One-Step Synthesis and Ring-Opening Polymerization of Novel Macrocyclic(arylene multisulfide) Oligomers

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ABSTRACT: A series of macrocyclic(arylene multisulfide) oligomers were synthesized under high dilution conditions by reacting diphenyl ether/diphenyl/diphenyl disulfide/diphenyl methane with dichloro disulfide in the presence of a trace amount of iron powder by a one-step reaction. From MALDI-TOF mass spectra, it was established that the repeating units of the cyclization ranged from two to seven and the unit of macrocyclic(arylene multisulfide) oligomers had one to seven sulfur atoms. The macrocyclic oligomers readily underwent ring-opening polymerization in the melt, resulting in linear, high molecular weight polymultisulfides. DSC thermograms demonstrated that the four polymultisulfides, derived from the macrocyclic(arylene multisulfide) oligomers, are amorphous in nature. The macrocyclic(arylene multisulfide) oligomers and polymers were analyzed by MALDI-TOF-MS, IR, HPLC, NMR, DSC, and TGA methods. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 735–741, 2004

Key words: macrocyclics; ring-opening polymerization; MALDI-TOF mass spectrum; oligomers; synthesis

INTRODUCTION

There has been an increasing interest in macrocyclic oligomers in recent years in view of their attractive applications as reactive intermediates for the synthesis of high-performance linear arylene polymers by ring-opening polymerization.[1–5] These macrocyclic oligomers exhibit lower melt viscosity compared to that of their corresponding polymers, which facilitate their melt processing. Macrocyclic oligomers can undergo the ring-opening polymerization without liberation of any byproducts at a relatively lower temperature. These advantages render them as potential candidates for application in the areas of high-performance polymers, matrices of composite materials, and high-temperature adhesives.

For preparing macrocyclic(arylene sulfide) oligomers, two main routes are generally adopted. In the first method, the macrocyclic(arylene disulfide) oligomers are usually synthesized under high dilution conditions by the catalytic oxidation of arylenedithiols with oxygen in the presence of a copper–amine catalyst as shown in Scheme 1. Cuprous chloride and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were used as copper and amine ligand, respectively.[6–8] These oligomers can readily undergo free-radical ring-opening polymerization upon heating. Another method is by one-step synthesis of cyclic(arylene monosulfide) oligomers through oxidation reaction of aromatic compounds containing aromatic electrophilic substitution. This proceeds under high dilution conditions at room temperature as depicted in Scheme 2.[9,10] 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was used as the oxidant. Several kinds of aromatic cyclic monosulfides bearing methyl, ether, sulfide, and disulfide groups were effectively prepared.

For the preparation of macrocyclic(arylene disulfide) oligomers, aromatic dithiols must be used as starting compounds. The synthesis of these compounds involves a two-step method in which the aromatic compounds react first with chlorosulfonic acid and then can be reduced by a suitable reducing agent. The synthesis procedure is rather complicated and the total yield is also low. Moreover, the catalyst of 2,2′-dithiobis(benzothiazole) is much more expensive and thus these cyclics are less practicable for the preparation of cyclic(arylene monosulfide) oligomers.

The varying sulfur contents in the macrocyclic(arylene sulfide) oligomers can lead to different ring-opening polymerization temperatures for these macrocyclics. It has been reported by Hay and coworkers[6–8] that the homocyclic(arylene disulfide)s can undergo

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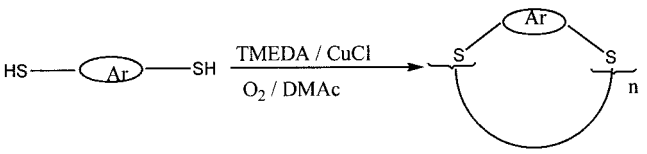
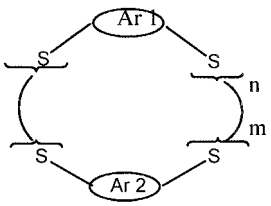


Scheme 1 Preparation of macrocyclic(arylene disulfide) oligomers.

ring-opening polymerization upon heating in the melt by a radical reaction mechanism. The ring-opening polymerization temperatures are generally higher than 200°C in the absence of any catalyst. Ding and Hay[11] performed copolymerization of homocyclic-(arylene disulfide) oligomers derived from 4,4′-isopropylidene bisbenzenethiol with S_8. The introduction of free sulfur results in a decrease in the ring-opening reaction temperature to 150°C. To decrease the ring-opening polymerization temperature, Meng et al.[12] rapidly polymerized several series of cocylic(arylene disulfide) oligomers at a temperature as low as 150°C without adding sulfur and any other catalysts. The structure can be depicted as follows:



For the cyclic(arylene monosulfide) oligomers, the ring-opening polymerization temperatures are generally higher than 300°C.[9,10] These cyclic oligomers were polymerized in the presence of 2,2′-dithiobis(benzothiazole) or elemental sulfur as an initiator.

According to the literature, larger amounts of aromatic compounds react with sulfur chloride in the presence of iron powder as catalyst for preparing linear sulfur-containing polymers.[13] In another report, the polymerization of diphenyl disulfide was carried by the S—S bond cleavage with a Lewis acid.[14] To date, however, there apparently are no studies, or successful approach, reported in the literature concerning the application of the above method to prepare the cyclic oligomers.

The main aim of this work was to synthesize macrocyclic(arylene multisulfide) oligomers in a one-step method and to polymerize them by free-radical ring-opening polymerization under mild conditions without using any catalyst. A series of new macrocyclic-(arylene multisulfide) oligomers were synthesized under high dilution conditions by reacting diphenyl ether/diphenyl/diphenyl disulfide/diphenyl methane with dichloro disulfide in the presence of trace amounts of iron powder by a one-step procedure. The resulting high yield macrocyclic products were then characterized by IR, HPLC, NMR, DSC, and MALDI-TOF-MS mass spectroscopic techniques.

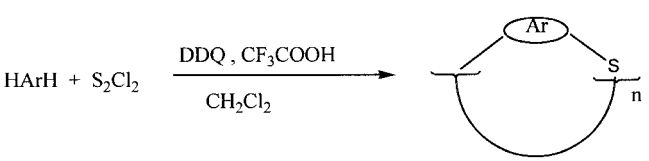
EXPERIMENTAL

Materials

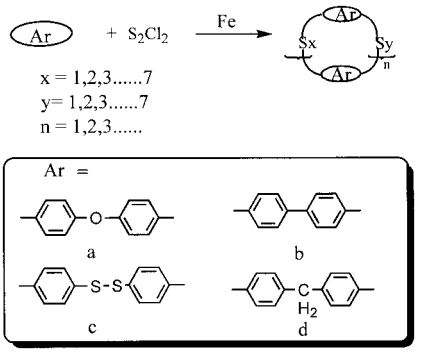
All the chemicals used were of reagent grade and purified by the standard methods. Diphenyl ether, diphenyl, diphenyl disulfide, and diphenyl methane were purchased from Aldrich. Dichloro disulfide and iron powder were obtained from Shanghai Chemical Reagent Co., Ltd., China. Methylene chloride and other solvents were supplied from commercial sources and used as received.

Measurements

Infrared spectra were recorded by the KBr pellet method using a Jasco FT/IR-5300 spectrometer (Jasco, Tokyo, Japan). The band resolution was maintained at 2 cm^{-1} for all measurements. ^{1}H-NMR spectra were recorded at 400 MHz on a Bruker DRX-400 NMR instrument (Bruker Instruments, Billerica, MA) 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. Gradient HPLC analysis was carried out on a Milton Roy CM4000 multiple solvent delivery system with a C18 Prime Sphere 4.6 × 200-mm column using THF and water as eluent solvents, and a UV detector operated at 300 nm. The gradient conditions were as follows: at 0 min, THF 0%; at 15 min, THF 100%; and at 25 min (end). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker MALDI-III TOF instrument with a maximum laser output of 6 mW at a wavelength of 337 nm (N_2 laser light, 3 nm pulse width, 100 mm diameter spot). The MALDI-TOF instrument was operated in a positive reflection mode. The ions produced from each laser shot were accelerated to 25 keV into a 1-m drift region. The matrix used for all experiments was 2,5-dihydroxy benzoic acid (Aldrich, Milwaukee, WI). The resolution and accuracy of the Bruker MALDI-III TOF instrument were 12,000 (the ratio of peak height to peak width at middle height) and <0.03%, respectively. Differential



Scheme 2 Preparation of macrocyclic(arylene multisulfide) oligomers.



Scheme 3 Preparation of macrocyclic(arylene multisulfide) oligomers.

scanning calorimetry (DSC) scans were obtained using a PE DSC-7 instrument (Perkin Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 20°C/min in N_2 (40 mL/min) atmosphere. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a Netzsch TG 209 instrument (Germany) at a heating rate of 20°C/min in N_2 (300 mL/min) atmosphere.

Preparation of macrocyclic(arylene multisulfide) oligomers

Macrocyclic(arylene multisulfide) oligomers were prepared by using the reagents described in Scheme 3. A typical procedure is as follows. Dichloromethane solution (40 mL) of diphenyl ether (5 mmol) was added dropwise to 80 mL of dichloromethane containing dichloro disulfide (5 mmol) and iron powder (50 mg) over a period of 4 h. The filtered solution was then poured into 200 mL of methanol to precipitate the oligomers. The resulting yellowish powders were washed with distilled water and methanol and dried at 30°C under vacuum for 20 h. Yield: 98.5%.

Macrocyclic(arylene multisulfide) oligomer ***1a***. ^{1}H-NMR ($CDCl_3$): 7.25–7.53 ppm (m, 4H), 6.75–7.01 ppm (m, 4H); IR (KBr, cm^{-1}): 3057, 3024, 1888, 1577, 1481, 1400, 1342, 1238, 1161, 1088, 1051, 1009, 868, 823.

Macrocyclic(arylene multisulfide) oligomer ***1b***. ^{1}H-NMR ($CDCl_3$): 7.54–7.71 ppm (t, 4H), 7.37–7.43 ppm (d, 4H); IR (KBr, cm^{-1}): 3018, 1587, 1471, 1448, 1373, 1250, 1113, 1084, 1003, 881, 808.

Macrocyclic(arylene multisulfide) oligomer ***1c***. ^{1}H-NMR ($CDCl_3$): 7.44 ppm (s, 8H); IR (KBr, cm^{-1}): 3049, 1896, 1718,1570, 1469, 1433, 1383, 1302, 1257, 1176, 1090, 1068, 1032, 1007, 810.

Macrocyclic(arylene multisulfide) oligomer ***1d***. ^{1}H-NMR ($CDCl_3$): 7.64 ppm (s, 4H), 6.90–7.19 ppm (m, 4H), 3.91 ppm (s, 2H); IR (KBr, cm^{-1}): 3024, 2918, 1595, 1489, 1452, 1398, 1182, 1111, 1074, 1034, 1014, 883, 841, 802.

Ring-opening polymerization of macrocyclic(arylene multisulfide) oligomers

Ring-opening polymerization (ROP) of macrocyclic-(arylene multisulfide) oligomers is described in Scheme 4.

The ROP of the cyclic oligomers was performed in the melt. A typical polymerization procedure is as follows: macrocyclic(arylene multisulfide) oligomer **1a** (3 mmol) was introduced into a 25-mL dry round-bottom flask with a provision for nitrogen inlet and outlet. The flask was then placed in a preheated salt bath at 300°C for 30 min. Upon finishing the ROP, the molten mixture was quenched by pouring into methanol, where a tough solid mass of the product was obtained. The product was ground to a fine powder and washed with chloroform to obtain poly(thio arylene)s in 80.4% yield.

Poly(thio arylene) ***2a***. IR (KBr, cm^{-1}): 2980, 2925, 2362, 1575, 1479, 1400, 1236, 1161, 1088, 1051, 1009, 818.

Poly(thio arylene) ***2b***. IR (KBr, cm^{-1}): 2926, 2372, 1580, 1443, 1368, 1252, 1078, 1001, 872, 802.

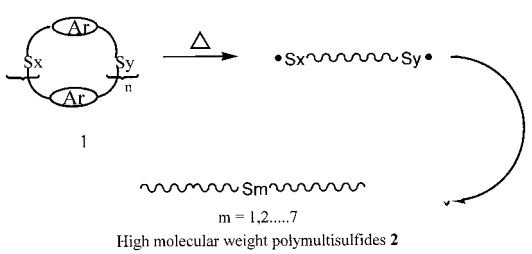
Poly(thio arylene) ***2c***. IR (KBr, cm^{-1}): 2927, 2367, 1564, 1466, 1425, 1379, 1294, 1088, 1005, 874, 806.

Poly(thio arylene) ***2d***. IR (KBr, cm^{-1}): 3051, 3012, 2367, 1583, 1485, 1448, 1394, 1178, 1107, 1072, 1011, 800.

RESULTS AND DISCUSSION

Preparation of cyclic(arylene multisulfide) oligomers

Pseudo-high dilution conditions were achieved by slowly adding the monomer solution into a solution of dichloro disulfide for a period of 2–12 h. It is well known that linear polymers are produced when the concentration of the monomer is high, whereas low or highly dilute concentration of monomer yields cyclic oligomers. Thus, to obtain the cyclic oligomers in a quantitative yield, the final concentration of the monomer is maintained below 0.08*M*. To ensure the formation of cyclic oligomers other than linear polymers, the addition of diphenyl ether needs about 4 h to complete, whereas the diphenyl/diphenyl disulfide/diphenyl methane system takes 12 h. For the syntheses of cyclic oligomers **1b–1d**, when the reaction time was



Scheme 4 Ring-opening polymerization of macrocyclic-(arylene multisulfide) oligomers.

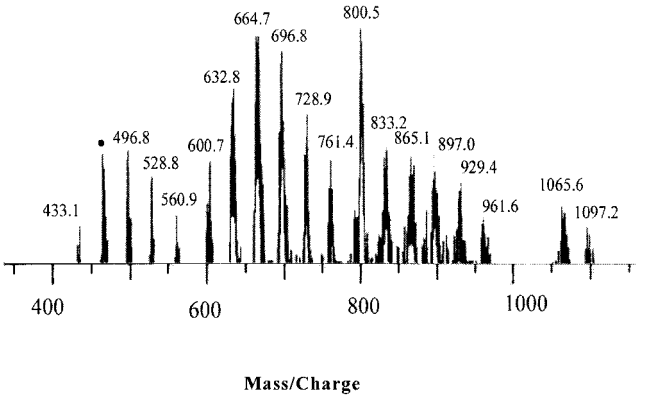


Figure 1 Positive ion MALDI-TOF-MS data for macrocyclic(arylene multisulfide) oligomer **1a** using 2,5-dihydroxy benzoic acid as the matrix. The peaks marked with solid circles (●) are attributed to contaminated linear oliomers.

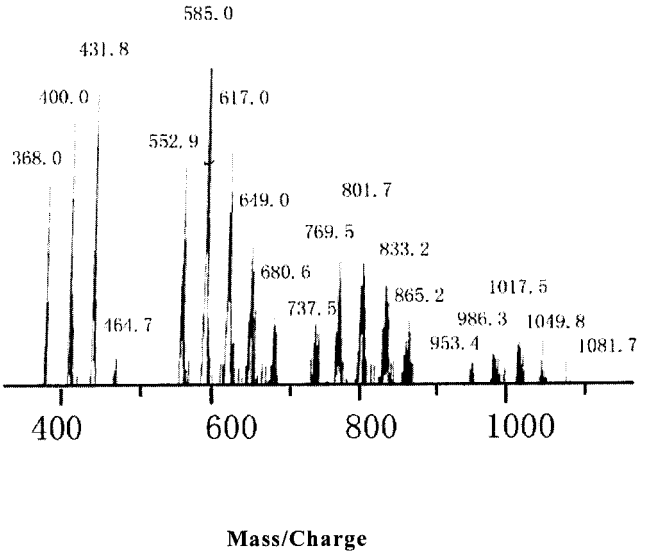


Figure 2 Positive ion MALDI-TOF-MS data for macrocyclic(arylene multisulfide) oligomer **1b** using 2,5-dihydroxy benzoic acid as the matrix.

less than 10 h, we obtained oil-like products only. Presumably, the resulting materials are linear products.

The FTIR spectrum of product **1c** (not shown) was found to be similar to that of linear(arylene sulfide) oligomers. However, two distinct peaks at 1090 and 1068 cm^{-1} were observed, which are characteristic of the cyclic(arylene sulfide) oligomer.[15] There was an absence of peaks around 690–740 cm^{-1} corresponding to an end phenyl group. In the ^{1}H-NMR spectrum, a single peak for the phenyl proton was observed at 7.44 ppm that confirms the formation of macrocyclic-(arylene multisulfide) oligomers. In combination with MALDI-TOF mass spectrum, the structure of macrocyclic oligomer **1c** is similar to that of cyclic(arylene sulfide)[9] but containing more sulfur atoms. No peaks attributable to –SH groups were observed.

MALDI-TOF-MS analyses (Figs. 1–4) also indicate that the resulting products are macrocyclic(arylene multisulfide) oligomers. In the present case, the correct molecular weight ion signals for the macrocyclic-(arylene multisulfide) oligomers are detected in the MALDI-TOF mass spectrum using 2,5-dihydroxy benzoic acid as matrix. The data of Figure 2 are given in Table I, representing the detailed structure of the macrocyclic(arylene multisulfide) oligomers. From this table, it is evident that no signals associated with the linear oligomers are observed. From the four MALDI-TOF mass spectra of macrocyclic(arylene multisulfide) oligomers, it is also apparent that the prepared products are a mixture of oligomers, having repeating units that bear one to seven sulfur atoms. The number of repeating units of arylene group varies from two to seven. From their structure, we can thus expect that these macrocyclic(arylene multisulfide) oligomers can readily undergo free-radical ring-opening polymerization like cyclic(arylene disulfide) oligomers.[12]

From the MALDI-TOF mass spectrum of macrocyclic **1b** (Table I), the presence of the peaks at 368.0, 552.9, and 737.5 *m/z* indicates that the oligomers are macrocyclic(arylene monosulfide) oligomers. However, on the basis of the presence of other peaks at 431.8, 649.0, 865.2, and 1081.7 *m/z*, we cannot firmly establish that they correspond to macrocyclic(arylene disulfide) oligomers. This uncertainty arises because there are two possibilities for the identification of the position of sulfur atoms in the unit. One possibility is that, on one side of the oligomer, there may be one sulfur atom, whereas on the other side, there may be three sulfur atoms. In another case, two sides of the oligomers can have two sulfur atoms each. The latter case establishes the formation of cyclic(arylene disulfide) oligomers. Further, the mass spectra and HPLC data for these oligomers provide different information. The mass spectra yielded 19 peaks, whereas

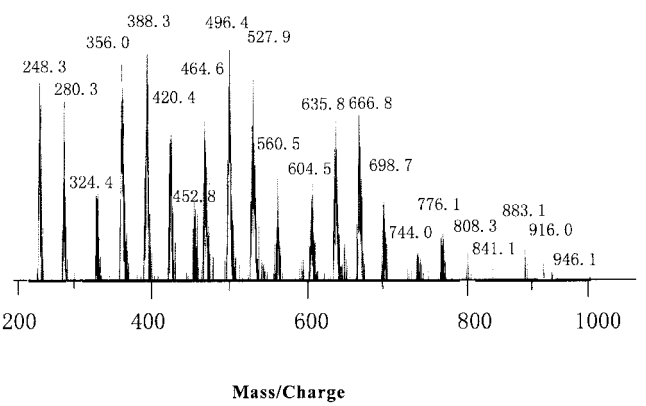


Figure 3 Positive ion MALDI-TOF-MS data for macrocyclic(arylene multisulfide) oligomer **1c** using 2,5-dihydroxy benzoic acid as the matrix.

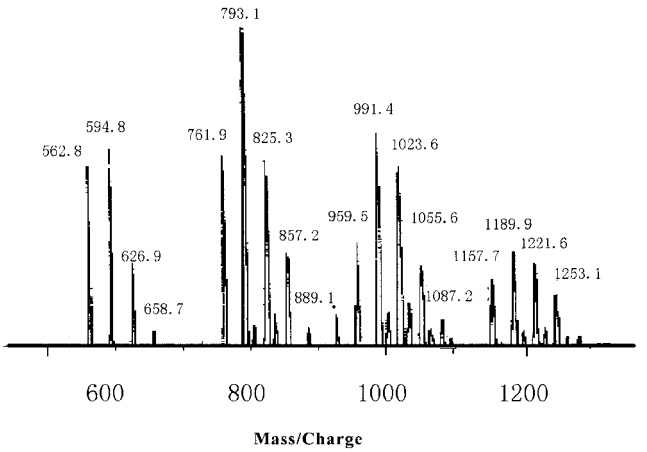


Figure 4 Positive ion MALDI-TOF-MS data for macrocyclic(arylene multisulfide) oligomer **1a** using 2,5-dihydroxybenzoic acid as the matrix. The peaks marked with solid circles (●) are attributed to contaminated linear oliomers.

HPLC analysis (Fig. 5) produced more than 19 peaks. So even when the unit of **1b** has four sulfur atoms, we cannot ensure that the oligomer formed is cyclic-(arylene disulfide). The complexity in the structure elucidation increases with increasing the number of sulfur atoms in each unit. Moreover, the HPLC peaks for **1b** (Fig. 5) are sharp, whereas those corresponding to oligomers **1a**, **1c**, and **1d** are broad (Fig. 6). These results indicate that the ingredients of **1a**, **1c**, and **1d** cannot be completely separated in the gradient HPLC analysis under the present experimental conditions.

TABLE I
Positive Ion MALDI-TOF-MS Data for Cyclic(arylene multisulfide) Oligomer 1b Using 2,5-Dihydroxy Benzoic Acid as the Matrix

Structure	Average value	Observed (m/z)	Deviation[a] (Da)
$(C_{12}H_8)_2S_2$	368.5	368.0	−0.5
$(C_{12}H_8)_2S_3$	400.6	400.0	−0.6
$(C_{12}H_8)_2S_4$	432.7	431.8	−0.9
$(C_{12}H_8)_2S_5$	464.7	464.7	0
$(C_{12}H_8)_3S_3$	552.9	552.9	0
$(C_{12}H_8)_3S_4$	584.8	585.0	0.2
$(C_{12}H_8)_3S_5$	616.9	617.0	0.1
$(C_{12}H_8)_3S_6$	649.0	649.0	0
$(C_{12}H_8)_3S_7$	681.0	680.6	−0.4
$(C_{12}H_8)_4S_4$	737.0	737.5	0.5
$(C_{12}H_8)_4S_5$	769.1	769.5	0.4
$(C_{12}H_8)_4S_6$	801.2	801.7	0.5
$(C_{12}H_8)_4S_7$	833.2	833.2	0
$(C_{12}H_8)_4S_8$	865.3	865.2	−0.1
$(C_{12}H_8)_5S_6$	953.4	953.4	0
$(C_{12}H_8)_5S_7$	985.4	986.3	0.9
$(C_{12}H_8)_5S_8$	1017.5	1017.5	0
$(C_{12}H_8)_5S_9$	1049.6	1049.8	0.2
$(C_{12}H_8)_5S_{10}$	1081.6	1081.7	0.1

[a] Deviation = (experimental value) − (average value).

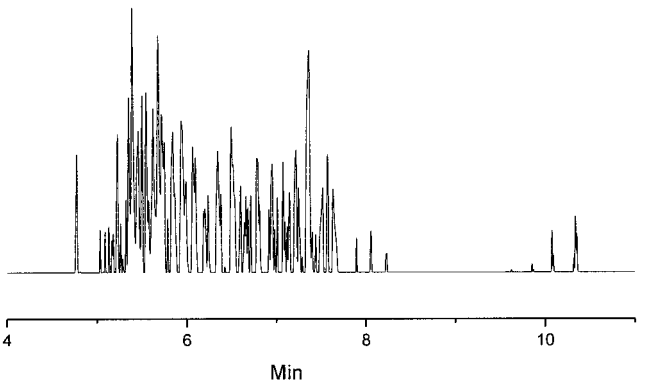


Figure 5 HPLC for macrocyclic(arylene multisulfide) oligomer **1b**.

From the DSC thermograms (not shown), it is deduced that the macrocyclic(arylene multisulfide) oligomers **1a**, **1b**, and **1c** are amorphous in nature. The glass-transition temperatures of **1a**, **1b**, and **1c** (Table II) were found to be 108.16, 173.48, and 104.46°C, respectively. The corresponding melt flow temperatures were in the range of 80–90, 125–131, and 105–115°C, respectively. Further, it is evident from the DSC studies that the macrocyclic(arylene multisulfide) oligomer **1d** is crystalline in nature with a melting temperature of 115.97°C.

Ring-opening polymerization of macrocyclic(arylene multisulfide) oligomers

The macrocyclic oligomers **1a** and **1d** were polymerized under nitrogen atmosphere at 300°C, whereas **1b** and **1c** were polymerized at 360°C in 0.5 h to obtain

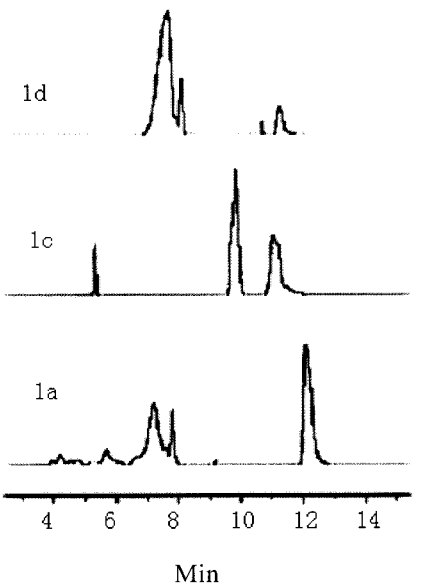


Figure 6 HPLC for macrocyclic(arylene multisulfide) oligomer **1a**, **1c**, and **1d**.

TABLE II
Thermal Properties of Macrocyclic(arylene multisulfide) Oligomers

Oligomer	Yield (%)	T_g (°C)	T_m (°C)	Range of melt flow temperature (°C)
1a	98.5	108.16	—	80–90
1b	95.4	173.48	—	125–131
1c	40.2	104.46	—	105–115
1d	54.1	—	115.97	—

TABLE III
Thermal Properties of Polymers Derived from the Ring Opening of Macrocyclic(arylene multisulfide) Oligomers

Polymer	T_g (°C)	TGA[a] (°C)	Range of melt flow temperature (°C)
2a	109.17	455	190–200
2b	176.99	494	308–314
2c	137.90	360	230–235
2d	118.58	476	270–280

[a] Temperature for 10% weight loss measured by TGA in N_2.

linear poly(thiophenylene). The DSC thermograms revealed that the four polymers made from the macrocyclic(arylene multisulfide) oligomers are amorphous in nature. The polymers are insoluble in common solvents at room temperature. Polymer **1a** is soluble in NMP above 200°C. Polymers **1c** and **1d** are only partially soluble in NMP at temperatures above 200°C, although polymer **1b** is insoluble in NMP at temperatures even above 200°C.

We found that the temperature of ring-opening polymerization is a vital factor to control the property of the polymer.

For macrocyclic oligomer **1a**, when the temperature of the ring-opening reaction was maintained at 250°C for 20 min, a product with a melt flow temperature in the range of 120–125°C was produced. As the temperature was increased to 300°C, the polymer synthesized had a melt flow temperature in the range of 190–200°C. The glass-transition temperature of polymer **2a** is 109.17°C (Table III). The $T_{d10\%}$ of polymer **2a** is at 455°C. In a comparison of the IR spectra (Fig. 7) of polymer **2a** and polymer prepared from homologous cyclic(arylene disulfide) oligomer **3**, it appears that they are similar. The absorption at 818 cm^{-1} is attributed to C—H out-of-plane deformation vibration of 1,4-disubstituted benzene, indicating the formation of 1,4-conjugated phenylene sulfide. The IR spectrum of macrocyclic(arylene multisulfide) oligomer **1a** is similar to that of linear polymer **2a**. The inherent viscosity of polymer **2a** is 0.22 dL/g, indicating high molecular weight of polymer was obtained.

For macrocyclic(arylene multisulfide) oligomer **1b**, when the temperature of the ring-opening reaction was maintained at 300°C, it did not undergo polymerization. In this case, when the temperature was increased to 360°C, the polymer synthesized had a melt

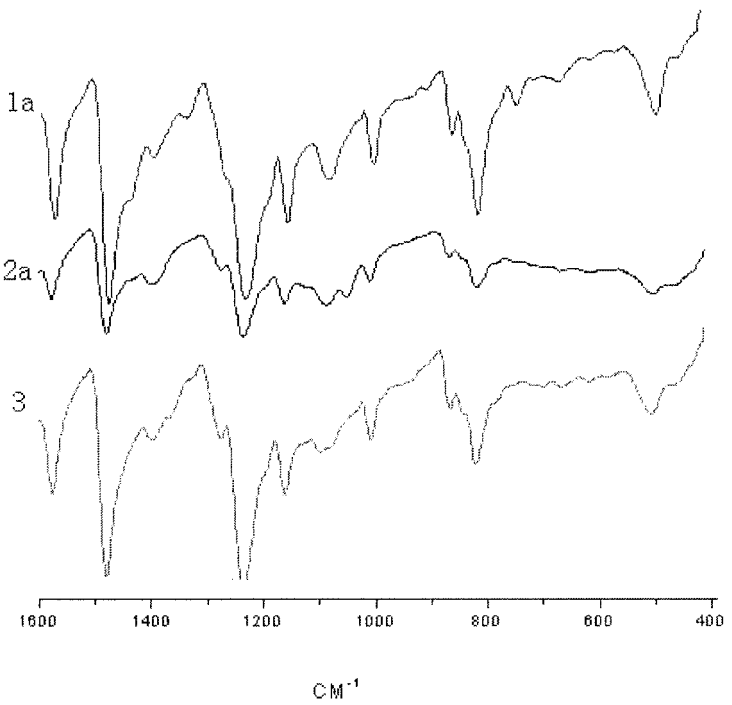


Figure 7 IR spectra of macrocyclic(arylene multisulfide) oligomer **1a** and polymer **2a** [**3** is the polymer prepared by corresponding cyclic(arylene disulfide) oligomer].

flow temperature in the range of 308–314°C. The glass-transition temperature of polymer **2b** is 176.99°C. Polymer **2b** shows high thermal stability with a $T_{d10\%}$ of 494°C and retains 80% of its original weight at 632°C under nitrogen atmosphere.

For macrocyclic(arylene multisulfide) oligomer **1c**, when the temperature of the ring-opening reaction was maintained at 300°C, the polymer synthesized had a melt flow temperature in the range of 230–235°C. When the temperature was increased to 360°C, the polymer synthesized had a melt flow temperature remaining in the same range. The glass-transition temperature of polymer **2c** is 118.58°C. The $T_{d10\%}$ of this polymer is 360°C. The high sulfur content in **2c** may be responsible for its low $T_{d10\%}$ value.

For cyclic(arylene multisulfide) oligomer **1d**, when the temperature of the ring-opening reaction was maintained at 250°C, we obtained a polymer with a melt flow temperature in the range of 220–230°C. When the temperature was increased to 300°C, however, the polymer synthesized had a melt flow temperature in the range of 270–280°C. The glass-transition temperature of polymer **2d** is 137.9°C. Polymer **2d** shows high thermal stability with a $T_{d10\%}$ of 476°C and retains 79% of its original weight at 662°C under nitrogen atmosphere.

CONCLUSIONS

In conclusion, macrocyclic(arylene multisulfide) oligomers were prepared by the reaction of diphenyl ether/diphenyl/diphenyl disulfide/diphenyl methane with dichloro disulfide in the presence of a trace amount of iron powder by one-step method under pseudo-high dilution conditions. The prepared cyclic oligomers are mixtures having repeating units with one to seven sulfur atoms. The number of repeating units vary from two to seven. This method provides a very effective way to synthesize cyclic(arylene sulfide) oligomers. Ring-opening polymerization of the macrocyclic(arylene multisulfide) oligomers led to the formation of linear poly(thio arylene)s. The DSC thermograms reveal that the four polymers prepared from the macrocyclic(arylene multisulfide) oligomers are amorphous in nature.

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