Synthesis and Nucleophilic Dealkylation of Poly[alkyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate]s

Agus Haryono, Kimihisa Yamamoto,[†] Eiichi Shouji, and Eishun Tsuchida*,[‡]

Advanced Research Institute for Science and Engineering, Department of Polymer Chemistry, Waseda University, Tokyo 169-8555, Japan

Received September 30, 1997; Revised Manuscript Received December 17, 1997

ABSTRACT: The dealkylation of sulfonium salts with nucleophiles such as halide ions takes place effectively to yield poly(phenylene sulfide). The kinetic analysis by means of UV−vis spectroscopy reveals that the dealkylation proceeds quantitatively to convert the sulfonium bond to a thioether bond. The reaction rate constants of the dealkylation by the halide ions are in the order $I^- > Br^- > Cl^-$. A propyl substituent on the sulfonium salt results in a lower dealkylation rate than that with methyl substituents, because of the steric hindrance of the propyl group. The demethylation of poly[methyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate] also proceeds efficiently on soaking thin films in dichloromethane solution containing tetraethylammonium halide for 20 h and results in the formation of a transparent and amorphous poly(*p*-phenylene sulfide) (PPS) film, because the synthetic procedure occurs under the glass transition temperature of PPS (90 °C), although PPS is well-known to be a highly crystalline polymer.

Introduction

Sulfonium salts have a proton or other cation species bound to the lone pair of electrons with a weak coordination bond. They have been synthesized by some synthetic routes.[1−10] Sulfonium salts have been known to undergo many synthetically useful reactions such as elimination,[11] addition[12] and alkylation.[13] The sulfonium group is also used as a soluble precursor of poly(*p*-phenylene vinylene)[14] and poly(arylene sulfide)s.[15−22] For these and other applications[23−26] as a new material, the chemical properties of not only the monomeric compounds but also the polymeric sulfonium salts should also be characterized.

Recently, we found that poly[methyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate] is synthesized through a sulfoxide−acid system and is converted to poly(*p*-phenylene sulfide) (PPS) through demethylation.[15,16] The synthetic interest in the method is the reaction temperature. PPS is well-known to be a highly crystalline polymer (crystallinity 40−60%).[27−29] The previously reported method gave a crystalline PPS, because the demethylation reaction was carried out at the reflux temperature of pyridine ($\geq T_g$ of PPS), despite the polymerization being carried out at room temperature. We have examined the demethylation of polysulfonium salts under room temperature ($<T_g$ of PPS) by halide ions to form an amorphous PPS with high molecular weight.

In this paper, novel polysulfonium salts which have a completely alternating structure of sulfide bonds and sulfonium bonds through the phenylene ring were synthesized and were examined for conversion to the poly(phenylene sulfide) chain through the dealkylation compared to those of the corresponding monomeric compound.

Experimental Section

Materials. Thioanisole was purchased from Tokyo Kasei Co., and methyl phenyl sulfoxide was prepared by the oxidation of thioanisole. Propyl phenyl sulfide was purchased from Lancaster Co., and propyl phenyl sulfoxide was prepared by the oxidation of propyl phenyl sulfide. Trifluoromethanesulfonic acid, methanesulfonic acid, sulfuric acid, tetraethylammonium iodide, tetraethylammonium bromide, tetraethylammonium chloride, potassium chloride, and pyridine were purchased from Kanto Chemical Co. Dichloromethane and 1,1,2,2-tetrachloroethane were purified by distillation in the usual manner. Methyl 4-(phenylthio)phenyl sulfoxide was synthesized in the previously reported manner.[15−16]

Synthesis of Methyl-(4-(methylthio)phenyl)phenylsulfonium Trifluoromethanesulfonate. A 300-mL four-necked round-bottom flask fitted with a thermometer, a dropping funnel, a N_2 gas inlet, and a Teflon-covered magnetic stirring bar was charged with methyl phenyl sulfoxide (7 g, 50 mmol), methyl phenyl sulfide (6.2 g, 50 mmol), and dichloromethane (50 mL). The reaction mixture was cooled to 0 °C. Trifluoromethanesulfonic acid (15 g, 100 mmol) in dichloromethane (50 mL) was added to the reaction with the dropping funnel over 20 min. The reaction mixture was stirred at 0 °C. After 30 min, the contents were gradually warmed to room temperature over a 30 min period. The reaction was continued for 20 h at room temperature. The reaction mixture was extracted with dichloromethane (100 mL) and water (300 mL). The organic layer was evaporated and recrystallized from diethyl ether. The obtained colorless crystal was dried under vacuum at room temperature for 20 h (16.5 g; yield, 83%). IR (KBr, cm^{-1}): 3023, 2932, 1571, 1478, 1422, 1258, 1161, 1067, 818, 638. Anal. Calcd for $C_{15}H_{15}S_3O_3F_3$: C, 45.44; H, 3.81. Found: C, 45.31; H, 3.82. ^1H NMR (CD_3CN, 500 MHz) δ: 7.35−7.90 (phenyl, 9H, m), 3.62 (methyl of sulfonium bond, 3H, s), 2.40 (methyl of sulfide bond, 3H, s). ^{13}C NMR (CD_3CN, 125 MHz) δ: 150.45, 135.16, 132.29, 131.19, 130.49, 128.78, 128.24 (phenyl C), 28.23 (methyl of sulfonium bond C), 14.55 (methyl of sulfide bond C).

Synthesis of Propyl-(4-(propylthio)phenyl)phenylsulfonium Trifluoromethanesulfonate (Scheme 1, eq 1). A 300-mL three-necked round-bottom flask fitted with a thermometer, a dropping funnel, a N_2 gas inlet, and a Teflon-covered magnetic stirring bar was charged with propyl phenyl sulfoxide (8.4 g, 50 mmol), propyl phenyl sulfide (7.6 g, 50 mmol), and dichloromethane (50 mL). The reaction mixture

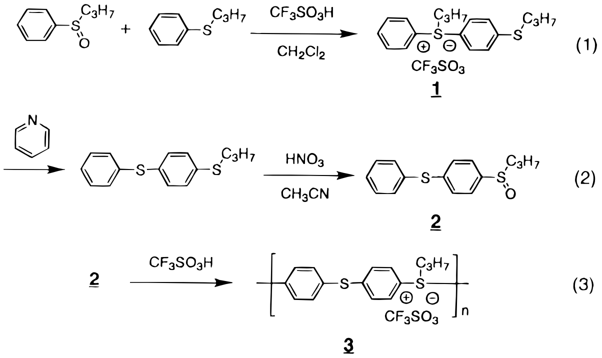
---

[†] Present Address: Department of Chemistry, Keio University, Yokohama 223, Japan.

[‡] CRESTO Investigator.

S0024-9297(97)01435-6 CCC: $15.00

Scheme 1



was cooled to 0 °C. Trifluoromethanesulfonic acid (15 g, 100 mL) in dichloromethane (50 mL) was added to the reaction mixture with the dropping funnel over 20 min. The reaction mixture was stirred at 0 °C. After 30 min, the contents were gradually warmed to room temperature over a 30-min period. The reaction was continued for 20 h at room temperature. The reaction mixture was extracted with dichloromethane (100 mL) and water (300 mL). The organic layer was dried over anhydrous sodium sulfate, evaporated, and dried under vacuum at room temperature for 20 h (19.5 g; yield, 86%). IR (KBr, cm^{-1}): 3023, 2938, 1571, 1478, 1422, 1258, 1161, 1067, 818, 638. Anal. Calcd for $C_{19}H_{23}S_3O_3F_3$: C, 50.43; H, 5.12. Found: C, 50.20; H, 5.15. ^{1}H NMR (CD_3CN, 500 MHz) δ: 7.40−7.83 (phenyl, 9H, m), 3.93 (propyl of sulfonium bond, 2H, t), 2.89 (propyl of sulfide bond, 2H, t), 1.49−1.67 (propyl, 4H, m), 0.94−1.00 (propyl of sulfonium bond, 3H, m), 0.86−0.93 (propyl of sulfide bond, 3H, m). ^{13}C NMR (CD_3CN, 125 MHz) δ: 149.01, 135.39, 132.27, 131.94, 131.24, 129.10, 126.23, 119.81 (phenyl C), 47.10, 22.69, 13.60 (propyl of sulfonium bond C), 34.03, 19.08, 12.76 (propyl of sulfide bond C).

Synthesis of Propyl 4-(Phenylthio)phenyl Sulfoxide (Scheme 1, eq 2). A 200-mL round-bottom flask with a Teflon-covered magnetic stirring bar was charged with propyl-(4-(propylthio)phenyl)phenylsulfonium trifluoromethanesulfonate (15 g, 33 mmol) and pyridine (30 mL). The reaction mixture was heated and stirred for 1 h at 100 °C. The reaction mixture was poured into MeOH−10% HCl (500 mL) and extracted with dichloromethane. The extract was evaporated and dried under vacuum at room temperature. Propyl 4-(phenylthio)phenyl sulfide was isolated with 94% yield (8.1 g).

A 500-mL round-bottom flask with a Teflon-covered magnetic stirring bar was charged with HNO_3 (20%, 120 mL) and propyl 4-(phenylthio)phenyl sulfide (7 g, 27 mmol) in acetonitrile (20 mL). The reaction mixture was mixed with vigorous stirring. The reaction was continued for 4 h at room temperature. The reaction solution became pale green. To the reaction mixture were added a saturated KCl solution and dichloromethane (100 mL). The aqueous layer was extracted twice with dichloromethane (2 × 50 mL) and dried over anhydrous sodium sulfate. After recrystallization from diethyl ether, white needle crystals were obtained (6.5 g; yield, 87%). IR (KBr, cm^{-1}): 3056, 2956, 2936 (ν_{C-H}), 1580, 1476, 1441 ($\nu_{C=C}$), 1046 ($\nu_{S=O}$), 849, 8222 (δ_{C-H}). ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ: 7.35−7.53 (phenyl, 9H, m), 2.66−2.81 (propyl, 2H), 1.56−1.71 (propyl, 2H), 0.97−1.01 (propyl, 3H). ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ: 148.8, 133.4, 132.0, 131.4, 130.5, 129.8, 128.0 (phenyl C), 50.2, 34.5, 19.3 (propyl C). Anal. Calcd for $C_{18}H_{14}S_1O_2$: C, 73.47; H, 4.76. Found: C, 73.32; H, 4.84.

Synthesis of Poly[propyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate] (Scheme 1, eq 3). A 100-mL round-bottom flask fitted with a Teflon-covered magnetic stirring bar was charged with propyl 4-(phenylthio)-phenyl sulfoxide (2.2 g, 8 mmol). The flask was cooled to 0 °C. Trifluoromethanesulfonic acid (10 mL, the concentration of monomer was 0.8 M) was added at 0 °C, and the solution was stirred. The trifluoromethanesulfonic acid acts as a solvent for the polymerization and a reagent for protonation to sulfoxide in this polymerization. The temperature was increased slowly to room temperature. Thereafter, the reaction was quenched by pouring the mixture into ice water. The precipitated polymer was then chopped in a blender, washed with water, and dried under vacuum at room temperature for 20 h (2.9 g; yield, 100%). IR (KBr, cm^{-1}): 3092, 1574, 1485, 1255, 1170, 872, 835, 638. Anal. Calcd for $C_{16}H_{15}S_3F_3O_3$: C, 47.05; H, 3.70. Found: C, 47.01; H, 3.73.

Synthesis of Poly[methyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate]. This polysulfonium salt was synthesized in the previous manner from polymerization of methyl 4-(phenylthio)phenyl sulfoxide in the presence of trifluoromethanesulfonic acid (0.8 M).[15,16]

Demethylation of Polysulfonium Salt at Low Temperature. A 100-mL round-bottom flask which had a Teflon-covered magnetic stirring bar was charged with poly[methyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate] (0.3 g, 0.79 mmol), acetone (15 mL), and acetonitrile (15 mL). The mixture was stirred vigorously in the dark at room temperature, until all of solid was dissolved. Sodium trifluoromethanesulfonate (0.26 g, 1.51 mmol) was put into the polysulfonium salt solution. Tetraethylammonium chloride (0.65 g, 3.95 mmol) was dissolved in an acetonitrile (3 mL) and water (1 mL) mixture. The small amount of water was added to dissolve the tetraethylammonium halide salt completely. This mixture was put into the polysulfonium salt solution and stirred vigorously at room temperature for 5 h. White, solid PPS, which appeared as the result of demethylation, was collected by filtration, washed with water, and dried under vacuum at room temperature for 20 h. IR (KBr, cm^{-1}): 3065, 1572, 1472, 1387, 1091, 1074, 1009, 810, 554, 481.

By using the same method, demethylation of poly[methyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate] by tetraethylammonium bromide (0.83 g, 3.95 mmol) and tetraethylammonium iodide (1.02 g, 3.95 mmol) was carried out.

Preparation of an Amorphous PPS Film. A poly[methyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate] film (0.03 mm) was prepared by casting from acetone solution at room temperature on a Teflon tray. The plate was inserted in a vacuum-dried box and dried for 20 h at 20 °C. The cast film of the polysulfonium salt was soaked in 0.01 M tetraethylammonium chloride (50 mL) for 20 h in the dark. After dipping, the transparent film was washed with water and EtOH and dried under vacuum for 20 h at 25 °C. IR (KBr, cm^{-1}): 3065, 1572, 1472, 1387, 1091, 1074, 1009, 812, 554, 481. Anal. Calcd for C_6H_4S: C, 66.63; H, 3.73. Found: C, 66.50; H, 3.83.

By using the same method, demethylation of the poly[methyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate] thin film in a tetraethylammonium−bromide 0.01 M dichloromethane solution was carried out.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded using a JEOL JNM-LA500. IR spectra were obtained with a JASCO Model IR-810 spectrometer using a potassium bromide pellet. DSC measurement was done in a nitrogen atmosphere using a SEIKO Model SSC/220 thermal analyzer: sample size, 7−10 mg; heating rate, 20 °C/min. Thermogravimetric (TG) measurements were done in a nitrogen atmosphere on a SEIKO Model TG/DTA 220 thermal analyzer: sample size, 7−10 mg; heating rate, 20 °C/min. UV spectra were observed using a Shimadzu UV-2100 spectrometer. Gas chromatography was recorded using a Shimadzu GC-14B. Elemental analysis was performed on a Perkin-Elmer PE-2400 II and a Metrohm 645 Multi DOSIMAT. Two parallel analyses were performed for each sample. The molecular weight of the polymer was determined by high-temperature gel-permeation chromatography (210 °C) on a Senshu VHT-GPC SSC-7000 equipped with a GPC-3506 column (GL Sciences Inc.) and a Soma Optics S-3750 UV−vis absorption detector set at 360 nm. 1-Chloronaphthalene was used as the eluent at a flow rate of 1.0 mL/min. Calibration was performed using narrow polydispersity polystyrene standards.

Results and Discussion

Formation of Monomeric and Polymeric Sulfonium Salts. Methyl-(4-(methylthio)phenyl)phenylsul-

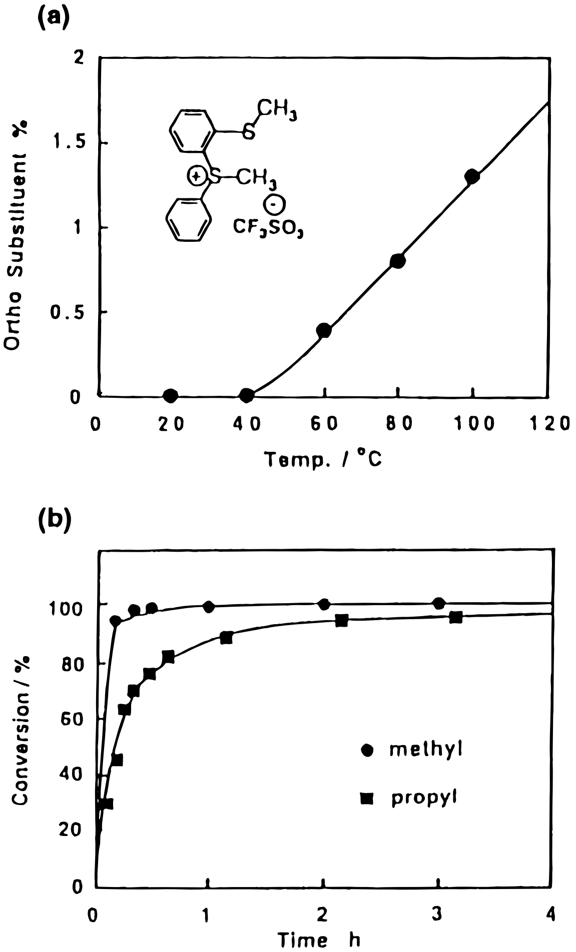


Figure 1. (a) Effect of reaction temperature in the electrophilic substitution reaction on the ortho/para selectivity. (b) Effect of substituent on the coupling reaction of the sulfide and sulfoxide compounds (R = methyl and propyl).

fonium salt was formed through a coupling reaction of methyl phenyl sulfoxide and thioanisole. This reaction was influenced by the acidity of the reaction mixture, as has already been reported in the previous paper.[16] Trifluoromethanesulfonic acid as the strongest protic acid is the most effective for the quantitative formation of the sulfonium cation in comparison with methanesulfonic acid and sulfuric acid. After a 30-min reaction at room temperature, the sulfonium salt was formed at approximately 100% conversion.[30]

The coupling reaction was initiated by protonation of methyl phenyl sulfoxide to give methylphenylhydroxysulfonium cation as an active species. The active species preferentially attacks the phenyl carbon of thioanisole at the para-position under room-temperature conditions. The para-selectivity was confirmed by the controlled reaction of methyl phenyl sulfoxide with thioanisole (Figure 1a). The para-selectivity was drastically influenced by the reaction temperature (Scheme 2).[31] The ortho-substituted product was not detected below 40 °C reaction conditions. At 100 °C, 1.3% of the ortho-substituted product (methyl-(2-(methylthio)phenyl)phenylsulfonium trifluoromethanesulfonate) was observed.

The coupling reaction of propyl phenyl sulfoxide with propyl phenyl sulfide also resulted in quantitative formation of the propyl-substituted sulfonium salt. The methylene proton in the propyl group is not eliminated during the reaction. The coupling reaction was slower than the methyl-substituted one because of the steric hindrance (Figure 1b). The propylphenyl-(4-(propylthio)phenyl)sulfonium salt was isolated as a stable salt having the empirical formula $C_{19}H_{23}S_3O_3F_3$. Depropylation proceeded quantitatively by pyridine reflux to yield propyl 4-(phenylthio)phenyl sulfide.

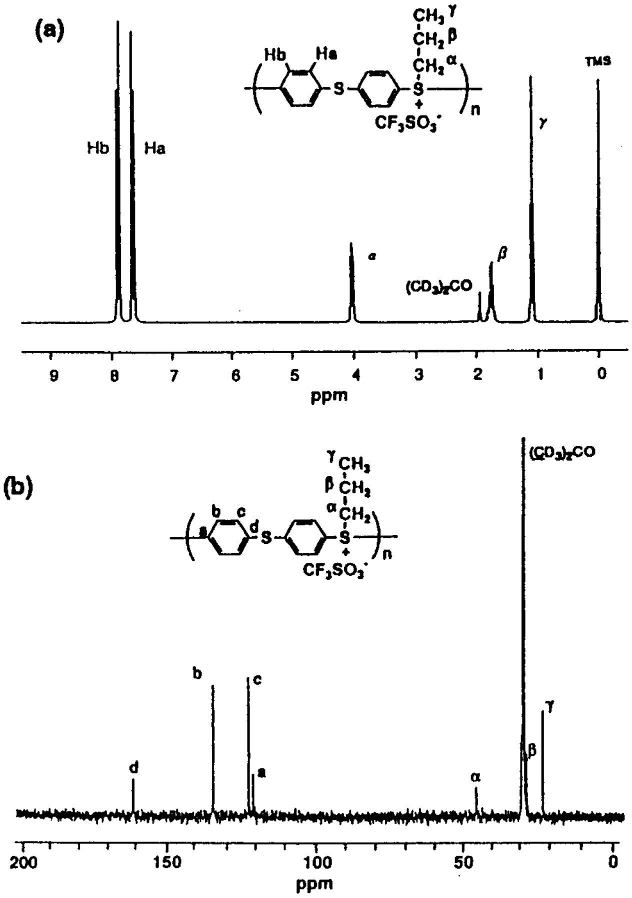
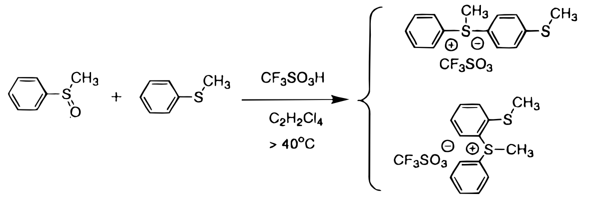


Figure 2. ^{1}H (a) and ^{13}C NMR (b) spectra of poly[propyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate] in $(CD_3)_2CO$ at 20 °C.

Scheme 2



The polymerization of propyl 4-(phenylthio)phenyl sulfoxide as a monomer was performed under the same conditions. The color of the reaction mixture changed to green at room temperature, and the viscosity of the reaction mixture gradually increased. After precipitation in water, the polysulfonium salt was quantitatively isolated as a white resin having the empirical formula $C_{16}H_{15}S_3F_3O_3$. The ^{1}H and ^{13}C NMR spectra of the resulting polymer are shown in Figure 2a and b, respectively. In the ^{1}H NMR spectrum, three kinds of peaks attributed to methyl protons (γ) and methylene protons (α, β) are observed at 1.09 and at 1.76 and 4.06 ppm, respectively. The α protons of the methylene group substituted by the sulfonium cation appear in a lower magnetic field than that of a neutral methylene sulfide group. The observation of AB quartet peaks at 7.63, 7.67, 7.88, and 7.92 ppm supports the formation of the polysulfonium salt which has the alternating

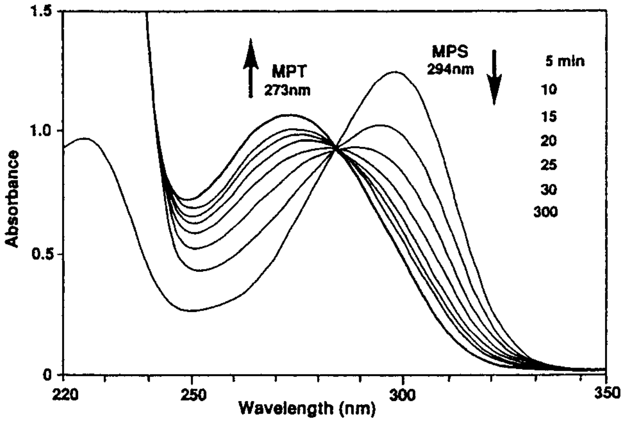


Figure 3. UV spectral changes in methyl-(4-(methylthio)-phenyl)phenylsulfonium trifluoromethanesulfonate demethylated by tetraethylammonium bromide (6.3 × 10^{-5} M, in acetonitrile at 25 °C).

structure of sulfide and sulfonium cations through the phenylene ring (Figure 2). In the ^{13}C NMR spectrum, three kinds of peaks (46.0, 28.6, 24.1 ppm) are attributed to the propyl carbon and four kinds of peaks (161.5, 135.0, 123.4, 121.8 ppm) are attributed to the phenyl carbon. The signal attributed to the propyl sulfinyl group as a terminal group was not detected in the ^1H and ^{13}C NMR spectra. The typical absorption band attributed to the C−H out-of-plane vibration of the 1,4-phenylene structure was observed at 816 cm^{-1}. The IR spectrum indicates that the resulting polymer contains $CF_3SO_3^-$ (1258, 638 cm^{-1}) and an alkyl group (2932 cm^{-1}). These spectroscopic data reveal the formation of poly[propyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate].

The polysulfonium salt is soluble in common solvents such as acetonitrile, acetone, dimethyl sulfoxide (DMSO), formic acid, and sulfuric acid. To convert to PPS from the polysulfonium salts, the dealkylation was carried out in the previously reported manner,[27,28] PPS was isolated in 100% yields, and the molecular weight of the polymer was determined to be 1.2 × 10^5 (20 h, 25 °C) and 6.7 × 10^4 (5 h, 25 °C) by high-temperature GPC.

Dealkylation of Sulfonium Salts. The demethylation of methyl-(4-(methylthio)phenyl)phenylsulfonium trifluoromethanesulfonate to methyl 4-(phenylthio)-phenyl sulfide was carried out using halide ions as nucleophiles. The S_N2-type reaction of nucleophiles such as pyridine, tetraethylammonium bromide, tetraethylammonium iodide, and tetraethylammonium chloride proceeds quantitatively to yield methyl 4-(phenylthio)-phenyl sulfide. Only methyl 4-(phenylthio)phenyl sulfide was detected from gas chromatography and ^1H NMR measurements.[32] Methyl-(4-(methylthio)phenyl)-phenylsulfonium trifluoromethanesulfonate (MPS) and methyl 4-(phenylthio)phenyl sulfide (MPT) show a λ_{max} at 294 nm (ϵ: 1.90 × 10^4 cm^{-1} M^{-1}) and at 273 nm (ϵ: 1.78 × 10^4 cm^{-1} M^{-1}), respectively, in acetonitrile. UV spectra of the sulfonium salts in acetonitrile have an isosbestic point at 282 nm (Figure 3) on addition of the nucleophile (tetraethylammonium bromide), which indicates the quantitative conversion to the sulfides from the sulfonium salts. The kinetics obey a pseudo-first-order reaction (Figure 4). After the demethylation, the equimolar formation of methylene bromide (2.69 ppm) is also confirmed by means of ^1H NMR. These results indicate that demethylation proceeds quantitatively through the nucleophilic attacks of the halide ion at the sulfonium cation to eliminate methylene halide. A PM3 molecular orbital calculation reveals that the two-center energy of the S−C (alkyl) bond (−14.8 eV) is estimated to be lower than that of the S−C (phenyl) bond (−15.9 eV) in the sulfonium molecules. The selective cleavage of the S−C (methyl) bond was supported by the semiempirical molecular orbital calculation.

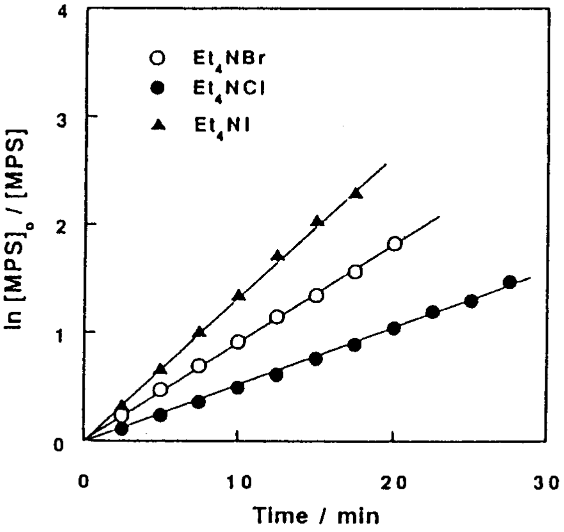


Figure 4. Plot of pseudo-first-order reaction on demethylation of methyl-(4-(methylthio)phenyl)phenylsulfonium trifluoromethanesulfonate (MPS) (at 25 °C, in acetonitrile). $[MPS]_0$ and [MPS] are the concentration of MPS at the initial time (before reaction) and after reaction time *t*, respectively.

Table 1. Rate Constant of Demethylation of Diarylalkylsulfonium

Nu[a]	temp/°C	solvent	permittivity	rate constant (k × 10^{-1}/M^{-1}·s^{-1})
Cl^-	25	CH_3CN	37.5	2.6
Br^-	25	CH_3CN	37.5	4.2
I^-	25	CH_3CN	37.5	6.6
Br^-	25	CH_2Cl_2	9.1	49
Br^-	25	NMP	32.0	13
Br^-	25	DMF	36.7	5.3
Br^-	25	DMSO	48.9	0.5
Br^-	15	CH_3CN	37.5	0.9
Br^-	32	CH_3CN	37.5	8.1
Br^-	41	CH_3CN	37.5	22

[a] The nucleophiles used were tetraethylammonium halide salts.

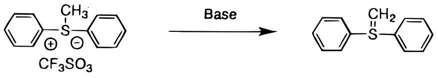
The kinetics of the reaction were evaluated by means of UV−vis measurement. On the basis of the kinetics results, the reaction rate constants of the dealkylation by halide ions are in the order I^- > Br^- > Cl^- (Table 1). The reaction behavior is typically observed in the nucleophilic reaction. Solvation on a small size ion such as chloride ion retards the substitution due to the large solvated coordination sphere. The effect of the counteranion on the rate constant was observed definitely as $SbCl^-$ > $CF_3SO_3^-$ = ClO_4^- (Table 2). This means that the polysulfonium salts are well-solvated in acetonitrile. The rate constant is also influenced by the substituents; for example, the demethylation proceeds more rapidly than that with a propyl group. The dealkylation selectively occurs in the presence of the nucleophiles, in the case of the sulfonium substituted with a methylene unit, which enables the formation of a sulfonium ylide structure in the presence of the base (Scheme 3).

On the basis of the van't Hoff analysis, activation energies (E_a) and frequency factors (A) were determined

Table 2. Effect of Counteranion on the Rate Constants of Demethylation of Diarylalkylsulfonium

Nu	counteranion	rate constant ($k \times 10^{-1}$/$M^{-1} \cdot s^{-1}$)
	ClO_4^-	2.6
Et_4NCl	$CF_3SO_3^-$	2.6
	$SbCl_6^-$	3.7
	ClO_4^-	4.1
Et_4NBr	$CF_3SO_3^-$	4.2
	$SbCl_6^-$	6.6
	ClO_4^-	6.7
Et_4NI	$CF_3SO_3^-$	6.6
	$SbCl_6^-$	

Scheme 3



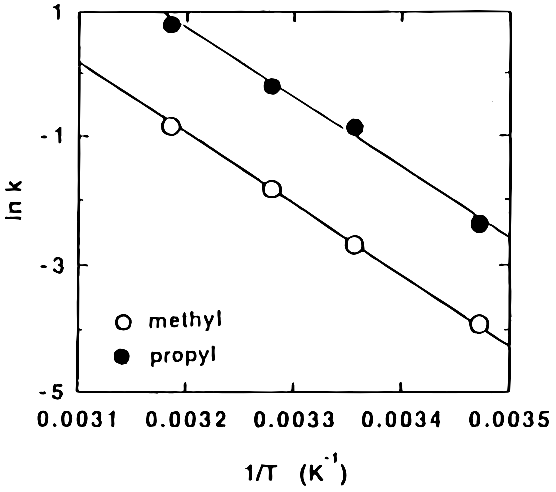


Figure 5. Arrhenius plot of dealkylation of the diarylalkylsulfonium salt (demethylated by tetraethylammonium bromide in acetonitrile; black plot is propyl group, and white one is methyl group).

Table 3. Obtained Kinetic Parameters

alkyl group	activation energy (E_a/kJ·mol^{-1})	frequency factor (A/M·s^{-1})	molar extinction coefficient (ϵ/cm^{-1}·M^{-1})
methyl	94	9.5×10^{15}	1.9×10^4
propyl	92	8.7×10^{14}	1.7×10^4

by Arrhenius plots (Figure 5 and Table 3). E_a and A in the nucleophilic reaction of tetraethylammonium bromide with methylphenyl-(4-(methylthio)phenyl)sulfonium trifluoromethanesulfonate are estimated to be E_a = 94 kJ·mol^{-1} and $A = 9.5 \times 10^{15}$ M·s^{-1}, respectively. Propylphenyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate gave the values E_a = 92 kJ·mol^{-1} and $A = 8.7 \times 10^{14}$ M·s^{-1}. The difference in the frequency factor is caused by the steric hindrance of the propyl group.

The kinetics also depend on the permittivity of the solvents (Figure 6). In dichloromethane with low permittivity ($\epsilon = 10$), the largest rate constant was observed. These results also support the typical solvent effect in the nucleophilic reaction, through the solvation of ionic species.

In the case of phenyl-(4-(phenoxy)phenyl)sulfonium trifluoromethanesulfonate, the nucleophilic reaction does not take place under the same conditions. The corresponding bromide salts were isolated through the exchange reaction of the counteranion. This indicates higher stability and lower reactivity of the triphenyl-substituted sulfonium salt toward nucleophiles due to resonance stabilization.

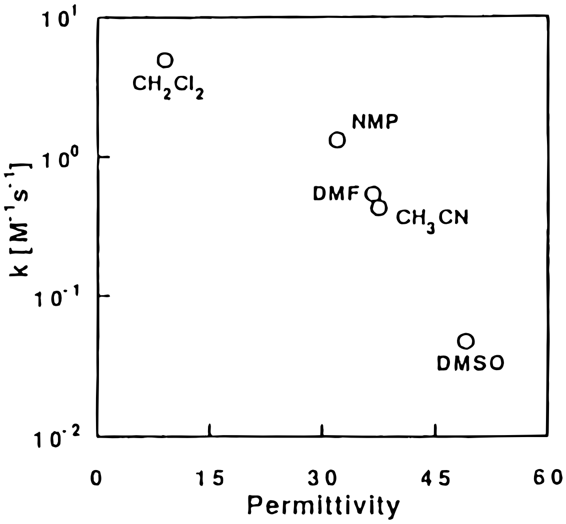


Figure 6. Dependence of the kinetics of dealkylation of sulfonium compounds on the solvent's permittivity.

Table 4. Demethylation of Polysulfonium

Nu	temp/°C	time/h	yield/%	T_g/°C	T_c/°C	T_m/°C	$T_{d\ 10\%}$/°C	10^5M_w
Cl^-	20	5	94	98	150	272	512	2.39
Br^-	20	5	94	99	152	272	516	1.87
I^-	20	5	100	95	141	276	517	0.99
Cl^-	0	5	91	99	161	263	511	6.21
Br^-	0	5	94	97	152	272	512	2.15
I^-	0	5	94	99	151	273	513	0.95
Cl^-	20	20[a]	91	96	141	276	520	2.16
Br^-	20	20[a]	97	96	140	276	520	1.11

[a] The demethylation of the polysulfonium cast film by dipping in dichloromethane.

Dealkylation of Polysulfonium Salts. The demethylation of poly[methyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate] was carried out in acetonitrile in the presence of tetraethylammonium halide at 5.0 molar equiv compared to the polymer unit because polysulfonium salts are soluble in acetonitrile (Table 4). During the demethylation, the reaction mixture became cloudy and then formed a white powder precipitate within 1 min. The demethylation of the polysulfonium salts proceeds more rapidly than that of the monomeric material due to the electron-donating effect of the thioether groups at both sides of the sulfonium unit.

The polymer was isolated in over 90% yield based on the theoretical weight of PPS. After the demethylation, the resulting polymers show different molecular weights and thermal properties. The demethylation by chloride ion results in a lower yield of PPS, due to the low reactivity. The polymer might contain a small amount of unreacted sulfonium moieties.

The nucleophilic dealkylation using chloride ion induces the formation of higher molecular weight poly(phenylene sulfide), because the reaction rate constant was smaller than those of the other nucleophiles. It is believed that the dealkylation has not been completed, and the resulting polymer contains trace amounts of unreacted sulfonium moieties. The resulting polymer shows a higher T_c and lower T_m in comparison with those of other polymers prepared using other nucleophiles. The contamination of the sulfonium moieties tends to cause a higher T_c and lower T_m of the resulting

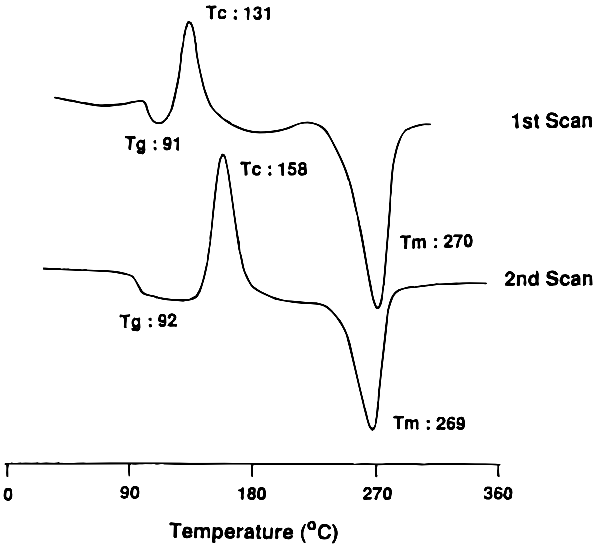


Figure 7. DSC (20 °C/min) thermograms of the resulting PPS which has been demethylated using tetraethylammonium bromide: (a) first scan; (b) second scan (after quenching).

polymer. The T_c of the polymer increases with an increase in the degree of unreacted moieties which act as a crystalline core during heating.

Formation of an Amorphous PPS. The demethylation of a cast film of polysulfonium salt (film thickness, 30 mm) was carried out heterogeneously by dipping the film in CH_2Cl_2 solution in the presence of TEACl or TEABr for 20 h. The resulting film retained its transparency without defect and was identified to be PPS ($T_{d\,10\%}$, 523 °C; M_w, 1.1×10^5). The IR spectrum of this resulting film agrees with that of the commercially available material. The absorption attributed to the methyl group disappeared, and a typical band attributed to a C−H out-of-plane vibration of the 1,4-phenylene structure was observed at 812 cm^{-1}. The CP/MAS ^{13}C NMR shows two peaks at 132.3 and 134.1 ppm which are attributed to the typical phenyl carbons of PPS.

The DSC thermogram of the resulting PPS film is shown in Figure 7. Especially, DSC analysis displays the T_g and T_c even in the first scan. The behavior is different from that of highly crystalline PPS, which is usually crystallized during the preparation by polycondensation at high temperature.[33] X-ray analysis (Cu Kα radiation) shows no diffraction peaks and only an amorphous halo. These results support the formation of an amorphous PPS film. After heating above the T_g, the crystalline structure was recovered. The demethylation of polysulfonium at room temperature provides a direct method of preparation of a transparent PPS film without any procedures involving rapid quenching after melting.

Conclusions

The sulfoxide−acid reaction of aryl sulfoxides provided the well-defined poly[alkyl-(4-(phenylthio)phenyl)-sulfonium trifluoromethanesulfonate]s. The conversion to poly(arylene thioether) was examined through the controlled reaction of the corresponding monomeric sulfonium salts. The dealkylation with halide ion as a nucleophile takes place quantitatively to convert the sulfonium bond to a thioether bond through the elimination of alkyl halide. The dealkylation of the polysulfonium salts with tetraethylammonium iodide results in the efficient formation of poly(*p*-phenylene sulfide). The procedures at room temperature could be applied to the formation of transparent and amorphous poly(*p*-phenylene sulfide) (PPS) (T_g, 91 °C; T_c, 131 °C; T_m, 270 °C; $T_{d\,10\%}$, 524 °C) by dipping a poly[methyl-(4-(phenylthio)phenyl)sulfonium trifluoromethanesulfonate] film in an HCl aqueous solution even though PPS is a well-known crystalline polymer.

Acknowledgment. This work was partially supported by a Grant-in-Aid for International Scientific Research Program (Joint Research No. 08044174), JSPS fellows (No. 085344) and for Scientific Research from the Ministry of Education Science and Culture (Nos. 09555297 and 09650982), and The Tokuyama Science Fundation.

References and Notes

(1) Roush, D. M.; Price, E. M.; Templeton, L. K.; Hethcock, C. H. *J. Am. Chem. Soc.* **1979**, *101*, 2971.
(2) Nesmeyanov, A. N.; Makarova, L. G.; Tolstaya, T. P. *Tetrahedron* **1957**, *1*, 145.
(3) Saeva, F. D.; Morgan, B. P.; Luss, H. R. *J. Org. Chem.* **1985**, *50*, 4360.
(4) Meerwein, H. *Org. Synth.* **1973**, *5*, 1080.
(5) Milligan, T. W.; Minor, B. C. *J. Org. Chem.* **1962**, *28*, 235.
(6) Smiles, S.; LeRossgnol, R. *J. Chem. Soc.* **1960**, *89*, 696.
(7) Wiegand, G. H.; McEwen, W. E. *J. Org. Chem.* **1968**, *33*, 2671.
(8) Miller, R. D.; Renaldo, A. F.; Ito, H. *J. Org. Chem.* **1988**, *53*, 5571.
(9) Hartke, K. *Chem. Ber.* **1979**, *112*, 2436.
(10) Minato, H.; Miura, T.; Kobayashi, M. *Chem. Lett.* **1976**, 677.
(11) Stirling, C. J. M. *Int. J. Sulfur Chem., Part C* **1971**, *6*, 41.
(12) Tillet, J. G. *Chem. Rev.* **1976**, *76*, 747.
(13) Shouji, E.; Nishimura, S.; Yamamoto, K.; Tsuchida, E. *Polym. Adv. Technol.* **1993**, *5*, 507.
(14) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1984**, *25*, 327.
(15) Yamamoto, K.; Shouji, E.; Nishide, H.; Tsuchida, E. *J. Am. Chem. Soc.* **1993**, *115*, 5819.
(16) Tsuchida, E.; Shouji, E.; Yamamoto, K. *Macromolecules* **1993**, *26*, 7144.
(17) Shouji, E.; Yamamoto, K.; Tsuchida, E. *Chem. Lett.* **1993**, 1927.
(18) Tsuchida, E.; Suzuki, F.; Shouji, E.; Yamamoto, K. *Macromolecules* **1994**, *27*, 1057.
(19) Shouji, E.; Nishimura, S.; Yamamoto, K.; Tsuchida, E. *Chem. Lett.* **1994**, 403.
(20) Yamamoto, K.; Shouji, E.; Suzuki, F.; Kobayashi, S.; Tsuchida, E. *J. Org. Chem.* **1995**, *60*, 452.
(21) Tsuchida, E.; Yamamoto, K.; Shouji, E. *Macromolecules* **1993**, *26*, 7389.
(22) Tsuchida, E.; Yamamoto, K.; Shouji, E.; Katoh, J.; Matsuo, M.; Kamiya, H. *Macromolecules* **1994**, *27*, 7504.
(23) Pappas, S. P.; Pappas, B. C.; Gatechair, L. R.; Schnabel, W. J. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 69.
(24) Ito, H.; Wilson, C. G. *Polym. Eng. Sci.* **1983**, *23*, 1012.
(25) Pappas, S. P.; Jilek, J. H. *Photogr. Sci. Eng.* **1979**, *23*, 140.
(26) Bordwell, F. G.; Boutan, P. J. *J. Am. Chem. Soc.* **1956**, *78*, 87.
(27) Boon, J.; Magre, E. P. *Makromol. Chem.* **1969**, *126*, 130.
(28) Boon, J.; Magre, E. P. *Makromol. Chem.* **1970**, *136*, 267.
(29) Brady, D. G. *J. Appl. Polym. Sci.* **1976**, *76*, 2571.
(30) The conversion was defined after nucleophilic demethylation of sulfonium salt by pyridine at reflux temperature and was calculated as [4-(methylthio)phenyl phenyl sulfide]/[(thioanisole) + (4-(methylthio)phenyl phenyl sulfide)].
(31) The temperature effect in the coupling reaction between thioanisole and methyl phenyl sulfoxide was studied in 1,1,2,2-tetrachloroethane solvent with the same reaction conditions, at 20, 40, 60, 80, and 100 °C. The ortho substituent was defined after nucleophilic demethylation of sulfonium salt by pyridine at reflux temperature, and calculated as {-[2-(methylthio)phenyl phenyl sulfide]}/{[2-(methylthio)phenyl phenyl sulfide] + [4-(methylthio)phenyl phenyl sulfide]}.
(32) ^1H NMR spectrum (2.35 ppm, methyl, s; 7.0−7.7 ppm, phenyl, m; at 20 °C in CD_3CN).
(33) Lopez, L. C.; Winlkes, G. L. *J. Makromol. Sci. Rev.* **1989,** *29*, 83.

MA971435I