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Cyclic Arylene Sulfides: A Novel Synthesis and Ring-Opening Polymerization

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ABSTRACT: Oxidative polymerization of aryl disulfides has been carried out under high dilution conditions for the preparation of cyclic arylene sulfides. The readily available diphenyl disulfide and dichloro disulfide with diphenyl sulfide, diphenyl ether, or *p*-xylene are useful monomers for the synthesis of the corresponding cyclic oligo(thio arylene)s in ∼ 69% yield. The cyclization of dichloro disulfide with *p*-xylene gives cyclic oligo(thio-2,5-dimethyl-1,4-phenylene) (**3c**) bearing a disulfide bond with the repeating units ranging from 3 to 10. The free radical ring-opening polymerization of the cyclics leads to the formation of linear poly(thio arylene)s. The obtained poly(thio-2,5-dimethyl-1,4-phenylene) (**6c**) has a melting temperature of 354 °C, which is 71 °C higher than that of the unsubstituted poly(thio phenylene).

Introduction

Much effort has been recently expended in preparing macrocyclic aromatic compounds in view of their significance as reactive intermediates for the synthesis of high-performance linear aromatic polymers by ring-opening polymerization.[1] The advantageous aspects of the ring-opening polymerization over the conventional polycondensation methods are the elimination of solvents, the absence of byproducts, and the rapid formation of high-molecular-weight polymers in high yields. Another noticeable attractive feature in using cyclics is their much lower melt viscosity compared with the polymers, which facilitates reactive injection molding. The ring-opening polymerization of cyclics has also potential applications for composite materials and structural adhesives. For these and other applications, a variety of macrocyclic aromatic compounds, including cyclic esters,[2] ethers,[3] amides,[4] ether ketones,[5] and ether ether ketones,[6] have been synthesized extensively in the past decade. Most of the synthetic procedures for these cyclics are based on nucleophilic aromatic substitution reactions in a polar solvent at high temperatures. In contrast to these reactions, aromatic electrophilic reations proceed efficiently under moderate conditions and have been utilized for the preparation of linear polymers; however, there have been few reports of taking advantage of the reaction for the synthesis of macrocyclic compounds. The very recent paper by Gibson et al. reported the synthesis of a cyclic ether ketone containing a sulfone group by the Friedel−Crafts acylation reaction.[7]

In attempts to develop a novel synthetic method for the preparation of high-molecular-weight poly(thio arylene), macrocyclic aromatic sulfides and disulfides have been prepared by several groups.[8] We have recently reported our preliminary results on the selective synthesis of cyclic oligo(thio-1,4-phenylene) through oxidative polymerization of diphenyl disulfide based on an aromatic electrophilic substitution reaction.[9] The reaction proceeds under high dilution conditions at room temperature and atmospheric pressure, resulting in the selective formation of cyclic hexamer in high yield. We describe herein our expanded results on the synthesis of cyclic sulfides by oxidative polymerization of dichloro disulfide with aromatics. Several kinds of aromatic cyclic sulfides bearing methyl, ether, and/or disulfide groups have been efficiently prepared. The cyclics are useful monomers for the thermal ring-opening polymerization to obtain linear poly(thio arylene)s. Thermal properties and molecular weights of the polymers are also discussed.

Results and Discussion

Synthesis and Characterization of Cyclic Oligo(thio arylene)s. The oxidative polymerization of diphenyl disulfide (DPDS) was carried out in acidic dichloromethane solution in the presence of an equimolar amount of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an oxidant (Scheme 1). To obtain cyclic oligo(thio phenylene), the reaction was done under high dilution conditions by slow addition of the monomer solution into an acidic oxidant solution over a period of 2 days so that the final DPDS concentration should not exceed 0.025 M. The yellow oxidant solution turned immediately to dark green with the addition of DPDS solution and gradually changed to pale brown. The reaction proceeds efficiently at room temperature and usual workup gives a white powder containing the cyclic product as the chloroform-soluble part in 60% yield (Table 1). The chloroform-insoluble part was confirmed to be a linear octakis(thio phenylene) bearing a disulfide bond by MALDI−TOF−MS (matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy) analysis. Our previous study shows that the disulfide bond is at the end of the chain.[10] The chloroform soluble part was characterized to be pure cyclic hexakis(thio-

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Scheme 1

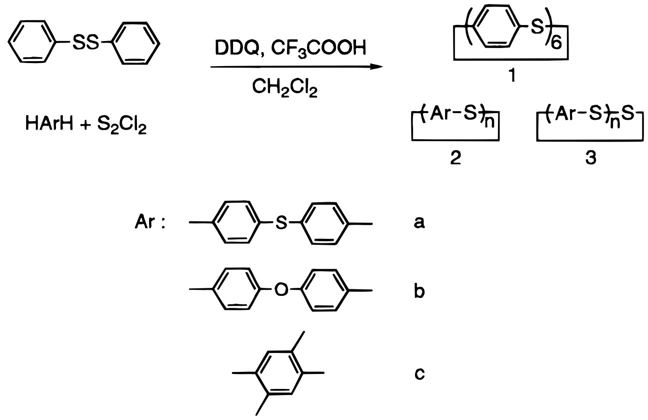


Table 1. Oxidative Polymerization of Disulfides for the Preparation of Cyclic Oligo(thio arylene)s

cyclic	yield (%) total	yield (%) cyclic	M_w	M_n	M_w/M_n	T_m (°C)
1	82	60	*a*	*a*	*a*	209
2a	83	51	570	490	1.2	180, 195
2b	89	60	600	570	1.1	122, 144
3c	80	69	520	400	1.3	250, 271

[a] A single product of hexamer confirmed by MALDI–TOF–MS analysis.

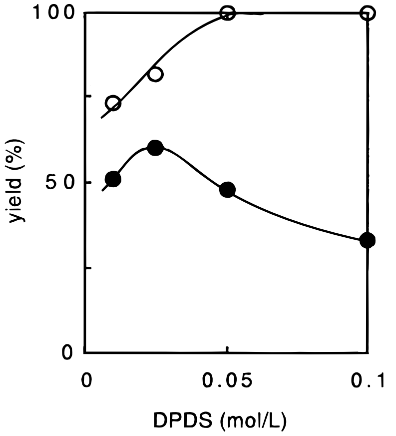


Figure 1. Effect of DPDS concentration on the total product yield (○) and cyclic hexamer (**1**) yield (●).

1,4-phenylene) (**1**). The MALDI–TOF–MS spectrum shows only a singlet corresponding to the correct molecular weight ion signal ($M^+ = 648$) for the cyclic hexamer with a good signal-to-noise ratio. In addition, gradient HPLC analysis showed the formation of a single product. The cyclic hexamer composed of the thio-1,4-phenylene unit was also well-characterized by IR and ^{1}H and ^{13}C NMR. These spectroscopic data give no indication of the presence of the end phenyl groups. GPC analysis shows a single sharp peak indicating that the cyclic product has M_w of 420 (a degree of polymerization of 4) relative to polystyrene standards.[11]

The yield of the cyclic depends on the feed concentration of DPDS (Figure 1). At 0.01 M DPDS concentration, the total yield of the oligomeric product was 73%, in which the yield of the cyclic product was 51%. Increasing the DPDS concentration results in an increase in the cyclic yield with a maximum of 60% at 0.025 M. At higher DPDS concentrations yields up to 100% can be obtained along with a significant decrease in the cyclic yield (<48%) with the addition time of 2 days. A higher monomer concentration would be possible by extending the addition period over 2 days.

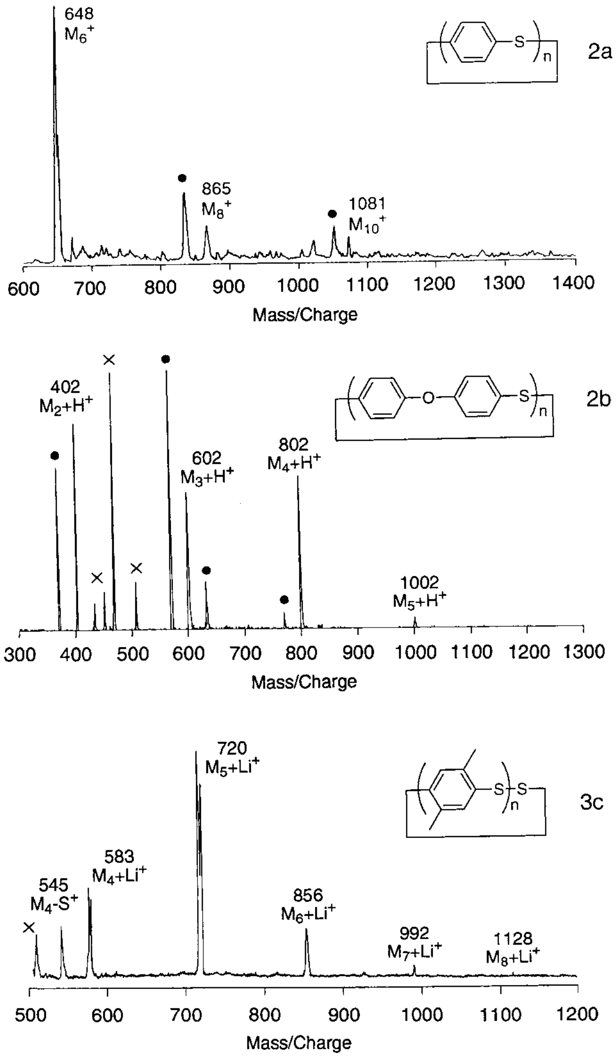


Figure 2. Positive ion MALDI–TOF–MS spectra of cyclic oligo(thio arylene)s prepared by the oxidative polymerization. The peaks marked with solid circles (●) are attributed to the contaminated linear oligomers. The peaks marked with a cross (×) are artifacts of the matrix (dithranol).

The method used for cyclization of DPDS by oxidative polymerization should be applicable to the reaction of dichloro disulfide (sulfur monochloride) with aromatics for the preparation of the corresponding cyclic oligo(thio arylene)s. The oxidative polymerizaiton of dichloro disulfide with diphenyl sulfide (DPS) was carried out under the same conditions as for DPDS to obtain the cyclic oligo(thio phenylene). The reaction proceeds efficiently and gives cyclic oligo(thio phenylene) (**2a**) in 51% yield. The IR and ^{1}H and ^{13}C NMR spectra of the cyclic **2a** are identical with those of **1**. GPC analysis shows that the cyclic products have a M_w of 570 and a M_n of 490 with polydispersity of 1.2. MALDI–TOF–MS analysis shows that **2a** consists of cyclic oligo(thio phenylene) with repeating units of 6, 8 and 10 (Figure 2). Two peaks of $M^+ = 834$ and 1050 show contamination with linear octamer and decamer products. From the reverse-phase gradient HPLC analysis, the main product is the hexamer by comparison with that of **1** (Figure 3). The cyclic **2a** contains 69.0% hexamer, 15.8% octamer, and 12.2% decamer. The minor peaks following the major peaks of the cyclics are due to the

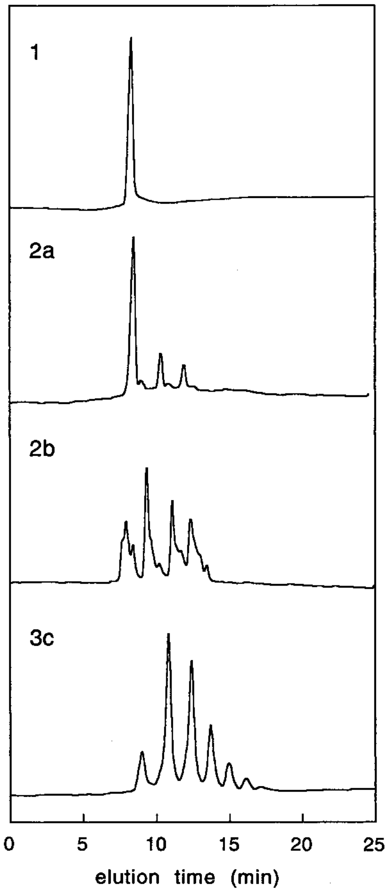


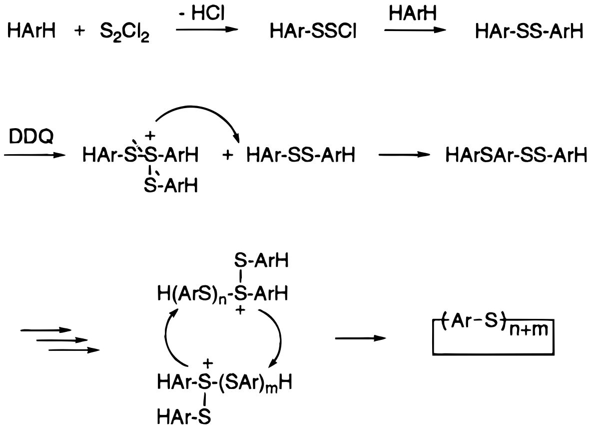
Figure 3. Reverse-phase gradient HPLC charts of cyclic oligo(thio arylene)s.

linear oligomers. The cyclic **2a** shows a melting endotherm with an onset temperature of 161 °C and an offset temperature of 210 °C peaking at 180 and 195 °C in the DSC analysis. The wide range of the melting peak is reasonable for a mixture of cyclics with different number of repeating units.

Diphenyl ether (DPE) can be also reacted with dichloro disulfide for the preparation of cyclic oligomers containing alternate oxyphenylene and thiophenylene units in the cyclic chain. The resulting cyclic **2b** shows a wide range of melting endotherm from 101 to 168 °C peaking at 122 and 144 °C. The combination of MALDI−TOF−MS and gradient HPLC analyses revealed that the product **2b** consists of 16.2% dimer, 28.7% trimer, 17.4% tetramer and 13.0%, pentamer. However, the contamination with linear oligomers (24.7%) was confirmed, which could not be removed after the extraction with hot chloroform.

The polymerization of dichloro disulfide with *p*-xylene (Xy) was performed to obtain the cyclic dimethylphenylene sulfide oligomers. It should be noted that the resulting cyclic oligo(thio-2,5-dimethyl-1,4-phenylene) (**3c**) contains a disulfide bond in a cyclic ring. The MALDI−TOF−MS spectrum clearly shows the correct molecular weight ion signals as the lithium adducts corresponding to **3c** with repeating units from 3 to 10. The contamination of linear oligomers could not be found in the spectrum. They are hardly soluble in hot chloroform and are easily separated from the cyclic products. In the ^{1}H NMR spectrum of the cyclic **3c**, three peaks attributed to methyl groups are observed at 2.22, 2.25, and 2.29 ppm. The two of them at lower magnetic field could be assigned to the methyl protons on a 1-sulfenyl-4-thiosulfenylphenylene, while the other could be assigned to the methyl protons on a 1,4-disulfenylphenylene. The three methyl peaks and the nine phenyl peaks in the ^{13}C NMR spectrum also support the structure of the cyclic oligomer with a disulfide bond. GPC analysis shows that **3c** has a rather large polydispersity of 1.3 compared to the other cyclics **2a** and **2b** (1.1−1.2). The gradient HPLC analysis revealed that **3c** consists of 7.6% trimer, 37.0% tetramer, 29.0% pentamer, 14.3% hexamer, 6.7% heptamer, 3.0% octamer, 1.5% nonamer, and 0.9% decamer. As for the cyclics **2a** and **2b**, the cyclic **3c** shows a wide melting endotherm peaking at 250 and 271 °C.

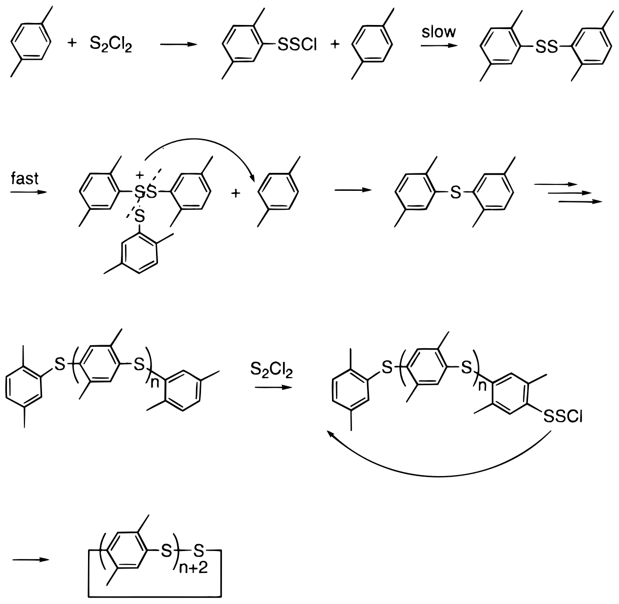
Scheme 2



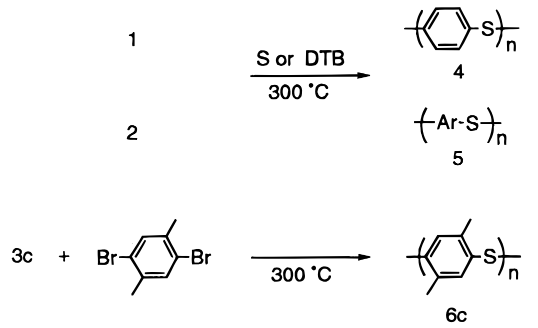
Cyclization Mechanism of the Disulfides. It has been already demonstrated that the oxidative polymerization of DPDS leads to the formation of a linear oligo(thio-1,4-phenylene) with a disulfide bond at the end of the chain.[12] The end disulfide group is oxidized to a dithio sulfonium cation, which is responsible for the electrophilic chain growth reaction. Under high-dilution conditions, the electrophilic substitution reaction by the oligomeric active sulfonium species takes place at its tail phenyl ring to form a cyclic oligo(thio-1,4-phenylene). The resulting cyclic is principally composed of the hexamer (**1**), because the cyclics with lower number of repeating units are difficult to form due to the ring strain. Since the linear octamer is precipitated out from the solution, the cyclics with a higher number of repeating units than six are also unavailable.

In the case of the oxidative polymerization of DPS with dichloro disulfide, the preferred starting monomer is bis(4-phenylthiophenyl) disulfide. This disulfide is too large to undergo the intramolecular head to tail reaction for the formation of the cyclic oligomer. For example, the formation of cyclic hexamer (**2a** with $n = 6$) by the intramolecular cyclization needs a linear decameric sulfonium cation, which is not soluble in dichloromethane. We assume that the reaction is based on a di- or trimolecular cyclization reaction as postulated in Scheme 2. The mechanism supports the formation of the cyclic **2a** of different number of repeating units ($n = 6$, 8, and 10): $2 + 4 =$ hexamer, $4 + 4 =$ octamer, and $2 + 4 + 4 =$ decamer. However, the selectivity for the cyclic is inferior to the case of DPDS, because of the contamination with linear oligomers which have a disulfide bond in the middle of the chain. The linear oligomers with a disulfide bond in the middle of the chain are less crystalline and more soluble than those

Scheme 3



Scheme 4



at the end and, therefore, result in contamination of the chloroform soluble fraction. The proposed cyclization mechanism could also hold for the case of DPE and dichloro disulfide.

In contrast to the above two cases, the oxidative cyclization of *p*-xylene with dichloro disulfide leads to the formation of the cyclic **3c** containing a disulfide bond. Through the measurement of kinetic constants, a different cyclization mechanism for the cyclic **3c** has been proposed as shown in Scheme 3. Bis(2,5-dimethylphenyl) disulfide has a 0.10 V lower oxidation potential at 1.60 V due to the four electron-donating methyl groups than the unsubstituted DPDS and has a faster oxidation rate at 1.1 M^{-1} s^{-1} (1.9×10^{-3} M^{-1} s^{-1} for DPDS).[13] The formation of bis(2,5-dimethylphenyl) disulfide (8.0×10^{-2} M^{-1} s^{-1})[14] by the Friedel–Crafts reaction of xylylthiosulfenyl chloride with another xylene monomer is rate-determining, and therefore, the cyclization occurs with the formation of a disulfide bond to give the cyclic **3c**. Due to the flexible disulfide bond present in the cyclic,[8g] homologues with repeating units from 3 to 10 could be obtained for **3c**.

Table 2. Ring-Opening Polymerization of Cyclic Oligo(thio arylene)s

polymer	initiator	yield (%)	M_w (10^3)	M_n (10^3)	M_w/M_n	T_m (°C)	TGA (°C)[a]
4	S	87	7.4	2.6	2.8	277	495
	DTB	98	10.4	2.5	4.2	283	514
5a	S	91	3.8	1.7	2.2	237	483
	DTB	100	6.5	2.1	3.1	250	490
5b	DTB	94	3.9	1.5	2.6	195	490
6c		100	3.9[b]	1.8[b]	2.2	354	492

[a] Temperature for 10% weight loss measured by TGA in N_2. [b] Soluble part of the product in 1-chloronaphthalene at 210 °C.

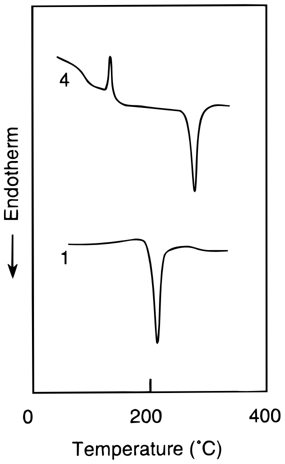


Figure 4. DSC thermograms of **1** and **4**.

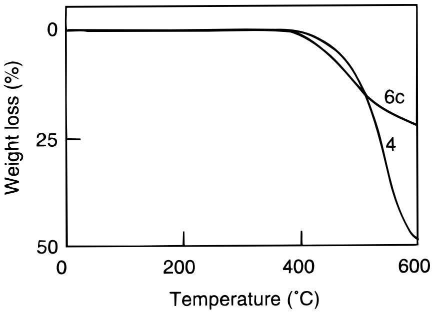


Figure 5. TGA thermograms of **4** and **6c**.

Thermal Ring-Opening Polymerization of Cyclic Oligo(thio arylene)s. The cyclic oligo(thio arylene)s **1**–**3** could be useful monomers for the preparation of the corresponding linear polymers by thermal ring-opening polymerization (ROP) in the presence of a small amount of an initiator (Scheme 4). The thermal ROP of the cyclic **1** was carried out with 1.0 mol % elemental sulfur at 300 °C under a nitrogen atmosphere. The reaction proceeds through free-radical mechanism in the solution of diphenyl ether, and a pale brown product of linear poly(thio phenylene) (**4**) was obtained in 87% yield after 1 h (Table 2). The IR spectrum of **4** supports the linear structure of the polymer without detectable cross-linking or branching. The polymer **4** is insoluble in hot chloroform and is only soluble in 1-chloronaphthalene above 200 °C. The molecular weight of **4** was determined by GPC analysis at 210 °C to be $M_w = 7400$ and $M_n = 2600$ ($M_w/M_n = 2.8$). No residual low molecular weight cyclic monomers were detected in the GPC chart. Instead of elemental sulfur, 2,2′-dithiobis(benzothiazole) (DTB) is also useful as the initiator for the thermal ROP in the melt without the solvent to give the linear polymer **4** with a higher M_w of 10 400 in 98% yield. DSC analysis revealed that the resulting **4** has a T_m of 283 °C, 74 °C higher than that of the starting cyclic **1** (209 °C) (Figure 4). A distinct T_g of 86 °C and a T_c of 131 °C were also observed. A high decomposition temperature for 10% weight loss ($T_{d_{10\%}}$) of 514 °C has been confirmed by TGA analysis (Figure 5). These thermal properties are comparable to those of the commercially available poly(thio phenylene) prepared by the traditional nucleophilic aromatic substitution reactions. The initiator DTB gives a higher molecular weight polymer in a higher yield than elemental sulfur. The polydispersity is somewhat wider when DTB is employed, probably because the polymerization has been carried out in the viscous melt.

The ROP of **2a** and **2b** were performed under the same conditions as that for **1**, however, the resulting polymers have rather low molecular weights and T_m: $M_w = 6500$, $M_n = 2100$, and $T_m = 250$ °C for **5a**, and $M_w = 3900$, $M_n = 1500$, and $T_m = 195$ °C for **5b**. A small amount of the linear oligomers contaminated with **2a** and **2b** causes the termination of the free-radical polymerization, resulting in the formation of lower molecular weight linear polymers than **4**.

Since the cyclic **3c** contains a disulfide bond itself, an initiator is not needed for the ROP. The ROP of the cyclic **3c** was carried out with an equimolar amount of 2,5-dibromo-*p*-xylene in diphenyl ether. The polymerization proceeds with elimination of bromine radical and leads to the formation of a linear poly(thio-2,5-dimethyl-1,4-phenylene) (**6c**) in 100% yield, which was very tough and only partially soluble (less than 20 wt %) in boiling 1-chloronaphthalene. DSC analysis revealed that the polymer **6c** is highly crystalline and has a T_m of 354 °C (Figure 6),[15] which is 48 °C higher than that of the linear poly(thio-2,5-dimethyl-1,4-phenylene) prepared by the oxidative polymerization of *p*-xylene and dichloro disulfide under the normal (not high dilution) conditions.[14] The T_m is 71 °C higher than that of the unsubstituted poly(thio phenylene) (**4**). The polymer **6c** shows high thermal stability with a $T_{d10\%}$ of 492 °C and keeps 78% of its original weight at 600 °C under nitrogen (Figure 5). High-temperature GPC analysis showed that the soluble part of **6c** in 1-chloronaphthalene has a M_w of 3900 and a M_n of 1800 ($M_w/M_n = 2.2$). We believe that the insoluble part is higher molecular weight with linear structure. In the IR spectrum, two peaks at 887 and 827 cm^{-1} assigned to C−H out-of-plane stretching of a 1,2,4,5-tetra-substituted benzene ring are observed. The absorption characteristic of penta-substituted benzene could not be found in the region of 890−910 cm^{-1}. A singlet peak of a methyl group (20.3 ppm) and three peaks of an aromatic group (124.1, 132.3, 140.9 ppm) in the CP−MAS ^{13}C NMR spectrum also support the linear structure of **6c** without detectable structural defects.

Conclusions

A novel synthetic method for the preparation of cyclic arylene sulfides has been developed by the oxidative polymerization of diphenyl disulfide, or dichloro disulfide with aromatics. The intramolecular head-to-tail reaction of the oligomeric sulfonium species occurs under high dilution conditions leading to the selective formation of the cyclic products. The cyclization of diphenyl disulfide gives a cyclic hexakis(thio-1,4-phenylene) in 60% yield, while the mixture of the cyclic with different repeating units was obtained from dichloro disulfide with diphenyl sulfide or diphenyl ether. The mechanism including a di- and/or trimolecular cyclization reaction has been proposed for the latter case. Cyclic oligo(thio-2,5-dimethyl-1,4-phenylene) bearing a disulfide bond has been obtained from dichloro disulfide and *p*-xylene in an oxidative reaction in which the rate-determining aryl disulfide bond formation (8.0×10^{-2} M^{-1} s^{-1}) builds up the cyclic structure. The free radical ring-opening polymerization of the cyclics gives the corresponding linear poly(thio arylene)s in quantitative yields. The poly(thio-2,5-dimethyl-1,4-phenylene) obtained is a crystalline polymer with a higher melting temperature of 354 °C than the other poly(thio arylene)s ($T_m \sim 283$ °C).

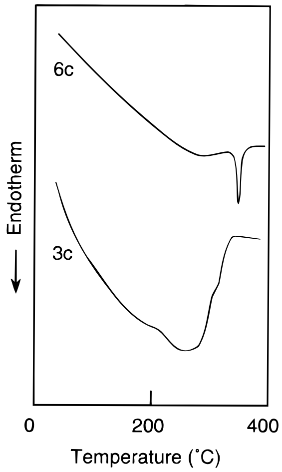


Figure 6. DSC thermograms of **3c** and **6c**.

Experimental Section

Measurement. Infrared spectra were obtained as KBr pellets using a JASCO FT/IR-5300 spectrometer. The band resolution was maintained at 2 cm^{-1} for all measurements. ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a JEOL JNM-LA500 (500 MHz ^{1}H, 125 MHz ^{13}C) spectrometer. The chemical shifts are calibrated using tetramethylsilane (0 ppm) as the internal standard. Elemental analysis was performed on a Perkin-Elmer PE−2400 II and a Metrohm 645 Multi-DOSIMAT. Two parallel analyses were performed for each sample.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectra were recorded on a Kratos Kompact 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 instrument was operated in a positive reflectron mode. The ions produced from each laser shot were accelerated to 20 keV into a 1 m drift region. An external calibration using bovine insulin and angiotension was used; this provides mass accuracy within 0.02% for this instrument. The matrix used for all experiments was 1,8,9-anthracenetriol (dithranol) (Aldrich). Samples were prepared by dissolving the cyclic oligomers in tetrahydrofuran (THF) at a concentration of 5.0 mg/mL. Lithium bromide was used as the ionization promoter with a stock solution of 5.0 mg/mL in THF. A 20 μL portion of the sample solution and a 20 μL portion of the lithium bromide solution were added to 200 μL of a 10 mg/mL solution of the matrix dissolved in THF. This final solution was shaken briefly, and 1 μL was applied to a stainless steel sample slide and air-dried prior to analysis.

Linear gradient HPLC was performed on a Milton Roy CM4000 multiple solvent delivery system with a C8 Prime Sphere 4.6 × 250 mm column, THF and water as eluent solvents, and a UV detector at 300 nm. The total running time for each injection was 30 min. The gradient condition was as follows: at 0 min, THF 70%; at 20 min, THF 90%; at 25 min, THF 100%; at 27 min, THF 70%; at 30 min (end), THF 70%. Gel permeation chromatography (GPC) was performed using a Shimazu LC-10A system equipped with two Asahipak columns (GS-510H and GS-310H) at 25 °C. Distilled THF was used as the eluent at a flow rate of 1.0 mL/min. The detector was a Shimazu SPD-10AV UV/vis spectrophotometer set at 265 nm. Calibration was performed using narrow polydispersity polystyrene standards. The molecular weight of the polymers was determined by high-temperature gel permeation chromatography (210 °C) on a Senshu VHT-GPC SSC-7000 equipped with a GPC-3506 column (GL Sciences Inc.) and a Soma Optics S-3750 UV−vis absorption detector set at 360 nm. 1-Chloronaphthalene was used as the eluent at a flow rate of 1.0 mL/min. Calibration was performed using narrow polydispersity polystyrene standards substituted by a fluorescent pyrene group.

Differential scanning calorimetry (DSC) was carried out on a Seiko DSC 220C thermal analyzer at a heating rate of 20 °C/min under nitrogen at a flow rate of 150 mL/min. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a Seiko TG/DTA 220 instrument at a heating rate of 20 °C/min under nitrogen at a flow rate of 300 mL/min. A 10 mg sample was used for each thermal analysis.

Materials. Commercial products dichloro disulfide, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), trifluoroacetic acid, trifluoroacetic anhydride, and elemental sulfur were purchased from Aldrich Chemical Co., Inc., or Kanto Chemical Company, Inc., and were used as received. Diphenyl disulfide (DPDS), 2,2′-dithiobis(benzothiazole) (DTB), and 2,5-dibromo-*p*-xylene were recrystallized twice from ethanol. Diphenyl sulfide (DPS), diphenyl ether (DPE), *p*-xylene (Xy), and dichloromethane were purified by distillation before use.

Preparation of Cyclic Oligo(thio phenylene) from Diphenyl Disulfide. A 40 mL dichloromethane solution of DPDS (4 mmol) was added dropwise to 120 mL of dichloromethane containing DDQ (4 mmol), trifluoroacetic acid (0.08 mol) and trifluoroacetic anhydride (16 mmol) over a period of 2 days. The mixture was stirred for another day to ensure the completion of the reaction and then poured into 500 mL of 37% hydrochloric acid diluted 1:9 with methanol to precipitate the oligomer. The crude product was treated with three portions of 100 mL of aqueous 5% NaOH solution to remove 2,3-dichloro-5,6-dicyano-1,4-hydroquinone. The resulting white powder was washed with water and methanol and dried at 20 °C under vacuum for 20 h to isolate cyclic hexakis(thio-1,4-phenylene) (**1**) in 60% yield.

Preparation of Cyclic Oligo(thio arylene) from Dichloro Disulfide and Aromatics. A typical procedure is as follows. A 40 mL dichloromethane solution of DPS (10 mmol) and dichloro disulfide (5 mmol) was added dropwise to 80 mL of dichloromethane containing DDQ (5 mmol), trifluoroacetic acid (0.1 mol), and trifluoroacetic anhydride (50 mmol) over a period of 2 days. The mixture was treated in a similar manner as described above to give a white powder of cyclic oligo(thio-1,4-phenylene) (**2a**) in 51% yield.

Cyclic Hexakis(thio-1,4-phenylene) (1). IR (KBr, cm^{-1}): 3063, 2924, 1570, 1472, 1387, 1096, 1074, 1009, 812. ^{1}H NMR ($CDCl_3$, 50 °C, ppm): 7.25 (s, 4H). ^{13}C NMR ($CDCl_3$, 50 °C, ppm): 131.7, 134.8.

Cyclic Oligo(thio-1,4-phenylene) (2a). IR (KBr, cm^{-1}): 3063, 2924, 1570, 1472, 1388, 1096, 1074, 1010, 813. ^{1}H NMR ($CDCl_3$, 50 °C, ppm): 7.25 (s, 4H). ^{13}C NMR ($CDCl_3$, 50 °C, ppm): 131.7, 134.7.

Cyclic Oligo(oxy-1,4-phenylenethio-1,4-phenylene) (2b). IR (KBr, cm^{-1}): 3060, 2925, 1580, 1481, 1236, 1163, 1098, 1082, 1011, 868, 826. ^{1}H NMR ($CDCl_3$, 50 °C, ppm): 6.93 (s, 2H), 7.30 (d, 2H). ^{13}C NMR ($CDCl_3$, 50 °C, ppm): 119.7, 129.8, 132.7, 156.4.

Cyclic Oligo(thio-2,5-dimethyl-1,4-phenylene) (3c). IR (KBr, cm^{-1}): 2973, 2917, 2853, 1474, 1451, 1379, 1080, 984, 885, 872. ^{1}H NMR ($CDCl_3$, 50 °C, ppm): 2.22, 2.25, 2.29 (t, 6H), 6.58−7.24 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 °C, ppm): 19.4, 19.5, 19.7, 19.8, 20.2, 130.8, 132.4, 132.6, 132.9, 133.2, 133.6, 134.3, 137.0, 138.0.

Ring-Opening Polymerization of Cyclic Oligo(thio arylene). The ring-opening polymerization of the cyclic oligomers was achieved in the melt using 2,2′-dithiobis(benzothiazole) (DTB). A typical polymerization procedure is as follows. Cyclic hexakis(thio-1,4-phenylene) (**1**, 3 mmol) was mechanically mixed with DTB (0.03 mmol) in a 10 mL dry test tube. After being swept with nitrogen for 5 min, the test tube was sealed with a septum which was equipped with a nitrogen inlet and outlet. The test tube was then placed into a preheated salt bath at 300 °C for 1 h. After the polymerization, quenching the melted mixture into methanol gave a tough solid mass of the product. The product was ground to a fine powder and washed with chloroform to obtain poly(thio-1,4-phenylene) (**4**) in 98% yield. The same conditions were applied for the ring-opening polymerization with elemental sulfur (0.03 mmol) as the initiator, except diphenyl ether (5 mL) was used as a solvent.

Poly(thio-1,4-phenylene) (4). IR (KBr, cm^{-1}): 3065, 2924, 1572, 1472, 1385, 1092, 1074, 1009, 812. Anal. Calcd for (C_6H_4S): C, 66.63; H, 3.73; S, 29.65. Found: C, 66.40; S, 3.88; S, 29.83.

Poly(oxy-1,4-phenylenethio-1,4-phenylene) (5b). IR (KBr, cm^{-1}): 3059, 2925, 1578, 1480, 1233, 1163, 1082, 1011, 869, 820. Anal. Calcd for ($C_{12}H_8OS$): C, 71.97; H, 4.03; S, 16.01. Found: C, 72.49; S, 4.55; S, 15.59.

Poly(thio-2,5-dimethyl-1,4-phenylene) (6c). IR (KBr, cm^{-1}): 2973, 2922, 1585, 1475, 1445, 1381, 1082, 887, 827. CP−MAS ^{13}C NMR (ppm): 20.3, 124.1, 132.3, 140.9. Anal. Calcd for (C_8H_8S): C, 70.54; H, 5.92; S, 23.54. Found: C, 70.22; S, 5.86; S, 23.84.

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