Synthesis of Polyphenylene Thioethers Through Cationic Oxidative Polymerization

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SYNTHESIS OF POLYPHENYLENE THIOETHERS THROUGH CATIONIC OXIDATIVE POLYMERIZATION

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ABSTRACT

Polyaromatic sulfides are efficiently and conveniently prepared by cationic oxidative polymerization. Diphenyl disulfides are quantitatively polymerized to yield poly(p-phenylene sulfide)s as white powders whose structure predominately contains 1,4-phenylene sulfide bonds. The disulfides are oxidized to phenylbis(phenylthio) sulfonium cations as active species of the polymerization. Repeating the oxidation and electrophilic reaction of the cation to the p-position of disulfides yields the polymer.

INTRODUCTION

It is well-known that aromatic compounds having mobile hydrogen, such as phenols [1], anilines [2], acetylenes [3], and pyrroles [4], are easily polymerized oxidatively to the corresponding polymers (Eqs. 1–4). This polymerization proceeds under mild or atmospheric conditions, and oxygen is essential for the polymerization. Oxygen-oxidative polymerization is one of the convenient and valuable methods to prepare aromatic polymers.

$$\text{(structure)} \longrightarrow \text{(structure)} \tag{1}$$

$$H_2N-\langle\bigcirc\rangle-NH_2 \longrightarrow \cdots-\langle\bigcirc\rangle-N{=}N-\langle\bigcirc\rangle-N{=}N-\langle\bigcirc\rangle-N{=}N-\cdots \tag{2}$$

$$HC{\equiv}C-\langle\bigcirc\rangle-C{\equiv}CH \longrightarrow \cdots-\langle\bigcirc\rangle-C{\equiv}C{-}C{\equiv}C-\langle\bigcirc\rangle-C{\equiv}C{-}C{\equiv}C-\langle\bigcirc\rangle-C{\equiv}C{-}C{\equiv}C-\cdots \tag{3}$$

$$\text{(pyrrole)} \longrightarrow \text{(polypyrrole structure)} \tag{4}$$
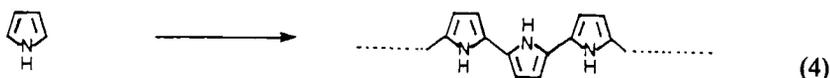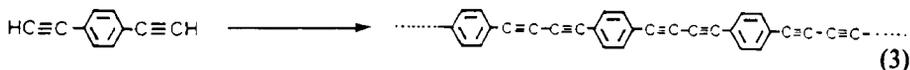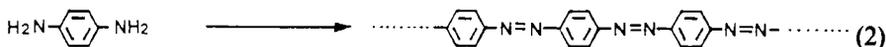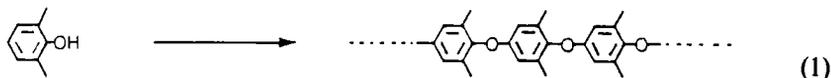
Thiophenol also has a mobile hydrogen, but is rapidly oxidized to yield thermodynamically stable diphenyl disulfide because formation of the S—S bond through the coupling of thiophenoxy radicals with each other [5] predominates over the formation of C—S—C bonds through coupling of the sulfur in the para position of the phenyl ring (Eq. 5).

$$\langle\bigcirc\rangle-SH \longrightarrow \left(\langle\bigcirc\rangle-S^*\!+{}^*S-\langle\bigcirc\rangle\right) \xrightarrow{\text{S-S Coupl.}} \langle\bigcirc\rangle-S{\cdot}S-\langle\bigcirc\rangle \tag{5}$$
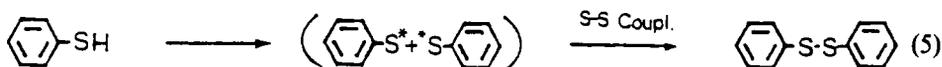
Poly(p-phenylene sulfide) (PPS) deserves much attention as an engineering plastic or as a conductive and sometimes specialty polymer with excellent performance. Lenz first reported that PPS is synthesized by the polycondensation of p-halothiophenoxy alkali-metal salts at high temperature (Eq. 6) [6]. PPS is now being commercially produced by the polycondensation of p-dichlorobenzene and sodium sulfide in N-methyl-2-pyrrolidone (Eq. 7) [7].

$$Br{-}\langle\bigcirc\rangle{-}SNa \longrightarrow {+}\!\langle\bigcirc\rangle{-}S\!\}_n \tag{6}$$

$$Cl{-}\langle\bigcirc\rangle{-}Cl + Na_2S \longrightarrow {+}\!\langle\bigcirc\rangle{-}S\!\}_n \tag{7}$$

These polymerizations proceed only under high pressure and high temperature. In addition, it is very difficult to remove the equimolar by-products, sodium chloride and metal halide, and to provide pure PPS

because salt contamination degrades, e.g., electrical performance and moldability.

Studies in our laboratory on the preparation of PPS have revealed that thiophenol and diphenyl disulfide can be oxidatively polymerized to PPS via cationic mechanisms by electrolytic, chemical, and catalytic oxidations [8-14]. This paper describes a novel and convenient synthesis route for poly(phenylene sulfide)s: diphenyl disulfides are polymerized to PPS with high purity in high yield in the presence of such equimolar oxidizing agents as quinones (Eq. 9) and Lewis acids (Eq. 10) or a catalytic amount of vanadylacetylacetonate ($VO(acac)_2$) under air atmosphere (Eq. 11) at room temperature (Table 1, Eqs. 8-11).

$$\frac{n}{2}\ \bigcirc\text{-S-S-}\bigcirc \quad \xrightarrow{\text{Electrolysis}} \quad \left(\bigcirc\text{-S}\right)_n + \frac{n}{2}\ H_2 \tag{8}$$

$$\frac{n}{2}\ \bigcirc\text{-S-S-}\bigcirc + \frac{n}{2}\ O=\bigcirc=O \quad \xrightarrow{\text{Ox. Agent}} \quad \left(\bigcirc\text{-S}\right)_n + \frac{n}{2}\ HO-\bigcirc-OH \tag{9}$$

$$\frac{n}{2}\ \bigcirc\text{-S-S-}\bigcirc + \frac{3n}{2}\ SbCl_5 \quad \xrightarrow{\text{Lewis Acid}} \quad \left(\bigcirc\text{-S}\right)_n + n\ HSbCl_6 + \frac{n}{2}\ SbCl_3 \tag{10}$$

$$\frac{n}{2}\ \bigcirc\text{-S-S-}\bigcirc + \frac{n}{4}\ O_2 \quad \xrightarrow{\text{Catalysis}} \quad \left(\bigcirc\text{-S}\right)_n + \frac{n}{2}\ H_2O \tag{11}$$
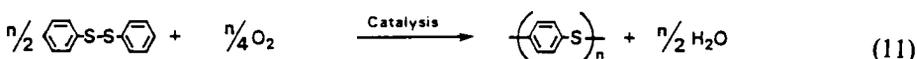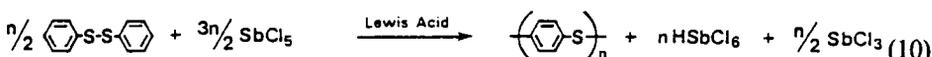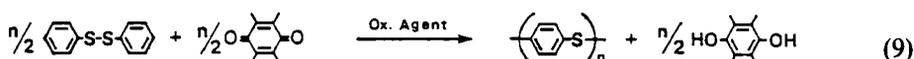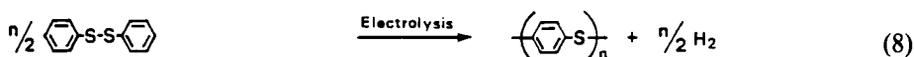
POLYMERIZATION OF DIPHENYL DISULFIDES THROUGH AN ELECTRON TRANSFER

Thiophenol is electrolytically oxidized to yield diphenyl disulfide at 1.7 V (vs Ag/AgCl) because the thiophenoxy radicals formed couple with each other. Although diphenyl disulfide is further oxidized under the given potential of 1.7 V, the cationic species formed are rapidly inactivated due to a nucleophilic reaction with the solvents and/or the supporting electrolytes, and do not yield PPS. We found that electrolytic oxidation of thiophenol and diphenyl disulfide [9] in the presence of acid effectively suppresses the nucleophilic side-reaction and yields PPS (Eq. 8).

A typical example of electro-oxidative polymerization is as follows. Thiophenol or diphenyl disulfide is dissolved in dry nitromethane containing 1.5 M trifluoroacetic acid in one compartment cell with a pair of platinum plates as a working and an auxiliary electrode. During electrol-

ysis at a controlled potential at 2.0 V (vs Ag/AgCl), the solution around the working electrode is colored brown and a white powder of PPS is precipitated. After electrolysis the polymer is isolated by filtration in 77% yield (empirical formula C_6H_4S). The polymerization is inhibited by such basic solvents as N-methylpyrrolidone and N,N-dimethyl-formamide and by water.

Chemical oxidation was applied to this polymerization instead of electrolytic oxidation [12]. Diphenyl disulfide was also allowed to react with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) in dichloromethane at room temperature (Eq. 9). The polymer was isolated as a pure white powder with nearly 100% total yield.

The IR spectrum of the PPS polymer obtained completely agreed with that of commercially available PPS. The absorption at 820 cm^{-1} was attributed to the C$-$H out-of-plane vibration of 1,4-substituted benzene, and there was no absorption at 860 and 880 cm^{-1} to be ascribed to tri- and tetra-substituted benzene. This indicates a linear or 1,4-conjugated phenylene sulfide structure. Absorption in the region of 1050 to 1100 cm^{-1} also agreed with a linear structure. Other spectroscopic

TABLE 1. Cationic Oxidative Polymerization of Diphenyl Disulfide at Room Temperature

Monomer	Oxidizing agent or catalyst	Concentration,[a] mol/L	PPS yield, wt%	mp of PPS, °C
Thiophenol	DDQ[b]	0.2	91	181
Thiophenol	Electrolysis	5.0[c]	77	162
DPS[d]	DDQ	0.1	96	192
DPS	SbCl$_5$	0.1	89	186
DPS	Electrolysis	4.0[c]	79	170
DPS	VO(acac)$_2$	0.001	93	182
2,5-Dimethyl-DPS	DDQ	0.1	98	338
3,5-Dimethyl-DPS	VO(acac)$_2$	0.001	72	198[e]

[a]Concentration of oxidizing agent or catalyst.
[b]2,3-Dichloro-5,6-dicyano-p-benzoquinone.
[c]Electricity.
[d]Diphenyl disulfide.
[e]T_g.

data indicated a poly(p-phenylene sulfide) structure without a cross-linking or a branching structure and excluded the oxidative side reactions that form sulfoxide groups.

The polymers prepared in this experiment were very pure PPSs compared with the ones prepared by the previously reported polycondensation procedure (Table 2). The molecular weight of the N-methylpyrrolidone-soluble part of the prepared PPS was about 10^3 as estimated by GPC measurement and the relationship between the molecular weight and the melting point of PPS [15].

Polymerization of diphenyl disulfide was carried out with various quinones in the presence of a small amount of trifluoromethane sulfonic acid (Table 3). The reduction peak potential (E_{pc}[acid]: Q + 2H$^+$ + 2e = QH$_2$) of quinones in the presence of acid corresponds to the driving force of the oxidation reaction with quinones that accompanies the proton elimination-addition reaction. 1,4-Benzoquinone with a higher E_{pc}[acid] in acidic solution did not promote polymerization even in the presence of a larger amount of acid. Polymerization is only promoted by quinones with a higher redox potential (E^0: Q + e = Q^{-*}, in the absence of acid). Strong electron-deficient quinones with a redox potential (E^0) above -0.3 V (vs Ag/AgCl) form a charge transfer complex with diphenyl disulfide and give PPS. That is, the E^0 of oxidant is a reliable parameter to estimate polymerizability.

TABLE 2. Elementary Analysis of PPSs

Monomer	Polymerization	Formula	Na, ppm	Cl, ppm	Cu, wt%	Br, wt%	N, ppm
DPS[a]	Oxidative polymerization	$C_{6.0}H_{4.1}S_{1.0}$	7	<10	0	0	<10
2,5-DMeDPS[b]	Oxidative polymerization	$C_{8.0}H_{8.1}S_{1.0}$	6	<10	0	0	<10
Na$_2$S + DCB[c]	Polycondensation	$C_{6.0}H_{4.2}S_{1.0}$	1500	4100	0	0	2900
4-BTC[d]	Polycondensation	$C_{6.0}H_{4.3}S_{1.4}$	4700	3500	>1	1.7	3200

[a]Diphenyl disulfide.
[b]Bis(2,5-dimethylphenyl) disulfide.
[c]p-Dichlorobenzene.
[d]Copper-4-bromothiophenoxide.

TABLE 3. Polymerization of Diphenyl Disulfide with Quinones in CH$_2$Cl$_2$ in the Presence of CF$_3$SO$_3$H

Quinone[a]	E^0,[b] V	E_{pc}[acid],[c] V	Diphenyl disulfide[d]	
			PPS yield, wt%	mp, °C
DDQ	0.41	0.68	92	189
p-Bromanil	−0.12	0.61	93	190
p-Chloranil	−0.13	0.51	90	185
p-Fluoranil	−0.15	0.57	80	185
2,6-Dichlorobenzoquinone	−0.33	0.67	36	180
p-Benzoquinone	−0.68	0.74	0	—
2,6-Ditertbutylbenzoquinone	−0.72	0.74	0	—
Naphthoquinone	−0.82	0.68	0	—

[a][Quinone] = 0.2 mol/L.
[b]Q + e = Q⁻*.
[c]Q + 2H$^+$ + 2e = QH$_2$.
[d][DPS] = 0.1 mol/L.

VO-CATALYZED POLYMERIZATION OF DIPHENYLDISULFIDES

The redox reaction of the oxygen-oxidative polymerization of phenol as catalyzed by a copper complex is schematically shown in Fig. 1. The redox potentials of oxygen and the copper complex are estimated at ca. −0.1 and 0.15 V, respectively, in the reaction atmosphere. The oxidation
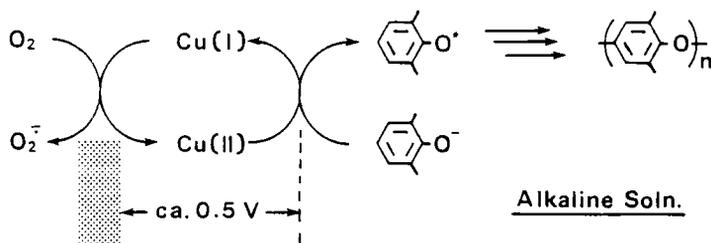
FIG. 1. Schematic redox reaction on O$_2$-oxidative polymerization of phenols catalyzed by copper complex.

potential of phenol is 0.4 V. The copper catalyst bridges the potential gap of 0.5 V between the potentials of oxygen and phenol. However, in the case of this polymerization of diphenyl disulfide, a similar redox reaction is not established. The redox potential of oxygen in the acidic atmosphere is ca. 0.5 V, and diphenyl disulfide shows a much higher oxidation potential at 1.6 V in comparison with that of phenol. The potential gap of ca. 1.0 V is so large that a single redox reaction cannot bridge the large gap between oxygen and disulfide.

Redox reaction systems of two electron-transfer mediators having different redox potentials and geared to each other can bridge the large gap. A strong oxidizer is effective for diphenyl disulfide oxidation because of the high oxidative potential of disulfide, but the reductant formed after oxidation is not easily reoxidized with oxygen. The catalyst should have more than two useful redox couple reactions in the redox potential gap between the oxidation of diphenyl disulfide and the reduction of oxygen.

Vanadyl compounds were selected as such catalysts. The redox potentials are placed in the potential gap region between 0.5 and 1.6 V [16]. Similar systems, such as oxyuranium or oxymanganese compounds, are out of the potential gap range (Table 4).

The oxidative polymerization of diphenyl disulfide was carried out with a catalytic amount of vanadyl compounds [11]. Diphenyl disulfide (0.1 M) was allowed to react with a catalytic amount of VO(acac)$_2$ (1 mM) in the presence of a strong acid such as trifluoromethane sulfonic acid (0.01 M), and trifluoroacetic anhydride (0.2 M) was added under air atmosphere and at room temperature (Eq. 11). The polymer was isolated in 93% yield after polymerization for 40 h. When thiophenol was used as a starting material, the polymerization also gave PPS. Thio-

TABLE 4. Electrode Potential of Metal Ions [16]

Redox reaction	Potential, V
$V^{3+} + e = V^{2+}$	-0.255
$VO^{2+} + 2H^+ + 2e = V^{3+} + H_2O$	0.337
$VO_2^+ + 2H^+ + 2e = VO^{2+} + H_2O$	1.00
$MO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$	1.208
$Mn^{3+} + e = Mn^{2+}$	1.51
$UO_2^{2+} + e = UO_2^+$	0.062
$UO_2^+ + 4H^+ + e = U^{4+} + H_2O$	0.62

phenol is believed to be first oxidized to diphenyl disulfide and then polymerized.

Diphenyl disulfide is not polymerized with only oxygen. In the presence of VO(acac)$_2$, polymerization is accompanied by a quantitative oxygen uptake. It does not proceed in the absence of oxygen. Vanadyltetraphenylporphyrin was also effective as a catalyst for this polymerization.

The oxidation state valences of the vanadium ion, $+5$, $+4$, and $+3$, corresponding to $(3d)^0$, $(3d)^1$, and $(3d)^2$, respectively, can be verified by spectroscopic measurements. ESR spectra of VO(acac)$_2$ in the absence and presence of acid revealed the valence state of the vanadyl ion. Signal intensity became weak after addition of the acid. Furthermore, $+5$ valence vanadium species were detected in the acidic solution by ^{51}V NMR after bubbling with oxygen. This result suggests that VO(acac)$_2$ disproportionates to the (III) and (V) species in the acidic atmosphere of this experiment. It is believed that the (V) valence species reacts with diphenyl disulfide to form an active polymerization species. This is supported by the result that equimolar VOCl$_3$ (V valence) reacts with diphenyl disulfide to yield PPS (ca. 90% yield) even under oxygen-free atmosphere. The (III) valence species was reoxidized to VO(acac)$_2$ (IV) with molecular oxygen, just as V(acac)$_3$ is promptly oxidized to VO(acac)$_2$ with oxygen. The redox potentials of VO(acac)$_2$ and V(acac)$_3$ are 1.1 and 0.7 V (vs Ag/AgCl) by cyclic voltammetry, respectively. That is, the VO catalyst acts as an excellent electron mediator to bridge a ca. 1.0 V potential gap between the oxidation potential of diphenyl disulfide (ca. 1.6 V vs Ag/AgCl) and the reduction potential of oxygen (ca. 0.5 V vs Ag/AgCl) (Figs. 2 and 3).

POLYMERIZATION MECHANISM

In this polymerization, the formation of PPS through the oxidation of diphenyl disulfide was confirmed by the following results. 1) The polymer yield corresponds to the electricity supplied. 2) In the polymerization of DDQ, 2,3-dichloro-5,6-dicyano-p-hydroquinone (DDH) was precipitated and isolated quantitatively in dichloromethane in the presence of acid, and the DDH yield corresponded to the formation of PPS. 3) In the presence of catalytic amounts of VO(acac)$_2$, PPS polymer yield was accompanied by a quantitative oxygen uptake. These mean that this polymerization is not a chain reaction initiated by an oxidative activator.
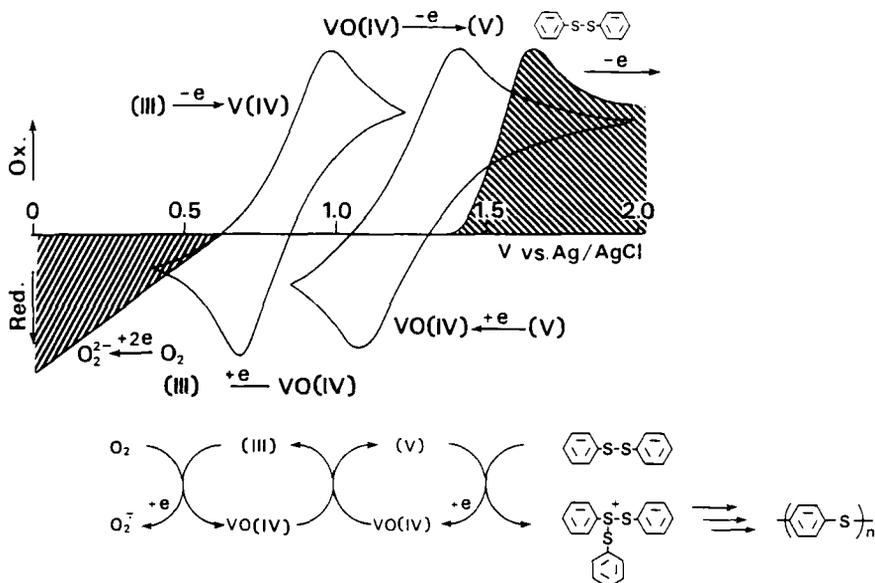
FIG. 2. Schematic redox reaction on O_2-oxidative polymerization of diphenyl disulfide catalyzed by $VO(acac)_2$ via cationic mechanism.

Since diphenyl disulfide is rapidly polymerized to PPS, we studied the active species of this polymerization by using nonpolymerizable dimethyl disulfide as a model compound. The reaction of dimethyl disulfide was carried out under the same conditions as for 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 $-40°C$. This result suggests that phenylbis-(phenylthio)sulfonium cation is produced by the oxidation of diphenyl disulfide in an acidic reaction mixture. This cation is believed to act as the active species for polymerization, and it reacts electrophilically with the p-position of the benzene ring to yield PPS [13]. The polymerization mechanism of diphenyl disulfide through an electron transfer is illustrated in Eq. (12).
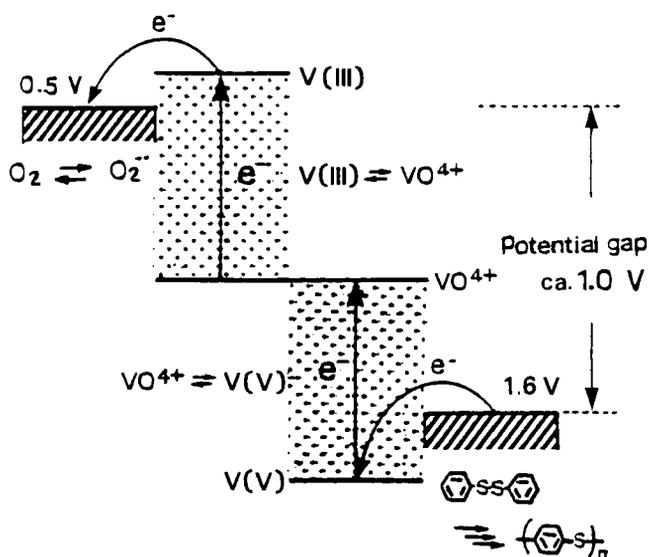
FIG. 3. Potential diagram of O_2-oxidative polymerization of diphenyl disulfide.

Oxidation
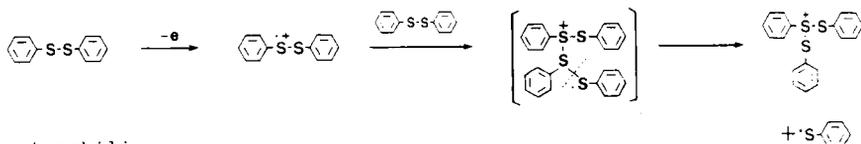
Electrophilic
Attack
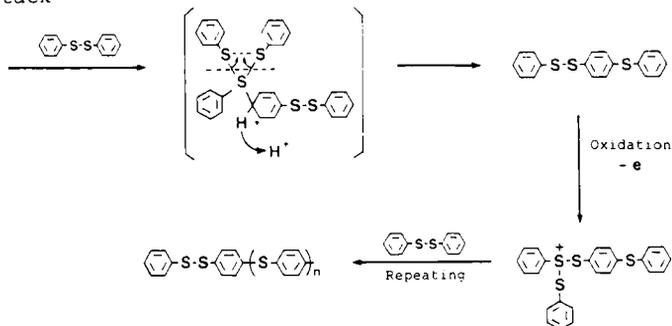
(12)

The cationic mechanism of the polymerization is supported by reference experiments in various solvents. The polymerization is suppressed by strong basic solvents such as acetonitrile and dimethylformamide. Hydrocarbon halide and nitrobenzene are preferable for the formation of PPS in this polymerization.

POLYMERIZATION OF SUBSTITUTED DIPHENYL DISULFIDES

The polymerization route can be applied for the formation of alkyl-substituted polyphenylene thioethers (Eq. 13) [10, 14].

$$
\left[\underset{R_3 \quad R_2}{\overset{R_4 \quad R_1}{}} S \right]_n
$$

R_1	R_2	R_3	R_4 =
CH_3	CH_3	H	H
CH_3	H	H	H
H	H	CH_3	H
CH_3	H	CH_3	H
H	H	CH_3	CH_3
OCH_3	H	H	H
CH_3	Cl	H	H

$$(13)$$
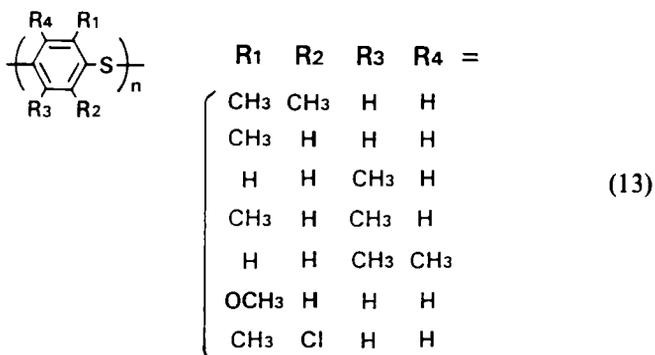
Bis(2,5-dimethylphenyl) disulfide is the most favorable monomer for this polymerization because of the higher melting point of poly(2,5-dimethyl-1,4-phenylene sulfide) and the higher polymerization yield. The structure was confirmed by CP-mass ^{13}C-NMR and IR spectra. The IR spectrum and elemental analysis agree with that of poly(2,5-dimethyl-1,4-phenylene sulfide) prepared by the polycondensation of sodium sulfide and 2,5-dichloro-*p*-xylene. The IR spectrum of the polymer showed only one absorption band at 880 cm^{-1}, and three kinds of carbon ascribed to the phenyl ring were observed in the NMR spectrum. These results indicate that the polymer has a linear structure.

The virgin poly(2,5-dimethyl-1,4-phenylene sulfide) formed has a melting point of 338°C after being annealed at 240°C. It is believed that this high melting point is caused by the higher symmetry of this polymer in comparison with the 3,5-dimethyl-substituted one. [The torsion angle of the C—S—C bond in poly(2,5-dimethyl-1,4-phenylene sulfide is estimated to be 45°, the same as that of poly(*p*-phenylene sulfide) by theo-

retical calculations, but poly(3,5- or 2,6-dimethylphenylene sulfides) show an angle of 90° due to steric hindrance of the dimethyl substituents.] On the basis of the annealing temperature, the glass transition temperature (T_g) of the polymer is estimated to be 230°C. Poly(3,5-dimethylphenylene sulfide) is completely soluble in N-methylpyrrolidone, α-chloronaphthalene, aromatic hydrocarbons, hydrocarbon halides, and polar solvents at room temperature. The solubility expands the available potential of PPSs.

COMPUTATION CALCULATION STUDY ON THE POLYMERIZATION MECHANISM

MO calculation (AM1) was used to investigate the reaction activity of the monomers. As mentioned above, the ends of a polymer chain play an important role in the growth reaction. Therefore, thioanisoles (TAs) were selected as the model compounds for this calculation.

First, the π-frontier electron density of nonsubstituted thioanisole (TA) was calculated. The electron density at the carbon atom in the para position is two or three times higher than those at the other carbons in the model compound. Calculation for anisole (AN), which is a homologous compound of sulfur, indicates that the electron is localized at the carbon atom in the para position in the compound. This is in contrast with TA where the frontier electron density is localized on the sulfur atom and the carbon atom in the para position. The ortho and para orientation in the electrophilic attack of the sulfonium cation is supported by using diphenyl ether and diphenyl sulfide. Furthermore, a much higher electron density at the carbon in the para position on S-substituted phenyl compounds causes para orientation in the electrophilic attack of the sulfonium cation to form linear PPS.

Next, the optimum conformation of the C—S—C bond of PPS was estimated because the torsion angle in the C—S—CH$_3$ plane and the phenyl ring plane affects the electronic state of the molecule.

The lowest energy of the structure was determined by means of the AM1 calculation by variation of the torsion angle. In the cases of 2,5-dimethyl-TA, 2-methyl-TA, and 3-methyl-TA, the TAs are represented as the optimum conformation for 0° or 180° torsion angles; i.e., the planes of C—S—CH$_3$ and the phenyl ring are coplanar, and the optimum conformation is caused by resonance stabilization through the overlap between the π-orbital of the sulfur and the 3pz, 2pz orbitals of the

phenyl ring. Stable 2,6-dimethyl-TA takes an angle of 60–90° because the steric hindrance of the two methyl groups in the ortho position is more predominant than resonance stabilization. The most stable structure was obtained at 60°.

Electron densities of substituted TAs in the optimum conformation are shown in Table 5. The π-frontier electron plays an important role in this reaction because the polymerization proceeds via a cation mechanism. Notice that the π-frontier electron is localized on the sulfur atom, and that the electron total is highest on the sulfur atom. This indicates that electrophilic attack of the cation also takes place on the sulfur atom [13, 17, 18]; that is, the exchange reaction of the sulfonium cation is induced during polymerization (Eq. 14).

$$\text{(14)}$$
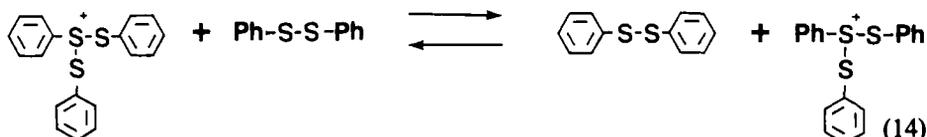
The propagation reaction of the polymer chain is the electrophilic attack of the cation on the para position of the phenyl ring. The polymerization rate is affected by the alternative electrophilic reaction. Thus, we calculated the p-C/S value, where p-C is the frontier electron density of the para carbon atom and S is the frontier electron density of the sulfur atom. The order of this ratio (p-C/S value) is as follows; 3,5-dimethyl-TA $\geq$ 2,5-dimethyl-TA > 3-methyl-TA > nonsubstituted-TA > 2-methyl-TA > 2,6-dimethyl-TA. The AM1 calculation indicates that

TABLE 5. Frontier Electron Density of the Thioanisole Model

Thioanisole derivatives	Electron density ratio		
	o-C/S	m-C/S	p-C/S
TA	0.139	0.050	0.265
2-Methyl-TA	0.102	0.083	0.260
3-Methyl-TA	0.169	0.045	0.291
2,5-Dimethyl-TA	0.079	0.000	0.316
2,6-Dimethyl-TA	–	0.034	0.153
3,5-Dimethyl-TA	0.129	–	0.313

3,5-dimethyl- and 2,5-dimethyl-substituted DPSs possess large electron densities in the para position of the phenyl ring, and this results in higher reactivity in the para position during polymerization.

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