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Synthesis of High Molecular Weight Poly(phenylene sulfide) by Oxidative Polymerization via Poly(sulfonium cation) from Methyl Phenyl Sulfoxide

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

Department of Polymer Chemistry, Waseda University, Tokyo 169, Japan

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ABSTRACT: High molecular weight poly(phenylene sulfide) (PPS), $M_w > 2 \times 10^5$) was synthesized via a poly(sulfonium cation) through oxidative polymerization of methyl 4-(phenylthio)phenyl sulfoxide. Polymerization proceeds in protic acid homogeneously. The poly(sulfonium cation) was soluble in common solvents such as formic acid and dimethyl sulfoxide. It was feasible to obtain high molecular weight poly(arylene sulfide) through the S_N2 reaction with pyridine as nucleophile. The poly(sulfonium cation) was available as a soluble intermediate for the synthesis of high molecular weight poly(phenylene sulfide).

Introduction

High molecular weight poly(phenylene sulfide) (PPS) deserves much attention as a high-performance engineering plastic because of its excellent chemical, thermal, and mechanical properties due to its the high crystallinity.[1-6] These excellent properties make it difficult to synthesize a high molecular weight PPS. Therefore, the preparation of PPS employs high-temperature and high-pressure processes in order to improve poor solvent solubility, e.g. commercial preparations of PPS are often carried out at temperature in excess of the boiling point of NMP, which requires the use of pressure vessels. Until now there had been much effort put into the formation of a high molecular weight poly(arylene sulfide) (PAS).[7-15] PPS is also obtained by other reaction mode, e.g. an electrophilic reaction and oxidative polymerization.[16-21] The polymerization proceeds at room temperature and provides pure PPS, but it results in a low molecular weight due to its poor solubility.

These synthetic difficulties are overcome by the use of a soluble precursor for the target polymer. Thus, conductive polymers such as poly(*p*-phenylenevinylene) (PPV)[22-25] and poly(*p*-phenylene) (PPP),[26-28] which are insoluble in common solvents, are synthesized via the soluble precursor. Thermostable plastics such as poly(ether ether ketone) (PEEK)[29] and poly(arylene sulfide ketone)[30] are also obtained via the soluble precursor with this elegant idea. We have found a new synthetic route for the formation of high molecular weight PPS via the soluble precursor under mild conditions using the sulfoxide–acid system.[31] This paper describes the new synthesis and the structure of the resulting PPS and also the polysulfonium cation as a soluble precursor.

Experimental Section

Materials. Thioanisole is purified by distillations in the usual manner. Methyl phenyl sulfoxide is prepared by the oxidation of thioanisole. Bromine, potassium hydrogen carbonate, anhydrous sodium sulfate, trifluoromethanesulfonic acid, and pyridine were purchased from Tokyo Kasei Co. Ltd. and used without further purification. Dichloromethane is purified by distillation in the usual manner.

Polymerization Method. i. Poly[methyl[4-(phenylthio)phenyl]sulfonium trifluoromethanesulfonate] (PPST). A 100-mL, round-bottom flask with a Teflon-covered magnetic stirring bar was charged with methyl 4-(phenylthio)phenyl sulfoxide (1 g, 4 mmol). The flask was cooled to 0 °C. Trifluoromethanesulfonic acid (5 mL, the concentration of monomer 0.8 M) was added at 0 °C and stirred. The trifluoromethanesulfonic acid acts as a solvent for the polymerization and a reagent for protonation to sulfoxide for this polymerization. The temperature was increased slowly to room temperature over a period of 0.5–1 h. The reaction solution turned from colorless to a pale blue. The reaction was continued for another 20 h at room temperature. The reaction was then quenched by pouring it into ice–water. The precipitated polymer was then chopped in a blender, washed with water, and dried in vacuum at room temperature for 20 h. Yield: 1.53 g (100%). IR (KBr, cm-1): 3086, 3023, 2932 (ν_{C-H}), 1570, 1478, 1422 ($\nu_{C=C}$), 1258, 638 (ν_{C-F}), 1161, 1067 ($\nu_{S=O}$), 816 (δ_{C-H}). ^1H and ^{13}C NMR are shown in Figure 2b. Anal. Calcd for $C_{14}H_{11}S_3F_3O_3$: C, 44.20; H, 2.91; S, 25.28. Found: C, 44.10; H, 2.73; S, 25.11.

ii. Poly(*p*-phenylene sulfide) (PPS). A 200-mL, three-neck, round-bottom flask equipped with a Teflon-covered magnetic stirring bar, reflux condenser, thermometer, and N_2 gas inlet was charged with PPST (1 g, 2.6 mmol) and pyridine (10 mL). The reaction mixture was stirred at room temperature. PPST is soluble in pyridine. The reaction solution become slightly pale yellow. After a few minutes, the reaction mixture turned into a white suspension. The reaction was continued for 1 h at room temperature and then the temperature was slowly raised to reflux. The reaction was continued for 20 h at reflux temperature. The reaction was then quenched by cooling it down to room temperature and then poured into methanol (200 mL, 10% HCl). The precipitate was washed with methanol and chloroform. The polymer was purified by continuous extraction in a Soxhlet apparatus with ethanol for 5 h and was dried in vacuo at 60 °C for 20 h. The resulting polymer was isolated as a white powder. Yield: 0.56 g 99%. IR (KBr, cm^{-1}): 3065 (ν_{C-H}), 1572, 1472, 1387 ($\nu_{C=C}$), 810 (δ_{C-H}), 1091, 1074, 1009, 554, 481. CP/MAS ^{13}C NMR (400 MHz, ppm): 132.1, 134.3 (phenyl C). Anal. Calcd for C_6H_4S: C, 66.63; H, 3.73; S, 29.64. Found: C, 66.80; H, 3.63; S, 29.61.

Synthesis of Methyl Phenyl Sulfoxide. A 500-mL, round-bottom flask with a Teflon-covered magnetic stirring bar was charged with dichloromethane (100 mL), 10% $KHCO_3$ (200 mL), and thioanisole (12.4 g, 100 mmol). To the reaction mixture was added bromine (16 g, 100 mmol) in dichloromethane (50 mL) over a period of 10 min with vigorous stirring. The reaction was continued for 30 min. The reaction solution became pale orange. To the reaction mixture was added KCl saturated solution and dichloromethane (100 mL). The aqueous layer was extracted with dichloromethane (2 × 50 mL) and dried over anhydrous sodium sulfate. After recrystallization from ether at −30 °C, an oily pale yellow solution was obtained 13.3 g at room temperature (yield 95%). The liquid was dried under vacuum at room temperature for 20 h and then used without further purification. IR (KBr, cm^{-1}): 3060, 2919 (ν_{C-H}), 1576, 1476, 1439 ($\nu_{C=C}$), 1051 ($\nu_{S=O}$), 812 (δ_{C-H}), 738, 689. ^1H NMR (400 MHz, ppm, $CDCl_3$): 7.72–7.40 (phenyl, 5 H, m), 2.72 (methyl, 3 H). Anal. Calcd

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for C_7H_8SO: C, 59.97; H, 5.75; S, 22.87. Found: C, 60.1; H, 5.7; S, 23.1.

Synthesis of Methylphenyl[4-(methylthio)phenyl]sulfonium Perchlorate (MSP). A 300-mL, three-neck, round-bottom flask, which had a thermometer and N_2 gas inlet and was equipped with a Teflon-covered magnetic stirring bar, was charged with methyl phenyl sulfoxide (7 g, 50 mmol) and thioanisole (6.2 g, 50 mmol). The reaction mixture was cooled to 0 °C. Methanesulfonic acid (100 mL) was added to the reaction. The temperature was gradually raised to room temperature over a 30-min period. The reaction was continued for 20 h at room temperature. The reaction mixture was then poured into perchloric acid (60%, 100 mL) and stirred for 1 h at room temperature, and then water (100 mL) and dichloromethane (100 mL) were added. The aqueous layer was extracted with dichloromethane (2 × 50 mL). The organic layer was dried over anhydrous sodium sulfate. After evaporation, a white residue was purified by recrystallization with ether. The white solid, 15.6 g (yield 90%), was dried under vacuum at room temperature for 20 h. IR (KBr, cm^{-1}): 3003, 2920 (ν_{C-H}), 1088, 625 (ν_{C-Cl}), 816 (δ_{C-H}). ^1H and ^{13}C NMR are shown in Figure 2a. Anal. Calcd for $C_{14}H_{15}S_2ClO_4$: C, 48.48; H, 4.36; S, 18.49. Found: C, 48.32; H, 4.40; S, 18.34; Cl, 10.22.

Synthesis of Methyl 4-(Phenylthio)phenyl Sulfide (MPS). A 200-mL, three-neck, round-bottom, flask which had a reflux condenser and N_2 gas inlet and was equipped with a Teflon-covered magnetic stirring bar, was charged with MPS (10 g, 28.8 mmol). Pyridine (50 mL) was added at room temperature and stirred for 30 min at room temperature. The temperature was increased to 100 °C, and reaction was continued for 10 min. The reaction mixture was poured into 10% HCl solution (300 mL) and was extracted with dichloromethane. The product was purified by flash column chromatography on silica gel using hexane–chloroform (3:1) as the eluent. After evaporation of the solvents, a colorless liquid (6.4 g, 95% yield) was obtained. The liquid was dried under vacuum at room temperature for 20 h. IR (KBr, cm^{-1}): 3057, 2919 (ν_{C-H}), 1580, 1476, 1437 ($\nu_{C=C}$), 810 (δ_{C-H}), 739, 689. ^1H NMR (400 MHz, ppm, $CDCl_3$): 7.29–7.01 (phenyl, 9 H, m), 2.26 (methyl, 3 H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$): 126.6, 127.1, 129.0, 130.1, 131.4, 132.2, 136.4, 138.2 (phenyl C), 15.6 (methyl C). Anal. Calcd for $C_{13}H_{12}S_2$: C, 67.2; H, 5.21; S, 27.6. Found: C, 67.0; H, 5.24; S, 27.4.

Synthesis of Methyl 4-(Phenylthio)phenyl Sulfoxide (PSO). A 500-mL, round-bottom flask with a Teflon-covered magnetic stirring bar was charged with dichloromethane (50 mL), 10% $KHCO_3$ (43 mL), and MPS (5 g, 21.6 mmol). To the reaction mixture was added bromine (3.45 g, 21.6 mmol) in dichloromethane (50 mL) over a period of 5 min with vigorous stirring. The reaction was continued for 30 min. The reaction solution became pale orange. To the reaction mixture was added a KCl saturated solution and dichloromethane (100 mL). The aqueous layer was extracted with dichloromethane (2 × 50 mL). The organic layer was washed with water, dried over anhydrous sodium sulfate, and filtered. After recrystallization from ether, the white solid was obtained (4.8 g, yield 90%). The white solid was dried under vacuum at room temperature for 20 h and then used without further purification for polymerization. MS (m/e): 248, 232, 217, 184, 108. IR (KBr, cm^{-1}): 3061, 2919 (ν_{C-H}), 1576, 1476, 1439 ($\nu_{C=C}$), 1051 ($\nu_{S=O}$), 816 (δ_{C-H}), 750, 639. ^1H NMR (400 MHz, ppm, $CDCl_3$): 7.30–7.57 (phenyl, 9 H, m), 2.67 (methyl, 3 H). ^{13}C NMR (400 MHz, ppm, $CDCl_3$): 124.5, 128.5, 129.7, 133.0, 133.5, 141.5, 144.3 (phenyl C), 46.0 (methyl C). Anal. Calcd for $C_{13}H_{12}S_2O$: C, 62.87; H, 4.87; S, 25.82. Found: C, 62.89; H, 4.91; S, 25.72.

Measurements. ^1H and ^{13}C NMR spectra were recorded using a 400-MHz FT-NMR GXS 400. 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 SEIKO Model SSC/220 thermal analyzer: sample size, 7–10 mg; heating rate, 20 °C/min. Thermogravimetric analyses (TG) 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. The determination of the molecular weight of the PPS was measured using a high-temperature GPC (Senshu Scientific Co. Ltd., SSC VHT-7000) with α-chloronaphthalene (flush column grade was purchased from Wako Jyunyaku Co. Ltd.) as the eluent. The absorption detector of this GPC is Soma Optics S-3750 UV/Vis absorption detector. Shodex GPC columns (AT-80M/s) were used for the measurement. In order to obtain a homogeneous polymer slurry, 6 mg of the polymer samples in 3 mL of α-chloronaphthalene was stirred and dissolved completely at 250 °C for 4 min and the solution was filtrated using Teflon membrane filter (purchased from ADVANTEC Co. Ltd.). The filtrated solution was quenched to room temperature. On each run, 500 μL of polymer slurry was injected at room temperature and redissolved at 250 °C through the capillary (0.5 mm i.d. × 1 m) in the preheater. The operating temperature was 210 °C (main column) and 250 °C (precolumn) with a flow rate of 1.0 mL/min. The detector was a UV–vis spectrometer (Senshu Scientific Co. Ltd., S-3750). A weak absorption at 354 nm (skirts) of PPS was employed to detect PPS after the injection of concentrated samples (2 mg/mL). This method has been reported by Stacy.[32] A well-defined polystyrene-substituted pyrene group was used as a standard sample (purchased from Polymer Standard Services Co. Ltd.) with MW ranging from 10^3 to 10^6. There were 10 samples in the region to calibrate the molecular weight. The molecules' weight distribution (MWD) were 1.0–1.2 (labeled). The polymer samples were dissolved at 2 mg/mL in the α-chloronaphthalene at 240 °C for 5 min and then cooled at 25 °C. The hot solution (240 °C) was filtered through 0.2-μm Teflon filters. The data acquisition was performed with a NEC-PC98 personal computer.

Computational Calculation. Reactivity (stability) of the sulfonium cations is evaluated as LUMO energies calculated by a semiempirical molecular orbital calculation PM3[33] (MOPAC Version 5.0). Nucleophilicity of the sulfonium cations are compared. LUMO energies and stability of bonds in the sulfonium cation are evaluated as a two-center energy using the keyword ENPAR. An optimized structure was obtained using the keyword PULAY. PM3 calculations were performed on a Fujitu VP2200 super computer.

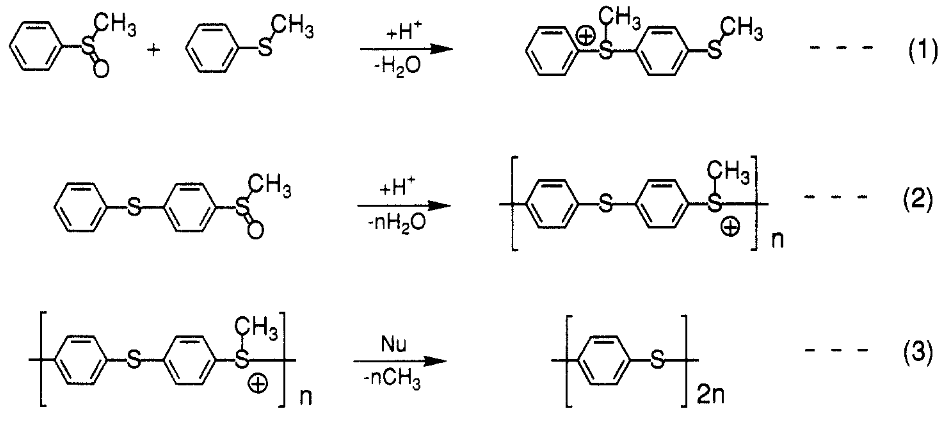
Results and Discussion

Coupling Reaction of Thioanisole and Methyl Phenyl Sulfoxide. The control experiment for the formation of sulfonium compounds were carried out in acidic media. Quantitative formation of the methylphenyl[4-(phenylthio)phenyl]sulfonium cation was confirmed by the model reaction between thioanisole and methyl phenyl sulfoxide in trifluoromethanesulfonic acid (Scheme I, part 1). The methylphenyl[4-(phenylthio)phenyl]sulfonium cation is isolated as a stable perchlorate salt having the empirical formula, $C_{14}H_{15}S_2ClO_4$, after the exchange of the counteranion from $CH_3SO_3^-$ by precipitation into perchloric acid (60%). ^1H NMR shows two peaks at 3.7 and 2.4 ppm attributed to methyl groups (Figure 2a). The former peak is assigned to methyl protons binding the sulfonium cation because the peak was observed at a field lower than that of the neutral methyl one due to the positive charge. A total of 10 peaks attributed to two methyl carbons and eight phenyl carbons in the ^{13}C NMR spectrum also indicates the formation of the MSP structure. Furthermore, the IR spectrum shows peaks at 1088 and 625 cm^{-1} which are ascribed to the perchlorate anion. The absorption band at 816 cm^{-1} indicates the formation of a typical 1,4-phenyl linkage. Combination of the COSY ^1H–^{13}C NMR and IR spectra reveal the formation of MSP.

The electrophilic substitution which proceeds through the protonation of the sulfoxide was accompanied by the elimination of water as a byproduct. Therefore, the reaction was influenced by the acidity of the mixture. Trifluoromethanesulfonic acid, which is the strongest protic acid, is the most effective for the formation of the sulfonium cation. The conversion to MSP in the reaction between thioanisole and methyl phenyl sulfoxide depends on the acidity function (H_o). In weak acids such as CH_3COOH and CF_3COOH, the electrophilic reaction scarcely proceeds (Figure 1).

Polymerization of PSO. The polymerization of PSO was performed in trifluoromethanesulfonic acid as the

Scheme I



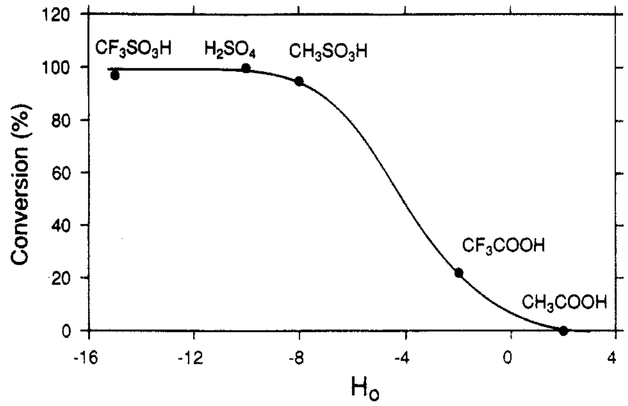


Figure 1. The reaction of thioanisole and methyl phenyl sulfoxide is performed in acid solvents. Conversion is defined as [methyl phenyl sulfoxide]/([thioanisole] + [methyl phenyl sulfoxide]).

solvent (Scheme I, part 2). The color of the reaction mixture changes from blue (<0 °C) to green (room temperature) and the viscosity of the reaction mixture gradually increases. After the precipitation in water, the poly(sulfonium cation) is quantitatively isolated as a white resin having the empirical formula, $C_{14}H_{11}S_3F_3O_3$.

^1H and ^{13}C NMR of the resulting polymer are shown in Figure 2b. In the ^1H NMR spectra, a peak attributed to methyl protons are observed at 3.78 ppm which is located at a lower field. The observation of AB quartet peaks is supported by the formation of the poly(sulfonium cation) which has the alternative structure of sulfide and sulfonium cations. ^1H NMR also shows that the integral ratio of methyl protons to aryl ones is 3:8. The ^{13}C NMR spectrum in formic acid shows four peaks assigned to aryl carbons and a methyl carbon. The typical absorption band attributed to a 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 a methyl group (2932 cm^{-1}). These spectroscopic data reveal the formation of poly(methyl[4-(phenylthio)phenyl]sulfonium trifluoromethanesulfonate) (PPST) (Figure 3a). The polycation is soluble in common solvent such as acetonitrile, acetone, dimethyl sulfoxide (DMSO), formic acid, and sulfuric acid.[34]

In order to convert to PPS from PPST, the demethylation was carried out using pyridine as a nucleophile (Scheme I, Part 3). PPST was dissolved in refluxing pyridine at 110 °C for 20 h. White powder was precipitated during the reaction. The IR spectrum of this resulting polymer (Figure 3b) agrees with the commercially available PPS (Ryton V-1 grade) (Figure 3c). The absorption attributed to the methyl group disappeared in the polymer. The resulting polymer also shows a band attributed to a C–H out-of-plane vibration of the 1,4-phenylene structure at 810 cm^{-1} which is a lower wavenumber than that of PPS (Ryton V-1). The result is caused by the high molecular weight of the resulting PPS. The absorption attributed to the methyl group disappeared in the polymer. The CP/MAS ^{13}C NMR shows two peaks at 132.1 and 134.3 ppm which are attributed to a typical phenyl carbon of PPS.

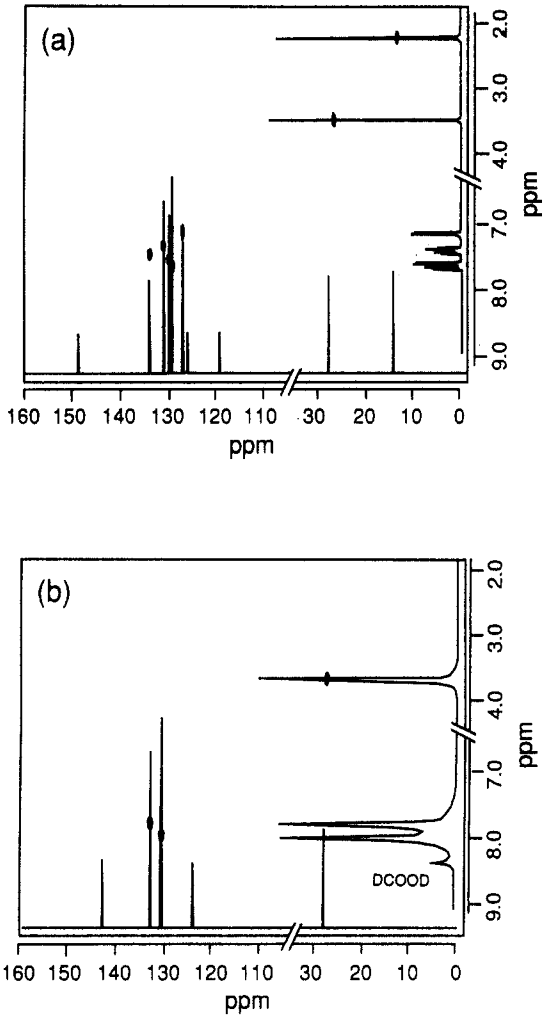


Figure 2. COSY ^1H–^{13}C NMR spectra of model sulfonium compound (MSP) in $CDCl_3$ (a) and obtained poly(sulfonium cation) (PPST) in DCOOD (b).

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, Table 1) by high-temperature GPC. Polymerization of PSO was carried out in various acids. The addition of P_2O_5 as a dehydrate agent in the media promotes the polymerization, e.g., the polymerization in trifluoromethanesulfonic acid–P_2O_5 results in a high molecular weight PPS with M_w 2.4

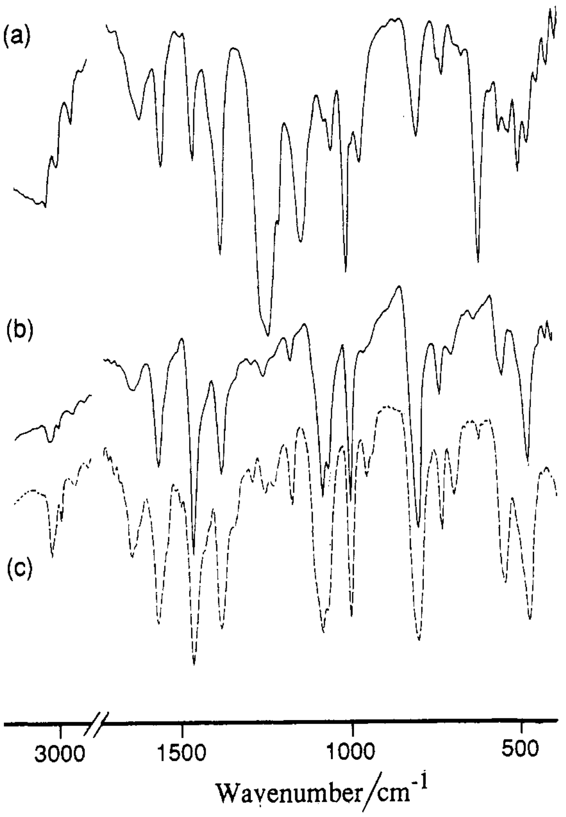


Figure 3. IR spectra of poly(sulfonium cation) (a), the resulting PPS (b), and commercial PPS (Ryton V-1) (c).

Table I. Relationship between Acid Derivative and Molecular Weight of Resulting PPS via Soluble Precursor[a]

acid	M_w	MWD	T_m (°C)
CF_3COOH	–[b]	–	–
CH_3SO_3H	2 710	1.9	275
CF_3SO_3H	120 000	4.6	260
CF_3SO_3H	67 000[c]	3.8	260
$CF_3COOH + P_2O_5$	24 000	2.3	273
$CH_3SO_3H + P_2O_5$	20 100	2.2	270
$CF_3SO_3H + P_2O_5$	249 000	5.6	260
$CF_3SO_3H + POCl_3$	17 800	2.1	277
Ryton V-1	21 600	2.7	280

[a] Polymerization temp 25 °C, time 20 h. [b] Cannot be obtained. [c] Temperature 25 °C, time 5 h.

$\times 10^5$. The high molecular weight PPS (M_w 2.4 $\times 10^5$) has a larger molecular weight distribution (M_w/M_n = 5.6), because of the high viscosity of the reaction mixture. The GPC elution curve of the resulting PPS (6.7 $\times 10^4$) shows M_w/M_n = 3.8 (Figure 4). DSC and TG measurements for M_w 2.4 $\times 10^5$ shows T_m 260 °C, T_g 96 °C, T_c 156 °C and $T_{d_{10\%}}$ 535 °C (Figure 5).[35] The T_m was lower than that of the Ryton V-1 grade (280 °C). The detectable difference in the structure between the resulting polymer and Ryton was not observed in these IR spectra. It is not denied that the lower melting points are caused by the existence of a small amount of the sulfonium cation unit or ortho substituents of the sulfide bond in the main chain of the PPS. However, existence of the ortho substituents was not observed in the NMR spectrum for the soluble precursor. MWD tends to increase with a rise in M_w and is larger than that of commercially available one, even though structural defects were not observed by spectrochemical analysis. We have measured molecular weight of PPS using high-temperature GPC. It cannot be denied that the high-temperature GPC overestimates MWD because the measure of MWD of standard polystyrene (labeled MWD 1.0–1.2) overestimately as MWD > 1.8 (after calibration with the polystyrene). Because of the overestimation in the measurement of MWD using high-temperature GPC system, we used our GPC to measure the molecular weight of the Ryton V-1. MWD of Ryton V-1 by our GPC was 2.1 (M_w 21 600). There is a correlation between T_m and M_w. T_m of obtained PPS were increase to 280 °C with decrease of molecular weight. The relationship can be seen as similar results of extensive study by Fagerburg.[36] The T_m of the resulting PPS did not change by annealing treatment at 200 °C, which means no existence of acid contamination in the resulting PPS.

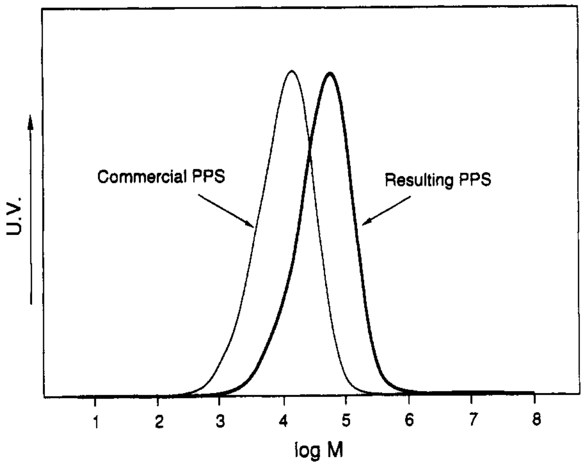


Figure 4. GPC trace of the resulting PPS and commercial PPS (Ryton V-1) with UV detectors (eluent, α-chloronaphthalene, 1 mL/min, 210 °C).

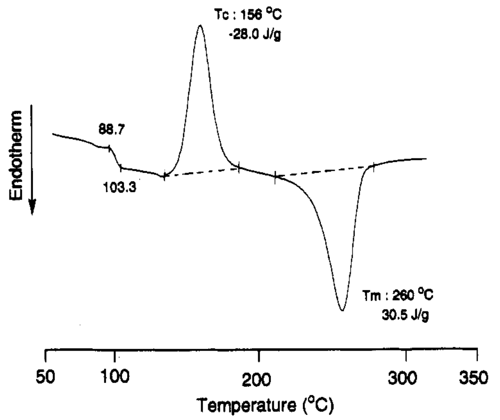
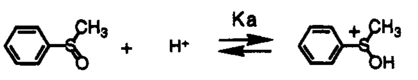


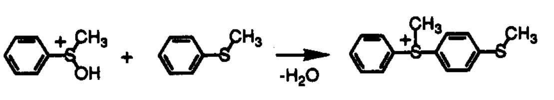
Figure 5. DSC thermogram of the resulting PPS (heating rate 20 °C/min, in N_2).

Methanesulfonic acid is not effective on the polymerization because of the weak acidity. This polymerization proceeds through an electrophilic reaction. The protonated sulfoxide, methylhydroxyphenylsulfonium cation, as an active species of the polymerization electrophilically attacks the phenyl ring of the monomer to yield a sulfonium cation of the dimer accompanied with the elimination of water. Formation of water as a byproduct during the polymerization decreases the acidity of the mixture and suppresses the polymerization. The sulfoxide–acid system is represented by the following equilibrium (1):



(1)

$$Ka = \frac{[SOH]}{[SO]\,[H^+]}$$



(2)

pK_a has been already estimated to be −2.3 mol^{-1} L.[37,38] Taking into account the pK_a of the acidification of

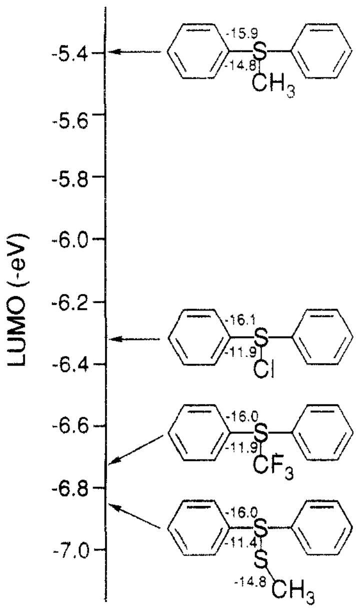


Figure 6. Examination of the relation between LUMO energy (PM3) and structure of the sulfonium cation.

sulfoxide, a protonic acid having an H_0 above 2.3 is predicted to be useful for the polymerization, that is, the poly(sulfonium cation) was not obtained using CH_3COOH ($H_0 = 2$) or CF_3COOH ($H_0 = -2$) as acid. Polymerization behaviors also support the idea that the polymerization is terminated by a decrease in the acidity (increase in H_0) due to water formation.

Computational Evaluation of Bond Elimination. The sulfonium cation and poly(sulfonium cation) are isolated as a stable salt. In addition, demethylation of MSP easily occurs through a S_N2 reaction with a base such as pyridine. Furthermore, PPST converts to PPS by demethylation. The reactivity and stability of the sulfonium cation were evaluated in the LUMO energy and two-center energies from the semiempirical molecular orbital calculation PM3. LUMO energies of the methyldiphenylsulfonium cation is compared with sulfonium cations derivatives, e.g., chlorodiphenyl-, diphenyl(trifluoromethyl)-, and (methylthio)diphenylsulfonium (Figure 6). LUMO energies of the diarylalkylsulfonium cation were the highest in these cations. Trityl cation is well-known to be stably isolated and possesses −6.3 eV as LUMO energy. The calculation supports the idea that MSP also exists as a stable salt because MSP possesses a higher LUMO energy than trityl cation. On the basis of two-center energies of diphenylmethyl sulfonium, which means bond strength, the phenyl $C-S^+$ bond is stronger than the methyl $C-S^+$ one. These results suggest that methyl $C-S^+$ bond is more cleavable than phenyl $C-S^+$ one by the S_N2 reaction. These calculation results support the idea that the poly[methyl[4-(phenylthio)phenyl]sulfonium cation] is also available as a soluble precursor with stability and reaction selectivity for the synthesis of PPS.

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(35) In the final stage of the polymerization, the solution viscosity of reaction mixture became very high. This event is considered as a property of a polycation. ^1H and ^{13}C NMR of the resulting poly(sulfonium cation) did not show the detectable ortho-linked spectrum. It is not denied that the electrophilic reaction occurs at ortho position and the resulting PPS which has ortho linkage shows a lower melting point rather than para-linked PPS, but the product of the model coupling reaction with thioanisole was isolated only para-substituted dimer. ^1H and ^{13}C NMR of the resulting poly(sulfonium cation) did not show the detectable ortho-linked spectrum. Fagerburg has reported an extensive study that the melting point of PPS decreases with increase of molecular weight (above $D_p > 50$, for D_p 183 has T_m 266 °C). It is difficult to conclude whether the lower melting point is caused by structural defect or by high molecular weight. The melt rheology of the PPS will give the formation.
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