Polymerization of Methyl Phenyl Sulfoxide under Acidic Conditions: Synthesis and X-ray Structure Analysis of a Phenylene Sulfonium Polymer

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ABSTRACT: Methyl phenyl sulfoxide was found to undergo self-polycondensation in triflic acid in the presence of diphenylamine to produce poly(methylsulfonio-1,4-phenylene triflate). Diphenylamine formed a charge-transfer (CT) complex with the hydroxy methyl phenyl sulfonium cation produced by the protonation of the sulfoxide, facilitating the electrophilic substitution reaction of the sulfonium cation onto the carbon atom of the terminal phenyl ring. The obtained polymer is a highly crystalline material whose structure was determined by X-ray analysis using the typical geometric parameters of the sulfoniophenylene dimer and trimer model compounds. The orthorhombic unit cell of the polymer (a = 10.875 Å, b = 10.449 Å, and c = 18.629 Å) contains eight monomeric units. The space group is *Pbcn* (#60). Two molecular chains along the c axis pass through the unit cell, one through the corner and the other through the center. The crystal structure of the polymer not only revealed a structural relevance to those of oxy- and thiophenylene polymers but also provided support for CT complex formation between the polymer and diphenylamine.

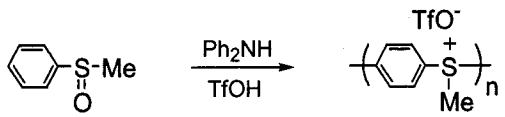
Introduction

Aromatic polymers containing heteroatoms have been developed extensively during the past half century for their industrial applications, originally as thermostable and processable engineering plastics and lately as optoelectronic materials as well. Among them are poly(phenylene oxide),[1] polyaniline,[2] polypyrrole,[2b] and their derivatives. Although they are classical polymers and have been well-studied, there are still great demands for new aromatic polymers to control both the physical and electronic properties and to tailor to a specific use. Some of the recent studies include, for example, polyphenylenes linked by boron[3] or selenium atoms.[4]

During the course of our study on oxidative polymerization of aromatic compounds, we have found and investigated sulfonium-containing aromatic polymers.[5] The polymers have good solubility, photoreactivity, and susceptibility to nucleophiles, which make them useful as a precursor for high-molecular-weight poly(arylene sulfide) and as a proton generator in photoresist technologies. Because of the strong electron-withdrawing nature of the sulfonium cation, the phenylene rings had to be linked alternatingly by sulfonio and electron-donating sulfide (or ether) bonds to build up the polymers. Our recent results show that the superacid-induced polymerization of benzene with sodium methanesulfinate[6] or the trans-methylation from methyl triflate to poly(phenylene sulfide) (PPS)[7] produces the simplest sulfonium-containing aromatic polymer **1**. This new polymer is, in addition to those above unique properties, expected to be crystalline.

We report herein that the polymerization of methyl phenyl sulfoxide can also afford the polymer by taking advantage of charge-transfer (CT) interaction (Scheme 1). The CT complex of protonated sulfoxide (hydroxy methyl phenyl sulfonium cation) and diphenylamine undergoes self-polycondensation in triflic acid. The polymerization mechanism is discussed in terms of the spectroscopic analyses of the CT complex. To ensure the CT complex formation during the chain propagation reaction, the crystal structure of the polymer **1** is analyzed and compared with its oligomer models **4** and **6**.

Scheme 1



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Experimental Section

Materials. Methyl phenyl sulfoxide was prepared by the oxidation of thioanisole as reported in the literature.[5b] Commercial reagents of diphenylamine, 3-chlorodiphenylamine, ditolylamine, phenothiazine, and *N*,*N*′-diphenylphenylenediamine were used as received. The oligomer compounds (diphenyl methyl sulfonium triflate (**3**), diphenyl methyl sulfonium hexafluoroantimonate (**4**), 1,4-bis(methyl phenyl sulfonio)-benzene bistriflate (**5**), and 1,4-bis(methyl phenyl sulfonio)-benzene bis(hexafluorophosphate) (**6**)) were prepared according to the literature.[7] Solvents were purified by distillation prior to use.

Measurement. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Lambda 500 spectrometer using D_2O or CD_2Cl_2 as a solvent. IR spectra were obtained using a KBr pellet on a Jasco FT/IR-5300 spectrometer. UV/vis spectra were measured on a Shimadzu UV-2100 spectrometer. Thermal analysis was performed by differential scanning calorimetry (DSC) using a Seiko DSC220C at a heating rate of 20 °C/min under nitrogen. Molecular weight measurement was done by gel permeation chromatography (GPC) at 210 °C using a Senshu Kagaku VHT-GPC SSC-7000 system equipped with a UV detector set at 365 nm. 1-Chloronaphthalene was used as eluent. Calibration was done with polystyrene standards.

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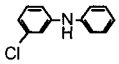
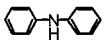
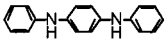
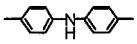
X-ray Crystallography. Colorless plate crystals of **4** were grown from 4 mL acetone solutions of the desired compound (0.10 g) after layering with diethyl ether. Colorless prismatic crystals of **6** were grown from 4 mL acetonitrile solutions of the desired compound (0.10 g) after layering with diethyl ether. Following microscopic examination in air in each case, a suitable crystal was mounted on a glass fiber at room temperature. All measurements were done on a Rigaku AFC7R diffractometer with a 7.5 kW rotating anode generator and graphite monochromated Mo Kα radiation (λ = 0.710 69 Å) for **4** and with a 12 kW rotating anode generator and filtered Cu Kα radiation (λ = 1.541 78 Å) for **6**. Unit cell parameters and an orientation matrix for data collection were determined by least-squares refinements using the setting angles of 25 carefully centered reflections in the range $23.46 < 2\theta < 24.85°$ for **4** and in $53.36 < 2\theta < 59.02°$ for **6**. The data were collected at a temperature of 25 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 55.0° for **4** and of 119.8° for **6**. Scans were done at a speed of 8.0°/min (in omega) for **4** and at speeds of 16.0, 8.0, and 4.0°/min (in omega) for each 2θ shell $4.0 < 80.0 < 100.0 < 120.0°$ for **6**. The weak reflections ($I < 3.0\sigma(I)$ for **4** and $I < 10.0\sigma(I)$ for **6**) were rescanned (up to two scans for **4** and seven scans for **6**), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflections. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm. The crystal-to-detector distance was 258 mm. The detector aperture was 9.0 × 13.0 mm for **4** and 6.0 × 6.0 mm for **6** (horizontal × vertical). The intensities of three representative reflection were measured after every 150 reflections. No decay correction was applied for **4**. Over the course of data collection for **6**, the standards decreased by 14.5%: a linear correction factor was applied to the data to account for this phenomenon. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.66 to 1.00 for **4** and 0.36 to 1.00 for **6**. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 1.4169×10^{-6}).

Structure Solution and Refinement. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement[8] was based on observed reflections ($I > 3.00\sigma(I)$) and converged with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ as listed in Table 3. Plots of $\sum w(|F_o| - |F_c|)^2$ vs $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. Data collection and structure solution parameters and conditions are listed in Table 3. Selected bond lengths and angles for **4** and **6** are listed in Table 4. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[9]

Polymerization. To a solution of diphenylamine (2.4 mmol) in 3 mL of triflic acid, methyl phenyl sulfoxide (2.4 mmol) was added. The mixture was stirred for 6 h at 25 °C. The reaction was then quenched by pouring it into 200 mL of diethyl ether. The precipitate was washed with diethyl ether and acetone to obtain a white powder of poly(methylsulfonio-1,4-phenylene triflate) **1** in 98% yield. IR (KBr): 3094, 3029, 2936 (ν_{C-H}), 1638, 1572, 1400 ($\nu_{C=C}$), 1258, 1160 ($\nu_{S=O}$), 1032, 639 (ν_{C-F}), 820, 758 (δ_{C-H}) cm^{-1}. ^1H NMR (D_2O): δ 3.85 (s, 3H), 8.30 (s, 4H). ^{13}C NMR (D_2O): δ 28.9, 133.5, 134.6. The demethylation of polymer **1** was carried out as previously reported.[5]

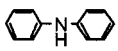
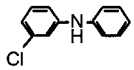
Poly(methylsulfonio-1,4-phenylene hexafluorophosphate) (7). To a solution of polymer **1** (2 mmol) in 20 mL of acetonitrile was added ammonium hexafluorophosphate (10 mmol). The mixture was stirred for 20 h in the dark at 20 °C. The mixture was evaporated to dryness to obtain a crude product, which was washed with tetrahydrofuran until no ammonium salts were detected in the filtrate. The white powder of polymer **7** was dried in a vacuum at 25 °C for 12 h.

Table 1. Polymerization of Methyl Phenyl Sulfoxide in Triflic Acid in the Presence of Aromatic Amine

amine	pK_b[a]	yield (%)[b]	T_m (°C)[c]
	31.1	22	220
	31.5	90	279
	34.2	100	278
	35.1	50	247
	35.7	0	-
	41.9	0	-

[a] Data taken from ref 13. [b] Yield of polymer **1**. [c] Melting temperature of polymer after demethylation.

Table 2. Equilibrium Constant *K* and Molar Extinction Coefficient ε of the 3/Amine CT Complex

amine	K (M^{-1})	ε (10^3 $cm^{-1}M^{-1}$)
	0.41	5.26
	0.48	3.06

Yield 89%. IR (KBr): 3098, 3029 (ν_{C-H}), 1641, 1402 ($\nu_{C=C}$), 835 (ν_{P-F}), 821 (δ_{C-H}) cm^{-1}.

X-ray Powder Diffraction. Crystallographic reflections for the polymer **7** were determined using a Cu Kα radiation. Thirty-one crystalline peaks were identified, 29 of which were considered significant enough to be included in an indexing procedure. The JADE software package of Molecular Structure Corporation was utilized to reconcile the difference between the calculated and the major observed powder diffraction *d*-spacings by unit cell parameter refinement. With the crystal class (orthorhombic) and the indices of a set of reflections assigned, the lattice parameters were successfully refined. The indexing was optimized for the significant minor (low intensity) reflections with the lattice parameters constrained.

Results and Discussion

Synthesis and Characterization of Phenylene Sulfonium Polymer 1. Methyl phenyl sulfoxide was assumed to be inactive in the acid-induced electrophilic polymerization, because the protonation of the sulfoxide lowers the electron density of the phenyl carbons significantly. The experimental behavior is supported by the PM3 semiempirical MO calculation, where the carbon net charges of the hydroxy methyl phenyl sulfonium cation (**2**) are more cationic and less susceptible to electrophilic substitution reaction than those of the parent compound (Figure 1). We hypothesized that a certain electron-donating compound should have CT

Table 3. Summary of X-ray Crystallographic Data for 4 and 6

complex	$[PhS^+(Me)Ph][SbF_6^-]$ (**4**)	$[PhS^+(Me)PhS^+(Me)Ph][PF_6^-]_2$ (**6**)
emp form	$C_{13}H_{13}SSbF_6$	$C_{20}H_{20}S_2P_2F_{12}$
fw	461.07	614.43
cryst syst	triclinic	monoclinic
space group	*P*1(#2)	*C*2/*c* (#15)
a (Å)	9.773(5)	23.433(2)
b (Å)	10.762(4)	10.113(4)
c (Å)	9.375(4)	10.651(4)
α (deg)	103.38(4)	
β (deg)	114.38(3)	91.16(1)
γ (deg)	103.36(4)	
V (Å^3)	812.2(7)	2523.5(9)
Z	2	4
density (calcd) (g/cm3)	1.885	1.617
crystal size (mm)	0.2 × 0.4 × 0.4	0.4 × 0.2 × 0.1
radiation	Mo Kα (*λ* = 0.71069 Å)	Cu Kα (*λ* = 1.54178 Å)
absn coeff *μ*	18.79 cm^{-1}	40.41 cm^{-1}
2*θ* max (deg)	55.0	119.8
no. of reflns cold	3957	2116
no. of unq reflns	3737	1993
no. of obsd reflns	2509 ($I > 3.00\sigma(I)$)	911 ($I > 3.00\sigma(I)$)
params	243	163
refln/param ratio	10.33	5.59
R	0.053	0.095
R_w	0.039	0.128
goodness-of-fit	2.73	1.84
max peak in diff map	0.83 e$^-$/Å^3	0.56 e$^-$/Å^3
min peak in diff map	−1.02 e$^-$/Å^3	−0.28 e$^-$/Å^3

Table 4. Selected Bond Lengths[a] and Angles[b] for $[PhS^+(Me)Ph][SbF_6^-]$ (4) and $[PhS^+(Me)PhS^+(Me)Ph][PF_6^-]_2$ (6) Characterized by X-ray Crystallography[c]

atoms	bond length or angle	atoms	bond length or angle
	$[PhS^+(Me)Ph][SbF_6^-]$ (**4**)		
S(1)−C(1)	1.804(8)	S(1)−C(2)	1.783(6)
S(1)−C(8)	1.782(6)	C(1)−S(1)−C(2)	103.9(4)
C(1)−S(1)−C(8)	103.9(4)	C(2)−S(1)−C(8)	103.6(3)
S(1)−C(2)−C(3)	123.8(5)	S(1)−C(2)−C(7)	115.3(5)
S(1)−C(8)−C(9)	121.3(5)	S(1)−C(8)−C(13)	116.9(5)
	$[PhS^+(Me)PhS^+(Me)Ph][PF_6^-]_2$ (**6**)		
S(1)−C(1)	1.81(1)	S(1)−C(7)	1.76(2)
S(1)−C(8)	1.77(1)	C(1)−S(1)−C(7)	101.6(7)
C(1)−S(1)−C(8)	103.8(6)	C(7)−S(1)−C(8)	104.7(7)
S(1)−C(1)−C(2)	115(1)	S(1)−C(1)−C(6)	121(1)
S(1)−C(8)−C(9)	115.5(8)	S(1)−C(8)−C(10)	124.2(9)

[a] Bond lengths are in angstroms. [b] Angles are in degrees. [c] Estimated standard deviations are given in parentheses.

2

Figure 1. Carbon net charges of methyl phenyl sulfoxide and **2** obtained by PM3 MO calculations.

interaction with the sulfonium cation. Among the various compounds bearing a lone pair of electrons such as amines and ethers, diphenylamine was chosen as a donor because it does not form a salt with triflic acid. The CT interaction could compensate the electron negativity of the sulfonium species and promote the polymerization of **2**.

The polymerization of methyl phenyl sulfoxide was carried out in triflic acid at 20 °C in the presence of an equimolar amount of diphenylamine. After 6 h, treatment of a viscous dark brown solution with diethyl ether gave a yellow powder of a crude product. Further washing of the product with acetone gave a white powder of polymer **1** in 98% yield. The chemical structure of the polymer was confirmed by ^{1}H, ^{13}C NMR, and IR spectra, which are consistent with the previously reported data[6,7] for poly(methylsulfonio-1,4-phenylene triflate) prepared by the polycondensation of sodium methanesulfinate with benzene or by the transmethylation of PPS. A single peak at 8.30 ppm assigned to phenylene protons in the ^{1}H NMR spectrum and only two aromatic peaks at 133.5 and 134.6 ppm in the ^{13}C NMR spectrum support the 1,4-disubstituted phenylene structure, indicating that the polymerization takes place predominantly at the position para to the sulfoxide group. In contrast to the results by Müllen et al.[10] in which they claim the acid-induced polymerization of an aryl sulfoxide having a diphenylamine moiety,[11] there is no evidence in the spectroscopies that polymer **1** contains diphenylamine in its structure.

Because the molecular weight of a polyelectrolyte is hard to determine by GPC or viscosity measurements, the polymer was converted to its sulfide analogue (PPS) by the precedented demethylation reaction with pyridine.[5] The molecular weight of the resulting PPS was determined by high-temperature GPC (at 210 °C in 1-chloronaphthalene relative to polystylene standards) to be M_w = 3600 and M_n = 1500. The rather low molecular weight of the polymer might be caused by the electric field effect of the polyelectrolyte and the multipositive charge on the oligomer which could prevent the sulfonium attacking on the terminal phenyl ring. Its melting temperature determined by DSC analysis is 278 °C, consistent with the reported value for PPS.[12]

Several other aromatic amines were examined for this polymerization (Table 1). It was found that the polymerization is quite sensitive to the basicity of the amine used. The reaction is quantitative with diphenylamine and with 3-chlorophenyl phenyl amine because of their appropriate basicity (pK_b 31.5−34.2)[13] to interact with the sulfonium cation. Weaker bases such as phenothiazine do not form a CT complex, and stronger bases such as *N*,*N*′-diphenyl-1,4-phenylenediamine, ditolylamine, and aniline rather form a stable triflate salt; they are not effective for the polymerization. The quantitative polymerization requires 60−100 mol % amount of amine as the monomer (Figure 2). The addition of more amine decreases the acidity of the system and produces the polymer in a lower yield.

Interaction of Sulfonium Cation with Diphenylamine. To confirm the formation of the CT complex, spectroscopic analyses were carried out using a nonpolymerzable model compound, diphenyl methyl sulfonium triflate **3**. Although both **3** and diphenylamine are transparent in the visible light, their mixed solution in dichloromethane has a yellow color based on the CT absorption. The CT absorption was observed at 400 nm as a shoulder of a large $\pi-\pi^*$ transition absorption of diphenylamine in the UV/vis spectrum. The stoichiometry of the CT formation was investigated by a continuous variation method, where the concentration of each component was changed to find the maximum absorbance while the total concentration was set to be constant at 0.1 M (Figure 3). At any points recorded (400, 410, and 420 nm), the absorbance[14] shows a maximum at the concentration of [**3**]/([**3**] + [Ph_2NH]) = 0.5, suggesting the 1:1 CT complex, i.e.,

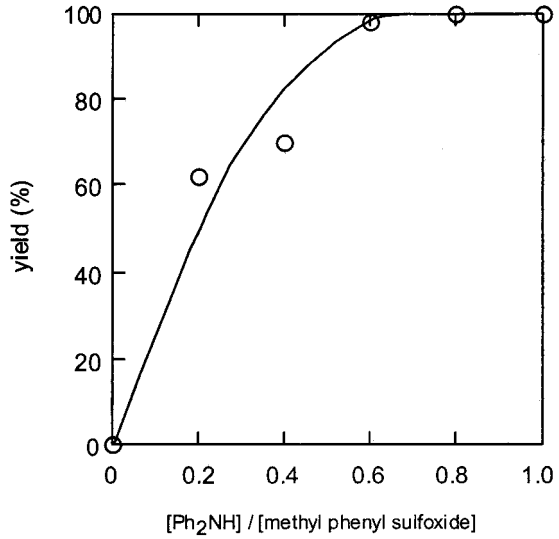


Figure 2. Effect of the amount of diphenylamine on the polymerization of methyl phenyl sulfoxide in triflic acid.

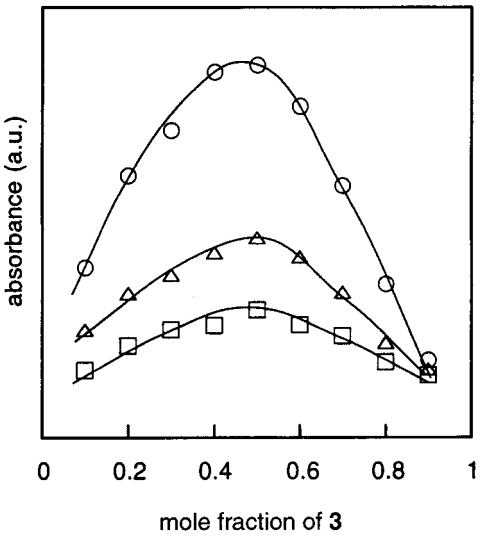


Figure 3. Effect of the molar fraction of **3** on the CT absorbance at 400 (○), 410 (△), and 420 nm (□) determined for a mixture of **3** and diphenylamine (total concentration = 0.1 M) in dichloromethane.

$$\mathbf{3} + \mathrm{Ph_2NH} \overset{K}{\rightleftharpoons} [\mathbf{3}\cdot\mathrm{Ph_2NH}]$$

The equilibrium constant, K, for the above reaction is defined by the following equation:[15]

$$\frac{[\mathbf{3}]l}{\mathrm{abs}} = \frac{1}{K\epsilon}\frac{1}{[\mathrm{Ph_2NH}]} + \frac{1}{\epsilon}$$

where abs = maximum absorbance of the complex, l = optical length, and ϵ = molar extinction coefficient of the complex. The K and ϵ were determined by the slope and the intercept in the Benesi−Hildebrand plots[15] (Figure 4) to be 0.41 M^{-1} and 5.26×10^3 cm^{-1} M^{-1}, respectively. This value of K indicates that 21 mol % of the sulfonium cation was tied up as the CT complex in dichloromethane solution of **3** and diphenylamine both in 0.8 M (the concentration used for the polymerization). The comparable values of K and ϵ were obtained for the **3**/3-chlorodiphenylamine complex (Table 2).

The formation of the CT complex was also confirmed by the ^{1}H NMR spectrum in CD_2Cl_2 (Figure 5). The peak

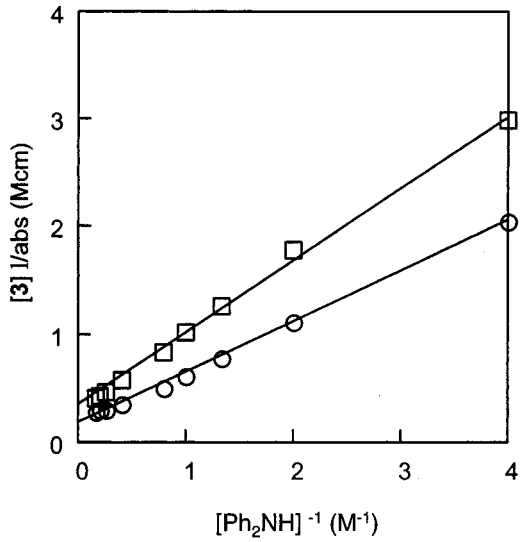


Figure 4. Benesi−Hildebrand plots for **3**/diphenylamine (○) and **3**/3-chlorodiphenylamine (□) complex.

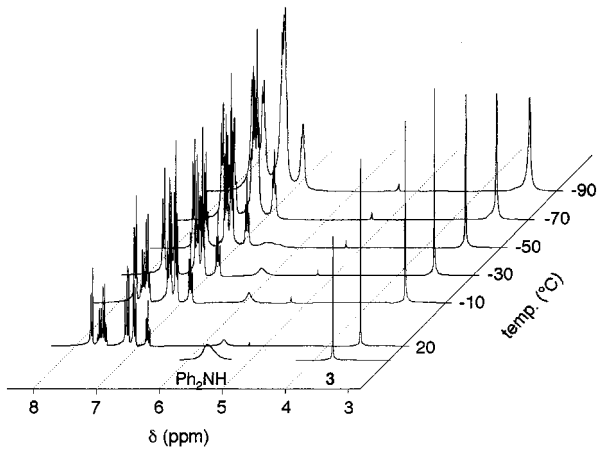
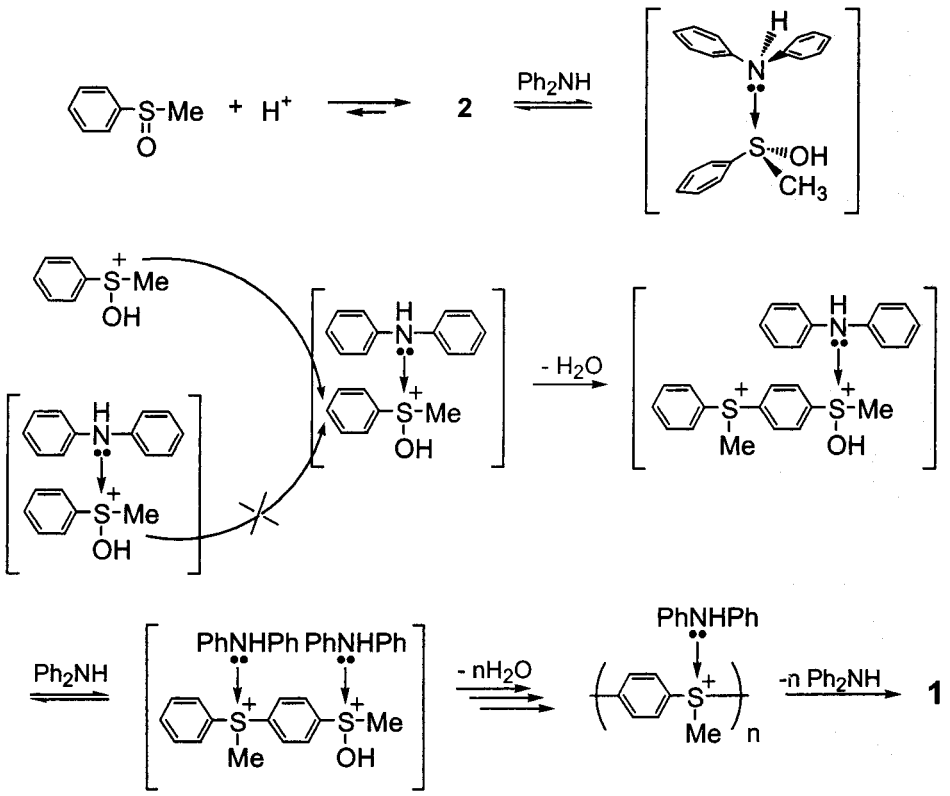


Figure 5. ^{1}H NMR spectra of an equimolar mixture of diphenylamine and **3** (both in 1.0 M) in CD_2Cl_2 at various temperatures.

of the methylsulfonio group of **3** is observed at 3.78 ppm, which shifted to 3.44 ppm with the addition of an equimolar amount of diphenylamine. The shift to a higher magnetic field is reasonable because the CT interaction should increase the electron density of the methyl substituent of **3**. The equilibrium should favor the CT complex at low temperatures, as indicated by the peak shift to 3.23 ppm at −90 °C. The opposite effect is observed for the imine proton of diphenylamine, which shifted from 5.72 ppm at 20 °C to lower than 7.00 ppm at −90 °C. (The peak was integrated into aromatic protons.) IR spectroscopy further supports the charge transfer from the amine to **3**, where the absorptions of the NH stretching vibration of diphenylamine (ν_s: 3382 cm^{-1} and ν_{as}: 3406 cm^{-1}) shifted to 3331 cm^{-1} as a broad peak in the 1:1 complex (Figure 6).[16]

Taking into account those spectroscopic results, the possible polymerization mechanism involving the CT complex is postulated in Scheme 2. Under strongly acidic conditions, methyl phenyl sulfoxide is protonated to hydroxy methyl phenyl sulfonium cation **2**. This intermediate has donor/acceptor interaction with diphenylamine to form the CT complex. The interaction could compensate the electron negativity of the sulfonium species and increase the reactivity of terminal phenyl

Scheme 2



ring to electrophilic substitution. The reaction takes place more probably between **2** and the complex than between the two complexed compounds, since there is no vacant sp^3 orbital of the sulfur atom in the complex to take part in the reaction. The assumption is not contradictory to the results in Figure 2 that 60−100 mol % of amine as the monomer is appropriate for the quantitative reaction. The successive reaction makes the chain propagation to give phenylene sulfonium polymer **1**. The amine attached to the polymer is removed by the treatment with acetone.

Syntheses and Crystal Structures of Oligomer Models. The reactivity of sulfonium compounds as electron acceptors and as electrophilic reagents should be strongly related to the atomic arrangement around the sulfur atom. A number of crystal structures of interesting sulfonium salts have been reported, such as those of dihalosulfonium salts[17] and an aurated sulfonium salt.[18] However, to our knowledge, no systemized study has been reported on the crystal structure of aromatic sulfonium salts. In attempts to obtain typical parameters for bond lengths and angles and torsional angles of aromatic sulfonium compounds to determine the crystal structure of the polymer **1**, the dimer and trimer model compounds were subjected to X-ray crystallographic analysis. However, the recrystallization of a triflate **3** met with failure. Reasoning that crystallization of a triflate salt might be disfavored because of the bulky anion, we turned to the crystallization of the product after anion exchange with various tetra-*n*-butylammonium salts. It was found that the crystallinity and the hygroscopicity of aromatic sulfonium salts depend on their counteranions. Anion exchange procedures were successfully employed to obtain suitable samples of aromatic sulfonium salts for diffraction studies. For the dimer model compound, good crystals were obtained only with the hexafluoroantimonate anion (**4**). X-ray diffraction study of the crystallized product (Table 3) revealed the structure of **4** (Figure 7a).

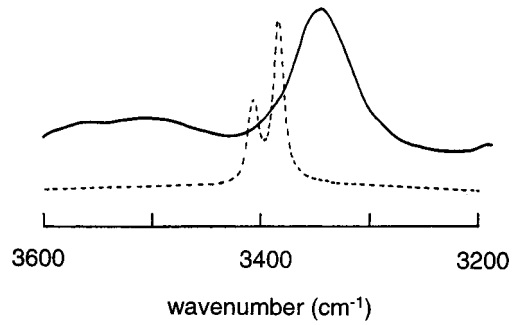


Figure 6. IR spectra of diphenylamine (dotted line) and a **3**/diphenylamine complex (solid line).

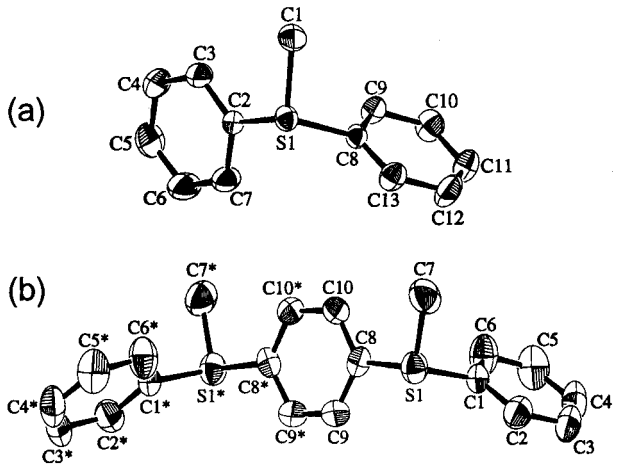


Figure 7. ORTEP view (30% probability ellipsoids) of the cation in (a) **4** and (b) **6**.

The S(1) atom covalently bonded with the three carbon atoms extends 0.747 Å above the C(1)C(2)C(8) plane. The arrangement of the four atoms represents a typical trigonal-pyramidal structure. The bond lengths of the sulfur atom and the phenyl carbons are indicative of the oxidation state of the sulfur atom (Table 4). Indeed, the S(1)−C(2) and S(1)−C(8) bond lengths (1.78 Å) are slightly longer than the C−S bond length of diaryl sulfides such as bis(4-methylphenyl) sulfide (1.75 Å) and bis(4-bromophenyl) sulfide (1.75 Å)[18] due to the decrease in the electron density of the 3p lone pair which resonate with the π electrons of the benzene ring. The enhanced p-character of the C−S bond and the s-character of the sulfur atom of the sulfonium compared to those of sulfides are also revealed by the significant decrease in the C−S−C bond angle upon the conversion of sulfide into sulfonium (**4**, 103.6(3)°; bis(4-methylphenyl) sulfide, 109°; bis(4-bromophenyl) sulfide, 109°; diphenyl sulfide, 113°).[19] The S(1)−C(1) bond length (1.804(8) Å) is comparable with the value of typical alkylsulfonium compounds.[20] The cation is separated by the almost spherical hexafluoroantimonate anion which is arranged in the proximity of the cations.

1,4-Bis(methyl phenyl sulfonio)benzene bistriflate (**5**) was synthesized from 1,4-bis(phenylthio)benzene by the same method as employed for **3**. Crystals suitable for X-ray analysis were obtained only for the hexafluorophosphate salt (**6**) after anion exchange with tetra-*n*-butylammonium hexafluorophosphate. X-ray analysis revealed the molecular structure of the cation as a hexafluorophosphate salt as shown in Figure 7b. The molecule occupies a C_2 crystallographic site symmetry. The S(1) atom, surrounded by the three carbon atoms, extends 0.755 Å above the C(1)C(7)C(8) plane which again represents a trigonal-pyramidal arrangement. The S(1)−C(1) and S(1)−C(8) bond lengths are longer than the C−S bond length of diaryl sulfides[19] as expected. The S(1)−C(7) bond length (1.76(2) Å) is again typical of the alkylsulfonium compounds.[20] The almost spherical hexafluorophosphate anion is located in the proximity of the sulfonium groups.

The positions of the three carbon atoms around the sulfonium in **4** and **6** show that a vacant sp^3 orbital should occupy the fourth position of the sulfur atom to accomplish the tetrahedral arrangement. The donor−acceptor interaction with diphenylamine is likely to occur with the protruding vacant sp^3 orbital of the sulfur atom.

An intriguing aspect is derived from the comparison of the crystal structures of **4** and **6**, which reveals good coincidence of the bond lengths and angles in the two cations. For instance, the S^+−C(phenyl) bond lengths in **4** are 1.783(6) and 1.782(6) Å, respectively, and those in **6** are 1.81(1) and 1.77(1) Å, respectively. The (phenyl)C−S^+−C(phenyl) bond angles in **4** and **6** are 103.6(3)° and 103.8(6)°, respectively. Moreover, the torsions of the best least-squares planes of the adjacent phenyl rings in **4** and **6** are also comparable (83.12° and 92.48°, respectively). In analogy to these oligomer models, one could estimate that the polysulfonium salt also has similar structural features. As the most typical parameter to characterize the crystal structure of **1**, one can estimate the spacing, or the distance between the repeating unit, along the polymer chain from the atomic distance between S1 and S1* in **6** (6.26 Å). These geometric parameters of the oligomer model compounds were used to determine the crystal structure of the polymer in Figure 9a (vide infra).

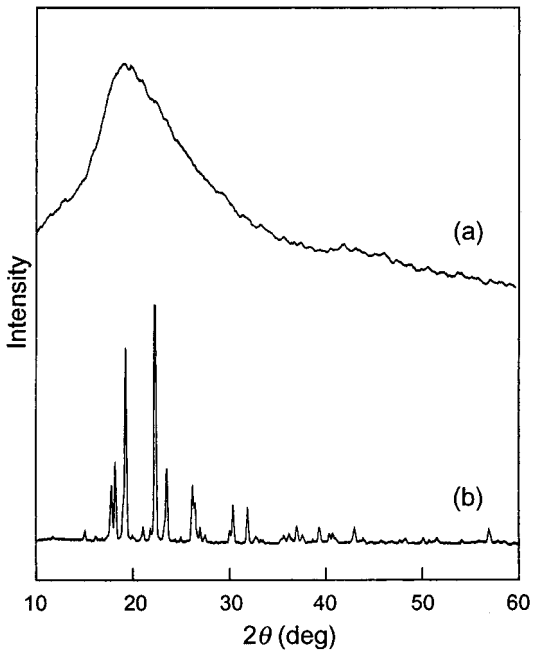


Figure 8. X-ray diffractograms of (a) poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene hexafluorophosphate) and (b) the polymer **7**.

Crystal Structure of the Methylsulfoniophenylene Polymers. PPS is known to be partly crystalline and shows relatively strong X-ray powder diffraction peaks superimposed on an amorphous halo, which allowed the crystal structure determination.[21] On the contrary, poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene hexafluorophosphate)[5] showed no X-ray diffraction peaks (Figure 8a), revealing that the polymer is amorphous. The increase in the spacing along the polymer chain, i.e., the size of the repeating unit, from that of PPS seems to prevent the polymer from forming good microcrystals.

The methylsulfoniophenylene polymer has a smaller repeating unit and is expected to be crystalline. Because the triflate polymer **1** was hygroscopic, the powder diffraction data were collected with the polymer **7** having hexafluorophosphate as the counteranion. The polymer **7** showed very sharp reflections without the amorphous halo (Figure 8b), indicating a high crystallinity. The sole unit cell of polymer **7** was induced by the following considerations. Previous studies showed that orthorhombic unit cells are the most frequently observed[22] for a number of structurally related aromatic polymers such as PPS,[21] poly(phenylene oxide),[23] and PEEK.[24] In Figure 8b, most of the recorded reflections could also be satisfactorily indexed by assuming an orthorhombic unit cell of dimensions $a = 10.875$ Å, $b = 10.449$ Å, and $c = 18.629$ Å. The lengths of the a and b axes are close to those determined for **4** and **6**. Table 5 shows good coincidence between the observed and calculated values of interplanar spacing d. A crystallographic density of 1.67 g/cm^3 was calculated for eight monomeric units per cell, which correlates acceptably with the crystal density of the oligomer model compounds considering that the polymer **7** could be highly crystalline.[25] In view of the molecular arrangement of the oligomer models (Figure 7) in the unit cell, the polymer chain is likely to be arranged along the long

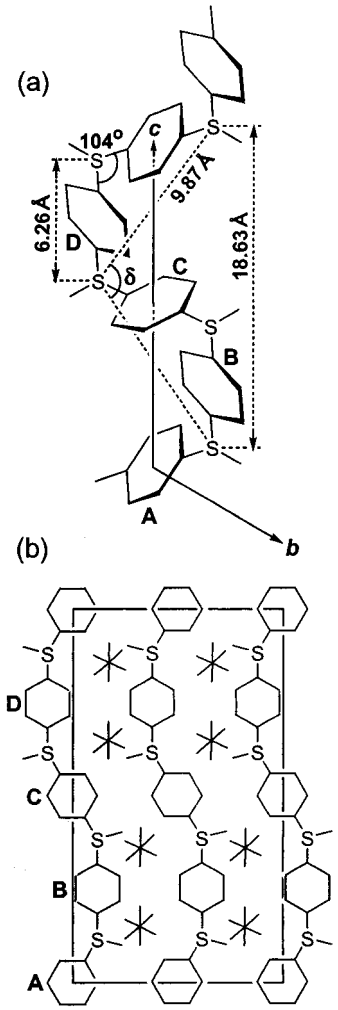


Figure 9. (a) Estimated conformation of a polymer chain in the crystal of **7**. Bond lengths and angles are from those in **6**. (b) Arrangement of the polymer chain in the unit cell projected along the *a*-axis. Positions for hexafluorophosphate anions are shown as asterisks.

c-axis. The systematic absence of the reflections *hk*0 with $h + k$ odd, 0*kl* with *k* odd, and *h*0*l* with *l* odd led us to the space group *Pbcn* (#60).[26] Figure 9a shows the structure of the polymer chain estimated from the typical bond parameters of the oligomer model compounds. Figure 9b shows the possible arrangement of the polymer chain in the unit cell projected along the *a* axis. Two molecular chains pass through the unit cell, one through the center and the other through the corner. In view of the symmetry of the space group, the centers of gravity of the phenylene groups labeled A and C were placed in the unit cell at the special positions 0, 0, 0; 0, 0, $^1/_2$; $^1/_2$; $^1/_2$, 0 and $^1/_2$, $^1/_2$, $^1/_2$, which are the centers of symmetry. Those labeled B and D were placed at the special positions 0, $-y$, $^3/_4$; 0, y, $^1/_4$; $^1/_2$, $^1/_2 + y$, $^1/_4$ and $^1/_2$, $^1/_2 - y$, $^3/_4$. This arrangement implies that four monomeric units are contained in the period of the *c*-axis, which is compatible with the estimated bond length and angles as shown in Figure 9a. The hexafluorophosphate anions occupy the eight general equivalent positions in the unit cell (Figure 9b). The angle of δ in Figure 9a is determined to be 141°, which characterizes the polymer structure. Thus, the crystal structure of **7** has a repeat distance different from that of the chemical structure of the polymer and consists of four benzene nuclei and four sulfonio linkages, yielding a repeat distance of 18.6 Å along the *c*-axis. Reflection intensity calculations to determine the rotation angle of the phenylene groups round the S−S axis were unsuccessful, due probably to the significant disorder of the hexafluorophosphate anions in the crystal.

Table 5. Observed and Least Squares Refined Diffraction Parameters for 7

hkl	I_{norm}	$2\theta_c$	$2\theta_o$	d_c	d_o
110	5	11.735	11.720	7.5347	7.5443
112	7	15.112	15.080	5.8580	5.8701
200	5	16.287	16.180	5.4377	5.4734
021	21	17.616	17.860	5.0303	4.9623
113	28	18.500	18.280	4.7920	4.8492
004	17	19.040	19.140	4.6572	4.6331
121	62	19.426	19.420	4.5656	4.5670
122	8	21.122	21.140	4.2026	4.1991
023	8	22.219	21.921	3.9977	4.0513
114	100	22.424	22.460	3.9615	3.9553
220	26	23.596	23.620	3.7674	3.7636
204	5	25.156	25.100	3.5372	3.5449
302	21	26.360	26.300	3.3783	3.3858
214	15	26.583	26.540	3.3504	3.3558
124	8	26.902	27.041	3.3114	3.2947
106	6	29.904	30.100	2.9855	2.9664
224	14	30.494	30.460	2.9290	2.9322
232	14	31.965	31.960	2.7975	2.7979
400	5	32.916	32.840	2.7188	2.7249
117	5	35.753	35.741	2.5093	2.5102
135	6	36.229	36.280	2.4774	2.4741
413	8	37.077	37.081	2.4227	2.4225
421	5	37.573	37.680	2.3918	2.3853
242	7	39.441	39.420	2.2828	2.2839
144	5	40.417	40.460	2.2299	2.2276
334	6	40.785	40.860	2.2106	2.2067
145	8	43.065	43.080	2.0987	2.0980
150	4	44.091	44.020	2.0522	2.0553
440	3	48.274	48.320	1.8837	1.8820

The crystal structure of **7** implies that the atomic arrangements around the sulfur atoms in **7** are similar to those of **4** and **6** and thus the polymer **7** has a vacant sp^3 orbital to allow the CT complex formation with diphenylamine.

Conclusions

The self-polycondensation of methyl phenyl sulfoxide was successfully accomplished by the reconciliation of the reactivity of hydroxy methyl phenyl sulfonium cation **2** as an electrophile by the electron donation from diphenylamine. The reaction was established as a convenient synthesis of poly(methylsulfonio-1,4-phenylene triflate) with a possible application to the polycondensation of a variety of aromatic sulfoxides. The high crystallinity of the polymer is reminiscent of PPS. Using the typical geometric parameters of the dimer and trimer model compounds, the atomic arrangement in the polymer crystal could be determined from the X-ray diffraction data.

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Supporting Information Available: Tables giving atomic coordinates, equivalent isotropic thermal parameters, and anisotropic displacement parameters for **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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