

Crosslinking of Poly(arylene disulfide)s and Poly(arylene sulfane)s Derived from Cyclic(arylene disulfide) Oligomers

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ABSTRACT: Cyclic(arylene disulfide) and polycyclic(arylene sulfide) oligomers were synthesized by catalytic oxidation of arylenedithiols or arylenetrithiols with oxygen in the presence of a copper-amine catalyst. These cyclic(arylene sulfide) oligomers can undergo free radical ring-opening polymerization at an elevated temperature in the melt or solution. Polycyclic(arylene sulfide) oligomers can be used to crosslink poly(arylene disulfide)s and poly(arylene sulfane)s derived from cyclic(arylene disulfide) oligomers and elemental sulfur. The crosslinking reactions were investigated by differential scanning calorimetry and by solubility of the cured products. The minimum concentrations of polycyclic(arylene sulfide) oligomers for producing a well crosslinked poly(arylene disulfide) and poly(arylene sulfane) are 7 wt % and 10 wt %, respectively. The crosslinking reactions between poly(arylene disulfide)s, poly(arylene sulfane)s, and triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT) were also investigated. TTT is more efficient for crosslinking than the synthesized polycyclic(arylene disulfide) oligomers. The crosslinkable poly(arylene disulfide)s and poly(arylene sulfane)s could be potentially used as high temperature coatings, sealants, adhesives, and as matrices for high performance thermoset composites. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3069–3077, 1999

Key words: cyclic(arylene disulfide); polycyclic(arylene disulfide); oligomer; crosslinking; ring-opening reaction; triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione

INTRODUCTION

Poly(aliphatic disulfide)s have long been commercialized and have had many applications since 1929. Crosslinked poly(aliphatic disulfide)s have high resistance to environmental degradation, good low temperature properties, low water-vapor transmission, and good adhesion to wood, metal, glass, and concrete. Moreover, they also have excellent resistance to organic solvents, acids, and bases.^{1–4} However, little information is available about poly(arylene disulfide)s owing to their in-

solubility. Several poly(arylene disulfide)s with low molecular weight (ca. 880) have been synthesized from difunctional sulphenyl chlorides and dithiols.⁵ Hay⁶ has prepared a series of poly(arylene disulfide)s that were not soluble in common organic solvents by using oxidative coupling with oxygen catalyzed by copper salts and an amine.

Recently, we have successfully synthesized high performance polymers from cyclic oligomers to solve processing problems such as poor solubility and high melt viscosities.^{7–10} In previous work, we have described the synthesis of a series of cyclic(arylene disulfide) oligomers by using oxidative coupling with oxygen catalyzed by copper salts and an amine by slow addition of the dithiol to the reaction mixture. Cyclic oligomers are ex-

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clusively produced.^{10,11} Some of these cyclic(arylene disulfide) oligomers have satisfactory solubility in common solvents, and can be highly purified. These cyclic(arylene disulfide)s 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.^{12–14} The polymerization is performed in the absence of a catalyst. Furthermore, poly(arylene sulfane)s can also be synthesized by a copolymerization reaction between cyclic(arylene disulfide)s and element sulfur.¹⁵ This provides a method for preparation of poly(arylene sulfane)s that might be useful as high temperature adhesives, coatings, sealants, etc.

In this work, we report the synthesis of a polycyclic(arylene disulfide) and its use as a crosslinking additive with poly(arylene disulfide)s and poly(arylene sulfane)s derived from poly(arylene disulfide)s and element sulfur. Commercial triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT) can also be used as a crosslinking agent, and the crosslinking efficiency of TTT is greater than that of the synthesized polycyclic(arylene disulfide). The crosslinked polymers possess better thermal stability, chemical resistance, and mechanical properties than the uncured polymers, especially for the poly(arylene sulfane)s with higher sulfur contents which are elastomers.¹⁵ Therefore, the crosslinked poly(arylene disulfide) and poly(arylene sulfane) potentially may be applied in the aforementioned applications. They could also be used as high-performance matrices for continuous-fiber reinforced composites, thermoset varnishes, and as cable insulators. Compared with poly(arylene imide)s or poly(arylene ether imide)s, the curing of poly(arylene disulfide) and poly(arylene sulfane) in the presence of a multifunctional crosslinking reagent can be performed under much milder conditions without the formation of any volatile by-product.

EXPERIMENTAL

Materials

4,4'-Isopropylidenediphenol (BPA) was kindly provided in high purity by the General Electric Company. Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT) was purchased from Aldrich Chemical and used without any further purification. 1,1,1-Tris(4-hydroxyphenyl)ethane, *N,N'*-dimethylthiocar-

bamoyl chloride, reagent grade diphenyl ether, cuprous chloride, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), and sublimed powdered sulfur were obtained from Aldrich. *N,N*-Dimethylacetamide (DMAc), tetrahydrofuran (THF), quinoline, methylene chloride, 1,1,2,2-tetrachloroethane, pyridine, methanol, chloroform, and potassium hydroxide were obtained from commercial sources and used as received.

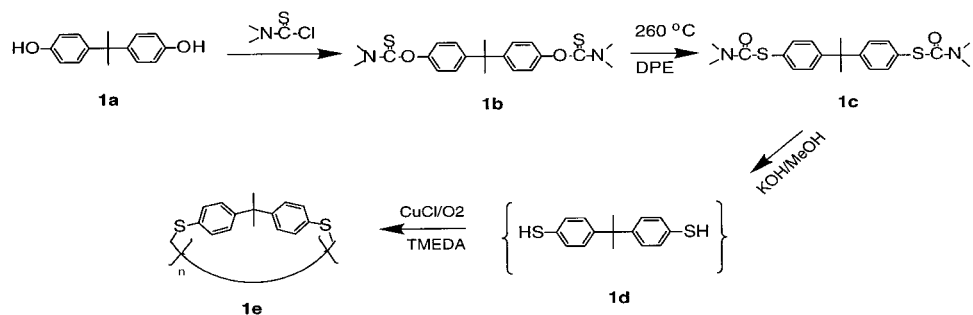
Instrumentation

The glass transition temperatures (T_g s) and 5% weight loss temperatures were determined on Seiko 5200 TGA/DTA and Seiko 220 DSC instruments at a heating rate of 20°C/min under nitrogen flow. 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 μm) of this analyte was spotted on the sample slot and air-dried. All spectra were obtained in the reflectron mode. Gel permeation chromatography (GPC) analyses were performed on a Waters 510 HPLC equipped with 5- μm Phenogel columns (linear, 4 \times 500 Å) arranged in series with THF as solvent and a UV detector at 254 nm. Gradient high pressure liquid chromatographies (HPLCs) were performed on a Milton Roy CM4000 multiple solvent delivery system with a C8 Prime Sphere 4.6 \times 250 mm column, THF and water as eluent solvents, and a UV detector at 300 nm. Nuclear magnetic resonance (NMR) data were recorded at 270 MHz on a Gemini 270 Hz NMR instrument (JEOL-270-CPF) and are listed in parts per million downfield from tetramethylsilane. Melting points were taken on a Fisher-Johns melting point apparatus.

The syntheses of cyclic(arylene disulfide) **1e** and polycyclic(arylene disulfide) **2e** are depicted in Schemes 1 and 2, respectively.

Preparation of 1b

BPA **1a** (20.0 g, 87.6 mmol) was added to 150 mL of ice-cold methanol solution which contained 11.8 g (210.2 mmol) of potassium hydroxide. The mixture was stirred at 0–5°C for 1.5 h and then *N,N'*-dimethylthiocarbamoyl chloride (28.2 g, 210.2 mmol) was added in two portions. The temperature was slowly raised to 60°C and stirring was continued for another 4 h at this tempera-



Scheme 1 Synthesis of cyclic(arylene disulfide).

ture. The white precipitate was collected by filtration and washed with cold methanol-water (3 : 1 v/v) three times. Pure (98.6%) white powder **1b** was obtained in good yield (32.5 g, 92.3%). Melting point, $194\text{--}195^\circ\text{C}$. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 7.24 (d, 4H, $J = 9.76$ Hz), 6.99 (d, 4H, $J = 9.76$ Hz), 3.47 (s, 6H), 3.32 (s, 6H), 1.71 (s, 6H). MALDI-TOF-MS: found 402.60; calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2$, 402.58.

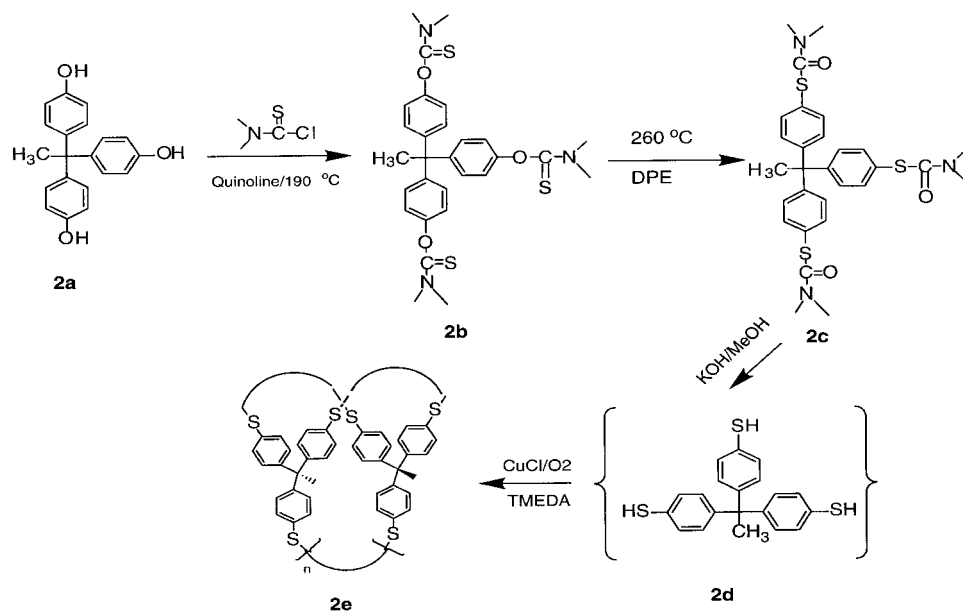
Preparation of **1c**

The mixture of **1b** (10 g) and diphenyl ether (5 mL) was placed in a salt bath preheated to 260°C for 2 h under nitrogen atmosphere. After cooling, the resultant solid was washed with cold methanol-water (3 : 1 v/v) three times and then recrystallized from *N,N*-dimethylformamide (DMF).

Pure (99.9%) white powder **1c** was obtained in good yield (8.1 g, 81.0%). Melting point $141\text{--}142^\circ\text{C}$. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 7.38 (d, 4H, $J = 8.65$ Hz), 7.26 (d, 4H, $J = 8.65$ Hz), 3.08 (s, 12H), 1.70 (s, 6H). MALDI-TOF-MS: found 402.60; calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2$, 402.58.

Preparation of **1d**

1d was synthesized by the method given in the literature.^{16,17} However, the resulting product was not separated out to avoid handling the compounds containing —SH groups. The resulting **1d** was extracted three times by methylene chloride and the solution was thoroughly dried over MgSO_4 for 5 h. The dry solution was directly used in the following reaction. The completion of hydrolysis of **1c** to **1d** was followed by HPLC (reten-



Scheme 2 Synthesis of polycyclic(arylene disulfide).

tion times of **1c** and **1d** are 2.73 and 8.26 min, respectively).

Preparation of **1e**

A 200-mL one-neck cylinder (height/diameter = 2.5/1) with an oxygen inlet in the bottom equipped with a high-speed vibromix stirrer was charged with 0.1 g of CuCl, 0.2 g of TMEDA, and 50–100 mL DMAc. The mixture was vigorously stirred for 15 min with oxygen bubbling directly into the reaction mixture. Then approximately 2.4 mmol (0.6 g) of **1d** in 20 mL of 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 filtered 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: > 90%. T_g and T_m are 80.5 and 219.3°C, respectively.

Preparation of **2b**

The mixture of **2a** (20.0 g, 87.6 mmol), quinoline, and *N,N'*-dimethylthiocarbonyl chloride (28.2 g, 210.2 mmol) was added in one portion to a 250-mL three-neck round-bottom flask equipped with a condenser and magnetic stirrer. The temperature was slowly raised to 190°C with stirring and the reaction was continued for 5 h at this temperature. The white precipitate that deposited was collected by filtration and washed with cold methanol-water (3 : 1 v/v) three times. Pure (98.6%) white powder **2b** was obtained in good yield (32.5 g, 92.3%). Melting point 229–232°C. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 7.10 (d, 6H, $J = 8.19$ Hz), 6.88 (d, 6H, $J = 8.19$ Hz), 3.47 (s, 9H), 3.34 (s, 9H), 2.21 (s, 3H). MALDI-TOF-MS: found 567.80; calcd for $\text{C}_{29}\text{H}_{33}\text{N}_3\text{O}_3\text{S}_3$, 567.79.

Preparation of **2c**, **2d**, and **2e**

The synthetic methods for **2c**, **2d**, and **2e** are similar to **1c**, **1d**, and **1e**, respectively. For **2c**: yield: 81.1%. Melting point 240–242°C. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 7.36 (d, 6H, $J = 7.27$ Hz), 7.13 (d, 6H, $J = 7.27$ Hz), 3.05 (s, 18H), 2.15 (s, 3H). MALDI-TOF-MS: found 567.80; calcd for $\text{C}_{29}\text{H}_{33}\text{N}_3\text{O}_3\text{S}_3$, 567.79. For the preparation of **2e**, the polycyclic product was insoluble in DMAc, and the resulting reaction mixture was poured

into 50–100 mL (equivalent volume to DMAc) of 5% HCl solution directly without filtration and stirred for 2 h to remove the copper salt. Yield: ~ 100%. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 7.37–7.20 (m, 6H), 6.99–6.78 (m, 6H), 2.15–2.10 (m, 3H).

General Procedure for the Melt Curing Reaction

The cyclic oligomer **1e** and polycyclic oligomers **2e** or TTT were dissolved in THF separately, and then were introduced (~10 mg) into a differential scanning calorimeter (DSC) aluminum crucible by micro-syringe. 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 a solubility test with a Soxhlet extractor using chloroform as solvent for 5 h. The residual sample was dried at 120°C for 24 h, weighed, and used to calculate the solubility.

RESULTS AND DISCUSSION

Synthesis of Cyclic- and Polycyclic(arylene disulfide) Oligomers

In a previous article, we reported the synthesis and characterization of a series of cyclic(arylene disulfide) oligomers.¹¹ Aromatic dithiophenols are difficult to separate and purify because of their ease of oxidation and their obnoxious odors. In this report, we describe in detail the synthesis of cyclic(arylene disulfide) **1e** and polycyclic(arylene disulfide) **2e**. For the preparations of bisthiophenol **1d** and trithiophenol **2d**, we did not separate them from the reaction mixtures, as depicted in Schemes 1 and 2, respectively. To ensure completion of the hydrolysis of **1c** and **2c**, HPLC was used to follow the reaction. Generally the hydrolysis reactions are very rapid and are complete in 30–60 min, in accordance with the literature.^{16,17} We demonstrated that **1d** or **2d** can be easily isolated by extraction because of the good solubility in methylene dichloride. Oxidation of dithiols has been performed by oxygen¹⁸ or iodine,¹⁹ and Hay⁶ found that dithiols can be oxidatively coupled to polydisulfides by reaction with oxygen in the presence of a mixture of tertiary amine and a copper salt. Using this method, the methylene chloride solution containing **1d** or **2d** was slowly

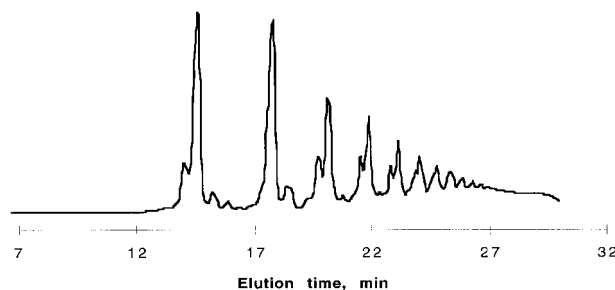


Figure 1 Gradient HPLC chart of cyclic(arylene disulfide) oligomer **1e**. (For gradient conditions, see text.)

introduced into the oxidizing mixture. Normally, cyclization reactions are completed in 3–5 h with the formation of cyclic oligomers in high yields.

Figure 1 shows the gradient HPLC chart of cyclic(arylene disulfide) oligomer **1e**. The gradient conditions were as follows: at 0 min, THF 70%, water 30; at 20 min, THF 90%, water 10%; at 25 min, THF 100%, water 0%; at 27 min (end), THF 70%, water 30%. By gradient HPLC, cyclic dimer to cyclic tetramer are shown to be the dominant products for cyclic oligomers **1e**. As expected, the polycyclic(arylene disulfide) oligomer **2e** was only partially soluble because the higher molecular weight species would be expected to be insoluble because they are crosslinked materials. There were no —SH groups (approximately 3–4 ppm) remaining as indicated by NMR, demonstrating the completion of oxidation. To obtain the soluble portion, the samples of **2e** synthesized under different conditions were extracted with THF, and the results are listed in Table I. It can be seen that the solubilities increase with increasing introduction time of **2d** into the reaction mixture. This means that high catalyst concentration, low concentration of **2d**, and long reaction times favor the formation of cyclic(arylene disulfide) oligomers; otherwise, aromatic polydisulfides with a crosslinked structure would be produced which are insoluble. The gradient HPLC

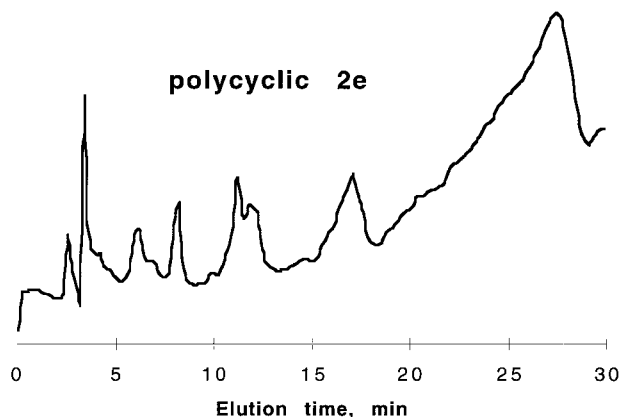


Figure 2 Gradient HPLC chart of polycyclic(arylene disulfide) oligomer **2e**. (For gradient conditions, see text.)

and GPC charts for the soluble portion of polycyclic **2e** are depicted in Figures 2 and 3, respectively. The gradient conditions were as follows: at 0 min, THF 80%, water 20; at 20 min, THF 90%, water 10%; at 25 min, THF 100%, water 0%; at 27 min (end), THF 80%, water 20%. It is apparent that the soluble portion still contains products with higher molecular weights although the oxidation reaction was performed under what should be optimal conditions.

Crosslinking Potential of Polycyclic (arylene disulfide) **2e**

It is well known that the disulfide bond ruptures to form radicals at elevated temperatures.^{14,20} Therefore, a poly(arylene disulfide) can be formed through ring-opening polymerization (ROP) from cyclic **1e** at elevated temperatures. Crosslinked poly(arylene disulfide) should be readily produced by using polycyclic **2e** as crosslinking agent. The curing results for poly(arylene disulfide)s from cyclic **1e** by addition of 10 wt % polycyclic **2e** under varying conditions are tabulated in Table

Table I The Solubilities of **2e** Obtained Under Different Conditions

Experiment No.	Ratio of CuCl/TMEDA/ 2d (g/drop/g)	DMAc (mL)	Addition Rate of 2d in 20 mL C ₂ H ₂ Cl ₂ , h	Soluble Portion (%)
1	0.1 : 8 : 1.5	35	2.0	10
2	0.2 : 20 : 1.5	80	2.0	22
3	0.2 : 20 : 1.5	150	4.0	49
4	0.3 : 30 : 1.5	150	6.0	46

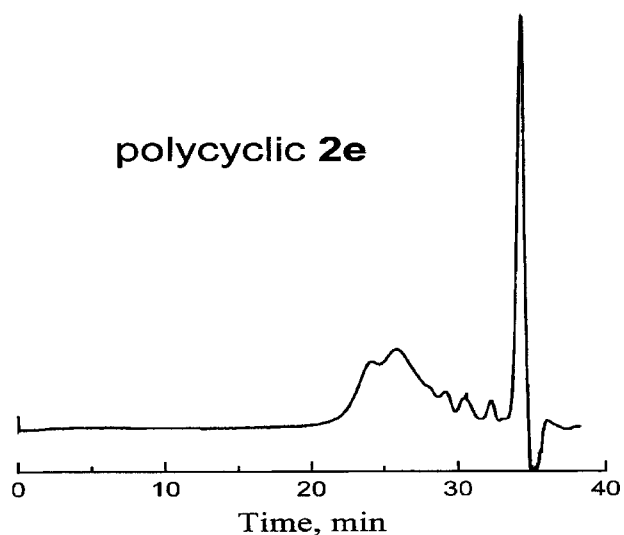


Figure 3 GPC chart of cyclic(arylene disulfide) oligomer **2e**.

II. Below 180°C, the ROP and crosslinking reaction are not complete because the T_m s of cyclic **1e** were still detectable, even for very long curing times (120 min). The T_g s located at approximately 120°C are the T_g s of crosslinked poly(arylene disulfide) from cyclic **1e**, which depend on its crosslinking degree. Solubility tests also showed that there was still unreacted cyclic **1e** remaining in cured samples. With curing temperatures up to or higher than 200°C, both cyclic **1e** and polycyclic **2e** underwent ring-opening reaction to form cured poly(arylene disulfide), indicating that temperature played a dominant role in

Table II Curing of **1e** by 10 wt % **2e**

Curing Condition	T_g (°C)	T_m (°C)	TGA _{-5%} (°C)	Solubility (%)
150°C				
30 min	82.5	224.8	339.6	51.9
120 min	93.1	222.9	339.5	44.0
180°C				
30 min	116.9	232.3	342.6	14.5
120 min	129.1	232.5 (NC)	367.3	3.3
200°C				
30 min	132.5	ND	350.4	2.4
120 min	133.8	ND	341.9	1.2
250°C				
30 min	133.9	ND	342.8	2.4
60 min	142.0	ND	350.5	1.9
120 min	ND	ND	368.5	1.1

NC, not clear; ND, not detectable.

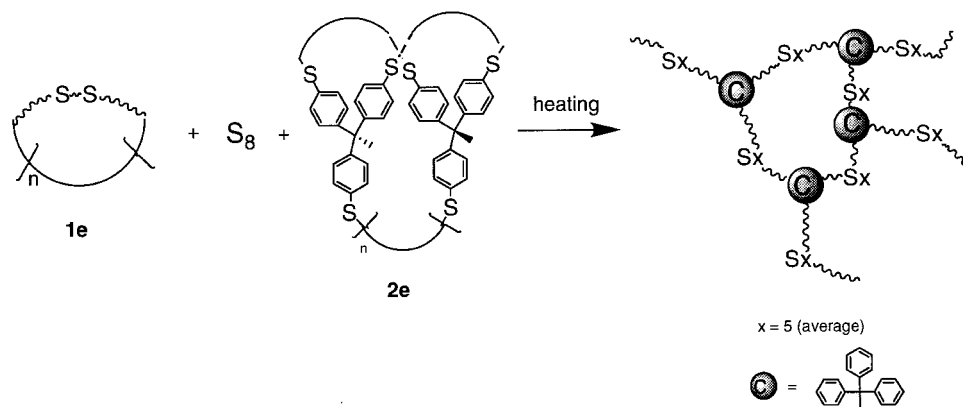
Table III Curing of **1e** at Different Concentrations of **2e**

Concentration of 2e , wt %	T_g (°C)	TGA _{-5%} (°C)	Solubility (%)
0	110.2	340.1	100
2	110.6	339.3	51.1
4	114.7	341.8	25.0
6	114.7	346.9	5.7
8	120.5	346.7	2.5
10	133.0	349.2	1.3

Curing 1 h at 200°C.

the curing reaction. It is believed that ROP and curing were complete at 200°C for 30 min with less than 2.5% uncrosslinked cyclic remaining, based on the solubility data.¹⁴ Generally, ROP takes place at temperatures approximately the T_m s of cyclic disulfides. With a further increase of temperature, for example 250°C, the cured poly(arylene disulfide) became black with a rough surface. Table III shows the curing results by using varying polycyclic **2e** contents. Similarly, it can be concluded that 7 wt % polycyclic **2e** was enough to crosslink poly(arylene disulfide) derived from **1e**. At this content, the cured poly(arylene disulfide) has a T_g of ca. 120°C with 5% weight loss temperature of ca. 345°C.

In previous work,¹⁵ we have obtained poly(arylene sulfane)s by copolymerizing cyclic(arylene disulfide)s with elemental sulfur. The poly(arylene sulfane)s with higher sulfur contents exhibited rubbery properties. In an effort to stabilize the poly(arylene sulfane)s, we have crosslinked them by using polycyclic **2e**. The curing reaction is shown in Scheme 3. The molar ratio of cyclic **1e** to elemental sulfur was selected as 1/3, which means that the poly(arylene sulfane) formed should contain an average of five S atoms per repeat unit. For the poly(arylene sulfane)s with higher sulfur contents, it is difficult to investigate the curing reaction because of the insolubility of the resulting polymers. The poly(arylene sulfane) obtained had a T_g of 65.5°C with a solubility of 57.4% in chloroform. It was rather thermally unstable (TGA_{5%} = 291.6°C), presumably because the resulting polymer contains small amounts of unreacted sulfur due to the ring chain equilibration with S₈. As is shown in Table IV, the T_g s of the poly(arylene sulfane)s increased with increasing amount of polycyclic **2e**. The T_g of crosslinked poly(arylene sulfane) with 10 wt %



Scheme 3 Crosslinking and stabilizing of poly(arylene sulfane) derived from cyclic **1e** and element sulfur by polycyclic **2e**.

polycyclic **2e** is 20°C higher than that without polycyclic **2e**. From both T_g and solubility data, we can conclude that 10 wt % polycyclic **2e** is enough to crosslink the poly(arylene sulfane). It should be noted that no obvious change in thermal stabilities was observed because only a small amount of polycyclic **2e** was incorporated.

In an effort to synthesize polycyclic disulfides with satisfactory solubility, we have attempted the synthesis of novel sulfur-bridged polycyclic-(arylene disulfide) oligomers from biphenol **3a**. The synthetic procedure is illustrated in Scheme 4 according to the related methods reported by Yamamoto et al.²¹ and Montaudo et al.²² As expected, the sulfur-bridged polycyclic **3f** was soluble in many solvents such as THF and chloroform. However, no curing reaction occurred when the mixture of cyclic **1e** and sulfur-bridged polycyclic **3f** was heated, and the resulting black material was still soluble in organic solvents. Probably, the reason is due to the formation of a more stable six-membered ring compound and the release of element sulfur. The model reaction is shown in

Scheme 4. The six-member ring structure cannot undergo further ring-opening reaction.

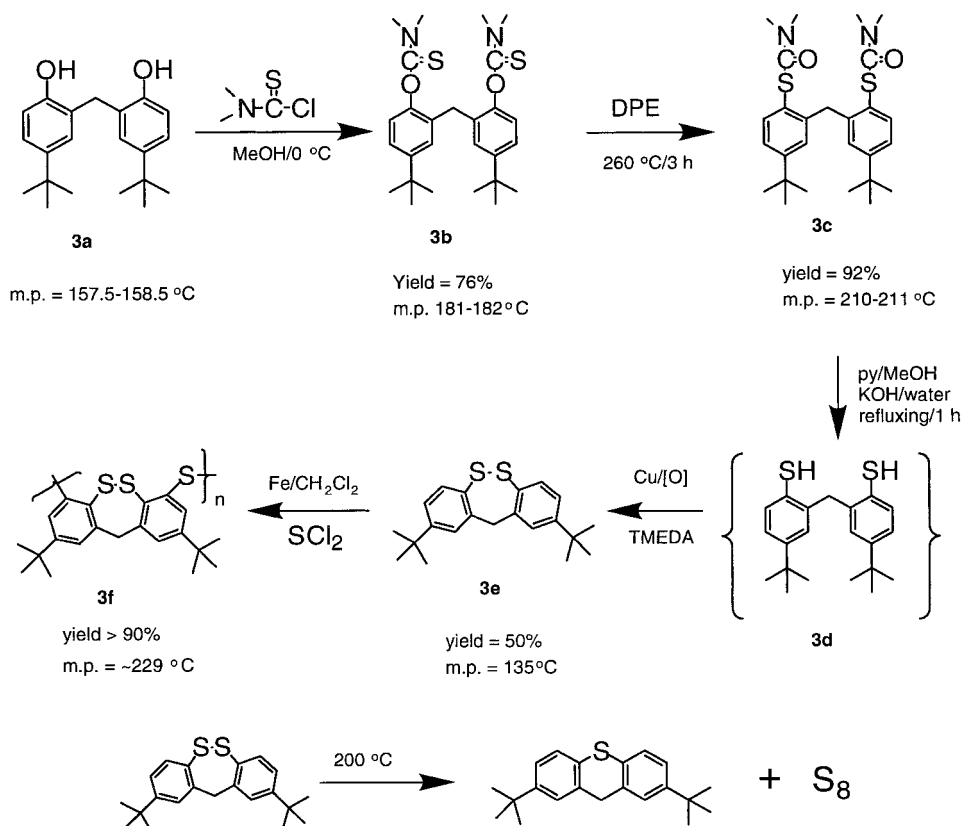
Curing of Poly(arylene disulfide) and Poly(arylene sulfane) by TTT

As discussed above, cyclic(arylene disulfide)s undergo rapid ROP upon heating through a free radical mechanism. Therefore, cyclic disulfides should also act as free radical initiators.^{23,24} The resulting radical species should initiate polymerization of compounds containing double bonds. Utilizing this property, TTT with three double bonds can be used as a crosslinking agent for cyclic(arylene disulfide)s (Scheme 5). TTT is a liquid at room temperature and has a flash point above 230°C. The curing results for cyclic **1e** with TTT are listed in Table V. It can be seen that with only 2% TTT, crosslinking occurs with cyclic **1e** and TTT as indicated by its low solubility. With increasing TTT content up to 6%, the T_g became undetectable, demonstrating that highly crosslinked poly(arylene disulfide) was obtained. Comparing Table V with Table III, we can conclude that TTT is more efficient than the polycyclic **2e** for the crosslinking of poly(arylene disulfide)s. Certainly, the higher functionality of TTT makes it easier to obtain a highly crosslinked material. Furthermore, TTT can increase and improve the mobility of the resulting free radicals in the melt because it is a liquid at room temperature. The cured poly(arylene disulfide) has a better appearance than that cured by polycyclic-(arylene disulfide) because liquid TTT can increase the fluidity of the solidifying melt. Similarly, poly(arylene sulfane) derived from cyclic **1e**

Table IV Curing of **1e**/Sulfur (1/3 Molar Ratio) at Different Concentrations of **2e**

Concentration of 2e , wt %	T_g (°C)	TGA _{-5%} (°C)	Solubility (%)
0	65.5	291.6	57.4
3	72.5	295.1	53.2
6	81.4	312.9	24.2
10	85.2 (NC)	294.0	9.73
15	95.5 (NC)	296.7	6.95

Curing 1 h at 200°C. NC, not clear.



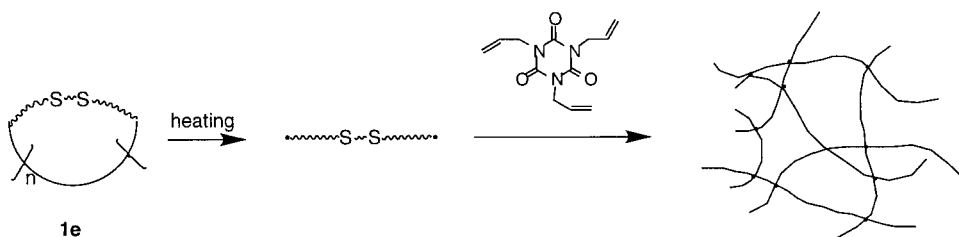
Scheme 4 Synthesis of sulfur-bridged polycyclic(arylene disulfide) oligomers.

and element sulfur can also be crosslinked by TTT as shown in Table VI. Approximately 8% TTT was enough to crosslink the poly(arylene sulfane). Although the ring-opening and free radical crosslinking reactions took place very rapidly, the incorporation of free sulfur in the polymer chain is slower. As is shown in Table VI, there is still a small portion of soluble sulfur and/or unreacted cyclic **1e** remaining, presumably due to the decreased mobility of reactive species in the solidifying melt.

CONCLUSIONS

Cyclic and polycyclic(arylene disulfide) oligomers were synthesized by a copper-catalyzed oxidation

of dithiols with oxygen. The direct oxidation procedure without the isolation of the synthesized thiophenols proved to be an effective method for preparation of cyclic(arylene disulfide)s. As-made polycyclic(arylene sulfide) oligomers can be used to crosslink poly(arylene disulfide)s derived from cyclic(arylene disulfide)s and poly(arylene sulfane)s derived from cyclic(arylene disulfide) oligomers and element sulfur. The minimum amounts required for crosslinking poly(arylene disulfide)s and poly(arylene sulfane)s are 7 wt % and 10 wt %, respectively. Commercially available TTT can be used to crosslink the poly(arylene disulfide)s and poly(arylene sulfane)s. Crosslinking with TTT is more efficient than that with polycyclic(arylene disulfide)s. These two kinds of



Scheme 5 Crosslinking of poly(arylene disulfide) derived from cyclic **1e** by TTT.

Table V Curing of 1e at Different Concentrations of TTT

Concentration of TTT (wt %)	T_g (°C)	TGA _{-5%} (°C)	Solubility (%)
0	110.2	340.1	100
2	112.9	339.9	34.0
4	131.1	338.0	7.5
6	ND	339.4	3.5
8	ND	340.6	4.8

Curing 1 h at 200°C. ND, not detectable.

Table VI Curing of 1e/Sulfur (1/3 Molar Ratio) at Different Concentrations of TTT

Concentration of TTT (wt %)	T_g (°C)	TGA _{-5%} (°C)	Solubility (%)
0	65.5	291.6	57.4
3	88.7	295.3	20.1
6	ND	297.4	8.2
10	ND	298.9	5.1

Curing 1 h at 200°C. ND, not detectable.

crosslinkable and sulfur-containing polymers potentially could be used as high-temperature coatings, sealants, adhesives, and as the matrices for high performance composites.

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