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Convenient Syntheses of Methylsulfonioarylene and Thioarylene Polymers from 1,4-bis(Methylsulfinyl)benzene

Kenichi Oyaizu^a; Hiroyuki Yonemaru^a; Tomokazu Iwasaki^a; Ryohei Matsubara^a; Eishun Tsuchida^a

^a Advanced Research Institute for Science and Engineering, Waseda University, Tokyo, Japan

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NOTE

Convenient Syntheses of Methylsulfonioarylene and Thioarylene Polymers from 1,4-bis(Methylsulfinyl)benzene

Kenichi Oyaizu, Hiroyuki Yonemaru, Tomokazu Iwasaki,
Ryohei Matsubara, and Eishun Tsuchida*

Advanced Research Institute for Science and Engineering,
Waseda University, Tokyo, Japan

Key Words: Polysulfonium salt; Electrophilic reaction; Polythioether; Thermal stability.

INTRODUCTION

It has been established that the protonation of aryl sulfoxides under strongly acidic conditions produces hydroxysulfonium cations which readily react with suitable aromatic molecules, thus yielding aromatic sulfonium cations.^[1] This reaction has been exploited for the synthesis of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) from 4-(methylsulfinyl)phenyl phenyl sulfide and triflic acid.^[2] The product can be converted to an engineering plastic poly(thio-1,4-phenylene) (PPS) by nucleophilic demethylation using pyridine.^[3,4] On the other hand, the superacidification of a more simple aryl sulfoxide compound, methylsulfinylbenzene, produces only the corresponding dimer, methyl{4-(methylsulfinyl)phenyl}(phenyl)sulfonium triflate; a further propagation reaction is impeded by the decrease in the electron density at the *para* position of the terminal phenyl ring due to the electron withdrawing effect of the sulfonio group.^[5] It has also been found that the admixture of methylsulfinylbenzene and triflic acid provides oligo(methylsulfonio-1,4-phenylene triflate) only when the reaction is carried out in

*Correspondence: Eishun Tsuchida, Advanced Research Institute for Science and Engineering, Waseda University, Tokyo, Japan; Fax: +813-3205-4740; E-mail: eishun@mn.waseda.ac.jp.

the presence of an external electron donor such as diphenyl amine to compensate for the inductive effect of the sulfonio group.^[6]

In this paper, we report that the protonation of a methylsulfinyl group by triflic acid is exclusively *not* impeded by the sulfonio group at the *para* position of the benzene ring, and hence 1,4-bis(methylsulfinyl)benzene can be used as a bifunctional monomer for the polycondensation with a wide variety of aromatic molecules to yield methylsulfonioarylene and thioarylene polymers conveniently (Sch. 1).

EXPERIMENTAL

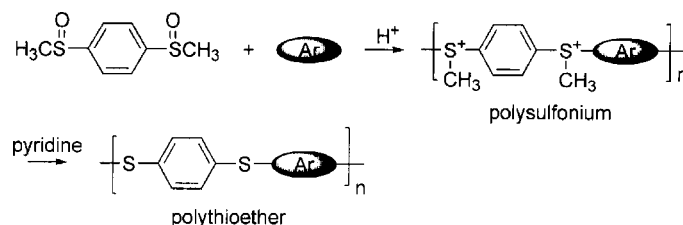
Materials

Commercial reagents of thioanisole, dimethyl sulfoxide, triflic acid, pyridine, hydrochloric acid, anhydrous sodium sulfate, 60% nitric acid, potassium carbonate, diphosphorus pentoxide, diphenyl sulfide, diphenyl ether, diphenyl selenide, naphthalene, biphenyl, pyridine, diphenylamine, bithiophene, diphenylmethane, and deuterated solvents for NMR measurements were used as received. All solvents were purified by distillation prior to use.

Synthesis

1,4-bis(Methylthio)benzene

To a solution of thioanisole (0.2 mol, 24.8 g) in dimethyl sulfoxide (0.2 mol, 15.6 g) was slowly added triflic acid (0.3 mol, 45 g) at 0°C. The resulting mixture was stirred at room temperature in the dark to provide a viscous suspension. After 4 h, unreacted thioanisole and dimethyl sulfoxide was removed by pouring the reaction mixture into diethyl ether and collecting the white precipitate by filtration. The collected crude product was dissolved in chloroform, and the solution was then evaporated to dryness at room temperature under reduced pressure. To the residue was added pyridine (100 mL) which was refluxed for 2 h to undergo demethylation of the sulfonium salt. After the demethylation reaction was completed, the resulting solution was neutralized with hydrochloric acid at 0°C. The demethylated product was extracted with chloroform.



Scheme 1.

**Methylsulfonioarylene and Thioarylene**

417

The chloroform layer was washed with H₂O repeatedly. Dehydration with anhydrous sodium sulfate followed by evaporation and purification by recrystallization from diethyl ether afforded 1,4-bis(methylthio)benzene as a white powder in 84% yield.

IR (KBr, cm⁻¹): 2914 ($\nu_{\text{C-H}}$), 887 ($\delta_{\text{C-H}}$).

¹H NMR (CDCl₃, TMS, ppm): δ = 2.46 (s, 6H, SCH₃), 7.22 (d, 4H, Ph).

¹³C NMR (CDCl₃, TMS, ppm): δ = 16.4 (SCH₃), 127.6, 135.1 (Ph).

MS (m/z): 170 (M⁺).

Elemental analysis: Calcd. for C₈H₁₀S₂: C, 56.46; H, 5.92; S, 37.62%. Found: C, 56.41; H, 5.81; S, 36.01%.

1,4-bis(Methylsulfinyl)benzene

1,4-Bis(methylthio)benzene (60 mmol, 10.5 g) was dissolved in a mixture of acetonitrile (60 mL) and dichloromethane (15 mL). To this solution was added 60% nitric acid (150 mL), and the resulting mixture was stirred at room temperature. The color of the mixture changed from green through orange to yellow as the reaction proceeded. After 6 h, neutralization with potassium carbonate at 0°C followed by the removal of water by evaporation, dehydration with anhydrous sodium sulfate, extraction with chloroform and rotary evaporation afforded the crude product as a white residue which was purified by recrystallization from ethanol to yield 1,4-bis(methylsulfinyl)benzene as a plate-like crystal in 92% yield.

IR (KBr, cm⁻¹): 2986 ($\nu_{\text{C-H}}$), 1038 ($\nu_{\text{S=O}}$), 881 ($\delta_{\text{C-H}}$).

¹H NMR (CDCl₃, TMS, ppm): δ = 2.78 (s, 6H, SCH₃), 7.83 (d, 4H, Ph).

¹³C NMR (CDCl₃, TMS, ppm): δ = 43.8 (S(O)CH₃), 124.5, 149.1 (Ph).

MS (m/z): 202 (M⁺).

Elemental analysis: Calcd. for C₈H₁₀O₂S₂: C, 47.52; H, 4.99; S, 31.66%. Found: C, 46.51; H, 4.41; S, 29.98%.

Coupling of Methylsulfinylbenzene and Aromatic Molecules

To a mixture of methylsulfinylbenzene (4 mmol, 0.28 g) and aromatic compounds such as diphenyl ether, diphenyl sulfide, biphenyl, naphthalene and bithiophene (2 mmol) maintained at 0°C in the dark was slowly added triflic acid (3 mL). The resulting solution was stirred at room temperature for 12 h. Then, pyridine (20 mL) was added to the solution which was refluxed for 2 h. After cooling, neutralization with hydrochloric acid followed by extraction with chloroform and rotary evaporation afforded the product which was

subjected to HPLC analysis to determine the composition of the product using a mixture of tetrahydrofuran and water in a volume ratio of 7:3 at a detection wavelength of 250 nm.

Polymerization of 1,4-bis(Methylsulfinyl)benzene and Diphenyl Sulfide

To a mixture of carefully weighed 1,4-bis(methylsulfinyl)benzene (2 mmol, 0.405 g), diphenyl sulfide (2 mmol, 0.373 g) and diphosphorus pentoxide (0.6 g) maintained at 0°C in the dark was slowly added triflic acid (6 mL). The resulting solution was stirred for 1 h in the dark at 0°C and then for 24 h at room temperature. As the reaction proceeded, the solution became highly viscous and showed a Weissenberg effect indicative of the formation of a high molecular-weight polymer. After the reaction, the solution was slowly poured into vigorously stirred diethyl ether to precipitate the product, poly{methylsulfonio-1,4-phenylenemethylsulfonio-1,4-phenylenethio-1,4-phenylene bis(triflate)}, as a white powder which was readily dissolved in pyridine. Refluxing the pyridine solution for 2 h followed by cooling to room temperature, neutralization with hydrochloric acid, washing with water and drying under vacuum yielded poly(thio-1,4-phenylene) (PPS) as a white powder in 95% yield.

IR (KBr, cm^{-1}): 3051 ($\nu_{\text{C-H}}$), 814 ($\delta_{\text{C-H}}$).

Elemental analysis: Calcd. for $\text{C}_6\text{H}_4\text{S}$: C, 66.66; H, 3.73; S, 29.61%. Found: C, 65.73; H, 3.10; S, 27.89%.

GPC (210°C, 1-chloronaphthalene, polystyrene standard): M_w , 1.4×10^5 ; M_n , 4.2×10^4 ; M_w/M_n , 3.4.

Polymerization of 1,4-bis(Methylsulfinyl)benzene and Diphenyl Ether

To a mixture of bis(methylsulfinyl)benzene (2 mmol, 0.405 g), diphenyl ether (2 mmol, 0.340 g) and diphosphorus pentoxide (0.6 g) maintained at 0°C in the dark was added triflic acid (6 mL). The resulting solution was stirred for 1 h in the dark at 0°C and then for 24 h at room temperature. After the reaction, the solution was poured into diethyl ether to precipitate the product, poly{methylsulfonio-1,4-phenylenemethylsulfonio-1,4-phenyleneoxy-1,4-phenylene bis(triflate)}, as a white powder which was subjected to ^1H NMR analysis (Figure 1) to confirm the linear 1,4-phenylene structure without branching (vide infra). The product was readily dissolved in pyridine which was refluxed for 2 h. After cooling to room temperature, neutralization with hydrochloric acid, washing with water and drying under vacuum afforded poly(thio-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylene) (PPSSO) as a white powder in 96% yield.

IR (KBr, cm^{-1}): 2924 ($\nu_{\text{C-H}}$), 1235 ($\nu_{\text{C-O}}$), 816 ($\delta_{\text{C-H}}$).

Elemental analysis: Calcd. for $\text{C}_{18}\text{H}_{12}\text{S}_2\text{O}$: C, 70.12; H, 3.92; S, 20.76%. Found: C, 70.52; H, 3.32; S, 19.27%.

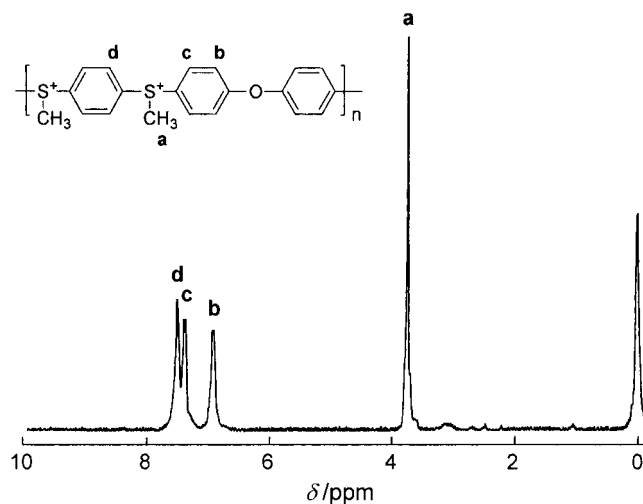


Figure 1. ^1H NMR spectrum of poly{methylsulfonio-1,4-phenylenemethylsulfonio-1,4-phenyleneoxy-1,4-phenylene bis(triflate)} in $\text{CF}_3\text{SO}_3\text{D}$. TMS was used as an external standard.

GPC (210°C, 1-chloronaphthalene, polystyrene standard): M_w , 2.6×10^4 ; M_n , 7.4×10^3 ; M_w/M_n , 3.5.

Polymerization of 1,4-bis(Methylsulfinyl)benzene and 1,4-bis(Methylthio)benzene

To a mixture of bis(methylsulfinyl)benzene (0.5 mmol, 0.101 g) and 1,4-bis(methylthio)benzene (0.5 mmol, 0.0852 g) maintained at 0°C in the dark was added triflic acid (1 mL). The resulting dark blue solution was stirred for 1 h in the dark at 0°C and then for 24 h at room temperature. After the reaction, the solution was poured into diethyl ether to precipitate the product, poly{methylsulfonio-1,4-phenylenemethylsulfonio-2,5-bis(methylthio)-1,4-phenylene bis(triflate)}, as a white powder. The product was then dissolved in pyridine (10 mL) which was refluxed for 3 h. After cooling to room temperature, the resulting solution was poured into methanol containing 5% hydrochloric acid to precipitate the demethylated product, poly(thio-1,4-phenylenethio-2,5-bis(methylthio)-1,4-phenylene) (MTPPS), which was collected by filtration, washed repeatedly with methanol and water and dried under vacuum. The final product was obtained as a white powder in 96% yield.

IR (KBr, cm^{-1}): 2914 ($\nu_{\text{C-H}}$), 809 ($\delta_{\text{C-H}}$).

^1H NMR (CD_2Cl_2 , TMS, ppm): δ = 2.38 (s, 6H, SCH_3), 7.12 (d, 4H, Ph), 7.16 (d, 2H, Ph).

^{13}C NMR (CD_2Cl_2 , TMS, ppm): δ = 16.1 (SCH_3), 127.9, 130.3, 131.7, 134.4, 143.7 (Ph).

Elemental analysis: Calcd. for $C_7H_6S_2$: C, 54.50; H, 3.92; S, 41.57%. Found: C, 55.39; H, 4.11; S, 38.89%.

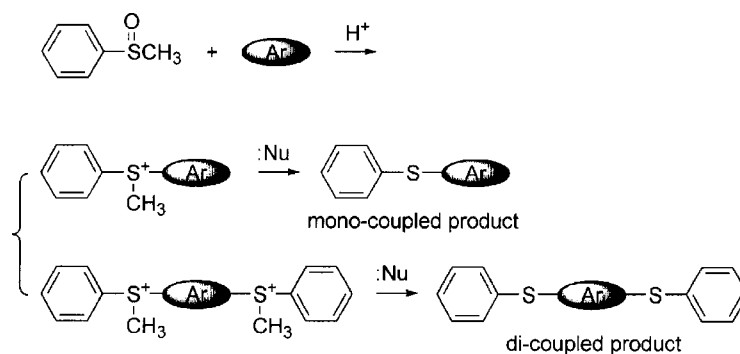
GPC (r.t., chloroform, polystyrene standard): M_w , 4.1×10^3 ; M_n , 2.4×10^3 ; M_w/M_n , 1.7.

Measurements

1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500 (500 MHz 1H , 125 MHz ^{13}C) spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Infrared spectra were obtained using a Jasco FT-IR 5300 spectrometer with potassium bromide pellets. Thermogravimetry and differential thermal analysis were performed using a Seiko TG-DTA 220 instrument at a heating rate of $10^\circ C/min$ under nitrogen with a flow rate of 300 mL/min. Differential scanning calorimetry was performed using Seiko DSC220C at a heating rate of $20^\circ C/min$ under nitrogen. A 5 mg sample was used for each thermal analysis. Molecular weight measurement was done by gel permeation chromatography (GPC) at $210^\circ C$ 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. Elemental analyses were performed using a Perkin-Elmer PE-2400 II and a Metrohm 645 multi-DOSIMAT. Two parallel analyses were performed for each sample. Mass spectra were obtained using a Shimadzu GCMS-QP5050 spectrometer.

RESULTS AND DISCUSSION

The coupling reactions of aryl sulfoxides with a variety of aromatic molecules were examined using methylsulfinylbenzene^[6] as a nonpolymerizable monofunctional compound (Sch. 2). A mixture of methylsulfinylbenzene (1 mol L^{-1}) and aromatic molecules such as diphenyl sulfide and diphenyl ether (0.5 mol L^{-1}) in triflic acid with constant stirring at room temperature for 2 h gave the products which were isolated after conversion to the corresponding thioethers by the subsequent treatment with refluxing pyridine for 12 h.



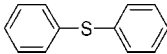
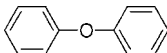
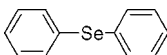
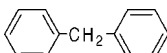
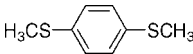

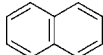
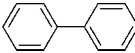
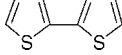

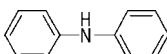
Scheme 2.

The coupled products were obtained almost quantitatively. The composition of the products, however, changed according to the reaction time (t). At the initial stage of the reaction ($t < \text{ca. } 1 \text{ h}$), the mono-coupled products were predominantly obtained over the di-coupled products while the di-coupled products prevailed at a prolonged time of the reaction ($t > 10 \text{ h}$) (Sch. 2), which indicates the stepwise mechanism of the coupling reaction. At higher temperatures (80°C), the coupling reaction was accelerated to yield only the di-coupled products even at the very initial stage of the reaction ($t < 0.5 \text{ h}$), but a small amount of the *ortho*-coupled side products were concomitantly produced. Aromatic molecules such as biphenyl, bithiophene and naphthalene were not susceptible to the coupling with methylsulfinylbenzene in triflic acid. These results suggest that linear, *para*-coupled polymers should be obtained using a bifunctional monomer, 1,4-bis(methylsulfinyl)benzene, in place of the monofunctional compound under conditions where the di-coupled products were exclusively obtained in high yields.

Table 1 summarizes the results of polymerization of 1,4-bis(methylsulfinyl)benzene with a variety of aromatic molecules in triflic acid. The most typical example that demonstrated the efficiency of this reaction was provided by the polymerization with an equimolar amount of diphenyl sulfide which gave the corresponding polysulfonium salt, poly{methylsulfonio-1,4-phenylenemethylsulfonio-1,4-phenylenethio-1,4-phenylene bis(triflate)}. Thus, the admixture of 1,4-bis(methylsulfinyl)benzene and diphenyl sulfide in triflic acid with constant stirring at room temperature for a sufficiently long time ($t = 24 \text{ h}$) gave the product which was isolated by pouring the mixture into diethyl ether. The high molecular weight of the product, determined after conversion to PPS by the treatment with pyridine, corroborated the high reactivity of the bifunctional monomer. Polymerization with diphenyl ether and diphenyl selenide also gave the corresponding polysulfonium salts. Their linear structures without branching or defects were confirmed by spectroscopic methods, which indicated that the electrophilic substitution by the hydroxysulfonium ion^[6] took place predominantly at the phenyl carbon *para* to the chalcogenide bond. Typically, the methylsulfonio protons in the polysulfonium salts appeared near $\delta = 3.8 \text{ ppm}$ in the ^1H NMR spectra (Fig. 1), and the two adjacent hydrogen atoms in the 1,4-phenylene units showed the out-of-plane vibrations near $\delta_{\text{C-H}} = 815 \text{ cm}^{-1}$ in the IR spectra. Because the molecular weight of a polyelectrolyte is hard to determine by GPC or viscosity measurements, the polysulfonium salts were converted to polythioethers by the treatment with pyridine (Sch. 1). Table 1 shows the molecular weights and thermal properties of the polythioethers. The molecular weight of the obtained PPS was much higher than that of the commercially available PPS prepared by the conventional polycondensation of *p*-dichlorobenzene and sodium sulfide,^[7] which resulted in significant increase in the temperatures for the glass transition (T_g) and the thermal degradation ($T_{d10\%}$). The melting point (T_m) of poly(thio-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylene) (PPSSO) was ca. 90°C lower than that of PPS as a result of an increased ΔS_m associated with the T_m , due to the lower symmetry of PPSSO. Indeed, it is known that C—O bonds (1.36 \AA) are significantly shorter than C—S bonds (1.74 \AA), and C—O—C angles (124°) are larger than C—S—C angles (110°).^[8] The low molecular weight of poly(thio-1,4-phenylenethio-1,4-phenyleneseleno-1,4-phenylene) (PPSSSe) could be ascribed to the low reactivity of diphenyl selenide to sulfonium nucleophiles.^[9]

Aromatic molecules which reacted with the strong acid such as diphenyl amine and pyridine were not applicable as the monomer. Polycondensation with benzene,

Table 1. Acid-induced polycondensation^a of 1,4-bis(methylsulfinyl)benzene with aromatic molecules (Ar).

Ar	Polythioether yield (%)	Abbr.	M_n^b ($\times 10^{-3}$)	M_w^b ($\times 10^{-3}$)	T_g^c (°C)	T_m^c (°C)	$T_{d10\%}^d$ (°C)
	100	PPS	42	140	105	280	540
	100	PPSSO	7.4	26	105	188	491
	70	PPSSSe	0.87	1.5	77	<i>e</i>	<i>e</i>
	Trace						
	70	MTPPS	2.4	4.1	<i>e</i>	<i>e</i>	<i>e</i>
	Trace						
	Trace						
	0						
	0						
	0						
	0						

^a Polymerization was carried out in $\text{CF}_3\text{SO}_3\text{H}$ (6 mL) using 1,4-bis(methylsulfinyl)benzene (2 mmol) and a monomer (Ar) (2 mmol) in the presence of P_2O_5 (0.6 g) for 24 h. The reaction was quenched by pouring the resulting mixture into diethyl ether to precipitate the polysulfonium salts which were then converted to polythioethers by the treatment with refluxing pyridine for 2 h and washing with HCl and H_2O .

^b Molecular weights were determined by GPC with 1-chloronaphthalene at 200°C as an eluent and polystyrene as a standard, respectively.

^c Glass transition temperatures (T_g) and melting points (T_m) were determined from DSC thermograms recorded under N_2 at a heating rate of 10°C/min.

^d Temperatures for the 10% weight loss ($T_{d10\%}$) were determined from TGA thermograms recorded under N_2 at a heating rate of 10°C/min.

^e Undetermined.



naphthalene or biphenyl did not proceed because they induced a significant decrease in the electron density upon substitution by the sulfonio group,^[5] which depressed the subsequent propagation reactions. On the other hand, 1,4-bis(methylthio)benzene having two electron-donating methylthio groups was susceptible to polycondensation with 1,4-bis(methylsulfinyl)benzene. The product, poly(thio-1,4-phenylenethio-2,5-bis(methylthio)-1,4-phenylene) (MTPPS), was a relatively low molecular-weight polymer (Table 1), which could be rationalized by the low reactivity due to steric effects.

CONCLUSION

The superacid-induced condensation of aryl sulfoxides was accomplished with aromatic molecules having electron donating substituents. The reaction was exploited for the polycondensation of 1,4-bis(methylsulfinyl)benzene with a variety of aromatic molecules, which provided the convenient synthetic route to methylsulfonioarylene and thioarylene polymers. Further studies on the properties of the obtained polymers and the effect of acidity on the polymerization are in progress, which will be reported in the future.

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