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Catechol-based macrocyclic aromatic ether-sulfones: Synthesis, characterization and ring-opening polymerization

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Dedicated to Professor Philip Hodge, recognising his contributions to polymers in synthesis over 45 years

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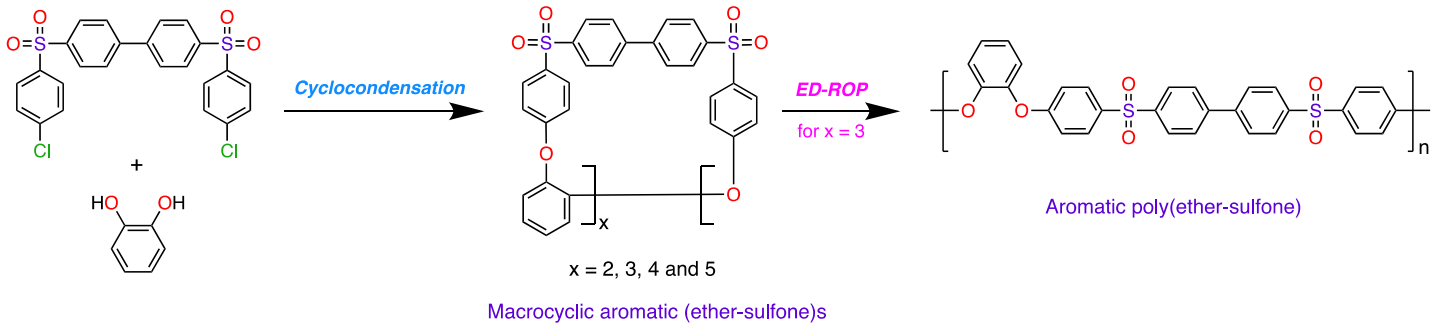
Abstract

Cyclocondensation between 4,4'-bis(4"-chlorobenzenesulfonyl)biphenyl and catechol, with subsequent chromatographic separation of the reaction products, led to the isolation of four novel ether-sulfone macrocycles (cyclic dimer, -trimer, -tetramer and -pentamer). Similarly, cyclocondensation of catechol with a novel seven-ring diketone/disulfone monomer allowed the isolation of the two new aromatic ether-ketone-sulfone macrocycles, a cyclic monomer and a cyclic dimer. Transannular shielding and deshielding effects in the cyclic monomer produce substantial chemical shift differences for chemically equivalent protons in the ^{1}H NMR spectra of the cyclic monomer and -dimer. Fluoride-initiated ring-opening polymerization of the ether-sulfone cyclic trimer affords a novel, high-molecular weight poly(ether-sulfone).



Keywords: Cyclocondensation, macrocycles, ring-opening polymerization, aromatic poly(ether-sulfone)s.

Introduction

The molecular structures of high-temperature engineering thermoplastics generally comprise linear chains of aromatic rings, linked together by thermo-oxidatively stable units such as direct arene-arene bonds, ether, ketone, sulfone, amide or imide groups.[1,2] Aromatic poly(ether-sulfone)s, exemplified in Chart 1, comprise an industrially-significant class of such polymers: these materials may in principle be accessed either by electrophilic chemistry (polysulfonylation)[3] or by activated nucleophilic substitution (polyetherification)[4] at the aromatic rings. In practice the nucleophilic route, involving the displacement of sulfone-activated chloride by phenoxide ion, has generally proved more selective and versatile both in the laboratory and in commercial production.[5,6] A more recently-discovered approach to polymers of this type involves the ring-opening polymerization (ROP) of *macrocyclic* aromatic (ether-sulfone)s.[7,8] Macrocyclic oligomers are present in small, equilibrium quantities (typically 1–3 wt%) in many linear step-growth polymers, including the poly(ether-sulfone)s,[9,10,11] but they may also be obtained in high yield either by *cyclo*-condensation of monomers under *pseudo*-high-dilution conditions,[12-16] or by ring-closing depolymerization of high molecular weight (MW) polymer at low concentration in solution.[7,17,18]

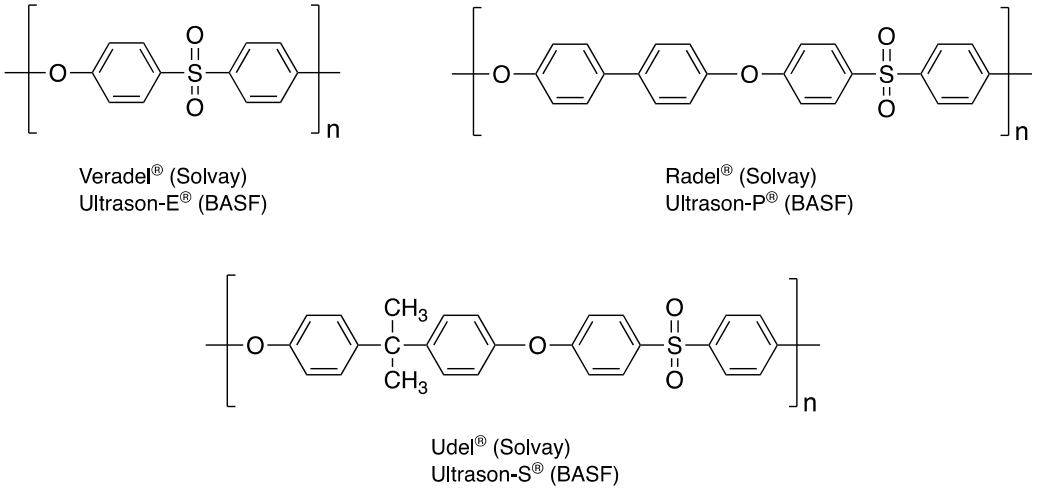


Chart 1. Industrially-significant aromatic poly(ether sulfone)s, showing current (2020) trade-names and manufacturers.

Both ring-opening polymerization and ring-closing depolymerization exploit the ring-chain equilibrium that can be established (generally in the presence of a suitable catalyst) between a high molecular weight, step-growth linear polymer and a homologous family of macrocyclic oligomers.[19-21] An important feature of such a system is that at *high* concentrations the equilibrium lies heavily in the direction of polymer, whilst at *low* concentrations it shifts to favor macrocylic oligomers. For example, under very concentrated or even solvent-free reaction conditions an equilibrated system would typically contain *ca.* 98 wt% polymer and only *ca.* 2% macrocycles, whilst under dilute conditions (say 1 wt% of solutes) the system can easily comprise >90% of macrocycles, and may even consist exclusively of these.[22] Thus, if a *neat* macrocyclic oligomer, or a mixture of homologous macrocylic oligomers, is allowed to undergo reversible cleavage, for example at high temperature in the presence of a catalyst, then ring-opening polymerization will occur. Such polymerizations involve only a shuffling of the linkages between repeat units and have several potentially valuable features. For example, no volatiles or other by-products are generated and, as the macrocycles are generally large

enough to be strainless, little or no heat is evolved. The latter process may therefore be described as an entropy-driven ring-opening polymerization (ED-ROP).[22] Conversely, when a *dilute* solution of high molar mass polymer is allowed to equilibrate by reversible chain-cleavage, then macrocyclic oligomers are formed in high yield by ring-closing depolymerization (RCDP).[7,17,18] It has been proposed that a combination of RCDP and ED-ROP could form the basis of a technique for recycling high-value step-growth polymers, and such processes have been investigated for several different polymers of this type,[18,23-25] including the poly(ether-sulfones).[24]

The vast majority of industrially-significant aromatic thermoplastics are based on 1,4-linked phenylene units,[1,2] although 1,3-linkages are found in a number of cases, as for example in the high-temperature polyamide poly(1,3-phenylene isophthalamide),[27] trademarked as *Nomex*®. Relatively little work has been reported on analogous systems based on the 1,2-phenylene unit, although a benzene-1,2-dioxy-based analogue of the all-*para* engineering poly(ether-ketone) known as PEEK has been obtained by Hodge and co-workers from polycondensation of benzene-1,2-diol (catechol) with 4,4'-difluorobenzophenone, and an equilibrium between this polymer and its homologous family of macrocylic oligomers (Chart 2; a) was shown to be established at high temperature in the presence of fluoride ions.[28] More recently, *o*-PEEK macrocycles have been employed to fabricate carbon fibre composites via ring opening polymerization reactions.[29] The present study might also lead the way to novel in-situ fabrication of high performance thermoplastic composites.

Other investigations on polymers containing catechol as co-monomer include work on poly(ester-imide)s, PEIs, synthesized by polycondensation of *N*-(4-carboxyphenyl) trimellitimide or *N*-(3-carboxyphenyl)trimellitimide with catechols or 5-methylresorcinol (Chart 2; b).[30] It is also noteworthy that catechol residues are present in the highly complex aromatic backbone of the biopolymer lignin, which is attracting increasing interest as a component of bio-thermoplastics as potential alternatives to petroleum-derived materials.[31]

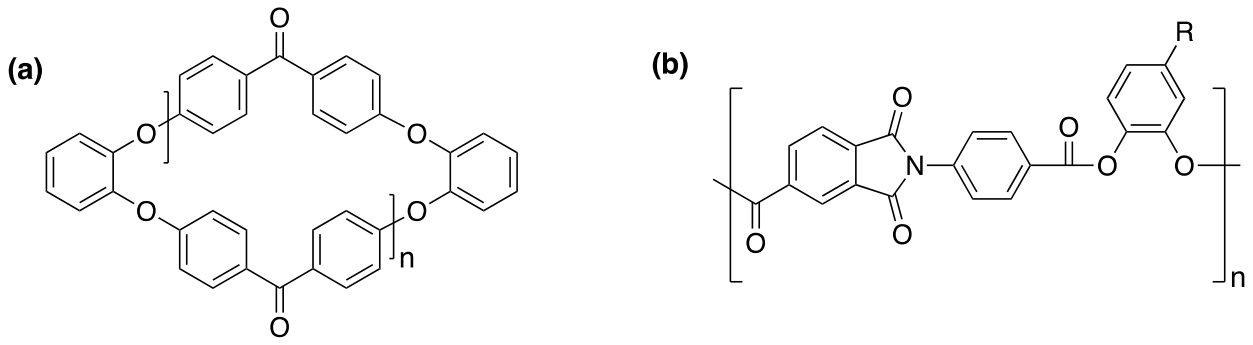
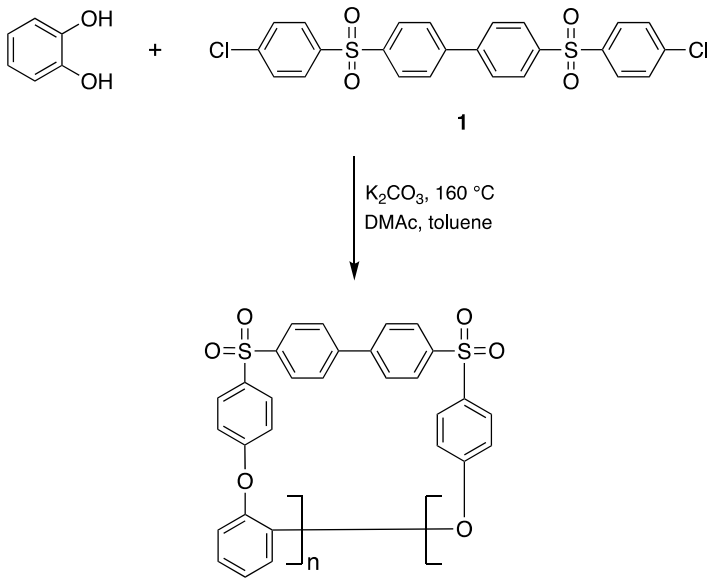


Chart 2. (a) Catechol-based macrocyclic aromatic ether-ketones[28,29]; (b) Catechol-based aromatic poly(ester-imide)s (R = H, Me, or *t*-Bu).[30]

In the present work, we report the synthesis, characterization, and entropy-driven ring-opening polymerization of a novel series of macrocyclic aromatic (ether-sulfone)s derived from catechol by nucleophilic *cyclo*-condensation with extended aromatic dichloro-compounds, activated towards nucleophilic (SNAr) substitution by the presence of sulfone groups *para* to the chloro-substituents.

Results and Discussion

Cyclo-condensation of catechol with 4,4`-bis(4"-chlorobenzenesulfonyl)biphenyl[32] (**1**) was achieved under *pseudo*-high dilution conditions by slow, continuous addition of a concentrated solution of **1** and catechol in dimethylacetamide (DMAc) to a suspension of potassium carbonate in DMAc/toluene at 160 °C, affording a mixture of macrocyclic aromatic (ether-sulfone)s (Scheme 1).



2 (n = 2), **3** (n = 3), **4** (n = 4), **5** (n = 5),

Scheme 1. Synthesis of cyclic oligomers **2**, **3**, **4** and **5** under *pseudo*-high dilution conditions.

Fractionation of the resulting mixture of cyclic oligomers by gradient elution chromatography afforded a series of macrocycles as pure compounds including the cyclo-dimer **2** (7.8%), -trimer **3** (3.4%), -tetramer **4** (2.0%) and -pentamer **5** (1.5%). The thermal characteristics and solubility properties of the four isolated macrocycles are summarized in Table 1. The cyclic oligomers with an even number of repeat units (dimer and tetramer) are crystalline, high-melting, and soluble only in strongly acidic solvent mixtures (e.g. chloroform/trifluoroacetic acid), while the cyclic trimer and pentamer are essentially amorphous compounds with good solubility in simple chlorinated solvents. Very similar odd/even behaviour has previously been reported for the corresponding cyclic oligomers of the commercial polysulfone known as Radel® (Chart 1).[7]

Table 1. Characterization of ether-sulfone cyclic oligomers **2**, **3**, **4** and **5** (Scheme 1)

	2	**3**	**4**	**5**
Yield (%)	7.8	3.4	2.0	1.5
[a] T_m (°C)	514	*nd*	425	*nd*
[b] T_c (°C)	280	*nd*	*nd*	*nd*
[c] T_g (°C)	*nd*	205	206	205
Solvent	$CHCl_3$/TFA[d]	$CHCl_3$	$CHCl_3$/TFA[d]	$CHCl_3$

[a] MPt (on heating); [b] Crystallization temperature (on cooling); [c] Glass transition (onset); [d] 5:1 v/v; *nd* = none detected

The ^{1}H NMR spectra of macrocycles **2**, **3**, **4** and **5** are very similar, with only small chemical shift differences as a function of ring size as reported in the Supplementary Material (SM). The ^{1}H NMR spectrum of cyclic trimer **3** is shown in Figure 1. The symmetrical pair of multiplets at 7.25 and 7.38 ppm is characteristic of the catechol residue, and the highest field doublet, at 6.87 ppm, is assigned to the protons *ortho* to the ether linkage and *meta* to sulfone. Detailed assignments of all ^{1}H NMR spectra are given in the Experimental Section and the SM.

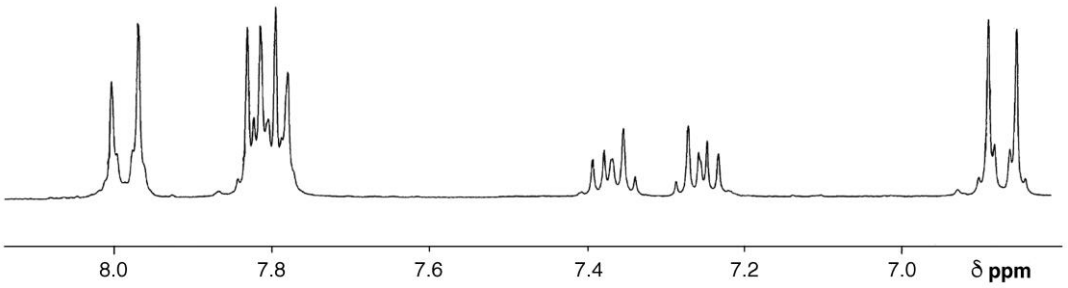
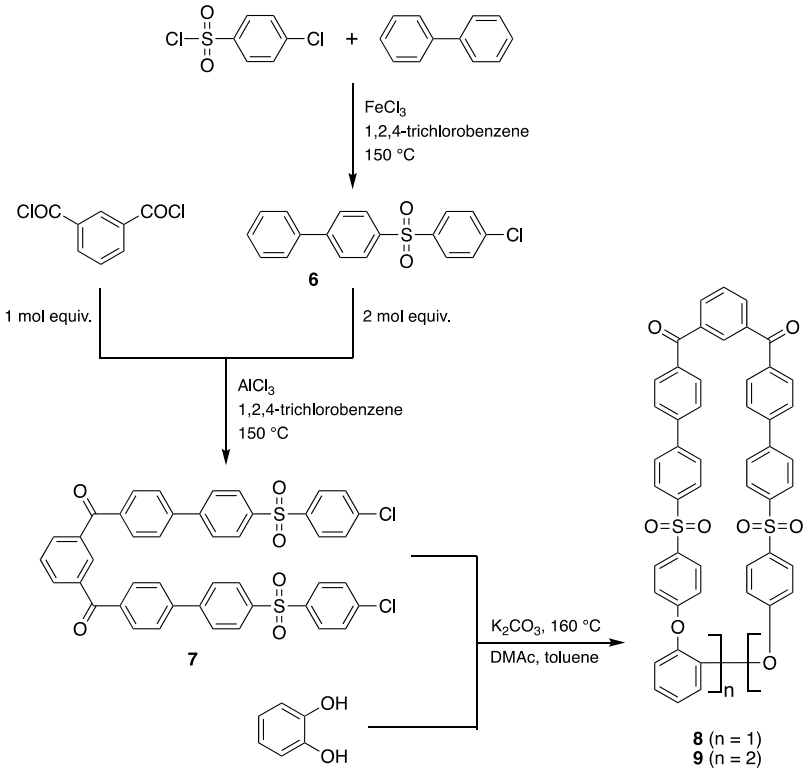


Figure 1. ^{1}H NMR spectrum (250 MHz, CD_2Cl_2/CH_3SO_3H, 4/1 v/v) of cyclic trimer **3**.

Each isolated macrocycle was identified by MALDI-TOF mass spectroscopy. The mass spectrum of the cyclic pentamer **5**, for example, showed only a strong molecular ion at *m/z* 2725, representing the sodium adduct $[M+Na]^+$ (*m/z* calc. 2726.0). Analogous mass spectra for macrocycles **2**, **3** and **4** are given in the SM.

Following the development of a successful *cyclo*-condensation procedure for aromatic (ether-sulfone)s from catechol and the four-ring dihalide **1**, we next investigated an analogous reaction between catechol and the seven-ring diketone/disulfone monomer **7**, synthesized by a two-stage route as shown in Scheme 2.



Scheme 2. Synthesis of monomer **7** and cyclic oligomers **8** and **9**.

The intermediate 4-(4'-chlorobenzenesulphonyl)biphenyl, **6**, was obtained in 50% yield from a Friedel-Crafts reaction between biphenyl and 4-chlorobenzenesulphonyl chloride using anhydrous ferric chloride as catalyst.[4] Subsequent reaction of **6** with isophthaloyl chloride afforded the seven-ring monomer **7** in 42% yield after recrystallization from DMF (Scheme 2). Its DSC thermogram showed a sharp melting peak at 284 °C. The ^{1}H NMR spectrum observed was fairly complex (see ESI) but was fully consistent with the proposed structure, as indeed were the MALDI-TOF mass spectrum, COSY NMR analysis and ^{13}C NMR spectrum.

Condensation of monomer **7** with catechol under *pseudo*-high dilution conditions (Scheme 3) afforded a range of oligomeric molecules, and analysis of the crude product by MALDI-TOF MS demonstrated that these oligomers comprised exclusively macrocyclic species – specifically the cyclic monomer **8**, cyclic dimer **9**, and trace amounts of a cyclic trimer which was not subsequently isolated. The cyclic monomer (27%) and cyclic dimer (2%) were recovered as pure compounds by gradient elution chromatography. Their structures were confirmed by MALDI-TOF MS, and by ^{1}H and ^{13}C NMR spectroscopy (see Experimental Section and SM).

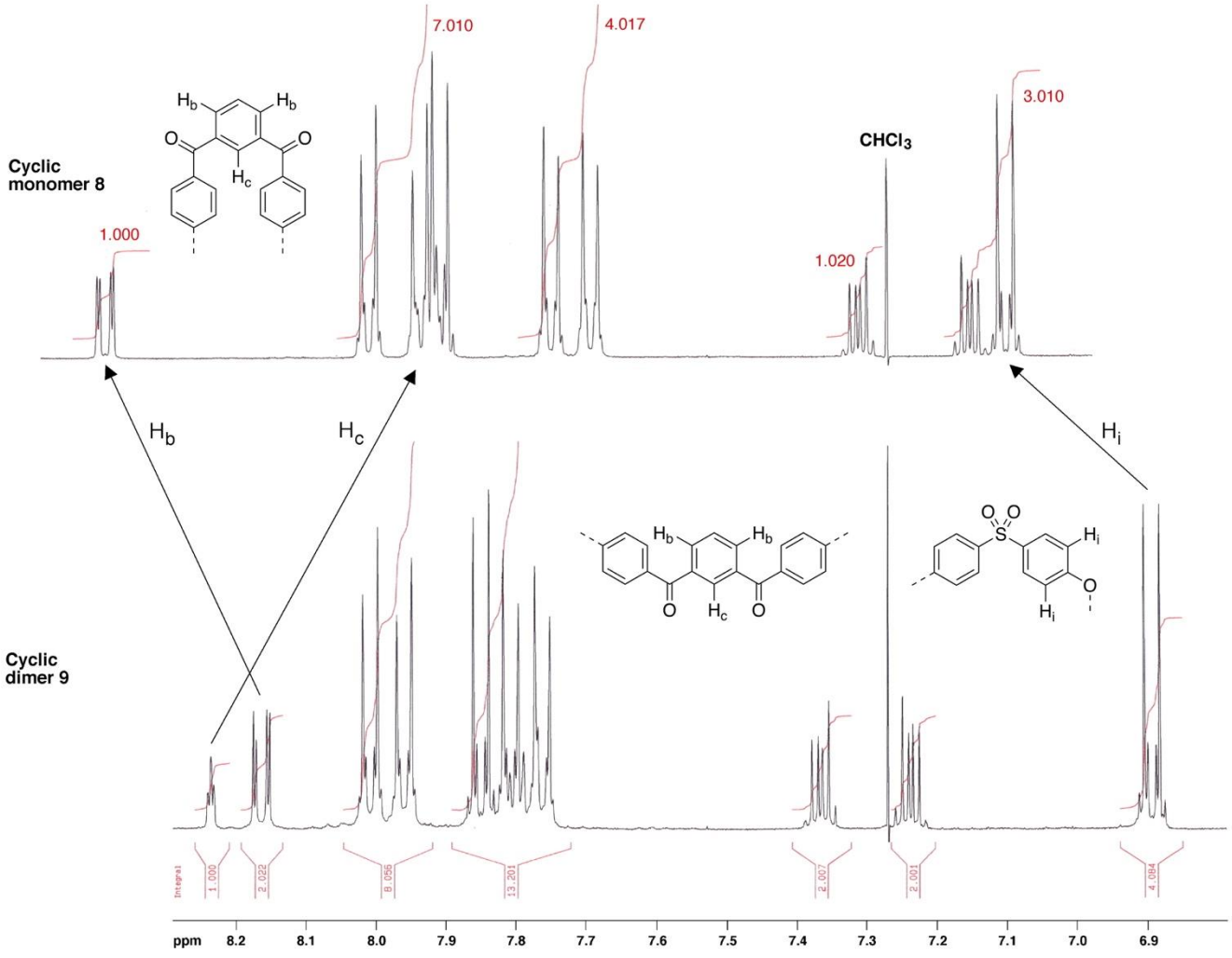


Figure 2. ^{1}H NMR spectra (400 MHz) of cyclic monomer **8** and cyclic dimer **9**. Integrals are shown in red.

In the ^{1}H NMR spectrum of cyclic monomer **8**, the resonance assigned to the isophthaloyl proton H_c, o*rtho* to both carbonyl groups, (identified by ^{1}H-^{1}H COSY analysis; see SM) lies at significantly higher field than the resonance for the corresponding protons in cyclic dimer **9**, the upfield shift being ca. 0.3 ppm (Figure 2).

This difference is however readily explained in terms of the allowed conformations at the isophthaloyl group. Energy-minimization of computational models for **8** and **9** (molecular mechanics with charge-equilibration, *Cerius2*) showed that the diarylisophthaloyl unit in cyclic monomer **8** is constrained to adopt a *syn* conformation in which the proton of interest (H_c) is "sandwiched" between two adjacent aromatic rings and is thus subject to significant ring-current shielding (Figure 3).

In contrast, the minimum-energy conformation of cyclic dimer **9** is much more open, with the diarylisophthaloyl units adopting an *anti* conformation in which there can be no intramolecular ring-current shielding of proton H_c. Moreover, in this model for cyclic dimer **9**, it is the isophthaloyl protons H_b, *meta* to H_c, that now lie in the ring-current shielding zones of the adjacent aromatic rings (Figure 3), accounting for their resonance position upfield (by ca. 0.2 ppm) relative to the corresponding signal in cyclic monomer **8** (Figure 2). Finally in comparing the ^{1}H NMR spectra of macrocycles **8** and **9**, the difference in chemical shift of ca. 0.2 ppm, seen for the protons H_i (Figure 2) may be accounted for in terms of mutual transannular *de*shielding effects between the adjacent ether-sulfone rings in cyclic monomer **8**. Further details of this modelling study, together with atomic coordinates for the final models of macrocycles **8** and **9**, are given in the SM.

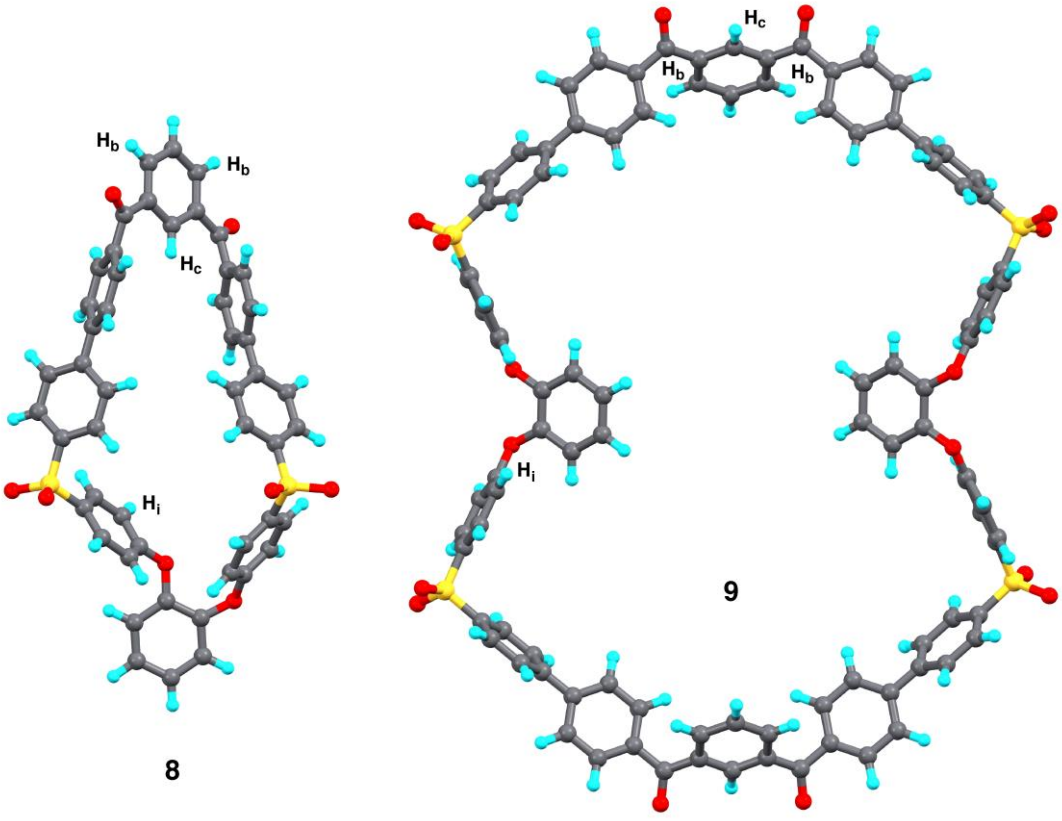
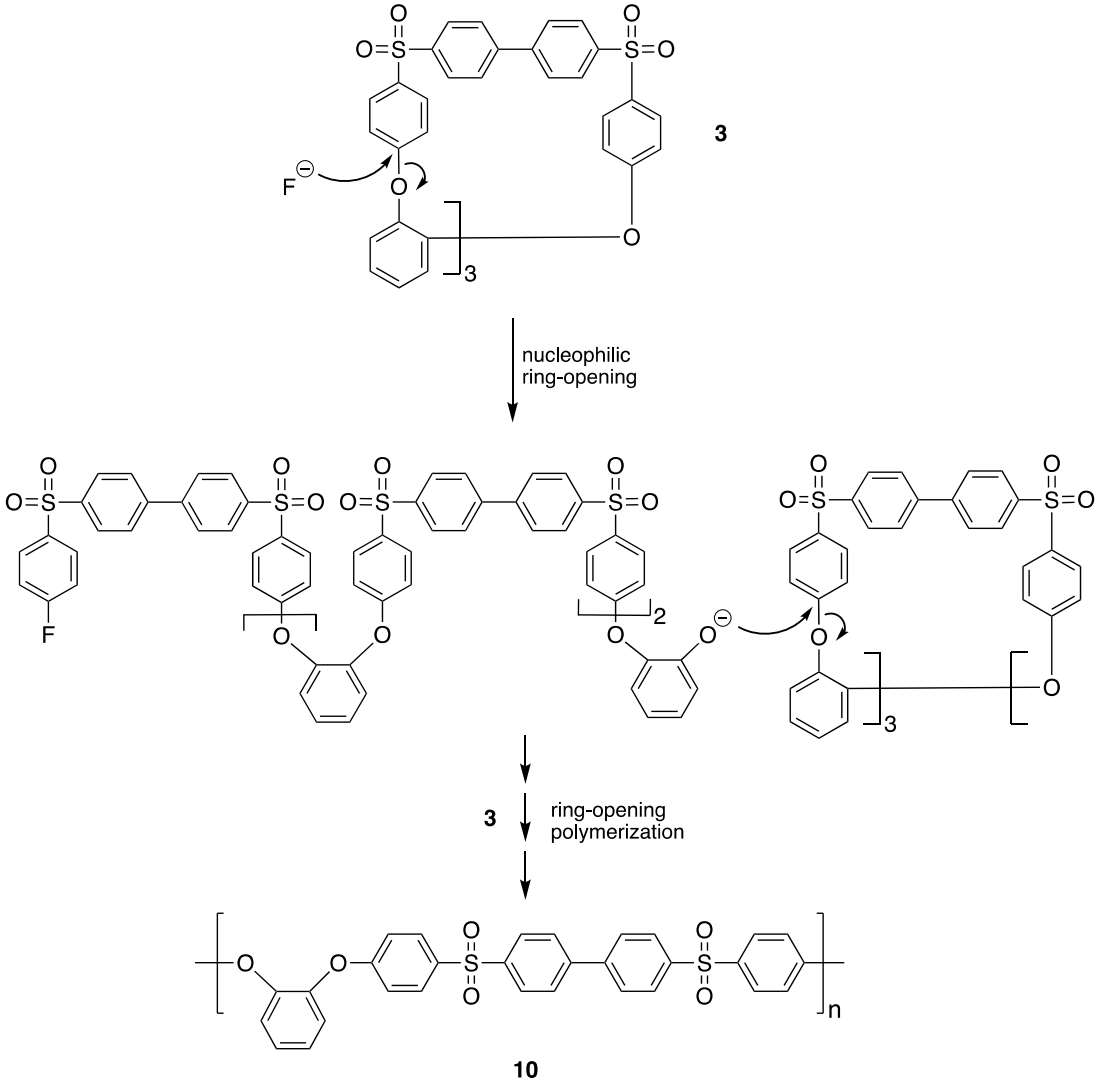


Figure 3. Energy-minimized models for the cyclic monomer **8** and cylic dimer **9**. The isophthaloyl proton H_c in **8** is constrained to lie within the ring-current shielding zones of the two adjacent aromatic rings by the *syn* conformation of the diarylisophthaloyl unit. Conversely, in **9**, the diarylisophthaloyl units can adopt the more open *anti* conformation, with no ring-current shielding of H_c but now with shielding of the protons H_b. Significant *de*shielding of the protons H_i is seen in the ^{1}H NMR spectrum of **8** relative to **9**, and this is ascribed to mutual, transannular, ring-current effects between the adjacent "ether-sulfone" rings in cyclic monomer **8**.

Entropy-driven ring-opening polymerization of macrocycle **3** was successfully achieved at high temperature (320 °C) in the melt phase, with anhydrous cesium fluoride as catalyst. In this type of process the fluoride ion acts as a nucleophilic initiator, cleaving the activated ether linkage of one macrocycle and generating a free phenoxide end-group which then attacks a second macrocycle, leading to chain-growth polymerization as shown in Scheme 3. The resulting linear polymer **10** was tough and flexible, and had an inherent viscosity of 0.45 dL g^{-1}, indicative of high MW and comparable with values for several commercial polyethersulfones including Radel® (also 0.45 dL g^{-1}; see Chart 1 and ref. 7). The new polymer was fully soluble in 96% sulfuric acid and in mixtures of dichloromethane and trifluoroacetic acid, indicating there was no significant degree of cross-linking between the chains.[6] In view of the extremely high melting points of **2**, **4**, **8** and **9** (> 400 °C), and the very low yield of **5** (1.5%), no comparable polymerizations were possible with these macrocycles.



Scheme 3. Nucleophilic ring-opening polymerization of macrocycle **3** leading to polymer **10** (note: the fluorophenyl and phenoxide end-groups of **10** are not shown).

Conclusions

This work reports two new families of aromatic ether-sulfone macrocycles. Cyclocondensation under *pseudo*-high dilution conditions between 4,4'-bis(4"-chlorobenzenesulfonyl)biphenyl and catechol, with subsequent chromatographic separation of the reaction products, led to the isolation of four novel ether-sulfone macrocycles (cyclic dimer, -trimer, -tetramer and -pentamer) that have all been fully characterized. Similarly, reaction between catechol and a novel seven-ring diketone/disulfone monomer allowed the isolation of two new aromatic ether-ketone-sulfone macrocycles, a cyclic monomer and a cyclic dimer, with the cyclic monomer being obtained in unexpectedly high yield (27%). Interestingly, proton NMR spectrum of the cyclic monomer showed a significant high field resonance-shift of the isophthaloyl proton *ortho* to both carbonyl groups relative to the corresponding resonance in the cyclic dimer. Potential reasons for this difference were explored by computational modelling, which revealed a constrained *syn* conformation of the diarylisophthaloyl unit in the cyclic monomer, contrasting with a more open conformation in the cyclic dimer where the diarylisophthaloyl units adopts an *anti* conformation. As a result, in the cyclic dimer there is no intramolecular ring-current shielding of the corresponding isophthaloyl proton. Finally, given the industrial relevance of poly(ether-sulfone)s, entropy-driven ring-opening polymerization of one of the new macrocycle**s** was studied using a catalytic amount of cesium fluoride as initiator. The resulting poly(ether-sulfone) showed good solubility, indicating an absence of cross-linking, and an inherent viscosity comparable to values for commercially available poly(ether-sulfone)s.

Experimental Section

General. Starting materials were obtained from Sigma-Aldrich. Potassium carbonate was used after drying under vacuum. Anhydrous aluminum chloride was sublimed under a nitrogen atmosphere before use. *N,N*-Dimethylacetamide (DMAc) was distilled from calcium hydride, and catechol was recrystallized from toluene. All other materials were used as received.

NMR data were obtained on Bruker AC250 and JEOL EX400 spectrometers, with chemical shifts recorded in δ (ppm) and referenced to residual solvent resonances. The abbreviations s, d, dd, t, m and br represent singlet, doublet, doublet of doublets, triplet, multiplet and broad respectively. Labelled structures for ^{1}H NMR assignments are given in the SM. Infra-red spectra were obtained from mulls in mineral oil (Nujol) and were recorded on a Perkin-Elmer FT1700 instrument.

Electron ionization mass spectra were run on a VG-BioQ triple quadrupole instrument in positive ion mode. MALDI-TOF mass spectra were obtained on an SAI LT3 Lasertof instrument using 1,8,9-trihydroxyanthracene as matrix. A typical sample preparation was as follows: 0.1 mL of a solution of the compound in THF (1 mg/mL), 0.1 mL of a solution of sodium trifluoroacetate in THF (1 mg/ml) and 0.1 mL of a solution of the matrix in THF (20 mg/ml) were combined, and an aliquot of the mixture was then carefully transferred to a sample plate and left to dry in a vacuum oven (40 °C) for 30 minutes prior to the analysis.

Differential scanning calorimetry (DSC) was performed using a Mettler DSC20 system (nitrogen atmosphere, scan rate 10 °C/min). Solution viscosimetry was carried out using a Schott-Gerate CT 150 semi-automated viscometer. The resulting time measurements are applied to the following equation:

$\eta_{inh} = \ln(t_s/t_0)/c$

Where η_{inh} is the inherent viscosity, (t_s) is the flow time for the polymer solution at concentration c (g/100 mL), and t_0 is the flow time for the pure solvent.

Synthesis of macrocycles 2, 3, 4, and 5. 4,4'-Bis(4''-chlorobenzenesulfonyl)biphenyl (5.00 g, 9.96 mmol) and catechol (1.10 g, 9.96 mmol) were dissolved in DMAc (120 mL) and the solution was added *via* a syringe pump under a nitrogen atmosphere, over 48 h, to a vigorously stirred suspension of K_2CO_3 (3.02 g, 21.9 mmol) in DMAc (150 mL) and toluene (80 mL) while the reaction mixture was heated under reflux. At the end of the addition, the mixture was refluxed for a further three hours. The brown solution was then filtered while hot to remove insoluble salts (K_2CO_3, $KHCO_3$, KCl), and distilled water (300 mL) containing HCl (0.5 mL) was then added slowly to the solution. A mixture of homologous cyclic oligomers precipitated as a grey solid which was collected by vacuum filtration and dried in a vacuum oven at 70°C overnight.

The cyclic dimer **2** (7.8%), -trimer **3** (3.4%), -tetramer **4** (2.0%), and -pentamer **5** (1.5%) were isolated (in that order) from the product mixture as pure compounds by gradient elution chromatography on silica gel, using dichloromethane/ethylacetate (100/0 to 97/3 v/v) as eluent.

The cyclic dimer **2** had mp 515°C, *m/z* (E/I) [100%, $(M)^+$] 1080, Calcd. For $C_{60}H_{40}S_4O_{12}$, 1080.1; ^{1}H NMR (CD_2Cl_2/CH_3SO_3H 4/1) δ (ppm) 6.78 (d, *J* 8.9 Hz, H_d), 7.22 and 7.38 (2m, H_e and H_f), 7.78 (d, H_a and H_c), 8.0 (d, *J* 8.56, H_b); ^{13}C ($CDCl_3$/CF_3COOH) δ (ppm) 117.7, 123.5, 127.9, 128.4, 128.9, 130.1, 133.1, 140.4, 145.1, 146.0; IR (KBr) 3073 ($\nu CH_{aromatic}$), 1576 (C-$C_{aromatic}$), 1480 and 1157 (νSO_2), 1263 cm^{-1} (νC-O); Anal. Calc. For $C_{60}H_{40}S_4O_{12}$: C, 66.65; H, 3.73%. Found: C, 66.41; H, 3.78%.

The cyclic trimer **3** showed no melting point and had *m*/z (E/I) [100%,$(M)^+$] 1620, Calc. For $C_{90}H_{60}S_6O_{18}$, 1620.2; ^{1}H NMR (CD_2Cl_2/CH_3SO_3H 4/1) δ (ppm) 6.87 (d, *J* 8.99 Hz, H_d), 7.26 and 7.36 (m, H_e and H_f), 7.78-7.83 (2m, H_a and H_c), 7.98 (d, *J* 8.6, H_b); ^{13}C (CD_2Cl_2/CH_3SO_3H 4/1) δ (ppm) 117.8, 124.2, 128.1, 128.8, 129.4, 130.7, 134.2, 141.4, 145.0, 146.3, 162.6; IR (KBr) 3073 ($\nu CH_{aromatic}$), 1581 (νC-$C_{aromatic}$), 1489 and 1153 (νSO_2), 1267 cm^{-1} (νC-O); Anal. Calc. For $C_{90}H_{60}S_6O_{18}$: C, 66.65; H, 3.73%. Found: C, 66.49; H, 3.78%.

The cyclic tetramer **4** had mp 424°C; *m/z* (E/I) [100%,$(M)^+$] 2160, Calc. For $C_{120}H_{80}S_8O_{24}$, 2160.3; ^{1}H NMR (CD_2Cl_2/CH_3SO_3H 4/1) δ (ppm) 6.88 (d, *J* 8.94 Hz, H_d), 7.22 and 7.34 (2m, H_e and H_f), 7.80 (t, H_a and H_c), 7.99 (d, *J* 8.55 Hz, H_b); ^{13}C (CD_2Cl_2/CH_3SO_3H 4/1) δ (ppm) 117.8, 124.1, 128.1, 128.8, 129.4, 130.7, 134.3, 141.4, 145.0, 146.4, 162.6; IR (KBr) 3073 ($\nu CH_{aromatic}$) 1576 (νC-$C_{aromatic}$), 1488, 1152 (νSO_2), 1267 cm^{-1} (νC-O). Anal. Calc. For $C_{120}H_{80}S_8O_{24}$: C, 66.65; H, 3.73%; Found: C, 66.32; H, 3.85%.

The cyclic pentamer **5** showed no melting point and had; *m/z* (E/I) [100%,$(M)^+$] 2700, Calc. For $C_{150}H_{100}S_{10}O_{30}$, 2700.3; ^{1}H NMR ($CD_2Cl_2$/$CH_3SO_3H$ 4/1) δ (ppm) 6.88 (d, *J* 8.95 Hz, H_d), 7.23 and 7.33 (2m, H_e and H_f), 7.76 (m, H_a and H_c), 7.97 (d, *J* 8.56 Hz, H_b); ^{13}C (CD_2Cl_2/CH_3SO_3H 4/1) δ (ppm) 117.9, 124.1, 128.1, 128.8, 129.5, 130.7, 134.17, 141.2, 145.0, 146.3, 162.6; IR (KBr) 3074 ($\nu CH_{aromatic}$) 1580 (νC-$C_{aromatic}$), 1488 and 1153 (νSO_2), 1267 cm^{-1} (νC-O); Anal. Calc. For $C_{150}H_{100}S_{10}O_{30}$: C, 66.65; H, 3.73%. Found: C, 66.37; H, 3.80%.

Synthesis of linear oligomer 7. Isophthaloyl dichloride (4.00 g, 0.0197 mol), 4-(4'-chlorophenylsulphonyl)-biphenyl **3.11** (14.24 g, 0.043 mol), and aluminium chloride (13.08 g, 0.043 mol) were heated with stirring in 1,2,4-trichlorobenzene (35 mL) at 150 °C for 3 hours, until HCl evolution virtually ceased. After cooling, the viscous solution was poured into a mixture of water and conc. hydrochloric acid (250 mL/20 mL). The aqueous phase was separated and the yellow viscous residue was stirred in hexane to solidify the product, which was then extracted twice with methanol (200 mL) and filtered off The resulting pale yellow powder was dried under vacuum overnight and recrystallized from DMF (100 mL) to give oligomer **7** as a white powder (6.00 g, 42%).

Oligomer **7** had mp 284°C *m/z* (E/I) [100%,$(M)^+$] 786.4, Calc. For $C_{44}H_{28}S_2O_6Cl_2$, 786.1; ^{1}H NMR ($CDCl_3$/CF_3COOH 5/1) δ (ppm) 7.57 (d, J_{ih} 8.72 Hz, H_i), 7.75-7.85 (H_d, H_e, H_a), 7.93-7.99 (m, H_h and H_f), 8.07 (d, J_{gh} 8.5 Hz, H_g), 8.14 and 8.17 (dd, J_{ba} 7.7 Hz, H_b), 8.28 (bs, H_c); ^{13}C ($CDCl_3$/CF_3COOH 5/1) δ (ppm) 128.2, 128.7, 129.0, 129.4, 130.5, 131.9, 135.0, 135.4, 136.1, 137.5, 140.0, 141.6, 144.9, 145.7; IR (KBr) 3052 cm^{-1} ($\nu CH_{aromatic}$), 1647 (νC=O), 1593, (νC-$C_{aromatic}$), 1475 and 1156 (νSO_2), 1107 cm^{-1} (νCl-$C_{aromatic}$).

Synthesis of macrocycles 8 and 9. Potassium carbonate (0.76 g, 5.5 mmol), DMAc (150 mL) and toluene (70 mL) were placed in a 500 cm^3 three-necked flask equipped with a magnetic stirrer, nitrogen gas inlet and a Dean-Stark trap with condenser and gas outlet. The reaction mixture was then heated until the toluene began to reflux (ca. 160 °C). Water was removed by azeotropic distillation with toluene over 2 hours. A solution of compound **7** (2.00 g, 2.54 mmol) and catechol (0.28 g, 2.54 mmol) in DMF (200 mL) was added with a syringe pump at a rate of 10 cm^3 per hour. After the end of the addition, the mixture was refluxed overnight. The resulting brown solution was filtered while hot to remove insoluble salts (K_2CO_3, $KHCO_3$, KCl). Distilled water (300 ml) containing HCl (10ml) was added slowly to the filtered solution until the desired cyclic oligomers precipitated as a brown solid. The mixture of oligomers was collected by vacuum filtration, washed with methanol, filtered again and dried in a vacuum overnight at 70°C to give a brown solid.

Gradient elution chromatography with DCM/EtOAc (100/0 to 97/3 v/v) on silica gel allowed only two of the macrocyclic oligomers to be isolated as pure compounds, specifically the cyclic monomer **8** (27.0%) and the cyclic dimer **9** (2.0%).

Cyclic monomer **8** had mp 404 °C, *m/z* (EI) [100%, $(M)^+$] 823.5, Calc. For $C_{50}H_{32}S_2O_8$, 824.1; ^{1}H NMR ($CDCl_3/CF_3COOH$ 5/1 v/v), δ (ppm) 7.11 (d, J_{ih} 8.9 Hz, H_i), 7.23 and 7.35 (m, H_l and H_m) 7.66-7.8 (m, H_d, H_e, H_a), 7.93-8 (m, H_h, H_f and H_c), 8.07 (d, J_{gh} 8.6 Hz, H_g), 8.38 and 8.42 (dd, J_{ba} 7.75 Hz, J_{bc} 1.6 Hz, H_b); ^{13}C ($CDCl_3/CF_3COOH$ 5/1 v/v) δ (ppm) 118.5, 122.3, 127.4, 128.0, 128.5, 130.3, 131.7, 133.8, 135.6, 135.9, 136.3, 140.2, 144.7, 145.2, 146.4, 162.3 (C *ipso* O ether), 199.4 (CO); IR (KBr) 3052 ($\nu CH_{aromatic}$), 1654 (νC=O), 1578, ($\nu C\text{-}C_{aromatic}$), 1487 and 1151 ($\nu SO_2$), 1222 cm^{-1} (νC-O); Anal. Calc. For $C_{50}H_{32}S_2O_8$: C, 72.80; H, 3.91%. Found: C, 72.61; H, 3.90%.

Cyclic dimer **9** had mp 413 °C, *m/z* (EI) [100%, $(M)^+$] 1647.8, Calc. For $C_{100}H_{64}S_4O_{16}$, 1648.3; ^{1}H NMR ($CDCl_3/CF_3COOH$ 5/1 v/v), δ (ppm) 6.90 (d, J_{ih} 8.93 Hz, H_i), 7.28 and 7.38 (2m, H_l and H_m) 7.75-7.87 (H_d, H_e, H_g and H_a), 7.95-8.03 (m, H_h, H_f), 8.16 and 8.18 (dd, J_{ba} 7.78 Hz, H_b), 8.28 (bs, H_c); ^{13}C ($CDCl_3/CF_3COOH$ 5/1) δ (ppm) 117.44, 123.77, 127.78, 128.21, 128.36, 128.93, 130.21, 131.92, 133.32, 135.97, 137.31, 140.34, 145.08, 145.45, 145.99, 162.53 (C *ipso* O ether), 199.5 (CO); IR (KBr) 2920 ($\nu CH_{aromatic}$), 1656 (νC=O), 1593, ($\nu C\text{-}C_{aromatic}$), 1487 and 1152 ($\nu SO_2$), 1265 cm^{-1} (νC-O).

Ring-opening polymerization of macrocycle 3. Polymerization of **3** was carried out in an aluminium DSC pan. The macrocycle was ground with 3 mol% of anhydrous cesium fluoride and a pelletized 20 mg sample of the mixture was heated at 320 °C for 1 hour under nitrogen in the DSC instrument and then cooled to room temperature. A subsequent DSC scan to 400 °C showed the resulting polymer to be amorphous (no melting transition) and to have a glass transition temperature (T_g) of 207 °C. On cooling, the polymer was recovered in the form of a tough, yellow, transparent pellet that dissolved completely in 96% sulfuric acid, in which solvent it showed an inherent viscosity (η_{inh}) of 0.46 dL g^{-1}.

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Supplementary Material

Spectroscopic data (^{1}H NMR, ^{13}C NMR, MALDI-TOF MS) for all products can be found in the supplementary material file, together with details of the computational modelling study. Atomic coordinates for the final models are available from the authors as electronic files in pdb format.

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