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Preparation of Poly(thioarylene)s from Cyclic Disulfide Oligomers

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ABSTRACT: A series of poly(thioarylene)s, including fluorinated poly(thioarylene)s, was prepared from cyclic disulfide oligomers and diiodo or dibromo aromatic compounds in diphenyl ether solution at 270 °C. The cyclic disulfide oligomers were derived from 4,4′-thiobis(benzenethiol) and 4,4′-biphenyldithiol, respectively. Diiodo monomers had to be used in excess (~4%) to obtain the highest molecular weight polymers, while equivalent amounts of dibromo monomers could be used. 1,4-Diiodobenzene gave poly(thio-1,4-phenylene) (PPS) with a T_g of 88 °C and a T_m of 286 °C, and 1,4-dibromobenzene gave PPS with a T_g of 92 °C and a T_m of 275 °C by reacting with the cyclic disulfide oligomers derived from 4,4′-thiobis(benzene thiol). Poly(thiobiphenylene) obtained from cyclic disulfide oligomers derived from 4,4′-biphenyldithiol had a melting point of 454 °C. Fluorinated diiodo or dibromo monomers have much lower reactivities toward the thiyl radical substitution reaction, and only low molecular weight polymers were obtained. All of the poly(thioarylene)s prepared have very high thermal stabilities as indicated by TGA.

Introduction

The synthesis of poly(thioarylene)s has been extensively studied, since poly(thio-1,4-phenylene) (PPS) is an excellent high-performance semicrystalline thermoplastic with outstanding thermal, oxidative and chemical resistance. Poly(thioarylene)s are generally prepared by the condensation of dichloroaromatic compounds with sodium sulfide in *N*-methylpyrrolidinone (NMP).[1−4] In recent years, several new synthetic methods have been developed. Oxidative polymerization of diaryl disulfides has been extensively studied by Tsuchida et al.[5−7] In addition, poly(thioarylene)s have been synthesized via electrophilic substitution reactions utilizing aryl alkyl sulfides,[8] methyl phenyl sulfoxide,[9] and sulfur chloride.[10] However, the use of large amount of strong acids in all of these reactions is a major drawback. Fagerburg *et al.* have developed a melt process for preparation of poly(thioarylene)s by reaction between sulfur and diiodo compounds. This process has been reported in several patents and papers.[11−16] The diiodo compounds can be prepared by reaction of iodine with aromatic compounds in the presence of oxygen generating water as the byproduct;[17] therefore, the iodine can be recycled. The products contain a significant amount of disulfide linkages, and a method for removal of these linkages has been patented.[18] Poly(thioarylene)s have also been prepared by reduction of the soluble precursor poly(arylene sulfoxide)s.[19−21] A transition-metal activated dichlorobenzene was used by Dembek to prepare soluble poly(thioarylene) precursors;[22] however, the demetalation method needs improvement. Several research groups have studied the melt ring-opening polymerization of cyclic(arylene thioether) oligomers.[23−28] Although a more feasible and economical preparation of cyclic oligomers is required, this process provides the possibility of easy material processing, since the cyclic oligomers have much lower melt viscosities compared to the linear high molecular weight polymers. The polymerization of bis(haloaryl disulfide)s in diphenyl ether solution was reported in 1991.[29,30] PPS obtained using this method after annealing had a T_m of 313 °C.[31]

A series of cyclic arylene disulfide oligomers have been prepared by oxidative coupling of dithiols with oxygen using a copper-amine catalyst.[32] The cyclic arylene disulfide oligomers undergo melt ring-opening polymerization to give high molecular weight poly(arylene disulfide)s by a free radical mechanism.[33] In a recent communication, we reported a novel method to prepare PPS from cyclic disulfide oligomers derived from 4,4′-thiobis(benzenethiol) and a 1,4-dihalobenzene.[34] This method can be easily extended to prepare other poly(thioarylene)s. It is the objective of this paper to describe detailed studies of this novel process and the preparation of some novel poly(thioarylene)s.

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Experimental Section

Measurements. Differential scanning calorimetry (DSC) was carried out with a Seiko 220 DSC instrument at a heating rate of 20 °C/min under nitrogen atmosphere. Thermogravimetry (TG) was carried out with a Seiko TG/TGA220 thermal analyzer at a heating rate of 20 °C/min under nitrogen atmosphere. Gel permeation chromatography (GPC) analyses were performed on a Waters 510 HPLC equipped with 5 m phenogel columns (linear, 3 × 500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. NMR data were recorded at 500 MHz on a Varian UNITY 500 NMR instrument and are listed in parts per million downfield from tetramethylsilane. FT-IR spectra were measured with an Analet AQS-18 FTIR spectrometer, and data were recorded with an Analet MAP-67 data system. Melting points for monomers were taken on a Fisher-Johns melting point apparatus, and the thermometer was uncorrected. Solid state ^{13}C-NMR spectra were recorded on a Chemagnetics CMX-300 spectrometer.

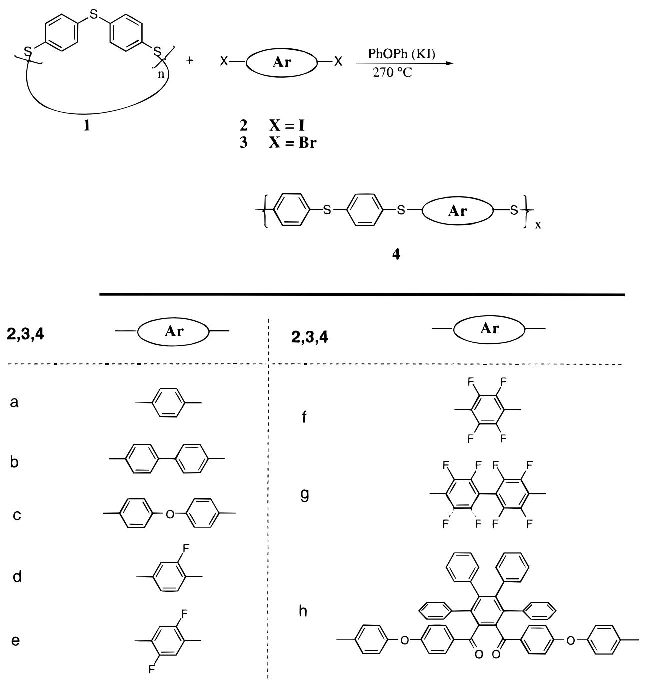
Materials. Cyclic disulfide oligomers **1** and **5** were prepared from 4,4′-thiobis(benzenethiol) and 4,4′-biphenyldithiol by copper−amine-catalyzed oxidation.[32] 1,4-Dibromobenzene, 1,4-diiodobenzene, bis(4-bromophenyl) ether, and diphenyl ether were purchased from Aldrich Chemical Co. and used without further purification. Commercially available 4,4′-dibromobiphenyl, 1,4-dibromo-5-fluorobenzene, 1,4-dibromo-2,5-difluorobenzene, 1,4-diiodotetrafluorobenzene, 1,4-dibromotetrafluorobenzene, and 4,4′-dibromooctafluorobiphenyl were recrystallized from absolute ethanol. 1,2-Bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene was synthesized according to the previously reported method.[35]

1,2-Bis(4′-bromophenoxybenzoyl)-3,4,5,6-tetraphenylbenzene (3h). A 100 mL three-neck flask was charged with 10.0 g (16.0 mmol) of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene, 5.53 g (32.0 mmol) of *p*-bromophenol, 8.83 g (64.0 mmol) of anhydrous K_2CO_3, 40 mL of DMAc, and 8 mL of toluene. The solution was heated to reflux, and water was removed by azeotropic distillation. The reaction mixture was kept at reflux for 5 h, cooled down to room temperature and poured into 400 mL of water. The solid product was filtered and washed with water and then with methanol. The product was recrystallized from toluene/ethanol, giving 14.2 g (95%) of the desired product. Mp: 215−217 °C. ^{1}H-NMR (500 MHz, $CDCl_3$) d 7.60 (d, 4H), 7.43 (d, 4H), 6.89−6.72 (m, 28H); ^{13}C-NMR (125 Mhz, $CDCl_3$) d 197.27, 160.18, 155.17, 142.00, 139.16, 138.56, 138.48, 137.98, 133.37, 132.64, 131.75, 131.03, 130.84, 126.96, 126.76, 126.37, 125.76, 120.93, 117.19, 116.42. FAB-MS *m/e* 933; Elemental analysis, calculated: C 72.11, H 3.89; found: C 72.08, H 3.86.

General Procedure for Polymerization of Cyclic Arylene Disulfide Oligomers with Diiodo Compounds. Cyclic disulfide oligomers **1** (0.248 g, 1.0 mmol), diiodoaromatic compound, and diphenyl ether (0.5 mL) were charged in a Pyrex test tube (1.5 × 15 cm) equipped with a mini magnetic stirring bar and a nitrogen inlet. The test tube was immersed in a salt bath preheated to 270 °C to a depth of about 2 cm to cover the contents inside for 10 h. 1-Chloronaphthalene (3 mL) was then added to dilute the polymer. The solution was poured into 300 mL of methanol to precipitate out the polymer, and the polymer was isolated by filtration and washed with hot methanol, hot chloroform, and then methanol, respectively. The product was dried at 100 °C under vacuum for 24 h and then subjected to analysis.

General Procedure for Polymerization of Cyclic Arylene Disulfide Oligomers with Dibromo Compounds. Cyclic disulfide oligomers **1** (0.248 g, 1.0 mmol), the dibromoaromatic compound (1.0 mmol), powdered potassium iodide (0.84 g, 5.1 mmol), and diphenyl ether (0.5 mL) were charged in a Pyrex test tube (1.5 × 15 cm) equipped with a mini magnetic stirring bar and a nitrogen inlet. The test tube was immersed in a salt bath preheated to 270 °C to a depth of about 2 cm to cover the contents inside for 24 h. 1-Chloronaphthalene (3 mL) was added to dilute the polymer. The solution was poured into 300 mL of methanol to precipitate out the polymer. The polymer was isolated by filtration and washed with hot water, hot methanol, hot chloroform, and then methanol. The product was dried at 100 °C under vacuum for 24 h and then subjected to analysis.

Scheme 1. Thermal Polymerization Reactions between Cyclic Disulfide Oligomers and Dihalo Aromatic Compounds



For the polymerizations of cyclic disulfide oligomers with 1,4-dibromo-2,5-difluorobenzene, 1,4-diiodotetrafluorobenzene, and 4,4′-dibromooctafluorobiphenyl, the washing with hot chloroform was either omitted or cold chloroform was used instead since the polymer products are soluble in hot chloroform.

Synthesis of polymer 4.3h. Cyclic disulfide oligomer **1** (0.248 g, 1.0 mmol), **3h** (0.933 g, 1.0 mmol), powdered potassium iodide (0.84 g, 5.1 mmol), and diphenyl ether (3.0 mL) were charged in a Pyrex test tube (1.5 × 15 cm) equipped with a mini magnetic stirring bar and a nitrogen inlet. The test tube was immersed in a salt bath preheated to 260 °C to a depth of about 4 cm to cover the contents inside for 40 h. After cooling down, 5 mL of chloroform was added to dilute the mixture. The solution was poured into 300 mL of vigorously stirred methanol to precipitate out the polymer. The polymer was dissolved in 20 mL of chloroform and filtered through a thin layer of Celite to remove the salt. The solution was concentrated and poured into 200 mL of methanol to precipitate the polymer. After filtration and drying at 100 °C under vacuum for 24 h, 0.944 g of white polymer was obtained. Yield: 92%.

Results and Discussion

Synthesis of PPS from Cyclic Disulfide Oligomers 1. The polymerization reaction is shown in Scheme 1. Throughout this paper, **4.2a−h** is used to represent the polymers prepared from diiodo compounds, while **4.3a−h** is used to represent the polymers prepared from dibromo compounds. The cyclic disulfide oligomers **1** used here have a number-average molecular weight M_n of 380 and a weight-average molecular weight M_w of 570 as determined by GPC (using polystyrene standards). The synthesis of PPS from cyclic disulfide oligomers **1** was first carried out. Because of the insolubility of PPS, the polymers formed were only examined by differential scanning calorimetry. The relationships between molecular weight and thermal properties have been established although they are probably not reliable.[16] No glass transition temperature

Table 1. Effect of Molar Ratio of Reactants on Thermal Properties of PPS

no.	yield (%)[a]	**2a/1**	T_g (°C)[b]	T_c (°C)[b]	T_m (°C)
1	97	1.00	85	123	284
2	98	1.01	85	125	286
3	94	1.02	88	127	287
4	97	1.04	88	132	286
5	96	1.06	82	125	286

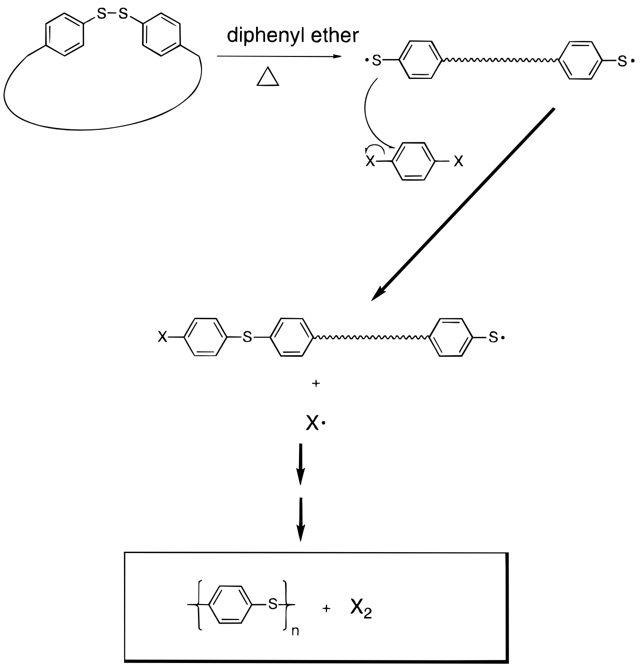
[a] Based on the amount of **1**. [b] Measured by DSC under nitrogen atmosphere at a heating rate of 20 °C/min. All the reported data were obtained by scanning of the quenched samples.

T_g was observed for any of the PPS polymers during the first heating scan. After quenching of the samples, a T_g, a crystallization temperature T_c, and a melting point T_m were observed. At the beginning, it was expected that stoichiometric amounts of **1** and 1,4-diiodobenzene (**2a**) would be required to obtain PPS with the highest molecular weight. However, with stoichiometric amounts, PPS with a glass transition temperature of 85 °C was obtained. It was found that an excess amount of **2a** is required to obtain PPS with higher glass transition temperatures. The effects of molar ratio of reactants on thermal properties of PPS is shown in Table 1. Although the glass transition temperature should be a monotonic function of molecular weight, we had difficulty in choosing the better condition between entry 3 and entry 4 in Table 1 since the difference of T_g is small. T_c is also a monotonic function of molecular weight, and it has much larger changes than T_g.[16] Although it may not be suitable to use the correlation equation from the reference directly to polymers synthesized by the present preparation method, the trend should be applicable, i.e., the higher the T_c detected by DSC, the higher the molecular weight for a series of polymers prepared by the same method using consistent measurements. The data in Table 1 shows that the molar ratio of cyclic disulfide oligomer **1** to 1,4-diiodobenzene has a significant influence on the T_c of the product. 1,4-Diiodobenzene has to be used in ~4% excess to obtain PPS with the highest T_c, which we assume represents the highest molecular weight according to the above arguments. Presumably, this is due to the decomposition of the diiodo compound at high temperatures. The need for excess diiodo compounds has been rationalized by other researchers in other polymerization reactions.[36] However, when *p*-dibromobenzene was used, the molar ratio of 1:1 of the reactants was found to be optimum. The PPS obtained after 24 h of reaction has a T_c of 150 °C, a T_g of 92 °C, and a T_m of 275 °C.

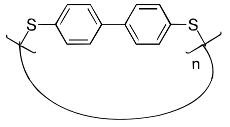
The structure of PPS prepared by the present method was studied by IR and solid state ^{13}C-NMR. The FT-IR spectra (KBr) of PPS **4.2a** and **4.3a** are identical. Both of them show strong absorptions at 814 cm^{-1} attributed to 1,4-substituted phenylene, which confirmed that they have linear, 1,4-phenylene sulfide structures. There is no visible absorption peak at 1234 cm^{-1} (−C−O−C−) for PPS **4.3a**, which was apparent when the polymerization was carried out in the absence of potassium iodide.[29,30] The solid state ^{13}C-NMR spectra of both PPS **4.2a** and **4.3a** are identical and show two peaks at 134.6 and 132.2 ppm, which are in accordance with the reported results.[29]

The polymerization mechanism is illustrated in Scheme 2, and is a typical free-radical *ipso*-substitution reaction. At high temperatures, disulfide linkages in cyclic disulfide oligomers are ruptured and give thiyl radicals. The thiyl radicals *ipso*-substitute the halogen atom and form diphenyl sulfide linkages and halogen radicals. The iodine radicals combine to form iodine which distills from the reaction mixture. However, the bromine radicals are very reactive and brominate the solvent diphenyl ether, which destroys the stoichiometric balance of reactants so that high molecular weight polymer is not formed. Potassium iodide serves as a reductant for the bromine atoms to suppress the side reactions caused by the reactive bromine radical and makes the use of dibromoaromatic compounds as monomers practical.

Scheme 2. Mechanism of Thermal Polymerization Reactions between Cyclic Disulfide Oligomers and Dihalo Aromatic Compounds



Synthesis of Poly(thioarylene)s from Cyclic Disulfide Oligomers. By applying the polymerization conditions described above, a series of poly(thioarylene)s were prepared from cyclic disulfide oligomers **1**, **5**, and different dihaloaromatic compounds. Generally, 4% excess of diiodo compounds were used, while equivalent amounts of dibromo compounds were used. Most of the polymers are insoluble in common organic solvents (except **4.3c**); therefore, we do not have a direct measurement of molecular weights. All of the polymers were obtained in very high yields. The thermal propertiers of the polymers are listed in Table 2. Polymer **4.3c** has the same glass transition temperature T_g as commercial PPS. However, the melting point is much lower than that of PPS due to the presence of ether linkages. It is interesting to note that this polymer has a much higher (~50 °C) melting point than poly(thio-1,4-phenyleneoxy-1,4-phenylene) (T_m = 191 °C).[37] As



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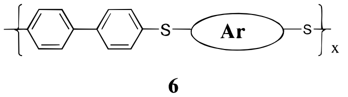

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Table 2. Thermal Properties of Poly(thioarylene)s

polymers	yield (%}[a]	T_g (°C)[b]	T_c (°C)[b]	T_m (°C)[a]	TGA (°C)[c]
4.3b	97	115			500
4.3c	96	85	139	238	493
4.3h	92	192			525
6.2a	83	146	230	295	520
6.3b	92			454[d]	496
6.3c	93	124	178	261	510

[a] Based on the amounts of cyclic disulfide oligomers. [b] Measured by DSC under nitrogen atmosphere at the heating rate of 20 C/min. All the reported data were obtained by scanning of the quenched samples. [c] Temperatures for 10% weight loss, which were measured under nitrogen atmosphere at a heating rate of 20 °C. [d] Obtained from the first heating scan. The second heating scan was not performed because of decomposition of the sample.

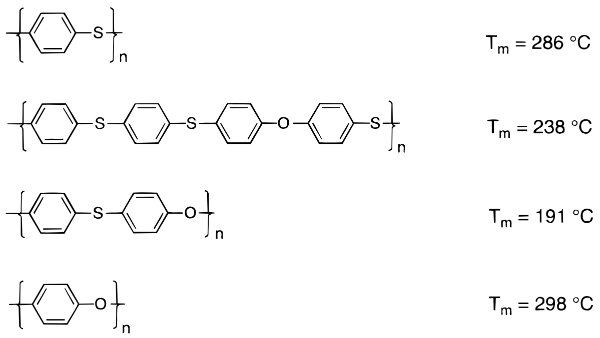

Figure 1. Thermal Properties of PPS and PPS Derivatives

shown in Figure 1, in all cases, polymers containing both thioether and ether linkages have lower melting points than PPS and poly(oxy-1,4-phenylene).[38] Poly(thio-4,4′-biphenylene), **6.3b**, is a highly crystalline polymer and has a melting point of 454 °C. This polymer has been previously prepared by reacting 4,4′-difluorobiphenyl or 4,4′-dibromobiphenyl with a alkali metal sulfide in NMP.[39,40] Polymer **6.3b** shows almost the same melting point as that prepared from 4,4′-difluorobiphenyl and sodium sulfide (445 °C),[39] while the melting point is much higher than that reported in another paper (387 °C);[40] however, these materials are believed to be low molecular weight oligomers. Polymers **4.3b** and **6.2a** can be viewed as the copolymer of PPS and poly(thio-4,4′-biphenylene) with molar ratios of 2:1 and 1:1, respectively. If one compares these results with the results reported by Park *et al.*,[40,41] the polymers prepared by the present method have much higher glass transition temperatures, which indicates that the polymers prepared by the present method have higher molecular weights. Polymer **4.3h** is an amorphous polymer, which is readily soluble in normal organic solvents, such as chloroform, THF. The number average molecular weight of **4.3h** was 11 000, and the weight average molecular weight was 29 000 as determined by GPC using polystyrene standards. If only a very small amount of solvent diphenyl ether was used, polymers with very broad molecular weight distribution were obtained, which indicates some branching reaction was taken place. This was also the case for the melt polymerization of bis(4-iodophenyl) disulfide.[42]

Synthesis of Poly(thioarylene)s from Fluorine-Containing Monomers. It was observed that the fluorine atom is unreactive toward the substitution reaction by thiyl radicals.[29,43] Therefore, it should be possible to prepare fluorinated poly(thioarylene)s by reaction of cyclic disulfide oligomers and dibromo- or diiodofluoroaromatic compounds. The study of fluorinated polymers has received extensive attention, since the introduction of fluorine into polymers can result in significant changes in polymer properties, such as low dielectric constant.[44,45] Several fluorinated poly(thioarylene)s were prepared by the reaction between cyclic disulfide oligomers **1**, **5**, and fluorinated aromatic compounds at high temperature. The thermal properties of all the polymers prepared are listed in Table 3. Polymers **4.3d**, and **4.3e** are not soluble in normal organic solvents, while polymers **4.2f**, **4.3f, 6.3f** and **6.3g** are soluble in hot chloroform. Polymer **4.3g** is soluble in chlorform at room temperature. If the thermal properties of polymers **4d**−**g** are examined, it is apparent that the higher the content of fluorine in the polymers, the higher the glass transition temperatures. Although melting points were observed in the first heating scans, only T_g's were observed after quenching the samples, which indicates that fluorinated moieties lower the rate of crystallization. Only low molcular weight polymers were obtained by the present method. The M_n of **4.3g** was 3200, and M_w was 6100 as determined by GPC. The thiyl radical is electrophilic and prefers to attack an electron-rich aromatic nucleus.[43] Fluorine is a strong electron-withdrawing group and significantly decreases the electron densities in the aromatic rings. The more fluorinated the monomer, the lower the reactivity. It is interesting to note that monomer **2f** gave a higher molecular weight polymer than monomer **3f**, indicated by the difference of T_g's. This observation indicates that iodinated monomers are preferable for electron deficient monomers.

Table 3. Thermal Properties of Fluorinated Poly(thioarylene)s

polymers	yield (%)[a]	T_g (°C)[b]	T_c (°C)[b]	T_m (°C)[b]	TGA (°C)[c]
4.3d	86	86	159	216	510
4.3e	84	86			498
4.2f	89	105			514
4.3f	72	94			498
4.3g	81	110			469
6.3f	61	159			520
6.3g	93	143			504

[a]Based on the amounts of cyclic disulfide oligomers. [b] Measured by DSC under nitrogen atmosphere at a heating rate of 20 °C/min. All the reported data were obtained by scanning of the quenched samples. [c] Temperatures for 10% weight loss, which were measured under nitrogen atmosphere at a heating rate of 20 °C.

Conclusion

A novel method for the preparation of poly(thioarylene)s from cyclic (arylene disulfide) oligomers and diiodo- or dibromoaromatric compounds has been demonstrated. A series of poly(thioarylene)s have been prepared from cyclic disulfide oligomers **1** and **5**, which are derived from 4,4′-thiobis(benzenethiol) and 4,4′-biphenyldithiol, respectively. Diiodo monomers had to be used in excess (~4%) to obtain the highest molecular weight polymers; however, equivalent amounts of dibromo monomers could be used. By reacting with cyclic disulfide oligomer **1**,1,4-diiodobenzene gave PPS with T_g of 88 °C and T_m of 286 °C and 1,4-dibromobenzene gave PPS with T_g of 92 °C and T_m of 275 °C. Fluorinated diiodo or dibromo monomers have much lower reactivities toward the thiyl radical substitution reaction, and only low molecular weight polymers were obtained. All of the poly(thioarylene)s prepared have very high thermal stabilities as indicated by TGA.

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