MATERIALS CHEMISTRY COMMUNICATIONS

# A macrocyclic aromatic thioether ketone: synthesis, structure and anionic ring-opening polymerisation

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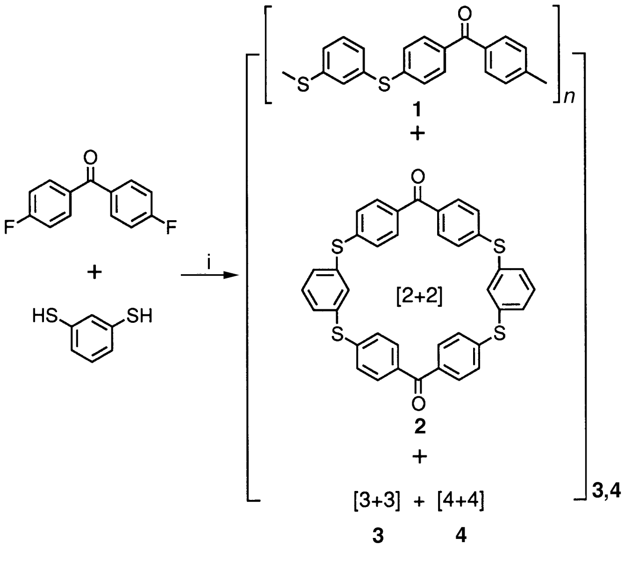
Nucleophilic polycondensation at high concentration between benzene-1,3-dithiol and 4,4′-difluorobenzophenone affords not only linear polymer **1** but also a significant yield (*ca.* 8%) of cyclic oligomers, mainly the [2+2] cyclodimer **2**. Under high-dilution conditions **2** becomes by far the major reaction product. Macrocycle **2** has been isolated, structurally characterised by single-crystal X-ray methods and found to undergo rapid anionic ring-opening polymerisation in the melt (330–360 °C), affording a linear, high molecular weight poly(arylthioether ketone).

Since the first reports of the synthesis and anionic ring-opening polymerisation of macrocyclic aromatic ethers,[1,2] there has been a rapid increase in interest in this potential approach to the production and fabrication of high-performance aromatic polymers.[3] In general, the very high melt viscosities of commercially available aromatic polyethers mean that their molecular weights (and dependent properties such as fracture-toughness) must be deliberately restricted if melt-processing is to be feasible.[4] However, no such restriction holds for *reactive* processing of low-viscosity cyclic oligomers which, once fabricated, can in principle be advanced to extremely high molecular weights. Moreover, the low initial viscosity of this type of material promotes rapid penetration and wetting of reinforcing fibres, so that cyclic oligomers are potentially attractive intermediates in the fabrication of very high fibre-content composite materials. Key features of this approach are that (i) there are no volatile co-products to generate voids in the final product, and (ii) the final polymer is linear rather than cross-linked, leading to much greater ductility and toughness than is possible for thermosetting materials such as the epoxy resins and bis(maleimide)s.

Recent results from Wang *et al.* suggest that the *thio*ether linkage may be a particularly versatile initiation site for the ring-opening polymerisation of aromatic macrocycles.[5] To date however only one specific macrocyclic thioether ketone, the all-*para* cyclic trimer $(SC_6H_4COC_6H_4)_3$, has been isolated and characterised in detail.[6] Here we report the high yield synthesis, structural characterisation and remarkably facile polymerisation chemistry of a new type of macrocyclic aromatic thioether ketone, obtained by nucleophilic cyclocondensation of benzene-1,3-dithiol with 4,4′-difluorobenzophenone.

Macrocycle **2** was initially isolated as a by-product of the polycondensation between benzene-1,3-dithiol and 4,4′-difluorobenzophenone (Scheme 1). The reaction was run at high concentration (*ca.* 25 wt% polymer) in *N*,*N*-dimethylacetamide (DMAc), and polymer **1** precipitated rapidly from the reaction mixture on cooling. This novel polymer was recovered in 86% yield by filtration, and proved to be crystalline in the 'as-made' state [$T_m = 195$ °C by differential scanning calorimetry (DSC)]. It did not, however, crystallise from the melt, showing only a glass transition ($T_g^{onset} = 107$ °C) on the second heating scan. The original filtrate slowly (over several days) deposited colourless crystals of a pure cyclic oligomer (3% yield) identified as the [2+2] cyclodimer **2** by mass spectrometry ($M^+$ 640) and $^{13}C$ NMR spectroscopy.‡ Further oligomeric material (2% yield) was precipitated by diluting the DMAc solution with MeOH, and mass spectrometry indicated that this comprised a mixture of the cyclodimer **2** with the homologous [3+3] and [4+4] cyclic condensation products **3** and **4** respectively.

In order to increase the yield of cyclic material, the reaction was next run at much lower concentration (1.5 wt% condensation products). The cyclic dimer **2** was now isolated in a remarkable 72% yield by column chromatography on silica gel (3:1 $CH_2Cl_2-CHCl_3$ as eluent), although yields of the higher cyclic oligomers **3** and **4** were still relatively modest at *ca.* 1% and 8%, respectively.



**Scheme 1** *Reagents and conditions:* i, $K_2CO_3$, DMAc, 160 °C

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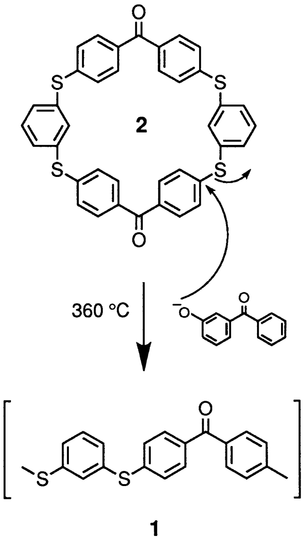
‡ *Selected data* for **2**: Mp (DSC) 329 °C; IR (KBr disc) n(C=O) 1650 cm$^{-1}$; $^{13}C$ NMR (300 MHz, $CD_2Cl_2-CH_3SO_3H$, 2:1 v/v): d 127.34, 128.19, 131.88, 132.73, 135.74, 137.22, 141.05, 155.69, 201.13 (Found: C, 70.9; H, 3.9; S, 20.2. Calc. for $C_{38}H_{24}O_2S_4$: C, 71.2; H, 3.8; S, 20.0%).



Scheme 2

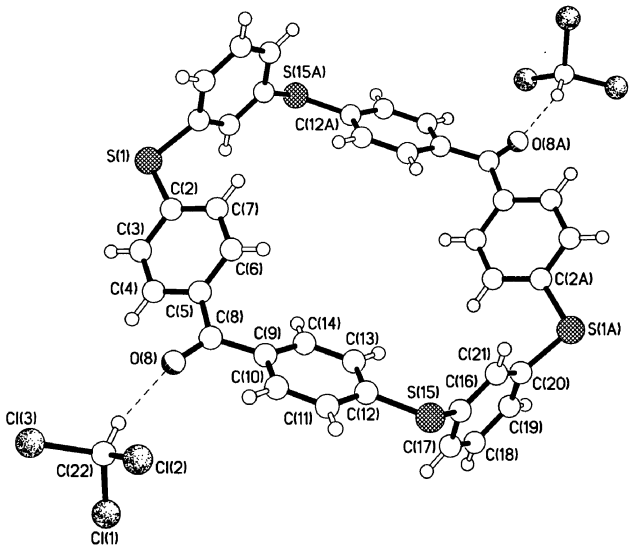


**Fig. 1** Molecular structure of macrocycle **2**, showing the solvating molecules of chloroform. Selected bond lengths and angles: S(1)–C(2), 1.762(3); C(12)–S(15), 1.769(3); C(5)–C(8), 1.485(4); S(15)–C(66), 1.781(3); C(8)–O(8), 1.223(3); C(20)–S(1A), 1.783(3); C(8)–O(9), 1.489(4)Å; C(8)–C(9)–C(14), 123.0(3); S(1)–C(2)–C(3), 115.9(2); C(11)–C(12)–S(15), 115.5(2); S(1)–C(2)–C(7), 124.9(2); C(13)–C(12)–S(15), 124.4(2); C(4)–C(5)–C(8), 117.9(2); C(12)–S(15)–C(16), 104.2(1); C(6)–C(5)–C(8), 123.7(3); S(15)–C(16)–C(17), 119.6(2); C(5)–C(8)–O(8), 118.8(3); S(15)–C(16)–C(21), 119.8(3); C(5)–C(8)–C(9), 121.3(2); C(19)–C(20)–S(1A), 119.9(3); O(8)–C(8)–C(9), 119.9(3); C(21)–C(20)–S(1A), 119.2(3); C(8)–C(9)–C(10), 118.6(3); C(20)–S(1A)–C(2A), 103.7(1)°.

Oligomer **2** was structurally characterised (Fig. 1) as its chloroform solvate by single crystal X-ray methods.§ The macrocycle has a rather open geometry with crystallographic inversion symmetry at its centre. The benzene-1,3-dithiolate residues are directed above and below the mean plane of the macrocycle (as defined by the four sulfur atoms) and are inclined at *ca.* 95° to this plane, leading to an overall chair-type conformation. Non-bonded repulsions within the diaryl thioether unit lead to significant bond-angle distortions at aromatic carbon atoms [C(2) and C(12)] linked to the thioether bridges.

The nominally trigonal bond angles C(3)—C(2)—S(1) and C(7)—C(2)—S(1) have, in this structure, values of 115.9(2) and 124.9(2)°, respectively. Similar distortions are also found in *linear* aryl ethers[7] and thioethers,[8] and in the present structure the bridge-bond angles at sulfur and the carbonyl carbon atoms are entirely normal at *ca.* 104 and 121° respectively. There is however clear evidence for some degree of ring-strain, in that the sulfur atoms lie *ca.* 0.16 Å out of the plane of the benzene-1,3-dithiolate residue. As shown in Fig. 1, the crystal contains two molecules of chloroform per macrocycle. Although the solvent molecules exhibit some orientational disorder in the crystal, both orientations result in their C–H bonds being directed almost linearly (C–H–O = 160°) towards the carbonyl oxygens of the macrocycle; the H , O separation of 2.14 Å being indicative of a reasonably strong hydrogen bond.

On heating to *ca.* 350 °C in the presence of an anionic initiator such as the potassium salt of 4-hydroxybenzophenone (2 wt%), macrocycle **2** was found to undergo rapid polymerisation in the melt (Scheme 2), to give tough, transparent, fully soluble, high molecular weight polymer **1**, identical by $^{13}$C NMR spectroscopy with the material produced by solution polycondensation. The ring-opening polymerisation however gives material of very much higher inherent viscosity (see below). This result suggests that the initiating benzoylphenoxide anion, which is present at a relatively high level (*ca.* 5 mol% relative to the cyclic oligomer), is ultimately displaced from the growing polymer chain, and thus behaves as a genuine catalyst for ring-opening polymerisation rather than as a classical, irreversible initiator.

This ring-opening polymerisation process can readily be followed by DSC, the characteristically sharp oligomer-melting peak observed at 329 °C in the initial heating scan (Fig. 2) being replaced in subsequent scans by the glass transition (onset at 110 °C) of the polymeric product. Given the timescale

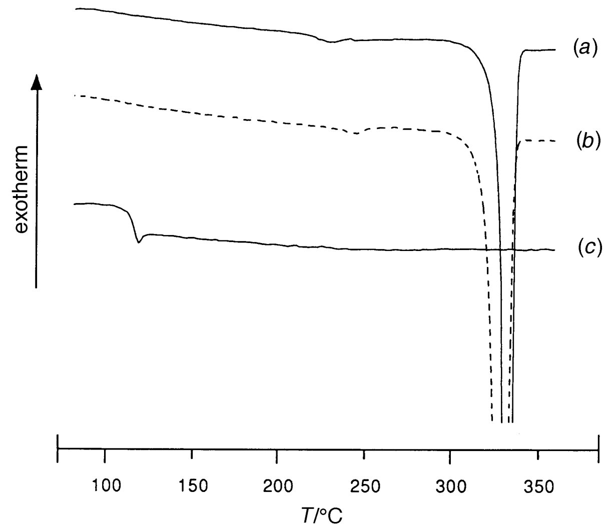


**Fig. 2** DSC thermograms (10 °C min$^{-1}$ heating rate) showing (*a*) the melting endotherm of pure macrocycle **2**, (*b*) the melting endotherm of macrocycle **2** containing 2 wt% of initiator, and (*c*) the glass transition of polymer **1** produced by ring-opening polymerisation during the course of scan (*b*)

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§ *Crystal data* for **2**: $C_{38}H_{24}O_2S_4 \cdot 2CHCl_3$, $M = 879.55$, triclinic, space group $P\bar{1}$, $a = 9.118(1)$, $b = 10.333(2)$, $c = 12.262(1)$, a = 102.40(1), b = 95.663(1), c = 114.052(1)°, $Z = 1$, $U = 1007.6(2)$ Å$^3$, $D_c = 1.449$ g cm$^{-3}$, $F(000) = 448$. The structure was solved by direct methods and the non-H atoms were refined anisotropically by full-matrix least-squares, based on $F^2$. The H atoms were refined isotropically (riding model). $R_1$ [$I > 2s(I)$] was 0.057, and $wR_2$ was 0.147 for 3043 independent observed reflections.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/23.

of the DSC experiment, in which the sample is simply heated to 360 °C at 10 °C $min^{-1}$ and then immediately allowed to cool, high molecular weight polymer must be produced within a few minutes of the macrocycle reaching its melting point.

Polymer **1** is amorphous when produced by ring-opening polymerisation in the melt, but it crystallises rapidly on contact with dipolar aprotic solvents such as *N*-methylpyrrolidone (NMP) or DMAc, in which solvents the crystalline polymer is insoluble. Viscosity and NMR measurements were therefore carried out using a mixture of $CH_2Cl_2$ and methanesulfonic acid (2 : 1 v/v) as solvent. Inherent viscosities of 2.98 and 1.15 dl $g^{-1}$ for the polymers derived from ring-opening and from polycondensation respectively clearly indicate that a high molecular weight polythioether ketone is very readily produced by anionic (nucleophilic) ring-opening polymerisation of macrocycle **2**, more readily indeed than by a conventional nucleophilic polycondensation reaction. Moreover, the absence of side reactions during ring-opening polymerisation (as indicated by the clean $^{13}C$ NMR spectrum and complete solubility in $CH_2Cl_2$–$MeSO_3H$ of the polymer produced) suggests that this class of macrocycle may prove to be of particular value in the development of ring-opening methodology for the synthesis of high-performance aromatic polymers.

This work was supported by the Engineering and Physical Sciences Research Council of the United Kingdom, the University of the West Indies Staff Development Programme and United Utilities plc. The award of a Royal Society Industry Fellowship to H. M. C. is gratefully acknowledged.

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*Communication* 6/07044B; *Received* 15*th October*, 1996