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Synthesis of cocyclic(arylene disulfide) oligomers and their adhesion properties as heating-melt adhesive

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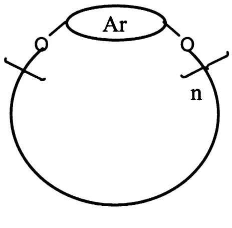
Abstract

Several series of homo- and cocyclic(arylene disulfide) oligomers were synthesized by the catalytic oxidation of arylenedithiols with oxygen in the presence of a copper-amine catalyst. These cyclic(arylene disulfide) oligomers can readily undergo free radical ring-opening polymerization at elevated temperatures in the melt. The cocyclic oligomers had much lower melt flowing temperatures than those of the homocyclic oligomers, which made it possible for the former to undergo ring-opening polymerization at relatively lower temperatures. The composition of the synthesized cyclic oligomers and their ring-opening polymerization were analyzed by proton NMR and gel permeation chromatography (GPC) analyses, respectively. The bonding strength of the cocyclic(arylene disulfide) as a heating-melt adhesive was determined using an Instron tester at a cross-head speed of 5 mm/min. The experimental results showed that the ring-opening polymerization of cocyclic(arylene disulfide) oligomers took place at a temperature as low as 150°C within a short time of 5 min. The ring-opening reaction temperature of the cocyclics was 50°C lower than that of the corresponding homocyclics. The shear-strength for the aluminum substrate prepared at 150°C utilizing the cocyclics was around 5.0 MPa. The cyclic(arylene disulfide) oligomers could be used potentially as high-temperature heating-melt adhesives, coatings, and sealants, as well as matrices for high-performance composites and nanocomposites.

Keywords: Cocyclic(arylene disulfide); Ring-opening reaction; adhesive

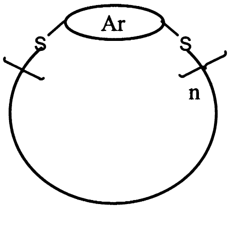
1. Introduction

Cyclic(arylene ether) oligomers (Structure 1) as precursors of high-performance polymers have attracted a great deal of attention [1–6] since the pioneering work of Brunelle et al. on macrocyclic carbonates [7–9].



These macrocyclic oligomers can be processed at a much lower temperature than the corresponding high molecular weight polymers because they have much lower melt viscosities. The macrocycles can undergo ring-opening polymerization without liberation of any by-products. These advantages make them potentially applicable in the areas of high-temperature adhesives, coatings and matrices for advanced thermoplastic composites. The ring-opening reaction temperatures of these macrocycles, however, are generally higher than 300°C. Moreover, the ring-opening reaction takes place only in the presence of proper catalysts, such as phenolic salts. These make the ring-opening reaction very difficult to complete; in all cases there is a large quantity of unreacted cyclics remaining in the melt because of its extremely high viscosity.

Recently, we have synthesized successfully a series of homocyclic(arylene disulfide) oligomers (Structure 2) by using oxidative coupling with oxygen catalyzed by copper salts and an amine.



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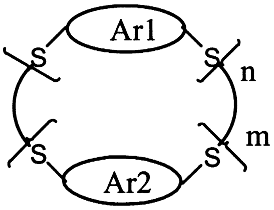
Cyclic oligomers are produced exclusively [10–12]. These homocyclic(arylene disulfide)s also undergo ring-opening polymerization upon heating to form high molecular weight poly(arylene disulfide)s in solution or in the melt via a radical reaction mechanism. The ring-opening polymerization is carried out in the absence of any catalyst at temperatures generally higher than 200°C. This temperature is still rather high, even though it is 100°C lower than that of cyclic(arylene ether) oligomers. High ring-opening reaction temperatures make it difficult to form high molecular weight polymers owing to the solidification of the resulting reactive species in the high viscous melt.

In this work, we report the synthesis of several series of homo- and cocyclic(arylene disulfide) oligomers (Structure 3).



We attempted to design and synthesize cyclic(arylene disulfide) oligomers with as low a melting point as possible, which in turn facilitates melt ring-opening polymerization. Compared with cyclic(arylene ether)s or homocyclic(arylene disulfide)s, the ring-opening polymerization of cocyclic(arylene disulfide)s can be carried out under much milder conditions without any volatile by-product being formed. Considering their high resistance to environmental degradation, good low temperature properties, low water-vapor transmission, excellent resistance to organic solvents, acids and bases, and good adhesion to metal, glass and concrete [13–16], these cocyclic(arylene disulfide)s with low melting point could find applications as adhesive resins for heating-melt adhesives used at high temperature, conductive adhesives, coatings and for high-performance matrices for filler-reinforced composites or nanocomposites, and high-temperature electronic insulators.

2. Experimental

2.1. Materials

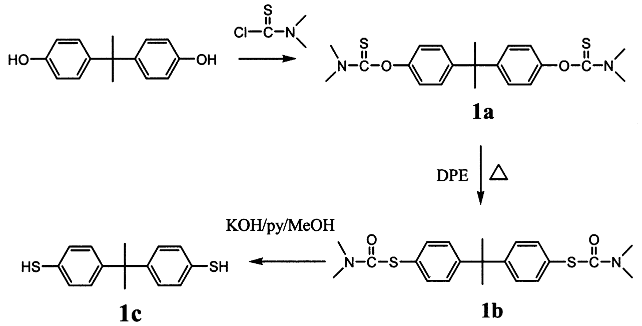
All the chemicals used were reagent grade and purified by standard methods. 4,4′-Isopropylidenediphenol (BPA) was kindly provided in high purity by the General Electric Company. The required 4,4′-thiobis(benzenethiol) was purchased from Aldrich Chemical and used without any further purification. Other arylenedithiols were synthesized according to the methods reported in the literature [10–12]. *N*,*N*′-dimethylthiocarbamoyl chloride, reagent grade diphenyl ether, chlorosulfonic acid, cuprous chloride, *N*,*N*,*N*′,*N*′-tetramethylethylethylene-diamine (TMEDA), and sodium hydrogen sulfide monohydrate were obtained from Aldrich. DMAc, THF, quinoline, methylene chloride, 1,1,2,2-tetrachloroethane (TCE), pyridine, methanol, chloroform, and potassium hydroxide were obtained from commercial sources and used as received.

2.2. Instrumentation

The glass transition and melting temperatures were determined on a Seiko 5200 TGA/DTA and Seiko 220 DSC instrument at a heating rate of 20°C/min under nitrogen flow. The second scan was performed after the sample was heated up to 200°C and held at that temperature for 5 min. 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 1:4:2 (wt) of sample, 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 reflection mode. Gel permeation chromatography (GPC) analyses were carried out on a Waters 510 HPLC equipped with 5-μm Phenogel columns (linear, 3×500 Å^2) arranged in series with chloroform as solvent and a UV detector at 254 nm. Gradient HPLCs were performed on a Milton Roy CM4000 multiple solvent delivery system with a C8 Prime Sphere 4.6×250 mm^2 column, THF and water (bubbled with nitrogen) as eluent solvents, and a UV detector at 300 nm. NMR data were recorded at 400 MHz on a Varian 400-Hz NMR instrument and are listed in parts per million downfield from tetramethylsilane (TMS). Melting points were taken on a Fisher-Johns melting point apparatus equipped with microscope. The bonding strength was determined by using an Instron tester (model 4206) at a crosshead speed of 5 mm/min. Thin aluminum plates were used as the substrates to prepare the joints bonded by synthesized cyclic(arylene disulfide) oligomers. The aluminum plates have dimensions of $5.0 \times 50 \times 0.2$ mm^3, and the joint area is about 5.0×5.0 mm^2. At least five samples for each composition were tested, and the average value was reported.

2.3. Preparation of bis(4-mercaptophenyl)2,2′-propane (*1c*)

The synthesis of bis(4-mercaptophenyl)2,2′-propane (**1c**) was illustrated in Scheme 1. Compounds **1a** and **1b** were synthesized according to the method described in the previous work [12]. Compound **1c** was prepared by the hydrolysis method similar to that given in the literature [13,14]. The product should be separated carefully at low temperature (~0°C) since arylenethiol could be oxidized easily, especially in the solution under basic condition. The resulting solid was dissolved in 5% NaOH solution and precipitated out by slowly adding diluted HCl. The final material was recrystallized from ethanol. Yield: 75.4%. M.p. 67–68°C. ^{1}H NMR ($CDCl_3$) δ 7.20 ppm



Scheme 1. Synthesis of bis(4-mercaptophenyl)2,2′-propane (**1c**).

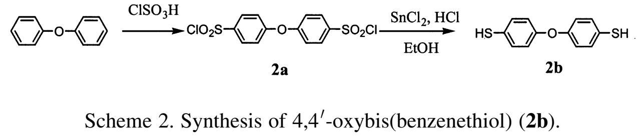
(d, 4H, $J = 8.1$ Hz), δ 7.08 ppm (d, 4H, $J = 8.1$ Hz), δ 3.39 ppm (s, 2H, –SH), 1.65 (s, 6H, $-CH_3$).

*2.4. Preparation of 4,4′-oxybis(benzenethiol) (**2b**)*

4,4′-oxybis(benzenethiol) (**2b**) was prepared according to the route given in Scheme 2. 4,4′-oxybis(4-chlorosulfonylphenyl) (**2a**) was synthesized following the reported procedure [15]. For the synthesis of **2b**, to a 1000-ml round-bottom flask, 30 g (81.7 mmol) of **2a** was introduced together with 300 ml of absolute ethanol, 300 ml of concentrated HCl and 300 g of stannous chloride dihydrate. The resulting mixture was heated to reflux for 7 h, and then cooled. The mixture was diluted with 1000 ml water and filtered. The resulting solid was dissolved in 5% NaOH solution and precipitated out by adding diluted HCl. The procedure was repeated twice. The final product was dried at room temperature under vacuum. Yield: 69.7%. M.p. 76–78°C. ^{1}H NMR ($CDCl_3$) δ 7.12 ppm (d, 4H, $J = 8.0$ Hz), δ 6.90 ppm (d, 4H, $J = 8.0$ Hz), δ 3.30 ppm (s, 2H, –SH). Other arylene dithiols were synthesized by the methods reported in the literature [13,14].

2.5. General procedure for oxidation synthesis of cyclic(arylene disulfide)s

A 150-ml one-neck cylinder (height/diameter = 2.5:1) with an oxygen inlet at the bottom equipped with a high-speed vibromix stirrer was charged with 0.15 g of CuCl, 0.3 g of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and ≥100 ml DMAc. The mixture was stirred vigorously at least for 15 min with oxygen bubbling directly into the reaction mixture. The color of the reaction mixture changed from light green to deep green. Then, approximately 4.0 mmol of arylenedithiol in 30 ml methylene chloride was introduced dropwise into the reaction mixture over 2–3 h. The resulting mixture was stirred for another hour to ensure the completion of the oxidation and then was filtrated through a layer of alumina. The filtrate was treated with 100 ml of 5% HCl solution and further stirred for 1 h. The precipitate was collected by filtration, washed with methanol twice and dried at room temperature under vacuum for 24 h. Yield: >85%.



Scheme 2. Synthesis of 4,4′-oxybis(benzenethiol) (**2b**).

2.6. General procedure for ring-opening reaction in the melt

The synthesized cyclic(arylene disulfide) oligomer powders were introduced (~10 mg) into a DSC aluminum crucible. The samples were dried overnight under vacuum and at room temperature. The crucible was then covered with an aluminum lid and heated under nitrogen atmosphere with a flow rate of 200 ml/min on a Seiko 220 TGA/DTA instrument. After cooling, part of the resulting sample was used to analyze T_g and T_m, and the other part was subjected to GPC analyses by using chloroform as solvent. The residual amount of unreacted cyclic in the sample was calculated upon GPC results.

2.7. General procedure for preparing aluminum joint samples

Thin aluminum plates with dimensions of $45 \times 5.0 \times 0.3$ mm^3 were selected and used as the substrates to determine the shear-strength of the joints bonded by synthesized cyclic(arylene disulfide) oligomers. A wide range of pretreatments for aluminum and its alloys is available. In this work, pretreatment of aluminum plates was combined with organic solvent washing and acid etching. First, the aluminum was washed with ethanol and acetone, respectively, in a supersonic vessel. The dried plates were then treated with 3 wt% phosphoric acid solution in ethyl acetate for 30 min followed by drying at 120°C. The joint samples were prepared on a melting point apparatus and the temperature was controlled at a fixed value. The cyclic powders were placed carefully between two aluminum plates and pressed manually. The joint samples were subjected to a tensile test after cooling to room temperature.

3. Results and discussion

3.1. Synthesis of arylene dithiol compounds

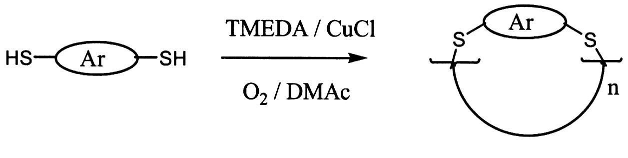
Three different methodologies have been reported to prepare arylene dithiols from various aromatic compounds [10,11]. All of the arylene dithiols used in this work, except for **1c** and **2b**, were made using the same methodologies as above. Compounds **1b** and **2a** were synthesized according to the method given in previous works [10,12]. Arylene dithiols **1c** and **2b** were prepared according to the synthetic routes shown in Scheme 1 and Scheme 2, respectively.

Compound **1c** should be precipitated carefully out at as low a temperature (~0°C) as possible because arylene thiolic salt is extremely easy to oxidize. The crude gum-like product contains a large amount of trapped water and it is difficult to remove by heating. Therefore, the crude solid was dissolved in 5% NaOH solution and precipitated out by slowly adding diluted HCl in order to remove the trapped water. Compound **1c** recrystallized from ethanol is a powder with light yellow color. 4,4′-oxybis(benzenethiol) (**2b**) was made from 4,4′-oxybis(4-chlorosulfonylphenyl) (**2a**) according to the route given in Scheme 2. When purifying crude **2b**, the crude solid should be dissolved in 5% NaOH solution at room temperature under protection of nitrogen flow to avoid its oxidation. Compound **2b** in light yellow was precipitated out by slowly adding diluted HCl.

Generally, aromatic dithiophenols are difficult to separate and purify because of their unstable properties and their obnoxious odors. In this work, we separated and purified **1c** and **2b** from the reaction mixtures at low temperatures in order to avoid their oxidation and unpleasant odors, as illustrated in Section 2. To avoid oxidation, all of the arylene dithiophenols were dried at room temperature under vacuum. The presence of the oxidized product, i.e. disulfide, can be detected easily by ^{1}H NMR. If there is any disulfide present, the proton signals of the benzene ring connecting to the disulfide linkage shift downfield. Therefore, the purity of arylene dithiols can be analyzed by the ^{1}H NMR technique.

3.2. Synthesis and properties of homocyclic(arylene disulfide) oligomers

DMSO, oxygen and iodine are used most frequently to fabricate disulfides and polydisulfides from the oxidation of thiols [16–18]. The catalytic oxidation of dithiols by oxygen has seldom been used. Hay found that poly(disulfide)s can be synthesized from dithiols by catalytic oxidation with oxygen in the presence of a mixture of tertiary amine and a copper salt [19]. In a previous paper, we have demonstrated that the catalytic oxidation of dithiophenols by oxygen is a very efficient and a novel method to prepare cyclic(arylene disulfide) oligomers [12]. The reactions are illustrated schematically in Scheme 3. Following this method, we have synthesized a series of homocyclic(arylene disulfide) oligomers **3** as listed in Table 1. However, only homocyclic(arylene disulfide) oligomers with high melting points (higher than 200°C) [10] were obtained. The high melting points are still a big obstacle for them to undergo ring-opening polymerization at a lower temperature than 150°C. In this sense, extremely dilute condition (1.0 g arylene dithiol/130 ml DMAc) and vigorous stirring (using a high-speed vibromix stirrer) were applied in order to synthesize cyclic oligomers with as small a size as possible.



Scheme 3. Catalytic oxidation cyclization of arylene dithiols.

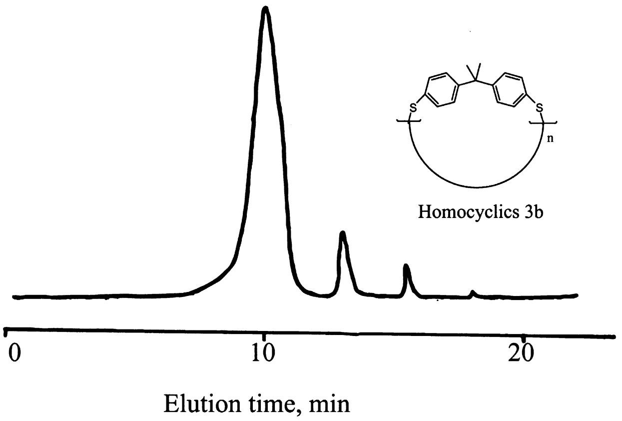
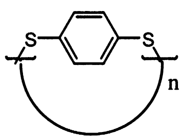
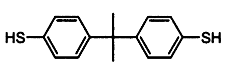
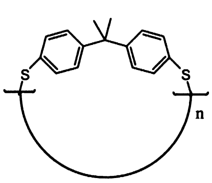
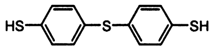
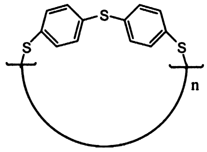
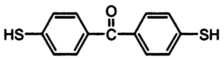
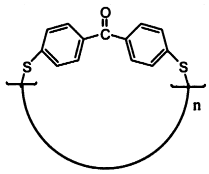
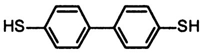
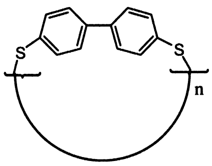
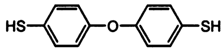
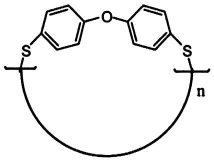
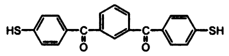
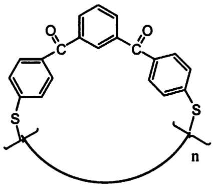


Fig. 1. Gradient HPLC chart of homocyclic(arylene disulfide) oligomers **3b** (for gradient conditions, see text).

Fig. 1 shows the gradient HPLC chart of cyclic(arylene disulfide) oligomer **3b**. The gradient conditions were as follows: at 0 min, THF 70%, water 30; at 20 min, THF 90%, water 10%; at 27 min, THF 100%, water 0%; at 27 min (end), THF 70%, water 30%. By gradient HPLC, the cyclic dimer is shown to be the dominant product for cyclic oligomers **3b** in which cyclic dimer content is higher than 70%. Unexpectedly, the melting point of cyclic oligomer **3b** (219.5°C) (Table 1) is the same as that of the corresponding cyclics (219.3°C) synthesized in a previous work [10]. Other thermal properties of synthesized homocyclic(arylene disulfide)s are also tabulated in Table 1. Basically, there is no obvious difference in melting points compared with the results from the previous work [10]. The results demonstrate that it is not effective to decrease the melting point by minimizing the size of the cyclic. It is considered that the size of cyclic does not change the molecular conformation, i.e. the regularity of the molecular chain. The regular molecular chain then results in the crystalline structure. A melting point of a compound or material is defined as its crystalline melting point. All of the homocyclics listed in Table 1 except homocyclic **3f** have melting points higher than 200°C. It is interesting to note that there is no melting point observed for homocyclic **3f** by DSC. However, the melt flowing temperature of homocyclic **3f**, as determined by the melting point instrument, ranges from 115 to 130°C, which is much lower than that for other homocyclics. This implies that homocyclic **3f** has an amorphous molecular structure. The low melt flowing temperature favors melt ring-opening polymerization of cyclics at a mild temperature.

Table 1
Thermal properties of homocyclic(arylene disulfide) oligomers (ND: not detected)

Entry	Homocyclic	1st scan		2nd scan, T_g (°C)	Melting range measured by melting point, (°C)
		T_g (°C)	T_m (°C)		
		ND	220.0	74.3	230–240
		80.5	219.5	120.0	225–240
		67.4	204.8	76.5	220–230
		ND	224.2	147.3	220–235
		67.5	325.4	176.0	295–320
		76.9	ND	78.7	115–130
		138.9	209.4	140.0	180–215

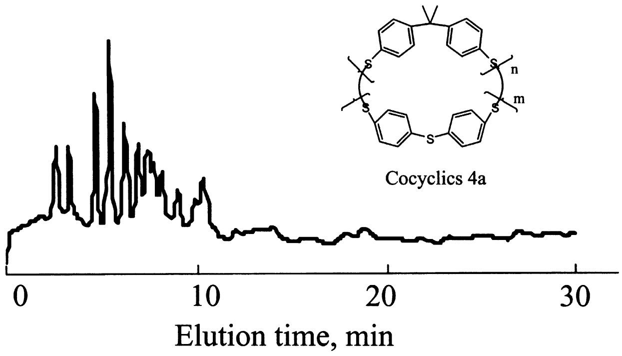


Fig. 2. Gradient HPLC chart of cocyclic(arylene disulfide) oligomers **4a**.

3.3. Synthesis and properties of cocyclic(arylene disulfide) oligomers

From the above results, it is believed that amorphous homocyclics can melt and flow at a very low temperature although it is difficult to synthesize the cyclics with this kind of molecular structure, even under what should be extreme or optimal conditions. However, the synthesis of cocyclics from two or more arylene dithiols may overcome this obstacle and result in an amorphous molecular structure. In an effort to synthesize cocyclic(arylene disulfide) oligomers with amorphous structure, we have attempted the syntheses of co- and tercyclic(arylene disulfide) oligomers from various dithiols. The synthetic procedure is similar to that illustrated in Scheme 3. As expected, the synthesized cocyclics **4** (Table 2) are all amorphous and there are no melting points observed. It is evident that cocyclization breaks up the regularity of the corresponding homocyclics. The melt flowing temperatures of the cocyclics, which range from 87 to 150°C, are much lower than those of the corresponding homocyclics as determined by the melting point instrument.

^{1}H NMR and gradient HPLC have been applied to characterize the structure and composition of the synthesized cocyclics. There were no –SH groups (around 3–4 ppm) remaining as indicated by all of the NMR spectra, demonstrating the completion of oxidation. By gradient HPLC, all of the cocyclics **4** except for cocyclic **4c** consist of the mixture of cocyclics derived from different dithiols as shown in Fig. 2. The cocyclics are difficult to separate owing to the cocyclization; hence they overlap and come out at almost the same retention time. It is surprising to note that cocyclics **4c** appeared as two series of peaks. By comparing them with their parent homocyclics **3c** and **3f**, it is easy to assign these two series of peaks as the mixture of homocyclics as given in Fig. 3. We have tried to confirm the mixture-formation of homocyclics by using matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) with and without an analyte consisting of 1:4:2 (wt) of sample, lithium bromide, and 1,8,9-trihydroxyanthracene (Dithranol) matrix. Unfortunately, the cyclic disulfides cannot be analyzed because of the instability [10] of these cyclics containing disulfide bonds. Supposedly, the homocyclic would have a crystalline structure and result in a high melting point. As listed in Table 2, however, cocyclics **4c** exhibit the lowest melt flowing temperatures ranging from 115 to 130°C. It is rather difficult to understand this behavior since free radical coupling reaction is a very rapid or instant reaction. Probably, the homocyclic formation resulted from the greater flexibility of homocyclics **3c** and **3f**, and the easy changes in their conformations favor the inner-molecular coupling of the resulting free radicals. We suggest that cocyclics **4c** are composed from the molecular blend of homocyclics **3c** and **3f**, which in turn breaks down the molecular regularity or crystalline structure of homocyclic **3c**. We have demonstrated by DSC measurement that there are no changes in the melting points of two components on blending two homocyclics together by the solution method. Based on the results in Table 2, all of the cocyclics have melt flowing temperatures lower than 150°C. This makes it possible for them to undergo ring-opening reaction under milder conditions. The glass transition temperatures (T_gs) of these cocyclics range from 54.4 to 86.5°C, while the T_gs of the polydisulfides derived from these cocyclics range from 54.4 to 140.3°C. The polydisulfide from cocyclics **4b** has an obnoxious odor because of its low T_g.

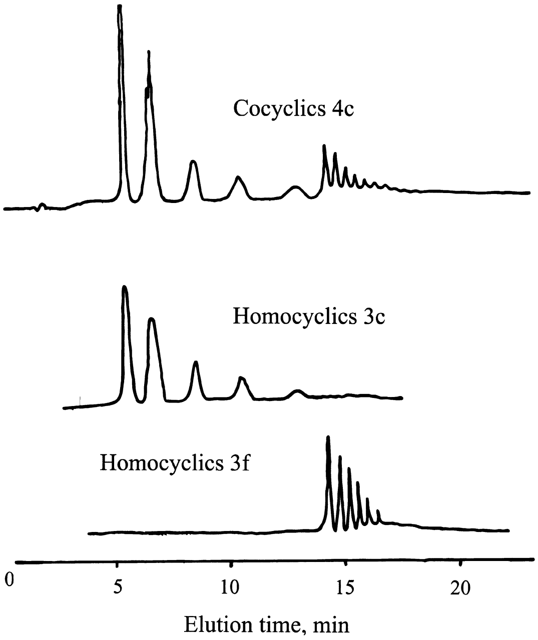
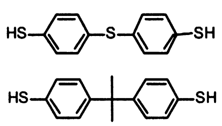
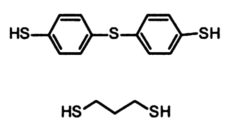
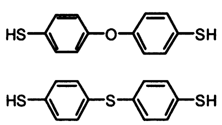
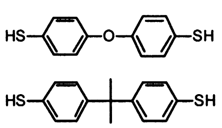
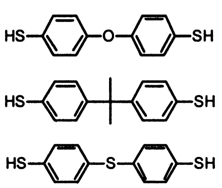
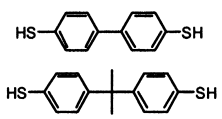
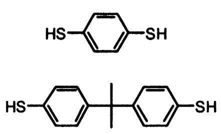


Fig. 3. Gradient HPLC charts of cocyclic(arylene disulfide) oligomers **4c**, homocyclic(arylene disulfide) oligomers **3c** and **3f**.

3.4. Ring-opening reaction of cocyclic(arylene disulfide) oligomers

It is well documented that the disulfide bond ruptures to form radicals at elevated temperatures [20,21]. Therefore, a poly(arylene disulfide) can be formed through ring-opening polymerization (ROP) from a cyclic(arylene disulfide)

Table 2
Thermal properties of cocyclic(arylene disulfide) oligomers (ND: not detected)

Entry	Cocyclic	1st scan		2nd scan, T_g (°C)	Melting range measured by melting point (°C)
		T_g	T_m (°C)		
	Mixture of cocyclics	78.4	185.8NC	104.5	110–125
	Mixture of cocyclics	54.4	ND	54.4	95–110
	Mixture of homcyclics	71.2	ND	77.0	87–100
	Mixture of cocyclics	84.5	ND	97.6	115–135
	Mixture of cocyclics	86.5	ND	91.3	110–125
	Mixture of cocyclics	ND	ND	140.3	135–150
	Mixture of cocyclics	71.9	ND	86.1	110–120

oligomer at elevated temperatures. However, the disulfide–disulfide bond interchange is rather 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 reacting with disulfide bonds can catalyze the exchange reaction at moderate temperatures [22]. Therefore, it is expected that the exchange reaction between disulfide bonds can speed up at high temperatures. In a previous work [20], we have obtained poly(arylene disulfide)s via the ring-opening reaction of cyclic(arylene disulfide) oligomers at a temperature higher than 200°C. We have also tested the same reaction for homocyclic(arylene disulfide) oligomers listed in Table 1 and have found that these homocyclics cannot undergo ring-opening reaction at a temperature lower than 150°C. This is because the melting points of these homocyclics are higher than 200°C; below

Table 3
GPC results of ring-opening polymerization of cocyclics **4a** in the melt

Ring-opening polymerization condition	M_n (g/mol)	M_w (g/mol)	DI[a]	Cyclic remaining (%)
170°C, 5 min	27,300	43,540	1.59	2.54
160°C, 5 min	27,812	44,509	1.60	2.45
150°C, 5 min	26,876	39,971	1.49	2.40
140°C, 5 min	23,601	42,222	1.79	33.0
20 min	25,398	43,577	1.72	12.1

[a] DI: Molecular weight distribution index (Mw/Mn).

this temperature, the resulting free radicals in the solid state cannot move anymore and react with each other. By co- or tercyclization methodology, we have synthesized a series of co- or tercyclic(arylene disulfide) oligomers with very low melt flowing temperatures, which is much lower than 150°C. It is worth, then, checking whether these cocyclics could undergo ring-opening reactions at a temperature lower than 150°C.

In order to study fully the ring-opening polymerization of these cocyclics, we have chosen cocyclics **4a** due to their reasonable solubility in chloroform, which facilitates the molecular weight analysis by GPC. Cocyclics **4a** start to melt flow at a temperature range from 110 to 125°C as detected by the melting point instrument. Therefore, we carried out the melt ring-opening polymerization at temperatures higher than the aforesaid temperatures. The sample was placed in a DSC crucible and ring-opening reaction performed in a TGA/DTA analyzer for 5 min under the protection of nitrogen flow. Subsequently, the resulting poly(arylene disulfide)s were dissolved in chloroform and subjected to GPC measurements. Table 3 shows the GPC results of the ring-opening polymerization of cocyclics **4a** in the melt. High molecular weight polymers were formed almost instantly at 170°C with only trace amounts of unreacted cocyclic oligomers remaining (less than 3.0%). Decrease of the ring-opening reaction temperatures results in no obvious changes in molecular weights and molecular weight distributions. With temperature decreasing down to or lower than 150°C, however, only 67% cocyclics (5 min) underwent ring-opening polymerization to form high molecular weight polydisulfide. Increasing ring-opening reaction time to 20 min, the resulting sample still has 12.1% unreacted cocyclics remaining, demonstrating that the melt ring-opening polymerization is a temperature-dominant reaction. Moreover, we found, by examining Table 3, that molecular weights formed are independent of reaction time and they depend on the reaction temperatures, which is a characteristic of a typical chain growth model for free radical polymerization. It is believed that ring-opening polymerization was complete at 150°C for 5 min with less than 2.5% unreacted cocyclics remaining, indicating that cocyclization is a very efficient way to decrease the melt ring-opening polymerization temperature. Generally, ring-opening polymerization takes place at temperatures around the T_ms of cyclic disulfides. With further decrease of temperature, for example 140°C, the interchange between disulfide–disulfide bonds becomes rather slow regardless of the low melt flowing temperatures for cocyclic oligomers. The results were depicted more clearly in Fig. 4.

Polydisulfides derived from cocyclics **4a**, **4d** and **4f** have high T_gs of ca. 100°C with 5% weight loss temperature of ca. 345°C, indicating that these polymers are thermally stable and can be used promisingly as high-temperature heating-melt adhesives as shown in Table 2. Moreover, it is easy to tailor the T_gs and melt flowing temperatures by changing the cocyclization arylene dithiol pair or their compositions.

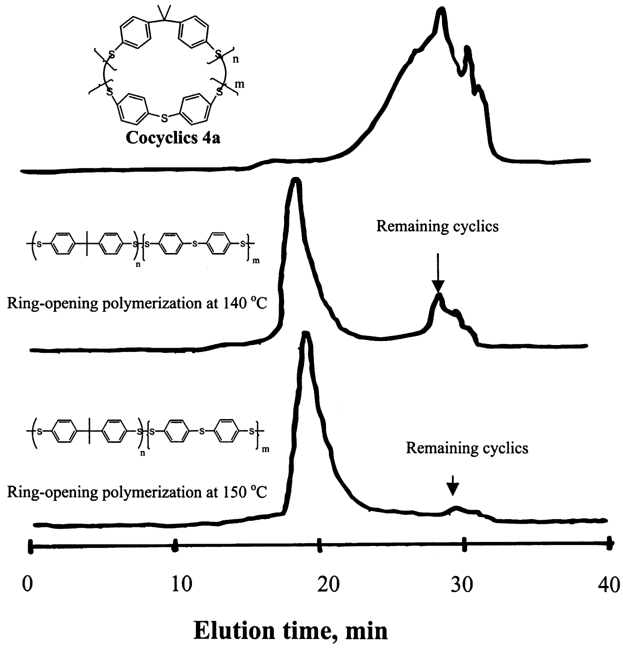


Fig. 4. GPC traces of poly(arylene disulfide) derived from melt ring-opening polymerization of cocyclic(arylene disulfide) oligomer **4a** at varying temperatures.

Table 4
Adhesion properties of the polydisulfide derived from homocyclics **3b** (AF: adhesive failure; CF: cohesive failure)

Ring-opening polymerization condition	Model of failure	Mean joint shear-strength (MPa)	Standard deviation (MPa)
180°C, 5 min	CF	0.814	0.0143
190°C, 5 min	CF	1.303	0.0136
200°C, 5 min	AF	4.670	0.0408

3.5. Adhesion properties of the polydisulfides derived from cocyclic(arylene disulfide) oligomers

As discussed above, cocyclic(arylene disulfide) oligomers undergo instant melt ring-opening polymerization upon heating through a free radical mechanism. In an effort to develop a conductive adhesive for bonding bipolar plates of a fuel cell, the adhesive resin must possess the following: (a) as low a melting point as possible for easy melt ring-opening polymerization; (b) a T_g higher than 100°C for thermal stability; (c) low melt viscosity to facilitate blending with a large amount of fillers; and (d) no volatile products produced during curing or ring-opening reaction. Considering the cocyclic(arylene disulfide) oligomers, especially for cocyclics **4a**, **4d** and **4f**, they satisfy all the above characteristics of a conductive adhesive resin. In addition to these factors, the other key is their adhesion strength.

To evaluate the bonding performance of the synthesized cyclics, thin aluminum plates are used as substrates for preparing joint samples. Our major objective is to develop aluminum bipolar plates as an alternative to stainless steel ones. The fabrication and measurement procedures are given in Section 2. Three different kinds of cyclic, i.e. homocyclics **3b** and **3f** and cocyclics **4a**, are selected for the evaluation of bonding strength. As discussed above, the molecular structures for these three kinds of cyclic are crystalline and amorphous, respectively. Table 4 lists the average joint shear-strength, taken from five replicate joints in each case, as a function of melt ring-opening polymerization temperature of homocyclic **3b**. Standard deviations are also provided. Because of the crystalline structure, homocyclic **3b** exhibits a distinct melting point at 219.5°C (ranging from 190 to 225°C) as determined by DSC. In this respect, it is reasonable to assume that the bonding strengths at 180 and 190°C are caused by cohesive failure because the resulting radical species in the solid cannot transit and initiate polymerization of cyclic disulfides. Increasing the temperature to 200°C, part of homocyclic **3b** starts to melt and flow, which in turn increases and improves the mobility of the resulting free radicals in the melt, leading to the formation of high molecular weight polydisulfide. The shear-strength at this temperature is very large associated with the adhesive failure model. Similarly, the adhesion performance of homocyclic **3f** is listed in Table 5. Homocyclic **3f** gives no melting point, but it begins to melt flow at a temperature of 115°C. The joint sample prepared at 160°C has no strength owing to cohesive failure. A maximum shear-strength (5.61 MPa) is achieved when the temperature is increased up to 180°C. Although homocyclic **3f** has a much lower melt flowing temperature compared to homocyclic **3b**, the melt ring-opening polymerization takes place at rather high temperatures.

Table 5
Adhesion properties of the polydisulfide derived from homocyclics **3f** (AF: adhesive failure; CF: cohesive failure)

Ring-opening polymerization condition	Model of failure	Mean joint shear-strength (MPa)	Standard deviation (MPa)
160°C, 5 min	CF	2.143	0.0183
170°C, 5 min	CF and AF	4.034	0.0336
180°C, 5 min	AF	5.611	0.0888

By utilizing cocyclization methodology, amorphous cocyclics with low melt flowing temperatures were synthesized as shown in Table 2. The shear adhesion strengths for cocyclics **4a** are tabulated in Table 6. Because of its low melt flowing temperature, we select the ring-opening temperature ranging from 140 to 170°C. However, low-temperature (140°C) treatment yields very low bonding strength, even extending the ring-opening time to 15 min. It is considered that the ring-opening reaction is not complete at this temperature. Also, the remaining small molecules, i.e. cocyclics, lead to poor strength. This is consistent with the result of the GPC measurement. From Table 6, adhesion strengths increase dramatically when the temperature is increased to 150°C. No obvious changes can be observed on prolonging the ring-opening time to 15 min. This means that long reaction time cannot increase the fluidity of the solidifying melt since the ring-opening reaction takes place instantly in the free radical mechanism. As shown in Table 6, the adhesion strength achieves an optimum value of 6.571 MPa as the temperature reaches 160°C, indicating that the ring-opening polymerization is a temperature-dependent

Table 6
Adhesion properties of the polydisulfide derived from cocyclics **4a** (AF: adhesive failure; CF: cohesive failure)

Ring-opening polymerization condition	Model of failure	Mean joint shear-strength (MPa)	Standard deviation (MPa)
140°C, 5 min	CF	0.886	0.0293
140°C, 15 min	CF	1.203	0.1170
150°C, 5 min	CF and AF	4.129	0.0232
150°C, 10 min	AF	4.739	0.0211
150°C, 15 min	AF	4.879	0.0240
160°C, 5 min	AF	6.571	0.0222
170°C, 5 min	AF	6.431	0.0351

reaction. Further increasing the temperatures does not result in additional improvement of adhesion properties.

4. Conclusions

Series cocyclic(arylene disulfide) oligomers were synthesized by the catalytic oxidation of arylene dithiols with oxygen in the presence of a copper-amine catalyst. These cocyclic oligomers possessed very low melt flowing temperatures and therefore could readily undergo free radical ring-opening polymerization at temperatures as low as 140°C in the melt. The low melt flowing temperature of these cocyclics resulted from their amorphous molecular structure. The composition of synthesized cyclic oligomers and their ring-opening polymerization were investigated and confirmed by proton NMR, gradient HPLC and gel permeation chromatography (GPC) analyses. The bonding strength of the cocyclic(arylene disulfide) as heating-melt adhesive was determined using an aluminum substrate. The experimental results demonstrated that the melt ring-opening polymerization of cocyclic(arylene disulfide) oligomers can be completed fully at a temperature as low as 150°C within a short time. The ring-opening reaction temperature of the cocyclics was 50°C lower than that of the corresponding homocyclics. The resulting polydisulfide bonds with the aluminum substrate very well with an optimum value of 6.571 MPa, indicating that the cocyclics could be used as heating-melt adhesive for various bonding applications. The cyclic(arylene disulfide) oligomers could be used potentially as high-temperature adhesive resin for conductive adhesives, heating-melt adhesives, coatings, and sealants, as well as matrices for high-performance composites and nanocomposites.

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