Ring−Chain Interconversion in High-Performance Polymer Systems. 1. [Poly(oxy-4,4′-biphenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene)] (Radel-R)

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Received February 28, 2002; Revised Manuscript Received May 29, 2002

ABSTRACT: At a polymer concentration of 1 wt % in dimethylacetamide, fluoride-promoted cleavage of ether linkages in Radel-R (an industrially important aromatic poly(ether sulfone) derived from 4,4′-biphenol) leads to ring-closing depolymerization. A high molar mass poly(ether sulfone) is thus converted in good yield to a family of macrocycles containing from eight up to at least sixty aromatic rings. Detailed analyses of the reaction products indicate a linear oligomer content of less than 4 wt %. Individual macrocycles containing eight, twelve, sixteen, and twenty aromatic rings have been isolated and characterized as pure, monodisperse oligomers (the first two by single-crystal X-ray analysis). The cyclic dimer and trimer both adopt open, flattened conformations with substantial free pathways through the ring centers, and the cyclic dimer packs to give a continuous-channel structure in the solid state. These macrocyclic oligomers undergo efficient ring-opening polymerization in the presence of phenoxide and especially thiophenoxide initiators to regenerate high-molar-mass polymer, demonstrating for the first time that the chemical recovery and recycling of high-performance aromatic polymers is—in principle—entirely feasible.

1. Introduction

Any polycondensation reaction proceeding to high molar mass generally affords not only linear polymer, but also a homologous series of macrocyclic oligomers—in amounts which are dependent both on the polymer system involved and on the reaction conditions.[1] Under equilibrium conditions, linear and cyclic species can interconvert via ring-opening polymerization of macrocyclic oligomers and ring-closing depolymerization (cyclodepolymerization) of linear chains, and depolymerizations of this type have recently been demonstrated for a number of aliphatic and semialiphatic polyesters.[2,3] The equilibrium mass ratio of cyclic oligomers to high-MW linear polymer increases with dilution, and within the general theoretical framework for ring−chain equilibria developed by Jacobson and Stockmeyer,[1] work by Mandolini and co-workers suggests the existence of a threshold concentration below which *only* cyclic species should be present.[4] This prediction has been confirmed experimentally for cyclodepolymerization of aliphatic polyesters, where the threshold concentration proved surprisingly high at around 2% w/v, but few other polymer systems have so far been studied in this respect. However, a number of important engineering thermoplastics, including the aromatic poly(ether sulfone)s and poly(ether ketone)s, are synthesized by nucleophilic displacement of halide ions from aromatic rings activated by electron-withdrawing substituents, and in the presence of fluoride ion, this process has been shown to be *reversible* (Scheme 1).[5,6] It thus seemed possible that fluoride-initiated cleavage of activated ether linkages might enable cyclodepolymerization to be achieved with, for example, aromatic poly(ether sulfone)s.

In practice it is the reverse reaction—ring-opening polymerization of macrocyclic aromatic ethers—which has been the focus of most research activity to date, as this chemistry offers a potentially valuable route to high-performance polymers.[7] Advantages of such an approach, in the production of composite structures, for example, include the very low initial viscosities of macrocyclic oligomers relative to the corresponding high-molecular-weight polymers, the absence of volatile byproducts, and the fact that ring-opening polymerizations of strain-free macrocycles are largely entropy-driven and thus thermally almost neutral.[8] Although ring-opening polymerization of macrocyclic aromatic ethers was first reported over a decade ago,[9,10] and has been widely investigated since,[11] the reaction proposed above—cyclodepolymerization via transetherification—was unknown when our work began. Our initial results demonstrating fluoride-catalyzed cyclodepolymerization of aromatic poly(ether sulfone)s have been described in preliminary communications,[12,13] and the occurrence of this process was subsequently confirmed by Kricheldorf and co-workers.[14] Of the commercially available poly(ether sulfone)s, polymer **1** (from 4,4′-biphenol and 4,4′-dichlorodiphenyl sulfone) has no potentially labile aliphatic units, unlike the better-known polysulfone derived from bisphenol A, and preliminary studies showed that

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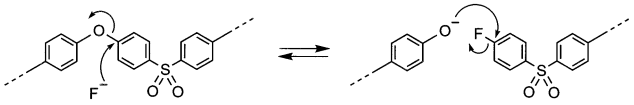
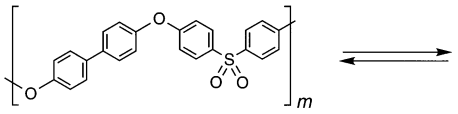
10.1021/ma020315u CCC: $22.00
Published on Web 07/27/2002

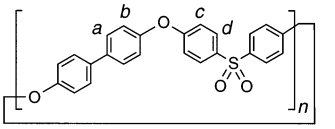
Scheme 1. Reversible, Fluoride-Induced Cleavage of an Aromatic Poly(ether sulfone) Chain



Scheme 2. Cyclodepolymerization and Ring-Opening Polymerization Processes for Polymer 1



Polymer **1** (number average $m \approx 60$)



Macrocyclic oligomers (number average $n \approx 4$)

both the polymer and its macrocyclic homologues are readily soluble in dipolar aprotic solvents. Polymer **1** was thus chosen for detailed study of its ring−chain interconversion chemistry, and we here present evidence that cyclodepolymerization of this polymer (trademarked as Radel-R)[15] is both high-yielding and reversible (Scheme 2). Our results indicate that ring−chain interconversions of this type could enable the chemical recovery and recycling of this and many other high-value engineering thermoplastics.

2. Results and Discussion

2.1. Cyclodepolymerization Studies. As a first step, polymer **1** (from Amoco Inc.) was purified by reprecipitation from solution in dimethylacetamide (DMAc), using acetone as the nonsolvent, to give a readily filterable, granular material which gel permeation chromatography (GPC) showed to contain only traces of low-MW species. The reprecipitated polymer (M_w 43000, M_n 23000, inherent viscosity 0.45 dL g^{-1}) was dissolved in anhydrous DMAc to give a 1% solution (w/v), and this was heated at reflux in the presence of cesium fluoride (50 mol % per polymer repeat unit) under dry nitrogen. Samples were removed every 12 h and analyzed by GPC. Over a period of 72 h, the broad, high-molar-mass peak progressively diminished and shifted to lower molar mass, and was largely replaced by a series of sharp, low-molar-mass peaks assignable to discrete oligomeric species (Figure 1).

A subsequent reaction was analyzed by solution viscometry over a more extended period (Figure 2), confirming both the progressive degradation in molar mass and the time scale required. The inherent viscosity (IV) fell sharply over the first 72 h, but then diminished only slightly in the second 72 h. An analogous reaction in dimethylformamide (DMF) produced almost identical results. In either case the reaction products were recovered by precipitation in water, and examination of the crude material by MALDI-TOF MS (Figure 3a) strongly suggested that the oligomers observed by GPC comprised a series of *macrocyclic* compounds, from cyclic dimer ($[M + Na]^+$ at *m/e* 823) to cyclic pentadecamer ($[M + Na]^+$ at *m/e* 6030). Use of alternative cationizing agents (H^+, Li^+) gave entirely analogous MALDI-TOF mass spectra. Importantly, no evidence for linear material could be found in these spectra, even though

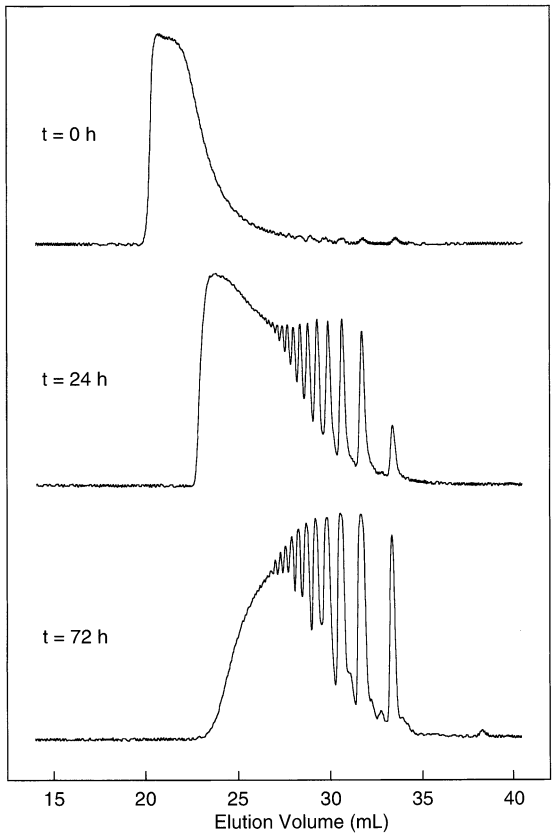


Figure 1. Cyclodepolymerization of polymer **1** in the presence of CsF, as shown by progressive loss of high-molar-mass material from the GPC trace and the appearance of a series of discrete peaks associated with homologous macrocyclic oligomers. The very weak peaks visible between those representing cyclic oligomers amount to ca. 2 wt % of the final product and are assigned to the linear hydroxy-ended oligomers detected by ^{1}H NMR.

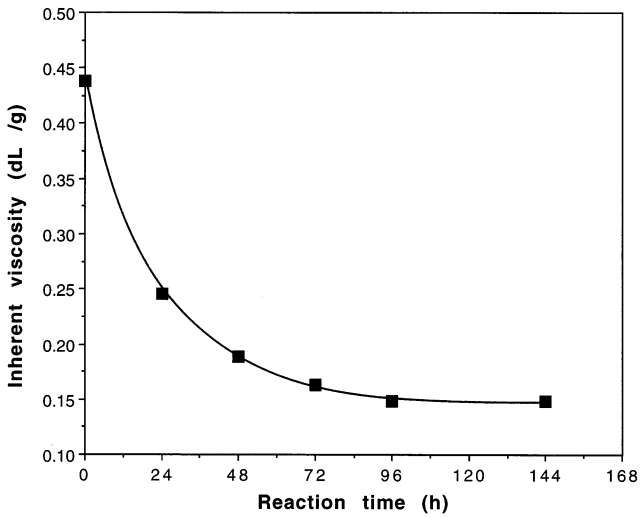


Figure 2. Cyclodepolymerization of polymer **1** in the presence of CsF, as shown by the progressive reduction in inherent viscosity with time.

MALDI-TOF analysis of a specifically synthesized sample of linear oligomers (average DP ≈ 4) showed that such species are easily detected by this technique (Figure 3b).

Similarly, a ^{1}H NMR spectrum for the linear-oligomer sample showed a well-resolved hydroxybiphenylene end-group resonance (an apparent doublet, $\delta = 6.95$) which in the corresponding spectrum for the products of

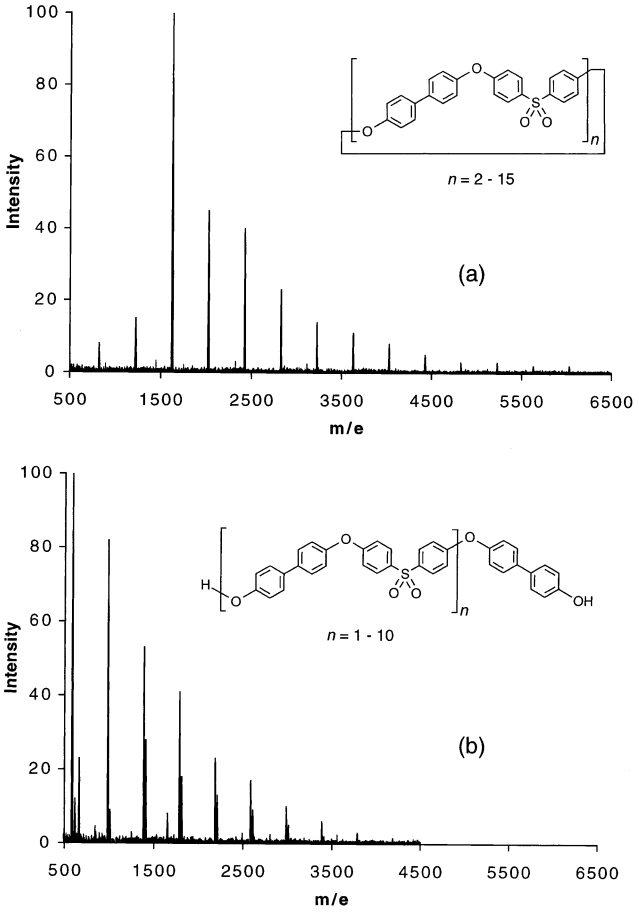


Figure 3. (a) MALDI-TOF mass spectrum of the products of cyclodepolymerization of polymer **1**. (b) MALDI-TOF mass spectrum of linear oligomers of polymer **1**. The principal peaks correspond to $[M + H]^+$ and the weaker lines at slightly higher mass to $[M + Na]^+$.

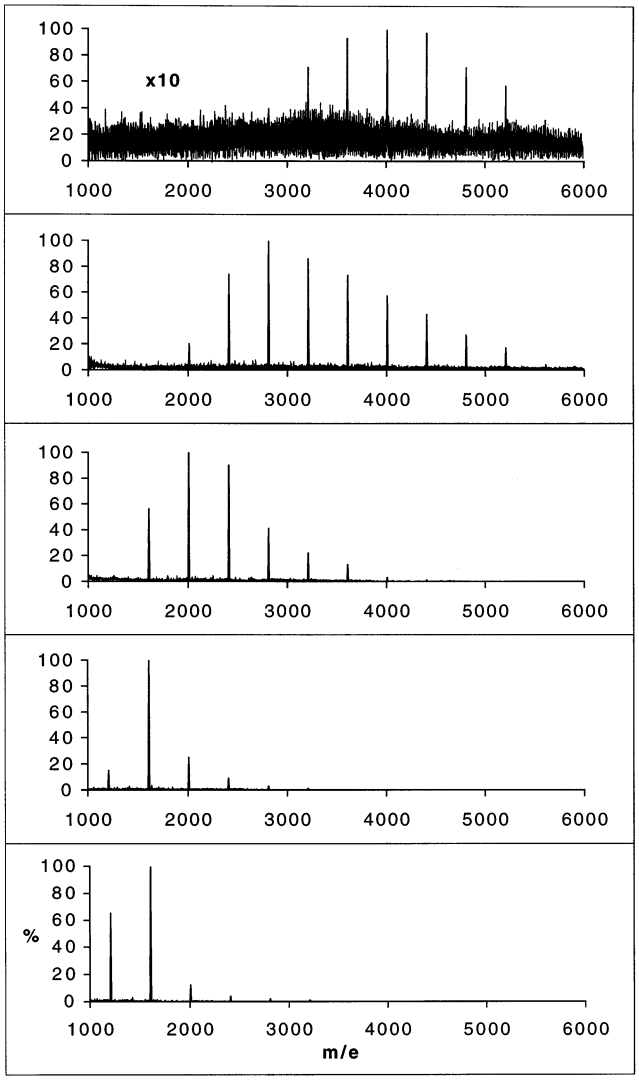


Figure 4. MALDI-TOF mass spectra of the fractions obtained by preparative GPC separation of the products from cyclodepolymerization of polymer **1**. Peaks correspond to $[M + Li]^+$.

cyclodepolymerization was observed only near the limit of detection. Integration showed that this resonance corresponded to 1 end group for every 62 polymer repeat units. On the basis that these end groups are associated with bis(hydroxybiphenylene)-ended oligomers, and given that M_n for this sample (by GPC) indicates an average DP of only 4.1, it is calculated that the proportion of such linear oligomers in the sample is no more than 3.3 wt %. To check for the presence of *fluorine*-ended linear material, ^{19}F NMR spectra were recorded using hexafluorobisphenol A as an internal quantification standard. Perhaps surprisingly, given the high levels of fluoride ion needed for efficient cyclodepolymerization (typically 1 mol of fluoride for every 2 polymer repeat units), NMR analysis of the products showed only ca. 1 fluorine atom per 1000 repeat units, giving a ratio of hydroxyphenyl to fluorophenyl end groups of 16:1. Elemental analysis showed only that any fluorine present was below the limit of detection (i.e., <0.1 wt %).

The results of MALDI-TOF analysis (above) had given no evidence for the presence of linear oligomers in the products of cyclodepolymerization. However, given that GPC failed to resolve individual oligomers of molar mass higher than ca. 5000 Da (at which point individual peaks merged into a high-molar-mass tail, as shown in Figure 1) and that MALDI-TOF MS showed neither cyclic nor linear species with masses above ca. 6000 Da, the composition of the unresolved GPC fraction at higher molar mass remained open to question. This fraction, comprising 11% of the total, was therefore isolated by preparative GPC and examined in more detail. Analytical GPC again failed to resolve individual oligomer peaks but gave $M_w = 8800$ and $M_n = 7300$, corresponding to an average DP of ca. 18. End-group analysis by ^1H NMR, as described above, indicated the presence of at most 5% linear oligomers, so that at least 95% of this fraction must comprise cyclic material. Four subsequent GPC fractions, of diminishing average molar mass, were also isolated, and these were each found to contain, by ^1H NMR, more than 97% cyclic oligomers. Analyses of all five fractions by MALDI-TOF MS are shown in Figure 4, where again no significant peaks assignable to linear oligomers can be detected. All available evidence thus indicates that cyclodepolymerization of the poly(ether sulfone) **1** leads to almost complete conversion of high-molar-mass polymer to cyclic oligomers.

Four previously unknown macrocycles were isolated from the products of cyclodepolymerization by column chromatography on silica gel. These were the cyclic dimer **2**, in 7.5% yield, cyclic trimer **3**, 6.4% yield, cyclic tetramer **4**, 5.8% yield, and cyclic pentamer **5**, 5.5% yield, characterized by differential scanning calorimetry (DSC), ^1H and ^{13}C NMR, MALDI-TOF MS, elemental

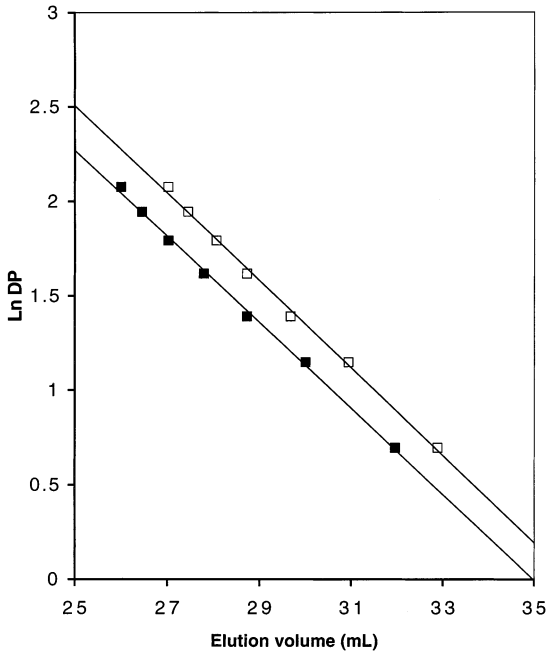


Figure 5. L_n DP versus elution volume for linear (■) and cyclic (□) oligomers of polymer **1**.

analysis, and (for the cyclic dimer and trimer) single-crystal X-ray methods (section 2.3). The lower macrocycles are crystalline and *extremely* high melting (T_m at 554, 389, and 455 °C for **2**, **3**, and **4**, respectively), but the cyclic pentamer is, like its parent polymer, entirely amorphous. The melting point of macrocycle **2** is even higher than that reported for the corresponding cyclic dimer of bisphenol A polysulfone (525 °C),[16] presumably reflecting the greater rigidity of direct arene−arene bonds relative to isopropylidene linkages.

With the isolation and characterization of these four macrocyclic species, and the availability of GPC data for the corresponding linear oligomers, it became possible to check individual GPC retention volumes against those for the original "oligomer" peaks observed during cyclodepolymerization. Their assignment to *cyclic* oligomers was thus confirmed. Moreover, plots of L_n DP against elution volume for cyclic and linear oligomers are essentially straight lines, as shown in Figure 5, and extrapolation of the "cyclics" line from the four characterized macrocycles confirms that *all* the GPC oligomer peaks found in the product mixture are indeed due to cyclic species, from dimer to dodecamer.

The mechanism of cyclodepolymerization must clearly involve initial nucleophilic attack by fluoride ion on sulfone-activated aromatic rings, cleaving the polymer chain into phenoxide-ended and fluorine-ended segments.[5] We have investigated the effects of fluoride ion concentration on cyclodepolymerization (Table 1) and find that the reaction slows dramatically as the mole ratio of fluoride to polymer (repeat unit) is reduced progressively from 0.5 to 0.05. These results, together with the very long time scale for cyclodepolymerization even at the highest fluoride concentration (Figures 1 and 2), suggest that the equilibrium position for cleavage and re-formation of the ether linkage is overwhelmingly toward ether *formation*. High levels of fluoride ion are therefore needed to generate even very small concentrations of phenoxide-ended chain segments. Once such a segment is formed however, it can undergo intramolecular cyclization at any activated ring (the so-called "back-biting" reaction, Scheme 3),[14] leading to a wide range of different macrocyclic ring sizes, as is indeed observed. Polymer end groups, in the form of chloro or hydroxyl substituents, would clearly be consumed under these conditions and are thus not accountable on a separate basis.

2.2. Macrocyclic Oligomers by Cyclopolycondensation. High yields (>90%) of macrocyclic oligomers were also obtained by carbonate-promoted polycondensation of 4,4′-biphenol with 4,4′-dichlorodiphenyl sulfone in DMAc under *pseudo*-high-dilution conditions (Scheme 4). Analysis by solution viscometry, MALDI-TOF MS, HPLC, and GPC indicated that the overall product distribution was virtually identical to that obtained by cyclodepolymerization of polymer **1**, and as found for the products of cyclodepolymerization, there was no evidence in these analyses for anything other than macrocyclic material.

2.3. Structural Analyses of Cyclic dimer 2 and Cyclic Trimer 3. Single crystals of **2** and **3**, suitable for X-ray analysis, were obtained by vapor diffusion of diethyl ether into solutions of the purified oligomers in dichloromethane. In the solid state, dimer **2** has crystallographic inversion symmetry and adopts a rather flattened, open conformation (Figure 6). The macrocycle exhibits partial disorder, with the C(2)−C(6) ring displaying two alternative orientations. As a consequence, two different geometries are observed for the diaryl sulfone units, with one molecule having a slightly skewed "open-book" conformation and the other a near-orthogonal arrangement of the rings. The diaryl ether fragment associated with O(8) has a skewed geometry, whereas that about O(21) is orthogonal. The biphenyl unit is twisted, with the two rings being mutually rotated by ca. 42°. The open conformation of the macrocycle provides a free pathway through the ring center of ca. 3.7 × 10 Å, which is populated by disordered molecules of dichloromethane solvent.

The macrocycles stack along the crystallographic *a* direction (Figure 7) to create continuous channels (from which the solvent diffuses rapidly on removing crystals from their supernatant). Adjacent channels are linked by $\pi-\pi$ stacking between symmetry-related pairs of the aromatic rings C(22)−C(27); the mean interplanar and centroid−centroid separations are 3.43 and 3.87 Å, respectively. There are no significant intermolecular interactions involving the biphenyl units.

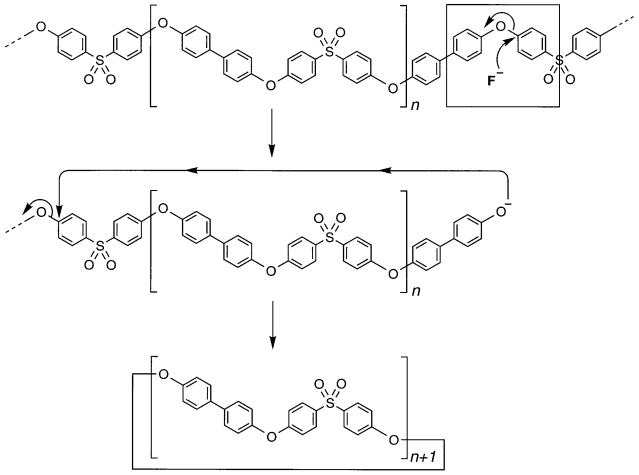
The trimer **3** has no molecular symmetry but, like its homologous dimer, adopts a distinctly flattened and open conformation with a very substantial free pathway (ca. 8.3 × 14.0 Å) through the macro-ring center (Figure 8). The geometries at two of the independent sulfone linkages are essentially open-book [at S(1) and S(28)], whereas that at S(55) tends more toward a skewed type of arrangement. For the diaryl ether components, rings A/B, I/J, and K/L adopt orthogonal-type conformations and rings C/D and G/H are skewed, whereas for the E/F pair of rings, the geometry is intermediate between these two conformations. All three biphenyl units are nonplanar, with torsional twist angles of ca. 38°, 14°, and 27° for the B/C, F/G, and J/K systems, respectively. In contrast to the well-defined channels formed by the cyclic dimer **2**, molecules of trimer **3** exhibit no distinct mutual alignment nor are there any dominant intermolecular interactions. Regions within the macrocyclic cavity are occupied by molecules of solvating dichloromethane, though these are severely disordered.

Table 1. Distribution of Cyclic Oligomers Formed in the Cyclodepolymerization of Polymer 1, as a Function of Fluoride Ion Concentration[a]

CsF concn (mM) [mol of CsF per polym repeat unit]	recovery (%) [yield of cyclics, from dimer to octamer (%)]	IV of recovered material (dL g^{-1})	weight percentages of cyclic oligomers $[-OArArOArS\,O_2Ar-]_n$ in recovered material, for $n = 1-8$[b]						
			$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
12.5 [0.5]	90 [74]	0.15	14.5	21.0	15.0	11.0	9.5	6.0	5.0
10.0 [0.4]	93 [67]	0.16	11.0	16.5	12.0	10.0	9.5	7.0	6.0
7.50 [0.3]	91 [40]	0.17	4.5	9.0	8.0	6.5	6.0	5.0	4.5
5.00 [0.2]	92 [36]	0.18	2.5	6.5	7.0	7.0	5.5	6.5	4.0
2.50 [0.1]	93 [10]	0.29	2.0	4.0	2.5	2.5			
1.25 [0.05]	94 [5]	0.45	2.0	3.0					

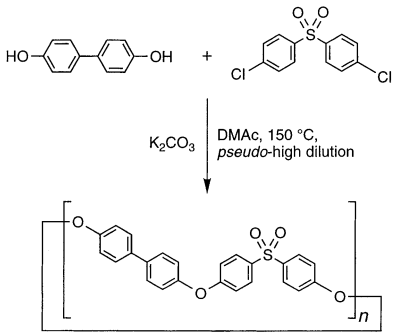
[a] Cyclodepolymerizations carried out in DMAc for 72 h, under the conditions described in section 3.2. [b] Analyses were by GPC; higher oligomers were not resolved.

Scheme 3. Cyclodepolymerization of Polymer 1 by Ether Cleavage and Back-Biting[a]



[a] *n* can take any value from 1 upward.

Scheme 4. Synthesis of Macrocylic Oligomers by Cyclopolycondensation



2.4. Ring-Opening Polymerization. Since the equilibrium position for ring−chain interconversion in any polymer system is highly dependent on concentration,[1,17] macrocyclic oligomers of polymer **1** should undergo ring-opening polymerization at high concentration, or in the melt, in the presence of a suitable initiator. Preliminary experiments showed that the mixture of macrocycles formed by either cyclopolycondensation or cyclodepolymerization melts in the range 210−230 °C, in contrast to the purified lower macrocyles which melt, as noted above, at anything up to 554 °C. Our attempts to simply reverse the cyclodepolymerization process by using cesium fluoride to initiate ring-opening polymerization of mixed macrocycles in the melt undoubtedly led to polymer formation, but the resulting materials were invariably cross-linked and insoluble, as noted also by Hay for analogous ring-opening of (ether ketone)-based macrocycles.[18] A search for alternative initiators showed

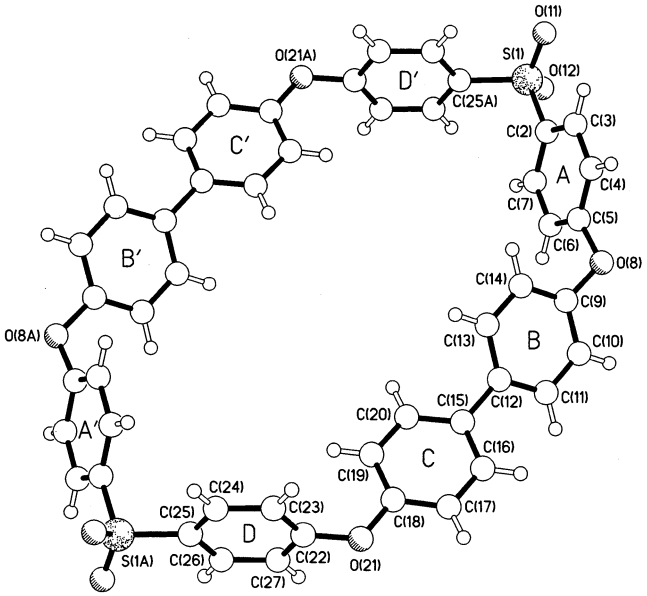


Figure 6. One of the two conformations adopted by cyclic dimer **2** in the solid state. The alternative conformation involves slight reorientations of rings A and A′ relative to their adjacent sulfone units.

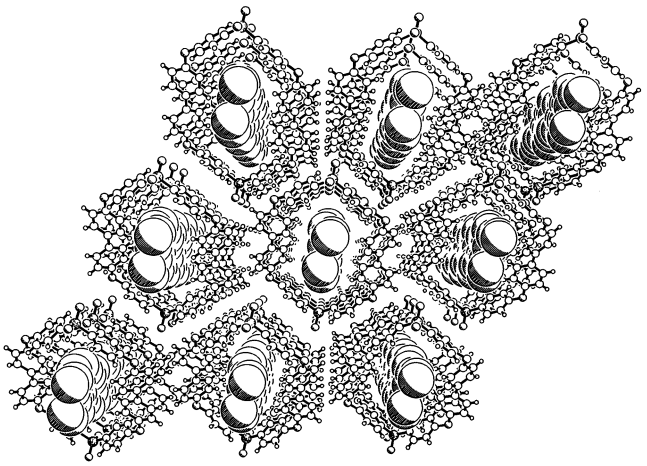


Figure 7. Continuous channels in the structure of **2**, showing the regions occupied by included molecules of dichloromethane.

that phenoxides derived from 4-hydroxybenzophenone, and more especially their *thiophenoxide analogues*, are highly effective so that, for example, polymerization of the mixed macrocyclic oligomers at 320 °C for only 5 min, initiated by 2 mol % cesium benzophenone-4-thiolate, yielded a deep brown, transparent polymer of very high molar mass (IV = 0.75, M_w = 151000, M_n = 26000 by GPC), which was yet fully soluble in DMAc

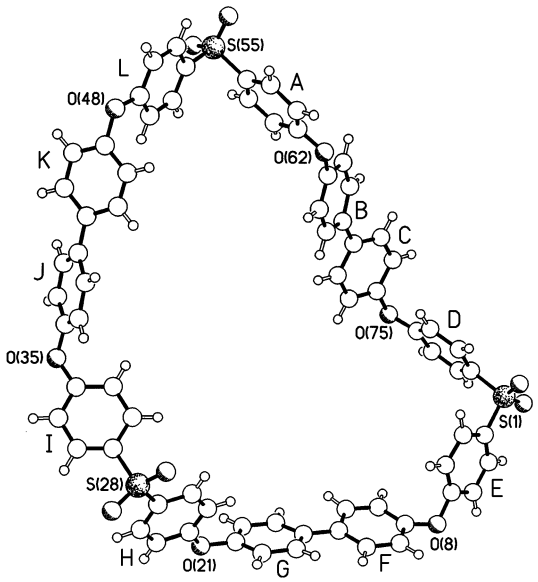


Figure 8. Structure of the cyclic trimer **3** in the solid state.

and THF. These values are far higher than for the commercial polymer (IV = 0.45), confirming the potential of in situ ring-opening polymerization as a fabrication technique for polymers of very high molecular weight, whose melt viscosities would render them unprocessable by normal methods. A small percentage of cyclic material invariably remained in the final polymer. Although this may be partly related to the very short reaction times, it should also be noted that macrocyclic oligomers do in any case comprise a percentage (typically 1−2 wt %) of the thermodynamic product mixture from polycondensations (not involving rigid-rod-type systems), even when these are carried out in the melt. The results of ring-opening polymerization studies for the present system using a range of different initiators are summarized in Table 2. Ring-opening of macrocyclic ether ketones initiated by the potassium salts of phenol and 4,4′-biphenol has been reported to give polymers of even higher molar mass, but these were invariably cross-linked to some degree.[18]

3. Experimental Section

3.1. General Methods and Instrumentation. All chemicals were standard reagent grade and were used, unless stated otherwise, without further purification. Dimethylacetamide and dimethylformamide were distilled from calcium hydride and stored under nitrogen. Granules of polymer **1** [Radel-R, from Amoco, inherent viscosity 0.45 dL g^{-1}] were milled to a fine powder using a Retsch ultracentrifuge mill, and the polymer was then dried at 80 °C. Benzophenone-4-thiol and benzophenone-4,4′-dithiol were synthesized by literature methods.[19,20] Air-sensitive and/or moisture-sensitive reactions were conducted under a dry nitrogen atmosphere. Thin-layer chromatography (TLC) was carried out on Polygram SIL G/UV_{254} SiO_2 plates. Column chromatography was conducted on Aldrich silica gel, 230−400 mesh, 60 Å. Proton and ^{13}C NMR spectra were recorded on Varian Gemini-200, Varian Unity Inova-300, and Varian Unity-500 spectrometers. Conventional mass spectra (EI/CI/FAB) were run on a Kratos Concept mass spectrometer, and MALDI-TOF MS analyses were obtained on Kratos Kompact and Micromass Tofspec instruments using dithranol as matrix and sodium or lithium trifluoroacetate or trifluoroacetic acid as cationizing agent. Elemental analyses were provided by the analytical service of Manchester University. Analytical samples were desolvated by prolonged heating at 200 °C under high vacuum. Solution viscosities were measured at 25 °C on 0.1% polymer solutions using a Schott-Geräte CT 150 semiautomated viscometer. DSC was performed under nitrogen using a Mettler DSC20 system at a scan rate of 10 or 20 °C min^{-1}. Conditions for GPC analysis of oligomer-containing samples were Gilson 307 pump, eluent chloroform, flow rate 0.3 mL min^{-1}, Polymer Labs 3 m "Mixed-E" columns (×4, in series), and GBC LC 1240 differential refractometer. For polymers, the analytical GPC system comprised a Knauer 64 pump, eluent THF, flow rate 1 mL min^{-1}, Polymer Labs 10 m "Mixed B" columns (×2, in series), and a Waters 410 differential refractometer. Preparative GPC was carried out using a Waters 590 pump, eluent chloroform, flow rate 10 mL min^{-1}, a Styragel 500 Å preparative column, and a Waters R403 differential refractometer. All GPC analyses were calibrated using polystyrene standards.

3.2. Cyclodepolymerization of Polymer 1. Polymer **1** (20.0 g) was purified by being dissolved in DMAc (200 mL) and slow addition of acetone (50 mL) with rapid stirring. The initially clear solution was stirred for 3 days, producing a white granular precipitate which was filtered off, washed with DMAc/acetone (4:1 v/v, 100 mL) and then with acetone (100 mL), and finally dried at 120 °C under vacuum. Recovery was 18.2 g. A solution of this polymer (2.00 g, 5.00 mmol based on the chemical repeat unit) and cesium fluoride (0.38 g, 2.50 mmol) in dry dimethylacetamide (200 mL) was heated at reflux (165 °C) under nitrogen. Samples (15 mL) were removed at 12 h time intervals and were precipitated in water. The solids were filtered off, washed with water, dried under vacuum, and analyzed by GPC. After 72 h the reaction mixture was cooled to room temperature and added to water (1000 mL) with stirring, and the precipitated solids were filtered off, washed copiously with water, and dried under vacuum. A similar reaction *without* sampling afforded 1.80 g of product (90% recovery). This material had an IV of 0.15 dL g^{-1}, and analysis by MALDI-TOF MS showed peaks $[M + Na]^+$ at *m/e* 823, 1223, 1624, 2024, 2425, 2826, 3627, 4027, 4428, 4828, 5229, 5630, and 6030, corresponding to the *cyclic* oligomers $[-ArSO_2-ArOArArO-]_n$, where Ar = 1,4-phenylene and n = 2−15. Gradient chromatography of this mixture on silica gel with dichloromethane/ethyl acetate as eluent afforded cyclic dimer **2** (7.5%), cyclic trimer **3** (6.4%), cyclic tetramer **4** (5.8%), and cyclic pentamer **5** (4.5% yield).

3.3. Characterization Data for Cyclic Oligomers. ^1H NMR assignments are referred to Scheme 2.

3.3.1. Cyclic Dimer 2. Mp: 554 °C (by DSC). ^1H NMR ($CDCl_3/CF_3COOD$, 300 MHz): δ = 6.94 (d, J = 8.8 Hz, 4H, H^b), 7.09 (d, J = 8.8 Hz, 4H, H^c), 7.43 (d, J = 8.8 Hz, 4H, H^a), 7.86 (d, J = 8.8 Hz, 4H, H^d). ^{13}C NMR ($CDCl_3/CF_3COOD$, 75 MHz): δ = 117.50, 120.61, 128.42, 129.59, 134.30, 136.45, 156.33, 162.38. Anal. Calcd for $C_{48}H_{32}O_8S_2$: C, 71.98; H, 4.02; S, 8.00. Found: C, 71.91; H, 4.06; S, 8.35. FAB-MS: *m/e* found 801 $[M + H]^+$.

3.3.2. Cyclic Trimer 3. Mp: 389 °C (by DSC). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.05 (d, J = 8.8 Hz, 4H, H^b), 7.14 (d, J = 8.8 Hz, 4H, H^c), 7.60 (d, J = 8.8 Hz, 4H, H^a), 7.90 (d, J = 8.8 Hz, 4H, H^d). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 117.39, 120.97, 128.64, 129.75, 135.56, 137.12, 154.25, 161.91. Anal. Calcd for $C_{72}H_{48}O_{12}S_3$: C, 71.98; H, 4.02; S, 8.00. Found: C, 71.03; H, 4.35; S, 8.52. FAB-MS: *m/e* found 1201 $[M + H]^+$.

3.3.4. Cyclic Tetramer 4. Mp: 455 °C (by DSC). ^1H NMR ($CDCl_3/CF_3COOD$, 300 MHz): δ = 7.15 (d, J = 8.8 Hz, 4H, H^b), 7.19 (d, J = 8.8 Hz, 4H, H^c), 7.66 (d, J = 8.8 Hz, 4H, H^a), 7.94 (d, J = 8.8 Hz, 4H, H^d). ^{13}C NMR ($CDCl_3/CF_3COOD$, 75 MHz): δ = 117.88, 120.83, 128.74, 129.63, 133.46, 137.36, 154.11, 162.64. Anal. Calcd for $C_{96}H_{64}O_{16}S_4$: C, 71.98; H, 4.02; S, 8.00. Found: C, 71.79; H, 4.01; S, 8.31. FAB-MS: *m/e* found 1602 $[M + H]^+$.

3.3.5. Cyclic Pentamer 5. T_g = 246 °C (by DSC). ^1H NMR ($CDCl_3$): δ = 7.00 (d, J = 8.8 Hz, 4H, H^b), 7.04 (d, J = 8.8 Hz, 4H, H^c), 7.51 (d, J = 8.8 Hz, 4H, H^a), 7.83 (d, J = 8.8 Hz, 4H, H^d). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 117.84, 120.65, 129.78, 135.66, 137.01, 139.73, 154.55, 161.78. Anal. Calcd for $C_{120}H_{80}O_{20}S_5$: C, 71.98; H, 4.02; S, 8.00. Found: C, 71.69; H, 3.80; S, 8.26. FAB-MS: *m/e* found 2004 $[M + H]^+$.

3.4. Synthesis of Macrocyclic Oligomers by Cyclopolycondensation. A solution of 4,4′-biphenol (1.77 g, 9.52 mmol)

Table 2. Ring-Opening Polymerization of Mixed Cyclic Oligomers of Polymer 1

initiator used[a]	mol % initiator per polymer repeat unit	conversion of cyclics to polymer (%, GPC)	polymer characterization data			
			IV[b] (dL g^{-1})	M_w[c]	M_n[c]	T_g[d] (°C)
CsF	4	*e*	*e*	*e*	*e*	*e*
CsOArCOAr	2	92	0.50	57000	15500	230
CsSArCOArSCs	2	94	0.56	76500	29500	225
CsSArCOArSCs	1	94	0.52	58500	16300	218
CsSArCOAr	2	96	0.75	151500	26000	229

[a] Polymerizations carried out in the melt at 320 °C for 5 min. [b] Solutions measured at 0.1% concentration (w/v) at 25 °C. [c] Values determined by GPC using polystyrene standards. [d] DSC onset value. [e] Insoluble.

and 4,4′-dichlorodiphenyl sulfone (2.73 g, 9.52 mmol) in DMAc (100 mL) was added dropwise under nitrogen, over a period of 5 h, to a stirred and refluxing suspension of potassium carbonate (1.31 g, 9.52 mmol) in DMAc (200 mL) and toluene (40 mL), with continuous removal of evolved water via a Dean−Stark apparatus. The mixture was refluxed (145 °C) for a further 15 h, then cooled to room temperature, and filtered. The filtrate was evaporated to ca. 50 mL under reduced pressure and added slowly to vigorously stirred dilute hydrochloric acid. The precipitate was filtered off, washed with water until the washings were neutral and then with methanol, and finally dried at 70 °C under vacuum. The yield of mixed oligomers was 3.60 g (94%). Analysis by MALDI-TOF MS showed peaks $[M + Na]^+$ at 823, 1224, 1625, 2025, 2426, 2826, 3226, 3627, 4028, 4428, 4828, 5229, 5630, and 6030, corresponding to macrocycles from cyclic dimer to cyclic pentadecamer.

3.5. Crystal Data for Macrocycles 2 and 3. 3.5.1. Macrocycle 2. $C_{48}H_{32}O_8S_2 \cdot 1.55CH_2Cl_2$, MW 932.49, triclinic, $P\bar{1}$, $a = 6.4067(7)$ Å, $b = 13.848(1)$ Å, $c = 14.139(1)$ Å, $\alpha = 118.40(1)°$, $\beta = 98.17(1)°$, $\gamma = 93.11(1)°$, $V = 1081.5(2)$ Å^3, $Z = 1$, $D_c = 1.432$ g cm^{-3}, μ(Cu Kα) = 33.5 cm^{-1}, $F(000) = 481$, $T = 293$ K. Crystal dimensions were 0.47 × 0.63 × 0.93 mm. From 3146 independent reflections measured ($2\theta \leq 124°$), 2460 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. Empirical absorption correction; refinement based on F^2 to give $R1 = 0.063$ and $wR2 = 0.164$.

3.5.2. Macrocycle 3. $C_{72}H_{48}O_{12}S_3 \cdot 3CH_2Cl_2$, MW 1456.06, monoclinic, $P2_1/c$, $a = 22.625(4)$ Å, $b = 10.033(2)$ Å, $c = 32.574(7)$ Å, $\beta = 94.18(2)°$, $V = 7375(2)$ Å^3, $Z = 4$, $D_c = 1.311$ g cm^{-3}, μ(Cu Kα) = 34.1 cm^{-1}, $F(000) = 3000$, $T = 183$ K. Crystal dimensions were 0.47 × 0.13 × 0.07 mm. From 10132 independent reflections measured ($2\theta \leq 120°$), 4218 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. Empirical absorption correction; refinement based on F^2 to give $R1 = 0.120$ and $wR2 = 0.234$. The high final value for $R1$ is a consequence of poor crystal quality and severely disordered, partial-occupancy dichloromethane molecules, few of which could be clearly resolved. Computations were carried out using the SHELXTL-PC program system. Tables of fractional atomic coordinates, bond lengths, bond angles, and thermal parameters for **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre; references CCDC-178440 (for **2**) and CCDC-178441 (for **3**). Contact information: The Director, CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K. E-mail: deposit@ccdc.cam.ac.uk.

3.6. Synthesis of Linear Oligomers of Polymer 1. To a solution of 4,4′-biphenol (6.75 g, 36.3 mmol mmol) and 4,4′-dichlorodiphenyl sulfone (7.81 g, 27.22 mmol) in DMAc (60 mL) were added anhydrous potassium carbonate (2.70 g, 19.56 mmol) and toluene (12 mL). The mixture was stirred under nitrogen and heated to reflux, with removal of water via a Dean−Stark trap. Toluene was progressively removed until the reflux temperature reached 150 °C, and after 2 h at this temperature the reaction mixture was cooled and precipitated into 5% hydrochloric acid (300 mL). The precipitate was filtered off and washed with hot water until the washings were neutral and then with hot methanol (300 mL), before drying at 70 °C under vacuum. The product had an IV of 0.20 dL g^{-1} in DMAc, and analysis by MALDI-TOF MS showed peaks $[M + H]^+$ and $[M + Na]^+$ corresponding to the linear oligomers $HOArArO[-ArSO_2ArOArArO-]_nH$, where Ar = 1,4-phenylene and $n = 1-10$.

3.7. Preparation of Thiophenoxide Initiators. To a stirred solution of cesium carbonate (3.80 g, 11.5 mmol) in water was added benzophenone-4-thiol (5.0 g, 23 mmol), giving a yellow solution which was then evaporated to dryness. The residue was stirred in diethyl ether (150 mL) for 0.5 h, filtered off, washed with diethyl ether, and dried under vacuum at 60 °C to give yellow, crystalline cesium benzophenone-4-thiolate (7.30 g, 92% yield). The orange dicesium salt of benzophenone-4,4′-dithiol was prepared similarly, in 91% yield.

3.8. Ring-Opening Polymerization of Mixed Macrocyclic Oligomers. The following procedure was typical. A powdered sample of mixed macrocyclic oligomers (0.20 g, 0.5 mmol based on the repeat unit), produced as in section 3.4**,** was added to a solution of the cesium salt of 4-benzoylthiophenol (0.0035 g, 0.01 mmol) in methanol (10 mL), and the mixture was sonicated to disperse the oligomers. The solvent was then removed on the rotary evaporator and the residue dried in a vacuum oven at 70 °C. A 20 mg sample was pelletized, encapsulated in an aluminum DSC crucible, and heated under nitrogen to 320 °C. After 5 min at this temperature the sample was cooled to room temperature, and a DSC heating scan was run at 20 °C min^{-1}. The polymeric product showed a glass transition temperature of 229 °C and, on removal from the DSC crucible, was found to be transparent, deep brown, and extremely tough. It was fully soluble in DMAc, THF, and 96% sulfuric acid, and had an inherent viscosity of 0.75 dL g^{-1}. Analysis by GPC in THF showed $M_w = 151000$, $M_n = 26000$, and a level of residual macrocylic oligomers of ca. 4%.

4. Conclusions

The industrially important poly(ether sulfone) based on 4,4′-biphenol (Radel-R) undergoes near-quantitative cyclodepolymerization at high temperatures, in the presence of fluoride ion as catalyst, to give a family of macrocyclic species containing from eight to at least sixty aromatic rings. A number of such oligomers have been isolated and characterized in detail. These macrocyclic materials, which can also be obtained by cyclopolycondensation under *pseudo*-high-dilution conditions, undergo ring-opening polymerization in the melt to give soluble polymer of high molar mass. The chemistry described here provides the first demonstration that the recycling of high-performance aromatic polymers via their macrocyclic homologues is—in principle—entirely feasible.

Acknowledgment. This work was supported by the Royal Society (an Industrial Fellowship to H.M.C.) and by the EPSRC under Grants GR/M66554 and GR/M67087.

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MA020315U