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Synthesis and polymerization of some macrocyclic (arylene ether sulfone) containing cardo groups and macrocyclic (arylene ether ketone sulfone) oligomers

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Some novel macrocyclic (arylene ether sulfone) containing cardo groups and (arylene ether ketone sulfone) oligomers have been synthesized in high yields by a nucleophilic aromatic substitution reaction of 4,4′-difluorophenylsulfone with bisphenols in the presence of anhydrous potassium carbonate under a pseudo-high-dilution condition. Detailed structural characterization of these oligomers by matrix-assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS), fast atom bombardment mass spectrometry (f.a.b.-m.s.), nuclear magnetic resonance spectrometry (n.m.r.) and single-crystal X-ray structure analysis confirms their cyclic nature, and the composition of the oligomeric mixtures is provided by g.p.c. analysis. Ring-polymerization of cyclic oligomers **3a** to a high molecular weight polymer with M_w of 59.1 k was achieved by heating at 290°C for 40 min in the presence of a nucleophilic initiator. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: high dilution; macrocyclic arylene ether sulfone oligomers; cardo groups)

INTRODUCTION

The discovery by Brunelle and co-workers of the high-yield synthesis and facile polymerization of bisphenol-A-based cyclic polycarbonates[1] has sparked much interest in the macrocyclic monomer technique. The cyclic oligomers offer a unique combination of low melt viscosity and the possibility of undergoing controlled polymerization in the melt without the liberation of volatile byproducts. These features are particularly valuable for the manufacture of advanced composite materials. In the past 10 years, this area has been rapidly extended to other systems such as cyclic esters[2–12], amides[13], ethers[14–34] and thioether ketones[35–39]. However, the studies of synthesis and ring-opening polymerization of cyclic (arylene ether sulfone)s, are relatively limited[14,15,26–34]. This paper reports the synthesis, characterization and ring-opening polymerization of some novel cyclic (arylene ether sulfone) oligomers containing cardo groups, as well as cyclic (arylene ether ketone sulfone) oligomers.

EXPERIMENTAL

Materials and instruments

Reagent-grade solvents and chemicals were used without further purification. Analysis by g.p.c. was performed on a Shimadzu LC-4A apparatus equipped with two columns of DuPont ZORBAX-PSM-60S and 1000S, and a UV detector (254 nm) using tetrahydrofuran (THF) as the eluent at a flow rate of 0.5 ml min^{-1}. The columns were calibrated with a mixture of six polystyrene standards. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectra were recorded on an LDI-1700 instrument at a wavelength of 337 nm (N_2 laser light) using 2,5-dihydroxybenzoic acid as the matrix. The MALDI instrument was operated in a positive linear mode. Fast atom bombardment (f.a.b.) mass spectrum was performed on a VG-QUATTRO mass spectrometer using 3-nitrobenzyl alcohol as the matrix. Nuclear magnetic resonance (n.m.r.) proton spectra were recorded on a Varian Unity-400 n.m.r. spectrometer at 400 MHz in $CDCl_3$ using TMS as a standard. Thermal analysis was carried out on a Perkin-Elmer 7 Series Thermal Analysis System. The heating rate was 10°C min^{-1} in nitrogen atmosphere.

General procedure for synthesis of cyclic oligomers

Adapting the method of Hay and co-workers[17–22] the synthesis of cyclic oligomers **3a** was used as an example. The cyclization reaction was conducted in a 500 ml four-neck round-bottom flask equipped with a nitrogen inlet, thermometer and condenser. The flask was charged with 300 ml of DMF, 30 ml of toluene and 2.0 g of anhydrous potassium carbonate. The solution was mechanically stirred and heated to 145°C. A solution of phenolphthalein (2.55 g, 8 mmol) and 4,4′-difluorophenylsulfone (2.03 g, 8 mmol) in 40 ml of DMF was added over a period of 10 h. After the addition was complete, the resulting solution was refluxed until the violet–red solution was turned pale yellow. The reaction was cooled and filtered to remove the salt. The solvent was then removed from the filtrate at reduced pressure. The residue was dissolved in 200 ml chloroform and filtered. The chloroform solution was concentrated to 50 ml and added to vigorously stirred methanol (200 ml). The desired cyclic oligomers precipitated as a pale yellow solid in the methanol. The precipitate was filtered and dried in a vacuum oven (100°C) for 12 h. The yield of **3a** was 2.94 g (69% yield). g.p.c Analysis of the product shows an

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M_w of 4.3 and an M_n of 1.4 k. *FT*i.r. (KBr): 1770.3 (ester C=O), 1322.5 (SO_2) cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ7.98 (m, 1H), 7.86 (m, 4H), 7.75 (m, 1H), 7.59 (m, 2H), 7.37 (m, 4H), 7.01 (m, 8H). A similar procedure was applied for the preparation of **3b** and **3c**. The yield of **3b** was 2.73 g (61% yield). Analysis of the product using g.p.c. shows an M_w of 5.3 and an M_n of 1.5 k. *FT*i.r.(KBr): 2920.1 (–CH3), 1771.2 (C=O), 1322.9 (SO_2); ^{1}H-n.m.r. ($CDCl_3$): δ7.97–7.99 (m, 1H), 7.12–7.78 (m, 5H), 7.58–7.62 (m, 2H), 7.28 (m, 2H), 7.16–7.18 (m, 2H), 6.91–6.96 (m, 6H), 2.19 (s, 6H, $-CH_3$). The yield of **3c** was 2.22 g (65% yield). Analysis of the product with g.p.c. shows an M_w of 1.3 and an M_n of 0.92 k. *FT*i.r. (KBr): 1651.0 (C=O), 1322.9 (SO_2) cm^{-1}. ^{1}H-n.m.r. ($CDCl_3$): δ7.82 (m, 4H), 7.22–7.25 (m, 4H), 6.94–6.98 (m, 8H).

*X-ray structure of cyclic dimer of **3c***

Cyclic oligomers **3c** were dissolved in a methylene chloride–ethanol mixed solvent (v/v, 10:1). As the solvent evaporates, some colourless crystals appear. The crystal chosen for analysis with dimensions $0.42 \times 0.20 \times 0.12$ mm was sealed in silica gel and mounted on a glass fibre. Intensity data were collected on a SIEMENS P4 4-Circle Diffractometer with graphite-monochromatized MoKα radiation at 293 K. The structure was solved by direct methods using SHELXTL PLUS (Release 5.0) and refined anisotropically (full-matrix least squares refinement on F2) for the non-hydrogen atoms. Crystal data for cyclic dimer of **3c**: monoclinic, space group Cc; $a = 20.583$, $b = 9.726$, $c = 32.019$ Å; $\beta = 93.83°$; $V = 6395.6$ Å^3; $Dc = 1.198$ Mg m^{-3}, $F(000) = 2380.0$, μ(Mo-Kα) = 0.16 mm^{-1}. $R = 0.1045$ for 4358 independent observed reflections [$I > 2\text{sigma}(I)$, $1.98° < \theta < 22.49°$].

*Ring-opening polymerization of **3a***

In a 50 ml flask, cyclic oligomers **3a** (0.50 g) were intimately mixed with potassium 4,4′-biphenoxide (0.01 g). The flask was heated in nitrogen atmosphere at 290°C for 40 min to give the corresponding polymer. The resulting polymer is partially insoluble in chloroform and THF. The reduced viscosity of the soluble fraction in chloroform is 0.23 dl g^{-1} which is approximately one third the value for the commercial phenolphthalein polyethersulfone (PES-C, 0.68 dl g^{-1}) sample. Analysis by g.p.c. shows that the high molecular weight fraction has an M_w of 59.1 and an M_n of 20.1 k.

RESULTS AND DISCUSSION

Adapting the method of Hay and co-workers[17–22] cyclic oligomers **3a–3c** were prepared, in high yields, by a nucleophilic aromatic substitution reaction from the potassium salt, prepared *in situ*, of the bisphenols **2a–2c** with 4,4′-difluorophenylsulfone under pseudo-high-dilution conditions (*Scheme 1*). A concentrated solution (0.2 M) of the reactants **1** and **2a** or **2b** or **2c** in *N*,*N*-dimethylformamide (DMF) was added dropwise into a mechanically stirred vessel containing solvent (DMF) and base (K_2CO_3) over a period of 10 h. The refluxing temperature was controlled at 145°C by varying the amount of the azeotropic solvent toluene. Following the addition of the reactants, the solution was refluxed for another 10 h to ensure the complete reaction. The cyclization reaction led to low molecular weight oligomers. The oligomeric materials are soluble in solvents such as DMF, dimethyl sulfoxide (DMSO), THF and chloroform. Analysis of the product **3a–3c** using g.p.c. reveals a series of resolved peaks in the low molecular weight region with M_n of 1.4, 1.5 and 0.92 k, respectively, and M_w of 4.3, 5.3 and 1.3 k, respectively (against polystyrene standard). A typical g.p.c. trace of **3a** is shown in *Figure 1*. Confirmation of the cyclic nature of these oligomers was obtained by employing matrix-assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS). MALDI-TOF-MS analysis indicates that the cyclic oligomers **3a** and **3b** consist principally of macrocycles with repeating units of 2–9. MALDI-TOF-MS spectra of **3a** and **3b**, using 2,5-dihydroxybenzoic acid as matrix, gives the correct molecular ion peaks for

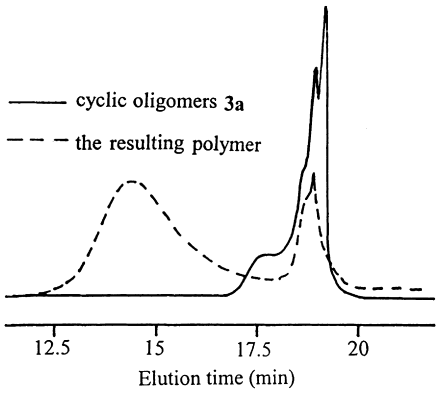
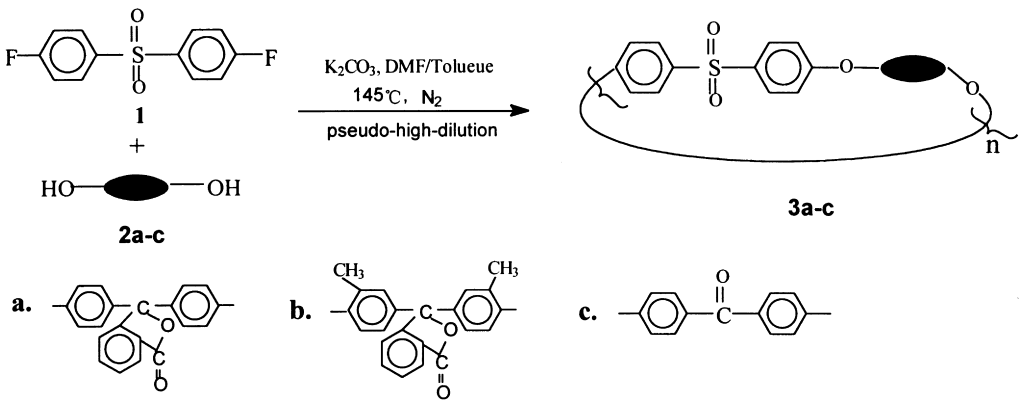


Figure 1 g.p.c. traces of cyclic oligomers **3a** and the resulting polymers



Scheme 1

$[Mn+H]^+$, sodium adducts $[Mn+Na]^+$ and potassium adducts $[Mn+K]^+$ of the desired macrocyclic oligomers with reasonable signal to noise ratio (*Figure 2*). For example, the signals for trimer of **3a** are located at 1598.7, 1620.7 and 1636.7 Da. The signal at 1598.7 Da corresponds to the protonated molecular ion peak $[Mn+H]^+$, that at 1620.7 Da is due to the adduct of the trimer with a sodium cation, while the signal at 1636.7 Da is due to the adduct of the trimer with a potassium cation which may result from the trace of potassium carbonate remaining in the products. Traces of linear oligomers were also observed, as an example, at $m/z = 1916.9$ (trimer of **3a** plus phenolphthalein) and $m/z = 1790$ and 1806 Da which have not been correctly ascribed. The level of detection for linear oligomers was about 6% for cyclic oligomers **3a**, and 5.5% for cyclic oligomers **3b** according to the relative abundance.

Unfortunately, the MALDI-TOF-MS technique for **3c** failed to produce clear and valuable spectrum for unknown reasons. However, the cyclic dimer of **3c** was clearly detected by using fast atom bombardment (f.a.b.-m.s.) techniques (*Figure 3*, $n = 2$, $m/z = 856.9$). The macrocyclic dimer of **3c** can be recrystallized from a methylene chloride–ethanol (v/v 10:1) mixed solution of the cyclic mixture **3c**. The structure of the macrocyclic dimer was conclusively proved by the single-crystal X-ray structure determination (*Figure 4*). X-ray analysis shows the macrocycle to adopt a rather open conformation, with a distance of 11.46 Å between O_5 and O_{10}, 15.74 Å between O_3 and O_8, 15.55 Å between S_1 and S_2, and 12.89 Å between C_{13} and C_{38}, respectively. Such dimensions could certainly accommodate the threading of a polymer chain and make the cyclic dimer a potential candidate for the polyrotaxane formation[32].

The diaryl sulfone unit adopts a characteristic 'open-book' type of conformation[34], with S–C–C–C torsion angles all in the range 176–179°. Similarly, the bridging oxygen atoms are almost co-planar with neighbouring phenyl rings with torsion angles in the range 174–179° except O_3–C–C–C in the range 168–171°. The other torsion angles of this type, relating bridging carbon atoms to neighbouring rings, are in the range 166–173°. The interplanar angles between neighbouring phenyl rings are all in the range 62–79°. Overall, the macrocycle displays a relatively planar conformation, with only the sulfone oxygen and carbonyl oxygen atoms projecting significantly above and below the aromatic envelope. The relatively high conformational rigidity of the macrocycle will afford a large increase in conformational entropy on ring-opening, which may be a motivating factor in the polymerization of such cyclic oligomers.

Based on the integration of the peak area, g.p.c. analysis indicates that macrocyclic oligomers **3a** contain 41.7% cyclic dimer, 20.6% cyclic trimer, 6.5% cyclic tetramer and 31.2% higher homologues ($n > 4$). Cyclics **3b** contain 46.0% cyclic dimer, 11.6% trimer, 8.1% tetramer and 34.3% higher homologues ($n > 4$). Macrocyclic oligomers **3c** contain 15.6% cyclic monomer, 44.3% cyclic dimer, 12.8% cyclic trimer and 27.3% higher homologues ($n > 3$).

Thermal analysis of macrocyclic oligomers **3a** shows a small T_g peak at 133.4°C ($\Delta Cp = 0.242$ J g^{-1} °C^{-1}) and another T_g peak at 246.8°C ($\Delta Cp = 0.553$ J g^{-1} °C^{-1}). No melt endotherm peak was observed up to 450°C indicating an amorphous material. Macrocyclic oligomers **3a** begin to soften at 275°C and form a homogeneous melt near 290°C. Macrocyclic oligomers **3b** show a small T_g peak at 145°C and another T_g peak at 229.5°C ($\Delta Cp = 0.299$ J g^{-1} °C^{-1}). No melt endotherm peak was observed up to 450°C, while

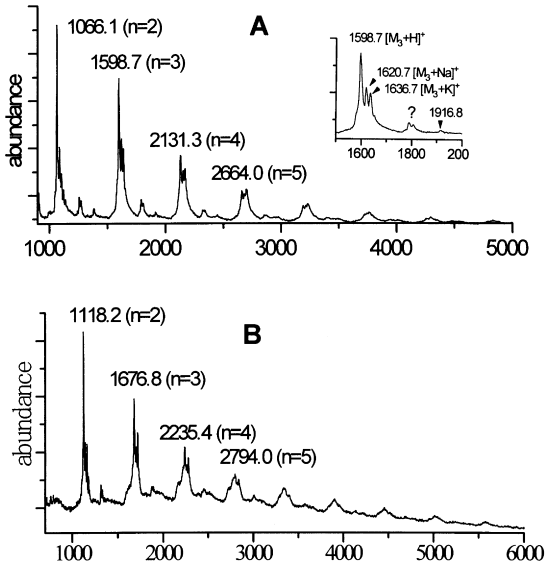


Figure 2 MALDI-TOF mass spectra of cyclic oligomers **3a** (A) and **3b** (B)

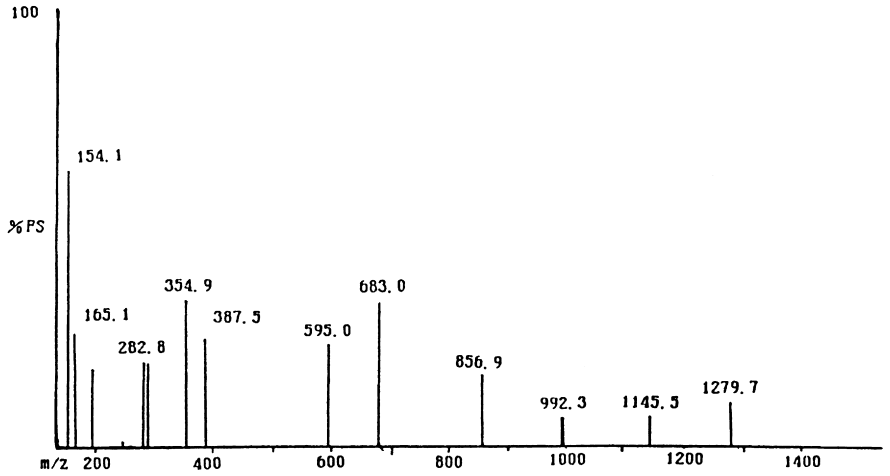


Figure 3 FAB-MS of cyclic oligomer **3**

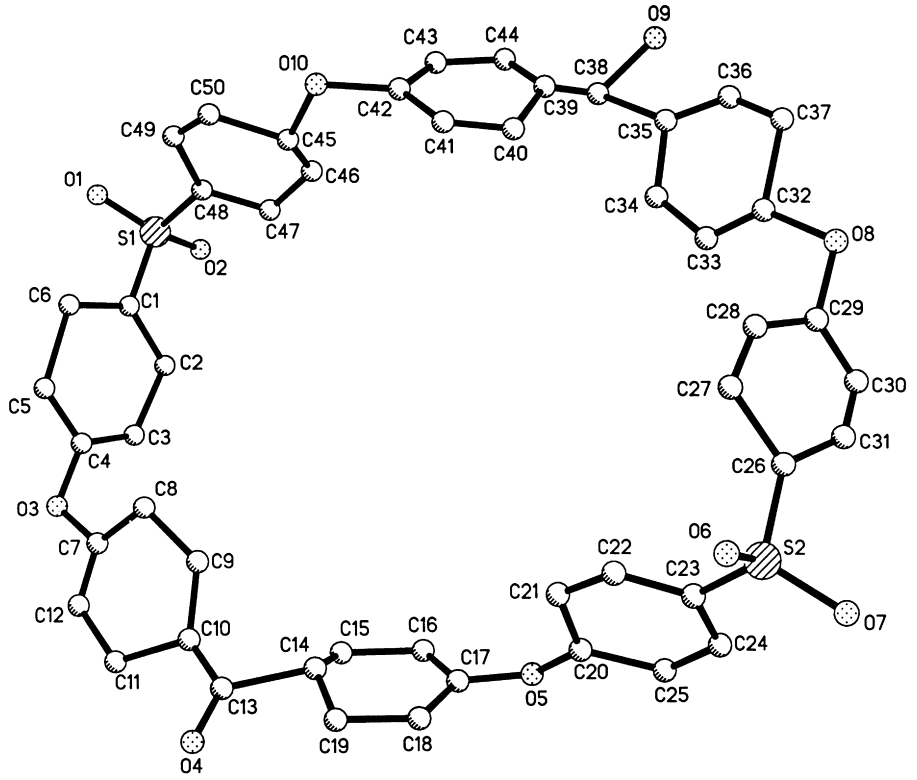


Figure 4 Single crystal X-ray structure of cyclic dimer of **3**

macrocyclic oligomer **3c** shows a broad endotherm peak at 374.7°C (midpoint) indicating a semicrystalline material.

The polymerization of macrocyclic oligomers **3a** was carried out in nitrogen atmosphere at 290°C in the presence of 2.0% (w/w) potassium 4,4′-biphenoxide for 40 min. Polymerization of macrocyclic oligomers **3a** resulted in a tough material which, unlike the commercial phenolphthalein polyethersulfone (PES-C)[40] sample, was partially insoluble in chloroform and tetrahydrofuran (THF). About 90% (weight) of the resulting polymer is soluble in THF. A g.p.c. trace of the soluble fraction is presented in *Figure 1*, which clearly shows the formation of high molecular weight linear polymer. The high molecular weight fraction has an M_w of 59.1 and M_n of 20.1 k with a molecular weight distribution of 2.9. Also, g.p.c. analysis shows that about 18.6% cyclic oligomers remained in the final polymer. Prolonging the polymerization time to 1 h gave a lesser amount of cyclic oligomers (10.5%) and the soluble fraction of the high molecular weight materials was considerably reduced to 80%. The insolubility of PES-C prepared from cyclics probably resulted from branching side reactions occurring at the high reaction temperatures employed. About 85% (weight) of the PES-C prepared from ring-opening polymerization is soluble in chloroform and the soluble fraction has a reduced viscosity of 0.23 dl g^{-1} (0.5% in chloroform at 25°C) which is approximately one third the value of the reduced viscosity of the commercial PES-C sample (0.68 dl g^{-1}). The lower viscosity of the polymer prepared from cyclics may originate from the presence of linear oligomers in the cyclic oligomers which acted as chain-transfer agents in the ring-opening polymerization reaction. Furthermore, the lower viscosity can also be attributed to the remaining of some cyclic oligomers in the final polymer. Thermal analysis of the resulting polymer from ring-opening polymerization shows a glass transition temperature of 251.3°C which is a little lower than that for the commercial PES-C sample (T_g = 260°C) and shows a 5% weight loss at 434.0°C in nitrogen atmosphere.

CONCLUSION

We have demonstrated the feasibility of using the ring-opening polymerization of cyclic oligomers to produce linear poly(arylene ether sulfone) polymers. These preliminary experiments produced good yields of the cyclic oligomers without a serious effort to optimize the preparative conditions. Ring-opening polymerization produced the corresponding polymers, while the polymers prepared from ring-opening polymerization have poor solubility in many common solvents. We believe that changes in catalyst structures and removal of linear oligomers from the cyclics will produce soluble polymers. Further work will be directed toward optimization of the cyclization reaction and detailed polymerization study.

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