Ring-opening polymerization of macrocyclic(aromatic disulfide) oligomer derived from 4,4′-oxybis(benzenethiol)

K. Chen[b], Z.A. Liang[b], Y.Z. Meng[a,b,*], A.S. Hay[c]

[a]*Institute of Energy and Environmental Materials, School of Physics and Engineering, Sun Yat-Sen University, 135 Xingang West, Guangzhou 510275, China*
[b]*Guangzhou Institute of Chemistry, Chinese Academy of Sciences, P.O. Box 1122, Guangzhou 510650, China*
[c]*Department of Chemistry, McGill University, 801 Sherbrooke West, Montreal, Que., Canada H3A 2K6*

Abstract

Ring-opening polymerization of macrocyclic(aromatic disulfide) oligomer derived from 4,4′-oxybis(benzenethiol) was studied. Ring-opening reactions were carried out in nitrogen and oxygen atmosphere, respectively. Oxidation reaction and cross-linking reaction took place in oxygen atmosphere. The melt copolymerization between cyclic **1** and elemental sulfur was studied using DSC, and TGA techniques. With increasing the contents of sulfur in the polymer, the T_g values, and 5% weight loss temperatures decreased. When the ratio of sulfur to cyclic reached 5, the polymer appeared as a rubber with a T_g of 23.0 °C and a 5% weight loss temperature of 269.4 °C. A series of poly(thiol aromatic)s were prepared from cyclic **1** and dibromo aromatic compounds in diphenyl ether at 260 °C. The dibromo aromatic compounds can be bis(4-bromophenyl) ether, 4,4′-dibromobiphenyl, and 1,4-dibromobenzene. 4,4′-Dibromobiphenyl gave poly(thiol aromatic) with a T_g of 122.2 °C and a T_m of 221.3 °C by reacting with the cyclic **1**.
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1. Introduction

For past decade, macrocyclic oligomers received considerable attention as precursors of high performance thermoplastics [1–10] since the pioneering work of Brunelle et al. on macrocyclic carbonates [11–13]. The macrocyclic oligomers offer a unique combination of low melt viscosity, and can be polymerized by ring-opening reaction without liberation of any byproduct. Especially for cyclic(aromatic disulfide) oligomers, they can undergo free radical ring-opening reaction upon heating in the absence of any catalyst. The resulting polymers exhibit high resistance to environmental degradation, low water–vapor transmission, excellent resistance to organic solvents, acids and bases, and good adhesion to metal, glass and concrete. Thus, these cyclics could find applications as hot-melt adhesives

used at high temperature and used for high temperature electronic insulators. Due to their importance in industry and academia, several papers have been devoted to this class of cyclics [14–19].

Little information is available about the ring-opening reaction of cyclic(aromatic disulfide) oligomers because of their insolubility of resulted polymers. In 1972, Hiatt found some cyclic sulfides bis(aromatic tetrasulfide)s undergo ring-opening reaction upon heating [20]. A 1,2,3-trithiane was reported to form a high molecular weight polymer upon standing in a closed flask at room temperature over 12 h [21]. It is well documented that the disulfides bond broken to form radicals at elevated temperature [22]. This characteristic has been utilized to initiate ring-opening polymerization (ROP) of cyclic oligomers containing thio-ether linkages [23,24] and cyclic(aromatic disulfide) oligomer derived from 4,4′-isopropylidene bisthiophenol [25]. Copolymerization reaction between cyclic(aromatic disulfide) oligomers synthesized from 4,4′-isopropylidene bisbenzenethiol and sulfur was also studied [26]. Ding et al. reported a novel method to prepare PPS from cyclic(aromatic disulfide) oligomers obtained from 4,4′-thiobis

* Corresponding author. Address: Institute of Energy and Environmental Materials, School of Physics and Engineering, Sun Yat-Sen University, 135 Xingang West, Guangzhou 510275, China. Tel.: +86-20-8523-1343; fax: +86-20-8523-2337.

E-mail address: mengyz@yahoo.com (Y.Z. Meng).
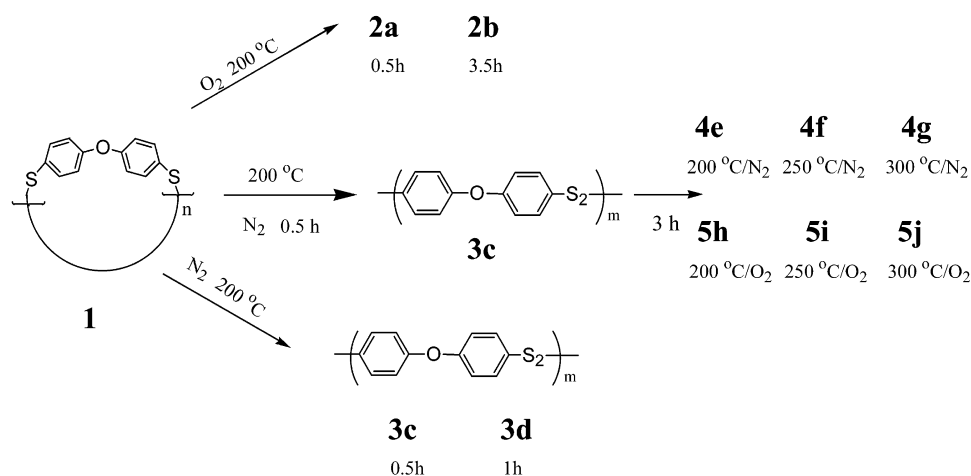
Scheme 1. Ring-opening polymerization of cyclic **1**.

(benzenethiol) and dibromo or diiodo aromatic compounds [27–29].

In previous work, we have prepared a series of homo- and cocyclic(aromatic disulfide) oligomers [19]. In the course of the study of these macrocyclics, we discovered that the homo cyclic(aromatic disulfide) oligomer derived from 4,4′-oxybis(benzenedithiol) possess low melt temperature, and can undergo ring-opening reaction upon heating under mild condition without any catalyst. Because of the low cost starting materials used, these macrocyclics show potential and practical applications. In this connection, we investigate the ROP in detail in order to optimize their properties of resulting polymers. For this purpose, we report in this paper the ROP in nitrogen and oxygen atmosphere respectively. Copolymerization with element sulfur and dibromo aromatic compounds are also presented.

2. Experimental

2.1. Materials

Cyclic **1** were prepared from the oxidation of 4,4′-oxybis(benzenethiol) with oxygen using a copper-amine catalyst as reported previously [19]. 4,4′-Dibromobiphenyl, 1,4-dibromobenzene, bis(4-bromophenyl) ether were purchased from Aldrich Chemical Co. Diphenyl ether, chloroform,1-methyl-pyrrolidone (NMP), N,N'-dimethylacetamide (DMAc), N,N'-dimethylformamide

(DMF), tetrahydrofuran (THF), potassium iodide and sulfur were obtained from commercial sources and used as received.

2.2. Instrumentation

Flourier-transferred Infrared spectra (FTIR) were recorded by KBr pellet method using a JASCO FT/IR-5300 spectrometer. The band resolution was maintained at $2 \, cm^{-1}$ for all measurements. Differential scanning calorimetry (DSC) scans were obtained using a Perkin–Elmer DSC-2C instrument at a heating rate of $20 \, °C \, min^{-1}$ in N_2 ($20 \, mL \, min^{-1}$) atmosphere. Thermogravimetry (TG), and differential thermal analysis (DTA) were performed on a Perkin–Elmer TG/DTA 6300 instrument at a heating rate of $20 \, °C \, min^{-1}$ in N_2 ($300 \, mL \, min^{-1}$) atmosphere. Elemental analysis (C, H, S) were performed by Elementar Vario EL instrument.

2.3. General procedure for ring-opening polymerization (ROP)

Small amount of cyclic **1** was introduced into a 25 mL dry round-bottom flask with a provision for oxygen/nitrogen inlet and outlet. The flask was then heated at 200 °C. Upon completing the ROP, the molten polymers **2a–b**, **3c–d** were obtained. The polymer **3c** was heated at 200, 250 and 300 °C for 3 h in oxygen and nitrogen, respectively, the molten polymers **4e–g**, **5h–j** were then obtained. The polymers

6k-p

x=(1-6) x 8   y=3-8
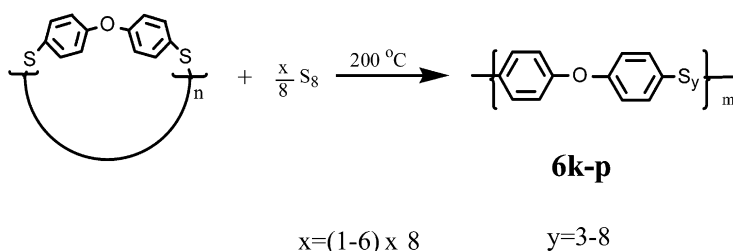
Scheme 2. Copolymerization of cyclic **1** with elemental sulfur.
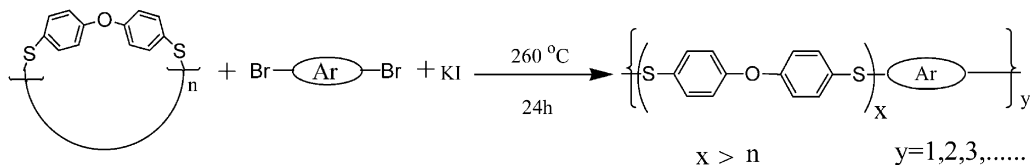
7q-s
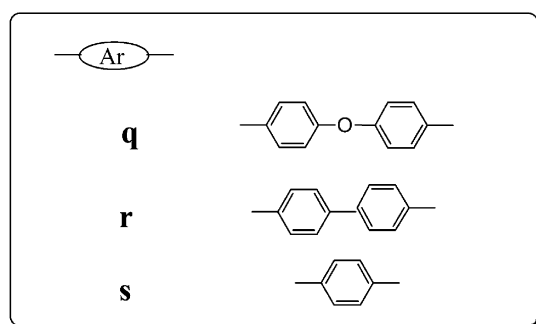
Scheme 3. Copolymerization of cyclic **1** with dibromo compounds.

were washed with DMAc, water and then dried at 100 °C under vacuum for 24 h. Yields: >95%. The reactions are illustrated in Scheme 1.

2.4. Melt copolymerization of cyclic *1* with sulfur

The mixture of cyclic **1** and elemental sulfur was placed on a piece of aluminum foil and the foil was folded. The mixture was then introduced into a 25 mL dry round-bottom flask with a provision for nitrogen inlet and outlet. The flask was heated at 200 °C for 30 min. Upon completion of the ROP, the molten polymers **6k–p** were obtained. The polymers were washed with DMAc, hot chloroform, water and then dried at room temperature under vacuum for 24 h. Yields: >95%. The copolymerization is illustrated in Scheme 2.

### 2.5. Copolymerization of cyclic *1* with dibromo compounds

Cyclic **1** (0.232 g, 1.0 mmol), the dibromo aromatic compound (1.0 mmol), powdered potassium iodide (0.84 g, 5.1 mmol), and diphenyl ether (2.5 mL) were charged into a 25 mL dry round-bottom flask equipped with a mini magnetic stirring bar and with a provision for nitrogen inlet and outlet. The round-bottom flask was immersed in a salt bath preheated to 260 °C for 24 h. 1-Chloronaphthalene

(3 mL) was added to dilute the polymer. The resulting viscous solution was poured into 300 mL of methanol to precipitate out the polymer. The polymer was isolated by filtration and washed with hot water, hot methanol, hot chloroform, and then methanol. The product was dried at 100 °C under vacuum for 24 h and then subjected to analysis. Yields: >85%. The procedure is illustrated in Scheme 3.

3. Results and discussion

3.1. Ring-opening polymerization of cyclic *1*

Catalytic oxidation of aromatic dithiols has been demonstrated using varying oxidants such as dimethyl sulfoxide (DMSO) [30], iodine [31]. Hay reported that dithiol compounds can be oxidized to form polydisulfides with oxygen using copper-amine catalysts [32]. In previous work, a series of homo- and co-cyclic(aromatic disulfide) oligomers were synthesized under high dilution condition using this method [14–19]. Following the method, cyclic **1** was synthesized under high dilution conditions (Scheme 4). Cuprous chloride and *N,N,N,N*-tetramethylethylene-diamine (TMEDA) were used as copper salt and amine ligand, respectively. The
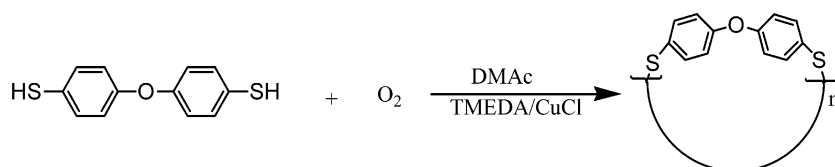
Scheme 4. Catalytic oxidation cyclization of aromatic dithiols.

Table 1
Ring-opening polymerization of cyclic **1** in different atmosphere

Polymer	Gas	Time (h)	T_g[a] (°C)	$T_{-5\%}$[b] (°C, N_2)
2a	O_2	0.5	80.7	369.9
2b		3.5	92.2	407.2
3c	N_2	0.5	77.8	370.3
3d		1	77.7	369.2
4e		3.5	80.2	375.3

[a] Measured in N_2 and at a heating rate of 20 °C min^{-1}.
[b] 5% Weight loss temperature obtained in N_2 at a heating rate of 20 °C min^{-1}.

4,4'-oxybis(benzenethiol) solution were added to the reaction mixture through a dropping funnel over a 4 h period. The final concentration of the reactants in the mixture was 0.05 M. It was observed that vigorous stirring is very important for the cyclic formation due to the well dispersion of oxygen. Similarly as reported in previous work [18], the ^1H NMR (CDCl$_3$) spectrum contained no –SH groups (3–4 ppm) indicating the completion of oxidation. Aromatic proton signals became more complicated because of the formation of cyclic(aromatic disulfide) oligomers. In previous work, the cyclic structures have been confirmed by MALDI-TOF-MS studies, and the repeating units of the cyclic were from 2 to 4 [14]. GPC analysis of cyclic **1** showed that the product had a number average molecular weight M_n of 506 Da and a weight average molecular weight M_w of 754 Da.

Various polymers can be synthesized via ROP of cyclic **1** as shown in Scheme 1.

All the polymers have poor solubility in common organic solvents like chloroform (CHCl$_3$), N,N'-dimethylacetamide

Table 2
Thermal properties of polymer **3c** annealed in different atmosphere

Polymer	Gas	Temperature (°C)	T_g[a] (°C)	$T_{-5\%}$[b] (°C, N_2)	Insoluble content (%)[c]
4e	N_2	200	80.2	375.3	0
4f		250	81.0	391.6	0
4g		300	90.3	409.6	0
5h	O_2	200	94.8	394.9	7.5
5i		250	96.0	405.4	14.0
5j		300	N/A	421.8	36.8

[a] Measured in N_2 and at a heating rate of 20 °C min^{-1}.
[b] 5% Weight loss temperature obtained in N_2 at a heating rate of 20 °C min^{-1}.
[c] Solvent: hot 1-methyl-pyrrolidone (NMP).

(DMAc), N,N'-dimethylformamide (DMF), tetrahydrofuran (THF), which is a typical characteristic for disulfide containing polymers. Therefore, no GPC data and NMR spectrum were available at room temperature. For all obtained polydisulfides, no melting point was observed in DSC scans indicated that they are amorphous in nature. The color of polymers **3c–d**, **4e–g** obtained via ROP in nitrogen is yellow, whilst the polymers **2a–b**, **5h–j** is black. Thermal properties of above polymers are listed in Tables 1 and 2. From Table 1, it can be seen that glass transition temperature (T_g) of polymer **2a** is slightly higher than that of polymer **3c**. The higher T_g of polymer **2a** was believed to result from the existence of sulfone or sulfoxide group. The rigid groups were yielded due to the oxidation of sulfides in oxygen. With the increase of reaction time from 0.5 to 3.5 h at 200 °C in oxygen, T_g of polymer **2a** increased from 80.7 to 92.2 °C

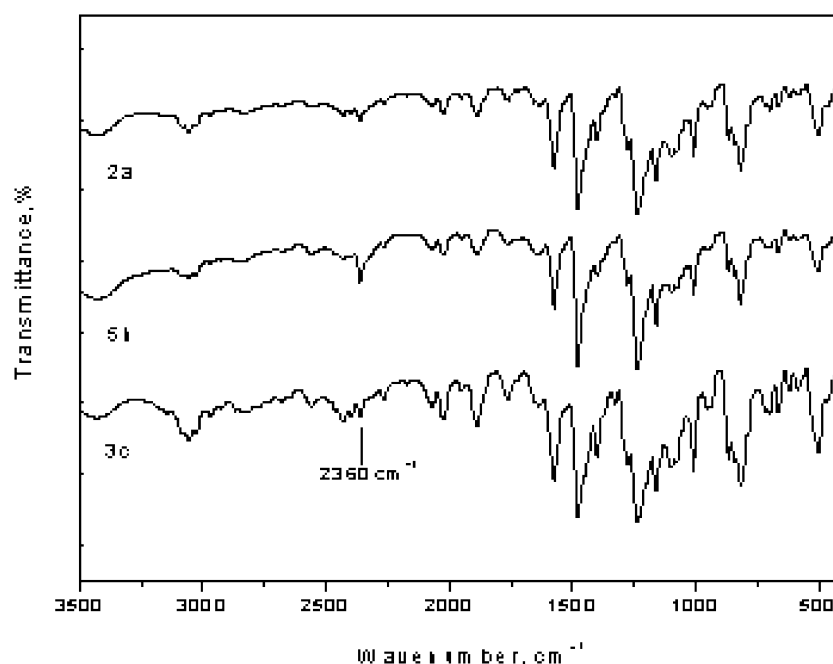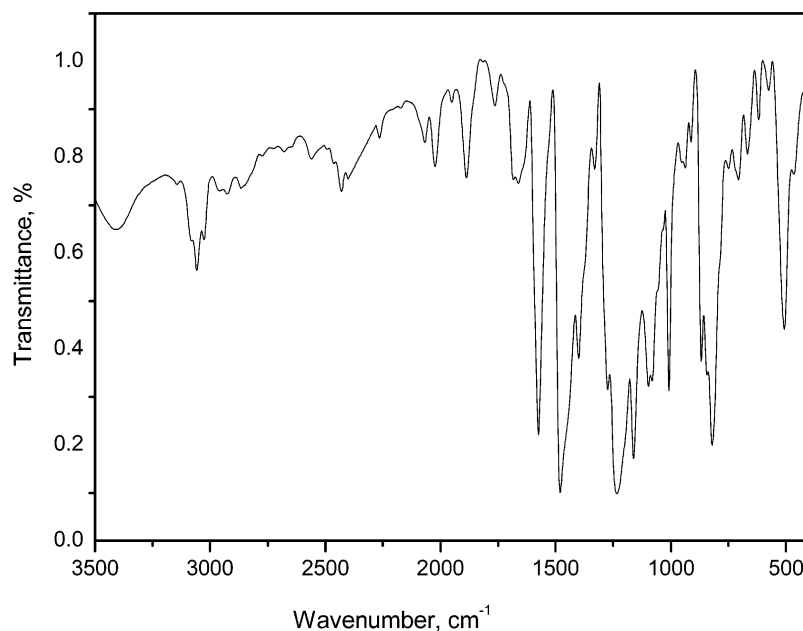In case of nitrogen, however, T_g of polymer **3c** increased

Fig. 1. FTIR spectra for polymers **2a**, **3c**, **5h**.

Fig. 2. FTIR spectra for the insoluble part of polymer **5h**.

merely from 77.8 to 80.2 °C, whereas the 5% weight loss temperature increased from 370.3 to 375.3 °C. We have reported that the ROP can generally finish in 10–30 min, implying that over 98% cyclics underwent ROP to form linear polydisulfide [18]. Extended ROP time can increase the molecular weight of polymer **3c** as indicated by the obvious increase of its T_g (Table 1). The inherent viscosity of polymer **3c** is measured to be 0.24 dL g^{-1} at hot 1-methyl-pyrrolidone, indicating that high molecular weight of polymer was obtained after ROP. The good solubility of polymers **3c–d**, **4e–g** in 1-methyl-pyrrolidone demonstrated that no cross-linking reaction happened during the ROP.

The properties of the polymer **3c** annealed in oxygen and nitrogen were tabulated in Table 2. By increasing anneal temperature from 200 to 250 °C in oxygen, the T_g of resulting polymer increased from 94.8 to 96.0 °C with increased insoluble content from 7.5 to 14.0%. Further increasing anneal temperature to 300 °C, the resulted polymer exhibited no T_g with insoluble content of as high as 36.8%. Clearly, cross-linking reaction became very serious at 300 °C. In contrast, when polymer **3c** annealed in nitrogen, all obtained polymers were soluble in hot NMP. With the increase of anneal temperature from 200 to 300 °C, the T_g of resulted polymer increased from 80.2 to 90.3 °C. Based on the above results, it is readily to tailor or control the thermal properties and cross-linking degree of resulted polymers.

The FTIR (KBr) spectra of polymers **2a**, **3c**, **5h**, are shown in Fig. 1. All the FTIR spectra are almost the same
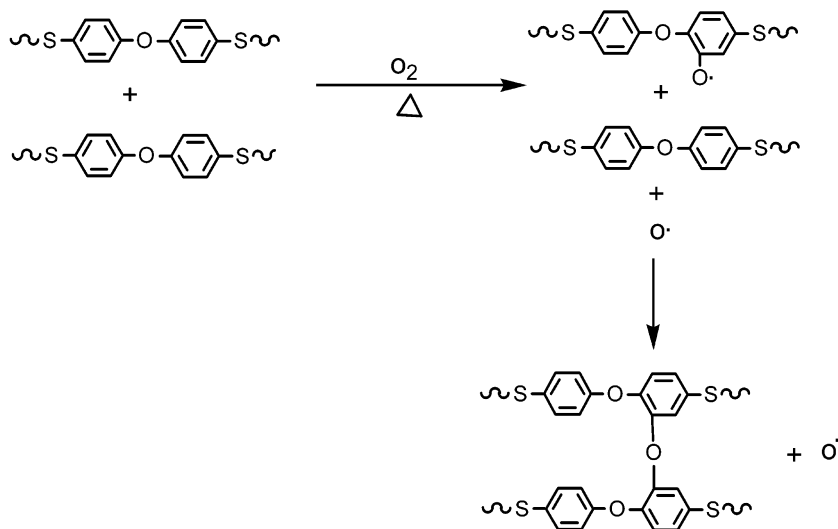

Scheme 5. Proposed cross-linking reaction mechanism of polymer **3c** in oxygen atmosphere.

Table 3
Element analysis of polymer **3c** annealed in oxygen and nitrogen atmosphere

Polymer	C (%)	H (%)	S (%)	O^a (%)	Structure
2b	61.27	3.684	27.16	7.886	$C_{10.21}H_{7.37}O_{0.99}S_{1.70}$
4e	60.88	3.910	26.85	7.764	$C_{10.15}H_{7.82}O_{0.97}S_{1.68}$
5h	60.95	3.621	27.14	8.289	$C_{10.16}H_{7.22}O_{1.04}S_{1.70}$
5h[b]	61.84	3.600	25.62	8.940	$C_{10.31}H_{7.20}O_{1.12}S_{1.60}$

[a] Oxygen content was obtained by subtracting the content of C, H and S from 100%.

[b] Insoluble part of **5h**.

Table 4
Thermal properties of polymers prepared from cyclic **1** and elemental sulfur

Polymer	$T_g{}^a$ (°C)	$T_{-5\%}{}^b$ (°C, N_2)
6k	52.3	331.6
6l	42.0	309.9
6m	37.9	299.0
6n	30.0	283.5
6o	23.0	269.4
6p	22.5	269.9

[a] Measured in N_2 and at a heating rate of 20 °C min^{-1}.

[b] 5% Weight loss temperature obtained in N_2 at a heating rate of 20 °C min^{-1}.

except the peak at 2360 cm^{-1} that presumably attributes to a stretching of $-SO_2-SO_2-$ or $-SO-SO-$bonds. For polymer **3c**, the peak at 2360 cm^{-1} appeared very weak, whereas for polymer **5h**, the peak at 2360 cm^{-1} became very strong. The peak intensity of 2360 cm^{-1} seems dependent upon anneal time in oxygen atmosphere.

As mentioned above, no 2360 cm^{-1} peak was observed for the insoluble part of polymer **5h** as shown in Fig. 2. It can be concluded that the oxidation part of polymer **3** was soluble in hot NMP. By separation, the insoluble part of polymer **5h** possessed a T_g of 138.6 °C and a 5% weight loss temperature of 383.0 °C. From Table 3, we can see that the oxygen content of the insoluble part of polymer **5h** was higher than those of polymers **2b** and **4e**. It can be deduced that the oxidation of polymer **3c** occurred in oxygen atmosphere. The oxidation reaction took place in two ways, i.e. the oxidation of sulfide and the cross-linking on benzene rings. The cross-linking reaction mechanism is depicted in Scheme 5. The cross-linking reaction mechan-

ism is thought to be the same as the hot cross-linking reaction of poly(p-phenylene sulfide) (PPS) when it subjects to melt processing. Upon heating in oxygen, free radicals were produced via the reaction between oxygen and benzene rings because oxygen can readily react with the *ortho* position on benzene rings. From the FTIR spectrum of the insoluble part of **5h** (Fig. 2), it is evident that the peak intensity of 1236 cm^{-1} was higher than that of polymer **3c**, implying the increase of the content of C–O–C bonds.

3.2. Melt copolymerization of cyclic *1* with elemental sulfur

Free radical copolymerization of cyclic **1** with element sulfur to form high molecular weight linear poly(aromatic disulfide)s has been disclosed previously [26]. In this work, we performed the copolymerization with molecular ratio of element sulfur to cyclic **1** ranging from 1:1 to 6:1. Because of the insolublity of resulted polymer at room temperature, no molecular weight information was available. Thermal properties of these polymers are presented in Table 4. From
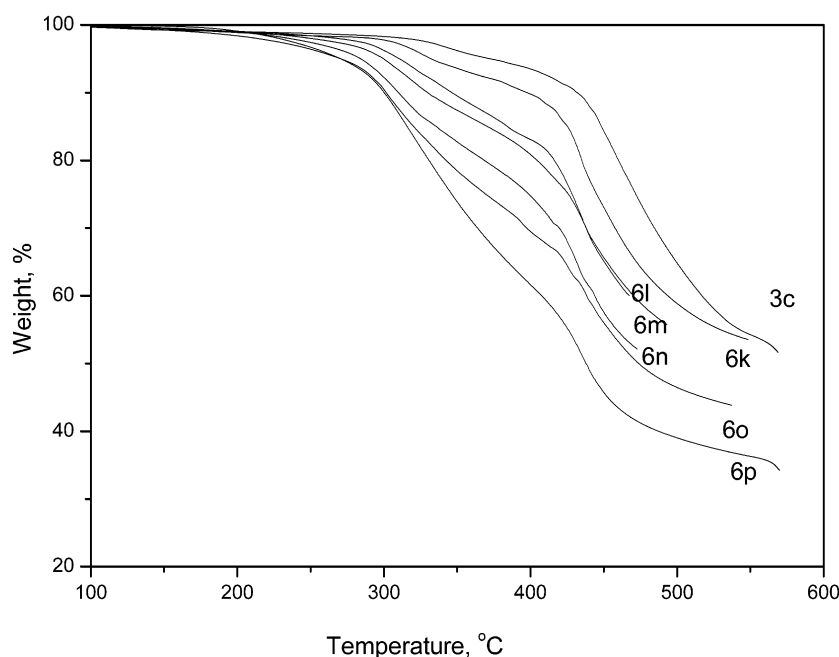

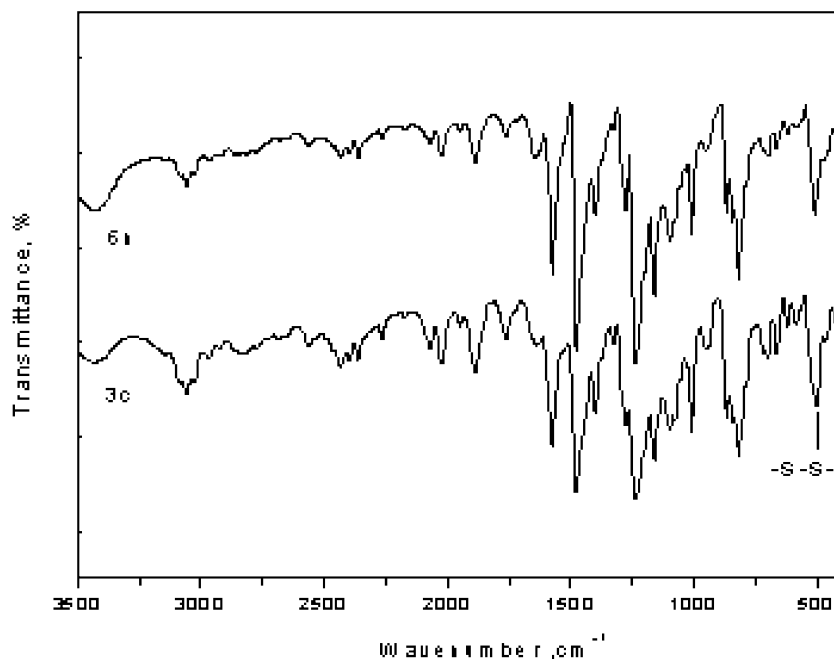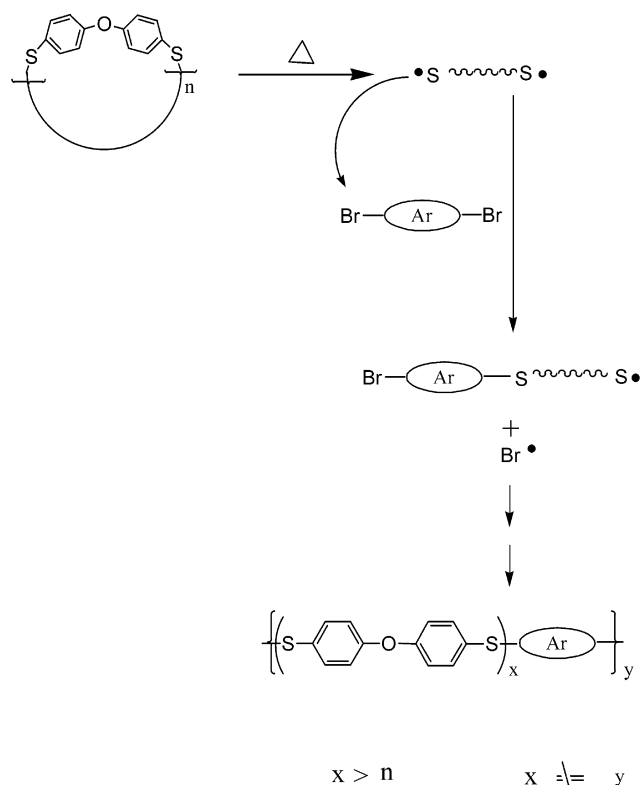Fig. 3. TGA traces for polymers **6k–p**.

Fig. 4. FTIR spectra for polymers **3c** and **6n**.

the TGA thermograms of polymers prepared by cyclic **1** and elemental sulfur (Fig. 3), we can see that the T_g and 5% weight loss temperatures of the polymers decreased with increasing sulfur content. Polymer **6o** has the lowest T_g of 23.0 °C and 5% weight loss temperature of 269.4 °C.

Scheme 6. The polymerization mechanism of cyclic **1** and dibromo compounds.

Because the T_g and 5% loss weight temperatures of polymers **6o** and **6p** were almost the same, the sulfur content of resulted polymer did not increase with increasing the element sulfur when the ratio of cyclic **1** to sulfur reached 5. With further heating the resulted polymers in oxygen for 30 min, the color changed from yellow to black and the 5% weight loss temperature increased by 30 °C over the polymer before heating. This means that further copolymerization of cyclic **1** and sulfur took place with the diminishing of free sulfur.

In all cases, flexible films were obtained by the following simple technique. Cyclics and sulfur were put on a piece of aluminum foil, and the foil was folded into a square around 1×1 cm^2. The square was placed on the surface of a hot plate preheated to 200 °C, and pressed with a piece of glass for copolymerization, the sample was quenched immediately by dipping into cold water. Finally, the aluminum foil was removed and a flexible film was obtained. Generally, polymers with higher sulfur content led to more flexible polymer films. The FTIR (KBr) spectra of polymers **3c** and **6n** are shown in Fig. 4. The FTIR spectra were nearly the same except for that the strong peak at 503 cm^{-1} (polymer **3c**) shifted to 510 cm^{-1} (polymer **6n**). The intensive peak was assigned to $-S-S-$ bond.

3.3. Copolymerization of cyclic **1** with dibromo aromatic compounds

The title copolymerization is represented in Scheme 3. All the polymers were obtained in high yields. Because of the insoluble nature, the polymers formed were only examined by DSC and TGA methods.

The polymerization mechanism is illustrated in Scheme

Table 5
Thermal properties of polymers prepared from cyclic **1** with dibromo aromatic compounds

Polymer	$T_g{}^a$ (°C)	$T_m{}^a$ (°C)	$T_{-5\%}{}^b$ (°C, N$_2$)
7q	78.8	185.2	482.7
7r	122.2	221.3	490.5
7s	92.4	N/A	418.8

[a] Measured in N$_2$ and at a heating rate of 20 °C min^{-1}.
[b] 5% Weight loss temperature obtained in N$_2$ at a heating rate of 20 °C min^{-1}.

6. The copolymerization can induce the group of dibromo aromatic compound into the polymer which prepared by the ring-opening reaction of cyclic **1**. At high temperature, the disulfide linkages in cyclic **1** were broken giving thiyl radicals. The thiyl radicals reacted with the bromine atom to form diphenyl sulfide linkages and bromine radicals. It is observed that usage of potassium iodide in this experiment is necessary to afford high molecular weight polymer. High molecular weight polymer cannot be formed because the bromine radicals are very reactive and brominates the solvent diphenylether, which destroys the stoichiometric balance of reactions. Potassium iodide can serve as a reducer for the bromine radicals to suppress the side reaction caused by the reactive bromine radical. Equivalent amounts of dibromo compounds were generally used, however, in the case of diiodo aromatic compounds, excess of dibromocompounds were used due to the decomposition of diiodo compound at high temperature. The need for excess diiodo compound has been rationalized by other researcher in other polymerization reaction [33].

The thermal properties of synthesized polymers are listed in Table 5. The 5% weight loss temperatures by TGA measurements were higher than 410 °C. From this table, it can be seen that the 5% loss weight temperature of polymer **7q** (482.7 °C) was 110 °C higher than that of polymer **3c** (370 °C).

The DSC trace for polymer **7q** showed a melting endotherm with a melting point of 185.2 °C and a melt enthalpy change of 5.6 kJ mol^{-1} (Fig. 5). Similarly, polymer **7r** showed a melting endotherm with a melting point of 221.3 °C and a melt enthalpy change of 3.4 kJ mol^{-1} (Fig. 5). Polymers **7r** and **7s** had a T_gs of 122.2 and 92.4 °C, respectively. Polymer **7q** had the same glass transition temperature as polymer **3c**.

4. Conclusions

The cyclic(aromatic disulfide) oligomer synthesized from 4,4′-oxybis(benzenethiol) can readily undergo ROP at elevated temperature. The resulted polymer in oxygen atmosphere had higher T_g than that in nitrogen atmosphere due to the oxidation of the sulfides in polymer. Cross-linking reaction became very serious at a higher temperature of 300 °C and in oxygen atmosphere. The polymer prepared at 300 °C and in oxygen had no T_g with insoluble content of 36.8%. The melt copolymerization between cyclic disulfide oligomers and elemental sulfur was performed at varying cyclic/sulfur ratios. The T_g's and 5% weight loss temperature of resulted polymers decreased with increasing sulfur contents. Very flexible films can be prepared from the copolymer of cyclics and sulfur. The T_g of the polymers can be tailored by charging the cyclic/sulfur ratio. A series of poly(thiol aromatic)s were synthesized from cyclic(aromatic disulfide) oligomers derived from 4,4′-oxybis(benzenethiol)
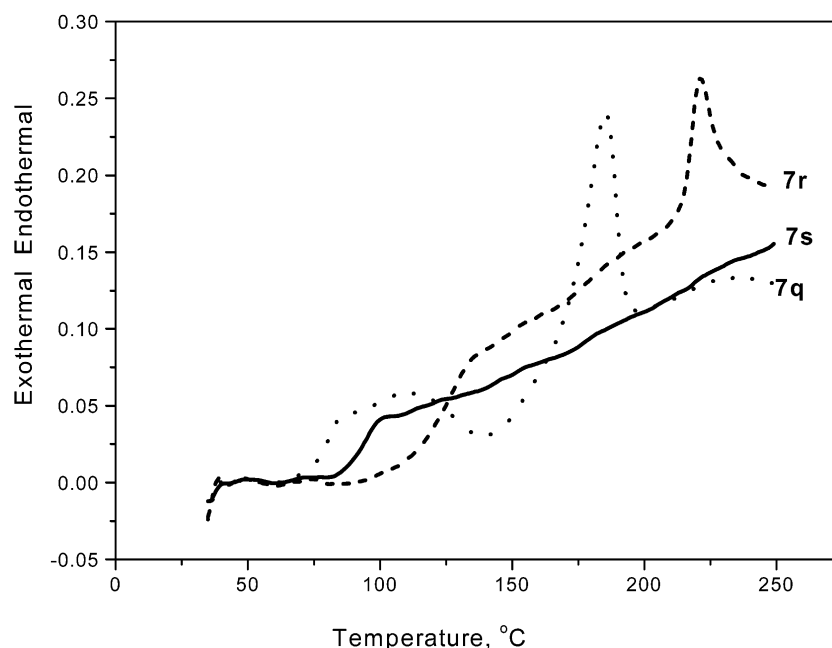

Fig. 5. DSC traces for polymers **7q–s**.

and dibromo aromatic compounds in diphenyl ether solution at 260 °C. The dibromo aromatic compounds can be bis(4-bromophenyl) ether, 4,4$'$-dibromobiphenyl, 1,4-dibromobenzene. All the poly(thio aromatic)s prepared had very high thermal stabilities as indicated by TGA measurements. Therefore, the thermal properties and molecular can be controlled by altering ROP conditions or melt copolymerization system.

Acknowledgements

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