Synthesis, Structure, and Ring-opening Polymerisation of Strained Macrocyclic Biaryls: a New Route to High-performance Materials†

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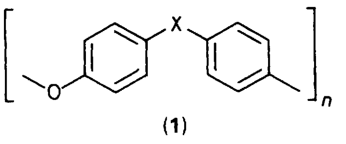
A series of new, all-aromatic, macrocyclic biaryls have been obtained by intramolecular, nickel-promoted coupling of bis(4-chlorobenzoylphenoxy)-terminated oligomers, and single-crystal *X*-ray analysis of one such macrocycle reveals extreme distortion of the biaryl unit; these highly strained materials undergo rapid ring-opening polymerisation in the presence of nucleophilic initiators to give high molecular weight polyetherketones.

High-performance polymers based exclusively on aromatic structures are rapidly increasing in technological importance as a result of their unique combination of toughness, lightness, dimensional stability at high temperatures, and resistance to thermo-oxidative degradation.[1] Linear materials such as polyethersulphone [(**1**); X = SO_2] and polyetherketone [(**1**); X = CO] are traditionally obtained either by nucleophilic polycondensation of bis-phenols with activated aromatic



(**1**)

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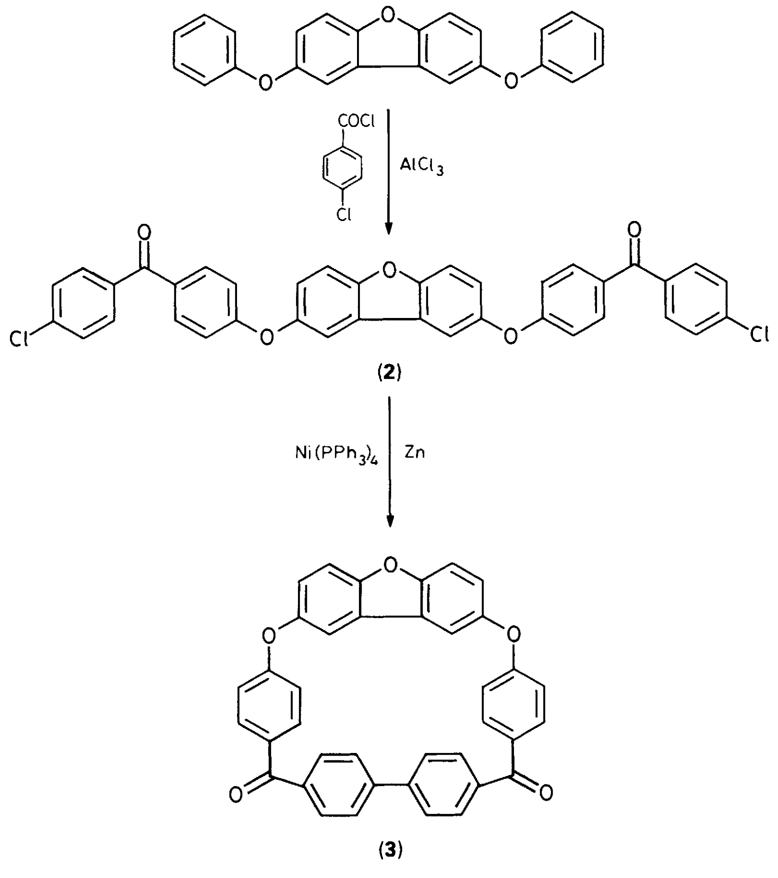
† H. M. Colquhoun, C. C. Dudman, and M. Thomas, European Patent Application 317,226 A2, published 1989, to ICI.



Scheme 1. Synthesis of macrocycle (3).

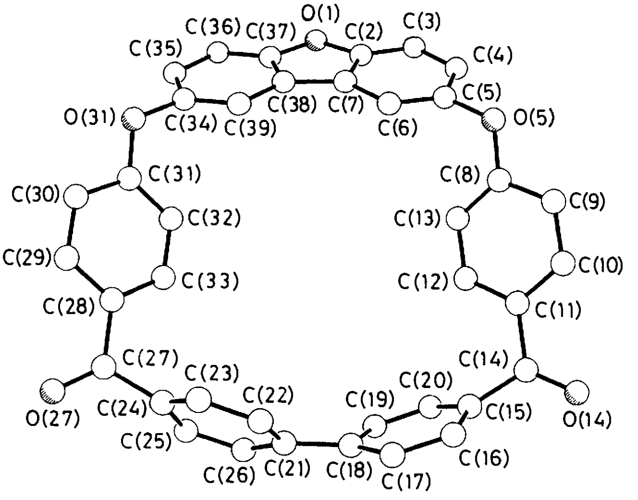
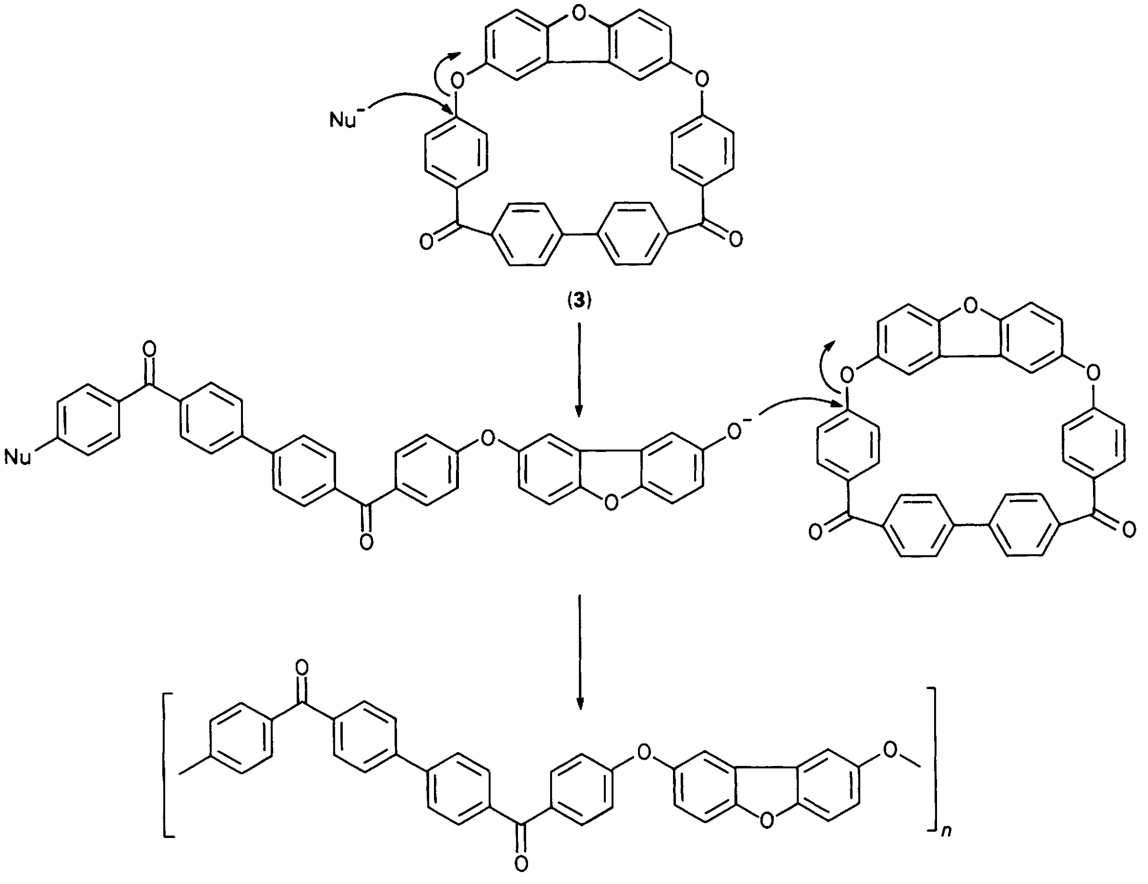


Figure 1. Molecular structure of (3). (The hydrogen atoms and solvent of crystallisation are omitted.) Selected torsion angles (°): C(6)–C(5)–O(5)–C(8) 66.0, C(5)–O(5)–C(8)–C(13) −3.8, C(12)–C(11)–C(14)–C(15) −21.1, C(11)–C(14)–C(15)–C(20) 63.5, C(23)–C(24)–C(27)–C(28) 75.6, C(24)–C(27)–C(28)–C(33) 24.0, C(32)–C(31)–O(31)–C(34) −4.5, C(31)–O(31)–C(34)–C(39) −59.6, (average e.s.d. 0.4°).

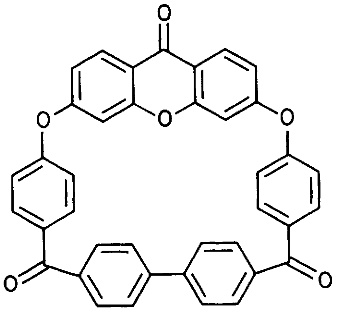
dihalides,[2] or by Friedel–Crafts self-polymerisation of phenoxyaroyl- and phenoxyarene-sulphonyl halides.[3] Such polymers are generally processable as thermoplastics, but the high temperatures required and more especially the very high melt viscosities combine to limit the application of these materials in areas such as fibre impregnation and microscale fabrication. In contrast, thermo*setting* aromatic resins such as the bismaleimides[4] are processable at lower temperatures and have relatively low viscosities, but their performance tends to suffer from the presence of oxidatively unstable aliphatic C–H groups and from the brittleness inherent in any highly cross-linked structure. We now introduce a new class of all-aromatic materials which have the potential to combine the performance of linear thermoplastics with the processing characteristics of thermosets.

During a programme to explore the synthesis and properties of monodisperse aromatic oligomers, it became evident to us that the recently-developed nickel(0)-promoted coupling of aryl halides[5] might be sufficiently rapid to provide a route into *cyclic* structures of this type, using the pseudo-dilution principle whereby progressive addition of starting material to a rapidly-reacting system maintains reactant concentration at a very low level. In practice we find that slow addition (*ca.* 4 h) of a dimethylacetamide (DMA) solution containing the bis(4-chlorobenzoyl)-terminated oligomer (**2**) to a DMA solution containing one molar equivalent of $Ni(PPh_3)_4$ (generated *in situ* from $NiCl_2$, $Bu^n{}_4NI$, PPh_3, and excess zinc dust)[5] leads to intramolecular coupling and formation of the new macrocylic biaryl (**3**) in 40% isolated yield (Scheme 1). The relative insolubility of (**3**) compared with linear coupling products allows straightforward isolation of the macrocycle, and the crude material may be purified by recrystallisation from toluene. The product contains 0.5 mole equivalents of toluene of crystallisation, but this can be removed by heating briefly under vacuum at 200 °C.

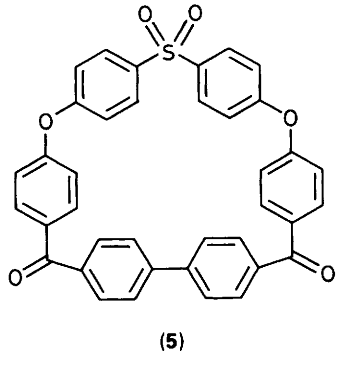
The single crystal *X*-ray structure of compound (**3**) (Figure



Scheme 2. Nucleophilic ring-opening polymerisation of (3).



(4)



(5)

1)‡ reveals extreme distortion of the biaryl unit, the normally co-linear bonds [C(14)–C(15)] and [C(24)–C(27)] subtending an angle of 65° as a consequence of (i) significant boat-like distortions of the aromatic rings {the interplanar angle between [C(16)–C(15)–C(20)] and [C(17)–C(18)–C(19)] for example is 17°} and (ii) pyramidalisation at the bridgehead carbon atoms C(15), C(18), C(21), and C(24). Furthermore, there is a twist angle of 31° between the two aromatic rings of the biaryl unit. So far as we are aware, this compound is the first macrocylic biaryl to have been structurally characterised and as a result the quite remarkable flexibility of the biaryl linkage has not been previously recognised.§ The toluene of

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‡ *Crystal data* for (3): $C_{38}H_{22}O_5 \cdot (C_7H_8)_{0.5}$, $M = 604.7$, triclinic, $a = 9.962(1)$, $b = 12.777(2)$, $c = 13.369(2)$ Å, $\alpha = 69.12(1)$, $\beta = 73.45(1)$, $\gamma = 89.13(1)°$, $U = 1517$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.32$ g cm^{-3}, $\mu(\text{Cu-}K_\alpha) = 7$ cm^{-1}. Data were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and refined anisotropically to give $R = 0.048$, $R_w = 0.057$ for 3555 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leqslant 58°$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ In a cyclophane based on 4,4′-bipyridinium units, some distortion of the bipyridyl units is also observed, the two $N^+–CH_2$ bonds subtending an angle of 24°;[10] a more recent study of a related structure has revealed a somewhat greater distortion, of *ca.* 30°.[11]

crystallisation does not insert into the molecular cavity, but is sandwiched between alternate pairs of macrocycles. The cavity is in fact already occupied to a large extent, as a result of the 'edge-on' orientation of the 4-oxybenzoyl groups.

Since the ether linkages in (**3**) are activated by *para*-carbonyl groups, they are potentially susceptible to nucleophilic cleavage,[6] suggesting that the highly-strained macrocycle might undergo nucleophilically initiated ring-opening polymerisation (Scheme 2). Indeed, bulk polymerisation of compound (**3**) is observed on heating to its melting point (353 °C) in the presence of a catalytic amount (1—5 mol%) of a nucleophilic initiator such as caesium fluoride or the potassium salt of 4-hydroxybenzophenone. The polymerisation, which is strongly exothermic, can be followed readily by differential scanning calorimetry (DSC) and is complete within 2—5 min depending on the reaction temperature and level of initiator.

The resulting all-aromatic polymer (Scheme 2) is tough, transparent, only partially soluble in concentrated sulphuric acid (perhaps indicating a slight degree of cross-linking), and amorphous by DSC, showing a glass transition (onset) at 225 °C. Fully soluble, though still tough, materials (inherent viscosities 0.40—0.70 $\mathrm{dl\,g^{-1}}$ at 25 °C for 0.1% solutions in sulphuric acid) can be obtained if the degree of polymerisation is limited by addition of a small amount (1—2 mol%) of an involatile end-capping agent such as 4-(benzoyl)-4′-(4-fluorobenzoyl)biphenyl. Polymerisation does not occur in the absence of initiator, even at 400 °C.

The macrocyclic compounds (**4**) and (**5**) have also been synthesised *via* nickel-promoted cyclisation of the corresponding chlorobenzoyl-terminated oligomers,¶ and although preliminary *X*-ray data indicate that these materials are rather less strained than compound (**3**), they nevertheless undergo facile ring-opening polymerisation under similar conditions.

Reactive processing of low-viscosity small-ring monomers is well-established in more conventional areas of polymer chemistry (for example in the various caprolactam-based processes for reaction injection moulding of Nylon-6),[7] and indeed the ring-opening polymerisation of *macrocyclic* compounds such as esters[8] and carbonates[9] has been known for many years. However, the work described here and in our associated patent† now allows extension of this concept to high-performance all-aromatic polyethers.††

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¶ Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

†† As this communication was about to be submitted, we learned that a related series of mixed aliphatic–aromatic cyclic ethers had been synthesised *via* nucleophilic etherification,[12a] and successfully polymerised.[12b]