Macrocyclic Arylene Ether Ether Sulfide Oligomers: New Intermediates for the Synthesis of High-Performance Poly(arylene ether ether sulfide)s

Yi-Feng Wang[†] and Allan S. Hay*

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

Received July 16, 1996; Revised Manuscript Received November 4, 1996[⊗]

ABSTRACT: A convenient and efficient synthetic route to a new class of macrocyclic aryl ether ether sulfide oligomers is described. This new class of cyclic oligomers is prepared, in excellent yield, by quantitative chemical reduction of macrocyclic aryl ether ether sulfoxide oligomers with oxalyl chloride and tetrabutylammonium iodide. The cyclic sulfoxide oligomeric precursors are prepared in high yield by an aromatic nucleophilic substitution reaction from bis(4-fluorophenyl) sulfoxide and potassium salts of bisphenols under high-dilution conditions. These novel cyclic oligomers were characterized by a combination of GPC, NMR, matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS), and thermal analyses. The cyclic nature of these oligomers was confirmed by NMR and MALDI-TOF-MS analyses of cyclic sulfoxide oligomers **4a** and its linear oligomers **6** and **7**. The cyclic sulfoxide oligomers are amorphous with T_gs varying from 140 to 199 °C. Upon chemical reduction, the corresponding sulfide oligomers are highly crystalline with T_m varying from 237 to 350 °C. The quantitative reduction of the cyclic sulfoxide oligomers to cyclic sulfide oligomers was confirmed by NMR and MALDI-TOF-MS analyses of sulfoxide **4c** and its corresponding sulfide **5c**. Ring-opening polymerization (ROP) of the cyclic aryl ether ether sulfide oligomers to corresponding high molecular weight linear polymers can be effected in the melt phase with the addition of a catalytic amount of 2,2′-dithiobis-(benzothiazole) (DTB) disulfide. A tough semicrystalline polymer obtained from ROP of **5a** has a T_g of 150 °C and T_m of 313 °C.

Introduction

Poly(aryl ether)s and poly(aryl thioether)s such as poly(arylene ether ketone)s, poly(arylene ether sulfone)s, and poly(phenylene sulfide) are well-known high-performance engineering thermoplastics with attractive property balances, namely high thermal, oxidative, and chemical stabilities, stiffness, and toughness.[1,2] Of particular importance are poly(phenylene ether ether ketone) (PEEK) and poly(1,4-phenylene sulfide) (PPS), which are semicrystalline high-melting polymers and are increasingly used in electronic/electric, aircraft, and aerospace industries. PEEK is commercially produced by nucleophilic substitution polycondensation in diphenyl sulfone above 335 °C.[3] PPS is commercially produced by polycondensation of 1,4-dichlorobenzene with sodium sulfide in polar solvents at high temperature and pressure.[4] The use of high-boiling solvent is necessary in order to attain relative high molecular weight of these insoluble crystalline materials. These severe reaction conditions, the use of additives, and different heat treatments may result in a large variability of the properties of the products. As a consequence, much research in recent years has been directed toward the development of new or improved thermoplastics.[5−10] Of particular interest is the development of semicrystalline poly(arylene ether ether sulfide)s[10] by first making the amorphous poly(arylene ether ether sulfoxide)s via nucleophilic substitution polycondensation of bis(4-fluorophenyl) sulfoxide and potassium salts of bisphenols and then converting them to the corresponding semicrystalline poly(arylene ether ether sulfide)s via a reduction reaction of the sulfoxide. The advantage of this process is that a controllable high molecular weight semicrystalline polymer can be conveniently prepared from an amorphous precursor.

With the development of high-performance thermoplastics such as PEEK and PPS, there is increasing interest in high-performance thermoplastic composites for their unique performance properties, such as excellent thermal, oxidative, and chemical resistance and damage tolerance superior to that of traditional thermosetting polymer matrix composites.[11] However, due to the high melting temperatures and high melt viscosities of the high molecular weight polymers, melt processing leads to fiber breakage and sometimes also leads to decomposition of the polymers. In addition, prepreg made from the high molecular weight polymers has poor tack and drape properties.[11] These problems are particularly severe for the fabrication of high-load continuous fiber thermoplastic composites. An ideal route for the fabrication of continuous fiber reinforced thermoplastic composites is to develop novel chemistry whereby tough, solvent resistant, high T_g or T_m, high molecular weight thermoplastics can be made during the fabrication process by polymerizing low molecular weight, low melt viscosity monomers or oligomers without evolution of volatiles.

In an effort to address the problems associated with high melt viscosities of high molecular weight polymers, development of low molecular weight macrocyclic oligomers as intermediates for the preparation of high-performance thermoplastics has attracted considerable attention in recent years.[12−27] The macrocyclic 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. The *in situ* transformation of macrocyclic oligomers such as carbonates,[12] esters,[13] aryl ethers,[14−17] aramids[18] and imides[19] via an anionic ring-opening polymerization route to high molecular weight linear polymers opens up the possibility of melt processing of aromatic thermoplastics in applications which are cur-

---

[†] Present address: GE Silicones, 260 Hudson River Road, Waterford, NY 12188.

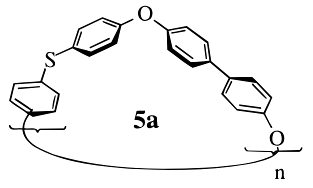
[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

S0024-9297(96)01044-3 CCC: $14.00

rently not accessible to the corresponding high molecular weight polymers due to their inherent high melt viscosities. In particular, the low viscosity of macrocyclic oligomers permits applications of high-performance thermoplastics in the fabrication of long or continuous fiber reinforced thermoplastic composites via processing methods such as compression molding, reaction injection molding, and melt-pultrusion.

The anionic ring-opening polymerization of macrocyclic aryl ether oligomers is achieved with nucleophilic initiators such as alkali fluoride[14−17] and alkali phenoxides.[20,21] Using alkali organic compounds as the initiator results in polymers containing inorganic salts and alkali phenoxide as the end groups, which is undesirable when the polymers are used in electric and electronic applications. Furthermore, the alkali phenoxide end groups would also contribute to the thermooxidative instability in the polymers at elevated temperatures.

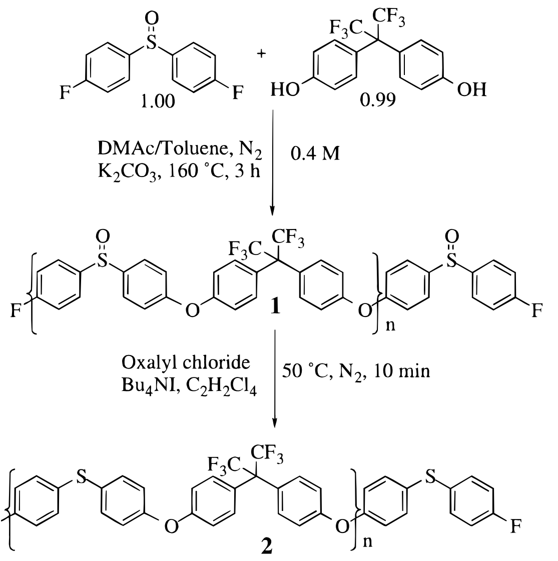
Recently, we reported that cyclic aryl ether thioether ketone oligomers containing a 1,2-dibenzoylbenzene moiety are thermally unstable in the melt[25] and undergo a novel free-radical ring-opening polymerization[28,29] to form high molecular weight linear polymers. The ring-opening polymerization is achieved via a transthioetherification reaction involving thiyl radical(s) and can be promoted by using a catalytic amount of elemental sulfur or disulfide organic compound such as 2,2′-dithiobis(benzothiazole). For the cyclic aryl ether thioether ketone oligomers containing a 1,2-dibenzoylbenzene moiety, the thioether linkage is activated by the electron-withdrawing carbonyl group. We were interested to learn whether this novel chemistry could be extended to other cyclic aryl thioether oligomers in which the thioether linkage is not activated by an electron-withdrawing group. We were also interested in exploring a facile route for the preparation of high-performance semicrystalline thermoplastic via macrocyclic aryl thioether oligomers. Thus, the original impetus behind the synthesis of macrocyclic aryl ether ether sulfide oligomers discussed in this article was to answer these questions. Preliminary studies of the synthesis and polymerization of cyclic oligomer **5a** has been reported in a recent communcation.[28] Cyclic oligomers **5a** undergo ring-opening polymerization readily in the melt in the presence of a catalytic amount of 2,2′-dithiobis(benzothiazole) (DTB) disulfide to form high molecular weight semicrystalline material. Hence, cyclic oligomers **5a** could be an attractive candidate as reactive intermediates for the fabrication of high-performance thermoplastic composites via reactive processing such as reaction-injection molding. This article describes the details of the synthesis and characterization of the cyclic aryl ether ether sulfide oligomers and their sulfoxide precursors. The preliminary study of the ring-opening polymerization of this novel class of macrocycles will also be discussed.



5a

Results and Discussion

Scheme 1



1

2

Preparation of Linear High Molecular Weight Poly(arylene ether ether sulfoxide) and Its Corresponding Poly(arylene ether ether sulfide). Recently, Riffle and co-workers[10] reported the synthesis of semicrystalline poly(arylene ether ether sulfide)s by first preparing a soluble, amorphous sulfoxide containing precursor, followed by reducing the sulfoxide moiety to sulfide. The poly(arylene ether ether sulfoxide)s were synthesized using conventional nucleophilic aromatic substitution reactions between bis(4-fluorophenyl) sulfoxide and potassium salts of bisphenols. The polymerization was conducted in *N*-methylpyrrolidinone (NMP) at 160 °C for 36 h, which implies that the displacement reaction is a relatively slow process. As we have discussed in previous publications,[22,26,27] the selective formation of macrocyclic aryl ether oligomers via an aromatic nucleophilic substitution reaction requires a fast displacement reaction and low concentration of unreacted end groups during the cyclization process. Therefore, we were interested in re-examining the reactivity of bis(4-fluorophenyl) sulfoxide toward nucleophilic substitution with bisphenoxides, prior to employing this chemistry for the synthesis of macrocyclic aryl ether sulfoxide oligomers.

^{19}F NMR chemical shifts are proven to be a simple and valuable tool for evaluating the reactivity of difluoro monomer toward nucleophilic aromatic substitution.[30] In general, bis(4-fluorophenyl) sulfone is considered to be the most activated monomer, 4,4′-difluorobenzophenone is the next most activated, and fluorobenzene is considered to be the least activated. The ^{19}F NMR chemical shift of the fluoro on C-4′ in bis(4-fluorophenyl) sulfoxide is found to be −107.6 ppm, which is comparable to that (−106.0 ppm) of 4,4′-difluorobenzophenone. Polymerization of bis(4-fluorophenyl) sulfoxide with 2,2′-bis(4-hydroxyphenyl)hexafluoropropane using *N*,*N*-dimethylacetamide (DMAc) as the solvent and potassium carbonate as the base at 160 °C for 3 h (Scheme 1) gave high molecular weight polymer **1** with M_n of 54 200 and M_w of 111 100. Thermal analysis showed that polymer **1** has a glass transition temperature of 190 °C, an intense exotherm peaked at 391 °C, and a 5% weight loss at 411 °C in nitrogen. By employing a reported procedure,[10] reaction of polymer **1** with 1.2 molar equiv of oxalyl chloride in conjunction with 2.5 molar equiv of tetrabutylammonium iodide, using 1,1,2,2-tetrachloroethane as the solvent at 50 °C, gave a quantitative yield of poly(aryl ether ether sulfide) **2** (see Scheme 1), which is very soluble in most organic solvents such as chloroform, tetrahydrofuran, and DMAc. GPC analysis

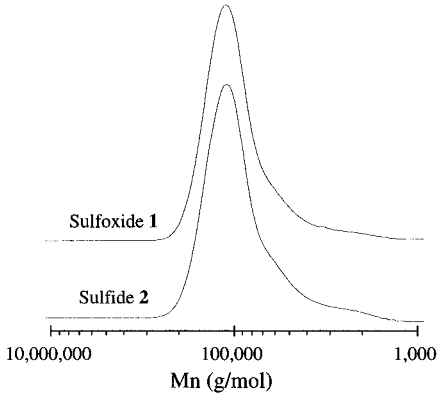


Figure 1. GPC traces of linear poly(aryl ether ether sulfoxide) **1** and linear poly(aryl ether ether sulfide) **2**.

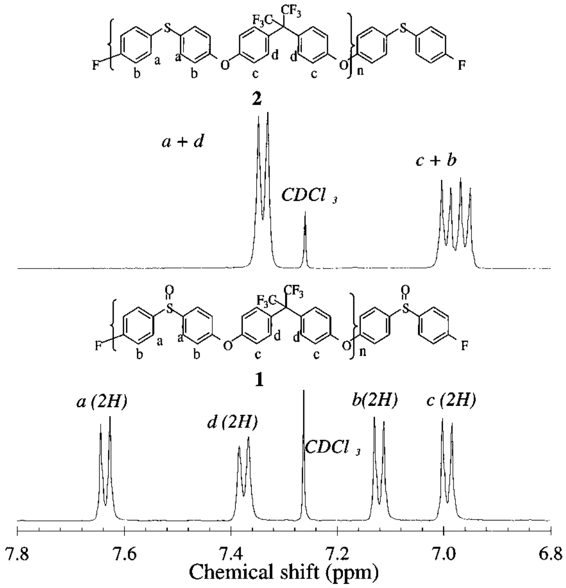
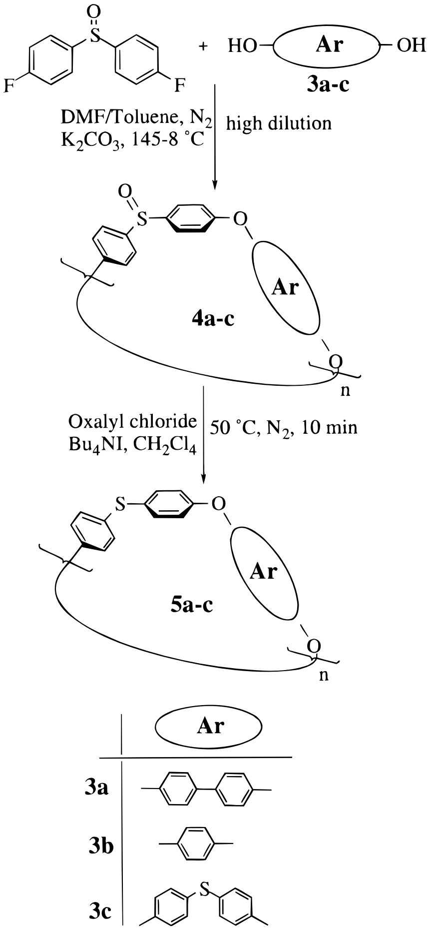


Figure 2. ^{1}H NMR spectra (in $CDCl_3$) of the linear poly(aryl ether ether sulfoxide) **1** and linear poly(aryl ether ether sulfide) **2**.

showed that **2** has a M_n of 54 000 and M_w of 111 800. The GPC traces of polymers **1** and **2** are essentially identical (see Figure 1). The result clearly indicates that no chain extension or chain scission occurred in polymer chains upon chemical conversion of sulfoxide to the sulfide. The quantitative reduction of sulfoxide to sulfide under the reaction conditions can be best confirmed by NMR analysis. The ^{1}H NMR spectra of polymers **1** and **2** in $CDCl_3$ are shown in Figure 2. Upon the reduction of sulfoxide to sulfide, the protons *ortho* to the sulfoxide at 7.63−7.64 ppm in the spectrum of **1** have shifted quantitatively upfield to 7.33−7.35 ppm in the spectrum of **2**. Thermal analysis showed that polymer **2** is amorphous with a T_g of 145 °C and a 5% weight loss at 534 °C in nitrogen. The degradation temperature of **2** is substantially higher than that of **1**, indicating that the sulfides have a significantly higher thermal stability compared with that of the sulfoxides.

Scheme 2



Preparation of Macrocyclic (Aryl Ether Ether Sulfoxide)s 4a−c. In the preceding section, we have demonstrated that bis(4-fluorophenyl) sulfoxide and 4,4′-difluorobenzophenone have similar reactivity toward nucleophilic aromatic substitution reaction (by ^{19}F NMR analysis), and high molecular weight polymer can be easily prepared from bis(4-fluorophenyl) sulfoxide and the potassium salts of bisphenol in a short reaction time by an aromatic nucleophilic substitution reaction. The classic approach of the condensation of monomers at low concentrations has proven remarkably successful in the synthesis of high yields of cyclic oligomers.[12−22,26] The preparation of cyclics from bis(4-fluorophenyl) sulfoxide and bisphenols under high-dilution conditions was next investigated. The cyclization reaction (Scheme 2) was conducted by the continuous addition of a concentrated solution of bis(4-fluorophenyl) sulfoxide and bisphenol monomers **3a**−**c** in DMF to a mixture of DMF and anhydrous potassium carbonate at 145 °C under argon over 8 h, followed by extended heating at 145−148 °C for another 8 h. This process led to a final concentration of product of 50 mM. A small amount of toluene was used for continuous azeotropic removal of water generated during the formation of potassium phenoxide salts. The cyclization reaction led to an essentially quantitative yield of a mixture of low molecular weight oligomers **4a**−**c** (Table 1). These oligomers have limited solubility in common organic solvents such as DMF, DMAc, and tetrahydrofuran (THF); however, they are very soluble in chlorinated solvents such as chloroform and 1,1,2,2-tetrachloroethane (TCE). GPC analysis using THF as the eluent indicates that the average degree of polymerization is about 3 (see Table 1). The GPC trace of cyclic oligomers **4a** is shown in Figure 3 along with those of linear oligomers **6** (M_n = 2300 and M_w = 3100) and **7** (M_n = 2900 and M_w = 4600). The linear oligomers **6** and **7** were prepared via the conventional condensation polymerization reaction by either prematurely terminating the polymerization or using an excess amount of bis(4-fluorophenyl) sulfoxide, respectively (Scheme 3). The GPC traces of linear oligomers **6** and **7** show the typical Gaussian distribution; on the other hand, the GPC trace of oligomers **4a** shows an exponential distribution in which

Table 1. Yields and Physical Properties of Macrocyclic Oligomers 4a–c and 5a–c

	cyclic oligomer					
	4a	**4b**	**4c**	**5a**	**5b**	**5c**
isolated yield (%)	96	92	98	97	96	98
M_n[a]	1200	950	1700			
M_w[a]	2900	1600	4900			
T_g (°C)[b]	199	165	141			82
T_m (°C)[b]				350[c] (275–372)[d]	237[c] (202–250)[d]	173, 267[c] (151–278)[d]
ΔH_m (kJ/mol)[e]				18.2	4.2	11.6
T_{ex} (°C)[f]	360[f] (325–373)[g]	350[f] (323–355)[g]	417[f] (350-467)[g]			
$T_{-5\%}$ (°C)[h]	363	363	370	530	501	518

[a] Measured by GPC and calibrated against polystyrene standards. [b] Measured by DSC under nitrogen (a flow rate of 150 mL/min) at a heating rate of 20 °C/min. [c] Peak temperature of melting endotherm. [d] Onset and offset temperature of melting endotherm. [e] Enthalpy change of the melting endotherm, measured by DSC and calibrated against indium. [f] Peak temperature of exothermic peak. [g] Onset and offset temperature of the exothermic peak. [h] 5% weight loss temperature, measured by TGA under nitrogen (a flow rate of 150 mL/min) with a heating rate of 20 °C/min.

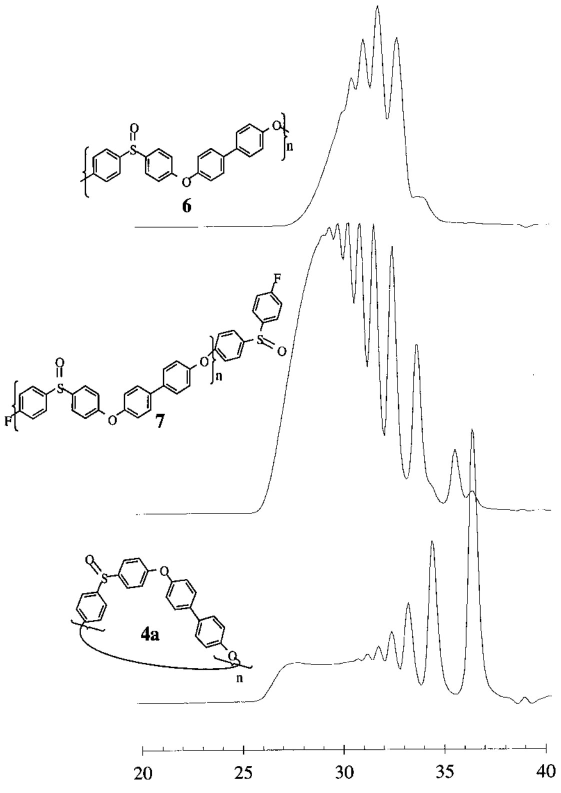
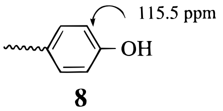


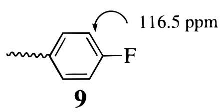
Figure 3. GPC traces of macrocyclic aryl ether ether sulfoxide oligomers **4a** and its linear analogs **6** and **7**.

the lowest molecular weight species have the highest concentration.

^{13}C NMR spectra (Figure 4) show that in the spectrum of **6** there are three intense signals at 116.71, 116.53, and 115.91 ppm, and in the spectrum of **7** there are two intense signals at 116.64 and 116.46 ppm. The signal at 115.9 ppm is due to the aromatic carbons *ortho* to the hydroxyl group (**8**), and the two signals at 116.5–116.7 ppm are due to the aromatic carbons *ortho* to the fluoro group (**9**). However, in the spectrum of **4a** there are no obvious signals in the range 117–115 ppm. Therefore, the presence of fluoro and/or phenolic end groups **8** and **9** in oligomers **6** and **7** is obvious. A more sensitive ^{19}F NMR analysis also shows that the end group **9** is only present in **6** and **7**. The ^{13}C and ^{19}F NMR analyses suggest the low molecular weight oligomers **4a** are macrocycles. Direct confirmation of the cyclic nature of the oligomers **4a–c** was provided by employing matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS).

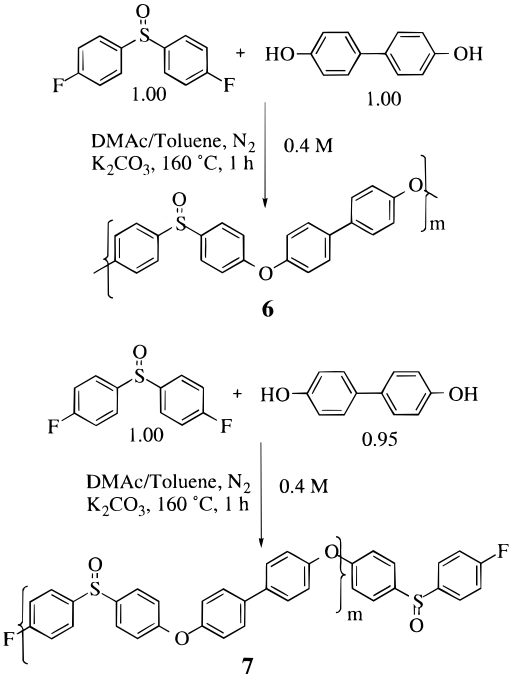


8



9

Scheme 3



MALDI-TOF-MS Analysis of Cyclic Oligomers 4a–c and Linear Oligomers 6 and 7. MALDI-TOF-MS is a recently introduced[31] soft ionization technique that allows desorption and ionization of very large molecules, and has been successfully used to determine the mass of large biomolecules and synthetic polymers.[31b,32] The great promise of MALDI-TOF is to perform the direct identification of mass-resolved polymer chains and the simultaneous determination of the end groups in polymer samples.

For the MALDI-TOF-MS analysis, the sample to be analyzed is mixed uniformly with a matrix. In an environment in which a large excess of the matrix is present, the sample molecules are surrounded by the matrix molecules in crystalline or amorphous states. The matrix, which has resonance absorption at the laser wavelength used (337 nm), absorbs the laser energy and causes rapid heating of the matrix, resulting in expulsion and soft ionization of the sample molecules without

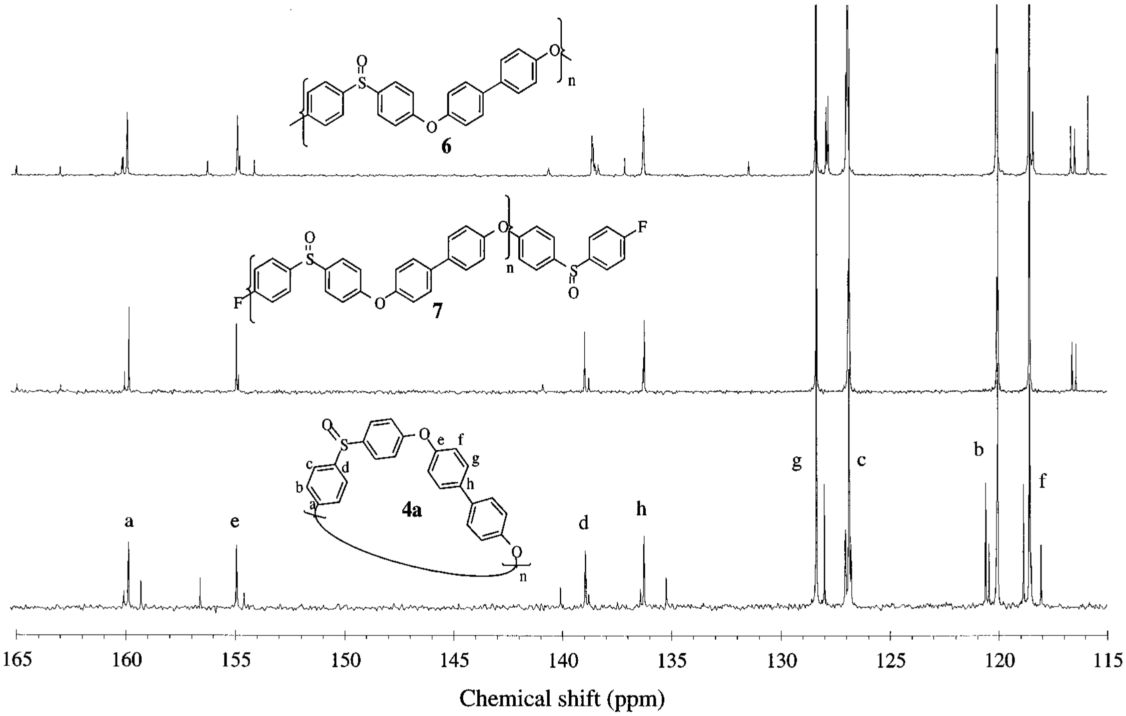


Figure 4. ^{13}C NMR spectra (in TCE-d_2) of macrocyclic aryl ether ether sulfoxide oligomers **4a** and its linear analogs **6** and **7**.

fragmentation. Once the analyte is ionized, it is accelerated and analyzed in a time-of-flight (TOF) mass spectrometer. As a result, the analyte is separated according to the molar mass of its components. The key to the successful application of this technique for synthetic polymeric materials is the dispersion of the polymer chains in the matrix at the molecular level and prevention of the entanglements between individual molecular chains. MALDI-TOF-MS is an ideal tool for the analysis of macrocyclic oligomers since there are little or no entanglements among the macrocyclic molecules.

The macrocyclic oligomers **4a**–**c** and linear oligomers **6** and **7** were analyzed by MALDI-TOF mass spectrometry using 1,8,9-anthracenetriol (dithranol) as the matrix. In order to promote the ionization, a small amount of silver trifluoroacetate was added to the sample. The positive ion MALDI-TOF mass spectra of **4a**–**c**, obtained in the reflectron mode, give the correct molecular ion signals for the desired cyclic oligomers, up to pentadecamer ($n = 15$) with excellent signal to noise ratio. A typical positive ion MALDI-TOF mass spectrum of **4a**, using silver trifluoroacetate as the ionization promoter, is presented in Figure 5a. The spectrum consists of a number of peaks of different intensity. In the mass range 600–2600, there are ten peaks which can be divided into two groups, in which one group consists of peaks having masses of 769.3, 1154.1, 1538.9, 1924.7, and 2309.1 and the other group consists of peaks having masses of 876.6, 1260.9, 1645.8, 2031.0, and 2416. In both groups, the peak-to-peak mass increment is 385. This mass increment equals the mass of the repeat unit in cyclic oligomers **4a** and, therefore, each peak represents one oligomer. The five peaks at m/z 769.3, 1154.1, 1538.9, 1924.7, and 2309.1 correspond to the protonated cyclic dimer, trimer, tetramer, pentamer, and hexamer, respectively. The other five peaks at m/z 876.6, 1260.9, 1645.8, 2031.0, and 2416.1 correspond to the silver adducts $[M_n + Ag]^+$ of cyclic dimer, trimer, tetramer, pentamer, and hexamer, respectively. For peaks having mass above 2600, there are only signals corresponding to the silver adducts $[M_n + Ag]^+$ of cyclics **4a** with repeating unit n from 7 to 15. The MALDI-TOF mass spectra of cyclic oligomers **4b** and **4c** using silver trifluoroacetate as the ionization promoter give the correct molecular ion signals for the desired protonated oligomers $[M_n + H]^+$ and/or the silver adduct $[M_n + Ag]^+$, up to pentadecamer ($n = 15$) and decamer ($n = 10$), respectively (see Tables 2 and 3), with excellent signal to noise ratio. Using lithium bromide (LiBr) as the ionization promoter, the MALDI-TOF mass spectrum (Figure 5b) of **4a** is simplified and there are only peaks corresponding to the lithium adduct $[M_n + Li]^+$ of the desired cyclic oligomers with repeating unit n from 2 to 14, although there are a few minor peaks (next to the main peaks) corresponding to the molecular ion signals for the desired protonated cyclic oligomers $[M_n + Li]^+$.

As we have discussed earlier, the ^{13}C and ^{19}F NMR analyses of **4a** did not reveal the presence of any phenolic and fluoro end groups, and for the MALDI-TOF mass spectra of **4a**–**c**, in the mass range (m/z) up to 5000, there was no indication of the presence of linear oligomers; therefore, it is fair to conclude that the low molecular weight oligomers **4a**–**c** are macrocycles. However, one could argue that, due to potential lower volatility and/or ionization of linear oligomers, MALDI-TOF-MS might not tell if the linear oligomers are present in the cyclics. Therefore it would be very useful to compare the MALDI-TOF mass spectra of the cyclics **4a** with those of the linear oligomers **6** and **7** and their mixtures in order to conclusively determine that the oligomers **4a** are completely macrocycles.

Figure 6 shows the positive ion MALDI mass spectrum of linear oligomers **6** obtained in the reflectron mode using dithranol as the matrix and silver trifluoroacetate as the ionization promoter. Statistically, there are three different end-capped linear oligomers (**6A**, **6B**, and **6C**) of **6** (see Chart 1), and for a given degree of polymerization, the concentrations of **6A** and **6C** are the same and are only half of that of **6B**. The inspection of the low mass range (up to m/z 1600) of the MALDI mass spectrum reveals that there are signals corresponding to the protonated linear dimer and trimer of **6A**, **6B**,

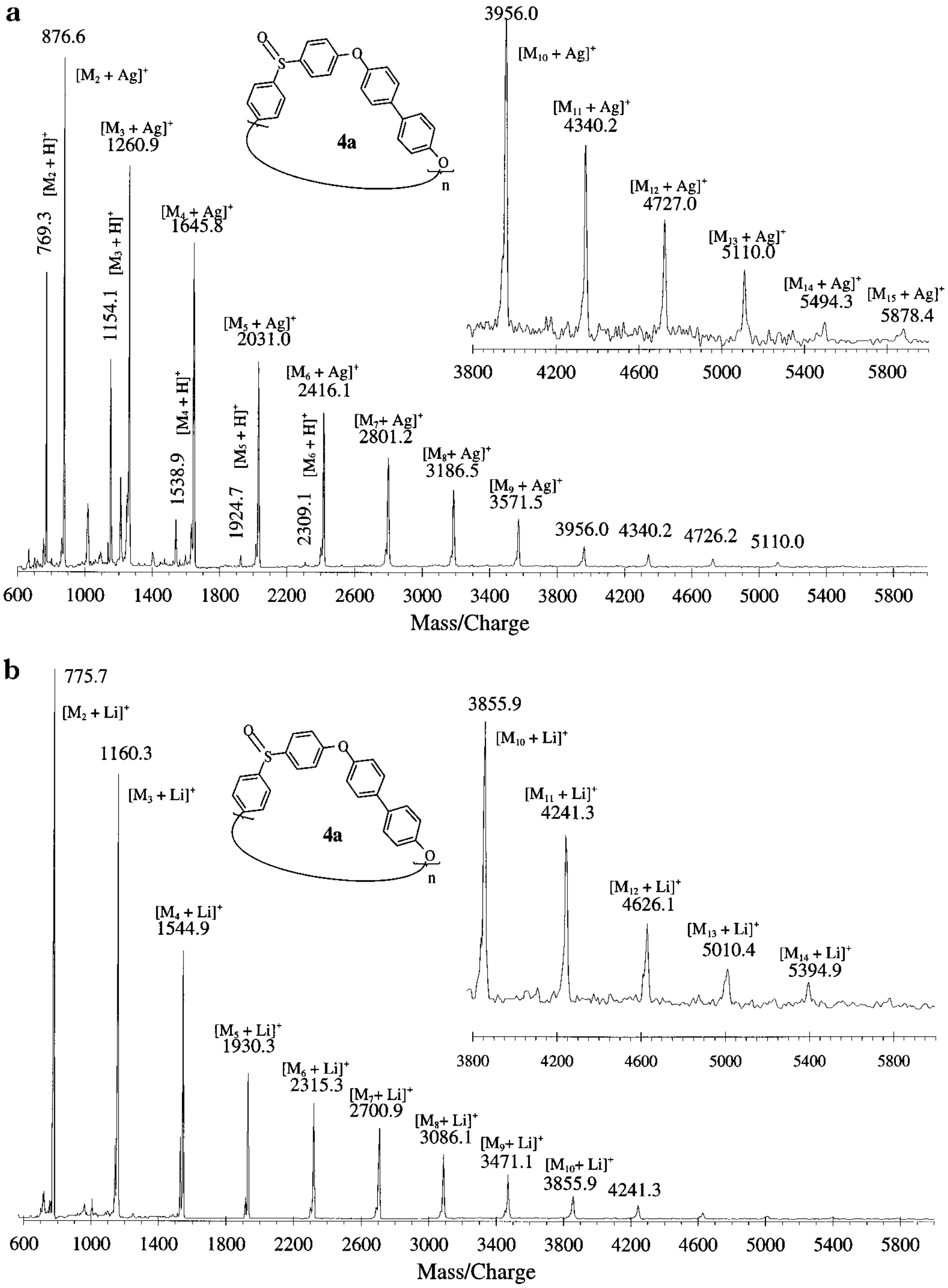


Figure 5. (a) Positive ion MALDI-TOF mass spectrum of cyclic oligomers **4a**. The data were acquired in the reflectron mode using dithranol as the matrix and silver trifluoroacetate as the ionization promoter (dithranol/$AgCO_2CF_3$/**4a** = 20:1:1 by weight). (b) Positive ion MALDI-TOF mass spectrum of cyclic oligomers **4a**. The data were acquired in the reflectron mode using dithranol as the matrix and lithium bromide as the ionization promoter (dithranol/LiBr/**4a** = 20:1:1 by weight).

and **6C** and signals corresponding to the silver adducts of linear dimer and trimer of **6A**, **6B**, and **6C**. However, in the higher mass range (above *m/z* 1600), there are only signals corresponding to the silver adducts of linear oligomers of **6B** and **6C** with a degree of polymerization from 4 to 8, and the relative intensities of the signals corresponding to **6B** and **6C** are essentially equivalent. This suggests that for the given matrix–sample system, the ionization of the difluoro end-capped linear oligomer **6C** is most efficient, the monofluoro end-capped oligomer **6B** is the next, and the dihydroxy end-capped linear oligomer **6A** is the least. Using the same matrix and ionization promoter, MALDI-TOF-MS analysis of difluoro end-capped linear oligomers **7** shows that linear oligomers with a degree of polymerization as high as 14 can be detected (Figure 7).

A positive ion MALDI mass spectrum, obtained in the reflectron mode using dithranol as the matrix and silver trifluoroacetate as the ionization promoter, of a mixture of cyclic oligomers **4a** with linear oligomers **7** is shown in Figure 8. This particular mixture consisted of 50 wt % of cyclics **4a** and 50 wt % of linear oligomers **7**. The spectrum consists of a number of peaks of different intensities. The peaks can be divided into two groups, in which one group consists of peaks having masses of 876.4, 1260.7, 1645.2, 2030.6, 2415.7, 2800.8, 3186.0, 3571.1, 3955.3, 4341.5, and 4726.8 and the other group consists of peaks having masses of 1114.5, 1499.0, 1883.9, 2268.8, 2654.2, 3039.5, 3424.7, 3809.4, 4194.4, 4579.5, 4963.7, 5349.3, and 5734.3. In both groups, the peak-to-peak mass increment is 385. This mass increment equals the mass of the repeat unit of cyclics **4a**

Table 2. Positive Ion MALDI-TOF-MS Data for Cyclic Oligomers 4b Using Dithranol as the Matrix and $AgCO_2CF_3$ as the Ionization Promoter

signal (m/z)	rel intens (%)	assignt[a]	calcd (m/z)	deviation (Da)[b]
616.9	23	$M_2 + H$	617.1	0.8
723.9	46	$M_2 + Ag$	724.7	0.8
925.6	37	$M_3 + H$	926.1	0.5
1032.4	98	$M_3 + Ag$	1033.1	0.7
1234.4	22	$M_4 + H$	1234.4	0.0
1340.9	100	$M_4 + Ag$	1341.4	0.5
1542.8	4	$M_5 + H$	1542.8	0.0
1649.8	40	$M_5 + Ag$	1649.8	0.0
1851.4	2	$M_6 + H$	1851.1	−0.3
1958.8	25	$M_6 + Ag$	1958.1	−0.7
2267.7	20	$M_7 + Ag$	2266.5	−1.2
2576.5	16	$M_8 + Ag$	2574.8	−1.7
2885.4	12	$M_9 + Ag$	2883.2	−2.3
3194.2	9	$M_{10} + Ag$	3191.5	−2.7
3503.1	5	$M_{11} + Ag$	3499.9	−3.3
3811.8	4	$M_{12} + Ag$	3808.2	−3.6
4120.8	2	$M_{13} + Ag$	4116.6	−4.3
4430.7	1	$M_{14} + Ag$	4424.9	−5.8
4735.9	0.8	$M_{15} + Ag$	4733.3	−2.6

[a] M_x ($x = 2-15$) represents the molecular ion with x repeating units. [b] Deviation = (experimental value) − (calculated value).

Table 3. Positive Ion MALDI-TOF-MS Data for Cyclic Oligomers 4c Using Dithranol as the Matrix and $AgCO_2CF_3$ as the Ionization Promoter

signal (m/z)	rel intens (%)	assignt[a]	calcd (m/z)	deviation (Da)[b]
833.1	89	$M_2 + H$	834.0	0.9
940	100	$M_2 + Ag$	941.0	1.0
1250.2	30	$M_3 + H$	1250.5	0.3
1357	54	$M_3 + Ag$	1357.5	0.5
1666.8	11	$M_4 + H$	1667.0	0.2
1773.9	32	$M_4 + Ag$	1774.0	0.1
2083.8	4	$M_5 + H$	2083.6	−0.2
2191	23	$M_5 + Ag$	2190.5	−0.5
2502.3	5	$M_6 + H$	2500.1	−2.2
2608.2	16	$M_6 + Ag$	2607.0	−1.2
2919.2	8	$M_7 + H$	2916.6	−2.6
3025.7	11	$M_7 + Ag$	3023.5	−2.2
3442.1	7	$M_8 + Ag$	3440.0	−2.1
3858.8	5	$M_9 + Ag$	3856.5	−2.3
4274.2	3	$M_{10} + Ag$	4273.1	−1.1

[a] M_x ($x = 2-10$) represents the molecular ion with x repeating units. [b] Deviation = (experimental value) − (calculated value).

and the linear oligomers **7**. The peaks in the first group correspond to the silver adducts $[M_n + Ag]^+$ of the cyclics **4a** with n from 2 to 12, and the peaks in the second group correspond to the silver adducts of the difluoro end-capped linear oligomer **7** with a degree of polymerization from 2 to 14. The ion signal at 769.1 corresponds to the protonated cyclic dimer of **4a**. It should be noted in Figure 8 that for oligomers having the same degree of polymerization, the intensities of the ion signals of the linear oligomers are higher than those of the cyclics. This is more obvious in the higher mass range (see Figure 8). This implies that in the same chemical environment, the ionization concentration of the difluoro end-capped linear molecules is higher than that of the cyclics. Therefore, MALDI-TOF mass spectrometry can be used as a tool to analyze the purity of cyclic oligomers. As we have shown in Figure 5, there are no peaks corresponding to the ion signals of the difluoro end-capped linear molecules or any other linear molecules; therefore one can conclude that oligomers **4a** are macrocycles and free of contamination with linear molecules.

Thermoanalyses of Cyclic Aryl Ether Sulfoxide Oligomers 4a−c. DSC analyses of cyclic oligomers **4a−c** were conducted in a nitrogen atmosphere (a flow of 150 mL/min) at a heating rate of 20 °C/min. A typical DSC trace of the cyclic oligomers **4a** is shown in Figure 9. The thermal properties of these oligomers are tabulated in Table 1. In general, the macrocyclic oligomers show a moderate T_g followed by an intense exothermic peak centered at 360 °C. There is no melting endothermic peak. TGA shows that cyclics **4a−c** undergo a sharp weight loss corresponding to ~4% around 360 °C under nitrogen. Although the true nature of the exothermic reaction associated with the sharp weight loss at 360 °C is unknown, we speculate that it is involved with the sulfoxide moiety.

Preparation of Macrocyclic (Aryl Ether Ether Sulfide)s 5a−c. Cyclics **5a−c** were prepared, in quantitative yield, by the reaction of cyclics **4a−c** with 1.2 molar equiv of oxalyl chloride in conjunction with 2.5 molar equiv of tetrabutylammonium iodide, using 1,1,2,2-tetrachloroethane as the solvent at 50 °C (see Scheme 2), according to a reported procedure.[10] Following the conversion of the sulfoxide moiety to sulfide, the resulting cyclics **5a** and **5b** become insoluble in most organic solvents, although they are soluble in hot 1-chloronaphthalene (at ~100 °C). Due to the insolubility of **5a** and **5b** in most organic solvents, molecular characterization methods such as solution NMR and GPC analyses cannot be performed.

TGA studies on the sulfide oligomers indicated that these cyclics have good thermal stability. Cyclics **5a−c** showed a 5% weight loss occurring at ~500 °C in nitrogen (see Table 1). These degradation temperatures are substantially higher than the corresponding values (~360 °C) for the sulfoxide precursors, indicating a significantly higher thermal stability for the sulfides as compared to the sulfoxides.

DSC analyses show that **5a** and **5b** are highly crystalline (see Table 1). A typical DSC trace of cyclic **5a** (see Figure 9) shows that there is only a melting endothermic peak centered at 350 °C with an onset temperature of 275 °C and an offset temperature of 372 °C. The fact that there is no exothermic peak in the temperature range 300−370 °C does indicate the absence of any sulfoxide functional groups in **5a**. Figure 10 shows the normal cross polarization magic angle spinning (CP-MAS) spectra of **4a** and **5a**. Comparing the CP-MAS spectrum of **4a** with its solution ^{13}C NMR spectrum in Figure 4, the broad peak at 166−150 ppm can be assigned as the C-a and C-e, the intense shoulder peak between at 150−140 ppm can be assigned as C-d, the peak at 140−130 ppm can be assigned as C-h, and the broad peak at 130−110 ppm can be assigned to C-c, C-g, C-b, and C-f. Following the conversion of the sulfoxide moiety to sulfide, there is no obvious shoulder peak between 150 and 140 ppm in the CP-MAS spectrum of **5a** (see Figure 10). This indicates that the reduction of sulfoxide to sulfide was complete.

Although cyclic **5c** is only partially soluble in solvents such as DMF, DMAc, THF, and chloroform, it is completely soluble in 1,1,2,2-tetrachloroethane (TCE) at temperatures above 50 °C. This facilitates the solution NMR and MALDI-MS analyses of **5c**. The ^1H NMR spectra of **4c** and **5c** are shown in Figure 11. The NMR spectra were obtained at 60 °C using TCE-d_2 as the solvent and TMS as the internal reference. Upon the reduction of sulfoxide to sulfide, the protons *ortho* to the sulfoxide at ~7.6 ppm in the spectrum of **4c** have shifted quantitatively upfield to ~7.3 ppm in the spectrum of **5c**. The MALDI-TOF mass spectrum of **5c** clearly gives the correct molecular ion signals for protonated cyclic oligomers and/or silver adducts of the cyclic oligomers (when silver trifluoroacetate was added as the ionization

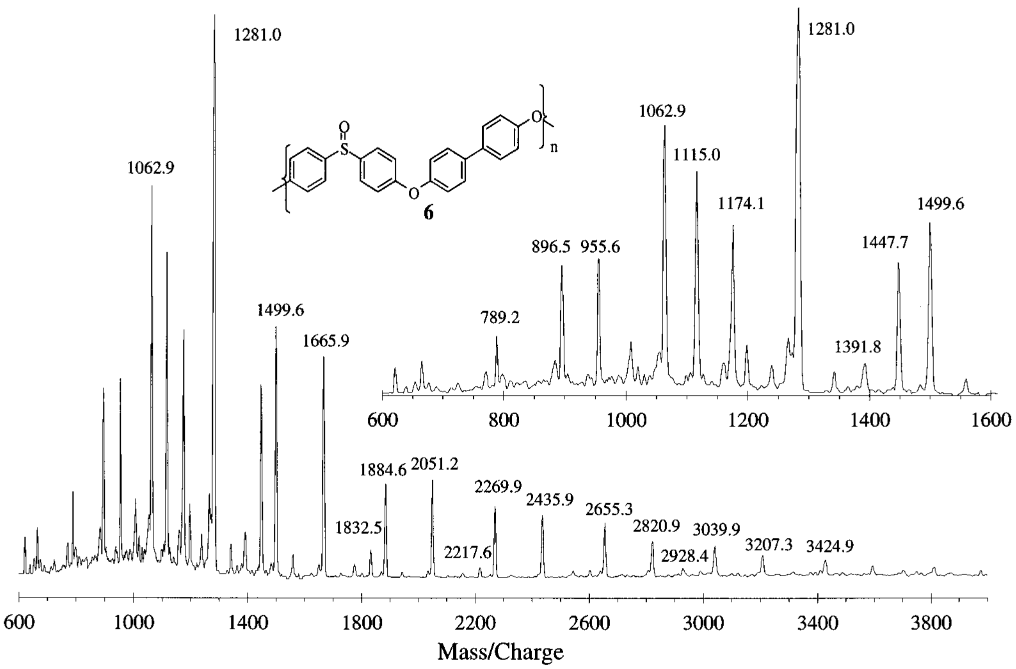
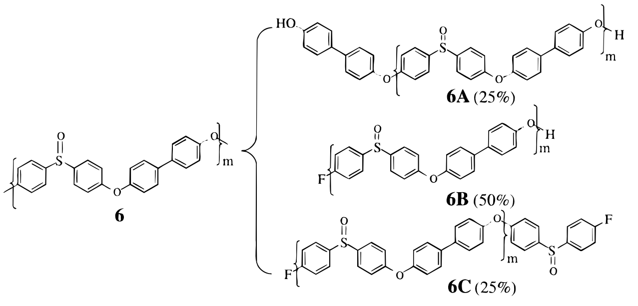


Figure 6. Positive ion MALDI-TOF mass spectrum of linear oligomers **6**. The data were acquired in the reflectron mode using dithranol as the matrix and silver trifluoroacetate as the ionization promoter (dithranol/$AgCO_2CF_3$/**6** = 20:1:1 by weight).

Chart 1



promoter) with repeating units from 2 to 9, and there is no indication of the presence of the molecular ion of **4c**. DSC analysis indicated that cyclics **5c** are semicrystalline with a T_g of 82 °C and have dual melting endothermic peaks centered at 173 and 267 °C. There is also no exothermic peak in the temperature range 300−360 °C.

Ring-Opening Polymerization of Cyclic Aryl Ether Sulfide Oligomers 5a−c. With the cyclic aryl ether sulfide oligomers available, polymerization reactions were next investigated. It was anticipated that the ring-opening polymerization of the macrocyclic aryl ether sulfide oligomers could be initiated through a transthioetherification reaction in the presence of a catalytic amount of organic disulfide such as 2,2′-dithiobis(benzothiazole) (DTB), a novel chemistry reported earlier.[29] Although DSC analysis showed that cyclic **5a** has a melting endotherm starting from 275 °C and ending at 372 °C with a peak temperature of 350 °C, the cyclics only become molten when heated at or above 350 °C. Therefore, the polymerization was conducted at 350 °C. In the presence of 1.0 mol % DTB, polymerization of cyclic oligomers **5a** at 350 °C for 1 h in a test tube under nitrogen led to the formation of polymer which was very tough and only partially soluble in boiling 1-chloronaphthalene. DSC analysis showed that the resulting material is highly crystalline and readily recrystallizes upon heating after quenching without the need of annealing (see Figure 12). The first DSC scan showed that the resulting polymer had a T_g of 150 °C and a T_m of 313 °C with a heat of fusion of 10.3 kJ/mol. It is interesting to note that the T_g and T_m of this material are very close to the corresponding values of the commercial poly(ether ether ketone) (PEEK) (T_g = 144 °C and T_m = 335 °C). After quenching the molten material from 370 °C to room temperature, the second scan showed a T_g of 149 °C, a recrystallization temperature (T_c) of 217 °C, and a T_m of 313 °C with a heat of fusion of 10.2 kJ/mol. The T_g and T_m of this material are essentially identical to those of a chemically identical high molecular weight linear polymer reported.[10]

Melt polymerization of cyclic **5b** at 340 °C for 1 h in the presence of 1.0 mol % DTB led to formation of a material only soluble in boiling 1-chloronaphthalene. DSC analysis showed that the material was highly crystalline and had a T_g of 98 °C, a T_m of 240 °C, and a heat of fusion of 8.3 kJ/mol. Although polymerization of cyclic **5c** at 300 °C for 1 h in the presence of 1.0 mol % DTB resulted in a tough material having only a T_g of 94 °C (a 12 °C increase compared to the starting oligomers **5c**), this material was not soluble in most organic solvents. Due to the insolubility of these materials, solution characterization methods such as viscosity measurement and GPC analysis cannot be performed. Undoubtedly, the materials resulting from ring-opening polymerization of the cyclics **5a−c** are high molecular weight materials as tough drawable films can be obtained directly from the ring-opening polymerization carried out at 300−350 °C.

Conclusions

A convenient and efficient synthetic route for the preparation of macrocyclic arylene ether ether sulfide oligomers via a chemical reduction reaction of sulfoxide precursors was developed. The cyclic aryl ether ether sulfoxide oligomer precursors, obtained in excellent yield, are prepared by an aromatic nucleophilic substitution reaction from the potassium bisphenoxides and bis(4-fluorophenyl) sulfoxide under high-dilution conditions. These oligomers were thoroughly studied by the combination of NMR, MALDI-TOF-MS, GPC, and ther-

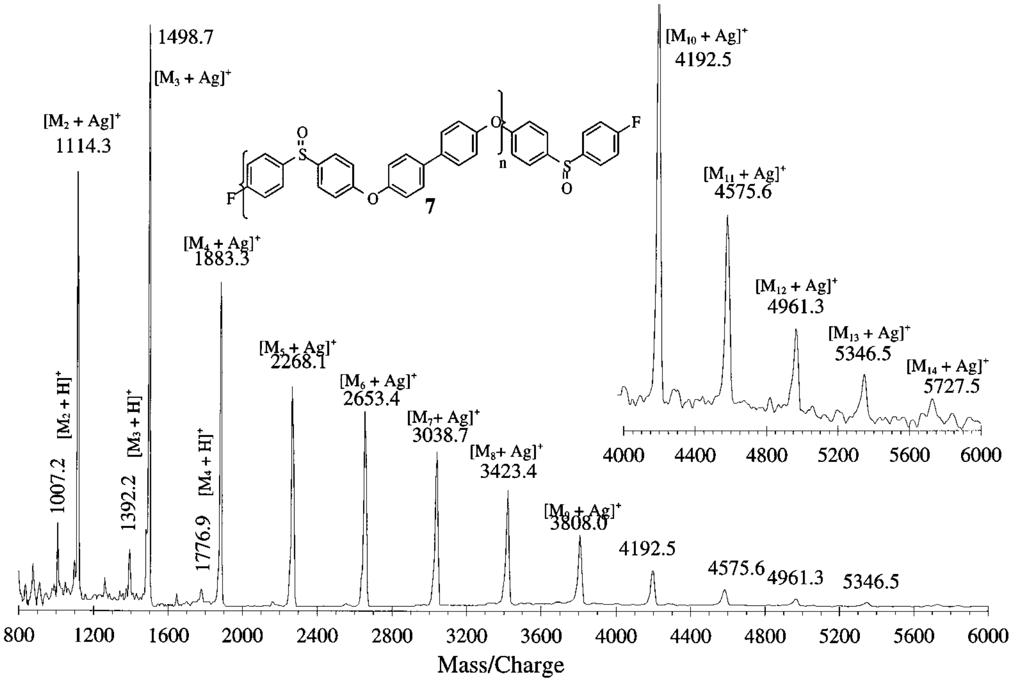


Figure 7. Positive ion MALDI-TOF mass spectrum of the fluoro end-capped linear oligomers **7**. The data were acquired in the reflectron mode using dithranol as the matrix and silver trifluoroacetate as the ionization promoter (dithranol/$AgCO_2CF_3$/**7** = 20:1:1 by weight).

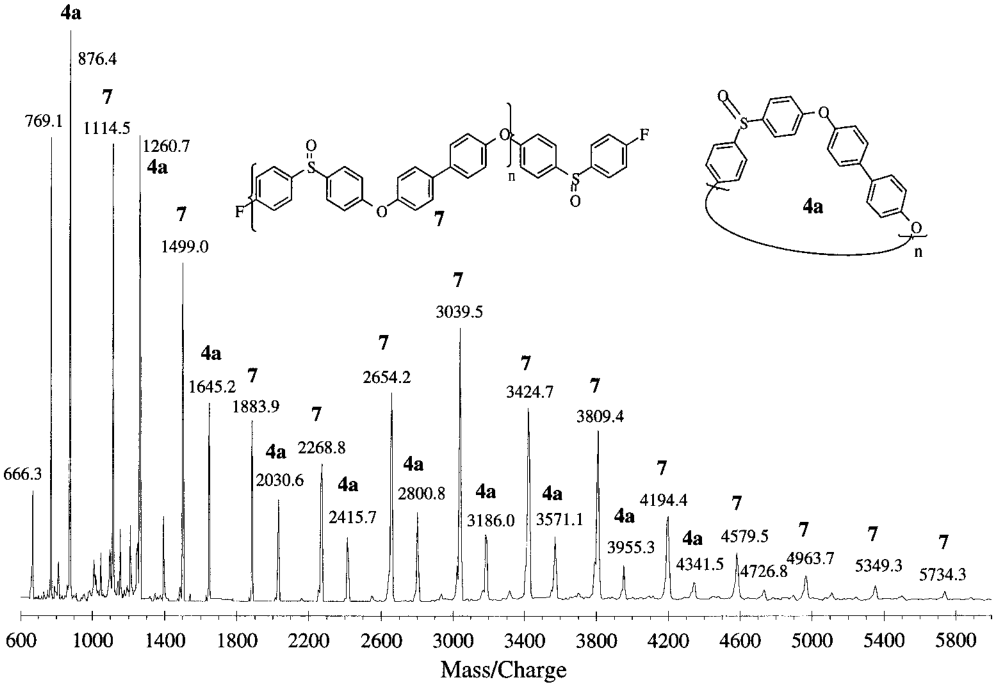


Figure 8. Positive ion MALDI-TOF mass spectrum of the mixture of the cyclic oligomers **4a** and the linear oligomers **7** (**4a**/**7** = 1:1 by weight). The data were acquired in the reflectron mode using dithranol as the matrix and silver trifluoroacetate as the ionization promoter (dithranol/$AgCO_2CF_3$/**4a**/**7** = 20:1:0.5:0.5 by weight).

mal analyses. MALDI-TOF-MS analysis of cyclic **5a**, its linear oligomeric analogs **6** and **7**, and their mixtures shows that MALDI-TOF-MS is a remarkable tool for the end-group analysis and proof of the cyclic nature of the oligomers. The cyclic arylene ether ether sulfide oligomers are prepared by quantitative chemical reduction of the cyclic sulfoxide oligomers with oxalyl chloride and tetrabutylammonium iodide. The quantitative reduction of the cyclic sulfoxide oligomers to cyclic sulfide oligomers was confirmed by NMR and MALDI-TOF-MS analyses of sulfoxide **4c** and its corresponding sulfide **5c**. Thermal analyses showed that the cyclic sulfoxide oligomers are amorphous with T_g varying from 140 to 199 °C. On the other hand, the corresponding cyclic sulfide oligomers are highly crystalline with T_m varying from 237 to 350 °C. Upon chemical reduction, the sulfide oligomers have much higher thermal stability than their sulfoxide precursors. Ring-opening polymerization of the molten oligomeric cyclics **5a** and **5b** in the presence of a catalytic amount of organic disulfide DTB leads to high molecular weight semicrystalline poly(arylene ether ether sulfide)s. A tough semicrystalline polymer obtained from ROP of **5a** has a T_g of 150 °C and a T_m of 313 °C. Further studies on the preparation of soluble poly(aryl ether ether sulfide)s via cyclic aryl ether sulfide oligomers and the fundamentals

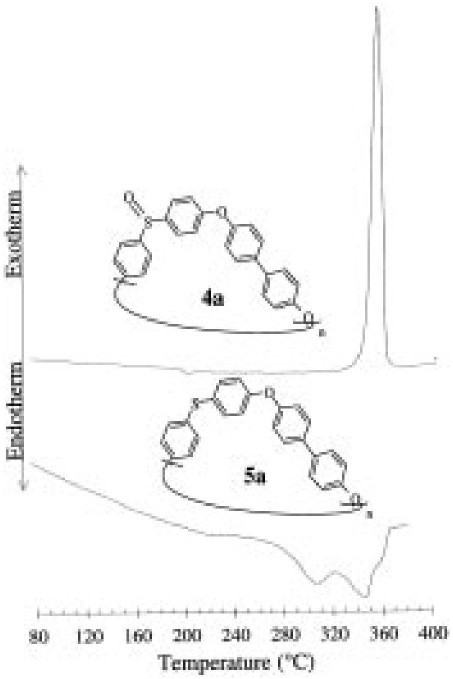


Figure 9. DSC traces of cyclic aryl ether ether sulfoxide oligomers **4a** and its corresponding sulfide oligomers **5a**.

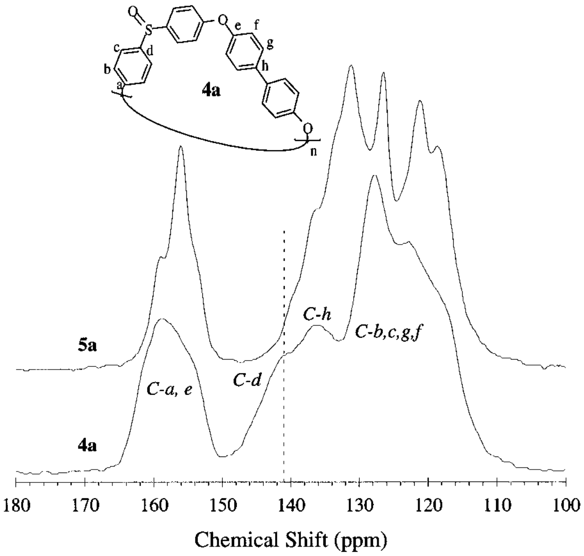


Figure 10. Solid-state ^{13}C CP-MAS NMR spectra of cyclic aryl ether ether sulfoxide oligomers **4a** and its corresponding sulfide oligomers **5a**.

of the polymerization reaction will be reported in due course.

Experimental Section

Instruments and Procedures. Nuclear magnetic resonance spectra were recorded on a Varian Unity-500 NMR spectrometer using $CDCl_3$ or $Cl_2DCCDCl_2$ as the solvents. Proton spectra were referenced to internal tetramethylsiliane (TMS), while ^{13}C NMR spectra were referenced to the $CDCl_3$ middle line at 77.0 ppm when $CDCl_3$ was used as solvent. ^{19}F NMR spectra were referenced to fluorobenzene at -112.67 ppm. The GPC analyses of the macrocyclic sulfoxide oligomers and linear polymers were carried out on a Waters 510 HPLC using four Phenogel 5 m columns in series (each 300 mm × 7.8 mm i.d., one linear and three 500 Å). HPLC grade tetrahydrofuran (THF) containing 0.5% w/v LiBr was used as the eluent with a flow rate of 1.0 mL/min, the UV detector was at 254 nm, and polystyrene standards were used for the calibration. Thermal analyses of macrocyclic oligomers were carried out on Seiko 220 DSC and 220 TGA/DTA instruments at a heating rate of 20 °C/min under nitrogen (a flow rate of 150 mL/min). Solid-state CP-MAS and DP-MAS ^{13}C NMR experiments were performed on a Chemagnetics CMX-300 spectrometer at 75 MHz with the spinning rate of 5 kHz.

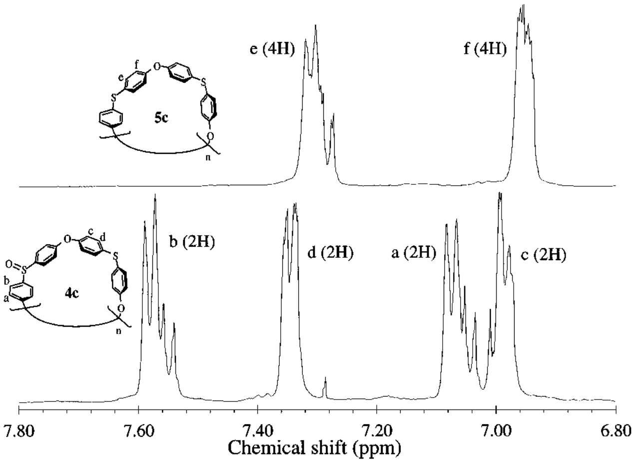


Figure 11. ^{1}H NMR spectra (in TCE-d_2) of cyclic aryl ether ether sulfoxide oligomers **4c** and its corresponding sulfide oligomers **5c**.

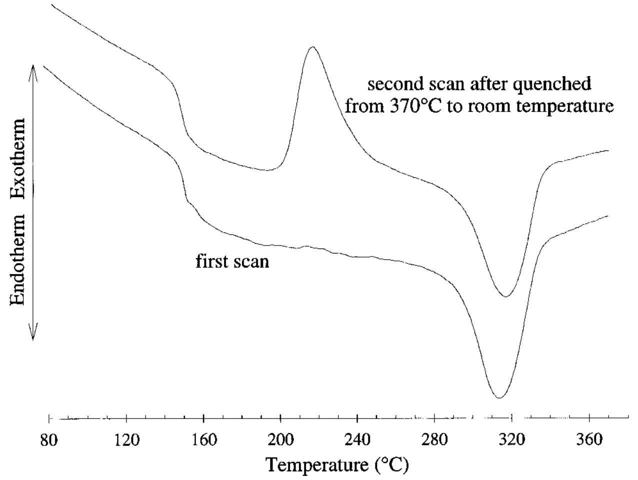


Figure 12. DSC traces of the polymer resulting from ring-opening polymerization of the cyclic aryl ether ether sulfide oligomers **5a** at 350 °C under nitrogen for 1 h in the presence of 1.0 mol % DTB.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Kratos Kompact MALDI-III TOF instrument with a maximum laser output of 6 mW at a wavelength of 337 nm (N_2 laser light, 3 ns pulse width, 100 mm diameter spot). The MALDI instrument was operated in a positive reflectron mode. The ions produced from each laser shot were accelerated to 20 keV into a 1 m drift region. An external calibration using bovine insulin and angiotension was used; this provides mass accuracy within 0.02% for this instrument. The matrix used for all experiments was 1,8,9-anthracenetriol (dithranol) (Aldrich). Samples were prepared by dissolving the cyclic oligomers in 1,1,2,2-tetrachloroethane (TCE) at a concentration of 5.0 mg/mL. Silver trifluoroacetate or lithium bromide was used as the ionization promoter with a stock solution of 5.0 mg/mL in THF. A 20 mL of the sample solution and 20 mL portion of the silver trifluoroacetate or lithium bromide solution were added to 200 mL of a 10 mg/mL solution of the matrix dissolved in chloroform. This final solution was shaken briefly, and 0.5 mL was applied to a stainless steel sample slide and air-dried prior to analysis.

Starting Materials. Reagent-grade solvents and chemicals were obtained from Aldrich and used without further purification. 2,2-Bis(4-hydroxyphenyl)hexafluoropropane was obtained from Kennedy & Klim Inc., and hydroquinone (99.9%) was obtained from Aldrich and used without further purification. 4,4′-Biphenol and 4,4′-thiobisphenol were obtained from Aldrich and recrystallized from methanol.

Bis(4-fluorophenyl) sulfoxide was prepared as follows. A 3 L three-neck round-bottom flask equipped with a mechanical stirrer, condenser, addition funnel, and nitrogen inlet was charged with 173.0 g (1.80 mol) of fluorobenzene, 320 g (2.29 mol) of anhydrous aluminum chloride, and 1.5 L of carbon disulfide. The mixture was stirred at room temperature under nitrogen. Then 60 mL (0.83 mol) of thionyl chloride was added slowly over 1 h. After stirring the reaction mixture for 16 h under gentle heating (the temperature was kept under 50 °C), the mixture was added to 4 kg of ice containing 100 mL of concentrated hydrochloric acid. The organic layer was separated and carbon disulfide was removed by distillation under nitrogen. The product was then recrystallized from a mixture of petroleum ether (bp 35−60 °C) and diethyl ether. Yield 95%; mp 51−52 °C; ^{1}H NMR (CDCl$_3$, TMS) δ (ppm) 7.17 (t, 4H), 7.63 (dd, 4H); ^{13}C NMR (CDCl$_3$) δ (ppm) 116.6, 116.8, 127.0, 127.1, 141.0, 163.3, 165.3; ^{19}F NMR (CDCl$_3$, FPh) δ −107.61 ppm.

Preparation of Poly(aryl ether ether sulfoxide) 1. The polymerization was conducted in a 50 mL three-neck round-bottom flask which was equipped with a magnetic stirrer, a nitrogen inlet, thermometer, Dean−Stark trap, and condenser. The flask was charged with bis(4-fluorophenyl) sulfoxide (2.3825 g, 10.0 mmol), 2,2′-bis(4-hydroxyphenyl)hexafluoropropane (3.3287 g, 9.9 mmol), anhydrous potassium carbonate (2.7640 g, 20.0 mmol), DMAc (25 mL), and toluene (10 mL). The mixture was magnetically stirred and heated under reflux for 30 min. The temperature range of the mixture was at 130−135 °C. Then the reaction temperature was gradually increased to 160 °C over 30 min by removal of toluene from the Dean−Stark trap. After another 3 h at 160 °C, the reaction mixture was cooled and precipitated into methanol. The precipitated fibrous product was filtered, redissolved into 30 mL of chloroform, and filtered through a layer of Celite. The filtrate was then concentrated to 10 mL and precipitated into methanol. The precipitate was filtered and dried at 150 °C in a vacuum oven to a constant weight to give polymer **1** (4.1 g, 77% yield, $M_n = 54\,200$ and $M_w = 111\,100$). ^{1}H NMR (CDCl$_3$, TMS) δ (ppm) 6.98 (d, $J = 8.8$ Hz, 2H), 7.11 (d, $J = 8.8$ Hz, 2H), 7.37 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ (ppm) 118.55, 119.72, 122.92, 122.94, 125.21, 126.98, 128.63, 131.91, 140.20, 156.69, 158.86.

Reduction of Sulfoxide Polymer 1 to the Corresponding Sulfide Polymer 2. Poly(aryl ether ether sulfide) **2** ($M_n = 54\,000$ and $M_w = 111\,800$) was prepared by chemical reduction of sulfoxide polymer **1** with oxalyl chloride and tetrabutylammonium iodide according to a reported procedure.[10] ^{1}H NMR (CDCl$_3$, TMS) δ (ppm) 6.95 (d, $J = 8.8$ Hz, 2H), 6.98 (d, $J = 8.8$ Hz, 2H), 7.33 (d, $J = 8.8$ Hz, 4H); ^{13}C NMR (CDCl$_3$) δ (ppm) 117.71, 120.42, 123.02, 125.29, 127.85, 130.91, 131.75, 132.82, 155.45, 157.63.

General Procedure for Synthesis of Macrocyclic Aryl Ether Sulfoxide Oligomers 4a−c from Bis(4-fluorophenyl) Sulfoxide. The synthesis of macrocyclic oligomers **4a** is used as an example. The cyclization was conducted in a 1 L three-neck round-bottom flask which was equipped with a Dean−Stark trap and condenser, a thermometer, and a nitrogen inlet. The reaction vessel was charged with DMF (560 mL), toluene (80 mL), and anhydrous potassium carbonate (8.706 g, 63.00 mmol). The mixture was magnetically stirred and heated under reflux under argon. The refluxing temperature was kept at 145 °C. Then a solution of bis(4-fluorophenyl) sulfoxide (7.1476 g, 30.0 mmol) and 4,4′-biphenol **3a** (5.5864 g, 30.0 mmol) in DMF (40 mL) was added over an 8 h period via a syringe pump. After the addition, the resulting solution was kept at 145−148 °C for another 8 h to ensure complete reaction. The reaction mixture was cooled and filtered to remove salts. The filtrate was then concentrated to 100 mL under reduced pressure and added dropwise into vigorously stirring distilled water (800 mL) containing 10 mL of concentrated hydrochloric acid. The desired oligomers precipitated as a white solid, which were collected by filtration and washed with distilled water until acid-free (checked with pH paper). Then the solid was stirred in 200 mL of methanol for 30 min, filtered, and dried in a vacuum oven at 150 °C for 24 h to give a white powder product (10.4 g, 96% yield). A similar procedure was applied for the preparation of the macrocyclic oligomers **4b** and **4c**. Yields of the products are listed in Table 1.

Preparation of Linear Oligomers 6. To a 25 mL three-neck round-bottom flask equipped with a magnetic stirrer, a nitrogen inlet, thermometer, Dean−Stark trap, and condenser were added bis(4-fluorophenyl) sulfoxide (2.3825 g, 10.0 mmol), 4,4′-biphenol (1.8621 g, 10.0 mmol), anhydrous potassium carbonate (2.073 g, 15.0 mmol), DMF (12.5 mL), and toluene (10.0 mL). The mixture was magnetically stirred and heated to reflux. The reaction temperature was raised to 140 °C over 10 min by partially removing toluene via the Dean−Stark trap. After another 1 h at 140 °C, the reaction mixture was cooled and precipitated into methanol. The precipitated product was filtered, redissolved into 30 mL of chloroform, and filtered through a layer of Celite. The filtrate was then concentrated to 10 mL and precipitated into methanol. The precipitate was filtered and dried at 150 °C in a vacuum oven to a constant weight to give linear oligomers **6** (2.7 g, 70% yield) ($M_n = 2300$ and $M_w = 3100$).

Preparation of Linear Oligomers 7. Linear oligomer **7** ($M_n = 2900$ and $M_w = 4600$) was prepared using an excess of bis(4-fluorophenyl) sulfoxide (5.3 mol % in excess) following the procedure described in the preceding paragraph.

Preparation of Macrocyclic Aryl Ether Ether Sulfide Oligomers 5a−c. The chemical reduction of sulfoxide cyclic oligomers **4a** to the corresponding sulfide cyclic oligomers **5a** is used as an example. To a 500 mL three-neck round bottom flask equipped with a magnetic stirrer, nitrogen inlet and condenser, were charged cyclic oligomers **4a** (7.69 g, 20.0 mmol), tetrabutylammonium iodide (18.81 g, 48.62 mmol), and 1,1,2,2-tetrachloroethane (250 mL). The mixture was magnetically stirred and heated to 50 °C under a slow stream of nitrogen. Once the mixture became a clear solution, oxalyl chloride (2.14 mL, 24.0 mmol) was added rapidly through a septum via syringe to the rapidly stirring solution. Immediately upon introduction of the oxalyl chloride, iodine was liberated, gas was evolved, and the corresponding sulfide cyclic oligomers precipitated in the form of fine particles. The reaction mixture was stirred at 50 °C for 10 min, then poured into vigorously stirred methanol (1000 mL), and filtered. The solid was washed several times with methanol and transferred into a beaker containing a 5% w/v aqueous solution of sodium thiosulfate (600 mL). After stirring for 2 h, the solid was again collected by filtration and washed several times with boiling distilled water (1 L) followed by methanol (400 mL). The solid was then dried in a vacuum oven (150 °C) for 24 h to give cyclic oligomers **5a** as a white powder (7.2 g, 97% yield).

Ring-Opening Polymerization Reaction of Cyclic Aryl Ether Ether Sulfides 5a−c. The ring-opening polymerization of the cyclic sulfide oligomers was achieved in the melt using disulfide DTB as initiator. A typical polymerization procedure is as follows: cyclic **5a** (1.0 g, 2.71 mmol) was mechanically mixed with disulfide DTB (9.0 mg, 0.027 mmol) in a 50 mL dry test tube. After sweeping with nitrogen for 5 min, the test tube was sealed with a septum which was equipped with a nitrogen inlet and outlet. The test tube was then placed into a preheated salt bath at 350 °C for 1 h. Upon disassembling the apparatus, a tough partly foamy product was obtained with a smooth surface on the bottom side next to the glass. Also found was a tough film which adhered to the surface of the bulk of the polymer and the wall of the glass test tube. This film was peeled away and was found to be both flexible and creasable and, hence, tough. The bulk of the polymer was so tough that a hammer had to be used to break it.

Acknowledgment. The authors acknowledge the financial support of this work by the Natural Sciences and Engineering Research Council of Canada. The authors are also grateful to Dr. Fred Morin for his assistance with solid-state NMR analyses.

References and Notes

(1) Seymour, R. B.; Kirshenbaum, G. S., Eds.; *High Performance Polymers: Their Origins and Development*; Elsevier: Amsterdam, 1986.

(2) Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* **1988**, *29*, 358.
(3) Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R. J.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, *22*, 1096.
(4) Geibel, J. F.; Campbell, R. W. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon: Oxford, U.K., 1989; Vol. 5, Chapter 32.
(5) Durvasula, V. R.; Stuber, F. A.; Bhattacharjee, D. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 661.
(6) Roovers, J.; Cooney, J. D.; Toporowski, P. M. *Macromolecules* **1990**, *23*, 1611.
(7) Hara, A.; Oishi, Y.; Kakikoto, M.-A.; Imai, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1933.
(8) Wang, Z. Y.; Hay, A. S. *Polymer* **1992**, *33*, 1779.
(9) Senn, D. R. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 1175.
(10) Bau, J. R.; Brink, A. E.; Konas, M.; Riffle, J. S. *Polymer* **1994**, *35*, 4949.
(11) Carlsson, L. A., Ed. *Thermoplastic Composite Materials*; Elsevier: Amsterdam, 1991.
(12) Brunelle, D. J. In *Ring-Opening Polymerization: Mechanisms, Catalysis, Structure, Utility*; Brunelle, D. J., Ed.; Hanser, New York, 1993; Chapter 11 and references cited therein.
(13) Guggenheim, T. L.; McCormick, S. J.; Kelly, J. J.; Brunelle, D. J.; Colley, A. M.; Boden, E. P.; Shannon, T. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 579.
(14) Fukuyama, J. M.; Talley, J. J.; Cella, J. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 581.
(15) Mullins, M. J.; Woo, E. P.; Chen, C. C.; Murray, D. J.; Bishop, M. T.; Balon, K. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (2), 174.
(16) Mullins, M. J.; Galvan, R.; Bishop, M. T.; Woo, E. P.; Gorman, D. B.; Chamberlain, T. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 414.
(17) Colquhoun, H. M.; Dudman, C. C.; Thomas, M.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 336.
(18) Memeger, M., Jr.; Lazar, L.; Ovenall, D.; Leach, R. A. *Macromolecules* **1993**, *26*, 3476.
(19) Takekoshi, T.; Terry, J. M. U.S. Patent 5,362,845, 1994.
(20) Chan, K. P.; Wang, Y.-F.; Hay, A. S. *Macromolecules* **1995**, *28*, 653.
(21) Chan, K. P.; Wang, Y.-F.; Hay, A. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36* (2), 132.
(22) Chan, K. P.; Wang, Y.-F.; Hay, A. S.; Hronowski, X. L.; Cotter, R. J. *Macromolecules* **1995**, *28*, 6705.
(23) Wang, Y.-F.; Chan, K. P.; Hay, A. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36* (2), 130.
(24) Wang, Y.-F.; Chan, K. P.; Hay, A. S. *J. Polym. Sci., Polym. Chem. Ed.* **1996**, *34*, 375.
(25) Wang, Y.-F.; Chan, K. P.; Hay, A. S. *J. Appl. Polym. Sci.* **1996**, *59*, 831.
(26) Wang, Y.-F.; Paventi, M.; Chan, K. P.; Hay, A. S. *J. Polym. Sci., Polym. Chem. Ed.* **1996**, *34*, 2135.
(27) Wang, Y.-F.; Chan, K. P.; Hay, A. S. *React. Polym.* **1996**, *30*, 205.
(28) Wang, Y.-F.; Chan, K. P.; Hay, A. S. *Macromolecules* **1995**, *28*, 6371.
(29) Wang, Y.-F.; Chan, K. P.; Hay, A. S. *Macromolecules* **1996,** *29*, 3717.
(30) Carter, K. R. *Macromolecules* **1995**, *28*, 6462.
(31) (a) Karas, M.; Hillenkamp, F. *Anal. Chem.* **1988**, *60*, 2299. (b) Hillenkamp, F.; Karas, M.; Beavis, R. C.; Chait, B. T. *Anal. Chem.* **1991**, *63*, 1193A.
(32) (a) Beavis, R. C.; Chait, B. T. *Rapid Commun. Mass Spectrom.* **1989**, *3*, 233. (b) Bahr, U.; Karas, M.; Hillenkamp, F. *Anal. Chem.* **1992**, *64*, 2866.

MA961044O