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Cyclic oligomers of poly(ether ketone) (PEK): synthesis, extraction from polymer, fractionation, and characterisation of the cyclic trimer, tetramer and pentamer

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Exhaustive extraction of poly(ether ketone) (PEK) with hot chloroform affords a novel range of cyclic oligo(ether ketone)s. The proportion of cyclic material extracted in this way ranged from as high as 13% for laboratory-synthesised PEK to as low as 2% for an industrial development-grade polymer. Extracts were characterised by ^{1}H NMR spectroscopy, GPC, and MALDI-TOF mass spectrometry, which indicated the presence of ring sizes from the cyclic trimer up to at least the cyclic decamer. These macrocyclic oligomers were also prepared (in *ca.* 80% total yield) by self-polycondensation of 4-fluoro-4′-hydroxybenzophenone under pseudo-high-dilution conditions. Column chromatography on silica gel enabled isolation of the cyclic trimer, cyclic tetramer and cyclic pentamer as pure compounds, characterised by NMR spectroscopy, mass spectrometry, elemental analysis and (for the cyclic trimer and cyclic tetramer) X-ray crystallography. Ring-opening polymerisation of mixed cyclic oligomers was achieved in the melt at 385 °C, using the potassium salt of 4-hydroxybenzophenone as initiator.

Introduction

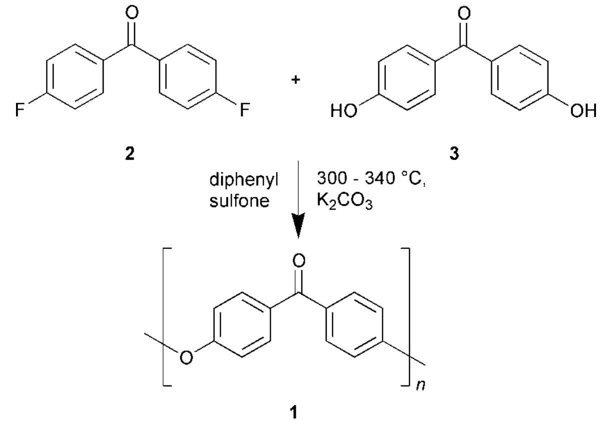
For statistical reasons a step-growth polymerisation invariably produces, in addition to the desired linear polymer, a cyclic oligomer fraction.[1–3] The former arises from *intermolecular* (second order) reactions between end groups whilst the latter results from analogous *intramolecular* (first order) reactions. The formation of linear polymer is therefore favoured at high reactant concentrations and, as the concentration falls, the probability of forming cyclic oligomers progressively increases.[3] Cyclic oligomers can often be separated easily from high molar mass linear material because they generally differ considerably in solubility from their parent polymers.[2a,4] In consequence the presence of cyclic oligomers in commercial step-growth polymers such as polyesters, polycarbonates, and poly(ether sulfone)s has been established for many years.[2a,5]

Syntheses of high performance aromatic polymers, such as the crystalline poly(ether ketone) (PEK) **1**, might be expected to produce larger cyclic oligomer fractions than melt-polymerised materials such as PET and nylon6.6 because aromatic polyetherifications are carried out *in solution*. Thus, PEK can be obtained by reaction of 4,4′-difluorobenzophenone **2** with 4,4′-dihydroxybenzophenone **3** in the presence of potassium carbonate, using diphenyl sulfone as solvent, at temperatures of up to 340 °C (Scheme 1).[6] This very high reaction-temperature is required, not to overcome any energy-barriers to etherification (which in fact proceeds readily below 200 °C) but to prevent the poly(ether ketone) from crystallising from solution before high molar mass has been achieved. In the present work we describe not only the extraction of cyclic oligomers **4** from an industrial development-grade of PEK, but also the pseudo-high-dilution synthesis of the same macrocycles **4**. The cyclic trimer **4a**, cyclic tetramer **4b** and cyclic pentamer **4c** were isolated as pure compounds and characterised in detail. Cyclic oligomers of several high-performance polymers are already known, for example the cyclic oligomers of poly(ether ether ketone) (PEEK) **5**,[7] and bisphenol-A polysulfone **6**,[8] but cyclic oligomers **4** of PEK have not been previously described. Cyclic oligomers related to step-growth polymers are currently of considerable interest as potential feedstocks for entropically-driven ring-opening polymerisation (ED-ROP),[9] as such polymerisations are in principle environmentally friendly in that no by-products are generated, and also, being essentially thermally neutral and evolving no volatiles, they seem ideally suited to the *in situ* production of composite materials.

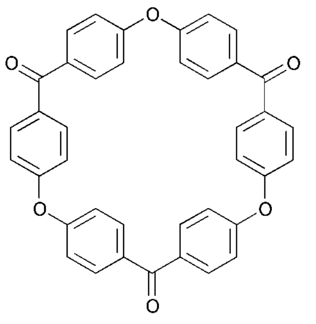
Experimental

General experimental details

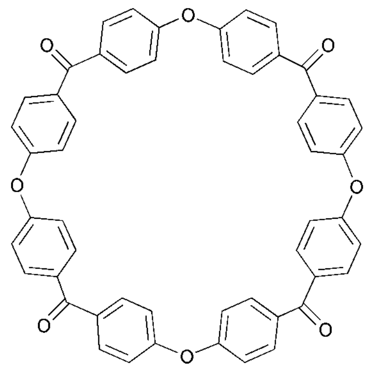
Abbreviations: *N*-methylpyrrolidone (NMP); trifluoroacetic acid (TFA); *N*,*N*-dimethylacetamide (DMAc); tetrahydrofuran (THF); and dimethyl sulfoxide (DMSO). Unless indicated



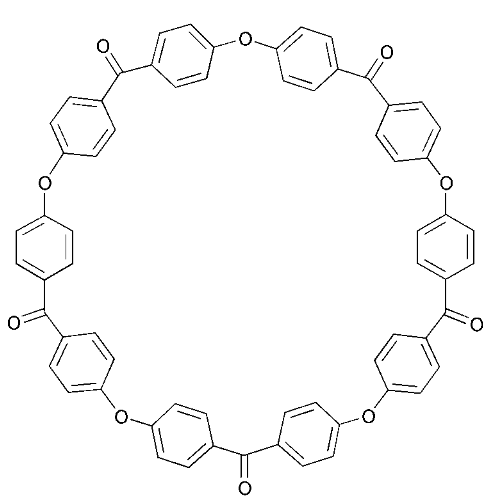
Scheme 1 The synthesis of poly(ether ketone) (PEK) **1**.



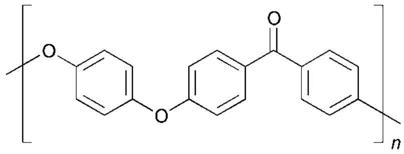
4a



4b



4c



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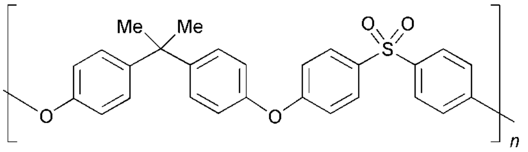

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otherwise melting points were determined under nitrogen using a Mettler DSC 20 instrument. Infra-red (IR) spectra were recorded on a Perkin-Elmer 1710 Fourier transform instrument using, unless indicated otherwise, KBr discs. ^{1}H Nuclear magnetic resonance (NMR) spectra were recorded at 500 Mz using a Varian Unity Spectrometer for, unless indicated otherwise, solutions in deuterochloroform. Mass spectra (EI/CI/FAB-MS) were obtained using a Kratos Concept Spectrometer; ionization by FAB was achieved using xenon atoms, with a matrix of *m*-nitrobenzyl alcohol. MALDI-TOF Mass spectra were obtained on a Micromass Tofspec instrument using 2,4-dihydroxybenzoic acid as matrix. Gel permeation chromatographic (GPC) analyses of oligomers were carried out in chloroform at 20 °C, using a series of four PL-Gel 30 cm mixed-E columns or a single 10 mm, 500 Å column, with a Polymer Laboratories GPC LC 1240 RI detector. The system was calibrated using polystyrene standards.

Synthesis of cyclic oligomers 4 and isolation of the cyclic trimer 4a, cyclic tetramer 4b and cyclic pentamer 4c

A mixture of potassium carbonate (2.00 g, 145 mmol), toluene (45 cm^3) and NMP (250 cm^3, freshly distilled from calcium hydride) was vigorously stirred in a 500 cm^3 round-bottomed flask equipped with a Dean–Stark trap, and the temperature was raised to 145–150 °C. A solution of 4-fluoro-4′-hydroxybenzophenone **7**^{10} (5.00 g, 23 mmol) in NMP (45 cm^3) was added over a 24 h period using a syringe pump. Water was removed *via* the Dean–Stark trap. When addition was complete the mixture was stirred for a further hour then cooled to ambient temperature and slowly added to cold methanol (300 cm^3). The white precipitate was filtered off, washed on the filter with water (300 cm^3), then with methanol (300 cm^3), and finally dried. The crude product (4.30 g, 94%) was placed in a Soxhlet thimble and extracted with hot chloroform for 24 h. The chloroform extract was evaporated and the residue, consisting essentially of cyclic oligomers (3.60 g, 79% total yield), was analysed by GPC. Integrated peak areas gave individual yields as follows: cyclic trimer **4a**, 12%; cyclic tetramer **4b**, 33%, cyclic pentamer **4c**, 9%; cyclic hexamer, 9%; cyclic heptamer, 7%; cyclic octamer, 7%; and cyclic nonamer, 1%. Mass spectrometry of the mixture (FAB-MS) showed peaks $[M+H]^+$ at 589, 784, 981, 1178, and 1374, representing cyclic trimer to cyclic heptamer, and MALDI-TOF analysis (no added cation) showed the same range of macrocycles, together with $[M+H]^+$ peaks at 1568 and 1765 (the latter very weak) associated with the cyclic octamer and cyclic nonamer. A portion (1.50 g) of the crude product was extracted with dichloromethane and this extract was subjected to column chromatography on silica gel (30 g) using gradient elution, initially with 0.5% ethyl acetate in dichloromethane and ending with a mixture containing 2% of the more polar solvent. This procedure gave successively the cyclic trimer **4a** (0.065 g), cyclic tetramer **4b** (0.190 g) and cyclic pentamer **4c** (0.055 g).

The cyclic trimer 4a. Mp 510 °C (by DSC); ν_{max} 1664 cm^{-1}; ^{1}H NMR: $\delta = 7.03$ (d, 12H, $J = 8.5$ Hz, Ar-H *ortho* to -O-) and 7.60 ppm (d, 12 H, $J = 8.5$ Hz, Ar-H *ortho* to carbonyl); ^{13}C NMR: $\delta = 118.59$, 131.99, 133.28, 160.22 and 198.07 ppm; mass spectrum (CI) 589 (100%, $[M+H]^+$); calcd for $C_{39}H_{24}O_6$: C 79.59, H 4.08; found: C 80.05, H 4.16%. Crystals suitable for X-ray analysis were grown by vapour diffusion of methanol into a chloroform solution.

The cyclic tetramer 4b. Mp 477 °C (by DSC); ν_{max} 1651 cm^{-1}; ^{1}H NMR (CDCl$_3$–TFA): $\delta = 7.21$ (d, 16H, $J = 8.7$ Hz, Ar-H *ortho* to -O-) and 7.89 ppm (16H, $J = 8.7$ Hz, Ar-H *ortho* to carbonyl); ^{13}C NMR: $\delta = 118.64$, 132.18, 132.72, 160.26 and 196.97 ppm; mass spectrum (CI): 786 (100%; $[M+H]^+$; calcd for $C_{52}H_{32}O_8$: C 79.59, H 4.08; found: C 79.58, H 4.07%. Crystals suitable for X-ray analysis were grown by slow evaporation of a solution in dichloromethane.

The cyclic pentamer 4c. Mp 326 °C (by DSC); ν_{max} 1656 cm^{-1}; ^{1}H NMR: $\delta = 7.21$ (d, 20H, $J = 8.7$ Hz, Ar-H *ortho* to -O-) and 7.89 ppm ($J = 8.7$ Hz, 20H, Ar-H *ortho* to carbonyl); ^{13}C NMR: $\delta = 118.66$, 132.36, 133.20, 159.87 and 194.09 ppm; mass spectrum (FAB): 982 (100%, $[M+2]^+$); calcd for $C_{65}H_{40}O_{10}$: C 79.59, H 4.08; found: C 79.44, H 4.24%.

Crystal data for macrocycles 4a and 4b†

Macrocycle **4a**: $C_{39}H_{24}O_6{\cdot}CH_2Cl_2{\cdot}2CH_3OH$, MW 737.59, monoclinic, $P2_1/c$, $a = 11.107(1)$, $b = 25.419(1)$,

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†CCDC reference number 1145/223. See http://www.rsc.org/suppdata/jm/b0/b000738m/ for crystallographic files in .cif format.

$c = 12.594(1)$ Å, $\beta = 96.91(1)°$, $V = 3529.8(2)$ Å^3, $Z = 4$, $D_c = 1.388$ g cm^{-3}, μ(Cu-Kα) = 21.2 cm^{-1}, $F(000) = 1536$, $T = 183$ K. Crystal dimensions were $0.30 \times 0.50 \times 0.60$ mm. From a total of 5870 independent reflections measured ($2\theta \leqslant 124°$), 5556 were found to have $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed.

Macrocycle **4b**: $C_{52}H_{40}O_8 \cdot 1.5CH_2Cl_2$, MW 912.17, triclinic, $P\bar{1}$, $a = 8.760(1)$, $b = 10.107(1)$, $c = 14.040(1)$ Å, $\alpha = 75.26(1)$, $\beta = 73.00(1)$, $\gamma = 80.20(1)°$, $V = 1143.6(1)$ Å^3, $Z = 1$ (the molecule is disposed about a center of symmetry), $D_c = 1.325$ g cm^{-3}, μ(Cu-Kα) = 22.7 cm^{-1}, $F(000) = 471$, $T = 293$ K. Crystal dimensions were $0.93 \times 0.33 \times 0.05$ mm. From a total of 3938 independent reflections measured ($2\theta \leqslant 125°$), 2816 were found to have $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed.

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, and allowed to ride on their parent carbon atoms. Refinements converged to $R_1 = 0.051$ and 0.061 for **4a** and **4b** respectively. Computations were carried out using the SHELXTL-PC program system.[11]

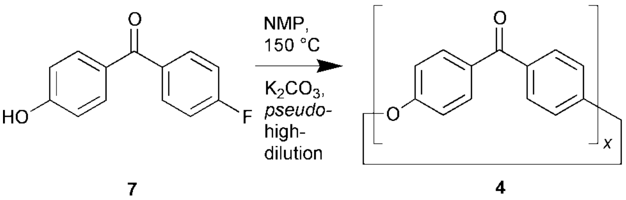
Laboratory synthesis of PEK 1 and extraction of cyclic oligomers 4

A mixture of 4,4′-dihydroxybenzophenone **3** (2.00 g, 9.30 mmol) and anhydrous potassium carbonate (1.70 g, 12.3 mmol) in diphenyl sulfone (13.30 g) was vigorously stirred at 200 °C under a nitrogen atmosphere for 1 hour. Solid 4,4′-difluorobenzophenone **2** (2.04 g, 9.30 mmol) was added rapidly and the temperature was gradually raised to 310 °C and held there for 3 hours. The hot, viscous mixture was then poured onto a clean aluminium sheet and allowed to cool. The resulting toffee-like solid was milled to a powder and extracted with refluxing methanol (2×150 cm^3) to remove diphenyl sulfone, and then with hot water (2×150 cm^3) to remove potassium fluoride and any residual carbonate. The solid remaining was finally dried at 80 °C, to give poly(ether ketone) (PEK, **1**, 3.41 g, 93%). A sample (1.50 g) of this polymer was extracted with hot chloroform for 24 hours using a Soxhlet apparatus. After drying, 1.30 g of polymer was recovered. Evaporation of the chloroform extract, followed by extraction of the residue with refluxing methanol (90 cm^3) to remove traces of diphenyl sulfone, gave a mixture of cyclic oligomers **4** (0.195 g, 13% w/w). By GPC ($CHCl_3$) this fraction was found to contain macrocycles from the cyclic trimer up to at least the cyclic octamer. Analysis by MALDI-TOF mass spectrometry (in the presence of lithium bromide) showed peaks at 596, 792, 988, 1184, 1380, 1577, 1774, 1969, 2165, 2361, and 2557, corresponding to $[M_x + Li]^+$ for $x = 3$–13.

Polymer **1**, after extraction as above, showed ν_{max} 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$–TFA): $\delta = 7.25$ ($J = 8.7$ Hz, 4H, Ar-H *ortho* to -O-) and 7.94 ppm ($J = 8.7$ Hz, 4H, Ar-H *ortho* to carbonyl); ^{13}C NMR ($CDCl_3$–TFA): $\delta = 119.08$, 132.22, 133.40, 160.78 and 198.87 ppm. Inherent viscosity (0.1% in conc. H_2SO_4 at 20 °C) was 0.65 dL g^{-1}. Analysis by DSC showed a strong melting endotherm ($\Delta H_{fusion} = 69$ J g^{-1}) at $T_m = 370$ °C. Partial reduction[12] of this material with triethylsilane and TFA gave a polymer in which 68% of the carbonyl groups had been converted to methylene linkages (as shown by ^{1}H NMR spectroscopy) and which was soluble in DMAc. By GPC the partly-reduced polymer had $\bar{M}_n$ 8400 and $\bar{M}_w$ 13 900.

Extraction of cyclic oligomers 4 from the industrial development polymer "PEK-390P"

Samples of a development grade of poly(ether ketone) (PEK-390P) were provided by ICI Plastics Division, Welwyn, UK, in the form of a free-flowing granular powder. Partial reduction[12] of this material with triethylsilane and TFA gave a polymer in which 74% of the carbonyl groups had been converted to methylene linkages (as shown by ^{1}H NMR spectroscopy) and which was soluble in DMAc. By GPC the partly-reduced polymer had $\bar{M}_n$ 10 300 and $\bar{M}_w$ 18 000.



Scheme 2 The synthesis of macrocyclic aromatic ether-ketones **4**.

A sample of PEK-390P (17 g) was extracted with chloroform using a Soxhlet apparatus. Evaporation of the solvent from the extracts gave a crude cyclic fraction (0.405 g, 2.4% w/w). Extraction of this crude product with methanol removed traces of diphenyl sulfone and left essentially pure cyclic material (0.326 g, 1.9% w/w). By GPC ($CHCl_3$) this purified extract was found to contain cyclic oligomers from the cyclic tetramer **6** up to at least the cyclic decamer. Analysis by MALDI-TOF mass spectrometry (in the presence of LiBr) showed peaks at 790, 986, 1182, 1379, 1575, 1772 and 1969, corresponding to $[M_x + Li]^+$ for $x = 4$–10.

Ring-opening polymerisation of cyclic oligomers

A mixed cyclic oligomer fraction (0.110 g), isolated as described above from PEK-390P, was powdered and suspended in methanol (8 cm^3) containing 0.0033 g of the potassium salt of 4-hydroxybenzophenone. After sonication for 40 min, the suspension was evaporated and the solid dried at 60 °C under vacuum overnight. Polymerisation was carried

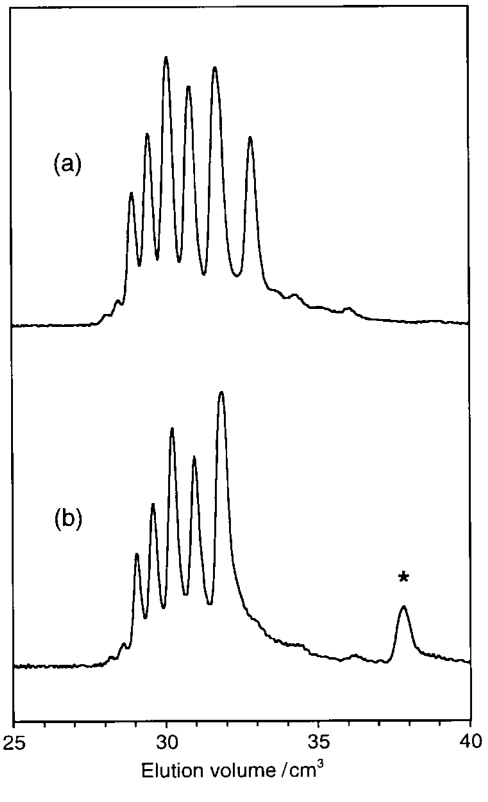


Fig. 1 Gel permeation chromatograms for cyclic oligomers extracted (a) from poly(ether ketone) **1** synthesised in the laboratory and (b) from a sample of the corresponding industrial polymer "PEK-390P". The absence of the cyclic trimer **4a** from chromatogram "b" is clearly evident. The peak marked with an asterisk is due to diphenyl sulfone.

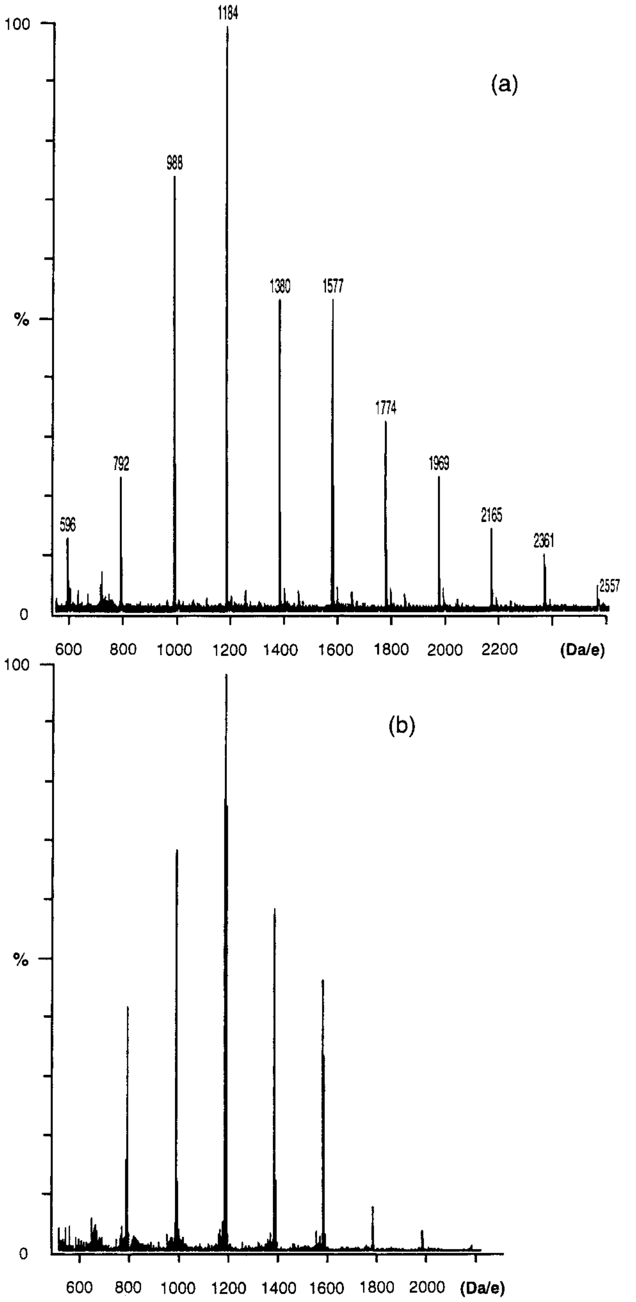


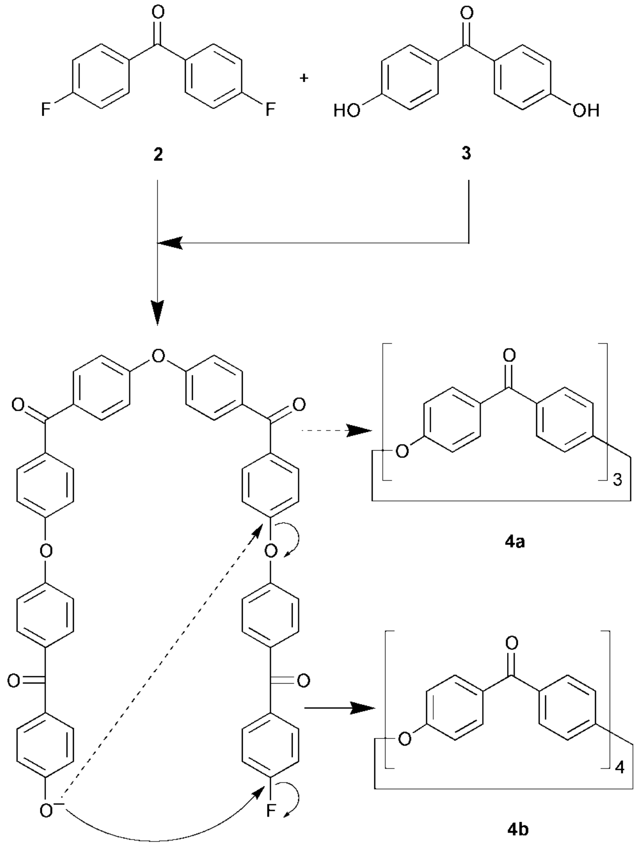
Fig. 2 MALDI-TOF mass spectra (with Li^+ as cationising agent) of the oligomers extracted (a) from PEK produced in the laboratory and (b) from the industrial polymer "PEK-390P". The peaks represent $[M+Li]^+$, where values of M correspond exclusively to *macrocyclic* species.

out in a DSC crucible containing 0.02 g of this material, which was heated under nitrogen to 410 °C to ensure complete melting of the oligomers, and then held at 385 °C for 25 min, before cooling to room temperature. The resulting polymer showed a crystalline melting point of 370 °C ($\Delta H_{\mathrm{fusion}} = 56\ \mathrm{J\ g^{-1}}$).

Results and discussion

Synthesis and characterisation of cyclic oligomers 4

To facilitate analysis of extracts from the various samples of PEK **1**, cyclic ether-ketone oligomers **4** were synthesised from 4-fluoro-4′-hydroxybenzophenone **7** and potassium carbonate in NMP at 145–150 °C using the pseudo-high-dilution technique (Scheme 2). The yield of cyclic oligomers was 79% and GPC analysis indicated that these macrocycles ranged in size from the cyclic trimer **4a** up to at least the cyclic decamer. Their identities were confirmed by FAB and MALDI-TOF mass spectrometry. Careful column chromatography afforded pure crystalline samples of the cyclic trimer **4a**, cyclic tetramer **4b** and cyclic pentamer **4c**. These showed relatively high melting points, at 510 °C, 477 °C and 326 °C respectively, but the trimer **4a** and pentamer **4c** were readily soluble in chloroform, dichloromethane, acetone and THF. The cyclic tetramer **4b** was less soluble in these solvents, but was sufficiently soluble in hot chloroform to permit extraction. All three isolated oligomers were fully characterised by FT-IR and NMR spectroscopy, mass spectrometry and elemental analysis, and crystals of the trimer **4a** and tetramer **4b** proved amenable to single-crystal X-ray analysis (see below).



Scheme 3 Formation of **4b** and **4a**, by end–end ring-closure and by "backbiting" respectively.

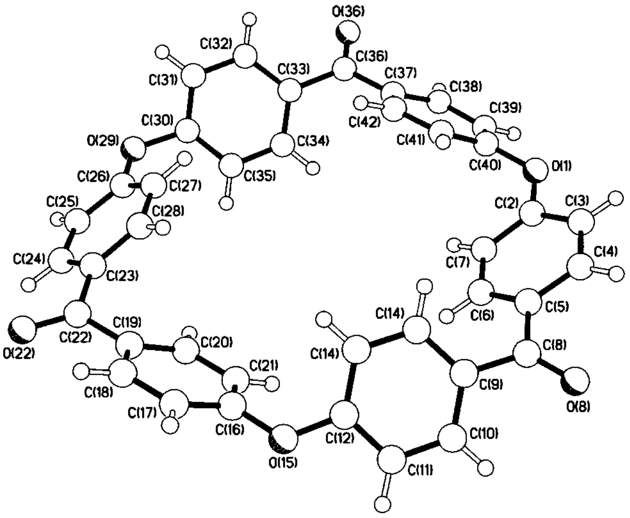


Fig. 3 Single crystal X-ray structure of the macrocyclic trimer **4a**.

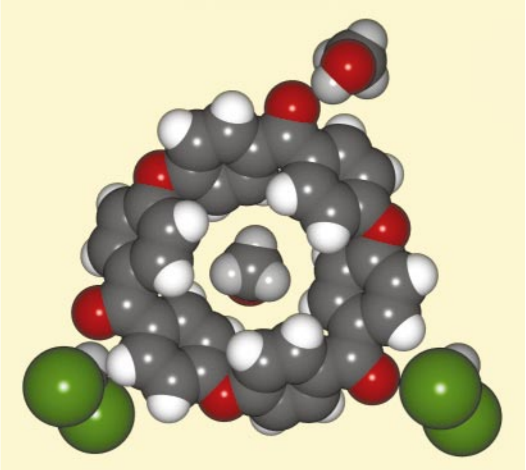


Fig. 4 Space-filling representation of macrocycle **4a** showing the inclusion of methanol in its central cavity, and peripheral hydrogen bonds to methanol and dichoromethane. Hydrogen bond geometries are: [C–H···O], [C···O] Å, [C–H···O]°; methanol 2.94, 2.05, 166; dichloromethane (LHS) 3.22, 2.39, 142; dichloromethane (RHS) 3.08, 2.23, 143.

Extraction of cyclic oligomers 4 from samples of PEK 1

A sample of poly(ether ketone) **1** was first synthesised in the laboratory, as shown in Scheme 1. Cyclic oligomers were carefully extracted from this crude polymer using hot chloroform, and were isolated in 13% total yield. Analysis by GPC (Fig. 1a) and MALDI-TOF mass spectrometry (Fig. 2) showed macrocycles from the cyclic trimer **4a** up to at least the cyclic tridecamer.

Although the single-monomer-based synthesis shown in Scheme 2 can obviously produce macrocycles **4** where *x* is both odd and even, it is of interest to note that the two-monomer synthesis of PEK, shown in Scheme 1, might be expected to give macrocycles containing only even numbers of the two-ring repeat unit. That this is not so is consistent with previous data suggesting that transetherification occurs in many aromatic poly-etherification and -thioetherification reactions, either by intramolecular ("back-biting") processes (Scheme 3)[13] or by reversible, fluoride-catalysed chain cleavage.[14]

An industrially-produced sample of PEK **1** was also extracted with hot chloroform. This material (PEK-390P; a development grade polymer provided by ICI Plastics Division, Welwyn) afforded cyclics in only 1.9% yield w/w. Analysis by GPC (Fig. 1b) and by MALDI-TOF MS (Fig. 2) indicated that the range of cyclics was broadly similar to that obtained for the polymer produced in the laboratory, but that *the trimer was absent*. The low cyclic-oligomer content of the development polymer suggests that the industrial polymerisation may have been carried out at a higher polymer concentration than was the case for our laboratory synthesis. Moreover, it appears that the soluble cyclic trimer **4a** is somehow removed during the manufacturing process.

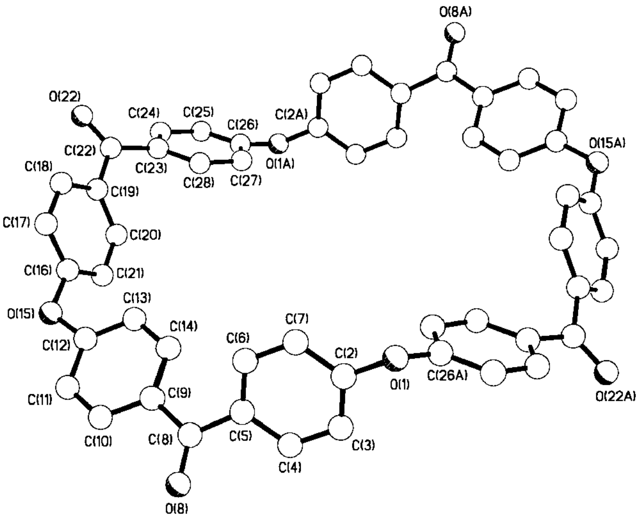


Fig. 5 Single crystal X-ray structure of the macrocyclic tetramer **4b**.

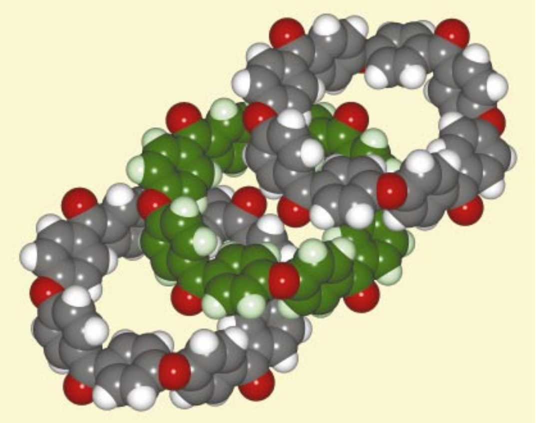
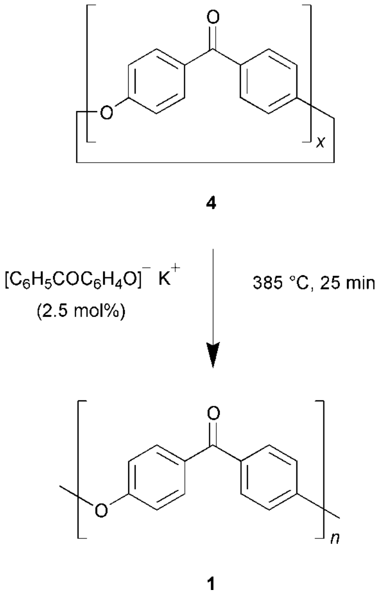


Fig. 6 Space-filling representation of three overlapping molecules of macrocycle **4b** in the crystal, showing how the macrocyclic cavity is filled by adjacent molecules entering from above and below. Contact at the centre of the macrocycle involves a complementary pair of C–H···O interactions with geometry [C–H···O], [C···O] Å, [C–H···O]°; 3.56, 2.70, 146.

Single-crystal X-ray analyses of the cyclic trimer 4a and cyclic tetramer 4b

The cyclic trimer **4a** (Fig. 3) has an unstrained geometry with approximate C_3 symmetry. Both the diaryl ether and diaryl ketone units have skewed geometries with torsional twists about their adjacent C–C and C–O bonds of between 29 and 37°. Overall, the molecule has a rather flat profile, with the centroids of the six aromatic rings being coplanar to within



Scheme 4 Ring-opening polymerisation of macrocyclic aromatic ether ketones **4**.

0.12 Å and the greatest (non-hydrogen atom) deviation from this plane being 0.86 Å, for C(35).

The crystals are solvated by both dichloromethane and methanol in a 1 : 2 mole ratio per macrocycle. One methanol molecule occupies the central void and the other forms a C–H···O hydrogen bond to the carbonyl oxygen O(36) whilst the dichloromethane and one of its symmetry-related counterparts utilises each of its methylene protons to form hydrogen bonds to the other carbonyl oxygen atoms O(8) and O(22) (Fig. 4). These interactions, coupled with (i) a face-to-face π-stacking arrangement (mean interplanar separation 3.8 Å) between the rings containing C(20) and C(40), (ii) an edge-to face-C–H···π interaction between the *ortho* C–H group adjacent to O(8) and the ring containing C(23) (H···π 2.85 Å, C–H···π 158°) and (iii) an edge-to-face C–H···π interaction between the *ortho* C–H group adjacent to O(29) and the ring containing C(5) (H···π 2.75Å, C–H···π 150°) lead to the formation of sheets of macrocycles within the crystal.

The centrosymmetric cyclic tetramer **4b** (Fig. 5) displays a more puckered conformation than the trimer, the centroids of the eight aromatic rings now being coplanar only to within 0.47 Å. There are marked departures from the symmetrical torsional twists at the ether and ketone linkages seen in the cyclic trimer, with the equivalent angles in the tetramer ranging between 9 and 67° (these values reflecting a geometry for one of the diphenyl ethers that more closely approaches orthogonal than it does the symmetrically-skewed conformation observed in the cyclic trimer).

The macrocycle **4b** crystallises in a stepped-layer arrangement such that the central cavity of each macrocycle is filled by the chains of two adjacent molecules entering one from above and one from below (Fig. 6). These molecules meet at the centre of the macrocycle, *via* a complementary pair of electrostatically favourable C–H···O contacts involving O(22) and its centrosymmetrically-related counterpart. The solvating dichloromethane is excluded from the molecular cavity and occupies voids between the stepped layers of macrocyclic oligomers.

Ring-opening polymerisation of cyclic oligomers

As noted in the Introduction, a major reason for the current interest in cyclic oligomers is their possible use as feedstocks for ED-ROP. Given the rather limited quantities of PEK-oligomers available from the present study, only a preliminary investigation of their ring-opening polymerisation proved possible. A mixed cyclic oligomer fraction (isolated from PEK-390P) with a melting range by DSC of 360–405 °C was heated briefly under nitrogen to 410 °C in the presence of potassium 4-benzoylphenoxide (2.5 mol% per monomer repeat unit), and then held at 385 °C for 25 min, before cooling to room temperature (Scheme 4). The polymer resulting from macrocyclic ROP was only partly soluble in concentrated sulfuric acid, indicating that the ring-opening process is accompanied by a slight degree of cross-linking. As a result, solution viscometry data could not be obtained. However, the polymer was tough and flexible, with a melting point by DSC of 370 °C and an enthalpy of fusion of 56 J g^{-1}. Assuming that the molar enthalpy of fusion of PEK is similar to that of PEEK (130 J g^{-1}),[15] the value of ΔH_{fusion} observed for the "ring-opened" polymer would correspond to a degree of crystallinity of approximately 40%.

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