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NEW SYNTHESIS OF POLY(PHENYLENESULFIDE)S THROUGH AN ELECTRON TRANSFER

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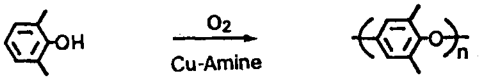
ABSTRACT

Poly(*p*-phenylenesulfide) (PPS) is efficiently and conveniently produced by a cationic and oxidative polymerization. Diphenyldisulfide is polymerized to PPS through one electron transfer at room temperature. The polymer is isolated as a white powder whose 1,4-structure is confirmed by IR. Phenylbis(phenylthio)sulfonium ion acts as an active species which is formed by oxidation of the S—S bond of diphenyldisulfide, and electrophilically substitutes on the phenyl ring. This polymerization is applicable to the polymerization of alkyl-substituted diphenyldisulfides to give PPSs, such as poly(2-methylphenylenesulfide) and poly(3,5-dimethylphenylenesulfide).

INTRODUCTION

Thiophenol has a mobile hydrogen similar to phenols, anilines, and acetylenes. The latter compounds are well-known to be oxidatively polymerized with a copper-amine catalyst under oxygen atmosphere at room temperature to yield polyphenylene oxides (Eq. 1; see Table 1 for all equations), polyanilines, and polyynes, respectively [1–3]. Oxidative polymerization is one of the most successful procedures for synthesizing aromatic polymers because of its ability to polymerize via selective oxidation by utilizing abundant and cheap oxidant molecular oxygen. It often

TABLE 1. Equations



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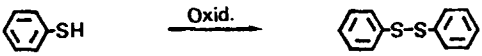

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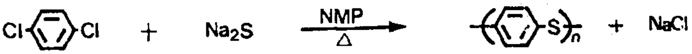

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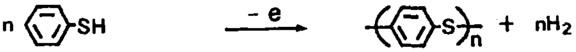

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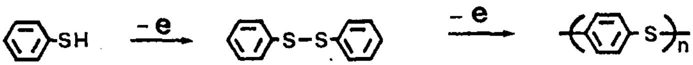

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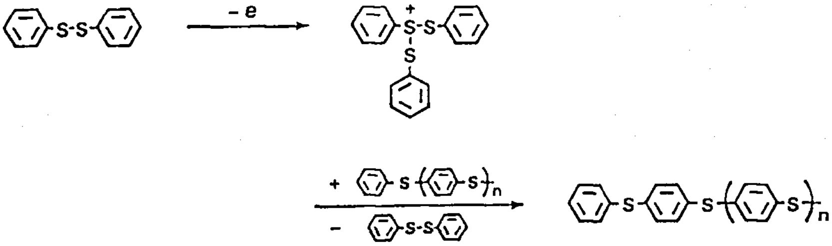

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represents a desirable low-cost method for upgrading the value of raw material. But if a similar oxidative polymerization procedure is applied to homologous thiophenol, diphenyldisulfide is formed due to the coupling of thiophenoxy radicals with each other (Eq. 2).

Poly(*p*-phenylenesulfide) (PPS) deserves attention as an engineering plastic or as a conductive polymer with excellent properties. Lenz first reported [4–7] that PPS is synthesized by the polycondensation of *p*-halothiophenoxy alkali-metal salts at high temperature (Eq. 3). PPS is now commercially produced by the polycondensation of *p*-dichlorobenzene and sodium sulfide in *N*-methyl-2-pyrrolidone (Eq. 4) [8, 9]. These polymerizations proceed only under high pressure and high temperature, with the formation of sodium chloride and metal halide. It is very difficult to remove the salts formed and to provide pure PPS; the salt contamination degrades the electrical performance and moldability. Our studies on the preparation of PPS have revealed that thiophenol and diphenyldisulfide can be oxidatively polymerized to PPS via a cationic mechanism by electrical or chemical oxidations [10–12]. This paper describes this novel and convenient synthesis route of poly(phenylene sulfide)s: Diphenyldisulfide is polymerized to PPS of high purity in high yield in the presence of an equimolar oxidizing agent such as quinones and Lewis acids or a catalytic amount of vanadylacetylacetonate ($VO(acac)_2$) under an air atmosphere at room temperature.

ELECTROPOLYMERIZATION OF DIPHENYLDISULFIDE

Thiophenol is easily electro-oxidized to yield diphenyldisulfide at 1.6 V (vs Ag/AgCl) based on the coupling of thiophenoxy radicals to each other [13]. Diphenyldisulfide is not electropolymerized to poly(phenylene sulfide) due to a nucleophilic reaction of the cationic species. The electropolymerization of thiophenol and diphenyldisulfide was carried out in the presence of acid to suppress the nucleophilic reaction (Eq. 5).

Thiophenol or diphenyldisulfide was dissolved in dry nitromethane containing 1.5 *M* trifluoroacetic acid in a one-compartment cell with a pair of platinum plates as a working electrode and an auxiliary electrode. During electrolysis with a controlled potential at 2.0 V (vs Ag/AgCl), the solution around the working electrode was colored brown and a white polymer was precipitated. The polymer was isolated by simple filtration after electrolysis in 77% yield as a white powder having the empirical formula C_6H_4S.

The polymerization also proceeded in the presence of other acids such as sulfuric acid, and stannic chloride, although the polymer yield and molecular weight were influenced by the added acid and solvent species. The polymerization was inhibited by basic solvents, such as methanol and *N,N*-dimethylformamide, and by water.

The cyclic voltammogram of thiophenol in the presence of trifluoroacetic acid is shown in Fig. 1. The first oxidation peak, which has been attributed to the oxidation of thiophenol to yield diphenyldisulfide, was observed at 1.6 V. The second peak current was measured at 1.8 V, and it has been attributed to the oxidation of diphenyldisulfide to its cation radical which reacts nucleophilically and irreversibly with the basic species. In the strongly acidic atmosphere of this experiment, this cationic species, formed by the oxidation at 1.8 V, leads to PPS formation.

See Table 2.

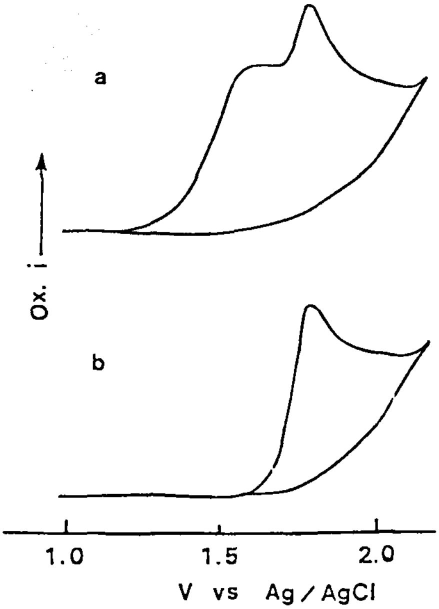


FIG. 1. Cyclic voltammograms of thiophenol (a) and diphenyldisulfide (b) in dichloromethane in the presence of CF_3COOH.

TABLE 2. Polymerization[a] of Diphenyldisulfides through Electron Transfer

Monomer	Oxidizing agent or catalyst	Concentration,[b] mol/L	PPS yield, wt%	mp of PPS, °C
Thiophenol	DDQ[c]	0.2	91	181
Thiophenol	Electrolysis	5.0[d]	77	162
DPS[e]	DDQ	0.1	96	192
DPS	$SbCl_5$	0.1	89	186
DPS	$AlCl_3$	1.0	51	213
DPS	Electrolysis	4.0[d]	79	170
DPS	$VO(acac)_2$	0.001	93	182
2-MethylDPS	$AlCl_3$	1.0	35	240
2,6-DimethylDPS	$AlCl_3$	1.0	85	245
3-MethylDPS	$VO(acac)_2$	0.001	65	173
3,5-DimethylDPS	$VO(acac)_2$	0.001	72	198

[a] At room temperature.

[b] Concentration of oxidizing agent or catalyst.

[c] 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone.

[d] Electricity.

[e] Diphenyldisulfide.

POLYMERIZATION OF DIPHENYLDISULFIDE WITH OXIDIZING AGENTS

Chemical oxidation was applied to this polymerization instead of electro-oxidation. Diphenyldisulfide was also allowed to react with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in dichloromethane at room temperature (Eq. 6). The polymerization proceeded in the presence of a small amount of trifluoromethane sulfonic acid as catalyst for the oxidation with the quinone. The polymer was isolated with >95% total yield as a pure white powder.

The polymer prepared in this experiment is very pure PPS in comparison with polymers prepared by the previously reported polycondensation procedure (N < 10 ppm, Na < 10 ppm). The latter PPS is 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 diphenyldisulfide with quinones at room temperature provides a large amount of pure PPS.

POLYMERIZATION OF DIPHENYLDISULFIDE WITH LEWIS ACIDS

Diphenyldisulfide was combined with various Lewis acids, such as aluminium trichloride and antimony pentachloride, and polymerized to PPS. The polymer was isolated in >80% yield as a white powder having the empirical formula C_6H_5S.

It has been reported [14-17] that a PPS-like polymer was prepared by the polymerization of benzene and sulfur with aluminum trichloride at the reflux temperature and that its main structure contained thianthrene units. The polymer prepared by us does not contain a thianthrene unit and has a linear structure. This is because of our PPS preparation conditions, i.e., reaction at room temperature.

VO-CATALYZED POLYMERIZATION OF DIPHENYLDISULFIDES

Diphenyldisulfide (0.1 *M*) was allowed to react with a catalytic amount of vanadylacetylacetonate (1 m*M*) in the presence of a strong acid, such as trifluoromethane sulfonic acid (0.01 *M*), and trifluoroacetic anhydride (0.2 *M*) under an air atmosphere and at room temperature (Eq. 7). The polymer was isolated in 93% yield. When thiophenol was used as the starting material, the polymerization also gave PPS (Eq. 8). Thiophenol is considered to be first oxidized to diphenyldisulfide and then polymerized.

This VO-catalyzed polymerization not only permits efficient PPS formation at room temperature but it is also applicable to the synthesis of alkyl-substituted PPSs (Eq. 9). For example, bis(3-methylphenyl)disulfide and bis(3,5-dimethylphenyl)disulfide yield poly(3-methyl-1,4-phenylene-sulfide) and poly(3,5-dimethyl-1,4-phenylenesulfide), respectively; these compounds were confirmed by IR, solid ^{13}C-NMR, and elemental analysis. They are soluble in benzene, chloroform, and dimethylformamide, and their molecular weights are 4200–5500 (vapor pressure osmometry).

Diphenyldisulfide is not polymerized with oxygen in the absence of a catalyst. In the presence of $VO(acac)_2$, polymerization is accompanied with by quantitative oxygen uptake. Additional oxygen uptake was observed whenever diphenyldisulfide was added to the reaction mixture. Vanadyltetraphenylporphyrin was also effective as a catalyst for this polymerization.

The typical blue color of $VO(acac)_2$ solution [λ_{max} = 604, 678 nm; ascribed to the d-d transition of V(IV)] immediately faded after the addition of a strong acid. These results suggest that $VO(acac)_2$ disproportionates to the (III) and (V) [18] species in the acidic atmosphere of this experiment. It is considered that the (V) valence species reacts with diphenyldisulfide to form an active species for the polymerization. This is supported by the fact that equimolar V_2O_5 (V valence) reacts with diphenyldisulfide to yield PPS ($\sim$90% yield) even under an oxygen-free atmosphere. The (III) valence species is reoxidized to $VO(acac)_2$ (IV) with molecular oxygen, just as $V(acac)_3$ is easily oxidized to $VO(acac)_2$ with oxygen. The redox potential of $VO(acac)_2$ and $V(acac)_3$ appear at 0.9 and 1.2 V (vs Ag/AgCl) respectively, with cyclic voltammetry. That is, the VO catalyst acts as an excellent electron-mediator to bridge the $\sim$1.0 V potential gap between the oxidation potential of diphenyldisulfide ($\sim$1.5 V vs Ag/AgCl) and the reduction potential of oxygen ($\sim$0.5 V vs Ag/AgCl).

STRUCTURE OF THE FORMED POLYMER

The structure that included the 1,4-phenylene unit was confirmed by IR (Fig. 2c). The absorption attributed to the C—H out-of-plane deformation vibration of 1,4-disubstituted benzene at 820 cm^{-1} indicates a

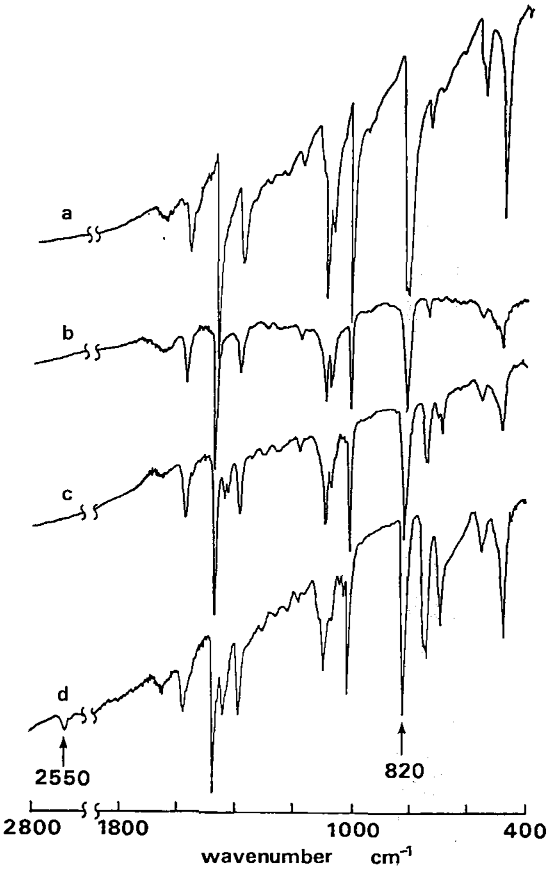


FIG. 2. IR spectra of commercially available PPS (noncuring type) (a), cyclic hexamer (b), the polymer obtained (c), and reduced product of the dichloromethane-soluble part of the polymer (d).

linear or 1,4-conjugated phenylenesulfide. This agrees with that of a reference PPS prepared by the polycondensation of *p*-halothiophenoxy alkali-metal salt. No typical absorption is observed at ∿850 cm^{-1}, which implies that no isolated ring hydrogen is present and excludes a branched or crosslinked structure. This IR spectrum is also consistent with that of a commercially available PPS (Fig. 2a). Weak absorption of the C—H out-of-plane vibration of monosubstituted phenyl rings appears at 680 cm^{-1}, which indicates a relatively small molecular weight for the PPS obtained.

For a cyclic hexamer of phenylenesulfide as reference (Fig. 2b) [19], IR absorption of the C—H out-of-plane vibration of the monosubstituted phenyl rings disappears. IR spectroscopy in the 1000–1150 cm^{-1} region reveals significant and diagnostic differences between cyclic and linear PPS [20]. This means that the polymer formed is linear. This region of the spectrum also shows that the polymer formed does not contain a sulfoxide or a sulfone structure, both of which show strong absorption in this region.

The polymer obtained also shows IR absorption at ∿480 cm^{-1}. Absorption in this region corresponds to S—S bond absorption for a *p*-substituted diphenyldisulfide such as bis(4-bromophenyl)disulfide at 478 cm^{-1} or for out-of-phase bending of the 1,4-disubstituted benzene between 446 and 552 cm^{-1} [21]. In order to prove the existence of a S—S bond in the polymer, the soluble PPS was reduced by lithium aluminum hydride in dichloromethane. The reduction product shows a new absorption at 2550 cm^{-1} (Fig. 2d), which is ascribed to the stretching vibration of the mercaptan group. This indicates that the prepared polymer contains disulfide bonds in the polymer chain. The melting point of the reaction product is lowered. The S—S bond is cleaved to SH by the reduction.

The x-ray diffraction pattern is similar to that of the commercial PPS Ryton as shown in Fig. 3. The molecular weight of the *N*-methylpyrrolidone-soluble part of the prepared PPS was about 10^3, which was estimat-

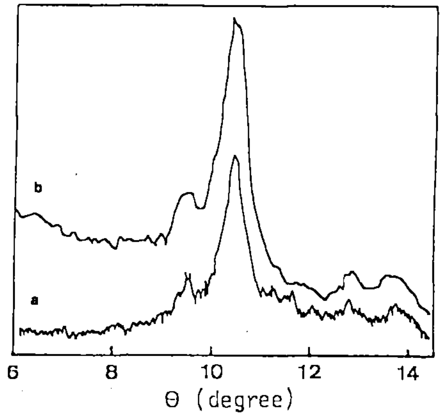


FIG. 3. X-ray diffraction patterns of the polymer formed (a) and commercially available PPS (b).

ed by the relationship between the molecular weight and the melting point of PPS [19].

POLYMERIZATION MECHANISM

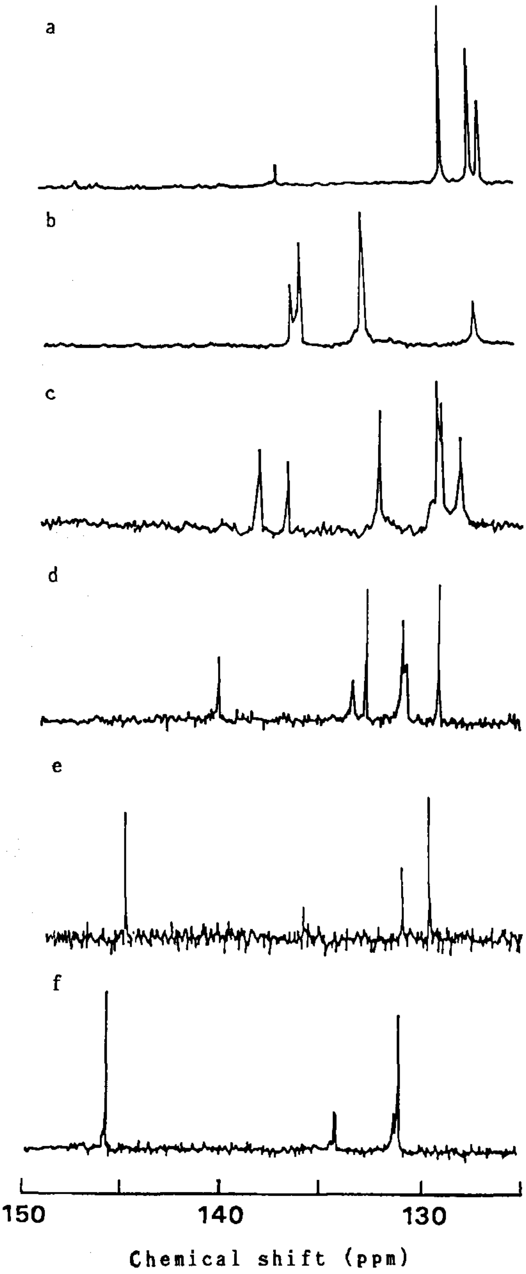
Since diphenyldisulfide is rapidly polymerized to PPS, we studied the active species of this polymerization by using nonpolymerizable dimethyldisulfide as a model compound. The reaction of dimethyldisulfide was carried out under the same conditions as was the polymerization except that tetrabutylammonium hexachloroantimonate was added in order to isolate the reaction intermediate as an hexachloroantimonate salt. Methyl(bismethylthio)sulfonium hexachloroantimonate was isolated from the reaction mixture at −40°C.

This result suggests that phenyl(bisphenylthio)sulfonium cation is produced by the oxidation of diphenyldisulfide in the acidic reaction mixture. Alkyl-substituted diphenyldisulfides also formed the corresponding sulfonium cations, as shown in Fig. 4. This cation is considered to act as the active species for the polymerization, and it electrophilically reacts with the *p*-position of the benzene ring to yield PPS. The polymerization mechanism of diphenyldisulfide through an electron transfer is illustrated in Eq. (10).

CONCLUSION

We have succeeded in synthesizing PPS and alkyl-substituted PPSs through a new and convenient route involving the oxidation of diphenyldisulfides or thiophenols. A cationic and oxidative polymerization mechanism has been discussed. This polymerization procedure expands the area of aromatic polymer syntheses through an electron-transfer process.

FIG. 4. ^{13}C-NMR spectra of diphenyldisulfide (a), the mixture of diphenyldisulfide and $SbCl_5$ (b), bis(2-methylphenyl)disulfide (c), the mixture of bis(2-methylphenyl)disulfide and $SbCl_5$ (d), bis(2,6-dimethylphenyl)disulfide (e), and the mixture of bis(2,6-dimethylphenyl)disulfide and $SbCl_5$ (f).


a
b
c
d
e
f
150
140
130
Chemical shift (ppm)

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