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Aromatic disulfide polymers back to macrocyclic disulfide oligomers via cyclo-depolymerization reaction

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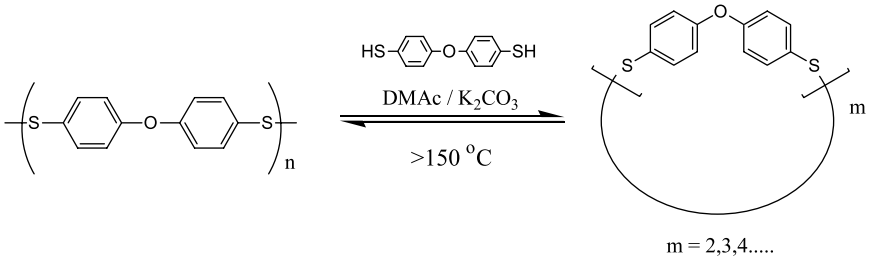
Abstract

A brand new and highly efficient method has been developed for the synthesis of aromatic macrocyclic disulfide oligomers. Cyclization was achieved by cyclo-depolymerization (CDP) of aromatic disulfide polymer in the presence of catalytic amount of thiols and weak base. The cyclic oligomers undergo a facile free-radical ring-opening polymerization to form high molecular weight polymer. Comparing with the conventional method for the preparation of macrocyclic aromatic oligomers by catalytic oxidation of dithiols, highly dilute condition was not necessary using the new method. The macrocyclics in high yield and with narrow molecular weight distribution were obtained. This method also provides a convenient technology for the recycle of aromatic disulfide polymers.



Keywords: Macrocyclics; Cyclo-depolymerization; Cyclization

1. Introduction

The study on the synthesis of aromatic macrocyclic disulfide oligomers has been started since Marschalk reported the first synthesis of aromatic cyclic disulfide in 1952 [1]. Nowadays, using aromatic cyclic disulfide oligomers as intermediate for the synthesis of high-performance polymers has attracted much attention of chemists [2–4]. In general, high-performance and better processing property for a polymer can hardly be achieved synchronously. But using small molecular intermediates can provide better processability, and polymers with good mechanical property can be obtained subject to a reactive processing.

The ring-opening polymerization (ROP) of aromatic cyclic oligomers can offer numerous advantages over conventional methodologies, including the elimination of using any solvent, the absence of volatile byproduct, and the capability of achieving very high molecular weights in a short reaction time [5]. The inherent low melt viscosities of aromatic cyclic oligomers endow them potential applications as high performance thermoplastics by simply melt processing methods such as compression molding, resin-transfer molding, melt pultrusion, and reaction injection molding etc. The ROP of aromatic cyclic oligomers with disulfide bonds is even more attractive

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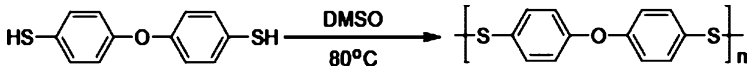
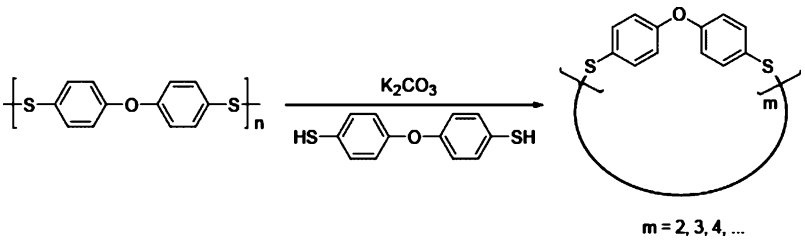
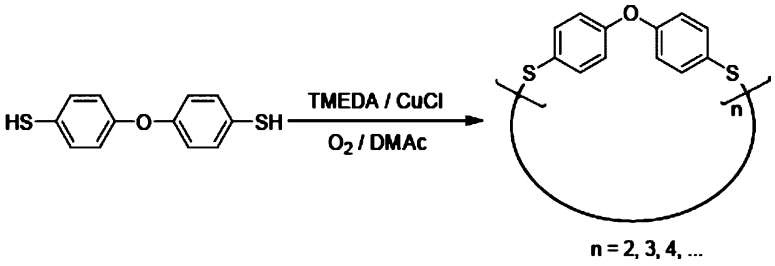


Scheme 1. Synthesis of aromatic disulfide polymer.



Scheme 2. Cyclo-depolymerization of aromatic disulfide polymer.



Scheme 3. Synthesis of aromatic macrocyclic disulfide oligomers by catalytic oxidation of dithiols.

for researchers, because the process can take place by simply heating without any catalyst or initiators [2,6].

Ideally aromatic macrocyclic disulfide oligomers are even perfect intermediates for polymer preparation. But the use of these outstanding materials was limited by their synthetic inconvenience. In past 50 years, the synthesis of cyclic disulfide oligomers was usually conducted in high-dilution conditions [3,4,7–9]. Because of the competitive side reaction to form linear byproduct, it is rather difficult to get high yield of macrocyclics, even if using a huge amount of solvent. This leads to an economical disadvantage and reactor scale limitation.

Herein this paper, we report a novel method for the preparation of aromatic macrocyclic disulfide oligomers by cyclo-depolymerization reaction of aromatic disulfide polymers. The cyclic structure of oligomers was proved by matrix-assisted laser desorption/ionization time-of-flight mass spectra and other technologies. The novel methodology can potentially used for both disulfide cyclics preparation and aromatic disulfide polymer reutilization.

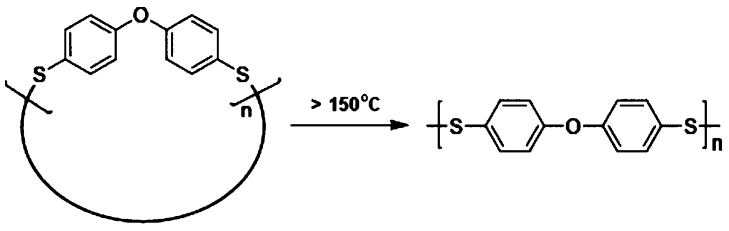
2. Experimental

2.1. Materials

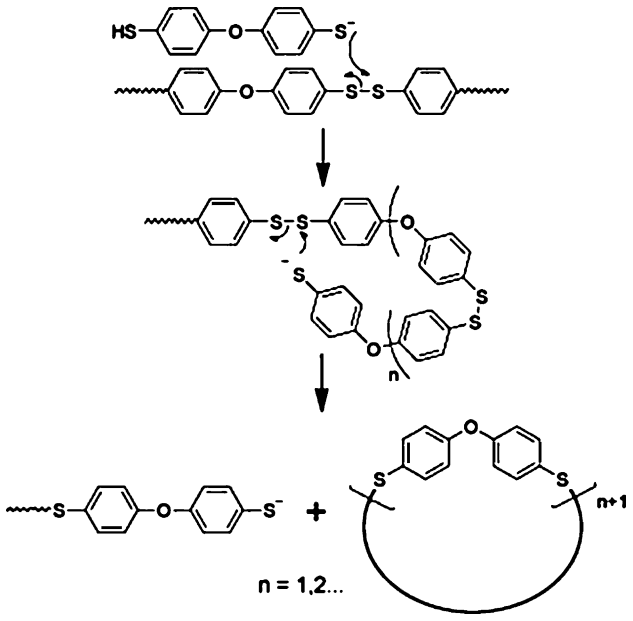
All the chemicals used were of reagent grade and purified by the standard methods. 4,4′-Oxybis(benzenethiol) was synthesized according to the methods described in the literature [10,11]. *N*,*N*′-Dimethylacetamide (DMAc) were obtained from commercial sources and used as received.

2.2. Instrumentation

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. Differential scanning calorimetric (DSC) scans were obtained using a Perkin–Elmer DSC-7C instrument at a heating rate of 20 °C/min in N_2 (20 mL/min) atmosphere.



Scheme 4. Ring-opening polymerization of aromatic macrocyclic disulfide oligomers.



Scheme 5. Cyclo-depolymerization mechanism of aromatic disulfide polymers.

Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TG/DTA 6300 instrument at a heating rate of 20 °C/min in N_2 (300 mL/min) atmosphere. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analyses were carried out on a Kratos KOMPACT MALDI-TOF-MS. The analyte consisted of 1:4:2 (weight) of sample, lithium bromide, and 1,8,9-trihydroxyanthracene (dithranol) matrix. A sample with about 0.2 μL of this analyte was spotted on the sample slot and dried at a temperature of about 50 °C. All spectra were recorded in the reflection mode. Fourier-transferred infrared spectra (FTIR) were recorded by KBr pellet method using a JASCO FT/IR 5300 spectrometer. The band resolution was maintained 127 at 2 cm^{-1} for all measurements. ^1H 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.

2.3. Preparation of aromatic disulfide polymer

The aromatic disulfide polymer used in this study was synthesized by oxidizing 4,4′-oxybis(benzenethiol) with DMSO (Scheme 1). A typical procedure for the synthesis of disulfide polymer is as follows: to a 25 mL flask was charged with 15 mL DMSO and 5 g 4,4′-oxybis(benzenethiol) that was prepared according to the method illustrated in literature [10,11]. The reaction mixture was stirred at 80 °C for 8 h. The polymer was then filtered, cut into small pieces, washed with methanol and dried at 80 °C under vacuum for 48 h. Like most disulfide polymers, the synthesized disulfide polymer is also insoluble in organic

Table 1
Synthesis of aromatic macrocyclic 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:0.005 g	150 mL DMAc	4	98	ND	71.1	75.4
b	1.00 g:0.30 g:0.005 g	15 mL DMAc	8	98	ND	71.7	74.6
c[c]	–	–	–	85	71.1		76.0
d[d]	1.00 g:0.30 g:0.005 g	150 mL DMAc	4	97	ND	71.6	75.6

[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.
[d] The polymer used was prepared by ROP of cyclic oligomers **a** at 180 °C for 30 min under N_2.

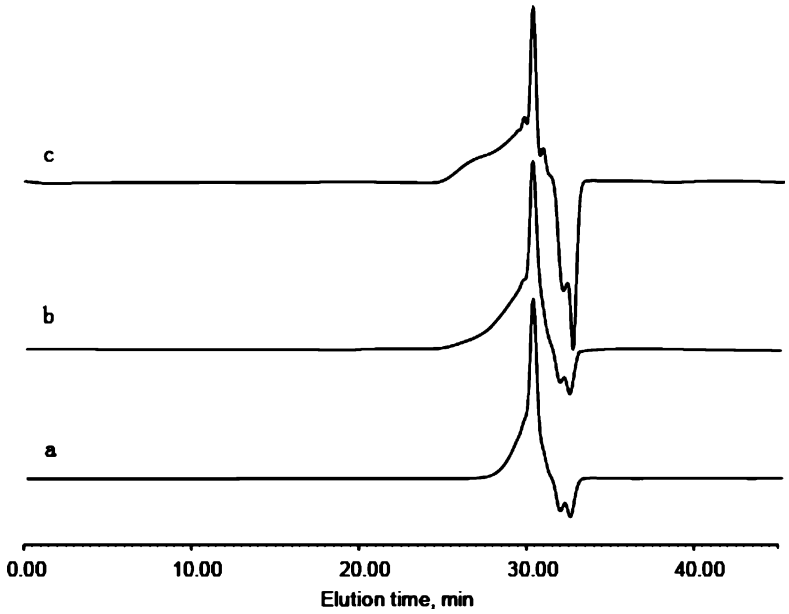


Fig. 1. GPC chart of marocyclic disulfide oligomers. **a**, Synthesized using 1 g polymer CDP in 150 mL DMAc; **b**, synthesized using 1 g polymer CDP in 15 mL DMAc; **c** synthesized by oxidative coupling [11].

solvent at room temperature. Therefore, the molecular weight of the disulfide polymer cannot be determined.

2.4. Synthesis of cyclic disulfide oligomers

Aromatic macrocyclic disulfide oligomers **a**, **b** and **d** were synthesized by using the method depicted in Scheme 2. Macrocyclics **a** and **b** were synthesized by cyclo-depolymerization (CDP) of disulfide polymer prepared by aforementioned method. Macrocyclic **d** was synthesized by CDP of aromatic disulfide polymer prepared by ring-opening polymerization (ROP) of cyclic oligomers **a**.

A typical CDP procedure for the synthesis of macrocyclics **a** and **d** is given as follows: to a 250 mL three-neck flask equipped with N_2 inlet, 1.00 g aromatic disulfide polymer, 0.30 g potassium carbonate, 0.0050 g 4,4′-oxybis(benzenethiol) and 150 mL *N*,*N*′-dimethylacetamide (DMAc) were introduced. The mixture was kept at 100 °C under N_2 with magnetic stirring for 4 h. The insoluble aromatic disulfide polymer disappeared into the DMAc solution upon completing the CDP. This can also be used as an indication of the completion of the CDP. The resulting solution was then filtered, and cyclic oligomers were precipitated by adding equivalent volume of 5% hydrochloric acid. The precipitates were collected by filtration, washed with 5% NaOH, water and methanol twice and dried at 50 °C under vacuum for 24 h. The yield was 98% for **a** and 97% for **d**. The cyclic oligomers have good solubility in both DMAc and THF, and can melt into liquid state.

Table 2
GPC results of aromatic macrocyclic disulfide oligomers

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

Macrocyclic oligomer **b** was prepared by similar method with only using a smaller amount of solvent (15 mL in a 25 mL three-neck flask) and longer reaction time (8 h). The yield of **b** was 98%. The resulting oligomers have also good solubility in both DMAc and THF, and can melt into liquid state.

For comparison, another cyclic oligomers **c** was prepared by oxidative coupling of 4,4′-oxybis(benzenethiol) with oxygen catalyzed by CuCl and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (Scheme 3) as described in previous works [11,12]. A 1 L three-neck flask with an oxygen inlet and a mechanical stirrer equipped was charged with 0.70 g of CuCl, 1.40 g of TMEDA and 500 mL DMAc. The reaction mixture was vigorously stirred for 10 min while oxygen was bubbled in. Then 3.0 g 4,4′-oxybis(benzenethiol) dissolved in 50 mL DMAc was drop-wise added to the reaction mixture over 3–4 h. The resulting mixture was stirred for another hour to ensure the completion of oxidation and then filtered. The filtrate was treated with 500 mL 5% HCl and stirred for 1 h to remove the copper salt. The precipitates were collected by filtration, washed with methanol twice and dried at 50 °C under vacuum for 24 h. The yield was 85%.

2.5. General ring-opening polymerization (ROP) procedure of macrocyclic oligomers

The ring-opening polymerization of aromatic disulfide oligomers is shown in Scheme 4. The ROPs of the macrocyclic oligomers were performed in the melt. A typical ROP procedure is given as follows: 0.5 g of cyclic oligomers was

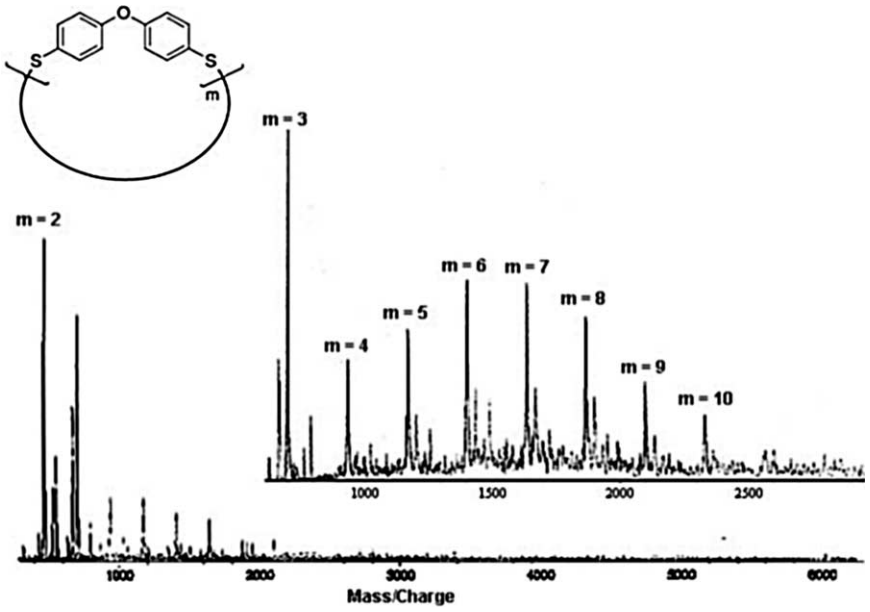


Fig. 2. MALDI-TOF-MS spectrum for aromatic macrocyclic disulfide oligomers **b** prepared by cyclo-depolymerization reaction of aromatic disulfide polymer.

introduced into a 25 mL dry round–bottom flask with a provision for nitrogen inlet and outlet. The flask was heated to 180 ± 5 °C and held for 30 min under N_2 atmosphere protection. Upon completion of the ROP, a molten material of aromatic disulfide polymer was obtained.

3. Results and discussion

3.1. Synthesis of macrocyclic aromatic disulfide oligomers

Aromatic macrocyclic disulfide oligomers are generally synthesized by the catalytic oxidation of aromatic dithiols in highly diluted solution. Iodine and DMSO are most frequently used oxidizing agent [8,13–15]. 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 [2]. However, the final concentration of the product based on the repeating unit was still very low (<0.04 M). Although both pseudo-high-dilution condition and extreme slowly addition of reactants into the reacting mixture has been employed to maintain low concentration of reactants in recent researches [2,11], very large amount of solvent and strong stirring are still necessary to afford highly diluted solution that favors the formation of cyclics. These conditions greatly limit the synthesis of the cyclics in large scale.

Cyclo-depolymerization (CDP) of aromatic disulfide polymers as depicted in Scheme 2 is a newly developed method for the synthesis of cyclic disulfide oligomers. The CDP reaction is

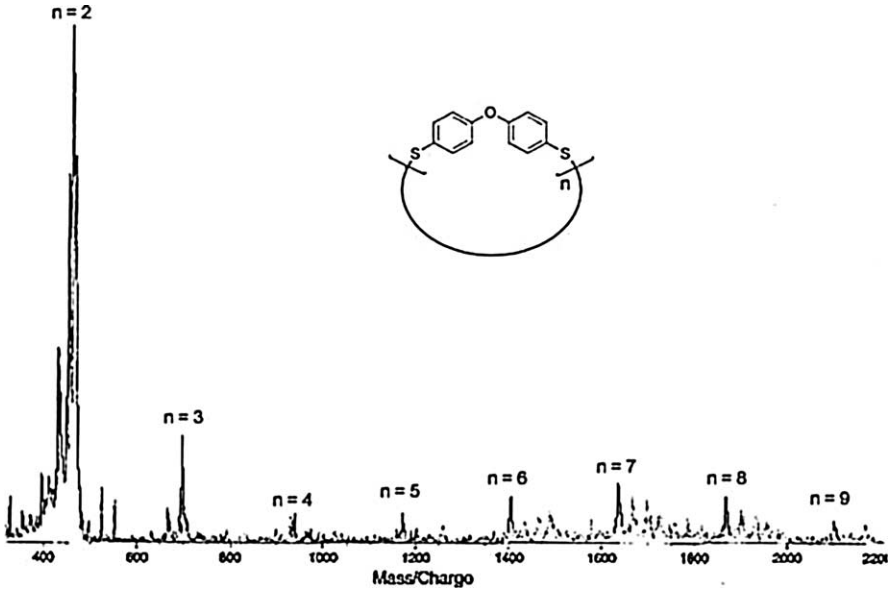


Fig. 3. MALDI-TOF-MS spectrum for macrocyclic oligomers **c** prepared by catalytic oxidation of dithiols.

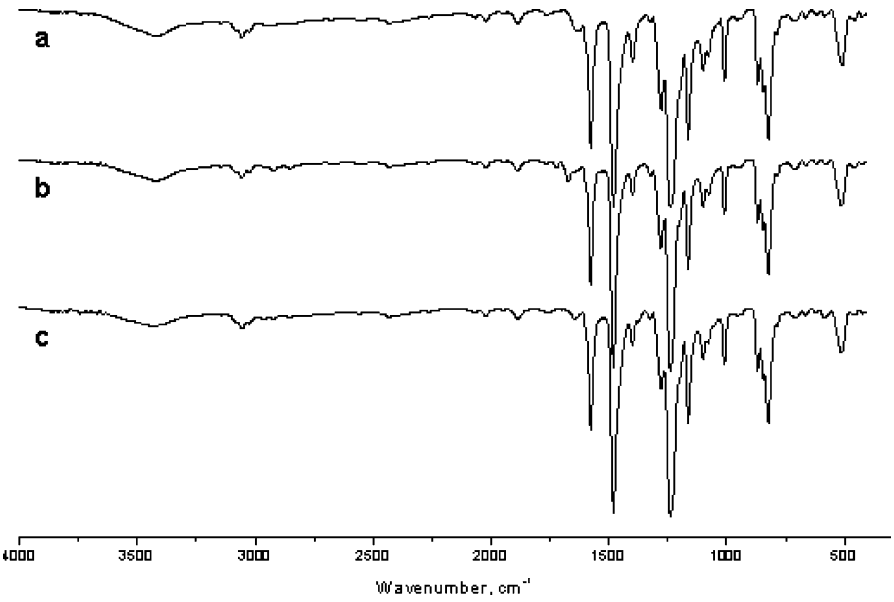


Fig. 4. Infrared spectra of aromatic macrocyclic disulfide oligomers. **a**, Synthesized using 1 g polymer CDP in 150 mL DMAc; **b**, synthesized using 1 g polymer CDP in 15 mL DMAc; **c**, synthesized by oxidative coupling [11].

initialized by sulfur anion generated by 4,4′-oxybis(benzenethiol) as catalyst (Scheme 5); and macrocyclic disulfide oligomers are finally formed via disulfide exchange. Though the disulfide exchange may cause equilibrium between cyclic oligomers and linear polymers, it has been proved that cyclic oligomers were only products under conditions that were not very concentrated. Several CDP reaction conditions and the physical properties of produced oligomers are listed in Table 1. Linear products with high molecular weight were not detected by Gel permeation chromatography (GPC) analysis under these conditions.

Macrocyclic oligomers **a**, **b** and **d** were prepared by CDP reaction of aromatic disulfide polymer; and **c** was prepared by catalytic oxidative coupling of dithiols. As can seen from Table 1, T_ms of **a**, **b** and **d** were detected by differential scanning calorimetric (DSC) while there was only a T_g for cyclic oligomer **c**. This can be explained by the following GPC results in Fig. 1. Cyclic oligomers **a** and **b** have much lower molecular weight distribution than oligomer **c**. There were many large molecules in oligomer **c**, whilst there were not in **a** and **b**. Therefore, the T_m of cyclic oligomer prepared by oxidation coupling was not very obvious, and only a T_g can be detected by DSC.

Cyclic oligomer **d** was prepared by CDP of aromatic disulfide polymer synthesized via ring-opening polymerization (ROP) of oligomer **a** at 180 °C for 30 min under N_2. This

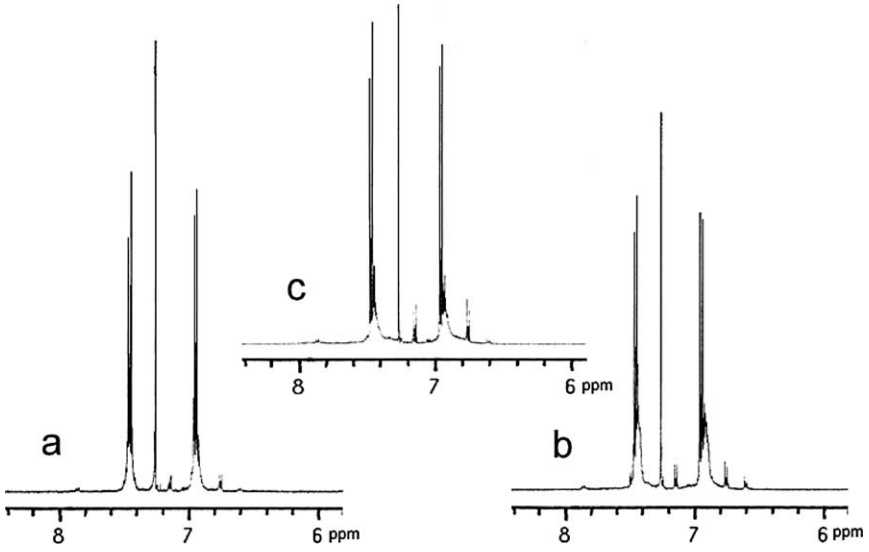


Fig. 5. ^{1}H NMR spectra of aromatic macrocyclic disulfide oligomers. **a**, Synthesized using 1 g polymer CDP in 150 mL DMAc; **b**, synthesized using 1 g polymer CDP in 15 mL DMAc; **c**, synthesized by oxidative coupling [11].

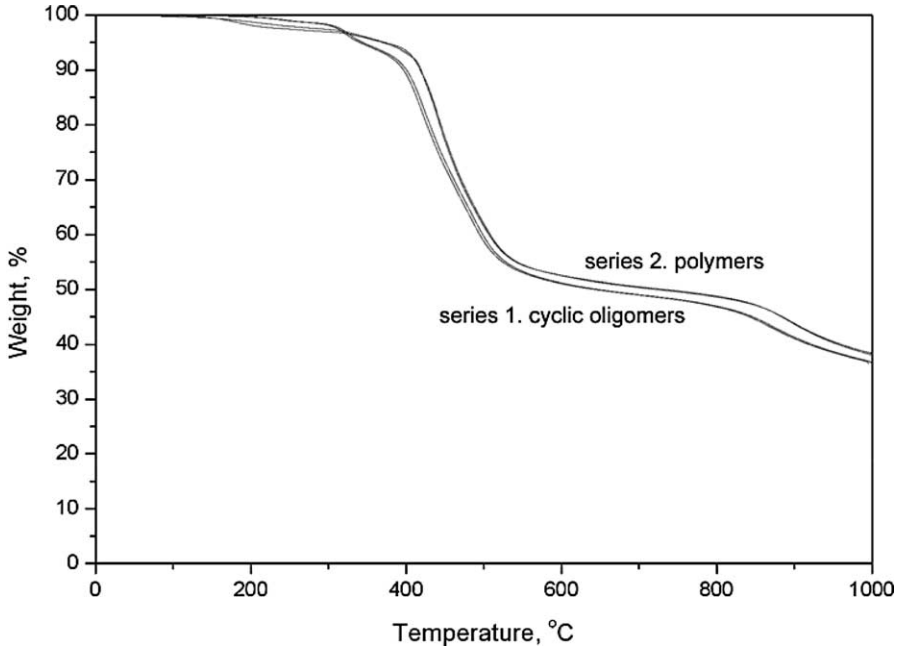


Fig. 6. TGA curves of macrocyclic oligomers (series **1**) and produced polymers (series **2**).

demonstrated the possibility of the recycle of aromatic disulfide polymers. This process provided a novel methodology for the recycle of aromatic disulfide polymer in a high yield.

3.2. Structure investigation

GPC curves of cyclic oligomers **a**–**c** are shown in Fig. 1. No linear and high molecular weight molecules were detected in all these three samples. The results were listed in Table 2. It can be seen from this table that polydispersity increased with the increase of solution concentration in CDP reaction, but it is still much smaller than that of the oligomers prepared by oxidative coupling. The polydispersity of cyclic oligomers **a** was only 1.1, which is very close to a monodispersed compound.

Fig. 2 shows the matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) of cyclic oligomers prepared by CDP in concentrated condition (oligomers **b**). Oligomers from cyclic dimer to cyclic decamer were well confirmed. From Fig. 2, it is evident that there was no signal attributed to the linear oligomers. These data present the detail structure of the macrocyclic disulfide oligomers prepared from CDP method. We can also conclude that the dimmer and trimmer are the predominant composition of the synthesized macrocyclic disulfide oligomers. The number of repeating units varied from two to ten. From their structure, therefore, we can predict that these macrocyclics can undergo free radical ring-opening polymerization.

To compare the results for the macrocyclic oligomers obtained by CDP and by catalytic oxidation of dithiols, the MALDI-TOF-MS spectrum of cyclic oligomers prepared by conventional oxidative coupling method (oligomers **c**) is shown in Fig. 3. It was found that the molecular masses of each oligomer shown in the spectra of **b** and **c** were almost the same. The molecular mass deviation for the oligomers from cyclic dimer to cyclic nonamer was no more than 0.9 dalton.

By carefully comparison, there was no any difference in absorption among the infrared spectra of macrocyclic oligomers synthesized by different methods (Fig. 4). This figure also proved that the synthesized oligomers had cyclic structure but linear one because there was no –SH bond detected in all ^{1}H NMR characterization. ^{1}H NMR has been also applied to investigate the structure and composition of synthesized oligomers. As shown in Fig. 5, the oligomers **a**, **b** and **c** had same chemical shift ($\delta = 7.463, 7.446, 6.954, 6.937$). These peaks correspond to the two group of hydrogens with $J = 8.5$ Hz. No –SH group (around 3–4 ppm) was observed in all NMR spectra demonstrating the completion of cyclic enclosure.

3.3. Thermal stability

The thermal stability of the macrocyclic disulfide oligomers and the corresponding polymers from these cyclics was evaluated by thermogravimetric analysis (TGA). Fig. 6 shows the TGA traces of the aromatic macrocyclic disulfide oligomers and corresponding polymeric counterparts. Series **1** are curves of cyclic oligomers, while series **2** are their corresponding polymeric counterparts. Both macrocyclics and polymers had 5% weight loss temperatures higher than 340 °C. The thermal stability of the polymers was slightly higher than the cyclic in high temperature region because of the difference in their molecular weights.

4. Conclusion

In conclusion, we have demonstrated that the cyclo-depolymerization of aromatic disulfide polymer provided an

efficient and easier way to synthesize corresponding macrocyclic disulfide oligomers. The novelty and merits of this work arises from (a) without the need of highly diluted condition and vigorously stirring, (b) high yield and narrow molecular weight distribution for as-made macrocyclics, (c) less costly and easier work-up 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.

Acknowledgements

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