Ring-closing depolymerisation of aromatic polyethers

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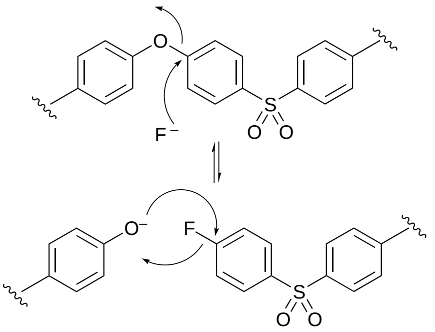
Equilibration of aromatic poly(ether sulfone)s and poly(ether ketone)s under conditions of fluoride-catalysed ether exchange leads, at low polymer concentrations in dipolar aprotic solvents, to efficient ring-closing depolymerisation.

Ring-opening polymerisation of macrocyclic aromatic ether ketones and ether sulfones offers a potentially valuable route to high-performance aromatic polymers,[1–3] and such chemistry has recently become the focus of significant research activity.[4] Advantages of this approach, in the production of composite structures for example, include the very much lower initial viscosities of macrocyclic oligomers relative to the corresponding high molecular weight polymers, the complete absence of by-products, and the fact that ring-opening polymerisations of strain-free macrocycles are largely entropy-driven and thermally neutral.

The synthesis and ring-opening polymerisation of macrocyclic aromatic ethers was first reported in 1989,[1] but the key reaction which would enable recycling of such materials (ring-closing depolymerisation)[5] has not so far been demonstrated. Aromatic poly(ether sulfone)s and poly(ether ketone)s do however undergo catalytic transetherification at high temperatures in the presence of strong but kinetically labile nucleophiles such as fluoride ion,[6] and the existence of this process (Scheme 1) strongly suggests a potential mechanism for polymer–macrocycle interconversion.

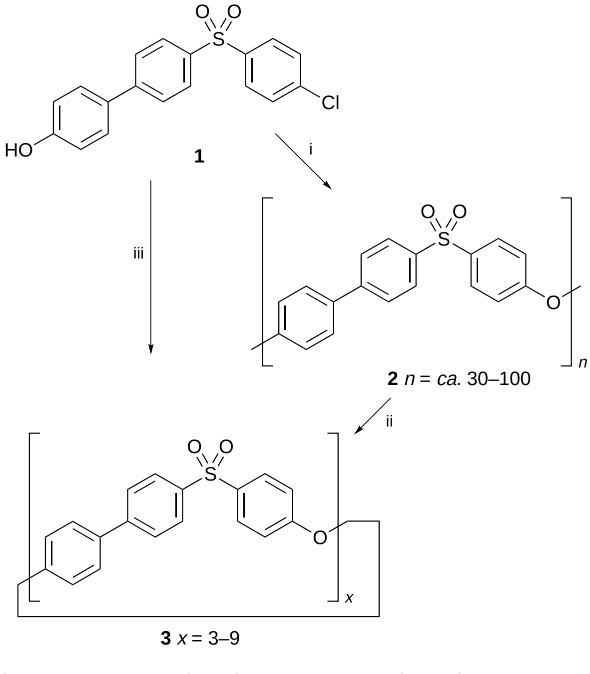


Scheme 1

We now report that efficient ring-closing depolymerisation of the aromatic poly(ether sulfone) **2** (M_w = 29 000, M_n = 8500 Da) can be achieved in dimethylacetamide (DMA) solution at 0.03 M monomer-equivalent concentration and at a temperature of 150 °C, using CsF (0.02 M) as catalyst (Scheme 2). Under these conditions the broad GPC peak associated with the starting polymer disappears over the course of about 12 h, and is progressively replaced by a series of sharp peaks representing macrocyclic oligomers in the approximate molecular weight range M_w = 800–4000 (Fig. 1). It should be noted that the macrocylic oligomers are present (as is often the case for condensation polymers) at a low level even in the starting polymer **2**. Indeed, when polycondensation of monomer **1** is carried out under high-dilution conditions these same macrocyles, identified by FAB-MS, come to represent the major fraction of the product (Scheme 2).

After equilibration of polymer **2** for 48 h in the presence of CsF there is no further change in the molar mass distribution, and the oligomers can be recovered in *ca.* 95% yield by precipitation in aqueous MeOH. Elemental analysis for fluorine (after repeated extraction with water to remove residual inorganics) reveals only very low levels of fluoride ion incorporation (*ca.* one fluorine for every thirty polymer repeat units) consistent with the formation of mainly cyclic species. Peak positions in the GPC and HPLC chromatograms of the depolymerised product are superimposable on those of the macrocyclic oligomers formed by polycondensation of monomer **1**. Moreover, FAB mass spectra of the products from macrocyclisation of **1** and from depolymerisation of **2** show an identical series of parent ions associated exclusively with cyclic species, from cyclotrimer ([M + H]$^+$ 925) to cycloheptamer ([M + H]$^+$ 2158).

The cyclic trimer, tetramer, pentamer and hexamer were isolated from the products of depolymerisation by column chromatography (silica gel; ClHC=CCl$_2$: CH$_2$Cl$_2$: EtOAc, 64 : 33 : 3) and were characterised by FAB mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, GPC, HPLC and DSC. Their well-resolved ^{1}H NMR spectra confirm that, as expected for pure cyclic oligomers, only three AA′BB′ systems are present in the aromatic region. Resonances assigned to protons *ortho* to the biphenyl linkage show significant variations of chemical shift as a function of ring-size, and are for example shifted upfield by *ca.* 0.1 ppm in the cyclic trimer **3** (x = 3), relative to the higher ring sizes. Crystals of **3** (x = 3) suitable for X-ray



Scheme 2 *Reagents and conditions*: i, K$_2$CO$_3$, PhSO$_2$Ph, 280 °C; ii, CsF, DMA, 150 °C; iii, K$_2$CO$_3$, DMA, 150 °C

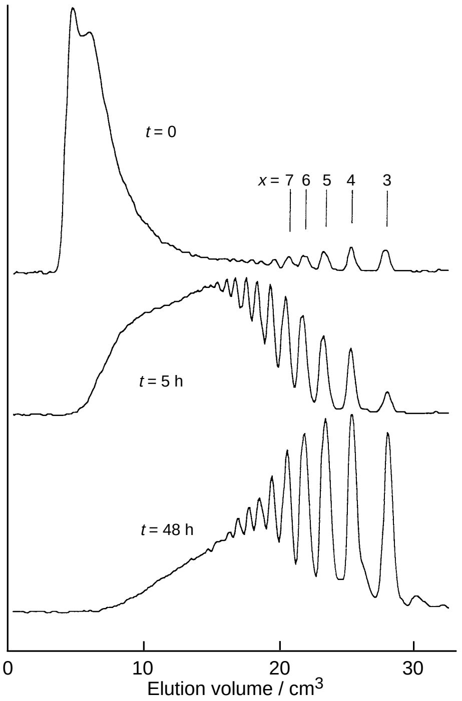


Fig. 1 Gel permeation chromatograms (eluent $CHCl_3$) showing progressive ring-closing depolymerisation of polymer **2** and formation of the macrocyclic oligomers $[OArArSO_2Ar]_x$ (Ar = 1,4-phenylene)

analysis, were isolated from $CHCl_3$. These melted sharply at 475 °C, but higher cyclic oligomers decomposed above 500 °C without melting. The structure of **3** (x = 3), determined by single-crystal X-ray diffraction,¶ is shown in Fig. 2. There is evidence for a slight degree of ring-strain in this macrocycle, in that all three C–S–C bond angles (101.6 ± 0.1°) are compressed by about 3.3° from their normal open-chain value of 104.9°. The biphenyl unit, which frequently adopts a coplanar conformation as a consequence of crystal packing and symmetry considerations,[7] here takes up a conformation close to its isolated minimum-energy position,[8] with inter-ring torsion angles for the three independent biphenyl residues in the range 34–38°.

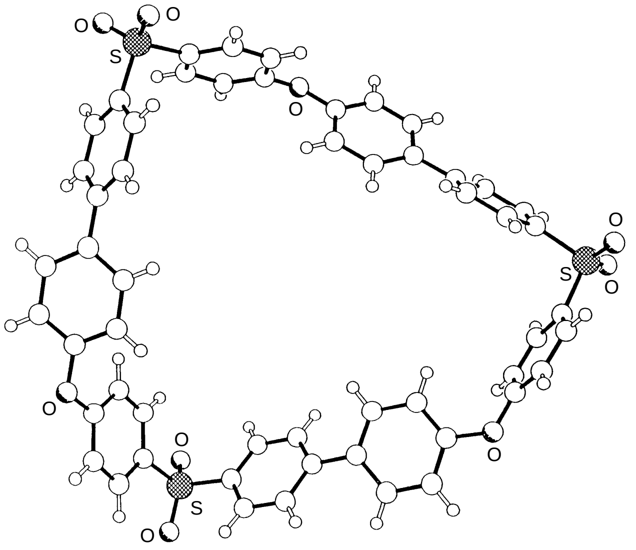
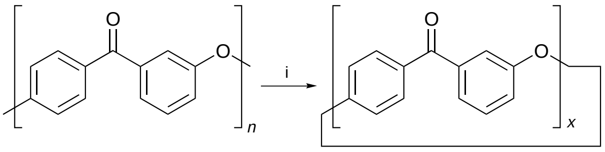


Fig. 2 Molecular geometry of the cyclic trimer **3** (x = 3) (the solvating molecule of $CHCl_3$, which partly fills the molecular cavity, has been omitted for clarity)



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x = 2–11

Scheme 3 *Reagents and conditions*: i, CsF, DMA, 155 °C

Ring-closing depolymerisation appears to be a quite general reaction for activated aromatic polyethers. The poly(ether ketone) **4** (Scheme 3), for example,[9] is cleaved to form macrocyclic species under very similar conditions and on much the same timescale as polymer **2**. Analysis of the product mixture by GPC, HPLC and FAB-MS demonstrates formation of macrocyclic ether ketone oligomers up to at least the cycloundecamer, and lower oligomers from cyclic dimer to cyclic hexamer have been isolated in pure form by column chromatography.

The potential of ring-closing depolymerisation chemistry for recycling (in every sense!) high-performance aromatic polyethers has thus been demonstrated for the first time. The possibility that non-equilibrium conditions might circumvent the current requirement for very low polymer concentrations in such reactions is now under investigation.

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Footnotes and References

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¶ *Crystal data* for **3** (x = 3): $C_{54}H_{36}O_9S_3{\cdot}CHCl_3$, M = 1044.38, monoclinic, space group $P2_1/n$, a = 7.468(2), b = 20.110(3), c = 34.099(5) Å, β = 95.68(2)°, Z = 4, U = 5096(2) Å^3, T = 213 K, D_c = 1.361 g cm^{-3}, μ(Cu-Kα) = 3.25 mm^{-1}, F(000) = 2152. A total of 7560 independent reflections ($2\theta \leqslant 120°$) were measured on a Siemens P4 rotating-anode diffractometer, with graphite-monochromated Cu-Kα radiation, using ω-scans. The structure was solved by direct methods and refined anisotropically using F^2 data to give R_1 = 0.062, wR_2 = 0.136 for 4988 independent observed reflections [$I > 2\sigma(I)$]. CCDC 182/533.

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