Cyclic Aromatic Disulfide Oligomers: Synthesis and Characterization

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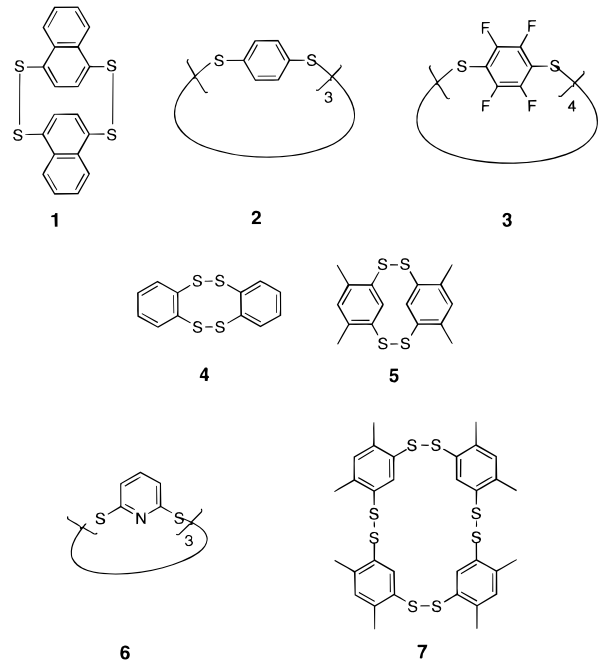
ABSTRACT: A series of cyclic aromatic disulfide oligomers have been synthesized in high yields by catalytic oxidization of arenedithiols in DMAc. The aryl groups contain moieties such as ketone, sulfone, isopropylidene, ether, thioether, and phenylphosphine oxide groups. The cyclic aromatic disulfide oligomers have been analyzed by gradient HPLC, GPC, ^{1}H-NMR, MALDI-TOF-MS, DSC, and TGA methods. Repeating units up to 9 for some cyclic aromatic disulfide ketone oligomers have been confirmed by MALDI-TOF-MS. In general, these cyclic aromatic disulfide oligomers are soluble in common organic solvents and have sharp melting points. Cyclic disulfide ketone oligomers and cyclic disulfide sulfone oligomers have higher glass transition temperatures and melting points than their ether or thioether counterparts.

Introduction

Although the first cyclic aromatic disulfide **1**, reported 40 years ago,[1] was synthesized with an unspecified yield from oxidation of 1,4-naphthalenedithiol with alkaline ferricyanide, only a few other cyclic aromatic disulfides have been reported since then. In 1976, Wong and Marvel synthesized a cyclic trimer **2** in 30% yield by oxidation of 1,4-dimercaptobenzene with iodine in ethanol and studied its application as a cross-linking agent.[2] Aimed at the synthesis of some novel complexing cyclics, Raasch was able to prepare a macrocyclic tetradisulfide **3** in 89% yield by using DMSO as oxidizing agent.[3] Cyclic aromatic disulfides **4**−**7** have been synthesized by using iodine as oxidizing agent,[4−6] and the structure of **7** has been confirmed by X-ray analysis.[6] The drive for the synthesis of most of these cyclics has been to study their structural geometry and their potential for complexation. Recently, extensive efforts have been devoted to the synthesis of cyclic oligomers for precursors of high molecular weight polymers,[7] since cyclic precursors have lower melt viscosities which facilitate the processing. Although aliphatic polydisulfides have long been prepared from cyclic aliphatic disulfides,[8] there is little work carried out on the synthesis of aromatic polydisulfides from cyclic aromatic disulfides.[9] The aromatic polydisulfides have been studied to a limited extent due to their insolubilities in common organic solvents.[10]

Disulfide−disulfide interchange is relatively slow at temperatures below 150 °C or in the absence of UV light. Trace amounts of sulfur, mercaptides, or alkaline agents capable of generating mercaptides by reaction with disulfide bonds catalyze the exchange reaction at moderate temperatures.[11] At high temperatures, the exchange reaction between disulfide bonds is much faster. Therefore, it is anticipated that cyclic aromatic disulfides would ring open and form high molecular weight polymers at high temperature without adding any catalyst. Since cyclic aromatic disulfide oligomers are readily soluble in organic solvents and can be easily purified, preparing aromatic polydisulfides from cyclic aromatic disulfide oligomers could be a practical way to apply aromatic polydisulfides in coatings, sealants, etc. Furthermore, cyclic aromatic disulfide oligomers could be potentially applied as cross-linking reagents. In 1991, Wang and Hay reported that poly(*p*-phenylene sulfide) (PPS) can be prepared by heating 4,4′-diiodophenyl disulfide.[12,13] Cyclic aromatic disulfide oligomers are also potentially very useful intermediates for the synthesis of aromatic polysulfides by reacting with diiodo or dibromo compounds.

Chart 1



Herein, we report the synthesis and characterization of a series of cyclic aromatic disulfide oligomers by copper-catalyzed oxidation of dithiol compounds with oxygen. Subsequent papers will report the details of studies on the ring-opening polymerization reaction of cyclic aromatic disulfide oligomers[14] and the synthesis of polysulfides from cyclic aromatic disulfide oligomers.[15]

Experimental Section

Gradient HPLCs were performed on a Milton Roy CM4000 multiple solvent delivery system with a C8 Prime Sphere 4.6 × 250 mm column, THF and water as eluent solvents, and a UV detector at 300 nm. Gel permeation chromatography (GPC) analyses were performed on a Waters 510 HPLC equipped with 5 μm Phenogel columns (linear, 3 × 500 Å)

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arranged in series with chloroform as solvent and a UV detector at 254 nm. Differential scanning calorimetry (DSC) scans were obtained using a Seiko 220 DSC instrument at a heating rate of 20 °C/min in N_2 (160 mL/min). The weight loss data were obtained from a Seiko 220 TG/TGA instrument at a heating rate of 20 °C/min in nitrogen. NMR data were recorded at 500 MHz on a Varian UNITY500 NMR instrument and are listed in parts per million downfield from tetramethylsilane. Elemental analyses (C, H, S) were performed by Fine Chemical Analysis (Ontario, Canada) and Galbraith Laboratories, Inc. (Knoxville, TN). Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analyses were performed on a Kratos KOMPACT MALDI-TOF-MS. The analyte consisted of 1.0:4.0:200 (w) of cyclic oligomers, lithium bromide, and 1,8,9-trihydroxyanthracene (Dithranol) matrix. A sample (0.2 μL) of this analyte was spotted on the sample slot and air-dried. All spectra were obtained in the reflectron mode. Melting points were taken on a Fisher-Johns melting point apparatus and the thermometer was uncorrected.

All the chemicals used were reagent grade and purified by standard methods. The required 4,4′-thiobis(benzenethiol) (**9a**) and *m*-benzenedithol (**9b**) were purchased from Aldrich Chemical Inc. Other arenedithiols were prepared according to the methods illustrated in Schemes 2−4. *N*,*N*′-Dimethylthiocarbamoyl chloride (Aldrich), chlorosulfonic acid (Omega), and sodium hydrogen sulfide monohydrate (Fluka) were used as received.

Starting materials 1,2-bis(4-fluorobenzoyl)benzene, 1,2-bis-(4-fluorobenzoyl)-3,6-diphenylbenzene, and 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene were prepared according to literature procedures.[16] 1,3-Bis(4-fluorobenzoyl)benzene was synthesized according to the published procedure.[17] Bis(4-fluorophenyl)phenylphosphine oxide was prepared by a Grignard technique.[18] Other starting materials were purchased from chemical suppliers.

4,4′-Biphenyldithiol (**9c**) and 4,4′-oxybis(benzenethiol) (**9d**) were prepared according to reported procedures.[19] 4,4′-Bis-(1-mercaptophenylene)-2,2′-propane (**9e**) was prepared by the route illustrated in Scheme 1. 1,4-Benzenedithiol (**9f**) and tetrafluoro-1,4-benzenedithiol (**9g**) were synthesized by the methods given in the literature.[3,20]

Bis(4-(chlorosulfonyl)phenyl)-2,2′-propane (8e). A 250 mL round-bottom flask was charged with 65 mL of chlorosulfonic acid and cooled to ca. −10 °C. 2,2′-Diphenylpropane (25.0 g, 0.127 mol) was added to the reaction mixture over 2 h via a dropping funnel. The resulting mixture was warmed to room temperature and kept at this temperature for 4 h. Then it was poured carefully into 1 kg of ice. The product was extracted with ca. 300 mL of toluene, and the organic solvent was evaporated to dryness with a rotary evaporator. The resulting solid was recrystallized from acetic acid and dried at room temperature under vacuum. Yield: 25.6 g, 50.7%. Mp 154−156 °C. ^{1}H NMR ($CDCl_3$): δ 7.98 (d, 4H, J = 7.81 Hz), 7.46 (d, 4H, J = 7.81 Hz), 1.79 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 156.9, 142.4, 128.1, 127.2, 44.3, 30.1.

Bis(4-mercaptophenyl)-2,2′-propane (9e). Compound **8e** (25.0 g, 0.063 mol) prepared above was added to a 1000 mL round-bottom flask charged with 300 mL of absolute ethanol, 300 mL of concentrated hydrochloric acid, and 250 g of stannous chloride dihydrate. The resulting mixture was heated to reflux for 8 h. After cooling, it was diluted with 1000 mL of water and filtered. The solid was dissolved in 600 mL of 5% NaOH solution and precipitated out by adding 10% HCl solution. This procedure was repeated three times and then the material was recrystallized from ethanol. Yield: 11.2 g, 77.6%. Mp 66−67 °C (lit.[21] 69−70 °C). ^{1}H NMR ($CDCl_3$): δ 7.17 (d, 4H, J = 8.1 Hz), 7.07 (d, 4H, J = 8.1 Hz), 3.38 (s, 2H, SH). ^{13}C NMR ($CDCl_3$): δ 148.1, 129.4, 127.6, 127.5, 42.3, 30.5.

4,4′-Dimercaptobenzophenone (9h). Sodium hydrogen sulfide monohydrate (22.2 g, 0.3 mol) was dissolved in DMF (100 mL) by heating to reflux. After cooling, 4,4′-difluorobenzophenone (10.91 g, 0.05 mol) was added carefully to the flask and the reaction mixture was kept at reflux for 5 h (**Caution: H_2S, which must be trapped and oxidized by passing through a 30% NaOH solution and a bleach solution (NaOCl), is produced during the reaction!**). The reaction mixture was then allowed to cool to room temperature and the precipitated salt was filtered. The filtrate was diluted with 200 mL of water and acidified with a 5% HCl solution. The precipitate was collected by filtration, then dissolved in 600 mL of 5% NaOH solution, and reprecipitated by adding 10% HCl solution. This purification process was repeated three times and the solid product was dried at room temperature under vacuum. Yield: 9.20 g (74.7%). Mp 171−174 °C (lit.[22] 178 °C, ethanol). ^{1}H-NMR ($CDCl_3$): δ 7.65 (d, 4H, J = 6.4 Hz), 7.33 (d, 4H, J = 6.4 Hz), 3.64 (s, 2H, SH).

The following compounds were similarly prepared but using the reagents described in Scheme 4. In all cases, the amounts of difluoro or dichloro compounds used were 0.05 mol.

1,3-Bis(4-mercaptobenzoyl)benzene (9i). Yield: 91.0%. Mp 178−181 °C. ^{1}H-NMR ($CDCl_3$): δ 8.10 (s, 1H), 7.97 (m, 2H), 7.70 (d, 4H, J = 8.3 Hz), 7.62 (m, 1H), 7.34 (d, 4H, J = 8.3 Hz), 3.67 (s, 2H, SH). HRMS: found, 350.0433 (64.8%); calcd for $C_{20}H_{14}O_2S_2$, 350.0435.

1,2-Bis(4-mercaptobenzoyl)benzene (9j). Yield: 91.4%. Mp 156−158 °C (toluene). ^{1}H-NMR ($CDCl_3$): δ 7.59 (s, 4H), 7.56 (d, 4H, J = 8.3 Hz), 7.22 (d, 4H, J = 8.3 Hz), 3.62 (s, 2H, SH). HRMS: found, 350.0433 (64.8%); calcd for $C_{20}H_{14}O_2S_2$, 350.0435.

1,2-Bis(4-mercaptobenzoyl)-3,6-diphenylbenzene (9k). Yield: 89.2%. Mp 165−168 °C (toluene). ^{1}H-NMR ($CDCl_3$): δ 7.59 (s, 2H), 7.40 (d, 4H, J = 7.8 Hz), 7.21 (m, 10H), 6.99 (d, 4H, J = 7.8 Hz), 3.46 (s, 2H, SH). HRMS: found, 502.1065 (100%); calcd for $C_{32}H_{22}O_2S_2$, 502.1061.

1,2-Bis(4-mercaptobenzoyl)-3,4,5,6-tetraphenylbenzene (9l). Yield: 93.2%. Mp 203−204 °C (toluene). ^{1}H-NMR ($CDCl_3$): δ 7.43 (d, 4H, J = 7.8 Hz), 7.00 (d, 4H, J = 7.8 Hz), 6.85(m, 20H), 3.46 (s, 2H, SH). HRMS: found, 654.1685 (100%); calcd for $C_{44}H_{30}O_2S_2$, 654.1687.

4,4′-Mercaptobenzil (9m). Yield: 96.2%. Mp 140−141 °C. ^{1}H-NMR ($CDCl_3$): δ 7.81 (d, 4H, J = 8.3 Hz), 7.33 (d, 4H, J = 8.3 Hz), 3.71 (s, 2H, SH). HRMS: found, 274.0124 (4.5%); calcd for $C_{14}H_{10}O_2S_2$, 274.0122.

Bis(4-mercaptophenyl)sulfone (9n). Yield: 61.0%. Mp 137−139 °C (toluene). ^{1}H-NMR ($CDCl_3$): δ 7.44 (d, 4H, J = 8.3 Hz), 7.32 (d, 4H, J = 8.3 Hz), 3.65 (s, 2H, SH). HRMS: found, 281.9844 (100%); calcd for $C_{12}H_{10}O_2S_3$, 281.9843.

Bis(4-mercaptophenyl)phenylphosphine Oxide (9o). Yield: Mp 74−76 °C. ^{1}H-NMR ($CDCl_3$): δ 7.63 (t, 2H, J = 7.8 Hz, PhH), 7.55 (d, 2H, J = 6.8 Hz, PhH), 7.50 (s, 1H, PhH), 7.47 (d, 4H, J = 10.3 Hz), 7.32 (d, 4H, J = 10.3 Hz), 3.63 (s, 2H, SH). HRMS: found, 342.0298 (100%); calcd for $C_{18}H_{15}OPS_2$, 342.0302.

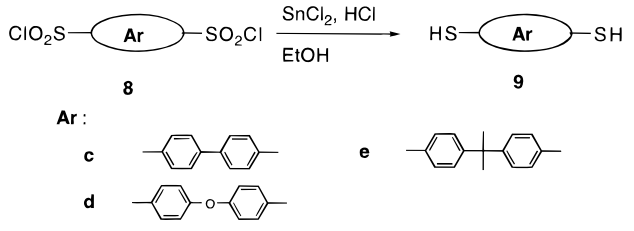
General Procedure for Preparation of Cyclic Aromatic Disulfide Oligomers. A 500 mL three-neck round-bottom flask equipped with a condenser, a dropping funnel, and oxygen inlet was charged with 0.5 g of CuCl, 1.1 g of tetramethylethylenediamine (TMEDA), and 200 mL of DMAc. The mixture was vigorously stirred for 15 min with oxygen bubbling directly into the reaction mixture. Then 0.01 mol of the arenedithiol dissolved in 50−100 mL of DMAc was added dropwise to the reaction mixture over 2 h. The resulting mixture was stirred for another hour to ensure the completion of the reaction and was then filtered through a layer of alumina. The filtrate was treated with 300 mL of 5% HCl solution and further stirred for 1 h. The precipitate was collected by filtration and dried at 50 °C under vacuum for 48 h.

For the preparation of **14c**, **14h**, and **14j**, the products are not soluble in DMAc, and the resulting reaction mixtures were poured into 500 mL of 5% HCl solution directly without filtration and stirred for 3 h to remove the copper salt. This procedure was repeated three times.

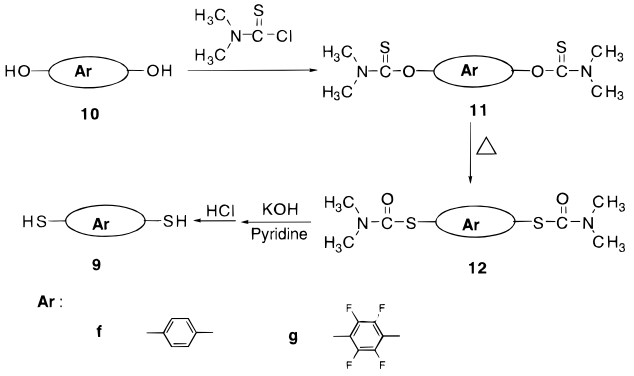
Results and Discussion

1. Synthesis of Aromatic Dithiol Compounds. Three different methodologies have been used to prepare arenedithiols, which are illustrated in Schemes 1−3. Compound **9e** was synthesized from 2,2′-diphenylpropane. Chlorosulfonation of 2,2′-diphenylpropane

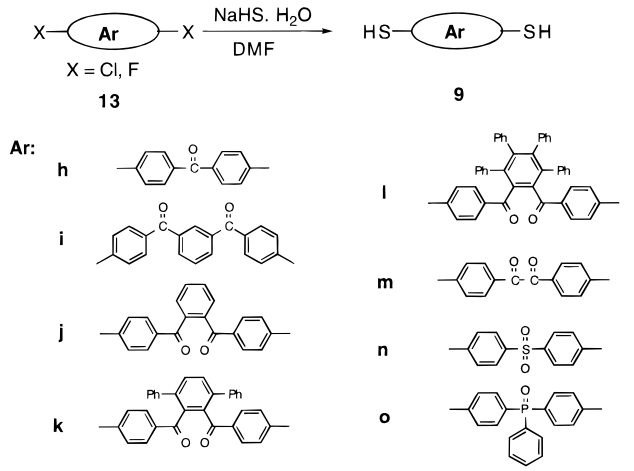
Scheme 1. Preparation of Arenedithiols from Arenedisulfonyl Chlorides



Scheme 2. Preparation of Arenedithiols from Dihydroxy Compounds

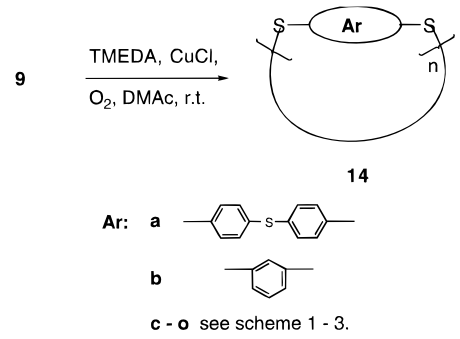


Scheme 3. Preparation of Arenedithiols from Sodium Hydrogen Sulfide



gave disubstituted products. The crude product precipitated out from water contained a large amount of trapped water which was very difficult to remove by heating. However, extracting the product with toluene and evaporation of solvent gave a material pure enough for the next reaction step. For the best results, the crude disulfonyl chloride should be recrystallized from hexane or acetic acid. The ketone, sulfone, or phosphine oxide containing arenedithiols could be synthesized from the corresponding dichloro or difluoro compounds and sodium hydrogen sulfide in DMF. This is a very easy synthesis that can be readily carried out on a 100 g scale in the laboratory. Monomers **9h**−**o**, which contain either ketone, sulfone, or phosphine oxide, are easily oxidized by air to form disulfide compounds at 80 °C. These disulfides cannot be dissolved in 5% NaOH solution. In contrast, **9a** can be dried at 100 °C for a very long time with little disulfide formation. The presence of disulfide in arenedithiols can be easily detected by ^{1}H-NMR. If there is any disulfide present, the proton signals of the benzene ring connecting to the disulfide linkage shift downfield. To avoid the oxidation, all of the arenedithiols were dried at room temperature under vacuum. For the present purpose, the presence of small amounts of disulfide does not interfere with the formation of cyclic oligomers. Compounds **9h** and **9n** have been made by other methods.[22,23] The phenylphosphine oxide and ketone containing dithiols, except **9h**, are new compounds.

Scheme 4. Synthesis of Cyclic Aromatic Disulfide Oligomers by Copper Catalytic Oxidation Reaction



2. Synthesis of Cyclic Aromatic Disulfide Oligomers. Iodine and DMSO are used most frequently to make disulfides or polydisulfides from thiols.[24] Catalytic oxidation of dithiols by oxygen has seldom been used. Hay found that dithiols can be transformed into polydisulfides by reaction with oxygen in the presence of a mixture of tertiary amine and a copper salt.[25,26] Here, it is demonstrated that catalytic oxidation of arenedithiols is a very efficient and a novel way to synthesize cyclic aromatic disulfide oligomers. The reactions are schematically illustrated in Scheme 4. The reaction products are cyclic mixtures as shown in the next sections. Several solvents have been used for the synthesis. DMAc was found to be the best solvent for all the systems. The oxidation reaction is very fast and unlike other cyclization reactions, which are run over 16 h under high-dilution conditions,[7] the present cyclization reactions are complete in 3−4 h with the formation of high yields of cyclic oligomers. The final concentration of the product based on the repeating unit is as high as 0.04 M, which is the same as the final concentration obtained for a typical nucleophilic process to make other cyclic oligomers.[7o,s] It should be pointed out that vigorous stirring is very important for the reaction since oxygen has to be well dispersed into the reaction media. By this method, very high yields of cyclic oligomers were obtained (Table 1).

3. Characterizations of Cyclic Aromatic Disulfide Oligomers. Elemental Analyses. Elemental analyses (C, H, S) for all of the cyclic oligomers are shown in Table 1. Generally, sulfur contents are lower than that of the calculated amount. We speculate that the cyclic aromatic disulfide oligomers form host−guest complexes with solvents[3] and the trapped solvents are extremely difficult to remove. The analysis results confirmed that disulfide is formed by the catalytic oxidation.

Composition Analyses of Cyclic Aromatic Disulfide Oligomers. The compositions of cyclic aromatic disulfide oligomers were analyzed by GPC and gradient HPLC techniques. The GPC results are listed in Table 2 and some representative GPC charts are shown in Figure 1. These GPC results indicate that the products obtained by the present methods are low molecular weight oligomeric mixtures, and their profiles are similar to those of typical cyclic oligomers.[7] Generally, ketone-containing cyclic disulfide oligomers show

Table 1. Elemental Analyses of Cyclic Aromatic Disulfide Oligomers

		measd[a]			calcd		
cyclic	yield (%)	% H	% C	% S	% H	% C	% S
14a	85	3.32	58.85	37.88	3.25	58.03	38.72
14b	74	2.91	51.30	44.90	2.88	41.44	45.68
14c	95	3.63	66.12	30.73	3.73	66.63	29.64
14d	84	3.43	61.87	27.14	3.47	62.04	27.60
14e	98	5.37	68.30	22.80	5.46	69.72	24.81
14f	76	2.87	51.37	45.74	2.88	51.44	45.68
14g	93		33.97	30.17		33.99	30.24
14h	98	3.53	65.21	24.42	3.30	63.91	26.24
14i	85	3.53	67.80	19.17	3.47	68.94	18.40
14j	91	3.55	67.86	17.43	3.47	68.94	18.40
14k	88	4.07	76.34	12.34	4.03	76.77	12.81
14l	99	4.47	80.94	9.89	4.32	80.95	9.82
14m	76	3.07	60.87	22.99	2.96	61.74	23.54
14n	99	2.89	52.45	32.97	2.88	51.41	34.30
14o	85	4.15	62.42	18.19	3.82	63.50	18.84

[a] *Elemental analyses (C, H, S) were performed by Fine Chemical Analysis (Ontario, Canada) and Galbraith Laboratories, Inc. (Knoxville, TN). Methods used are based upon those found in *Standard Methods for the Examination of Water and Waste Water*, 7th ed.; American Public Health Association: Washington, DC.

Table 2. GPC Analyses of Cyclic Aromatic Disulfide Oligomers

cyclic	M_n (g/mol)[a]	M_w (g/mol)[a]
14a	560	720
14b	110	140
14c	700	760
14d	690	900
14e	1000	1700
14f	160	320
14g	370	390
14h	730	930
14i	880	1300
14j	640	700
14k	1400	2300
14l	1800	2800
14m	590	660
14n	470	490

[a] Measured by GPC and calibrated against polystyrene.

higher apparent molecular weights since they are bulky molecules. Cyclic disulfide **14l** shows the highest apparent molecule weight because of the presence of the very bulky tetraphenylbenzene moiety. Cyclic disulfide oligomers **14c** and **14j** are only slightly soluble in chloroform. Their GPC results represent only the soluble portion. It is unclear from these results whether they contain higher oligomers or linear polymers. Cyclic **14o** has a very strong interaction with the column and hence its GPC data are not available with chloroform as eluent.

The gradient HPLC charts for cyclic aromatic disulfide oligomers **14a**−**n** (except **14j**) are shown in Figure 2. The gradient conditions were as follows: at 0 min, THF 70%, H_2O 30%; at 20 min, THF 90%, H_2O 10%; at 25 min, THF 100%; at 27 min, THF 70%, H_2O 30%; at 30 min (end), THF 70%, H_2O 30%. Cyclic **14j** and **14o** are totally insoluble in THF; hence their gradient HPLC results are not available. The separation of cyclic oligomers by gradient HPLC is determined by the solubilities of and polarities of the substrates to be analyzed. Although we can generally apply the gradient conditions given above to analyze all of the cyclics obtained, cyclic oligomer **14n** was not well separated. The HPLC chart of **14n** was obtained by using the following gradient conditions: at 0 min, THF 60%, H_2O 40%; at 20 min, THF 80%, H_2O 20%; at 25 min, THF

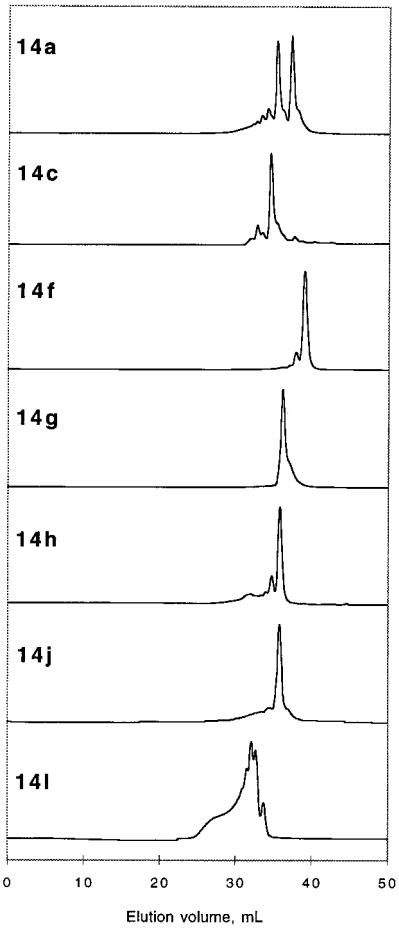


Figure 1. Gradient HPLC charts of cyclic aromatic disulfide oligomers. (For gradient conditions, see text.

100%; at 27 min, THF 60%, H_2O 40%; at 30 min (end), THF 60%, H_2O 40%.

From gradient HPLC and GPC results, we can assign repeating units for the cyclic aromatic disulfide oligomers. The smallest repeating units of **14c** and **14f** are 3 (i.e. $n = 3$), while that of **14g** is 4 (i.e. $n = 4$). All other cyclic aromatic disulfide oligomers **14** contain the smallest repeating unit, 2.

Cyclic oligomer **14a** contains 33% of cyclic dimer and 33% of cyclic trimer, respectively, as determined by gradient HPLC, while **14d** contains 7.5% of cyclic dimer and 31% of cyclic trimer. This result may be because the C−O bond is more rigid than the C−S bond and cyclics from the former could be more strained. Cyclic oligomer **14b** contains 47% of cyclic dimer due to the favorable conformation. However, cyclic oligomer **14f** does not contain any cyclic dimer due to the conformation of the starting material. All of the cyclic oligomers **14e**, **14h**, **14i**, and **14n** contain more cyclic dimer than cyclic trimer. Cyclic trimer and cyclic tetramer are dominant products for cyclic oligomers **14k**, **14l**, and **14m**. This is believed to be due to the ring strain in the cyclic dimers.

By gradient HPLC, **14f** contains 66% of trimer and 20% of tetramer, while **14g** contains 95% of tetramer. This distribution of cyclic oligomer is consistent with the results obtained from other synthetic methods. By using iodine as oxidizing agent and ethanol as solvent, the trimer of **14f** was obtained in 30% yield.[2] By the present method, cyclic oligomer **14f** was obtained in 76% yield in which 66% of trimer is present. It is surprising to note that the tetramer of **14g** was the predominant

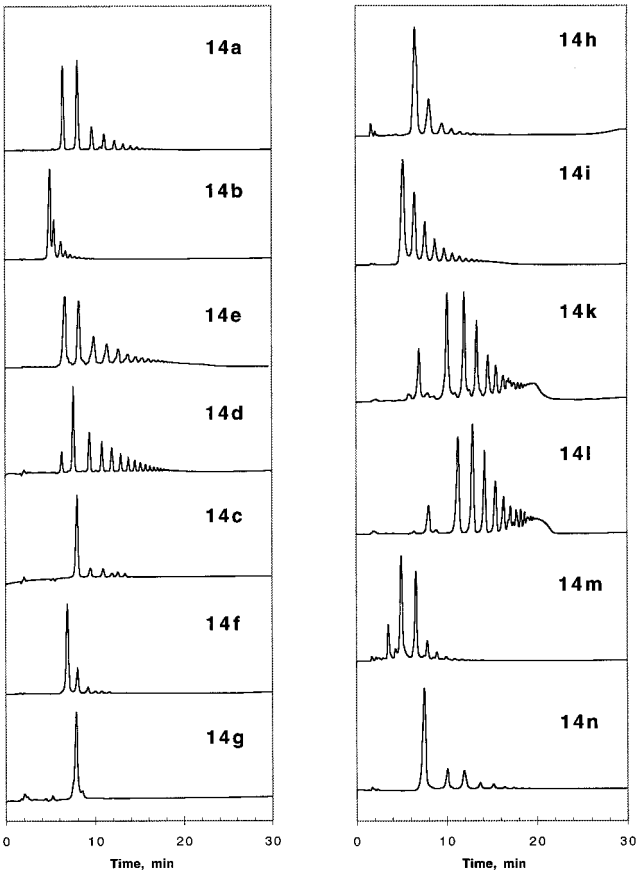


Figure 2. GPC charts of cyclic aromatic disulfide oligomers.

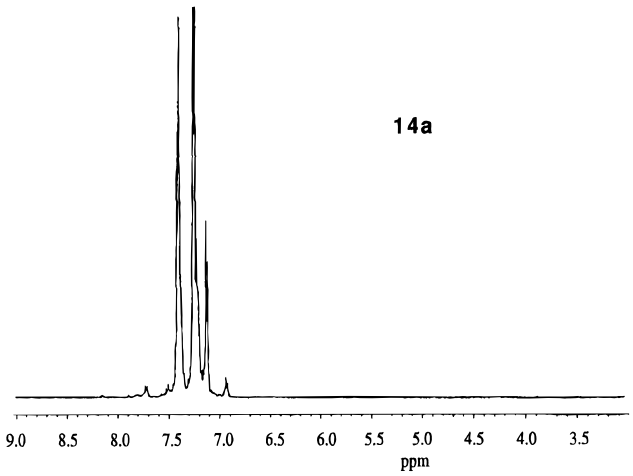


Figure 3. ^{1}H-NMR spectrum of **14a** in chloroform-*d*.

product both in this method and in the DMSO method.[3] Apparently, structural effects play an important role here. In particular, the fluorine atoms seem to exert some electrostatic repulsion which prevents the formation of a smaller cyclic oligomer ($n = 3$) as in **14f,** with the analogous hydrogen-substituted ring.

Cyclic Properties from NMR and MALDI-TOF-MS Studies. ^{1}H-NMR spectra have been taken for all of the products to detect the presence of end groups. The ^{1}H-NMR spectrum of **14a**, shown in Figure 3, clearly shows that there is no proton signal due to the SH group in the range of 3−4 ppm. This indicates that there is no detectable SH end group present in the products. The profiles of the HPLC and GPC chromatograms are consistent with those already reported for other oligomeric cyclic mixtures.[7] Therefore, we can reasonably

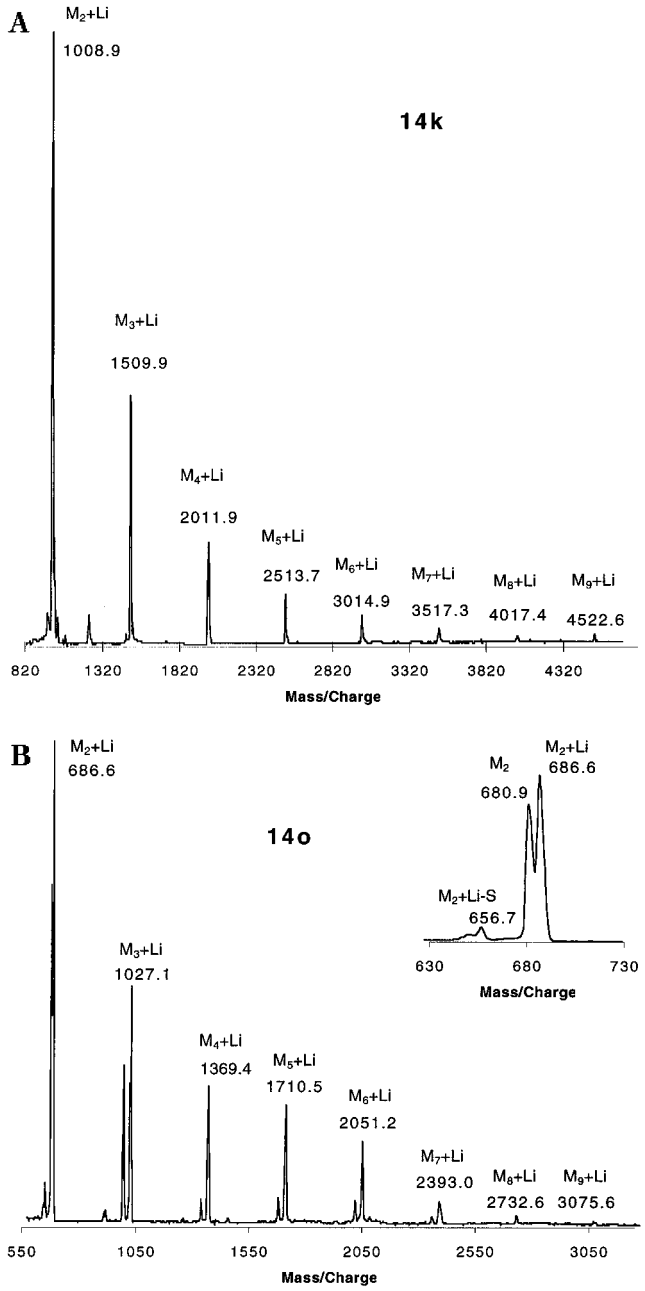


Figure 4. MALDI-TOF-MS spectra for cyclic aromatic disulfide oligomers.

state that the products obtained here are cyclic oligomers.

The cyclic structures have also been confirmed by MALDI studies. The MALDI-TOF-MS technique has been used recently to analyze linear polymers and has been particularly successful for oligomeric cyclic mixtures.[27] In the analysis of cyclic aromatic oligomers, no clean spectra were obtained without any matrix. By using 1,8,9-trihydroxyanthracene (dithranol) as matrix, a relatively clean spectra was obtained for **14o**. Repeating units up to 6 can be detected. However, no clean spectrum was obtained for other cyclic aromatic disulfide oligomers under similar conditions. It was found that by adding LiBr as cationization agent, very clean MALDI spectra were obtained for **14i**, **14k**, and **14l** (Figure 4). Cyclic oligomers **14j** with repeating units up to 3 are also detected by this technique, although the signal to noise ratio is low. When silver was used as the cationization agent, no clean spectra were recorded. The repeating units up to 9 for **14k** (4523,

Table 3. Thermal Properties of Cyclic Aromatic Disulfide Oligomers

	DSC[a]				
	1st scan			2nd scan	TGA[c]
cyclic	T_g (°C)	T_m (°C)	ΔH (kJ/mol)[b]	T_g (°C)	(−5%, N_2)
14a	69.8	208.9	9.45	73	466
14b		155	9.14	38.1	376.3
14c		336.9	l17.76		455.3
14d	76.9			78.7	407.1
14e	80.5	219.3	1.94	ND[d]	376.4
14f		220	7.01	74.3	380.2
14g		248.3	9.55	ND[d]	450.4
14h		226.3	9.7	149.7	433.6
14i	138.9	209.4	5.51	139	428.5
14j		318.3 (dec)	39.48	187.4	358.7
14k	189.9			190	441.2
14l	253.2	318.4, 339.2	10.12	258	462.1
14m		260, 285	18.36	118.9	381.6
14n		303.4	16.88	214.5	336.9
14o	131.8	275.5	3.06	202.1	392.7

[a] Measured under N_2; heating rate was 20 °C/min. [b] Calculated based on repeating units. [c] Temperature at which 5% weight loss was observed under a N_2 atmosphere; heating rate was 20 °C/min. [d] Not detected.

M_9 + Li), **14l** (5890, M_9 + Li), and **14o** (3076, M_9 + Li) and up to 10 for **14i** (3494, M_{10} + Li) are clearly detected by this technique. The representative MALDI spectrum of **14k** is shown in Figure 4A. In the MALDI spectra for **14k**, **14i**, and **14l**, small peaks corresponding to cyclic oligomers with one less sulfur atom are observed. The MALDI spectrum for cyclic oligomer **14o** consisted of two sets of molecular peaks (Figure 4B). One corresponds to cyclic oligomer peaks without the attachment of a Li cation. Another set corresponds to cyclic oligomers with the attachment of the Li cation. Without addition of any cationization agent, a relatively clean MALDI spectrum can be obtained. This indicates that cyclic oligomers **14o** can be easily charged. The addition of LiBr improved the analysis so that cyclic oligomers with repeating units up to 9, instead of 6 without the addition, were detected. Unfortunately, the MALDI-TOF-MS technique for other cyclic aromatic disulfide oligomers failed to produce any spectra under various conditions tried.

Thermoanalyses of Cyclic Aromatic Disulfide Oligomers. The cyclic aromatic disulfide oligomers were tested using DSC and TGA, carried out at a heating rate of 20 °C/min under a N_2 atmosphere (Table 3). All samples were tested twice. The samples were first subjected to DSC heating as prepared. After the first heating scan, the sample was cooled to room temperature and subjected to a second DSC scan. Generally, the temperature limit for the first DSC heating scan was set at 320 °C. If no thermal features were detected below this temperature, the temperature limit was raised to 380 °C. For **14c** the limit was set at 400 °C to observe the thermal features, and at this temperature significant weight loss occurred. Therefore, the second DSC heating scan for **14c** was not taken. All cyclic aromatic disulfide oligomers, except **14d** and **14k**, show strong endothermal peaks in the first DSC heating scan which are due to melting; this may be due to the presence of significant amounts of a cyclic dimer and trimer. Cyclic oligomer **14j** has the highest melting enthalpy. As expected, the biphenyl group increased the melting point significantly. Although the second DSC heating scans show that **14a** and **14d** have almost the same glass transition temperature, cyclic oligomer **14d** does not show any melting point or any crystallinity. Even though the second DSC heating scan suggested that cyclic aromatic disulfide oligomers containing ketone, sulfone, and phosphine oxide groups have higher glass transition temperatures than their ether or thioether counterparts, they only show a slight increase in their melting points (Table 3). Therefore, the melt ring-opening polymerization of cyclic aromatic disulfide oligomers is very feasible and practical since melt ring-opening polymerization of cyclic oligomers has to be carried out above the melting points. The T_gs of cyclic oligomers from the second heating scan show the same correlation with structure effects as other polymer systems. The T_g of sulfone-containing cyclic oligomer **14n** is 50 °C higher that that of ketone-containing **14h**. The tetraphenylbenzene moiety-containing cyclic oligomer **14l** has the highest T_g among those studied.

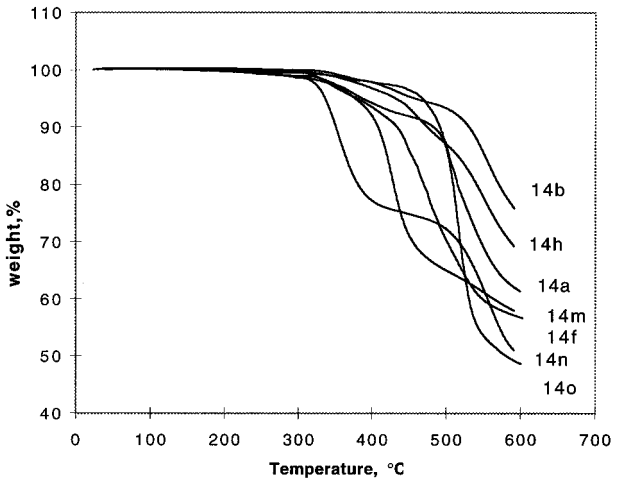


Figure 5. TGA scans of cyclic aromatic disulfide oligomers.

The 5% weight loss temperatures from TGA tests for these cyclic aromatic disulfide oligomers are above 350 °C, and even up to 450 °C; an exception was **14n**, which showed 5% weight loss at 337 °C. Weight loss generally starts from ca. 320 °C (Figure 5). At high temperatures, there is an equilibrium reaction existing for diphenyl disulfide.[28] Diphenyl disulfide produces diphenyl sulfide and sulfur by a thermolysis reaction and diphenyl disulfide can also be formed by reaction of diphenyl sulfide and sulfur. This equilibrium reaction explains the thermal stability characteristics of cyclic aromatic disulfides. This is also the reason why cyclic aromatic disulfide oligomers lose weight starting around 320 °C. **14n** has the least thermal stability, which is due to loss of sulfur dioxide. Oae *et al.* have shown that the reaction of diphenyl sulfone and diphenyl disulfide produces sulfur dioxide at 300 °C.[29] It can be seen that the initial weight loss of cyclic oligomer **14n** is roughly equal to the weight loss of sulfur dioxide.

Conclusions

A series of cyclic aromatic disulfide oligomers have been synthesized by a copper-catalyzed oxidation reaction with oxygen and characterized by several techniques. The cyclic aromatic disulfide oligomers generally have solubilities in common organic solvents, such as DMAc and chloroform. Repeating units up to 10 have been detected by the MALDI-TOF-MS technique for some cyclic disulfide oligomers. Almost all of the cyclic aromatic disulfide oligomers show sharp melting points by DSC, which indicates they are semicrystalline. TGA

of cyclic aromatic disulfide oligomers indicates that 5% weight loss values are above 350 °C and some up to 450 °C.

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