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Synthesis of a Novel Macrocyclic Arylene Ether Sulfone

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ABSTRACT: The present work reports the synthesis of a macrocyclic arylene ether sulfone, **4**, in two steps. In the first step dichlorodiphenyl sulfone (**1**) was substituted with two Bisphenol A (**2**) moieties by a nucleophilic substitution reaction using three solvents and reagent systems: (a) potassium carbonate/dimethylacetamide, (b) sodium hydride/dimethylformamide, or (c) aqueous caustic/dimethyl sulfoxide. The product **3** was cyclized with dichlorodiphenyl sulfone to form **4** using the first and second procedures. For economy and convenience, the first system is the method of choice for this synthesis. The products were characterized by elemental analysis, solubility, IR, NMR, GPC, MS, TGA (in air and nitrogen atmospheres), and DSC.

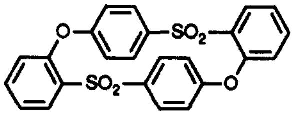
Introduction

In recent years polyrotaxanes have received considerable attention,[1-10] which is amply justified in view of their dynamic nonbonded components. In polyrotaxanes macrocycles may be involved in microtransport along the backbone of the polymer. Polymers of various structures such as block, star, graft, etc., have been well established, whereas the chemistry of large (i.e., greater than 30-membered) macrocycles needs more attention. An overall clear concept of polymers and macrocycles will help us to explore the dynamic microworld.

According to the physical nature of the macrocycle, it may be categorized as (a) flexible,[11] (b) semirigid,[12] or (c) rigid.[13] On the other hand, from an electronic structural point of view we may classify macrocycles as (i) electron donors or acceptors such as crown ethers[11] and bipyridinium dication based systems,[14] (ii) neutral macrocycles like cyclic polystyrene,[15] or (iii) polar macrocycles, e.g., a tetracarboxylic macrocycle[16] and bis(5-carboxy-1,3-phenylene)-32-crown-10.[17]

So far considerable work has been done on crown ethers. Gibson et al. have studied their threading in detail.[1-6] Crown ethers are mostly flexible and semirigid types. Crown ethers with aromatic groups are of present interest to many research groups. A naphthyl-substituted crown has been observed to have a folded U-shaped structure[18] such that the naphthyl groups are in a parallel orientation. Hence, aromatic substitution in crown ethers may give a folded or twisted shape which will be a negative factor in threading. Furthermore, crown ethers possess limited thermal stability.

To overcome the disadvantages of crown ethers, the present work highlights the synthesis of a novel macrocyclic arylene ether sulfone. Low-cost starting materials, a short synthesis route, and thermal stability are the attractive features of the present compound. Furthermore, the rigid and open structure of the macrocyclic may help threading. A 16-membered cyclic dimer **5** of sulfone ether has been reported.[19] However, it is not suitable for polymeric rotaxane formation; rings of at least 24 atoms are required.[1,4]



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The present work reports the synthesis of macrocyclic arylene ether sulfone **4** in two steps. The first step is the nucleophilic disubstitution of dichlorodiphenyl sulfone (**1**) with 4,4′-isopropylidenediphenol (Bisphenol A, **2**) and the second step is the cyclization of the above product **3** with another molecule of dichlorodiphenyl sulfone to the macrocyclic arylene ether sulfone **4** (Scheme I).

Experimental Section

Materials. Bisphenol A, dichlorodiphenyl sulfone, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and toluene (Aldrich Chemicals) were used as supplied. Chloroform-*d* (D, 99.8%) for NMR was supplied by Cambridge Isotope Laboratories.

Measurements. A Harvard syringe infusion pump Model 22 was used to control the cyclization reaction. Melting points were determined on a Haake-Buchler capillary melting point apparatus and are corrected. The FT-NMR (proton) spectra were recorded on Bruker WP 270-MHz and 200-MHz instruments using tetramethylsilane as the internal standard. GPC analyses of the linear and cyclic compounds were performed in THF and $CHCl_3$, respectively, using a Waters system (RI and UV detectors) after calibration with PS standards. Infrared spectra (KBr pellets) were recorded on a Nicolet MX-1 FTIR spectrometer. The mass spectrum was measured with a VGA 7070E analytical mass spectrometer, the latter being equipped with a fast atom bombardment (FAB) facility using a high-energy beam of neutral argon atoms in conjunction with a 3-nitrobenzyl alcohol matrix. Column chromatography was performed using silica gel 60 (32–63-μm mesh, Universal Scientific Inc.). Elemental analyses were performed by Atlantic Microlab of Norcross, GA. TGA and DSC were performed on a Perkin-Elmer Model TGA-7 and Unix DSC 7 models under nitrogen and air at heating rates of 40 and 10 °C/min, respectively.

Synthesis of Compound 3 Using K_2CO_3. Bisphenol A (**2**; 45.70 g, 0.200 mol) was placed in a 500-mL four-necked flask equipped with a mechanical stirrer, nitrogen gas inlet, thermometer, and Brand–Barrett trap along with condenser. DMAC (120 mL) was added to dissolve the Bisphenol A. Potassium carbonate (27.60 g, 0.200 mol) was added, and the solution was mechanically stirred under a nitrogen atmosphere. To this solution was added approximately 75 mL of toluene as an azeotroping agent. This reaction mixture was then heated until the toluene began to reflux. A reflux temperature of 150 °C was maintained. Water was thoroughly removed by azeotropic distillation with toluene. Dichlorodiphenyl sulfone (**1**) (11.5 g, 0.0400 mol) in 150 mL of DMAc was added dropwise over 3–4 h. The solution was further refluxed with stirring for 6–8 h. The color of the solution became pale yellow to orange to deep green or purple depending on the concentration of the Meisenheimer complex formed. A very fine suspension of Bisphenol A dipotassium salt and excess potassium carbonate appeared. After

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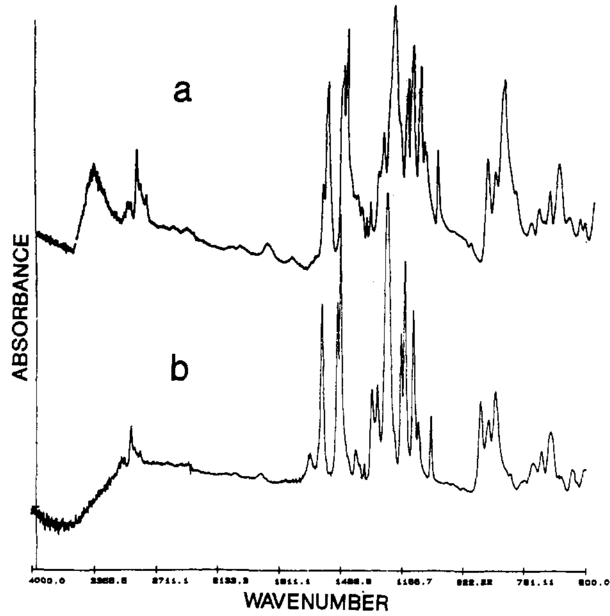
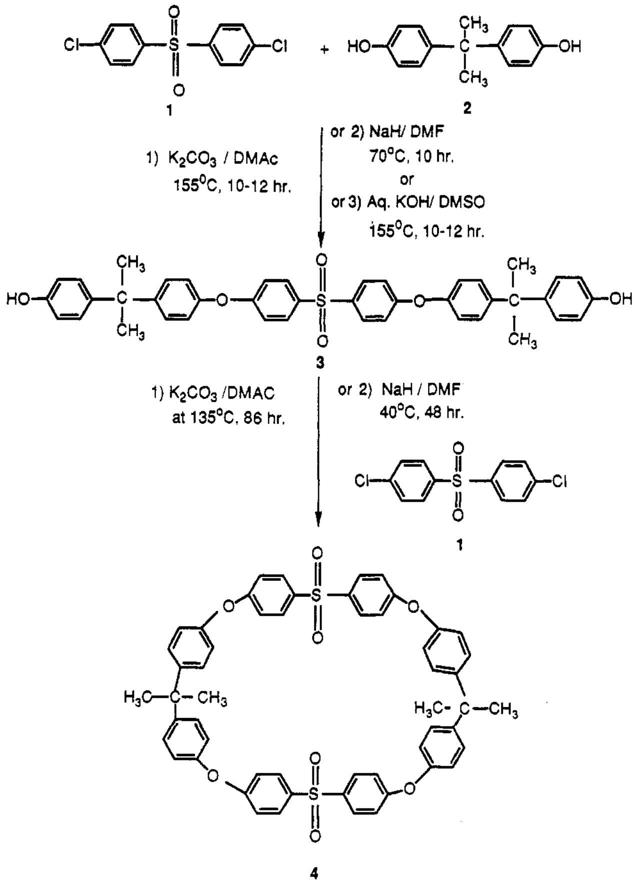


Figure 1. IR spectra of (a) compound 3 and (b) compound 4.

Scheme I. Two-Step Route for the Synthesis of a Novel Macrocyclic Arylene Ether Sulfone



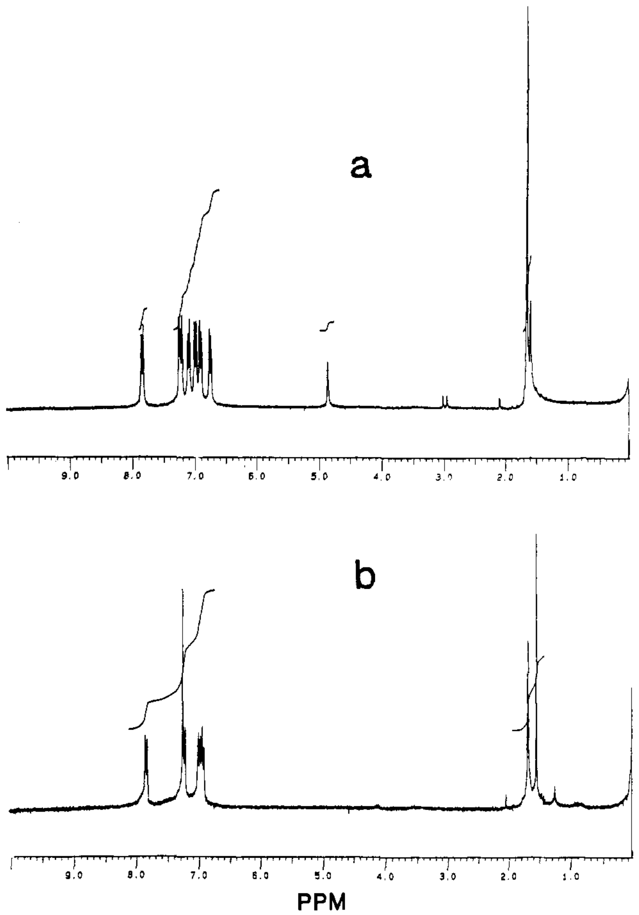


Figure 2. 270-MHz ^{1}H NMR spectra of (a) compound 3 and (b) compound 4. Impurity peaks in the solvent ($CDCl_3$) are observed at 1.5 ppm (H_2O) and 7.3 ppm ($CDCl_3$).

filtration, the filtrate was treated with a 10% HCl solution to pH 2–3 which gave a separate layer containing compound 3. Bisphenol A was soluble in DMAc in this condition. DMAc was decanted. The product was washed with water and finally dissolved in chloroform in which Bisphenol A is practically insoluble. The $CHCl_3$ layer was filtered and evaporated to dryness using a rotary evaporator at 60 °C. The yellowish white product was dissolved in ether and treated with a 5% NaOH solution to give a separate layer of the Meisenheimer complex. The ether layer was separated, washed three times with 5% HCl and three times with distilled water, and evaporated to dryness using a rotary evaporator. The product was further treated with warm toluene to remove traces of the Meisenheimer complex and finally precipitated from hexane. TLC indicated the absence of compounds 1 and 2. The white product was finally dried in vacuo at 60 °C for several hours. The yield was 24.26 g (90%). There was no sharp melting point; it softens at 100 °C and melts at 145 °C. Anal. Calcd for $C_{42}H_{38}O_6S$ (MW 670): C, 75.20; H, 5.71; S, 4.78. Found: C, 75.00; H, 5.77; S, 4.86. IR: 3422 (ArOH), 2965.1 ($-CH_3$), 1587 (aromatic C=C), 1508 and 1488 (S=O), 1244 (CO for ether and phenol), 1171, 1144, 1104 (COC) cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.83 (d, H_a, J = 9.0 Hz), 7.22 (d, H_c, J = 8.8 Hz), 7.10 (d, H_f, J = 8.7 Hz), 6.99 (d, H_b, J = 9.0 Hz), 6.91 (d, H_d, J = 8.8 Hz), 6.75 (d, H_e, J = 8.7 Hz), 4.9 (s, phenolic H), 1.7 (s, CH_3) ppm.

Synthesis of Compound 3 Using DMF and NaH. NaH (16 g, 0.40 mol) was washed three times with hexane and transferred into a 1-L flask using 150 mL of DMF. Bisphenol A (2; 45.70 g, 0.200 mol) was dissolved in 150 mL of DMF and added to the above mixture during 1 h at 70 °C under a nitrogen atmosphere. A total of 11.50 g (0.04 mol) of DCDPS (1) was dissolved in 180 mL of DMF and added dropwise over about 3 h at 70 °C. The reaction mixture changed to dark green. It was further refluxed at 150 °C for 8 h. The product was cooled and treated with water to remove unreacted NaH. The filtrate was treated with dilute HCl to pH 2–3, and the product was purified as before. The yield was 21.10 g (78%).

Synthesis of Compound 3 Using KOH and DMSO. Into a 1-L round-bottomed flask, fitted with an inert gas (N_2) tube, mechanical stirrer, thermometer, dropping funnel, moisture trap (Dean–Stark), and condenser, were placed 45.70 g (0.2000 mol) of Bisphenol A (2), 100 g of dimethyl sulfoxide (DMSO), and 300 g of chlorobenzene. The mixture was heated to 60–80 °C, whereupon a clear solution was obtained. KOH (22.44 g, 0.400 mol) in 200 mL of water was added over about 10 min with good stirring. Two liquid phases appeared; one was predominantly chlorobenzene, and the other was the disodium salt dissolved in aqueous DMSO. The system was refluxed. Water was removed from the system as an azeotroping mixture with chlorobenzene. Around 120–140 °C a precipitate of disodium salt of Bisphenol

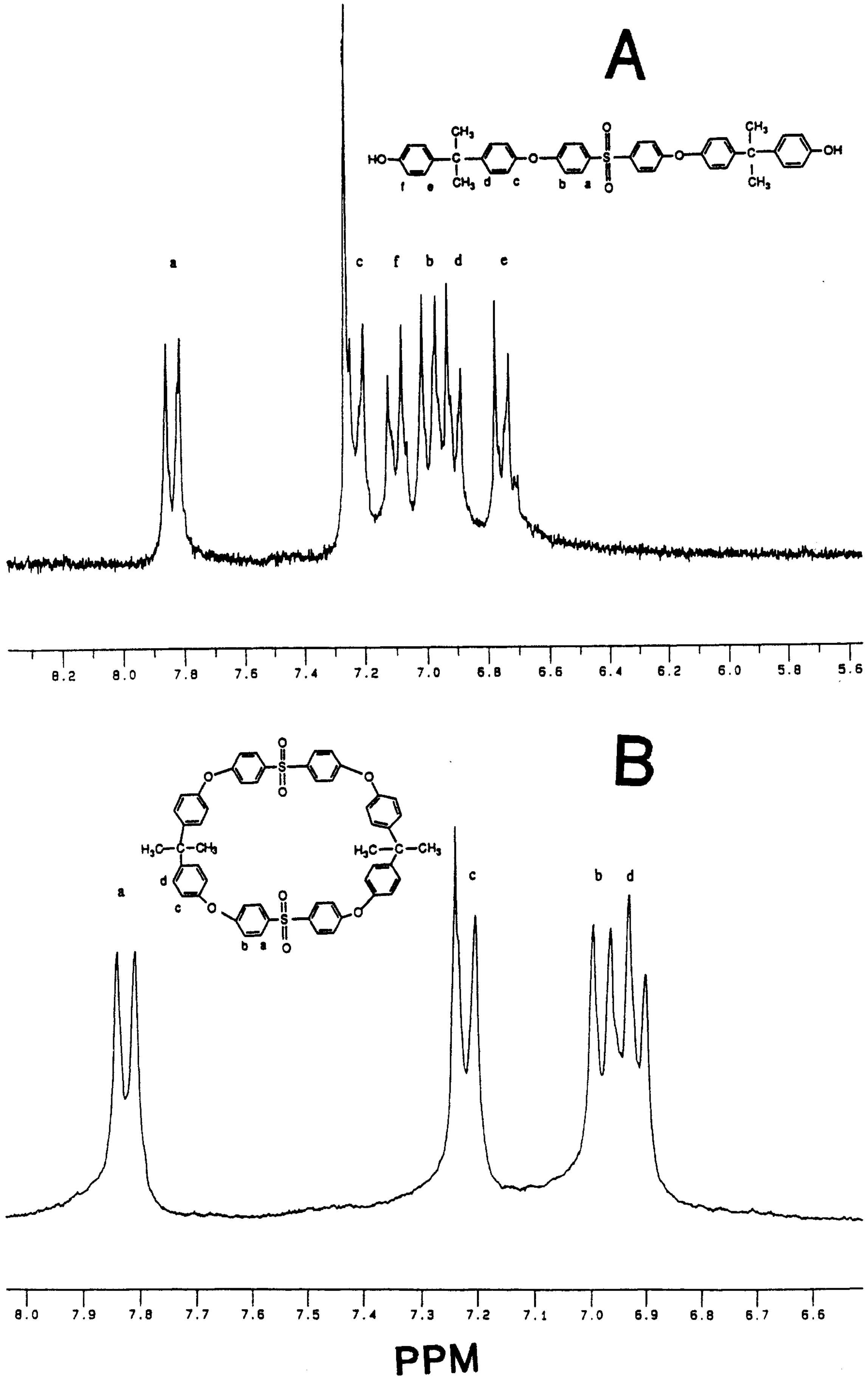


Figure 3. ^1H NMR spectra of (A) compound 3 (200 MHz) and (B) compound 4 (270 MHz) aromatic regions only. The peaks at 7.26 and 7.24 ppm in (a) and partially in (b), respectively, are due to $CHCl_3$.

A appeared on removal of water. Excess azeotropic solvent was distilled off from the system. At 155–160 °C, the precipitate redissolved with the formation of a very viscous solution. It was believed at this point that only traces of water remained. A

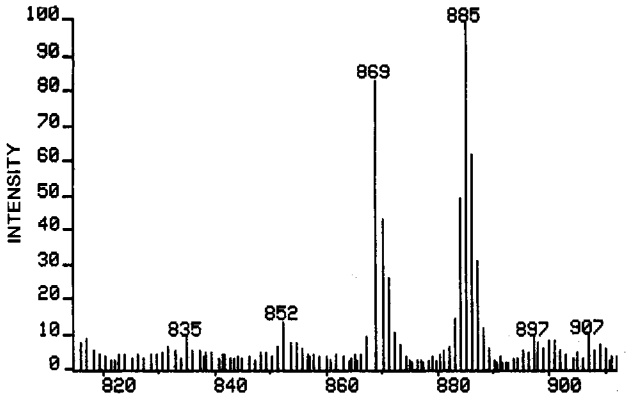


Figure 4. Mass spectrum of compound 4.

solution of 11.50 g (0.043 mol) of DCDPS (1) in 125 mL of chlorobenzene was added over a period of 2 h via an addition funnel, and the reaction mixture was refluxed for 10 h. The reaction mixture was cooled and filtered. The filtrate was treated with 10% HCl solution to pH 2-3, which gave a thick precipitate of compound 3. The layer of DMSO was decanted, and the product was washed several times with water to remove traces of DMSO. The product was dissolved in chloroform, filtered, and evaporated to dryness using a rotary evaporator at 60 °C. The product was dissolved in ether and freed from the Meisenheimer complex using dilute alkali as before. The yield was 15.24 g (56%).

Synthesis of Macrocyclic Arylene Ether Sulfone 4 Using DMAC/K_2CO_3. A three-necked flask equipped with a nitrogen gas inlet, thermometer, and Dean–Stark trap along with condenser was preheated with 5.52 g (0.02 mol) of K_2CO_3 in 100 mL of DMAc along with 40 mL of toluene at 135 °C. A total of 12.5 g (0.019 mol) of compound 3 in 60 mL of DMAc and 5.74 g (0.02 mol) of compound 1 in 60 mL of DMAc were added via separate syringes at a rate of 0.70 mL/h using a syringe infusion pump. The reaction was carried out for 89 h. Finally the solution was filtered and the filtrate was treated with dilute HCl to pH 2-3. The mass was poured into ice with stirring and kept overnight. The pale yellowish solid was filtered and washed several times with water to remove traces of acid and dried under vacuum. The dried powered product was stirred several hours in ethanol to remove traces of compound 3. The residue was stirred in ethyl acetate to free the cyclic compound from oligomers which are insoluble in ethyl acetate. The macrocycle along with compound 1 was further extracted with ether. The fast-moving (R_f = 0.76) fraction was the macrocycle 4, and the slow-moving (R_f = 0.71) fraction was 1 with diethyl ether and dichloromethane as eluent on silica gel TLC, whereas the reverse happens in ethyl acetate/hexane as eluent. Finally the macrocycle was purified by column chromatography using ether/dichloromethane as eluents. The weight of white solid was 2 g (11%), solvent loss at 188 °C. MS (FAB): m/z 885 (M^+, molecular ion), 884 ($M^+ - H$), 883 ($M^+ - 2\ H$), 869 ($M^+ - CH_4$), 852 ($M^+ - H - 2\ CH_4$), 835 ($M^+ - 2\ CH_4 - H_2O$). IR: 2965.1 (CH_3), 1587 (aromatic C=C), 1508 and 1488 (S=O), 1244 (CO for ether and phenol), 1171, 1144, 1104 (COC) cm^{-1}. ^1H NMR ($CDCl_3$): 7.82 (d, H_a, J = 8.6 Hz), 7.22 (d, H_c, J = 8.4 Hz), 6.98 (d, H_b, J = 8.6 Hz), 6.91 (d, H_d, J = 8.4 Hz), 1.7 (s, CH_3) ppm.

Synthesis of Macrocyclic Arylene Ether Sulfone 4 Using DMF/NaH. 60% NaH (1.76 g, 0.04 mol) was washed three times with hexane and transferred to a 500-mL three-necked flask under nitrogen with 100 mL of DMF at 150 °C. Compound 3 (13.4 g, 0.02 mol) in 30 mL of DMF and 1 (5.75 g, 0.02 mol) in 30 mL of DMF in separate syringes were added at a rate of 0.70 mL/h using a syringe infusion pump. After 48 h at 40 °C, excess NaH was destroyed with water and the mixture was filtered. The filtrate was treated with dilute HCl to pH 2-3. A white precipitate was filtered and washed with water, methanol, ethyl acetate, and toluene to remove traces of parent compounds. Finally column chromatography was performed in ether/dichloroethane solvents to produce pure product.

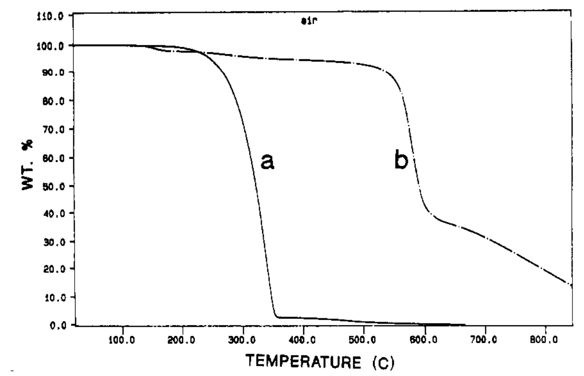


Figure 5. TGA curves of (a) compound 3 and (b) compound 4 in air.

Results and Discussion

Compound 3, produced as white flakes, was highly soluble in chloroform, dichloroethane, ethanol, methanol, acetic acid, tetrahydrofuran, ether, ethyl acetate, and benzene and insoluble in hexane, toluene, and water. However, in alkaline hot water solubility was observed. Macrocyclic arylene ether sulfone 4 was obtained as white crystals which were soluble in chloroform, dichloroethane, or toluene. Unlike compound 3, the macrocycle is insoluble in ethanol and methanol and soluble in toluene.

Complete isolation of the cyclic compound needs some improved procedures; the mass from the extract using ethyl acetate has shown the presence of the cyclic compound in GPC traces. Furthermore, the ethyl acetate extract releases the cyclic compound in ether medium leaving a product insoluble in ethyl acetate; we believe this is due to rotaxanes which with time release macrocycles that are insoluble in ethyl acetate.

Figure 1 compares the IR spectra of compounds 3 and 4 and reveals the absence of phenolic stretching at 3422 cm^{-1} in compound 4; otherwise, all the peaks are common to both compounds.

The NMR spectra of the above compounds are compared in Figures 2 and 3. The protons at 1.7 ppm (TMS = 0 ppm) are due to the aliphatic protons from the isopropylidene group; the relative integration is reduced in macrocycle 4 compared to precursor 3 due to the change of ratio of aromatic hydrogen to aliphatic hydrogen. A phenolic hydrogen singlet appears at 4.9 ppm in compound 3 but is absent in compound 4. The aromatic doublets which appear in compound 3 but are absent in compound 4 are (I) the doublet at 7.10 ppm for protons (f) ortho to the hydroxyl group and (II) the doublet at 6.75 ppm for protons (e) ortho to the isopropylidene group but meta to the phenolic hydroxyl group. Note in Figure 3 that the signals for macrocycle 4 are broader than those for linear precursor 3. This presumably reflects the slower conformational motions of the macrocycle, which CPK models show to be relatively rigid. Molecular mechanics calculations[21] predict a low-energy conformation with cavity inner dimensions 8 × 11 Å.

Figure 4 shows part of the mass spectrum of compound 4. The molecular ion peak at 885 (100% intensity) is characteristic of the cyclic compound and distinguishes it from the linear precursor. Isotopic masses of 886 (63% intensity), 887 (30% intensity), and 888 (11% intensity) were recorded in agreement with calculated ratios. Other prominent peaks appear at 884, 883, 869, 852, and 835; these are due to the elimination of H, 2 H, CH_4, 2 CH_4 + H, and 2 CH_4 + H_2O, respectively.

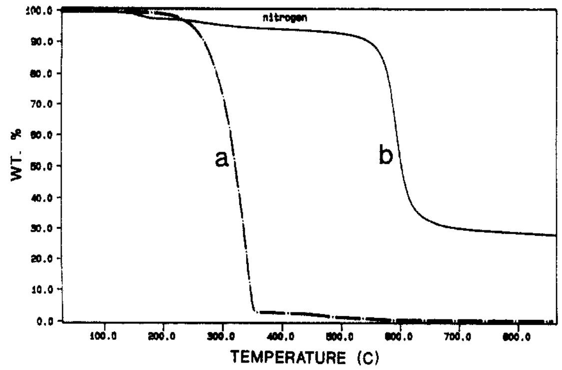


Figure 6. TGA curves of (a) compound 3 and (b) compound 4 in nitrogen.

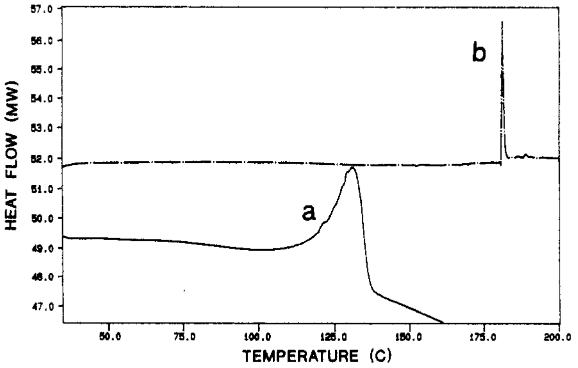


Figure 7. DSC thermograms of (a) compound 3 and (b) compound 4.

Figures 5 and 6 compare the TGA of compounds 3 and 4 in air and in nitrogen, respectively. In Figure 6, compound 3 shows a very considerable rate of weight loss in the range of 287–358 °C (94.8%), while cyclization to compound 4 causes tremendous improvement in the initial thermal stability to 572 °C with 60% degradation at 616 °C; the weight loss at ca. 180 °C is believed to be due to the loss of solvent; see DSC results below. Further with macrocycle 4 25% char remains at 850 °C. The thermal stability of compound 3 is unaffected by the change of atmospheres. These results clearly demonstrate the devastating effect of phenolic end groups on the thermooxidative stability of poly(ether sulfone)s.

Figure 7 compares the DSC thermograms in which compound 3 shows an initiation of phase change around 100 °C, giving a peak at 138 °C as we have observed by capillary melting point measurement. Compound 4 shows a sharp endotherm at 181 °C, which we attribute to loss of residual solvent (dimethylacetamide; bp 165 °C). No transitions are observed up to 220 °C on subsequent scans. Thus, macrocycle 4 appears to be amorphous.

Conclusion. The present synthesis for a 40-membered macrocyclic arylene ether sulfone provides a relatively rigid, open, thermally stable macrocyclic component for the synthesis of a variety of polyrotaxanes. Polymeric rotaxanes or molecular composites[20] may reduce the difficulty and expense of composite fabrication of this type of thermally and environmentally stable polymer.

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