Synthesis of Poly(arylene sulfide)s by Cationic Oxidative Polymerization of Diaryl Disulfides

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ABSTRACT: Alkyl-substituted poly(arylene sulfide)s (PASs) are prepared by the oxidative polymerization of diaryl disulfides with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The structures of the formed poly(arylene sulfide)s are confirmed by spectroscopic measurements. The linear structure of poly(2-methyl-1,4-phenylene sulfide) is confirmed by comparing its spectroscopic data with those of the polymer prepared from bis(2-methylphenyl) disulfide, bis(3-methylphenyl) disulfide and (4-bromo-2-methylthiophenoxy) copper salt. Bis(2,5-dimethylphenyl) disulfide is easily polymerized to poly(2,5-dimethyl-1,4-phenylene sulfide) with high yield and high melting point in comparison with the other methyl-substituted poly(arylene sulfide)s, due to the symmetry of the polymer structure. The polymerization reaction, with the exception of bis(3,5-dimethylphenyl) disulfide, produces low molecular weight polymers because of the solvent insolubility of PASs and the low reactivity of diaryl disulfides. Soluble poly(2,6-dimethylphenylene sulfide) is isolated by the polymerization of bis(3,5-dimethylphenyl) disulfide as a white powder with ca. 3×10^4 weight-average molecular weight.

Introduction

Poly(*p*-phenylene sulfide) (PPS) is classed as an engineering plastic because of its excellent chemical, thermal, and mechanical properties.[1] The commercially important preparative route to PPS is a polycondensation of 1,4-dichlorobenzene and sodium sulfide in a polar solvent, such as *N*-methylpyrrolidone, at high temperature and high pressure.[2] Lenz and co-workers reported that PPS is also prepared by the polycondensation of the (*p*-halothiophenoxy)metal salt.[3,4] Recently, much effort has been exerted in the development of new synthetic routes to poly(arylene sulfide)s (PASs).[5,6] Until now, surprisingly, few papers have been reported[7,8] on the preparation of substituted poly(arylene sulfide)s.

We have found and reported that diphenyl disulfide as a monomer reacts with DDQ which cleaves its S–S bond and easily polymerizes to a linear poly(*p*-phenylene sulfide) at room temperature and atmospheric pressure.[9–14] This polymerization not only is an efficient synthesis of PPS but also is applicable to the synthesis of substituted PASs. Methyl groups were introduced in diphenyl disulfide at the meta position of the benzene ring to improve the solubility of the polymer. Poly(2,6-dimethylphenylene sulfide) with its high molecular weight and melting point was formed through the oxidative polymerization with DDQ in high monomer feed concentration.

This paper describes the structures of the formed poly(arylene sulfide)s and the polymerization behavior of alkyl-substituted diphenyl disulfides such as bis(2-methyl-, 3-methyl-, 4-methyl-, 2,6-dimethyl-, 2,5-dimethyl-, 3,5-dimethyl-, and 2,4-dimethylphenyl) disulfides. The effect of the methyl substituents in the cationic oxidative polymerization is also discussed.

Experimental Section

Materials. Solvents, dichloromethane, 1,1,2,2-tetrachloroethane, and nitrobenzene, were purified by two distillations in the usual manner. Diphenyl disulfide was purified by two recrystallizations from ethanol–water and drying in vacuo for 1 day at 30 °C and was obtained as white needles: mp 59 °C. Bis(2-methylphenyl)disulfide, bis(3-methylphenyl) disulfide, bis(4-methylphenyl) disulfide, bis(2-methoxyphenyl) disulfide, bis(2,6-dimethylphenyl) disulfide, bis(2,6-dichlorophenyl) disulfide, bis(2,5-dimethylphenyl) disulfide, and bis(2,4-dimethylphenyl) disulfide were prepared by the oxidation of the corresponding thiophenols with I_2 in alkaline methanol. Bis(2,6-diethylphenyl) disulfide, bis(3,5-dimethylphenyl) disulfide and bis(2-chloro-6-methylphenyl) disulfide were prepared by the Leuckart reaction[15] from the corresponding substituted anilines as a starting material. Bis(2,5-dimethoxyphenyl) disulfide was prepared by the reported method from *p*-dimethoxybenzene.[16] Bis(3-methylphenyl) disulfide and bis(3,5-dimethylphenyl) disulfide were purified by column chromatography on silica gel. Other diaryl disulfides were purified by double recrystallizations. The structures of all monomers were confirmed by spectroscopic measurements before the polymerization. The purities of the diaryl disulfides were over 99.5% as measured by gas chromatography. Trifluoromethanesulfonic acid (3M Co., >98%), trifluoroacetic acid (Kantoh Chemical Co., >99.5%), and DDQ (Merck, >98%) were used without further purification and were handled under a dry nitrogen atmosphere.

Measurements. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a 90-MHz JEOL FX-100. IR spectra were obtained using a JASCO Model IR-810 spectrometer. Mass spectra were obtained using an ionization energy of 20 eV on a JEOL Model JMS-DX300 spectrometer. Melting points and softening points were determined on a hot stage microscope with a heating rate of 2 °C/min. DSC measurement was done in a nitrogen atmosphere on a SEIKO Model SSC/500 thermal analyzer: sample size, 7–10 mg, heating rate, 20 °C/min. The melting point of poly(2,5-dimethylphenylene sulfide) was measured by DSC after annealing for 10 min[17] in a nitrogen atmosphere at 240 °C. The glass transition temperature of poly[bis(3,5-dimethylphenyl) disulfide] was measured using the DSC at a 20 °C/min heating rate. The determination of molecular weight of the soluble part of PASs in *N*-methylpyrrolidone (NMP) was carried out using a Shimadzu LC-9A. Asahipac (GS 501H and 310H) columns were used for the analysis. The operating temperature was 25 °C with a flow rate of 1.0 mL/min of NMP solution. The detector was a UV–vis spectrophotometer (Shimadzu SPD-6AV, 265 nm). The data acquisition was performed with a Shimadzu Chromatopac C-R6A. The polymer samples were dissolved at 0.5 wt % in the distilled NMP. The solution was filtered through 0.2-μm Teflon filters just before injection. The GPC was calibrated with five monodisperse polystyrene samples with M_w ranging from 1400 to 87 000. The samples were purchased from Showa Denko K.K. (Shodex SM-105). The number-average molecular weights of the polymers were determined by vapor pressure osmometry (VPO). Measurements were made on benzene solutions at 40 °C with a Corona 119 osmometer, calibrated with a monodisperse polystyrene standard (M_n = 10 300) supplied by Showa Denko K.K. The instrument was checked for accuracy with a variety

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of polymers of known M_n.

Polymerization Method. A typical experiment was done in a three-necked glass vessel where 0.01 mol of diphenyl disulfide was dissolved in 50 mL of dichloromethane. The mixture was rapidly poured into 0.2 mol/L of DDQ in 50 mL of dichloromethane in the presence of trifluoromethanesulfonic acid (0.01 mol/L) and kept at 20 °C in a nitrogen atmosphere for 20 h. After the polymerization, the reaction mixture was poured into 500 mL of hydrochloric methanol (5 wt %) to precipitate a polymeric material. The polymer was purified by the previously reported method.[13] The polymer did not contain more than 10 ppm of DDQ, 2,3-dichloro-5,6-dicyano-*p*-hydroquinone (DDH), and metal ions.

Spectroscopic Data. Bis(3,5-dimethylphenyl) disulfide: ^{1}H-NMR ($CDCl_3$, ppm) 2.2 (methyl, 12 H); 6.8, 7.1 (phenyl, 6 H). ^{13}C-NMR ($CDCl_3$, ppm) 21.2 (methyl C); 125.3, 129.0, 136.9, 138.6 (phenyl C). IR (KBr, cm^{-1}) 2920, 2960, 3030 (ν_{C-H}); 1460, 1580 ($\nu_{C=C}$); 680, 840 (δ_{C-H}). MS (*m/e*) 105, 137, 274. Bis(2,6-diethylphenyl) disulfide: ^{1}H-NMR ($CDCl_3$, ppm) 1.1, 2.8 (ethyl, 20 H); 7.1 (m, phenyl, 6 H). ^{13}C-NMR ($CDCl_3$, ppm) 15, 28 (ethyl C); 126, 130, 134, 150 (phenyl C). IR (KBr, cm^{-1}) 2960, 3050 (ν_{C-H}); 1460 ($\nu_{C=C}$); 750 (δ_{C-H}). MS (*m/e*) 165, 330. Bis(2-methyl-6-chlorophenyl) disulfide: ^{13}C-NMR ($CDCl_3$, ppm) 22 (methyl C); 128.3, 128.7, 130.3, 134.5, 140.7, 145.2 (phenyl C). IR (KBr, cm^{-1}) 2925, 2960 (ν_{C-H}); 1400, 1500 ($\nu_{C=C}$); 745, 860 (δ_{C-H}). Bis(2,5-dimethoxyphenyl) disulfide: ^{1}H-NMR ($CDCl_3$, ppm) 3.9 (methoxy, 12 H); 6.8 (m, phenyl, 6 H). ^{13}C-NMR ($CDCl_3$, ppm) 56 (methoxy C); 112, 113, 117, 124, 152, 154 (methoxy C). IR (KBr, cm^{-1}) 2920, 2960, 3040 (ν_{C-H}); 1460 ($\nu_{C=C}$); 740, 800, 860 (δ_{C-H}).

Poly(*p*-phenylene sulfide): Anal. Calcd for (C_6H_4S): C, 66.67; H, 3.70; S, 29.63. Found:[18] C, 66.51; H, 3.85; S, 29.55. IR is shown in Figure 1a. MS (*m/e*) 756, 648, 540, 434, 326, 218, 110. These data suggested that a monomer unit of 109 existed.

Poly[bis(2-methylphenyl) disulfide]: Anal. Calcd for (C_7H_6S): C, 68.80; H, 4.95; S, 26.25. Found:[18] C, 68.66; H, 4.91; S, 26.12. IR is shown in Figure 1b. ^{1}H-NMR ($CDCl_3$, ppm) 7.1 (m, phenyl, 3 H); 2.3 (s, methyl, 3 H). ^{13}C-NMR is shown in Figure 2. MS (*m/e*) 368, 490, 612.

Poly[bis(3-methylphenyl) disulfide]: Anal. Calcd for (C_7H_6S): C, 68.80; H, 4.95; S, 26.25. Found: C, 68.77; H, 4.98; S, 26.21. IR is shown in Figure 1c. ^{1}H-NMR ($CDCl_3$, ppm) 7.1 (m, phenyl, 3 H); 2.3 (s, methyl, 3 H). ^{13}C-NMR is shown in Figure 2. MS (*m/e*) 490, 612.

Poly[bis(3,5-dimethylphenyl) disulfide]: Anal. Calcd for (C_8H_8S): C, 70.54; H, 5.92; S, 23.54. Found: C, 70.51; H, 5.93; S, 23.47. IR is shown in Figure 1d. ^{1}H-NMR ($CDCl_3$, ppm) 6.7 (s, 2 H); 2.3 (s, 6 H). ^{13}C-NMR ($CDCl_3$, ppm) 125.1, 127.2, 140.1, 144.3 (phenyl C); 21.9 (methyl C). MS (*m/e*) 408, 544, 682.

Poly[bis(2,6-dimethylphenyl) disulfide]: Anal. Calcd for (C_8H_8S): C, 70.54; H, 5.92; S, 23.54. Found: C, 70.33; H, 6.09; S, 23.47. IR is shown in Figure 1e. ^{1}H-NMR ($CDCl_3$, ppm) 7.0 (m, phenyl, 2 H); 2.3 (s, methyl, 6 H). ^{13}C-NMR ($CDCl_3$, ppm) 124.1, 128.6, 136.1, 140.4, 141.5, 144.0 (br, phenyl C); 21.5 (methyl C). MS (*m/e*) 408, 544, 682, 819.

Poly[bis(2,4-dimethylphenyl) disulfide]: Anal. Calcd for (C_8H_8S): C, 70.54; H, 5.92; S, 23.54. Found:[18] C, 70.01; H, 6.02; S, 23.47. IR is shown in Figure 1f. ^{1}H-NMR ($CDCl_3$, ppm) 7.0 (m, phenyl, 2 H); 2.3 (s, methyl, 6 H). ^{13}C-NMR ($CDCl_3$, ppm) 130 (broaden, phenyl C); 21.5 (methyl C). MS (*m/e*) 408, 544, 682, 819.

Poly[bis(2,5-dimethylphenyl) disulfide]: Anal. Calcd for (C_8H_8S): C, 70.54; H, 5.92; S, 23.54. Found:[18] C, 70.25; H, 5.97; S, 23.38. IR is shown in Figure 1g. CP-MASS ^{13}C-NMR (ppm, 400 MHz) 124, 132, 141 (phenyl C); 20 (methyl C). MS (*m/e*) 408, 544.

Poly[bis(2-methyl-6-chlorophenyl) disulfide]: Anal. Calcd for (C_7H_5ClS): C, 53.67; H, 3.22; S, 20.48; Cl, 22.63. Found: C, 53.55; H, 3.23; S, 20.39; Cl, 22.63. IR (KBr, cm^{-1}) 2920, 2950, 3050 (ν_{C-H}); 1330, 1380, 1440, 1560 ($\nu_{C=C}$); 860 (δ_{C-H}). ^{1}H-NMR ($CDCl_3$, ppm) 7.0 (m, phenyl, 2 H), 2.2 (s, methyl, 3 H). ^{13}C-NMR ($CDCl_3$, ppm) 122.8, 128.3, 129.2, 130.4, 137.3, 145.7 (phenyl C); 22.1 (methyl C).

Poly[bis(2-methoxyphenyl) disulfide]: Anal. Calcd for (C_7H_6OS): C, 60.84; H, 4.38; S, 23.21. Found: C, 60.73; H, 4.39; S, 23.15. IR (KBr, cm^{-1}) 2830, 2930 (ν_{C-H}); 1440, 1480, 1560 ($\nu_{C=C}$); 1180 (ν_{C-O-C}); 860, 820 (δ_{C-H}).

Poly[bis(2,5-dimethoxyphenyl) disulfide]: Anal. Calcd for ($C_8H_8O_2S$): C, 57.12; H, 4.79; S, 19.07. Found:[18] C, 57.01; H, 4.76; S, 19.02. IR (KBr, cm^{-1}) 2830, 2930, 2970 (ν_{C-H}); 1360, 1440, 1480, 1560 ($\nu_{C=C}$); 1180, 1205 (ν_{C-O-C}); 860 (δ_{C-H}).

Preparation of Poly(arylene sulfide)s through Polycondensation. Poly(2-methyl-1,4-phenylene sulfide) was prepared[3,4] by the polycondensation of (4-bromo-2-methylthiophenoxy) copper salt at 350 °C. Poly(2,5-dimethyl-1,4-phenylene sulfide) was prepared[2] by the Phillips method as a reference. 2,5-Dichloro-*p*-xylene and sodium sulfide were reacted in *N*-methylpyrrolidone at 250 °C under 2–5 atm in the presence of lithium acetate.

Rotating Ring Disk Voltammetry (RRDV) of Diaryl Disulfides. RRDV was carried out in a two-compartment cell kept in a nitrogen atmosphere in the presence of 5 mmol/L of the substrate. A platinum disk (0.126 cm^2), platinum wire, and Ag/AgCl were used as a working, an auxiliary, and a reference electrode, respectively. The disk potential was controlled by a Nikko Keisoku DPGS-1 dual potentiogalvanstat and a Nikko Keisoku NFG-3 function generator with a scanning rate of 5 mV/s. The rotating rate was 2500 rpm. We previously reported[9] that diphenyl disulfide was electrooxidized to its cation radical and chemically reacted to form the sulfonium cation as an active species of this polymerization. The reduction peak potentials of the radical cation and the sulfonium cation were estimated at 1.3 and 0.5 V, respectively, by cyclic voltammetry. The ring disk potential was applied at 1.2 and 0.5 V for each measurement of the cation. The theoretical collection efficiency (N^0_k) was 0.42 for this ring disk electrode. The collection efficiencies ($N_k = i_r/i_d$) in this measurement were calculated by dividing of the limiting current of the ring disk electrode (i_r) by that of the disk electrode (i_d).

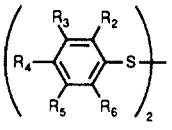
Model Reaction of the Electrophilic Reaction of the Cation. The chemically prepared methylbis(methylthio)sulfonium cation (0.04 mol)[19] was dissolved in 20 mL of dichloromethane. Diphenyl sulfide (20 mL, 0.1 mol/L) was added to the reaction mixture. We previously reported[14] that methylthio-substituted diphenyl sulfide was quantitatively formed as a main product through an electrophilic reaction. The reaction conversion was confirmed by gas chromatography.

Results and Discussion

Structure of Polymers. Diaryl disulfides such as bis(methylphenyl) disulfide, bis(dimethylphenyl) disulfide, and bis(dimethoxyphenyl) disulfide are polymerized with DDQ to yield the corresponding PASs in high yield. Cationic oxidative polymerization is a convenient method to prepare the PPS and the PASs (Table I). However, low molecular weight PASs are produced by the polymerization, with the exception of bis(3,5-dimethylphenyl) disulfide, because these polymers are precipitated in the reaction mixture.[20] To avoid confusion, source-based names are used in Table I and in the discussion to define the polymers obtained from polymerization of the different disulfides. Structure-based names are used exclusively to define the actual structures of the polymers formed. This nomenclature has been adopted because the polymerization of a particular disulfide may give rise to more than one type of repeat unit and because two different disulfides can yield polymers of identical structure.

Bis(3-methylphenyl) disulfide is allowed to react with DDQ in tetrachloroethane for 20 h at room temperature. The polymer, poly[bis(3-methylphenyl) disulfide], is isolated in over 90% yield as a white powder. The IR spectrum of the formed polymer agrees with that of poly(2-methyl-1,4-phenylene sulfide) prepared by the polycondensation. Both the IR and the NMR spectra also agree with those of the poly[bis(2-methylphenyl) disulfide] prepared by the polymerization of bis(2-methylphenyl) disulfide. Possible structural units for poly[bis(3-methylphenyl) disulfide] are shown in Scheme I. The

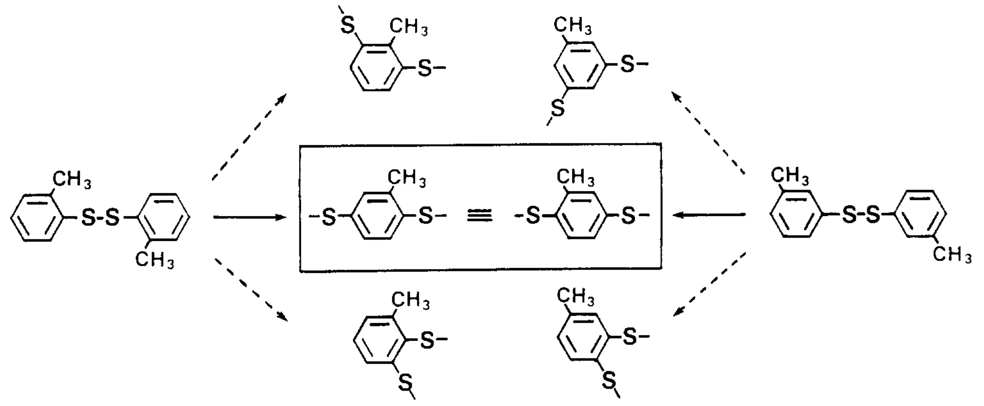
Table I
Oxidative Polymerization[a] of Diaryl Disulfides with DDQ



source-based name of PAS	R_2	R_3	R_4	R_5	R_6	PAS yield, wt %	mp,[b] °C	M_n[c]
poly(diphenyl disulfide)	H	H	H	H	H	95	195[d]	1000[e]
poly[bis(2-methylphenyl) disulfide]	CH_3	H	H	H	H	76	140	1600
poly[bis(3-methylphenyl) disulfide]	H	CH_3	H	H	H	92	150	3800
	H	H	CH_3	H	H	0		
poly[bis(2-methoxyphenyl) disulfide]	OCH_3	H	H	H	H	60	150	2400
poly[bis(2,6-dimethylphenyl) disulfide]	CH_3	H	H	H	CH_3	91	210	2350
poly[bis(2,5-dimethylphenyl) disulfide]	CH_3	H	H	CH_3	H	97	338[d]	800[e]
poly[bis(3,5-dimethylphenyl) disulfide]	H	CH_3	H	CH_3	H	93	185[f]	3200 9600[g]
poly[bis(2,4-dimethylphenyl) disulfide]	CH_3	H	CH_3	H	H	69	100	1300
poly[bis(2,5-dimethoxyphenyl) disulfide]	OCH_3	H	H	OCH_3	H	80	170	800[e]
	Cl	H	H	H	Cl	0		
poly[bis(2-methyl-6-chlorophenyl) disulfide]	CH_3	H	H	H	Cl	98	185	2050

[a] Reaction time 40 h. [b] Hot stage of microscope. [c] Vapor pressure osmometry. [d] DSC measurement. [e] Benzene-soluble part of polymer. [f] Glass transition temperature by DSC. [g] M_w.

Scheme I



polymer structure containing an ortho linkage could be excluded because the reaction on the ortho position of the benzene ring leads to the formation of thianthrene as a side reaction.[14] One notices that poly(2-methyl-1,4-phenylene sulfide) and poly(3-methyl-1,4-phenylene sulfide) have identical structures. Both poly[bis(2-methylphenyl) disulfide] and poly[bis(3-methylphenyl) disulfide] are linear structures or 1,4-linked, which is supported by the agreement of their IR and NMR spectra (Figures 1b,c and 2).

The linearity of the polymers is also supported by the existence of the absorption bands at 820 and 880 cm^{-1}, which correspond to the adjacent 2H C–H out-of-plane deformation vibration and the isolated 1 H C–H out-of-plane vibration,[21] respectively. Difference absorptions at 790 and 750 cm^{-1} appear in the IR spectra of each polymer (Figure 1b,c), which correspond to the adjacent 3H C–H out-of-plane vibration and the adjacent 4H one, respectively. These results are based on a difference in end groups.

Bis(3,5-dimethylphenyl) disulfide gives a white and pure polymer with >95% yield by the oxidative polymerization. The polymer structure including 1,4-phenylene units was confirmed as follows. The IR spectrum of poly[bis(3,5-dimethylphenyl) disulfide] agrees with that of poly(2,6-dimethyl-1,4-phenylene sulfide) prepared by polycondensation from (4-bromo-2-methylthiophenoxy)copper salt. An IR absorption band between 800 and 900 cm^{-1} was observed at 880 cm^{-1}, which is ascribed to an isolated C–H out-of-plane vibration on the benzene ring. These results mean the formation of linear poly(2,6-dimethyl-1,4-phenylene sulfide), taking into account the symmetry of each polymer structure.

Bis(2,6-dimethylphenyl) disulfide is also polymerized to give the polymer. The elemental analysis and mass spectroscopic data of the polymer support the formation of poly(2,6-dimethylphenylene sulfide). However, the IR spectrum does not agree with the linear poly(2,6-dimethyl-1,4-phenylene sulfide), and the adjacent 2H C–H out-of-plane deformation vibration is observed at 820 cm^{-1} (Figure 1e). The disagreement is not based on the fact that the monomer units couple through the methylene sulfide bonds[22] because the NMR signals of the methylene proton and carbon were not observed at 3.6 and 60 ppm, respectively. It is considered that poly[bis(2,6-dimethylphenyl) disulfide] contains not only a 1,4-linkage but also a 1,3-linkage structure (Scheme II).

The spectroscopic data also support the formation of poly(2,6-diethylphenylene sulfide) by the polymerization of bis(2,6-diethylphenyl) disulfide. The complete polymerization of bis(2,6-diethylphenyl) disulfide is indicated by a decrease in the absorption band at 760 cm^{-1} attributed to the adjacent 3H C–H out-of-plane vibration of the monomer. The polymer also contains 1,3-phenylene and 1,4-phenylene structures similar to the poly[bis(2,6-dimethylphenyl) disulfide] because the absorption band at

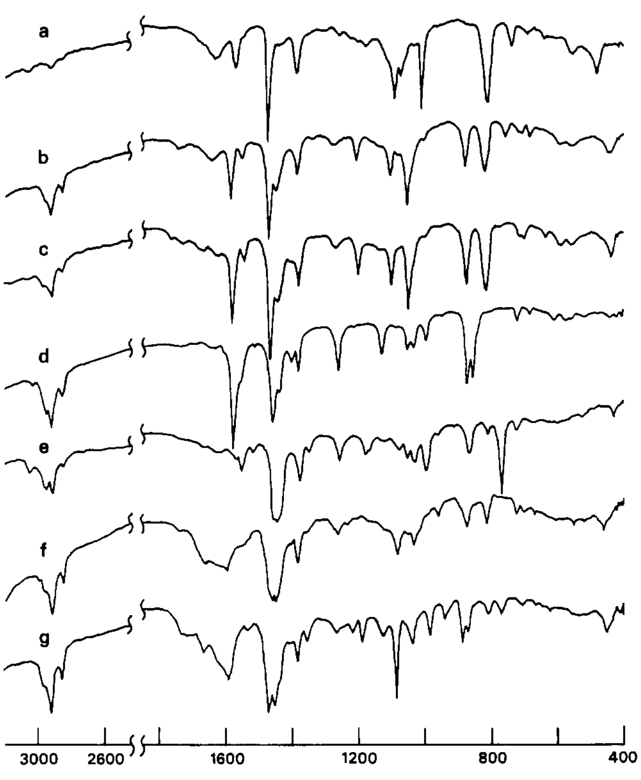


Figure 1. IR spectra of poly(diphenyl disulfide) (a), poly[bis(2-methylphenyl) disulfide] (b), poly[bis(3-methylphenyl) disulfide] (c), poly[bis(3,5-dimethylphenyl) disulfide] (d), poly[bis(2,6-dimethylphenyl)disulfide] (e), poly[bis(2,4-dimethylphenyl) disulfide] (f), and poly[bis(2,5-dimethylphenyl) disulfide] (g).

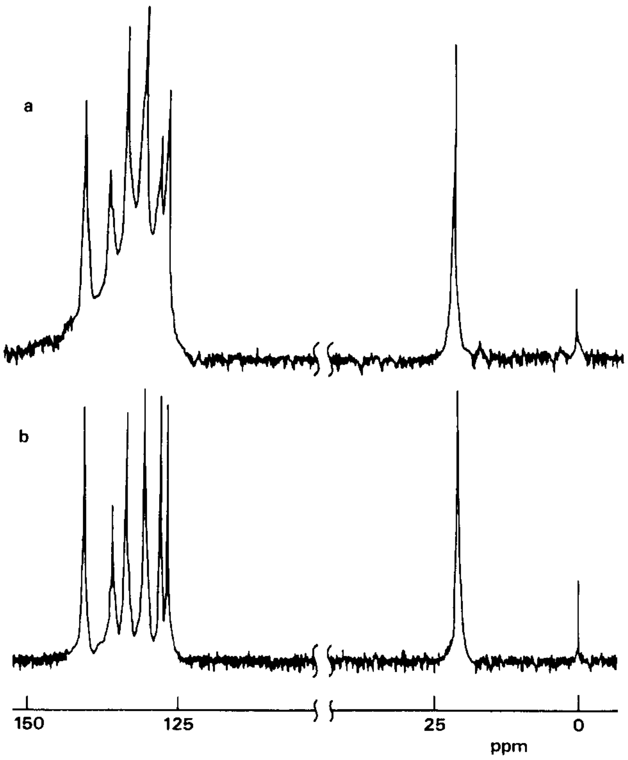
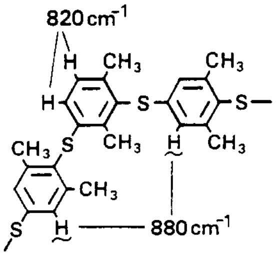


Figure 2. ^{13}C-NMR spectra of poly[bis(2-methylphenyl) disulfide] (a) and poly[bis(3-methylphenyl) disulfide] (b).

820 cm^{-1} exists.

Bis(2,5-dimethylphenyl) disulfide is a more favorable monomer for this polymerization, from the viewpoint of the higher melting point and high yield of poly[bis(2,5-dimethylphenyl) disulfide]. The structure was confirmed by CP-MASS ^{13}C-NMR and IR spectra. The spectroscopic data agreed with those of poly(2,5-dimethyl-1,4-phenylene sulfide) prepared by the Phillips method.[2] The IR spectrum of the polymer shows an absorption band at 880 cm^{-1} (Figure 1g). Three signals ascribed to the carbon atoms of the phenyl ring are observed in the NMR spectrum. These results indicate that the polymer has a linear structure.

Scheme II



The formed virgin polymer has no melting point; however, it shows a high melting point at 338 °C after annealing at 240 °C for 10 min.[17] It is considered that the higher melting point is caused by the higher symmetry of this polymer in comparison with poly(2,6-dimethylphenylene sulfide) or poly(2-methylphenylene sulfide).[23] The glass transition temperature (T_g) is estimated at 200 °C by means of a DSC measurement. This polymer was completely soluble in hot *N*-methylpyrrolidinone and α-chloronaphthalene but was not soluble in any common solvents at room temperature, similar to the solvent solubility of commercially available PPS.

In the case of bis(2,4-dimethylphenyl) disulfide, oxidative polymerization proceeds in spite of having a substituent in the para position of the benzene ring. The IR spectrum is similar to that of poly[bis(2,6-dimethylphenyl) disulfide]. The data indicate that poly[bis(2,6-dimethylphenyl) disulfide] contains the 2,6-dimethyl-1,3-phenylene structure (Figure 1f). However, bis(4-methylphenyl) disulfide, which has a substituent in the para position, was not efficiently polymerized to PAS.

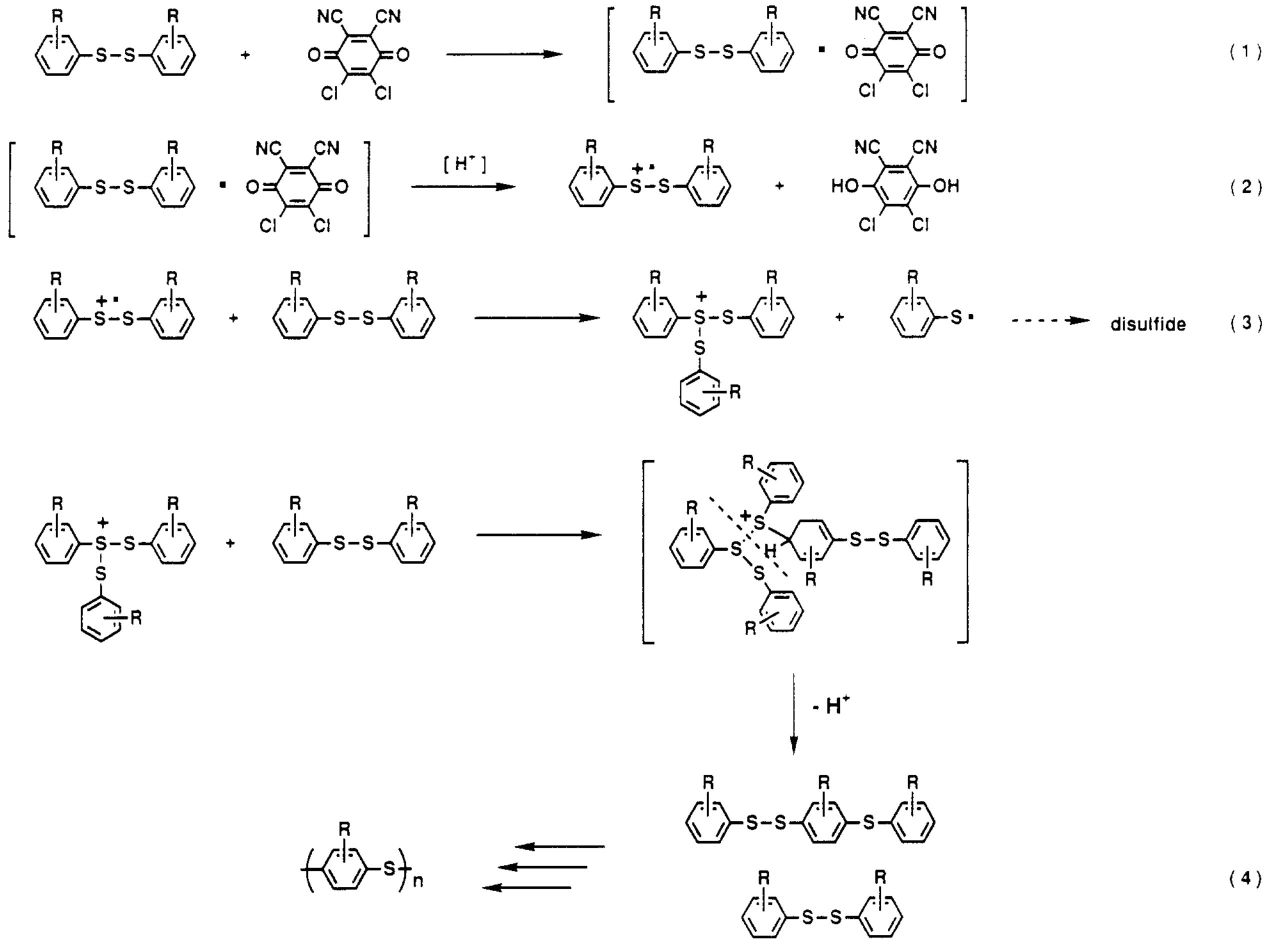
To study the effect of electron-withdrawing substituents on the polymerization, oxidative polymerization of chloro-substituted diaryl disulfides was carried out. Bis(2,6-dichlorophenyl) disulfide does not react with DDQ. The monomer is not oxidized by DDQ because the dichloro-substituted monomer has the higher oxidation potential.

Bis(2-methyl-6-chlorophenyl) disulfide and bis(3-chlorophenyl) disulfide are allowed to polymerize to poly(2-methyl-6-chlorophenylene sulfide) and poly(3-chlorophenylene sulfide), respectively. However, the molecular weight of the polymer does not drastically increase in comparison with the other PASs.

Polymerization Behavior. Polymerization curves of each monomer are shown in Figure 3 in order to compare the reactivity of the monomers. Bis(3,5-dimethylphenyl) disulfide and bis(2,5-dimethylphenyl) disulfide are more rapidly polymerized than the other diaryl disulfides to yield the corresponding polymers.

In a previous paper we reported[13,14] that the polymerization proceeded via a cationic mechanism with electron transfer through the formation of a charge-transfer complex with DDQ and disulfide. Diphenyl disulfide is oxidized with a one-electron transfer[24] to yield the cation radical. The cation radical reacts with a neutral disulfide to yield phenylbis(phenylthio)sulfonium cation[25] accompanied with a thiophenoxy radical. The radical is coupled to the disulfide. The sulfonium cation is an active species and electrophilically reacts with the para position of the

Scheme III



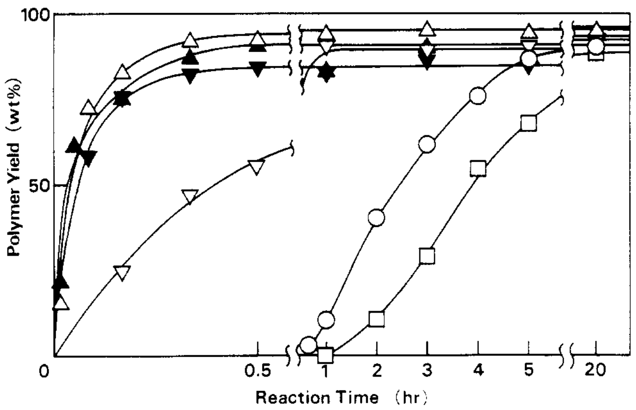


Figure 3. Cationic oxidative polymerization of diphenyl disulfides. Diphenyl disulfide (○), bis(2-methylphenyl) disulfide (▽), bis(3-methylphenyl) disulfide (▼), bis(2,5-dimethylphenyl) disulfide (△), bis(3,5-dimethylphenyl) disulfide (▲), and bis(2,6-dimethylphenyl) disulfide (□).

benzene ring of the monomer or the oligomer.[25] The same oxidation and the electrophilic reaction process are continuously repeated to yield PPS.

It is reasonable to consider that the polymerization process consists of four elementary reactions as follows (Scheme III): (1) formation of a charge transfer (CT) complex between diaryl disulfide and DDQ (eq 1), (2) oxidation of diaryl disulfide (eq 2), (3) formation of the sulfonium cation from the cation radical (eq 3), and (4) the electrophilic reaction (eq 4). The substituents effects of each elementary reaction are discussed in the following section.

Diaryl disulfides form charge-transfer complexes with DDQ. Formation constants of the CT complexes (K) were calculated using the Benesi–Hildebrand procedure[26] (Table II). One notices that each CT formation constant of bis(2,5-dimethylphenyl) disulfide is larger but not enough to result in the drastic increase in the polymerization rate (Table II). Substituents of the diaryl disulfides do not significantly influence the CT complex formation.

Table II
CT Complex Formation Constant of Diaryl Disulfides with DDQ

disulfide	CT formn const k, 10 × mol/L	oxidn rate, 10^4 × mol/s	oxidn potl, V vs Ag/AgCl	collect eff A,[a] %	collect eff B,[b] %
diphenyl	4.5	1	1.70	1	28
2-methylphenyl	8.9	4	1.65	27	33
3-methylphenyl	2.4	23	1.65	1	18
3,5-dimethylphenyl		50	1.55	1	10
2,6-dimethylphenyl	6.9	0.5	1.70	33	33
2,5-dimethylphenyl	2.4	35	1.60	7	20

[a] Collection efficiency of cation radical. Ring electrode potential: 1.3 V. [b] Collection efficiency of cation radical and sulfonium cation. Ring electrode potential: 0.5 V.

Table III
Polymerization of Bis(3,5-dimethylphenyl) Disulfide

[monomer], mol/L	reacn time, h	polymer yield, wt %	M_w	M_n
0.1	40	93	9600	3200
2.0	20	91	17000	5400
2.0	40	97	18000	7500
2.0	120	97	28000	10000
3.0	40	93	20000	8200
4.0	40	99	21000	6100

The oxidation process, an electron transfer to DDQ from diphenyl disulfide, was examined from the formation reaction of 2,3-dichloro-5,6-dicyano-*p*-hydroquinone (DDH).

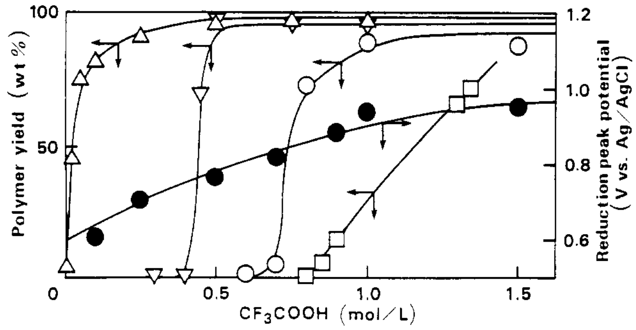


Figure 4. Effect of the concentration of CF$_3$COOH on the oxidative polymerization of diaryl disulfide. Diphenyl disulfide (○), bis(2-methylphenyl) disulfide (▽), bis(2,5-dimethylphenyl) disulfide (△), bis(2,6-dimethylphenyl) disulfide (□), and reduction peak potential of DDQ (●).

The order of the oxidation rate of the disulfides is as follows: bis(3,5-dimethylphenyl) disulfide > bis(2,5-dimethylphenyl) disulfide > bis(3-methylphenyl) disulfide > bis(2-methylphenyl disulfide) > diphenyl disulfide > bis(2,6-dimethylphenyl) disulfide.

We have reported[27] that the oxidation process is promoted by the acidity of the reaction mixture due to an increase in the oxidation ability of DDQ. The requisite concentrations of trifluoroacetic acid for efficient PAS formation depend on the monomer (Figure 4). Bis(3,5-dimethylphenyl) disulfide reacts with DDQ even in the presence of 0.05 mol of trifluoroacetic acid for 20 h, giving the polymer with 80 wt % yield. Bis(3,5-dimethylphenyl) disulfide and bis(2,5-dimethylphenyl) disulfide are efficiently polymerized in the presence of smaller amounts of trifluoroacetic acid (Figure 4). The result suggests that these diaryl disulfides are easily oxidized with quinone because of the lower oxidation potential. Since the polymerization of diaryl disulfides is carried out at the same acid concentration, the polymerizations of bis(3,5-dimethylphenyl) disulfide and bis(2,5-dimethylphenyl) disulfide proceed rapidly in comparison with diphenyl disulfide.

We studied the formation reaction of the sulfonium cation (eq 3) and the electrophilic reaction (eq 4) by rotating ring disk voltammetry since diphenyl disulfide could yield PPS by electrooxidation[10] instead of the chemical oxidation with DDQ in the same manner. Diphenyl disulfide is oxidized with one electron transfer at 1.7 V to yield the cation radical. A cyclic voltammogram of the disulfide shows two reduction peaks at 1.5 and 0.5 V, which are ascribed to the reduction of the cation radical and the sulfonium cation, respectively.

The collection efficiencies (N_k) of the radical cation and the sulfonium cation are estimated as the rate of the eq 3 and eq 4 reactions, respectively (Table II).[27] 2,6-Disubstituted diaryl disulfides show higher collection efficiencies of the radical cation in comparison with diphenyl disulfide. This means that the formation reaction of the sulfonium cation (eq 3) was retarded by the 2,6-disubstituents due to its steric hindrance.

The electrophilic reaction of the sulfonium cation with a benzene ring is also influenced by the substituents. Taking into account the collection efficiencies of the sulfonium cation, the order of the electrophilic reaction rate of the diaryl disulfides is estimated as follows (see Experimental Section): bis(3,5-dimethylphenyl) disulfide > bis(3-methylphenyl) disulfide > diphenyl disulfide.[28] The substituents effects on the electrophilic reaction are also supported by the model reaction of the methylbis(methylthio)sulfonium cation with substituted diphenyl sulfides. The rate constants of bis(3,5-dimethylphenyl) sulfide, bis(2,5-dimethylphenyl) sulfide, and diphenyl sulfide are 2.1×10^5, 3.8×10^3, and 6.7 L mol^{-1} h^{-1}, respectively. These results support the idea that the alkyl substituents on the diphenyl disulfide promote the electrophilic substitution of the cation.

A methyl group substituted at the meta position of the monomer is most effective in the polymerization and results in a high yield and high polymerization rate. Poly(2,6-dimethylphenylene sulfide) is isolated with a molecular weight of 2.8×10^4 by polymerization in 2 mol/L of monomer concentration for 120 h. It is suggested that the electrophilic reaction of the cation is accelerated in such high concentration. The formed polymer is completely soluble in common solvents such as chloroform, *N*-methylpyrrolidone, and α-chloronaphthalene even with a 3×10^4 molecular weight. The virgin polymer is amorphous and shows a T_g at 185 °C and gives a film after casting from solution. The detailed physical and thermal properties will be reported in a following paper.

Conclusion

Substituent effects on the polymerization are as follows. (1) An electron-donating substituent, methyl, at the meta position increases the linearity of the formed polymer because of the facilitated electrophilic substitution of the cation in the para position. (2) Methyl substituents at the 2,6-position decrease the linearity of the formed polymer. The S atom is more effective in increasing the electron density at the carbon in the para position of the disulfide monomer than the methyl group, taking into account that the polymers produced from diphenyl disulfide and bis(2-methylphenyl) disulfide are linear. (3) Methyl substituents at the meta position of diphenyl sulfide promote not only the oxidation process but also the electrophilic substitution. (4) Electron-withdrawing substituents retard the polymerization because of the high oxidation potential of the disulfide such as bis(2,6-dichlorophenyl) disulfide.

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(17) Poly[bis(3,5-dimethylphenyl) disulfide] exhibits no melting point even after annealing for 2 h at 240 °C under a nitrogen atmosphere. Increase in the molecular weight by annealing

was not observed by GPC measurement. It is considered that PASs undergo less easily the curing reaction than PPS.

(18) Calculated values do not take into account that these polymers are low molecular weight and contain S–S bonds in the chain.[14]

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(20) The polymerization of diphenyl disulfide was carried out in *N*-methylpyrrolidone to improve the poor solvent solubility of PPS. However, the basic solvent retards the polymerization because of the deactivation of the cation. The polymerization was also carried out at high temperature, 100 °C, in tetrachloroethane. However, the polymer yield decreased in comparison with that at room temperature, and a cross-linking reaction and thianthrene formation occurred at high temperature.[13]

(21) The IR absorption bands are assigned using 1,4-bis(phenylthio)benzene and 1,4-bis(2,5-dimethylphenyl)-2,5-dimethylbenzene as model compounds of the polymers. The former exhibits the adjacent 2 H C–H out-of-plane deformation vibration at 825 cm^{-1}. The latter exhibits the isolated 1 H C–H out-of-plane vibration at 885 cm^{-1}.

(22) This means that the electrophilic attack of the sulfonium cation occurs completely on the phenyl ring and the methyl protons of the disulfide are not eliminated by the electrophilic reaction.

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(24) The number of electrons transferred in the oxidation of diphenyl disulfide was confirmed by cyclic voltammetry. The oxidation peak current indicates one-electron-transfer oxidation. Yamamoto, K.; Yoshida, S.; Nishide, H.; Tsuchida, E. *J. Electrochem. Soc.*, in press.

(25) The sulfonium cation contains three sulfur atoms. On the basis of the formula of the structure, the sulfur atom in the center of the cation bears the positive charge. Generally, the reactivity of a cation in an electrophilic reaction is determined by the LUMO level and the direction. LUMO levels of the sulfur atoms on the sulfonium cation have already been calculated by the molecular orbital method (PM3 method). The results indicate that the reactive center of the cation is the sulfur atoms on both sides. We will publish the results in the near future.

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(28) $N_k = A/k + B$ (k is the rate constant in a semi-first-order reaction; A and B are constants). An accurate k cannot be determined in this experiment, but the order of the rate is estimated from the N_k value. The electrophilic reactions of bis(2,6-dimethylphenyl) disulfide, bis(2-methylphenyl) disulfide, and bis(2,5-dimethylphenyl) disulfide are not examined exactly by RRDV because the N_k values of these cation radicals are not equal (the N_k of these reactions contain the N_k of these cation radicals).