The poly(ether ketone)s were white solids. The polymers **2a** and **2c** were soluble only in concentrated sulfuric acid and methanesulfonic acid. In contrast, polymers **2b** and **2d** were soluble both in strong acids and in polar aprotic solvents. In particular, polymer **2d** was soluble in haloalkane. A film, cast from the solution of polymer **2d** in dichloromethane shows a high degree of toughness.

The degree of polymerization (n) was calculated from the chlorine analyses (Table V), assuming that both polymer ends have chlorine atoms. This estimation evidently gave higher values for n since it did not consider the side reactions, such as reduction of the aryl chloride ends of the polymers during the polymer-isolation step.[8]

Therefore, the molecular weight of polymer **2d** having an inherent viscosity of 0.87 $dL \cdot g^{-1}$ was determined by means of GPC. The chromatogram indicated that the M_n and M_w values were 28 000 and 140 000, respectively, for standard polystyrene, and the ratio of M_w/M_n was 5.0. Generally, the value of M_w/M_n increases with the extents of reaction and approaches 2 in the limit of large extents of reaction. At this time we cannot explain this large value of 5.

The thermal stability of the polymer was examined by thermogravimetry (TG). A typical trace for polymer **2d** is shown in Figure 8. The polymer showed a 10% weight loss at 570 °C both in air and in nitrogen. Differential scanning calorimetry on powder showed weak but reproducible endotherms at 154 °C, which reflected the glass transition temperature. These data are presented in Table VI.

In summary, our studies indicate that poly(ether ketone)s with high molecular weights can readily be prepared by nickel-catalyzed coupling polymerization of aromatic dichlorides containing ether–ketone structures. This method is advantageous for the formation of poly(ether ketone)s because of the rapidity and simplicity of the reaction and mild conditions compared to conventional methods. The disadvantage of this method is that crystalline poly(ether ketone)s with high molecular weights cannot be prepared because of the limited solubility of the polymers.

Acknowledgment. We are indebted to Sadao Kato for the technical assistance and to Takeyoshi Takahashi for performing the elemental analyses. We also thank Idemitsu Kousan Ltd. for the chlorine analyses and the GPC analyses.

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Registry No. **1a**, 63175-37-1; **1a** (homopolymer), 124418-68-4; **1a** (SRU), 124418-76-4; **1b**, 124418-66-2; **1b** (homopolymer), 124418-69-5; **1b** (SRU), 124418-77-5; **1c**, 29924-09-2; **1c** (homopolymer), 124418-70-8; **1c** (SRU), 88099-20-9; **1d**, 124418-67-3; **1d** (homopolymer), 124418-71-9; **1d** (SRU), 124418-75-3; DMF, 68-12-2; DMAc, 127-19-5; NMP, 872-50-4; HMPA, 680-31-9; DMSO, 67-68-5; $NiCl_2$, 7718-54-9; PPh_3, 603-35-0; ZN, 7440-66-6; diphenyl ether, 101-84-8; *p*-chlorobenzoic acid, 74-11-3; *m*-chlorobenzoic acid, 535-80-8; 1,4-diphenoxybenzene, 3061-36-7; bipyridine, 37275-48-2.

Oxidative Polymerization of Diphenyl Disulfides with Quinones: Formation of Ultrapure Poly(*p*-phenylene sulfide)s

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ABSTRACT: Poly(*p*-phenylene sulfide)s are prepared through the oxidative polymerization of diphenyl disulfides or thiophenol with quinones at room temperature. The formed polymer is isolated as a white and pure powder having a 1,4-conjugated structure. The oxidative polymerization preferentially proceeds through a novel cationic mechanism. Diphenyl disulfide forms a charge-transfer complex with quinones and is oxidized to a sulfonium cation. The cation electrophilically substitutes on the phenyl ring to yield poly(*p*-phenylene sulfide). Influences of the quinones on this polymerization are discussed in connection with their redox potentials.

Introduction

Poly(*p*-phenylene sulfide) (PPS) is available as an engineering plastic having excellent performances,[1-6] such as high order of moldability, thermal stability, and good electrical characteristics. It is well-known that PPS is commercially produced by polycondensation of *p*-dichlorobenzene with sodium sulfide in *N*-methylpyrrolidone at ca. 200 °C under high pressure.[7-9] Lenz and co-workers have reported[10-16] the preparation of PPS by the poly-

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condensation of *p*-halothiophenoxy metal salts. These polycondensation reactions proceed with the formation of sodium chloride or metal halide. It is very difficult to remove the formed salts and to provide pure PPS. This PPS has been characterized by using commercial PPS contaminated with salt. For example, the salt contamination degrades the electric performance and moldability.[17]

Some papers have reported[18-22] on the preparations of PPS-like polymers. However, these polymers showed no melting point and also contained a small amount of metal catalyst.

Recently we found and preliminarily reported[23-25] that diphenyl disulfide is polymerized to yield poly(*p*-phenylene sulfide) with Lewis acids, such as antimony pentachloride at room temperature. In this paper we describe that pure PPSs are quantitatively formed by a cationic and oxidative polymerization[26] with oxidizing agents such as quinones and discuss the mechanism of this polymerization.

Experimental Section

Materials. The monomer diphenyl disulfide was purified twice by recrystallization from ethanol and dried in vacuo for 1 day at 30 °C and was obtained as a white needle, mp 59 °C. Thiophenol was distilled twice under reduced pressure and was stored under nitrogen atmosphere. Commercial guaranteed reagents of quinones were used without further purification. A guaranteed reagent of trifluoromethanesulfonic acid was used under dry nitrogen atmosphere. All solvents (dichloromethane, nitrobenzene, α-chloronaphthalene, and *N*-methylpyrrolidinone) were purified by distillation in the usual manner. 3,5-Dimethylthiophenol was synthesized by the Leuckart reaction from 3,5-dimethylaniline as a starting material.[27] Bis(3,5-dimethylphenyl) disulfide was prepared by the oxidation of 3,5-dimethylthiophenol with iodine in alkaline ethanol, whose structure was confirmed spectroscopically. Bis(3,5-dimethylphenyl) disulfide: yellow liquid; IR (KBr, cm^{-1}) 2920, 2960, 3030 (ν_{C-H}), 1460, 1580 ($\nu_{C=C}$), 680, 840 (δ_{C-H}); ^1H NMR $CDCl_3$, ppm) δ 2.2 (12 H, CH_3), 6.8, 7.1 (6 H, phenyl); ^{13}C NMR ($CDCl_3$, ppm) δ 21.2 (CH_3 C), 125.3, 129.0, 136.9, 138.6 (phenyl C); mass, *m/e* 274, 137, 105.

Polymerization Method. A typical experiment is as follows. Diphenyldisulfide (0.01 mol) was dissolved in 50 mL of dichloromethane and was poured into the 50 mL of dichloromethane solution containing 0.02 mol of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and 0.001 mol trifluoromethanesulfonic acid. The solution immediately changed from light yellow to deep black and was kept at 20 °C under a dry nitrogen atmosphere for 20 h. White powder separated out and the deep black color of solution faded with time. The precipitated powder was collected and washed with 5% hydrochloric methanol. The polymer was extracted with tetrahydrofuran to remove 2,3-dichloro-5,6-dicyano-*p*-hydroquinone (DDH) and was then dissolved in hot α-chloronaphthalene. The α-chloronaphthalene solution was poured in tetrahydrofuran. This reprecipitated purification was repeated twice to yield a white polymer powder. After filtration of the precipitate from the reaction mixture, the residue was poured into 500 mL of 5% hydrochloric methanol to precipitate a dichloromethane-soluble part of the product, which is the oligomer of PPS. The dichloromethane–methanol reprecipitation was repeated twice to yield also a white powder. Poly(*p*-phenylene sulfide) (dichloromethane-insoluble part): IR (KBr, cm^{-1}) 3025, 2960, 2925 (ν_{C-H}), 1395, 1480, 1580 ($\nu_{C=C}$), 820 (δ_{C-H}), 480, 560, 740, 1015, 1080, 1100; mass, *m/e* 756, 684, 540, 434; X-ray diffraction pattern 2Θ = 19, 21. Anal. Calcd for C_6H_4S: C, 66.67; H, 3.7; S, 29.63. Found: C, 66.52; H, 3.85; S, 29.60. Oligo(*p*-phenylene sulfide) (dichloromethane-soluble part): IR (KBr, cm^{-1}) 3025, 2960, 2925 (ν_{C-H}), 1395, 1480, 1580 ($\nu_{C=C}$), 820 (δ_{C-H}), 480, 560, 740, 1015, 1080, 1100; ^1H NMR ($CDCl_3$, ppm) δ 7.2 (phenyl, 4 H); ^{13}C NMR ($CDCl_3$, ppm) main signals δ 131.5, 129.0, 127.5 (phenyl C); mass *m/e* 540, 434, 326. Anal. Calcd for C_6H_4S: C, 66.67; H, 3.7; S, 29.63. Found: C, 66.50; H, 3.94; S, 29.54. Number-average molecular weight of the formed PPS is ca. 500 (vapor pressure osmometry, solvent benzene). Bis(3,5-dimethylphenyl) disulfide was similarly polymerized with DDQ. Poly(3,5-dimethyl-1,4-phenylene sulfide): IR (KBr, cm^{-1}) 2850, 2920, 2950, 2975, 3040 (ν_{C-H}), 1370, 1450, 1570 ($\nu_{C=C}$), 875 (δ_{C-H}), 850, 1050; ^1H NMR ($CDCl_3$, ppm) δ 2.31 (6 H, CH_3), 6.70 (2 H, phenyl); ^{13}C NMR ($CDCl_3$, ppm) δ 21.9 (CH_3 C), 125.1, 127.2, 140.1, 144.3 (phenyl C). Anal. Calcd for C_8H_8S: C, 70.54; H, 5.982; S, 23.54. Found: C, 70.02; H, 5.99; S, 23.39.

Isolation of Methyl Bis(methylthio)sulfonium Antimony Hexachloride. Dimethyl disulfide (0.1 mol) was poured into a dry dichloromethane (200 mL) solution of DDQ (0.1 mol) and trifluoromethanesulfonic acid (0.2 mol). DDH was precipitated during the time passage and was removed from the reaction mixture. By the addition of tetrabutylammonium antimony hexachloride to the solution at −20 °C, the mixture changed to a yellowish slurry. The precipitate was filtered and recrystallized in dichloromethane. A slightly yellowish microcrystalline product was obtained in 63% yield. Methyl bis(methylthio)sulfonium antimony hexachloride: yellow needlelike solid; mp 118–120 °C; IR (KBr, cm^{-1}) 3020, 2925, 2850 (ν_{C-H}), 1415, 1310, 1115, 1040, 995; ^1H NMR (CH_2Cl_2, ppm) δ 3.0, 3.6; UV (CH_2Cl_2, nm) λ_{max} = 272. Anal. Calcd for $C_3H_9S_3SbCl_6$: C, 7.57; H, 1.91; S, 20.20; Sb, 25.59; Cl, 44.71. Found: C, 7.69; H, 1.96; S, 19.79; Sb, 25.81; Cl, 44.71.

Measurement. ^1H and ^{13}C NMR spectra were measured on a 90-M Hz JEOL FX-100. The IR spectrum of the polymer was measured by using a JAS IR-810 spectrometer. Mass spectra were obtained by using an ionization energy of 20 eV on a JMS-DX 300 spectrometer. Melting points were determined on a hot stage of a microscope with a heating rate of 2 °C/min. DSC measurements were made on a SEIKO thermal analyzer SSC/580 with a heating rate of 20 °C/min. The molecular weight of the dichloromethane-soluble part of the polymer was measured by using a benzene solution with vapor pressure osmometry. Sodium, copper, chloride, and bromide in the polymer were analyzed by inductively coupled plasma emission spectroscopy. Nitrogen was analyzed by micro Kjeldahl method.

UV spectrum of the reaction solution was measured on a Shimazu UV-240 spectrometer. ^1H NMR spectroscopy on the reaction mixture was carried out in a double-compartment cell probe of which the internal sample was CD_3OD/tetramethylsilane. Oxidation and reduction potentials of diphenyl disulfide and quinones were measured by cyclic voltammetry which was carried out in a two-compartment cell kept under nitrogen atmosphere. Platinum disk (0.126 cm^2), platinum wire, and Ag/AgCl were used as a working, an auxiliarly, and a reference electrode, respectively. The potential was controlled by a Nikko Keisoku DPG-3 dual potentiogarvanostat and a Nikko Keisoku DPG-3 function generator with a scanning rate of 100 mV/s. Rotating disk voltammetry was also carried out in the same apparatus and under the same conditions. The rotating rate of the electrode and the scanning rate of the potential were 2000 rpm and 5 mV/s, respectively.

Results and Discussion

Structure of the Formed Polymer. Diphenyl disulfide is allowed to react with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in dichloromethane at room temperature. The polymerization proceeds in the presence of a small amount of trifluoromethanesulfonic acid as a catalyst for the oxidation with the quinone. The polymer is isolated with >95% total yield as a white and pure powder having an empirical formula of C_6H_4S and is soluble in hot *N*-methylpyrrolidinone and α-chloronaphthalene. The IR spectrum of the obtained polymer completely agrees with that of the commercially available PPS. The absorption at 820 cm^{-1} attributed to the C–H out-of-plane vibration of 1,4-substituted benzene and no absorption at 860 and 880 cm^{-1} ascribed to tri- and tetrasubstituted benzene indicate a linear or 1,4-conjugated phenylene sulfide structure. There is a weak absorption of the C–H out-of-plane vibration of the monosubstituted end phenyl ring of the polymer. Absorption in

Table I
Elemental Analyses of PPS Prepared through Various Methods

no.	polymerization method	monomer	exptl formula	Na,[a] ppm	Cu,[a] wt %	Cl,[b] ppm	Br,[b] wt %	N,[c] ppm
1	polycondensation	sodium sulfide–*p*-dichlorobenzene	$C_{6.0}H_{4.2}S_{1.0}$	1500	0	4700	0	2900
2	polycondensation	copper *p*-bromothiophenoxide	$C_{6.0}H_{4.3}S_{1.4}$	4700	>1	3500	1.7	3900
3	oxidative polymerization	diphenyl disulfide	$C_{6.0}H_{4.1}S_{1.0}$	7	0	125	0	<10
4	oxidative polymerization	bis(3,5-dimethylphenyl) disulfide	$C_{8.0}H_{8.2}S_{1.0}$	5	0	85	0	<10

[a] Inductively coupled plasma emission spectrometry. [b] Ion chromatography. [c] Micro Kjeldahl method.

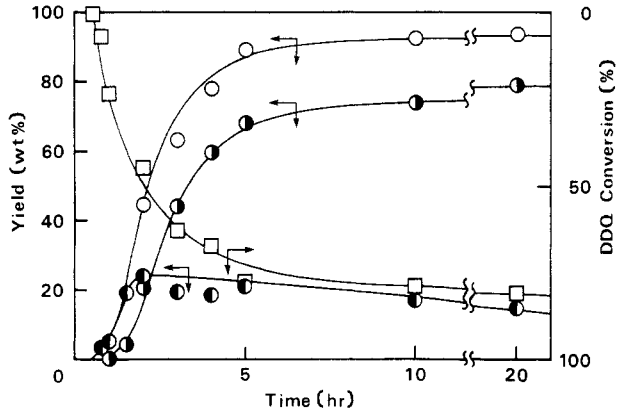


Figure 1. Polymerization of diphenyl disulfide with DDQ (0.1 mol/L) in the presence of CF_3COOH (1 mol/L): total yield of PPS (○); yield of CH_2Cl_2-soluble PPS (◐); yield of CH_2Cl_2-insoluble PPS (◑); yield of DDH (□).

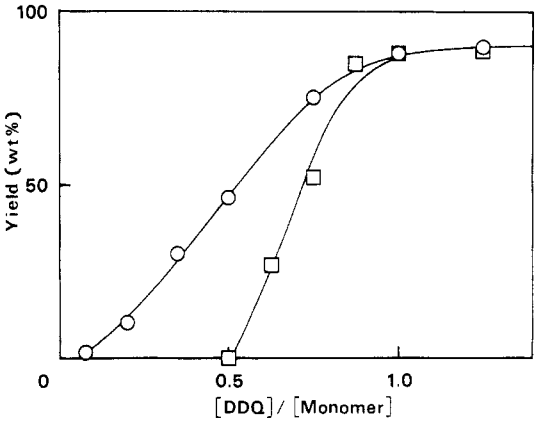


Figure 2. Oxidative polymerization of diphenyl disulfide (○) and thiophenol (□) as a starting material ([diphenyl disulfide] = 0.1 mol/L; [thiophenol] = 0.2 mol/L).

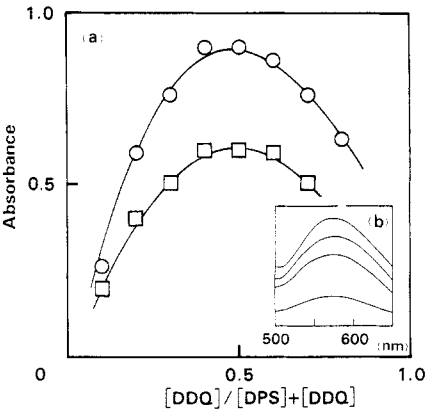
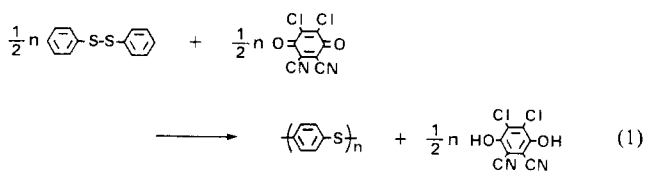


Figure 3. (a) Job plots for diphenyl disulfide–DDQ mixture in CH_2Cl_2 at 20 °C ([diphenyl disulfide] + [DDQ] = 0.05 mol/L): 575 nm (○), 650 nm (□). (b) Visible absorption spectra of diphenyl disulfide–DDQ mixture.

the region of 1050–1100 cm^{-1} also agrees with that of linear one.[28] The other spectroscopic data also indicate a poly(*p*-phenylene sulfide) structure without cross-linking, branching, and cyclic structure. The molecular weight of the dichloromethane-soluble part of this PPS (ca. 20% of the total) was ca. 500, which indicates the formation of oligo(*p*-phenylenesulfide). The molecular weight of the dichloromethane-insoluble polymer is estimated to be more than 10^3, which is based on the relationship between the molecualr weight and the melting point of PPS.[9]

The polymer prepared in this experiment is highly pure in PPS in comparison with ones prepared by the previously reported polycondensation procedure (Table I). The latter PPS are usually contaminated with metal salts, halogen, and nitrogen because metallic halide is stoichiometrically formed through the polycondensation and a nitrogen-containing compound is used as the reaction solvent at high temperature. The oxidative polymerization of diphenyl disulfide with quinones at room temperature provides a relatively pure PPS.

Polymerization Mechanism. DDQ is a strong oxidizing reagent. In this polymerization, oxidation of diphenyl disulfide with DDQ was confirmed by the stoichiometric formation of 2,3-dichloro-5,6-dicyano-*p*-hydroquinone (DDH) in the presence of an acid. DDH formation corresponds yielding PPS (Figure 1). Figure 2 shows that DDQ is required with a little more than an equimolar amount of diphenyl disulfide. Diphenyl disulfide is not polymerized in the absence of DDQ even with an acid. DDQ acts as the oxidizing agent of diphenyl disulfide as shown in eq 1.



(1)

By the addition of DDQ to the diphenyl disulfide solution, the mixture immediately turns dark brown (λ_{max} = 575 nm) from light yellow in the presence and absence of an acid. This visible absorption is enhanced with a decrease in temperature. It has been reported[29-32] that diphenyl disulfide forms a charge-transfer (CT) complex with acceptors such as tetracyanoethylene and iodine. In the accordance that DDQ is a strong electron-deficient molecule with high electron affinity,[33] it is reasonable that a charge-transfer complex is formed between DDQ and diphenyl disulfide and the absorption band is attributed to a CT complex of DDQ with diphenyl disulfide. The stoichiometry of the complex was studied by Job's method[34] of continuous variation (Figure 3). The result clearly indicates a maximum absorbance at a 1:1 DDQ to diphenyl disulfide molar ratio. Using the Benesi–Hildebrand procedure,[35] the association constant was calculated and is given in Table III (mentioned later). Rotating disk voltammograms of diphenyl disulfide and DDQ were measured in an acidic mixture. The reduction of DDQ and the oxidation of diphenyl disulfide appear

Table II
Polymerization[a] of Diphenyl Disulfide in Various Solvents

solvent	donor[39] no.	PPS yield, wt %	mp, °C
CH_2Cl_2		95	189
$(CHCl_2)_2$		90	191
CH_3NO_2	2.7	83	113
$C_6H_5NO_2$	4.4	93	172
CH_3CN	14.1	0	...
PC[b]	15.1	0	...
DMF[c]	26.6	0	...

[a] [DDQ] = 0.1 mol/L; [CF_3SO_3H] = 0.01 mol/L. [b] Propylene carbonate. [c] *N,N*-Dimethylformamide.

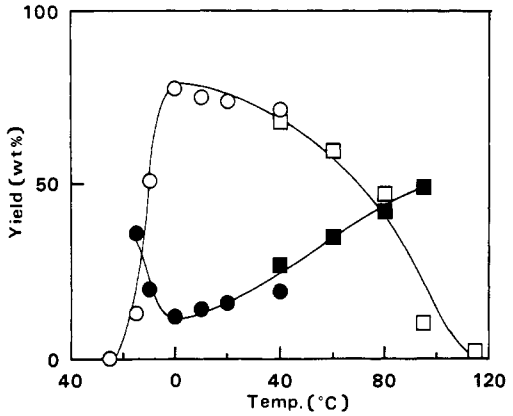
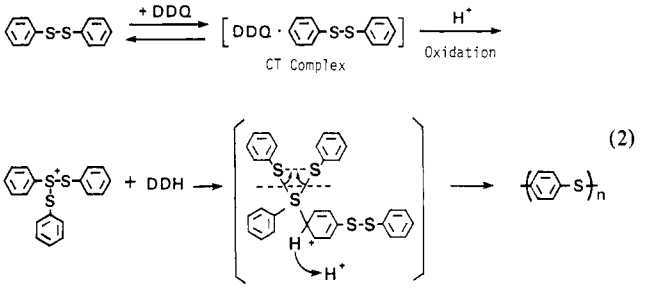


Figure 4. Temperature effect on the polymerization of diphenyl disulfide with DDQ: yield of CH_2Cl_2-soluble PPS (●); yield of CH_2Cl_2-insoluble PPS (○); yield of $(CHCl_2)_2$-soluble PPS (■); yield of $(CHCl_2)_2$-insoluble PPS (□).

at 1.3 and 1.6 V, respectively, and do not overlap each other. This denies a direct electron transfer oxidation from diphenyl disulfide to DDQ or an outer-sphere oxidation process.[36]

Diphenyl disulfide is not polymerized with DDQ below −30 °C while DDH is isolated from the medium and an oxidation reaction proceeds. The ^{13}C NMR spectrum of the reaction mixture at −30 °C shows four main signals, which are not assigned to diphenyl disulfide and the other sulfides.[37,38] In a previous paper[25] we concluded that the sulfonium cation is the active species for the polymerization of diphenyl disulfide. In this experiment, diphenyl disulfide is oxidized with DDQ to yield the phenylbis(phenylthio)sulfonium cation.

Since diphenyl disulfide is rapidly polymerized to PPS, we studied the structure of an active species by using nonpolymerizable dimethyl disulfide as a model compound. The reaction of dimethyl disulfide with DDQ was carried out under the same conditions as in the polymerization except that tetrabutylammonium antimony hexachloride was added in order to isolate the reaction intermediate as an antimony hexachloride salt. Methylbis(methylthio)sulfonium antimony hexachloride was isolated from the reaction mixture at −40 °C and was identified by ^1H NMR spectroscopy and elemental analysis (see Experimental Section). These results suggest that the phenylbis(phenylthio)sulfonium cation is produced by the oxidation of diphenyl disulfide with DDQ in the acidic reaction mixture. This cation is considered to act as the active species for the polymerization and electrophilically reacts with the benzene ring to yield PPS. The polymerization mechanism of diphenyl disulfide with DDQ is illustrated in eq 2.



(2)

The cationic mechanism in the polymerization is also supported by the reference experiments in various solvents. The polymerization is suppressed by a strong basic solvent such as acetonitrile and dimethylformamide. Hydrocarbon halide and nitrobenzene are preferable to the formation of PPS in this polymerization (Table II).

Figure 4 shows the effect of the temperature on the polymerization of diphenyl disulfide in dichloromethane and tetrachloroethane. PPS is efficiently yielded with a higher molecular weight at 0–20 °C. The reaction above 80 °C results in a low yield and side reactions of the cationic intermediate species. Below −30 °C the polymer is not given while DDH is precipitated in the reaction mixture. The oxidation of diphenyl disulfide only proceeds at low temperature although the polymerization does not. That is, the intermediate cation, phenylbis(phenylthio)-sulfonium, exists stable but does not electrophilically react with oligophenylene disulfide below −30 °C. The electrophilic reaction of the cation significantly influences the formation of PPS.

Polymerization of diphenyl disulfide was carried out with various quinones in the presence of a small amount of trifluoromethanesulfonic acid (Table III). The reduction peak potential (E_{pc}[acid]: $Q + 2H^+ + 2e^- = QH_2$) of the quinones in the presence of acids has been reported

Table III
Polymerization of Diphenyl Disulfide or Thiophenol with Quinones in CH_2Cl_2 in the Presence of CF_3SO_3H

					diphenyl disulfide[f]		thiophenol[g]	
quinone[a]	$E°$,[b] V	E_{pc}[acid],[c] V	$10K$,[d] M^{-1}	10^5V_0,[e] M s^{-1}	PPS yield, wt %	mp, °C	PPS yield, wt %	mp, °C
DDQ	0.41	0.68	4.5	3.2	95	189	91	181
o-chloranil	−0.01	0.76	1.6	3.4	88	190	60	189
p-bromanil	−0.12	0.61	4.0	0.8	96	190	44	132
p-chloranil	−0.13	0.51	*h*	0.7	93	185	89	186
p-fluoranil	−0.15	0.57	*h*		83	185	71	158
2,6-dichlorobenzoquinone	−0.33	0.67	5.6		36	180	0	...
p-benzoquinone	−0.68	0.74	0	...	0	...	0	...
2,6-di-*tert*-butylbenzoquinone	−0.72	0.74	0	...	0	...	0	...
naphthoquinone	−0.82	0.68	0	...	0	...	0	...

[a] [Quinone] = 0.2 mol/L. [b] $Q + e^- = Q^{-\bullet}$. [c] $Q + 2H^+ = 2e^- + QH_2$. [d] Formation constant of CT complex between diphenyl disulfide and quinone. [e] Polymerization initial rate calculated by the formation of hydroquinones. [f] [Diphenyl disulfide] = 0.1 mol/L. [g] [Thiophenol] = 0.2 mol/L. [h] K could not be determined with Benesi–Hildebrand plot, although strong CT absorption was observed.

to correspond to the oxidizing ability of quinones concerned with the proton elimination–addition reaction.[40-43] But *p*-benzoquinone with a higher E_{pc}[acid] in the acidic mixture does not yield PPS. One notices in Table III that the polymerization only occurs with quinones with a higher redox potential ($E°$: Q + e⁻ = Q⁻*, in the absence of acid) which forms the CT complex with disulfide. A strong electron-deficient quinone such as DDQ forms a CT complex with diphenyl disulfide and initiates the oxidation for the polymerization to give PPS. The oxidative polymerization occurs and gives PPS with quinones with a redox potential ($E°$) above −0.3 V (vs Ag/AgCl in dichloromethane).

One also notices in Table III that the E_{pc}[acid] of quinones is related to the polymerization rate. Diphenyl disulfide is more rapidly polymerized with quinones having higher E_{pc}[acid], such as DDQ and *o*-chloranil in comparison with bromanil and *p*-chloranil.

The presence of a strong acid, such as trifluoromethanesulfonic acid and trifluoroacetic acid, is a requisite of this polymerization. Acids influence the polymerization rate. The acid acts as a catalyst for the quinone reaction and retards the nucleophilic reactions of the solvent to the cationic active species.

Polymerization of Thiophenol. Polymerization with thiophenol as the starting material was carried out similarly to that of diphenyl disulfide (Table III). Molar DDQ is also necessary for the molar PPS formation (Figure 2). However, PPS is not formed with half equimolar amount of DDQ because thiophenol is first oxidized to diphenyl disulfide with DDQ. Diphenyl disulfide is quantitatively isolated from the reaction mixture in the presence of half equimolar amount of DDQ to that of thiophenol. It has been reported[44] that the formation constant of CT complexation between thiophenol and iodine was about 10 times larger than that of diphenyl disulfide. Probably the preferential formation of diphenyl disulfide with DDQ argues that thiophenol easily forms a CT complex with DDQ in comparison with the disulfide. That is, in Figure 2 half equimolar amount of DDQ oxidizes thiophenol quantitatively to diphenyl disulfide, and excess DDQ initiates the polymerization.

Polymerization of Bis(3,5-dimethylphenyl) Disulfide. Bis(3,5-dimethylphenyl) disulfide was also polymerized with DDQ. Poly(3,5-dimethyl-1,4-phenylene sulfide) formation was confirmed by elemental analysis and ^{13}C and ^{1}H NMR and IR the spectroscopic data (see Experimental Section). The polymer is highly pure in PPS in comparison with ones prepared by the polycondensation procedure (Table I). The molecular weight of the benzene-soluble part of the polymer was ca. 5×10^3. The completely polymerized polymer has its melting point at ca. 195 °C. The degree of the polymerization of the disubstituted PPS is much higher than that of poly(*p*-phenylene sulfide) prepared under the same conditions because of the disubstituents. Anyway, the oxidative polymerization of diphenyl disulfides with quinones conveniently and efficiently provides pure poly(*p*-phenylene sulfide)s.

Physical and mechanism properties of PPS will be reported in a following paper.

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References and Notes

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(26) In this polymerization of diphenyl disulfide the molecular weight of the dichloromethane-soluble part of the obtained polymer was ca. 500 and of the dichloromethane-isoluble part of the polymer was ca. 10^3. This indicates the formation of oligo(*p*-phenylene sulfide), which is caused by the insolubility of PPS in dichloromethane at room temperature. However, the molecular weights for alkyl-substituted poly(*p*-phenylenesulfide)s were $>10^4$. In this paper we describe these reactions of diphenyl disulfides as polymerizations.
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(37) ^{13}C NMR ($CDCl_3$, ppm, −30 °C): diphenyl disulfide, δ 128.4, 128.8, 130.9, 138.1; diphenyl sulfide, δ 126.9, 129.1, 131.1, 136.0; thianthren, δ 127.5, 128.6, 135.5; thiophenol: δ 125.4, 128.9, 129.3, 130.7. The reaction mixture of diphenyl disulfide with DDQ in the presence of acid: δ 127.7, 133.2, 136.0, 136.8.
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