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Formation of crystalline macrocyclic phases during electrophilic precipitation–polycondensation syntheses of poly(arylene ether ketone)s

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Abstract

Elongated crystalline particles formed as by-products during poly(arylene ether ketone) synthesis by electrophilic precipitation–polycondensation of 4,4′-diphenoxybenzophenone with terephthaloyl chloride or isophthaloyl chloride, thought previously to be polymer-whiskers, have now been identified as macrocyclic phases. Single crystal X-ray analysis of the needle-like particles formed in the reaction with terephthaloyl chloride, using the microdiffraction technique with synchrotron radiation, revealed that they consist of a macrocylic compound containing ten phenylene units, i.e. the [2 + 2] cyclic dimer. An analogous structure has also been demonstrated for the corresponding macrocycle derived from the reaction of 4,4′-diphenoxybenzophenone with isophthaloyl chloride. Chloroform extraction of the products of the two polycondensations dissolved the macrocyclic material (but not the linear polymer), and analysis of the extracts by MALDI-TOF mass spectrometry demonstrated the presence in both cases of homologous families of macrocyclic products. Higher yields of macrocycles were obtained under pseudo-high dilution conditions, enabling the [2 + 2] cyclodimers from reactions of 4,4′-diphenoxybenzophenone with both terephthaloyl and isophthaloyl chloride to be isolated as pure compounds and fully characterised.

1. Introduction

It is known that, under certain conditions, chain-growth polymerisation can continue in a polymer precipitated from an initially homogeneous reaction medium. Such reactions, generally referred to as ‘precipitation–polycondensations’, have been established particularly for aromatic polyesters [1–3], polyarylenes [4,5], polyheteroarylenes [6] and poly(arylene ether ketone)s [7]. Depending on the reaction conditions and monomer structures, the precipitated polymer generally forms solvent-swollen particles a few tens of μm in diameter. The polymer-forming reactions within these particles proceed analogously to solution polycondensations [8,9], so that for example, molecular weight and molecular weight distribution do not depend on the particle size [8].

Precipitation of well-defined crystalline structures during the course of aromatic polyester syntheses has been widely observed [10–23], and it is now known that these structures are polymeric crystals, mainly of the whisker type. In an apparently analogous type of reaction, the synthesis of poly(ether ketone ether ketone ketone) (PEKEKK) by precipitation–polycondensation of 4,4′-diphenoxybenzophenone with terephthaloyl chloride in the presence of aluminium chloride (Scheme 1) was shown to produce a small proportion of elongated, needle-like structures in addition to globular polymeric particles [24].

A study by electron diffraction (at 76 kV) of the needle-like particles showed well-defined crystalline reflections [25], and it was suggested that such particles (which were also observed in polycondensations of 4′4-diphenoxybenzophenone with isophthaloyl chloride and 2,6-naphthalenedicarboxylic acid chloride) might also be polymer whiskers [26]. However, we have recently noted, in a preliminary study, that the elongated, crystalline particles obtained as

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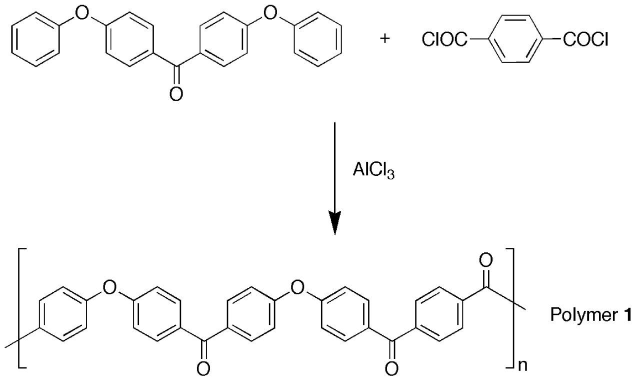


Scheme 1. Synthesis of PEKEKK (polymer **1**) by electrophilic polycondensation. Polymer **2** is obtained from the corresponding reaction with isophthaloyl chloride.

by-products of electrophilic polycondensation between 4,4′-diphenoxybenzophenone and terephthaloyl chloride in fact represent a macrocyclic phase [27]. The present paper confirms and extends this result, and gives detailed characterisation data, including single-crystal X-ray analyses, of two macrocyclic oligomers formed during the synthesis of aromatic poly(ether-ketones) by electrophilic precipitation–polycondensation.

2. Experimental

2.1. Materials

Terephthaloyl chloride, isophthaloyl chloride, 1,2-dichloroethane and dichloromethane were obtained from Aldrich and were distilled under dry nitrogen before use. The diether monomer, 4,4′-diphenoxybenzophenone, was prepared as described in the literature [24] and was purified by recrystallization from methanol/benzene. Analysis of the recrystallised material by DSC showed mp 146 °C and purity 99.92%. Anhydrous aluminium chloride was sublimed under vacuum before use.

2.2. Instrumental methods

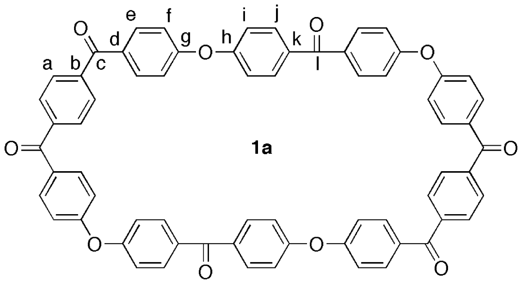
Scanning calorimetry (DSC) measurements were carried out under nitrogen using a Mettler DSC-20 system at a scanning rate of 20 °C min^{-1}. Mass spectra (MALDI-TOF) were obtained using an SAI TofSpec instrument with dithranol as matrix and with sodium trifluoroacetate as cationising agent. Proton and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer using CF_3-$COOH/CDCl_3$ as solvent and ca. 6% (w/v) solutions. Solution viscometry was carried out with 0.2% (w/v) polymer solutions in concentrated sulfuric acid, at 25 °C, using a Schott-Gerate CT semi-automated viscometer.

2.3. Synthesis of polymers *1* and *2*

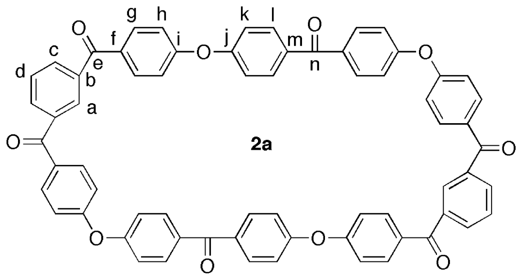
Precipitation–polycondensation syntheses of aromatic polyetherketones were carried out according to methods described in the literature [9,24]. As shown in Scheme 1, condensation of 4,4′-diphenoxybenzophenone with terephthaloyl chloride afforded polymer **1**. Reaction with isophthaloyl chloride gave the isomeric polymer **2**. Inherent viscosities of polymers **1** and **2** were 1.56 and 1.80 dl g^{-1}, respectively.

2.4. Synthesis of macrocycles *1a* and *2a* under pseudo-high dilution conditions

Anhydrous aluminium chloride (36.40 g, 0.273 mol) and dichloromethane (DCM, 300 ml) were placed in a 1 l three-necked flask equipped with a mechanical strirrer, nitrogen gas inlet and outlet. A solution of terephthaloyl chloride or isophthaloyl chloride (5.55 g, 0.027 mol) and 4,4′-diphenoxybenzophenone (10.00 g, 0.027 mol) in DCM (100 ml) was added to the flask using a syringe pump at a rate of 4 ml h^{-1}. At the end of the addition, the mixture was stirred for a further 3 h. The light orange suspension was precipitated in 2 l of water and left to stir. After 24 h, the product was filtered off, washed with water, dried and extracted with boiling chloroform (6 × 200 ml). On evaporating the extract, a white powder (1.40 g for terephthaloyl chloride, 2.40 g for isophthaloyl chloride) was recovered and found by MALDI-TOF MS to contain cyclic oligomers ranging from dimer to pentamer. This product was fractionated by gradient elution chromatography on silica gel with a mixture of DCM and ethyl acetate as eluent. The cyclic dimers **1a** (isolated solvent-free) and **2a** (isolated initially as an ethyl acetate solvate) were obtained in 3 and 4% overall yields, respectively.



1a



2a

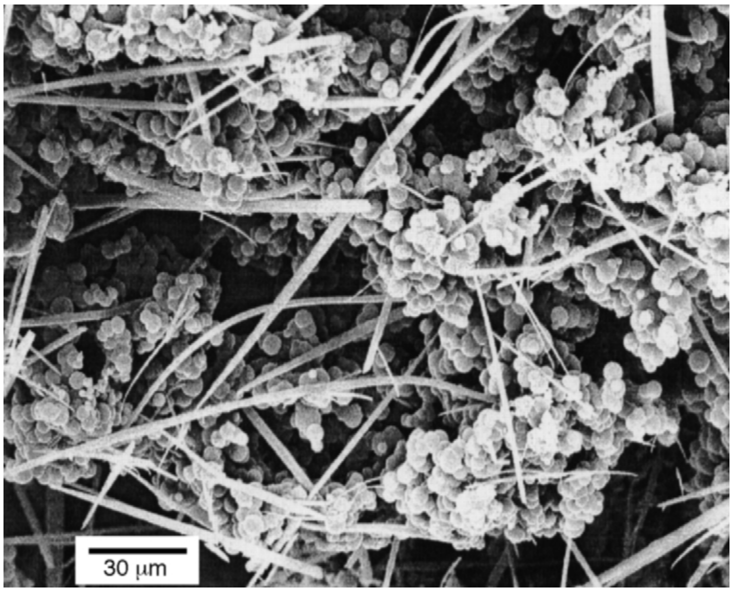


Fig. 1. Scanning electron micrograph showing spherical particles of polymer **1** and needle-like crystals of macrocycle **1a**.

Cyclic dimer **1a** had mp 427 °C (by DSC); *m/z* (MALDI-TOF, dithranol) [100%, $(M + Na)^+$] 1016; ν_{max} (Nujol) 1659, 1588 cm^{-1}; ^1H NMR ($CDCl_3/F_3COOH$, 250 MHz) δ (ppm) 7.83 (d, $J = 8.8$ Hz, $4H_e$), 7.80 (s, $4H_a$), 7.78 (d, $J = 8.8$ Hz, $4H_j$) and 7.10 (m, $4H_f$, $4H_i$); ^{13}C NMR ($CDCl_3/CF_3COOH$, 62.8 MHz) δ (ppm) 198.37 (C_l), 198.20 (C_c), 161.71, 160.92 (C_g, C_h), 140.95 (C_b), 133.87, 133.62 (C_e, C_j), 132.80, 132.00 (C_d, C_k), 130.39 (C_a) and 119.59, 119.42 (C_f, C_i); calculated for ($C_{66}H_{40}O_{10}$): C 79.83%, H 4.06%; Found C 79.25%, H 4.20%.

Cyclic dimer **2a** had mp 393 °C (by DSC); *m/z* (MALDI-TOF, dithranol) [100%, $(M + Na)^+$] 1016; ν_{max} (Nujol) 1657, 1591 cm^{-1}; ^1H NMR ($CDCl_3/CF_3COOH$, 250 MHz) δ (ppm) 8.18 (dd, $J = 7.7$ and 1.6 Hz, $2H_c$), 8.11 (t, $J = 1.6$ Hz, H_a), 7.94 (d, $J = 8.8$ Hz, $4H_l$, $4H_g$), 7.81 (t, $J = 7.7$ Hz, H_d) and 7.23 (m, $4H_h$, $4H_k$); ^{13}C NMR ($CDCl_3/CF_3COOH$, 62.8 MHz) δ (ppm) 198.70 (C_n), 198.41 (C_e), 161.60, 160.70 (C_i, C_j), 137.29 (C_b), 135.00 (C_c), 133.70, 133.80 (C_g, C_l), 132.81 (C_f), 132.63 (C_a), 131.87 (C_m), 130.07 (C_d), 119.60, 119.20 (C_h, C_k); calculated for ($C_{66}H_{40}O_{10}\cdot C_4H_8O_2$): C 78.93%, H 4.54%; Found C 78.97%, H 4.05%.

2.5. X-ray data collection, structure solution and refinement

Synchrotron X-ray data were recorded at the ID13 Microfocus Beamline at the European Synchrotron Radiation Facility (ESRF). Several crystals were tested before selecting one of suitable quality for data collection. Each sample was mounted on a very fine glass fibre made from borosilicate glass with a micro-pipette puller. A typical crystal size was $20 \times 3 \times 1\ \mu m^3$. Data were collected using the ID13 microdiffractometer [28] by the oscillation technique, using a two-dimensional CCD detector (Mar-CCD; ca.130 mm diameter, 2048×2048 pixels and a pixel size of $0.06445 \times 0.06445\ mm^2$) and with the glass fibre axis approximately parallel to the oscillation axis. The oscillation range of each exposure was 6°, and 100 images were collected with three passes of 4 s exposure time for each individual pass at a wavelength of 0.775 Å. The beam size was defined by a 10 μm diameter aperture. Crystal to detector distance was ca. 45 mm. The diffraction images were indexed and the reflections integrated using the XDS software suite [29]. The crystal structure (non-hydrogen atoms) was determined by direct methods using SHELXS97 and refinement in space group $P21/c$ was carried out with SHELXL97 [30]. After a few least-squares cycles, anisotropic displacement parameters were employed on all O and C atoms. Phenylene rings were refined without any constraints.

Crystal data for ***1a***. $C_{66}H_{40}O_{10}$, monoclinic, space group $P2_1/c$, $a = 7.031(1)$, $b = 16.875(1)$, $c = 20.352(1)$ Å, $\beta = 94.391(1)$, $V = 2407.6(4)$ Å^3, $M = 992.98$, $T = 100(2)$ K, $Z = 2$, $D_c = 1.370\ g\ cm^{-3}$, $F(000) = 1032$, synchrotron radiation, $\lambda = 0.775$ Å, 4344 independent reflections, $R_1 = 0.0522$, $wR_2 = 0.1184$ for 3356 independent observed reflections [$2\theta \leq 56°$, $I > 2\sigma(I)$].

A high-quality crystal from a sample of **1a** which had been annealed for several hours at 300 °C was also selected for data collection and structure refinement (**1a***). Data for this sample were recorded at 85(2) K at a wavelength of 0.784 Å; the sample-detector distance was ca. 55 mm.

Crystal data for ***1a****. $C_{66}H_{40}O_{10}$, monoclinic, space group $P2_1/c$, $a = 7.022(1)$, $b = 16.875(2)$, $c = 20.168(2)$ Å, $\beta = 94.400(2)$, $V = 2382.8(5)$ Å^3, $M = 992.98$, $T = 85(2)$ K, $Z = 2$, $D_c = 1.384\ g\ cm^{-3}$, $F(000) = 1032$, synchrotron radiation, $\lambda = 0.784$ Å, independent measured reflections 2907, $R_1 = 0.0394$, $wR_2 = 0.0924$ for 2379 independent observed reflections [$2\theta \leq 50°$, $I > 2\sigma(I)$].

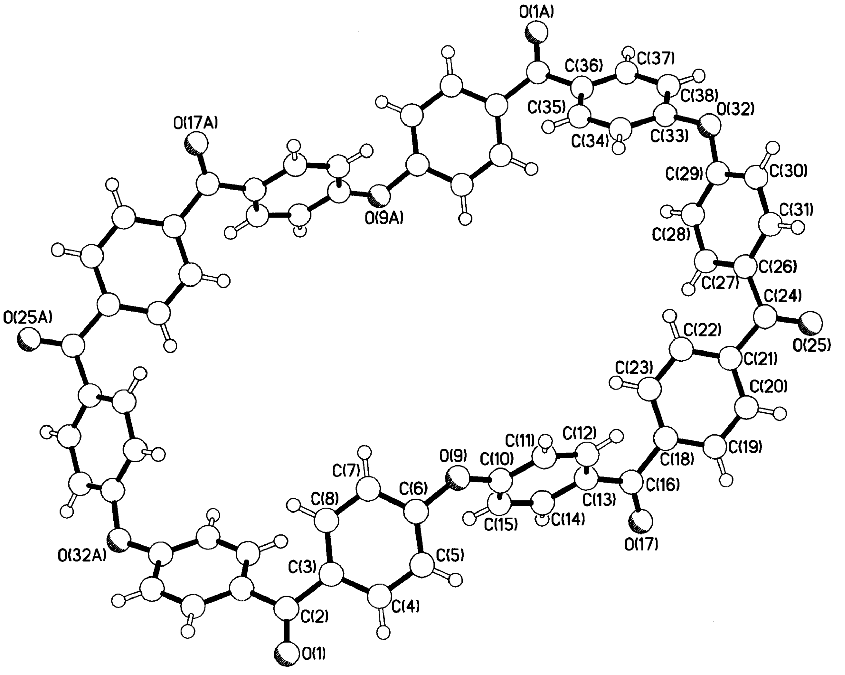


Fig. 2. Molecular structure of cyclic dimer **1a**.

Solution and refinement were as for **1a**. The structures of **1a** and **1a*** are isotypic.

Laboratory X-ray data for **2a** were measured at 183(2) K using a Bruker P4 diffractometer and monochromated Cu Kα radiation (rotating anode source). Structure solution and refinement were carried out using the SHELXTL program system.

Crystal data for ***2a***. $C_{66}H_{40}O_{10}$, triclinic, space group $P\bar{1}$, $a = 7.2002(6)$, $b = 11.2371(8)$, $c = 15.2382(14)$ Å, $\alpha = 78.649(8)$, $\beta = 78.744(9)$, $\gamma = 77.605(8)°$, $V = 1165.2(2)$ Å^3, $M = 992.98$, $T = 183(2)$ K, $Z = 1$, $D_c = 1.415$ g × cm^{-3}, $F(000) = 516$, Cu Kα radiation, independent measured reflections 3851, $R_1 = 0.0514$, $wR_2 = 0.1298$ for 3142 independent observed reflections [$2\theta \leq 120°$, $I > 2\sigma(I)$].

3. Results and discussion

3.1. Characterisation of macrocyclic products from a precipitation–polycondensation reaction

Polycondensation of 4,4′-diphenoxybenzophenone with terephthaloyl chloride in the presence of aluminium chloride (Scheme 1) was carried out using the procedure reported in the literature [24]. The reaction proceeded as a

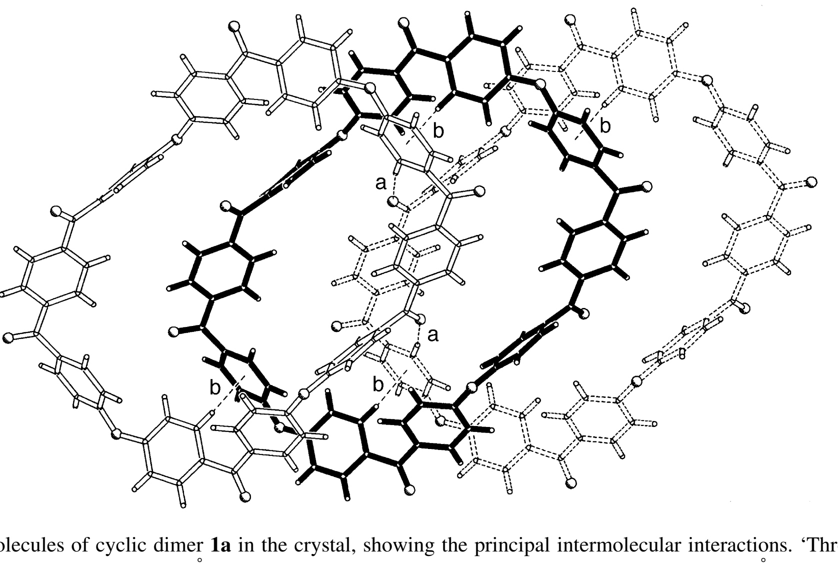


Fig. 3. Packing of adjacent molecules of cyclic dimer **1a** in the crystal, showing the principal intermolecular interactions. 'Through-ring-centre' C–H···O hydrogen bonds ('a') have C···O, H···O, 3.34, 2.39 Å, C–H···O, 171°; C–H···π interactions ('b') have H···π, 2.59 Å, C–H···π, 131°.

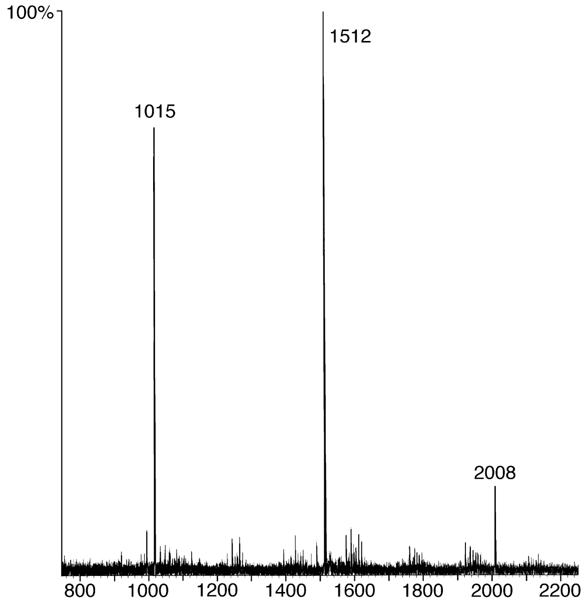


Fig. 4. Mass spectrum (MALDI-TOF) of the macrocyclic fraction extracted from polymer **1**. Principal peaks represent cyclic dimer, trimer and tetramer (all $[M + Na]^+$).

precipitation–polycondensation and, as previously described [24], elongated needle-shaped crystals were observed along with spherical polymer particles after work up of the reaction products (Fig. 1). The proportion of needle-like particles was estimated at ca. 1%.

Although mixed with globular particles of polymer **1**, the birefingent, needle-like crystals were physically free and individual crystals could be separated manually from the polymer, using a needle under an optical microscope. Because of the very small crystal volume and weak X-ray scattering power, synchrotron radiation was required for the crystal structure determination. Data were recorded by means of a microdiffractometer at the ID13 beamline of the European Synchrotron Radiation Facility (ESRF), and analysis revealed that the needle-like crystals shown in Fig. 1 in fact comprise a cyclic [2 + 2] dimer (**1a**).

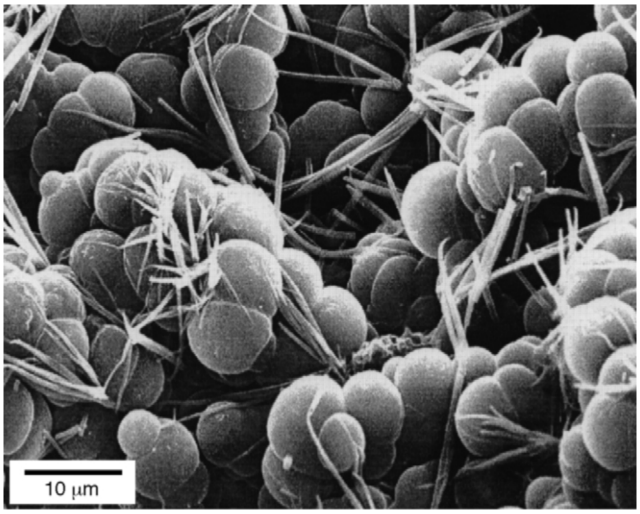


Fig. 5. Scanning electron micrograph showing spherical particles of polymer **2** and elongated crystals containing macrocycle **2a**.

As shown in Fig. 2, the cyclic dimer **1a** has crystallographic inversion symmetry and a very open conformation, with a free pathway through the macro-ring centre of dimensions ca. 7.9 × 12.9 Å. The conformations at the diarylene ether and diarylene ketone units are all asymmetrically skewed, with torsional twists about the bonds linking adjacent aromatic ring systems ranging from ca. 18 and 57°. The sum of adjacent torsion angles at each of these linkages is, however, in the much narrower range of ca. 57–75°, the average (67°) being fairly typical of that observed in many ether–ketone systems. The bond angles at ether-oxygen and ketone-carbon atoms are in the very narrow range 118.8–120.2°.

Despite the open conformation, the crystal is unsolvated, the macrocyclic cavity being filled by terephthaloyl residues of adjacently-stacked molecules (Fig. 3). This packing arrangement is stabilized by 'through-ring-centre' C–H···O hydrogen bonds ('a' in Fig. 3) between alternate macrocycles, and short C–H···π contacts between adjacent molecules ('b' in Fig. 3).

It proved impractical to obtain sufficient macrocycle for spectroscopic and elemental analysis by manual segregation of the crystals, and an attempt was therefore made to separate the macrocyclic fraction from the polymer by solvent extraction. It is known that the semicrystalline poly(arylene ether ketone) **1** is insoluble in chloroform at its boiling point, and so a number of samples of polymer **1** containing needle-crystals were extracted repeatedly with boiling chloroform and the soluble material was recovered by evaporation of the solvent. Scanning electron micrographs of the polymer remaining after extraction revealed only spherical particles of polymer; the needle-like particles were no longer present. Mass spectrometry (MALDI-TOF) revealed (Fig. 4) that in fact the extract contained not only cyclic dimer **1a** but also higher macrocycles (mainly cyclic trimer and tetramer), formed as by-products during condensation of 4,4′-diphenoxybenzophenone with terephthaloyl chloride.

Despite the clear evidence from MALDI-TOF MS that higher macrocycles are present in polymer **1**, identical X-ray diffraction data and derived lattice parameters were obtained for all needle-like crystals separated manually from this polymer. It therefore seems that these structures comprise essentially pure macrocyclic dimer, and that the other macrocycles detected spectroscopically do not crystallize separately from the polymer fraction.

The synthesis of polymer **2** by an analogous precipitation–polycondensation reaction between 4,4′-diphenoxybenzophenone and isophthaloyl chloride proceeded very similarly to that of polymer **1**, again affording a dispersion of polymer particles. Moreover, SEM analysis of the polymeric product also revealed the presence of elongated crystals mixed with the globular polymer particles (Fig. 5). These structures were, however, physically embedded in the

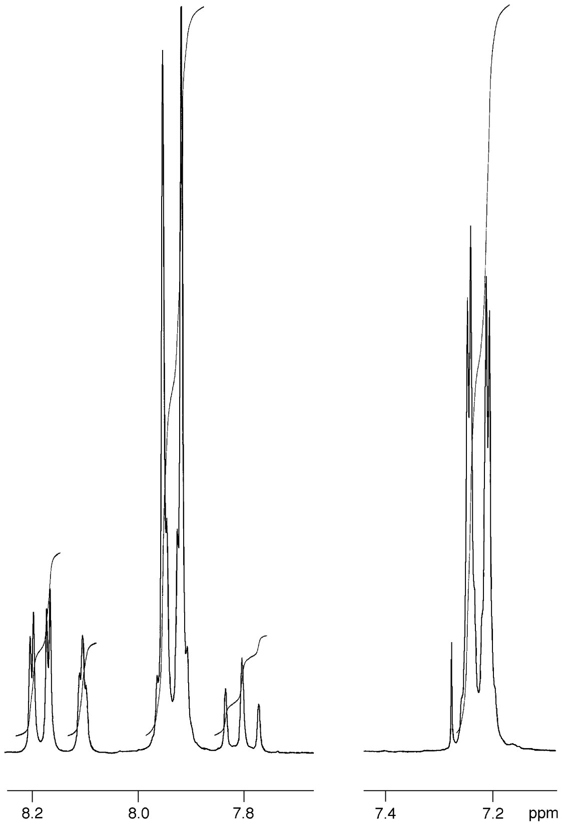


Fig. 6. ^{1}H NMR spectrum (250 MHz) of macrocycle **2a**. Assignments are given in Section 2.4.

polymer, and could not readily be detached under the optical microscope. However, extraction of polymer **2** with hot chloroform dissolved the majority of the crystals away from the insoluble polymer, and analysis of the extract by MALDI-TOF MS showed it to comprise a mixture of cyclic dimer **2a** and cyclic trimer.

In view of the very small quantities of cyclic oligomers available from reactions carried out under conventional precipitation–polycondensation conditions, syntheses of polymers **1** and **2** were next carried out under pseudo-high dilution conditions [31–40], with the aim of enhancing the yields of macrocycles.

3.2. Macrocyclic products from condensation under pseudo-high dilution conditions

Earlier work on the synthesis of macrocyclic aromatic etherketones focused mainly on nucleophilic cyclo-condensation between activated aromatic dihalides and alkali metal diphenoxides [32–39], carried out under pseudo-high dilution conditions where the reactants are brought together so slowly that only a very low concentration of end-groups is ever present in the reaction mixture. Arylene ether ketone cyclic oligomers can be produced by electrophilic aromatic (Friedel-Crafts) substitution, but only one such reaction has previously been reported [40]. In the present work, a pseudo-high dilution version of the reaction shown in Scheme 1 yielded a chloroform-soluble material which MALDI-TOF MS showed comprised cyclic oligomers from cyclic dimer to at least cyclic pentamer. Fractionation by column chromatography afforded cyclic dimer **1a** as a pure compound, m.p. 427 °C.

An analogous pseudo-high dilution reaction between 4′4-diphenoxybenzophenone and isophthaloyl acid chloride yielded, after chromatographic fractionation of the products, pure cyclic [2 + 2] dimer **2a**, with mp 393 °C. This

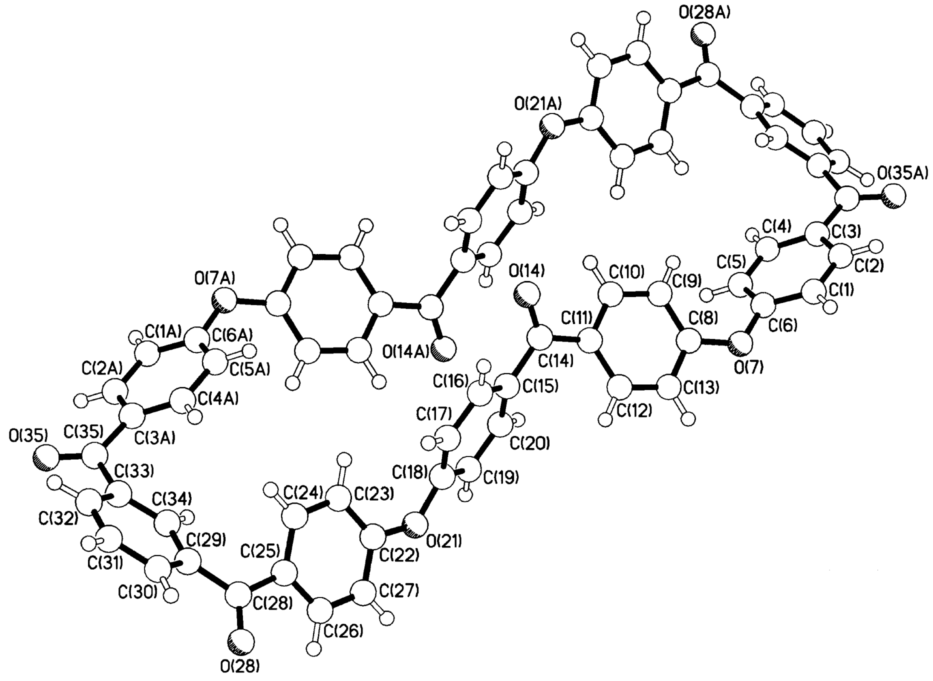


Fig. 7. Molecular structure of cyclic dimer **2a**.

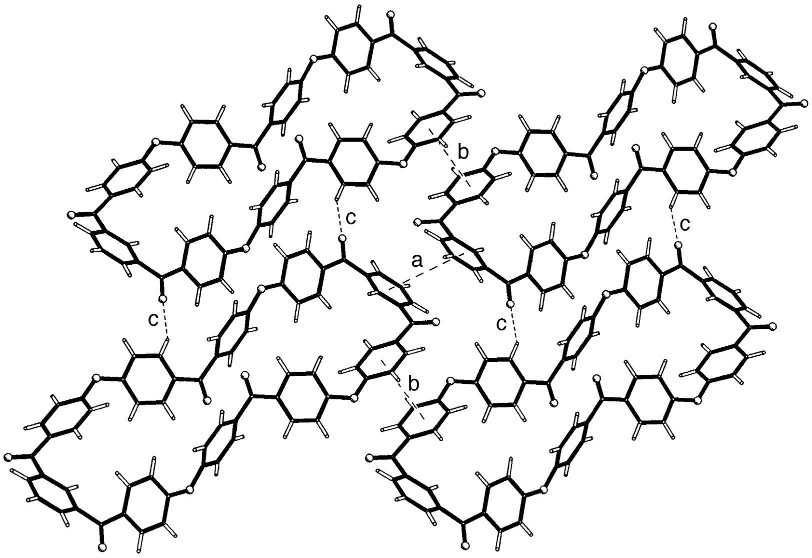


Fig. 8. Packing of adjacent molecules of cyclic dimer **2a** in the crystal, showing the principal intermolecular interactions. The π–π stacking interactions have centroid–centroid and mean interplanar separations (Å), ('a') 4.52, 3.10 and ('b') 3.76, 3.38; C–H···O hydrogen bonds ('c') have C···O, H···O, 3.24, 2.37 Å, C–H···O, 149°.

macrocycle gave a well-resolved ^{1}H NMR spectrum, as shown in Fig. 6.

The structure of cyclic dimer **2a** was confirmed by single-crystal X-ray analysis (Figs. 7 and 8). The macrocycle possesses crystallographic inversion symmetry but in contrast to the open conformation adopted by **1a**, here the macrocyle is essentially self-filling, adopting a collapsed pseudo-figure-of-eight geometry. The central region is closely packed and contains a pair of short transannular C–H···π contacts between C(10)–H and the C(15A)–C(20A) aromatic ring and also between their symmetry-related counterparts; the H···ring-centroid distance is 3.04 Å.

A range of geometries for the diarylene ether and diarylene ketone units is observed, with approximately symmetric twists occuring either side of the C(14) and C(28) carbonyl carbons and of the O(21) ether oxygen. The geometries at the O(7) ether linkage and C(35) carbonyl carbon are unusual, having torsional twists about the C(6)–O(7) and C(33)–C(35) bonds of ca. 45° and of ca. 16° about O(7)–C(8) and C(35)–C(3A). The sum of these angles is, however, in each case ca. 60°, resulting in conventional values for the relative orientations of adjacent aromatic rings. A combination of π–π stacking ('a' and 'b' in Fig. 8) and weak C–H···O interactions ('c' in Fig. 8) result in the formation of loosely-linked sheets of macrocycles; there are no significant inter-sheet contacts.

4. Conclusions

Electrophilic precipitation–polycondensation of 4,4′-diphenoxybenzophenone with terephthaloyl or isophthaloyl acid chloride, in the presence of aluminium chloride, occurs with the formation of by-product macrocyclic oligomers which can precipitate separately from the polymer as discrete, crystalline phases. Single crystal X-ray microdiffraction studies of the needle-like particles formed in the reaction with terephthaloyl chloride show that these represent the [2 + 2] cyclic dimer (**1a**). An analogous cyclic dimer (**2a**) was isolated from the corresponding polymerisation reaction with isophthaloyl chloride. Extraction of the polymers with hot chloroform afforded, in both cases, not only the cyclic dimers but also higher macrocycles. Oligomers **1a** and **2a** were obtained in higher (though still small) yields from reactions carried out under pseudo-high dilution conditions and, after chromatographic purification, were fully characterised. It is remarkable that, despite polymerisations being carried out in the presence of a large excess of aluminium chloride which would normally complex strongly with aromatic ketone units, macrocycle **1a** is found to crystallise directly from the reaction as a pure, aluminium-free phase.

Acknowledgements

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