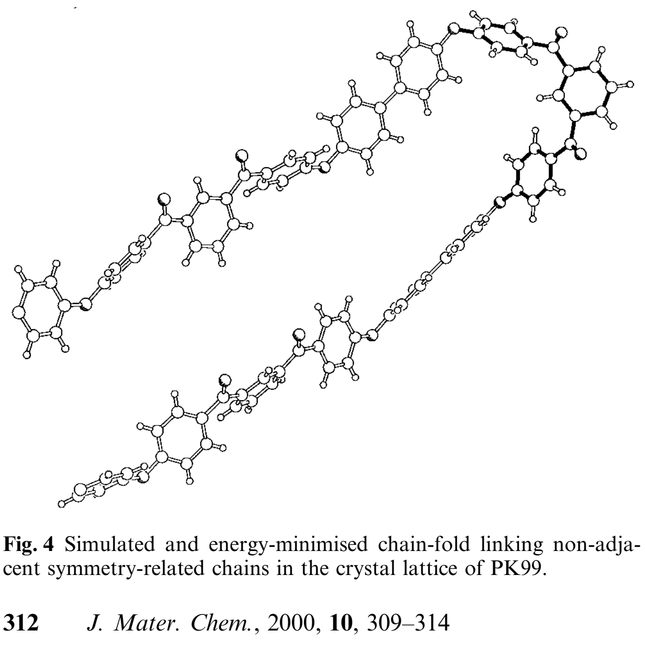


Fig. 4 Simulated and energy-minimised chain-fold linking non-adjacent symmetry-related chains in the crystal lattice of PK99.

Ring-opening polymerisation of the cyclic [3+3] trimer **5** was achieved by heating a sample containing 1 wt% cesium fluoride as initiator for 30 min at 300 °C in a standard aluminium DSC crucible.[7] In order to achieve homogeneous mixing of the initiator with the macrocycle, the sample for polymerisation was prepared by concentrating to dryness a methanolic suspension of the macrocycle in which was dissolved the appropriate quantity of caesium fluoride. The newly formed polymer showed a T_g at 168 °C and, after annealing at 250 °C for 90 minutes, a strong crystal melting endotherm at 302 °C (*cf.* 305 °C reported for PK99). In an experiment modelling the production of a composite material, ring-opening polymerisation of **5** was conducted in a crucible within which the sample rested on a woven stainless steel cloth (150 µm mesh). In a control experiment, a sample of conventional, high molar mass PK99 was heated for the same time and at the same temperature in contact with the same type of cloth. Scanning electron micrographs of the two samples (after removal of the cloth) are shown in Fig. 5. While the high molar mass polymer has clearly not penetrated into the stainless steel cloth, extensive flow of the low-viscosity molten

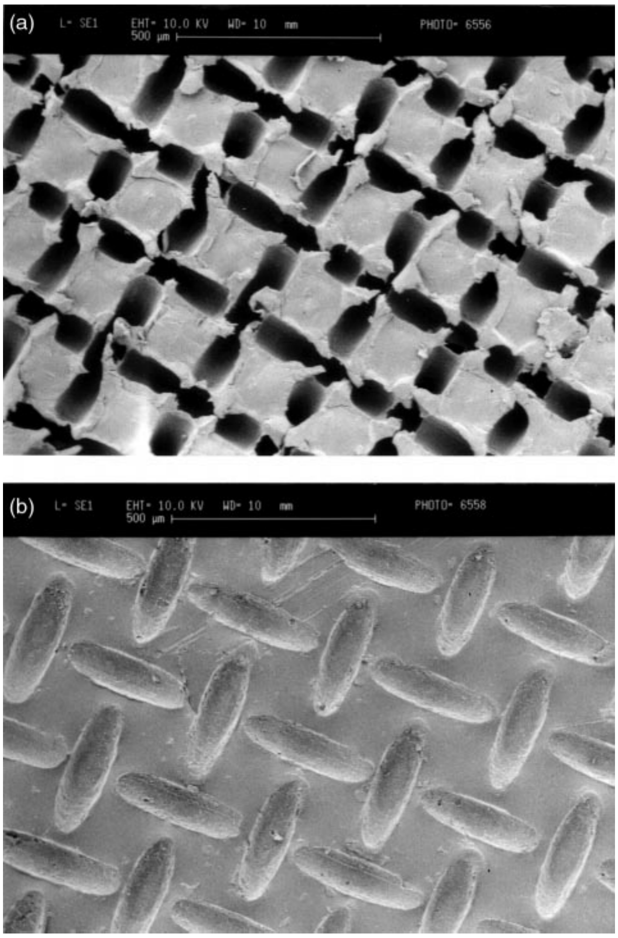


Fig. 5 (a) Scanning electron micrograph of a sample of PK99, produced by ring-opening polymerisation of macrocycle **5** at 300 °C for 30 min, while in contact with a stainless-steel cloth (150 µm mesh size); (b) Sample of conventionally-produced PK99, heated in contact with the same type of cloth under conditions identical to those used to produce specimen (a).

macrocyle into the mesh has obviously occurred during the ring-opening polymerisation process, demonstrating the potential advantages of ROP in this situation.

The cyclic [5 + 5] macrocycle shows thermal behaviour analogous to that of the [3 + 3] macrocycle. In principle it should be just as suitable for ROP synthesis of PK99 but, as it was obtained in considerably lower yield, ring-opening polymerisation of this oligomer has not yet been attempted.

Conclusions

We have demonstrated that *cyclo*-condensation of 4,4′-dihydroxybiphenyl with 1,3-bis(4-fluorobenzoyl)benzene affords a series of [$n+n$] macrocyclic oligomers homologous with the polyetherketone known as "PK99". A characteristic feature of these macrocyclic oligomers is that, for odd values of n, the macrocycles are readily-soluble, non-crystalline glasses, whereas the even-numbered members of the series are crystalline, high-melting and relatively insoluble. The X-ray structure of the [2 + 2] cyclodimer structure provides a new model for chain-folding within lamellar crystallites of PK99. The potential value of macrocyclic ring-opening polymerisation in composite materials fabrication has been demonstrated using the amorphous [3 + 3] cyclotrimer which polymerises readily in the presence of fluoride ion, to give tough, semi-crystalline polymer.

Experimental

Instrumentation

Proton and ^{13}C NMR spectra were recorded on Varian Gemini-200, Varian Unity Inova-300 and Varian Unity-500 spectrometers. Conventional mass spectra (EI/CI/FAB) were run on a Kratos Concept spectrometer, and MALDI-TOF MS analyses were obtained on Kratos Kompact and Micromass Tofspec instruments. Differential scanning calorimetry (DSC) was performed under nitrogen using a Mettler DSC20 system. Conditions for HPLC analyses were: Perkin-Elmer LC-480 diode array system, phenosphere silica gel column 8 mm × 10 cm, eluent 5% EtOAc in DCM, flow rate 2 cm^3 min^{-1}. Single crystal X-ray studies were carried out on a Siemens P4 diffractometer using graphite-monochromated Cu-Kα radiation. Molecular models were constructed using *Cerius2* (MSI, Cambridge, UK) running on a Silicon Graphics O2 workstation. Elemental analyses were provided by the analytical service of Manchester University.

Crystal data for 4

$C_{64}H_{40}O_8.2CH_2Cl_2$, MW 1106.8, triclinic, $P\bar{1}$, $a = 10.800(1)$, $b = 11.016(1)$, $c = 12.414(1)$ Å, $\alpha = 107.85(1)$, $\beta = 100.95(1)$, $\gamma = 96.48(1)°$, $V = 1356.9(2)$ Å^3, $Z = 1$ (the molecule is disposed about a center of symmetry), $D_c = 1.354$ g cm^{-3}, μ(Cu-Kα) = 24.6 cm^{-1}, $F(000) = 572$, $T = 293$ K. Data for a clear crystalline prism of dimensions 0.10 × 0.13 × 0.47 mm were measured at 20 °C using ω-scans. From a total of 4171 independent relections measured ($2\theta \leqslant 124°$), 3173 were found to have $|F_o| > 4\sigma(|F_o|)$ and these were considered to be observed. The data were corrected for Lorentz and polarisation factors but not for absorption. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The included molecule of dichloromethane proved to be disordered over four partially overlapping sites, each of different occupancy. The positions of the hydrogen atoms were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares, based on F^2, and converged to give $R = 0.064$. Computations were carried out using the SHELXTL-PC program system.[8] Tables of fractional atomic coordinates, bond lengths, bond angles and thermal parameters for **4** have been deposited at the Cambridge Crystallographic Data Centre; CCDC reference number 1145/196. See http://www.rsc.org/suppdata/jm/a9/a908414b/ for crystallographic files in .cif format.

Synthesis of the cyclic oligomers

1,3-Bis(4-fluorobenzoyl)benzene (1.45 g, 4.5 mmol) and 4,4′-dihydroxybiphenyl (0.84 g, 4.5 mmol) were dissolved in dimethylacetamide (DMAc) (45 cm^3) and introduced with a syringe-pump over 30 h, under a nitrogen atmosphere, into a vigorously stirred and refluxing suspension of K_2CO_3 (0.76 g, 5.5 mmol) in DMAc–toluene (150 cm^3, 4 : 1). At the end of the addition the reaction mixture appeared as a clear solution. The mixture was then cooled to room temperature while being stirred overnight. During this period a white precipitate was formed. This was filtered off and washed on the filter with methanol–water (3 × 10 cm^3, 2 : 1). These washings were added to the filtrate and the mixture was diluted with water (1 l). The resulting milky suspension was filtered. This second solid residue was washed on the filter with methanol–water (3 × 10 cm^3, 2 : 1) and combined with that obtained from the first filtration. This procedure allowed a quantitative recovery of the organic products of the reaction.

A small sample of the crude solid was suspended in DCM and analysed by TLC (SiO_2, DCM–EtOAc 97.5 : 2.5). The soluble fraction was visualised under UV light and by treatment with iodine vapour. Three major components having R_f values 0.5, 0.4, and 0.2 could be identified as well-defined spots. The crude product was subjected to Soxhlet extraction with dichloromethane. Fractional crystallisation of the extract (which gave some [2 + 2] macrocycle) and column chromatography (SiO_2, DCM–EtOAc from 99 : 1 to 94 : 6) afforded three compounds that in order of elution were characterised as follows.

The [2 + 2] cyclic dimer **4**: (158 mg, 7.7%) mp 406 °C (DSC, recrystallised from hot *N*-methylpyrrolidone or by slow evaporation of a DCM solution); ^{1}H NMR (300 MHz, CD_2Cl_2–CH_3SO_3H): δ 8.39 (br s, 2H, H$_c$), 8.14–8.11 and 8.13 (m, 4H, H$_b$ overlapping with d, 8H, $J = 9.1$ Hz, H$_g$), 7.93 (t, $J = 7.8$ Hz, 2H, H$_a$), 7.78 (d, 8H, $J = 8.6$ Hz, H$_d$), 7.30 (d, 8H, $J = 8.6$ Hz, H$_e$), 7.22 (d, 8H, $J = 9.1$ Hz, H$_f$); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.13, (d, 4H, $J = 7.5$ Hz, H$_b$), 7.94 (br s, 2H, H$_c$), 7.87 (d, 8H, $J = 8.8$ Hz, H$_g$), 7.75 (t, 2H, $J = 7.5$ Hz, H$_a$), 7.57 (d, 8H, $J = 8.8$ Hz, H$_d$), 7.14 and 7.11 (2 × d, 16H, $J = 8.8$ Hz, H$_e$ and H$_f$); ^{13}C NMR (75 MHz, CD_2Cl_2–CH_3SO_3H): δ 200.8, 168.9, 153.0, 138.7, 138.3, 137.6, 133.8, 132.9, 129.9, 128.8, 125.4, 121.5, 118.0; Positive FABMS: 937, $(M+1)^+$; calcd for $C_{64}H_{40}O_8$: C 82.04; H 4.30; found C 81.66; H 4.39 %.

The [3 + 3] cyclic trimer **5**: (323 mg, 15%), glass, T_g 153 °C onset (DSC); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.08–8.06 (m, 9H, H$_b$ and H$_c$), 7.86 (d, 12H, $J = 8.8$ Hz, H$_g$), 7.69 (t, 3H, $J = 7.7$ Hz, H$_a$), 7.65 (d, 12H, $J = 8.8$ Hz, H$_d$), 7.20 (d, 12H, $J = 8.8$ Hz, H$_e$), 7.11 (d, 12H, $J = 8.8$ Hz, H$_f$); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 194.1, 161.7, 154.9, 137.8, 136.7, 132.8, 132.3, 131.6, 130.9, 128.8, 120.4, 117.3; Positive FABMS: 1405, M$^+$; calcd for $C_{96}H_{60}O_{12}{\cdot}C_4H_8O_2$: C 80.41; H 4.59; found C 80.50; H 4.44%.

The [5 + 5] cyclic pentamer **7**: (67 mg, 3%); glass, T_g 153 °C onset; ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.96 (br s, 5H, H$_c$), 7.90 (d, 10H, $J = 7.8$ Hz, H$_b$), 7.78 (d, 20H, $J = 8.8$ Hz, H$_g$), 7.54 (t, 5H, $J = 7.8$ Hz, H$_a$), 7.50 (d, 20H, $J = 8.8$ Hz, H$_d$), 7.06 (d, 20H, $J = 8.8$ Hz, H$_e$), 6.99 (d, 20H, $J = 8.8$ Hz, H$_f$); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 193.5, 161.0, 154.3, 137.2, 136.0, 132.2, 131.7, 130.9, 130.2, 128.0, 127.8, 119.7, 116.6; Positive FABMS: 2341, M$^+$; calcd for $C_{160}H_{100}O_{20}{\cdot}2(C_4H_8O_2)$: C 80.12, H 4.63; found: C 79.96; H 4.39 %.

Acknowledgements

This work was supported by the Royal Society, the University of Messina, the UK Engineering and Physical Sciences Research Council (grant numbers GR/K87999 and GR/K73442) and the Royal Society of Chemistry (a travel grant to FHK). We wish to thank Mr P. R. Ashton of the University of Birmingham for carrying out preliminary MALDI-TOF MS analyses.

References

1 J. J. Liggat and P. A. Staniland, *Polym. Commun.*, 1991, **32**, 450.
2 D. J. Blundell, J. J. Liggat and A. Flory, *Polymer*, 1992, **33**, 2475; M. Bellomo, L. Franco and M. Hill, *Polymer*, 1997, **38**, 5643.
3 I. Baxter, H. M. Colquhoun, F. H. Kohnke, D. F. Lewis and D. J. Williams, *Polymer*, 1999, **40**, 607.
4 H. F. Kay and B. A. Newman, *Acta Crystallogr., Sect. B*, 1968, **24**, 615; P. Groth, *Acta Chem. Scand.*, 1979, **A33**, 199; T. Trzebiatowski, M. Dräger and G. R. Strobl, *Makromol. Chem.*, 1982, **183**, 731.
5 For recent reviews of macrocyclic ring-opening polymerisation see:Y. F. Wang, K. P. Chan and A. S. Hay, *React. Funct. Polym.*, 1996, **30**, 205; P. Hodge, H. M. Colquhoun and D. J. Williams, *Chem. Ind. (London)*, 1998, 162.
6 H. M. Colquhoun, C. A. O'Mahoney and D. J. Williams, *Polymer*, 1993, **34**, 218.
7 H. M. Colquhoun, C. C. Dudman, M. Thomas, C. A. O'Mahoney and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1990, 336.
8 SHELXTL/PC version 5, Bruker AXS Analytical Instruments, Madison WI, 1996.

Paper a908414b