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Communications to the Editor

Novel Synthesis of Macrocyclic Aromatic Disulfide Oligomers by Cyclodepolymerization of Aromatic Disulfide Polymers

Z. A. Liang,[‡] Y. Z. Meng,*[,†,⊥] L. Li,[⊥] X. S. Du,[‡] and A. S. Hay[§]

Institute of Energy & Environmental Materials, School of Physics & Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China; Guangzhou Institute of Chemistry, Chinese Academy of Sciences, P.O. Box 1122, Guangzhou 510650, P. R. China; Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec H3A 2K6, Canada; and School of Mechanical & Production Engineering, Nanyang Technology University, North Sprine (N3) 639798, Singapore

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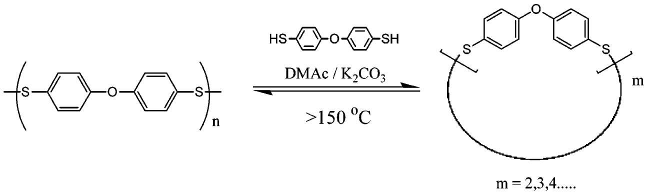
Aliphatic polydisulfides are polymers with many useful properties, such as high resistance to environmental degradation, good adhesion to wood, metal, glass, and concrete, and excellent resistance to organics, water, acids, and bases. Aliphatic disulfide polymers have long been commercialized and have found many applications,[1,2] but the applications of aromatic disulfide polymers are limited by their processing problems mainly due to their insolubility and high melt viscosities.[1] The synthesis of cyclic aromatic and aliphatic disulfide oligomers as intermediates for preparing linear polymers continues to be actively studied in recent years.[3−8] To fabricate high molecular weight polymers via ring-opening polymerization of cyclic oligomers offers numerous advantages over other polymerization methods, including the elimination of the need for using solvents, the absence of volatile byproducts, and the capability of achieving very high molecular weight in a short reaction time.[9]

Macrocyclic aromatic disulfide oligomers are generally synthesized by the catalytic oxidation of aromatic dithiols in highly diluted solution. Iodine and DMSO are most frequently used oxidizing agents.[10−13] Hay has reported the synthesis of a series of cyclic aromatic disulfide oligomers using oxidative coupling of dithiols with oxygen catalyzed by copper salts and an amine. However, the final concentration of the product based on the repeating unit is extremely low ($\ll$0.04 M).[5] Large amounts of solvent and vigorous stirring have to be used to afford the quasi-high-dilution conditions that favor the formation of cyclics. This greatly limits the synthesis of the cyclics on a large scale. In this respect, we reported herein an effective, easy, and rapid method for the synthesis of macrocyclic aromatic disulfide oligomer from 4,4′-oxybis(benzenethiol) by cyclodepolymerization (CDP) of the linear aromatic disulfide polymer. The synthesis can be conveniently carried out in a large scale without the necessity of high-dilution conditions. The realization of the CDP reaction is demonstrated in Scheme 1.

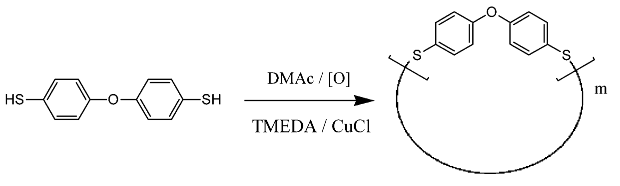
Scheme 1. Cyclodepolymerization of an Aromatic Disulfide Polymer



The 4,4′-oxybis(benzenethiol)-derived aromatic disulfide polymer was prepared by oxidizing 4,4′-oxybis(benzenethiol) with DMSO. A typical procedure for the synthesis is as follows: a 25 mL flask was charged with 15 mL of DMSO and 5 g of 4,4′-oxybis(benzenethiol) following the procedure described elsewhere.[14,15] The reaction mixture was stirred at 80 °C for 8 h followed by filtration to collect the precipitated polymer. The polymer was then chopped in blender into small pieces, washed with methanol, and dried at 80 °C under vacuum for 48 h.

As depicted in Scheme 1, the CDP was then performed under both diluted and concentrated conditions (Table 1). The concentration of the CDP reaction is 10 times greater than that of the conventional method. The disulfide polymer was depolymerized in *N,N*′-dimethylacetamide (DMAc) at 100 °C for several hours in the presence of a catalytic amount of potassium carbonate and 4,4′-oxybis(benzenethiol) with stirring. Upon filtration, macrocyclic oligomers were precipitated by adding an equivalent volume of 5% hydrochloric acid, followed by filtration, washing with 5% NaOH, water, and methanol twice, and drying at 50 °C under vacuum for 24 h. The yields were >98% in both cases. The macrocyclic oligomers have good solubility in both DMAc and THF and melt upon heating, implying the formation of low molecular weight oligomers.

For comparison, conventional synthesis of cyclic aromatic disulfide oligomer was conducted by oxidative coupling of 4,4′-oxybis(thiophenyl) with oxygen catalyzed by CuCl and *N,N,N*′,*N*′-tetramethylethylenediamine (TMEDA), as illustrated in previous studies.[14,15]



[†] Sun Yat-Sen University.

[‡] Chinese Academy of Sciences.

[§] McGill University.

[⊥] Nanyang Technology University.

* Corresponding author: e-mail mengyz@yahoo.com; Tel and Fax +8620-84114113.

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Table 1. Synthesis of Macrocyclic Aromatic Disulfide Oligomers

	polymer:K_2CO_3:dithoil	solvent	time (h)	yield (%)	$T_g{}^a$ (°C)	$T_m{}^a$ (°C)	ROP^b $T_g{}^a$ (°C)
a	1.00 g:0.30 g:0.0050 g	150 mL of DMAc	4	98	ND	71.1	75.4
b	1.00 g:0.30 g:0.0050 g	15 mL of DMAc	8	98	ND	71.7	74.6
c^c				85	ND	71.1	76.0

[a] The T_g and T_m were measured by DSC under N_2 at a heating rate of 20 °C/min. [b] The aromatic disulfide polymers were prepared by ROP of macrocyclics at 180 °C for 30 min under N_2. [c] The macrocyclic aromatic disulfide oligomer was synthesized by conventional catalytic oxidation of 4,4′-oxybis(benzenethiol) with oxygen in the presence of a copper−amine catalyst.[14]

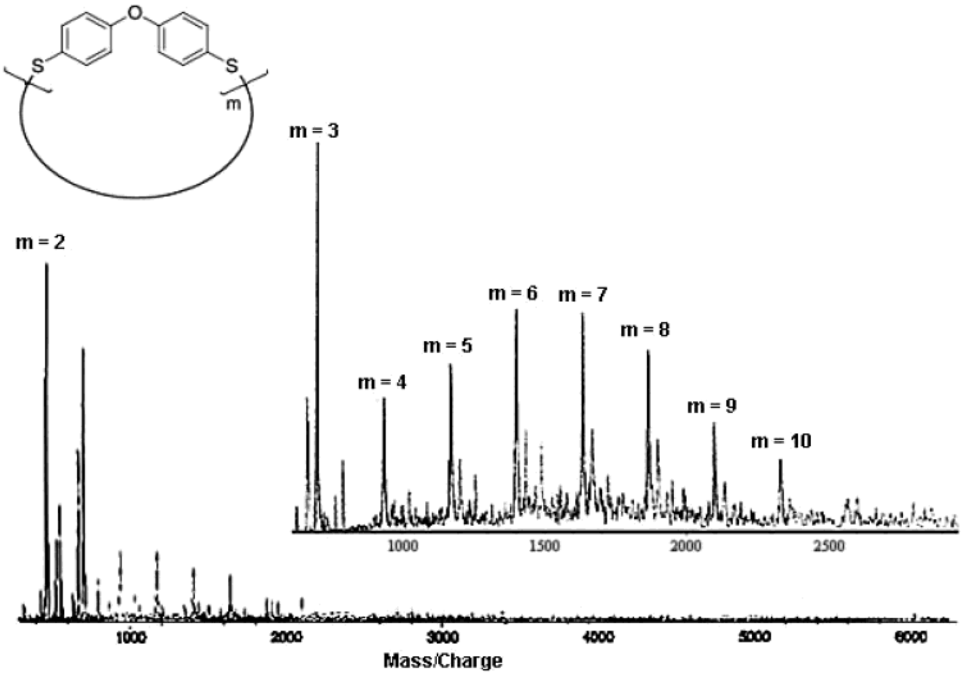


Figure 1. MALDI-TOF-MS spectrum of macrocyclic disulfide oligomers **b** synthesized by the CDP method (1 g of polymer/15 mL of DMAc).

Table 2. GPC Results of Aromatic Macrocyclic Disulfide Oligomers^a

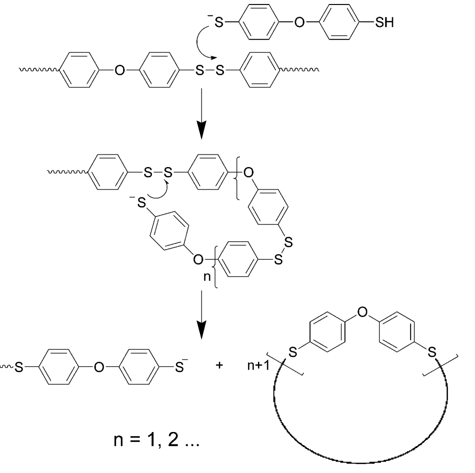
	M_n	M_w	M_z	polydispersity
a	729	806	961	1.1052
b	844	1469	4775	1.7393
c	704	1765	5552	2.5083

[a] Gel permeation chromatography (GPC) analysis was carried out using a Waters 510 HPLC instrument equipped with 5 μm Phenogel columns (linear, 3 × 500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. Polystyrene with molecular weights ranging from 500 to 10^6 Da was used as calibrating standard.

The solubility and gel permeation chromatography (GPC) data (Table 2) proved that the polydisulfides have converted into small molecules. Moreover, the sample prepared by CDP possessed smaller molecular weight dispersity. The fact that melting points of the oligomers can be detected with differential scanning calorimeter (DSC) also demonstrated the formation of cyclic oligomers because corresponding polydisulfides had no melting point but only glass transition temperatures (T_g).

The matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF-MS) technique has been used recently to analyze linear polymers and has been particularly successful for oligomeric cyclic mixtures.[16−19] In MALDI-TOR-MS[20] spectra of the oligodisulfides synthesized by the CDP method (Figure 1), macrocyclics were detected which corresponds to cyclics $(C_{12}H_8S_2)_m$ (calcd 232.32 × m) with m = 2, 3, 4, 5,... Dimer and trimer were predominant compositions based on the results of GPC measurements. No monomeric disulfide ring (n = 1) was formed because of ring strain. Only very low molecular weight oligomers were detected in GPC traces, indicating that cyclic dimer and trimer were predominant compositions. This was in accordance with MOLDI-TOF-MS results (Figure 1), considering the calibrating standard deviation of the GPC method. Figure 2 shows the spectrum of cyclic oligomers prepared by the conventional oxidative coupling method. Regardless of mass signal intensity, the mass signal positions of each cyclic composition were same as those of oligomers prepared by the CDP method.

^{1}H NMR[21] has been also applied to investigate the structure and composition of oligomers synthesized using different methods. As shown in Figure 3, the oligomers **a**, **b,** and **c** had the same chemical shift (δ = 7.463,



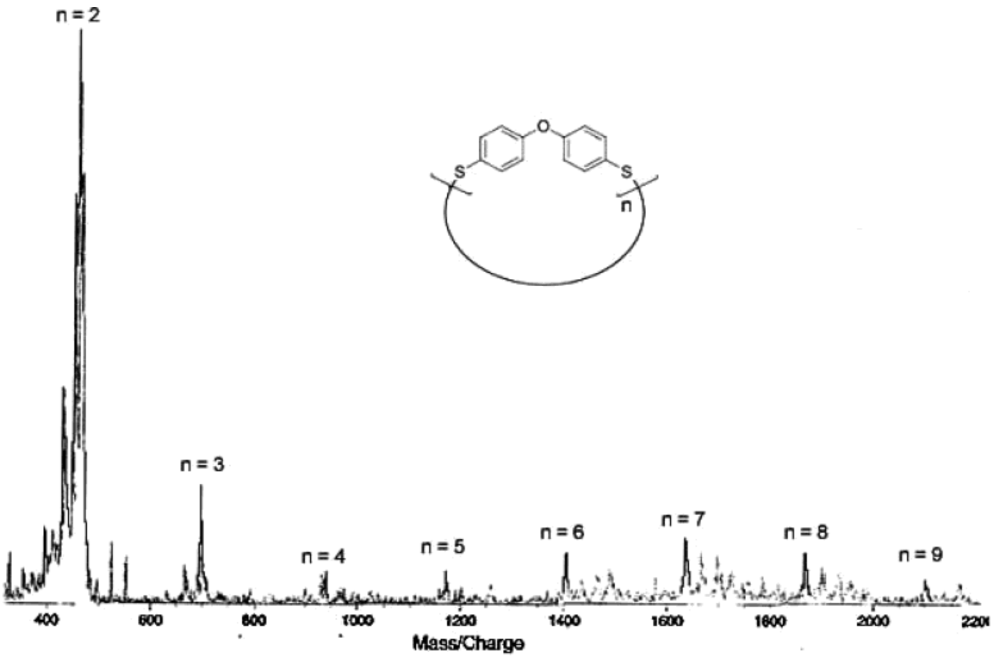


Figure 2. MALDI-TOF-MS spectrum of macrocyclic disulfide oligomers **c** synthesized by the oxidative coupling method.

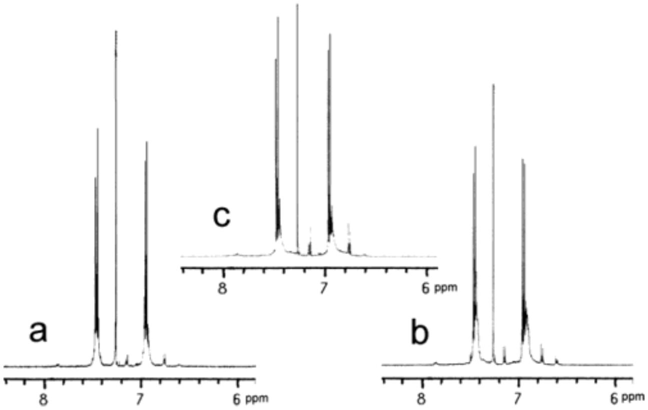


Figure 3. ^{1}H NMR spectra of cyclic disulfide oligomers: **a**, synthesized using 1 g of polymer CDP in 150 mL of DMAc; **b**, synthesized using 1 g of polymer CDP in 15 mL of DMAc; **c**, synthesized by oxidative coupling.[14]

7.446, 6.954, 6.937). These peaks correspond to the two groups of protons with $J = 8.5$ Hz. No −SH group (around 3−4 ppm) was observed in all NMR spectra, demonstrating the completion of cyclic enclosure.

It was found that the yield and purity of resulting macrocyclic oligomers were related to the amount of aromatic dithiol because the aromatic dithiol acted as an initiator and therefore participated in the CDP reaction via a thiol−disulfide exchange. In this case, the two thiol groups can act as end groups and form one linear molecule. After enough equilibration time, all the aromatic disulfide polymers can depolymerize into small linear molecules while dissolving in the reaction solvent. After removing N_2 protective atomosphere, the small linear molecules or dithiols were instantly oxidized to yield cyclic disulfides because dithiols can be easily oxidized, particularly in basic solution.

The feasibility of the CDP method for cyclic oligomers preparation resulted from two factors: the solubility difference of the oligomers and their polymeric counterparts and the highly reactivity to forming cyclics. When original polymers are soluble but the resulting oligomers are soluble, the oligomers are favorable products and very high yield can be achieved. Like ring-opening polymerization in melt conditions, this is also an entropically driven reaction.

Melt ring-opening polymerizations of the macrocyclic oligomers prepared by CDP and oxidative coupling were performed at 180 ± 5 °C for 30 min in a N_2 protective atmosphere (Scheme 1). Both of the resulting polymers were insoluble in both DMAc and THF and behaved as an elastic material when heated to their glass transition temperatures. The molecular weights of the polymers were not determined owing to their insolubility.

In conclusion, we have demonstrated that the cyclodepolymerization of aromatic disulfide polymers is an efficient and easier way to synthesize the corresponding macrocyclic disulfide oligomers. The novelty and merits of this work arises from (a) elimination of the need for highly diluted condition and vigorous stirring, (b) high yield and narrow molecular weight distribution for as-made macrocyclics, (c) less costly and easier workup for purifying product, and (d) a convenient technology to recycle aromatic disulfide polymers. To our knowledge, this new methodology has not been reported so far.

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(20) 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 1:2 (wt) of sample and 1,8,9-trihydroxyanthracene (dithranol) matrix.
(21) ^{1}H NMR spectra were recorded at 500 MHz on a Varian INOVA-500NB NMR instrument, and the chemical shifts were listed in parts per million downfield from tetramethylsilane (TMS). The chemical shifts were calibrated using TMS as the internal standard.

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