

Cyclodepolymerisation of bisphenol A polysulfone: evidence for self-complementarity in macrocyclic poly(ether sulfones)

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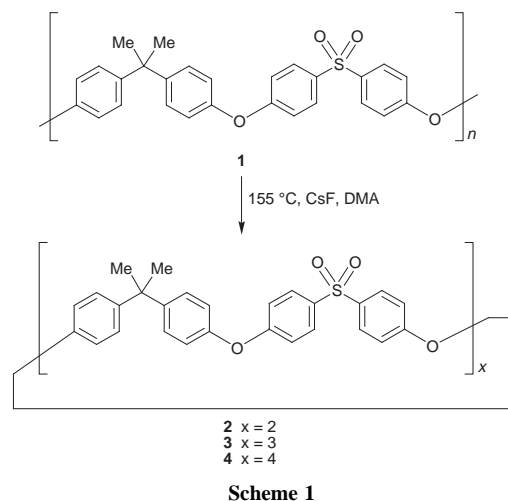
The engineering thermoplastic generally referred to as 'bisphenol A polysulfone' undergoes fluoride-promoted cyclodepolymerisation; high molar mass polymer is thus transformed into a series of macrocyclic oligomers containing up to at least 72 aromatic rings; those containing up to 24 rings have been isolated as pure compounds, and single-crystal X-ray studies of the cyclotrimer and cyclotetramer reveal shape-complementary pairs and chains of macrocycles, respectively.

Polycondensation reactions generally afford not only high molar mass linear polymers, but also (in amounts depending on reaction conditions) homologous series of macrocyclic oligomers.¹ As a result, significant quantities of cyclic materials are found in many important commercial polymers. Under equilibrium conditions, linear and cyclic species can interconvert *via* ring-opening polymerisation of macrocyclic oligomers and/or ring-closing depolymerisation (cyclodepolymerisation) of linear chains. Such interconversions have recently been demonstrated for polyesters,² polycarbonates,³ and certain aromatic polyethers.⁴ A theoretical framework for ring-chain equilibria in dilute solution has been developed by Mandolini and co-workers, indicating the existence of a threshold concentration below which *only* cyclic species should be present.⁵

Here we report that the high-performance engineering thermoplastic **1**, generally referred to as 'bisphenol A polysulfone' (formed by polycondensation of bisphenol A with 4,4'-dichlorodiphenyl sulfone, and trademarked as *Udel* by the Amoco Corporation and *Ultrason-S* by BASF) undergoes clean cyclodepolymerisation at high temperatures in the presence of fluoride ion. The polymer is transformed, *via* fluoride-promoted ether interchange reactions,⁶ into a series of macrocyclic oligomers, ranging from the [2+2] cyclodimer to the [18+18] cyclooctadecamer (Scheme 1).

Heating a 0.5 wt% solution of bisphenol A polysulfone at reflux in DMA with 0.5 equiv. of CsF per polymer repeat unit leads to the disappearance of high molar mass polymer and formation (as evidenced by GPC and HPLC) of a well-defined series of oligomeric compounds.¶ Analysis of the isolated products by MALDI-TOF mass spectrometry (Fig. 1) demonstrates that the oligomers comprise exclusively *macrocyclic* species, with molar masses in the range m/z 906 (cyclodimer) to 7980 (cyclooctadecamer). Chromatographic fractionation yielded a series of pure, monodisperse oligomers from cyclodimer (**2**) to cyclohexamer, characterised by elemental analysis, ¹H and ¹³C NMR spectroscopy, mass spectrometry and, in the cases of the cyclotrimer (**3**) and cyclotetramer (**4**), by single crystal X-ray diffraction.**

The cyclodimer (**2**), which crystallises spontaneously from solutions of the commercial polymer, has already been characterised in some detail;⁷ the higher macrocycles were however previously unknown. The macrocyclic oligomers from cyclotrimer to cyclohexamer may be isolated as crystalline solvates from solvents such as CHCl₃ and CH₂Cl₂, but these



readily lose solvent on heating to give amorphous, glassy materials. Single crystal X-ray analysis of the cyclotrimer **3**, as its MeCN solvate, shows the molecule to adopt a folded geometry, reminiscent of a tennis ball seam (Fig. 2). As with the cyclodimer,⁷ the diphenyl sulfone units adopt 'open book' type conformations, while the diphenylisopropylidene rings are skewed. The diphenyl ether linkages on the other hand appear to be conformationally rather flexible, here adopting both near-orthogonal *and* skewed geometries.

Remarkably, it appears that centrosymmetrically-related pairs of cyclotrimers have self-complementary surfaces, since these interact in the solid state to create supramolecular 'dimers' as shown in Fig. 3. Isopropylidene groups centred on C(71) mutually insert through the loops of complementary oligomer chains between O(8) and S(57). Residual clefts in the surface of the dimer are populated by included MeCN solvent molecules. Dimer stabilisation appears to be achieved through a combination of electronically-complementary face-to-face π -stacking

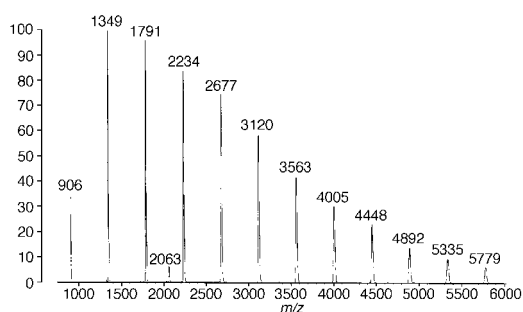


Fig. 1 Partial MALDI-TOF mass spectrum of the macrocyclic products ($M + Na^+$) formed by cyclodepolymerisation of bisphenol A polysulfone (the small peak at m/z 2063 is due to an impurity in the dithranol matrix.)

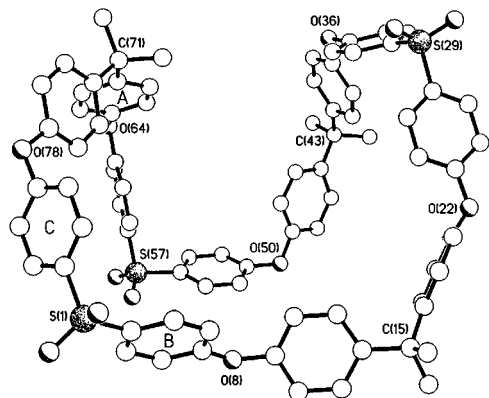


Fig. 2 Structure of **3**, illustrating the tennis ball seam-like conformation adopted in the solid state. Ring torsion angles relative to the plane of the C–X–C bridge (X = S, C, or O) are: at S(1), 86 and 86°; at S(29), 85 and 81°; at S(57), 84 and 79°; at C(15), 76 and 19°; at C(43), 62 and 31°; at C(71), 49 and 46°; at O(8), 79 and 7°; at O(22), 64 and 13°; at O(36), 73 and 4°; at O(50), 60 and 29°; at O(64), 85 and 3°; at O(78), 74 and 28°.

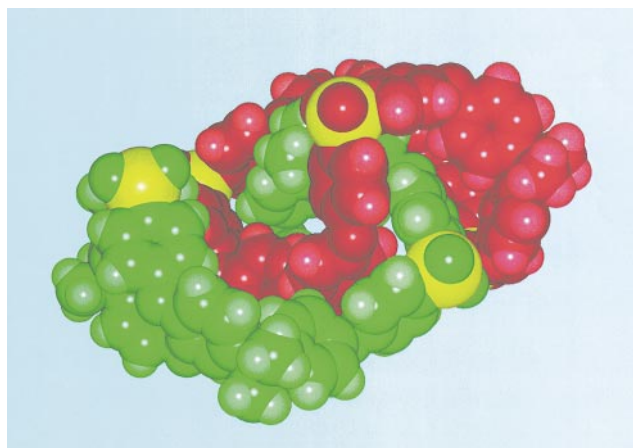


Fig. 3 Space-filling representation of **3**, showing the mutual interpenetration of enantiomeric macrocycles. The centroid–centroid and mean interplanar spacings between rings ‘A’ and ‘B’ in centrosymmetrically related molecules of the cyclo-trimer are 3.96 and 3.57 Å respectively; the H– π distance and C–H– π angle are 2.71 Å and 175°, respectively; and the H–centroid vector is inclined by 82° to the ‘C’ ring plane.

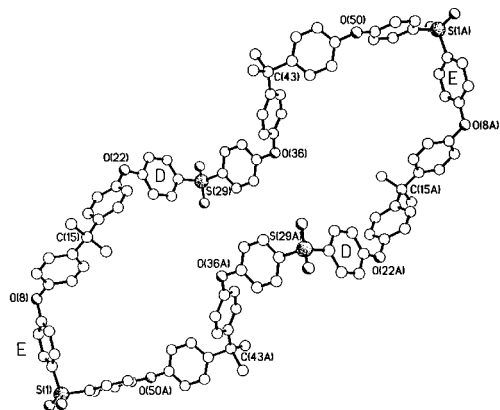


Fig. 4 Structure of **4**. Ring torsion angles relative to the plane of the C–X–C bridge (X = S, C, or O) are: at S(1), 89 and 84°; at S(29), 89 and 76°; at C(15), 57 and 26°; at C(43), 62 and 34°; at O(8), 70 and 27°; at O(22), 76 and 1°; at O(36), 79 and 33°; at O(50), 79 and 2°.

between ring ‘A’ of one molecule and ring ‘B’ of another, as well as a C–H– π interaction between the *ortho*-hydrogen *syn* to O(64) and the ‘C’ ring of an adjacent molecule.

The X-ray structure of the cyclo-tetramer **4** (Fig. 4) shows it to possess crystallographic inversion symmetry. The individual

conformational features closely resemble those of the cyclo-trimer and generate an elongated macrocycle, of approximately 33.6×15.5 Å, containing two distinct cavities. Again there is significant interpenetration of the isopropylidene unit of one macrocycle into the cavity of an adjacent molecule but here, instead of generating isolated pairs of cyclic oligomers, continuous chains of intertwined macrocycles are created.

A valuable new approach to the structural characterisation of non-crystalline polymers emerges from the present work, as it is becoming clear that even *very large* cyclic oligomers of such materials, when *monodisperse*, can afford single crystals of a size and morphology suitable for X-ray analysis. The position is somewhat analogous to that in protein crystallography, where macromolecules are monodisperse for genetic reasons and where strong intramolecular interactions lead to the adoption of compact conformations, allowing macroscopic single crystals to be obtained.

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Notes and references

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|| Fractionation of the recovered solid by gradient chromatography on silica (CH_2Cl_2 –trichloroethene–EtOAc) afforded the cyclodimer **2** (6%), cyclo-trimer **3** (6.5%), cyclotetramer **4** (5.5%), cyclopentamer (4.5%) and cyclohexamer (2.5% yield). Satisfactory elemental analyses, NMR and mass spectra have been obtained. MALDI-TOF mass spectrometry used 1,8,9-trihydroxyanthracene as matrix and sodium trifluoroacetate as cationising agent. Solvated single crystals of **3** and **4** were obtained by slow evaporation of solutions in CHCl_3 –MeCN and benzene–MeOH respectively.

** *Crystal data for 3*: $\text{C}_{81}\text{H}_{66}\text{O}_{12}\text{S}_3 \cdot 4\text{MeCN}$, $M_r = 1491.73$, triclinic, space group $P\bar{1}$, $a = 14.608(2)$, $b = 16.356(1)$, $c = 17.368(1)$ Å, $\alpha = 89.17(1)$, $\beta = 85.49(1)$, $\gamma = 67.60(1)^\circ$, $V = 3823.8(7)$ Å³, $T = 183$ K, $Z = 2$, $D_o = 1.296$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 14.28$ cm⁻¹, $F(000) = 1712$. $R_1 = 0.050$, $wR_2 = 0.126$ for 9088 independent observed reflections [$2\theta \leq 120^\circ$, $I > 2\sigma(I)$]. For **4**: $\text{C}_{108}\text{H}_{88}\text{O}_{16}\text{S}_4 \cdot 6.6\text{C}_6\text{H}_6 \cdot 1.4\text{MeOH}$, $M_r = 2330.40$, triclinic, space group $P\bar{1}$, $a = 10.541(1)$, $b = 15.432(1)$, $c = 21.602(1)$ Å, $\alpha = 105.10(1)$, $\beta = 91.03(1)$, $\gamma = 109.71(1)^\circ$, $V = 3172.2(4)$ Å³, $T = 203$ K, $Z = 1$, $D_o = 1.220$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 12.18$ mm⁻¹, $F(000) = 1230$. $R_1 = 0.083$, $wR_2 = 0.206$ for 5470 independent observed reflections [$2\theta \leq 124^\circ$, $I > 2\sigma(I)$]. Data for both compounds were measured on a Siemens P4/RA diffractometer with graphite-monochromated Cu–K α radiation using ω -scans. Both sets of data were corrected for Lorentz and polarisation effects, and semi-empirical absorption corrections (from ψ -scans) were applied. The structures were solved by direct methods and non-hydrogen atoms were refined anisotropically using the SHELXTL program package. CCDC 182/992.

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