Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Electrophilic Reaction of Phenyl Bis(Phenylthio) Sulfonium Cation as an Active Species for the Oxidative Polymerization of Diphenyl Disulfide

Eishun Tsuchida; Kimihisa Yamamoto; Eiichi Shouji

To cite this Article Tsuchida, Eishun , Yamamoto, Kimihisa and Shouji, Eiichi(1994) 'Electrophilic Reaction of Phenyl Bis(Phenylthio) Sulfonium Cation as an Active Species for the Oxidative Polymerization of Diphenyl Disulfide', Journal of Macromolecular Science, Part A, 31: 11, 1579 — 1589

To link to this Article: DOI: 10.1080/10601329408545869

URL: http://dx.doi.org/10.1080/10601329408545869

J.M.S.—PURE APPL. CHEM., A31(11), pp. 1579-1589 (1994)

ELECTROPHILIC REACTION OF PHENYL BIS(PHENYLTHIO) SULFONIUM CATION AS AN ACTIVE SPECIES FOR THE OXIDATIVE POLYMERIZATION OF DIPHENYL DISULFIDE

EISHUN TSUCHIDA,* KIMIHISA YAMAMOTO, and EIICHI SHOUJI

Department of Polymer Chemistry
Waseda University
Tokyo 169, Japan

ABSTRACT

Computer modeling predicts that the methyl bis(methylthio) sulfonium cation can act as an efficient electrophile for sulfide bond formation in which the sulfur atoms at the side position of the cation react with the phenyl ring of an aromatic molecule. The electrophilic reaction mechanism of phenyl bis(phenylthio) sulfonium cation with anisole was examined using computer simulation. The reaction between phenyl bis(phenylthio) sulfonium cation, which is a homogeneous structure of the cation, and anisole shows the efficient formation of 4-phenylthioanisole with diphenyl disulfide as a by-product. In the oxidative polymerization of diphenyl disulfide, the formation process of poly(*p*-phenylene sulfide) includes an elementary reaction between the phenylthio group at each side position of the phenyl bis(phenylthio) sulfonium cation and the carbon at the para position of the phenyl ring.

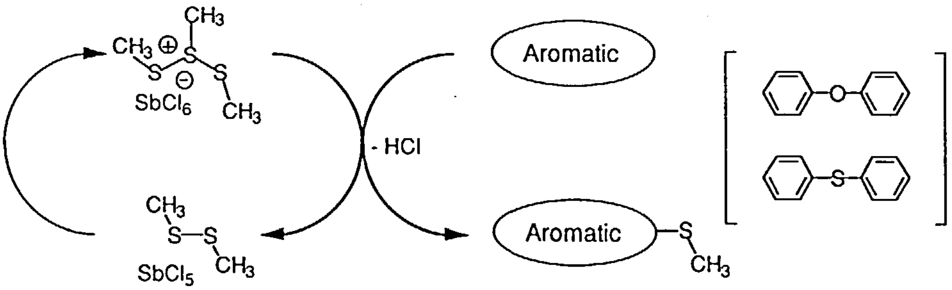
INTRODUCTION

Sulfonium cations possessing a pyramidal structure with a trivalent sulfur atom are of interest as optically active reagents in asymmetric synthesis. They are widely used as an electrophile because of their facile exchange reaction with sulfur compounds. Binding of substituent groups to the sulfur atom of the sulfonium cation can have a drastic influence on its stability and reactivity [1]. Sulfonium cations with chloro [2, 3] alkoxy [4–9], or thioalkoxy [10, 11] substituents have high reactivity; e.g., dimethyl methylthio sulfonium antimony hexachloride is added electrophilically to unsaturated hydrocarbons to form an episulfonium cation. Sulfonium cations with two methylthio and methyl substituents on the sulfur atom have been synthesized; e.g., methyl bis(methylthio) sulfonium antimony hexachloride (MMS) [12, 13]. This sulfonium cation efficiently introduces methylthio substituents in unsaturated hydrocarbons by electrophilic addition.

So far, aryl sulfide bonds have generally been constructed by nucleophilic reaction of an alkylthiolate anion with an arylhalide at high temperature accompanied by salt elimination. However, introduction of the alkylthio bond to the aromatic ring by nucleophilic substitution results in the formation of side products, such as thiophenol, by cleavage of the bond between the sulfur and the alkyl carbon atom [14]. MMS reacts electrophilically with aromatic compounds to yield the corresponding methylthio-substituted aromatics [15]. The electrophilic substitution of methylthio groups at the para position of aromatic compounds, such as diphenyl ether and diphenyl sulfide, which have an electron-donating group, has been observed experimentally. MMS acts as an efficient electrophile for the formation of the aryl sulfide bond (Scheme 1).

We have developed a new synthetic route to poly(*p*-phenylene sulfide) (PPS), which is well known as an excellent engineering plastic having good thermal and chemical resistance, by the oxidative polymerization of diphenyl disulfide derivatives under mild conditions [16]. The active cationic species in the system is believed to be the homogeneous structure of MMS. Some computational examinations of the mechanism of electrophilic substitution between MMS and aromatics leads to an understanding of the electrophilic reaction of the cation formed by the oxidation of diphenyl disulfide as the active species.

The present paper describes the electronic structure and accounts for the reac-



SCHEME 1.

tivity of sulfonium cations with two disulfide bonds in the electrophilic reaction with aromatics on the basis of molecular orbital calculations.

EXPERIMENTAL

Materials

The guaranteed reagents, dimethyl disulfide, diphenyl disulfide, antimony pentachloride, anhydrous sodium sulfate, and hexane, were purchased from Tokyo Kasei and used without further purification. Dichloromethane was purchased from Tokyo Kasei and purified twice by distillation in the usual manner.

Synthesis of MMS

A 200-mL round bottom flask with a Teflon-covered magnetic stirring bar was charged with dichloromethane (50 mL) and antimony pentachloride (7.5 g, 25 mmol). The reaction mixture was cooled to 0°C, and dimethyl disulfide (2.4 g, 25 mmol) in dichloromethane (25 mL) was added over a 20-minute period with vigorous stirring. The reaction was continued for 30 minutes at 0°C. The reaction mixture turned orange, and pale yellow crystals were observed in the reaction mixture. To the reaction mixture was added cooled ($<0°C$) hexane (100 mL). The reaction mixture was filtered and then washed with cooled ($<0°C$) hexane (100 mL). Slightly yellow needles were obtained after vacuum drying at room temperature (7.5 g, yield = 95%). IR (KBr, cm^{-1}): 3020, 2925, 1415, 1310, 1115, 1040, 995. ^1H-NMR (90 MHz, ppm, $CDCl_3$) is shown in Fig. 1(a). CP/MAS ^{13}C-NMR (400 MHz, ppm, $CDCl_3$) is shown in Fig. 1(b).

Analysis. Calculated (%) for $C_3H_9SbCl_5$: C, 7.57; H, 1.89; S, 20.22; Sb, 25.60; Cl, 44.70. Found: C, 7.66; H, 1.91; S, 19.99; Sb, 25.72; Cl, 44.71.

Synthesis of Methyl-4-phenylthiophenyl Sulfide

A 200-mL round bottom flask with a Teflon-covered magnetic stirring bar was charged with dichloromethane (50 mL) and diphenyl disulfide (6 g, 32.4 mmol). MMS (5.12 g, 10.8 mmol) was added to the reaction mixture with vigorous stirring. The reaction mixture turned brown. The reaction was continued for 20 hours at room temperature. To a 10% HCl solution (500 mL) was added the reaction mixture and dichloromethane (200 mL). The reaction mixture was washed with 10% aqueous HCl and water. The organic layer was evaporated and dried over anhydrous sodium sulfate. The product was purified by flash column chromatography on silica gel using hexane:chloroform (3:1) as the eluent (6.5 g, yield = 87%). IR (KBr, cm^{-1}): 3060, 2920, 1580, 1475, 820, 710. ^1H-NMR (90 MHz, ppm, $CDCl_3$): 2.42, 7.17, 7.23. ^{13}C-NMR (90 MHz, ppm, $CDCl_3$): 15.9, 126.7, 127.5, 129.1, 130.4, 132.2, 132.5, 136.5, 138.1. MS: *m/e* 232, 217, 184, 124, 108. Rf: 0.26 (*n*-hexane).

Synthesis of Methyl-4-phenoxyphenyl Sulfide

A 200-mL round bottom flask with a Teflon-covered magnetic stirring bar was charged with dichloromethane (50 mL) and diphenyl ether (5.5 g, 32.4 mmol). To the reaction mixture was added MMS (5.12 g, 10.8 mmol) with vigorous stirring.

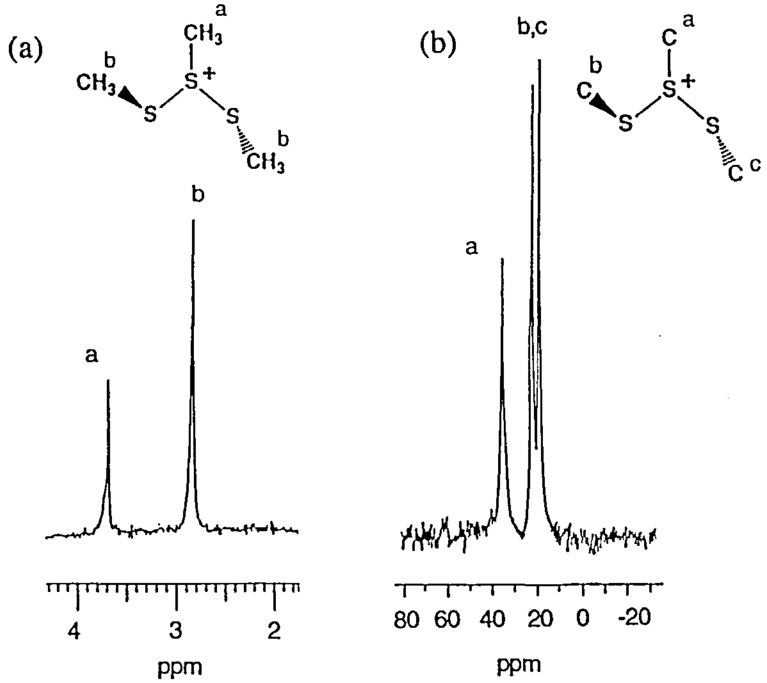


FIG. 1. ^{1}H-NMR spectrum (−20°C, in $CDCl_3$) (a) and CP-MAS ^{13}C-NMR spectrum (b) of methyl bis(methylthio) sulfonium antimony hexachloride.

The reaction mixture turned brown. The reaction was continued for 20 hours at room temperature. To a 10% HCl solution (500 mL) was added the reaction mixture and dichloromethane (200 mL). The reaction mixture was washed with 10% aqueous HCl and water. The organic layer was evaporated and dried over anhydrous sodium sulfate. The produce was purified by flash column chromatography on silica gel using hexane:chloroform (3:1) as the eluent (6.2 g, yield = 89%). IR (KBr, cm^{-1}): 3040, 2920, 1583, 1485, 1236, 1167, 833, 754; ^{1}H-NMR (90 MHz, ppm, $CDCl_3$): 2.45, 6.98, 7.20, 7.24, 7.31. ^{13}C-NMR (90 MHz, ppm, $CDCl_3$): 17.4, 118.7, 119.6, 123.2, 129.5, 129.7, 132.4, 155.5, 157.3. MS: *m/e* 216, 201, 139. Rf: 0.22 (*n*-hexane).

Computational Calculation

The structure and reactivity of sulfonium cation were examined using molecular orbital calculations (PM3, ab initio 6-31G*). For the PM3 calculation, MOPAC ver 5.0 was used [17]. The stable structure of MMS and PSC required using Keyword STEP in the PM3 calculation. The two parameters σ and ψ (degree) are defined as twist angles of the two disulfide bonds in sulfonium cations. The stable structure obtained (which was a lower heat of formation species) was re-optimized by energy minimization using PM3.

The reaction mechanism of MMS and phenyl bis(phenylthio) sulfonium cation (PSC) for aromatics was examined by electrophilical substitution simulation using anisole. The stable conformation of anisole was obtained after energy minimization, and this optimized structure was used. There are two models in the simulation between MMS and anisole. The Side S model is defined as a reaction model of the reaction between the sulfur atom of the side position of MMS and the carbon para position of anisole. The Center S model is defined as a reaction model of the reaction between the sulfur atom in the center position of MMS and the carbon para position of anisole. Heat of formation energy and bond orders [between the sulfur atom of the side position and the carbon atom of the para position (anisole), and between the sulfur atom of the center position and the side sulfur atom] were calculated. Each model was energy optimized continuously. The reaction coordinate was changed to decrease from 3.2 to 1.6 Å within steps of 0.1 Å. In the PM3 calculation, Keyword CHARGE = 1 was used for all compounds with a sulfonium cation structure.

RESULTS AND DISCUSSION

The structure of MMS with its three sulfur atoms and three methyl groups was confirmed by a combination of ^1H, ^{13}C-NMR, and IR. The ^1H-NMR spectrum at −20°C shows two peaks at 2.81 and 3.70 ppm with an intensity ratio of 2:1. The peak at 2.81 ppm is attributed to methyl protons substituted on both sides of the MMS molecules. The peak at 3.70 ppm is attributed to methyl protons binding in the center of MMS, which is moved to a lower field due to the positive charge of the sulfur atom. CPMAS ^{13}C-NMR of MMS reveals the existence of three kinds of carbon atoms (18.5, 22.0, 34.0 ppm) in the solid state. Raman reflection spectroscopy shows peaks at 680-690, 490, 440 cm^{-1}, attributed to symmetric vibrations of C—S, S—S—S, and S—S structures, respectively [18]. These results indicate that each methyl group on both sides of MMS has different chemical environments in the solid state. Semiempirical molecular orbital calculations were performed to examine the stable conformation of MMS. Heats of formation of MMS in various conformers were calculated by PM3 using the Keyword STEP. The minimum energy was estimated to be 179.2 (kcal/mol) at $\theta = 169.1°$ (38.1°) and $\psi = 38.1°$ (169.1°) (Fig. 2). The contour map indicates free rotation around the two S—S bonds in MMS because of the low potential barrier for S—S bond rotation. These results are supported by the spectroscopic observations of only two peaks attributed to methyl proton with an intensity ratio of 2:1 in the CD_2Cl_2 solution. The electron density in the LUMO on the sulfur atoms at both sides (0.572 [19]) of MMS is larger than that on the central sulfur atom (0.550 [19]). The calculated (ab initio 6-31G*) LUMO function results in an advantage for the large overlapping with the localized HOMO on the carbon atom at the para position of anisole, and the LUMO near the two off-center sulfur atoms undergoes an electrophilic reaction with anisole as a aromatic compound.

Using anisole as a model, the electrophilic substitution reaction with MMS was simulated by a semiempirical molecular orbital calculation (PM3) to examine the reactivity of MMS and to determine the relative reactivity of the three sulfur atoms. In the Center S model, the heat of formation energy of the system increases monotonically with the approach of the center sulfur atom to the carbon atom at the para position of anisole (Figs. 3 and 4a). In contrast, the reaction simulation for

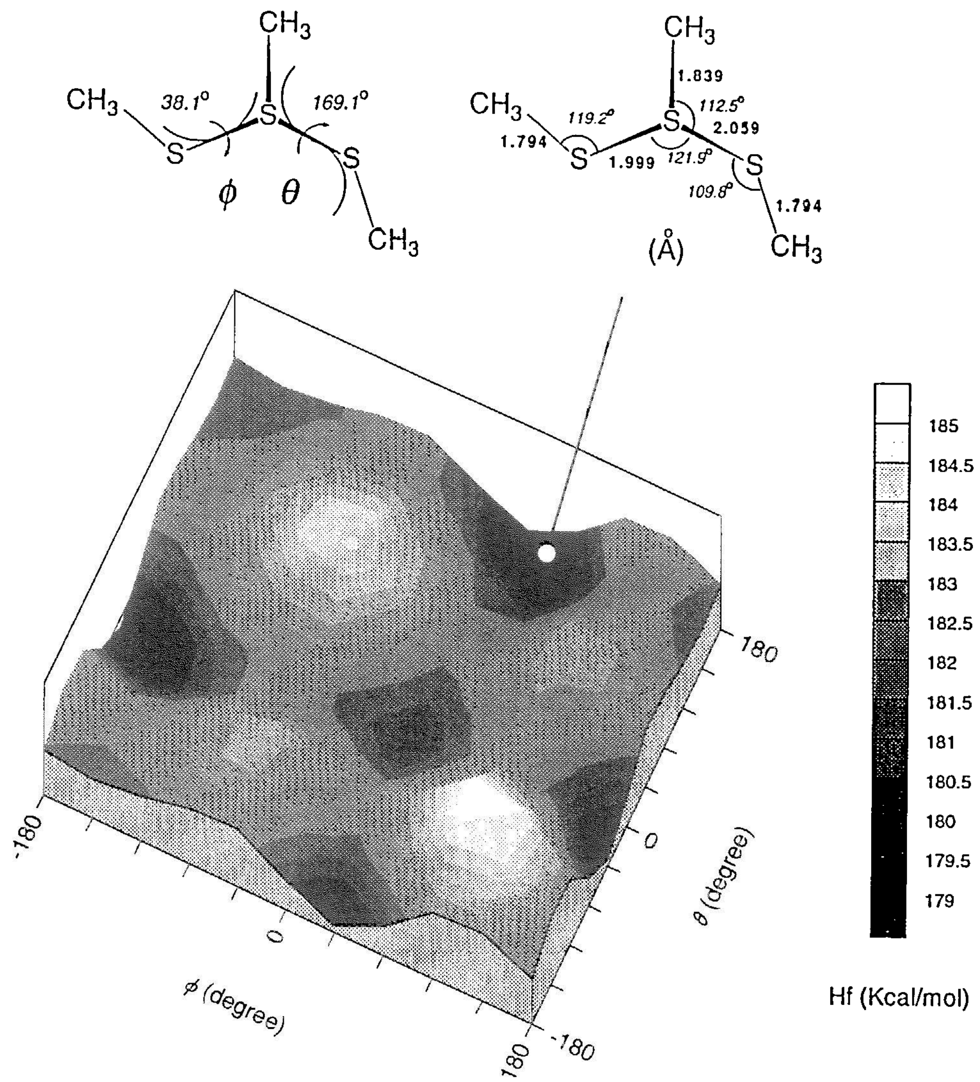
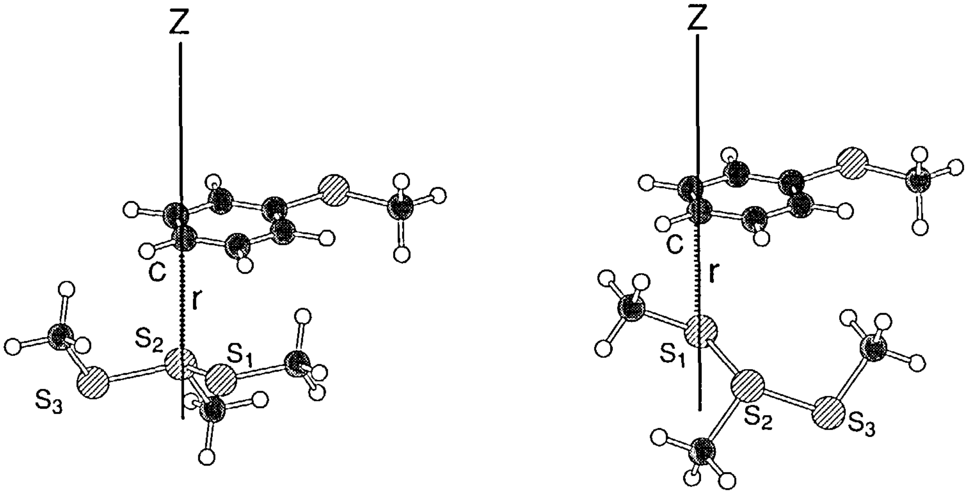


FIG. 2. PM3 calculated contour map of formation of methyl bis(methylthio) sulfonium cation.

the Side S model in which the off-center sulfur atoms approaches anisole shows a minimum energy (Fig. 4b). In the Side S model, bond formation between the sulfur atom in the side position and the carbon atom at the para position manifests itself through an increase in the bond order and a synchronized decrease in the S—S bond order in MMS. These behaviors show that 4-methylthio anisole is produced via formation of the σ-complex accompanied by elimination of dimethyl disulfide. Introduction of the methylthio group into diphenyl ether and diphenyl sulfide using MMS occur, and methyl-4-pheoxyphenyl sulfide and methyl-4-phenylthiophenyl sulfide are obtained, respectively.



(a) Central S model

(b) Side S model

r: Reaction coordinate(Å)

FIG. 3. Initial coordinate of reaction simulation for the MMS-anisole system. Center S model (a) is defined as a reaction between the sulfur atom of the center position in MMS and the carbon atom at the para position of anisole. Side S model (b) is defined as a reaction between the sulfur atom of the side position in MMS and the carbon atom at the para position of anisole.

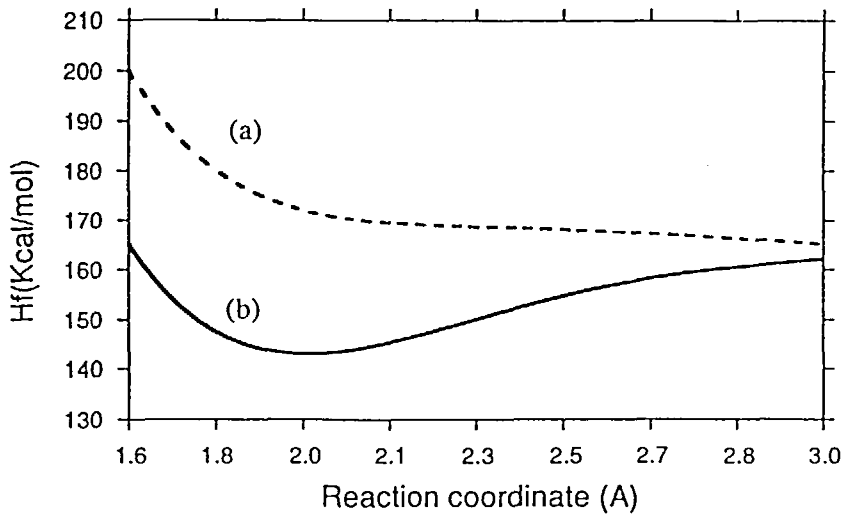
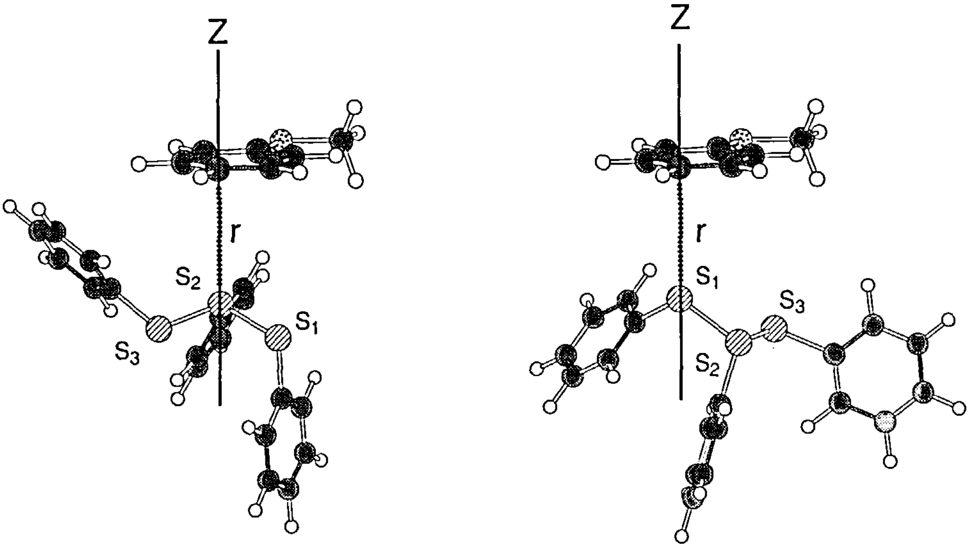


FIG. 4. PM3 calculated heat of formation energy in Center S model (a) and Side S model (b).



(a) Central S model (b) Side S model

r: Reaction coordinate(Å)

FIG. 5. Initial coordinate of reaction simulation for the PSC–anisole system. Center S model (a) is defined as a reaction between the sulfur atom of the center position in PSC and the carbon atom at the para position of anisole. Side S model (b) is defined as a reaction between the sulfur atom of the side position in PSC and the carbon atom of the para position of anisole.

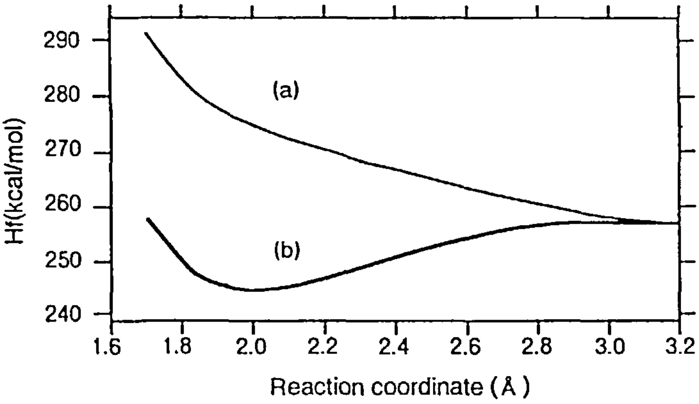
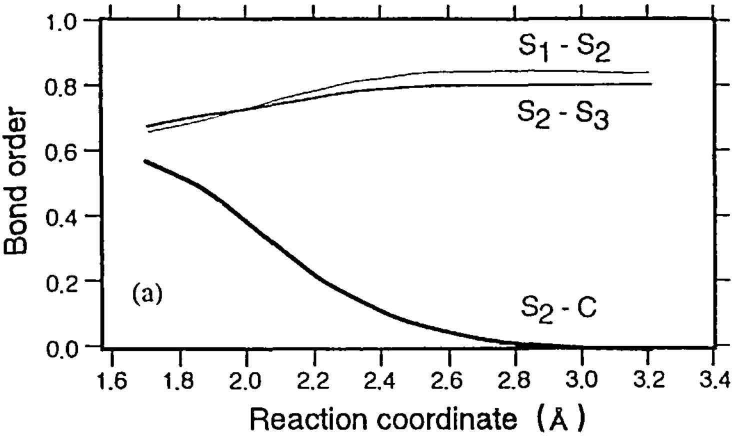


FIG. 6. PM3 calculated heat of formation energy in Center S model (a) and Side S model (b).



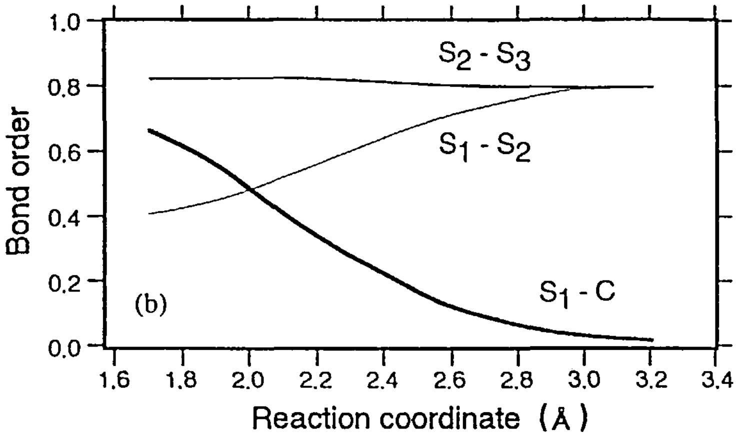
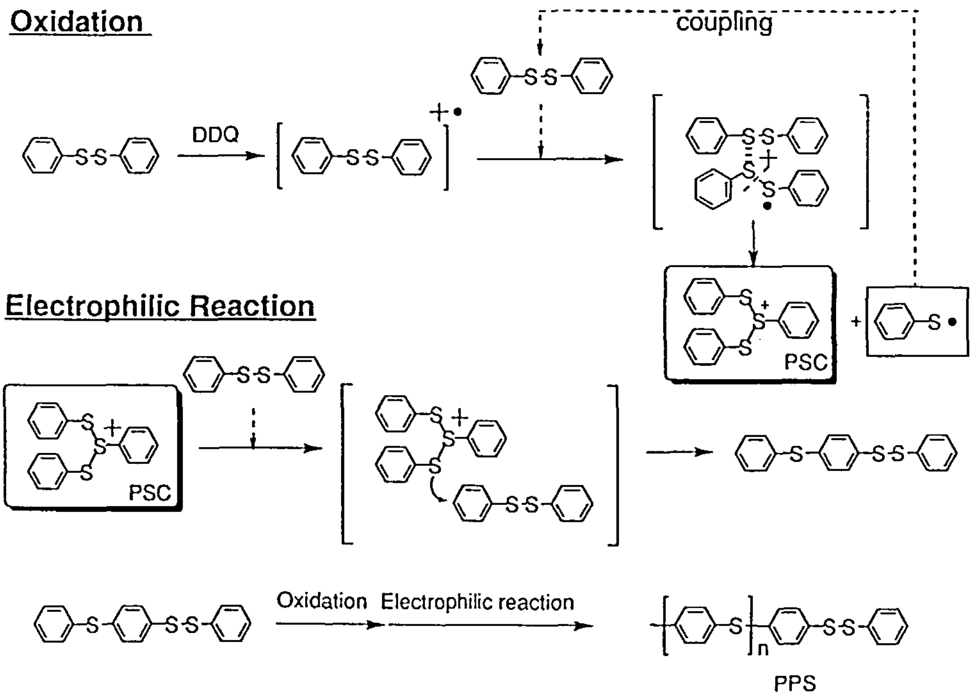


FIG. 7. PM3 calculated bond order changes in the reaction simulation in Center S model (a) and Side S model (b). Sulfur atoms as S_1, S_2, and S_3, and carbon atom as C is defined in Fig. 5.

We have reported a new synthetic route to poly(*p*-phenylene sulfide) (PPS) by the oxidative polymerization of diphenyl disulfide with 2,3-dicyano-5,6-dichloro quinone (DDQ). In this system, the phenyl bis(phenylthio) sulfonium cation (PSC) is believed to be an active cation species. The propagation reaction of the phenylene sulfide chain was examined by computational simulation using anisole and PSC. Similarly, Side S and Center S models are defined (Fig. 5). Semiempirical molecular orbital calculations were performed to obtain the more stable conformation of PSC. By using this stable conformation of PSC, simulation of the electrophilic substitution reaction with anisole was performed.

In the Center S model, the heat of formation energy of the system increases monotonically with the approach of the center sulfur atom to the carbon atom at



SCHEME 2.

the para position of anisole (Fig. 6), and this behavior is similar to the MMS-anisole system in the Center S model. The bond order of S(central)—S(side) in the Center S model slightly decreases, and that of S(central)-C(carbon para position of anisole) increases. Reaction simulation for the Side S model in which the off-center sulfur atoms approach anisole shows an energy minimum (Figs. 5b and 6b). The bond order of S(side)—S(central) effectively decreases and that of S(side)—C(carbon para position of anisole) increases (Fig. 7). Moreover, the bond order of S(opposite side against this Side S)—S(central) slightly increases in the Side S model. The Side S model shows the formation of 4-phenylthio anisole as a main product with the elimination of diphenyl disulfide as a by-product. In oxidative polymerization (Scheme 2), the diphenyl disulfide formed was oxidized with DDQ [16], and PSC was formed again. The continuous reaction results in PPS formation under mild conditions.

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Development Scientific Research 04555223 and Scientific Research 05650865 from the Ministry of Education, Science and Culture, Japan.

REFERENCES AND NOTES

[1] D. L. Butler, *J. Am. Chem. Soc.*, *74*, 1846 (1952).
[2] K. Hartke, *Arch. Pharm.* (*Weinham*), *315*, 153 (1982).
[3] K. Hartke, *Chem. Ber.*, *112*, 2436 (1979).
[4] K. Torssell, *Acta Chem. Scand.*, *21*, 1 (1967).
[5] W. Epstein and J. Ollinger, *J. Chem. Soc.*, *Chem. Commun.* p. 1338 (1970).
[6] C. R. Johnson, *Acc. Chem. Res.*, *6*, 341 (1973).
[7] R. Kuhn, *Angew. Chem.*, *69*, 570 (1957).
[8] H. Meerwein, *Org. Synth.*, *5*, 1080, 1096 (1973).
[9] S. G. Smith and S. Winstein, *Tetrahedron*, *3*, 317 (1958).
[10] G. K. Helmkamp, B. A. Olsen, and D. J. Pettit, *J. Org. Chem.*, *30*, 676 (1965).
[11] T. Mukaiyama and K. Suzuki, *Chem. Lett.*, p. 1 (1993).
[12] A. S. Gybin, W. A. Smit, V. S. Bogdanov, M. Z. Krimer, and J. B. Kalyan, *Tetrahedron Lett.*, *21*, 383 (1980).
[13] G. C. Capozzi, O. DeLucchi, V. Lucchini, and G. Modena, *Synthesis*, p. 677 (1976).
[14] L. Testaferri, M. Tingoli, and M. Tiecco, *J. Org. Chem.*, *45*, 4376 (1980).
[15] E. Tsuchida, K. Yamamoto, H. Nishide, S. Yoshida, and M. Jikei, *Macromolecules*, *23*, 2101 (1990).
[16] K. Yamamoto, M. Jikei, K. Oi, H. Nishide, and E. Tsuchida, *J. Polym. Sci.*, *Polym. Chem. Ed.*, *29*, 1359 (1991).
[17] J. J. P. Stewart, *J. Comput. Chem.*, *10*, 221 (1989).
[18] Dimethyl disulfide shows two peaks at 670 (ν_{C-S}) and 510 (ν_{S-S}) cm^{-1} in Raman spectrum.
[19] Electron density was calculated from $2(c_x^2 + c_y^2 + c_y^2)$ in which c_x, c_y, and c_z are coefficients of the atomic orbitals $3p_x$, $3p_y$, and $3p_z$ of the sulfur atom.