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Notes

Synthesis of Poly(phenylene sulfide) by O_2 Oxidative Polymerization of Methyl Phenyl Sulfide

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Introduction

The polymerization via selective oxidation utilizing oxygen as the oxidant presents potentially a desirable low-cost method for upgrading the value of raw materials. The most successful example is the oxidative polymerization of 2,6-dimethylphenol to yield poly(2,6-dimethyl-1,4-phenylene oxide) using a copper–amine catalyst in an oxygen atmosphere at room temperature.[1] Our studies on the preparation of poly(*p*-phenylene sulfide) (PPS), which is an excellent and general-purpose engineering plastic,[2] have revealed that thiophenol and diphenyl disulfide are oxidatively polymerized to PPS via a cationic mechanism by electrochemical or chemical oxidations.[3–6] The oxovanadium catalyst acts as an efficient catalyst for the O_2 polymerization of diphenyl disulfide.[7] The polymerization provides very pure PPS in high yield but of low molecular weight because of the insolubility of PPS in dichloromethane at room temperature.

Recently, we proposed a new synthetic route for the synthesis of high molecular weight PPS via a soluble precursor under mild conditions which overcomes the synthetic difficulties presented by poor solubility.[8] In the previous paper we reported the polymerization of methyl 4-phenylthiophenyl sulfoxide to make poly[methyl-(4-phenylthiophenyl)sulfonium trifluoromethanesulfonate] as a poly(sulfonium cation) in the presence of trifluoromethanesulfonic acid. That is, a conversion from sulfoxide to sulfonium has been examined. Recently, we have found that sulfoxide was oxidatively polymerized directly to poly(sulfonium cation) catalyzed by cerium ammonium nitrate (CAN) with atmospheric oxygen in the presence of methanesulfonic acid. The present paper describes the Ce-catalyzed O_2 polymerization of a sulfide as a novel and convenient synthetic route to high molecular weight PPS ($M_w > 10^5$) via a soluble precursor.

Experimental Section

Measurements. The IR spectra were obtained using a Jasco FT-IR 5300 with a potassium bromide pellet. The ^{1}H-NMR spectra and ^{13}C-NMR spectra of the poly(sulfonium cations) were obtained using a JEOL FT-NMR GSX400. The CP/MAS spectrum of PPS was obtained using the same NMR spectrometer. The gas chromatograms were measured with a Shimadzu GC-12 gas chromatograph instrument. The molecular weight of the obtained PPS was obtained with a high-temperature gel permeation chromatograph (Senshu Scientific Co. Ltd., SSC VHT-7000) with α-chloronaphthalene as eluent at 210 °C and equipped with Shodex GPC columns (AT-80M/s) and a UV–vis spectrophotometer (Senshu Scientific Co. Ltd., S-3750) as a detector. Polystyrene standard samples were used to correct the calibration curve.

Materials. Thioanisole, diphosphorus pentoxide (P_2O_5), and cerium ammonium nitrate (CAN) (extra reagent grade) were purchased from Tokyo Kasei Co. and used without further purification. Methyl phenyl sulfoxide was prepared by the oxidation of thioanisole with nitric acid and purified by distillation under reduced pressure. Methyl 4-phenylthiophenyl sulfide (MPS) was prepared by the demethylation of methyl-(4-methylthiophenyl)phenylsulfonium perchlorate (MSP) with pyridine, which was synthesized by the reaction of thioanisole and methyl phenyl sulfoxide in methanesulfonic acid. Anhydrous magnesium sulfate was obtained from Tokyo Kasei Co. and used without further purification. Methanesulfonic acid was also purchased from Tokyo Kasei Co. and used after purification by vacuum distillation.

Oxidation of Thioanisole in an O_2 Atmosphere. CAN (109 mg, 0.2 mmol) and methanesulfonic acid (10 mL) were added to a 100-mL flask and stirred with a magnetic stirrer to give an orange solution or suspension. Thioanisole (1.24 g, 10 mmol) was added to the flask and stirred for 20 h at 25 °C under an oxygen atmosphere. Pyridine (30 mL) was added to the flask, and the reaction mixture was refluxed for 30 min to demethylate the sulfonium cations. The mixture was cooled to room temperature (25 °C), neutralized with hydrochloric acid, extracted with chloroform, washed with water, dried over anhydrous magnesium sulfate, and concentrated by evaporation. The product was confirmed by means of gas chromatography (GC) and GC–mass spectrometry.

Oxygen Uptake Measurement. (i) Poly[methyl-(4-phenylthiophenyl)sulfonium perchlorate] (PPSP). CAN (109 mg, 0.2 mmol) and P_2O_5 (1.4 g, 10 mmol) were dissolved in methanesulfonic acid (5 mL) in a closed vessel maintained at 25 °C (or 70 °C), and the resulting mixture was stirred for 1 h until a steady state was reached under a dry argon atmosphere. A similar vessel equipped with a manometer and a buret was connected to it with a tube. The atmosphere in the vessel was replaced by oxygen. The instrument was kept airtight. A solution of MPS (1.16 g, 5 mmol) in methanesulfonic acid (5 mL) was added. 1,1,2,2-Tetrachloromethane was carefully added from a buret to the second vessel to keep the pressure at 1 atm. The oxygen consumption was measured from the net amount of tetrachloromethane added during the reaction. After the reaction, the mixture was added to 100 mL of water. The reaction mixture was precipitated in perchloric acid, and the product was isolated as a pale yellow solid. The solid was filtered, thoroughly washed with water, and dried in vacuo over P_2O_5 for 10 h at 25 °C to give poly[methyl-(4-phenylthiophenyl)sulfonium perchlorate] (PPSP; 1.59 g. Yield: 96:. IR (KBr, cm^{-1}): 3084, 3021, 2932 (ν_{C-H}), 1568, 1476, 1395, 1092 (ν_{Cl-O}), 1009, 982, 816 (δ_{C-H}), 745, 698, 623 (ν_{Cl-O}), 554, 494. ^{1}H NMR (DCOOD, TMS): δ 7.7–7.9 (d, 8H), 3.8 (s, 3H). ^{13}C NMR (DCOOD, TMS): δ 141.7, 132.3, 130.2, 124.0 (phenyl C), 27.5 (S^+-CH_3). [η]: 1.7 [in CH_3CN/H_2O = 65/35 (v/v) with CF_3SO_3Na (50 mM)].

(ii) Poly(*p*-phenylene sulfide) (PPS). The obtained poly(sulfonium cation) (PPSP; 0.7 g) was dissolved in 10 mL of pyridine at 25 °C and stirred for 1 h. The clear reaction mixture became a white suspension after 10 min. The reaction mixture was refluxed for 12 h. The product was isolated and then poured into 200 mL containing 10% HCl. The precipitate was filtered, washed with methanol, and refluxed in ethanol for 2 h, and the product was dried in vacuo for 12 h at 50 °C to give 0.45 g of PPS. Yield: 98%. IR (KBr, cm^{-1}): 3065, 1572, 1472, 1389, 1092, 1074, 1009, 812 (δ_{C-H}), 743, 706, 556, 482. CP/MAS ^{13}C-NMR: δ 134.4,

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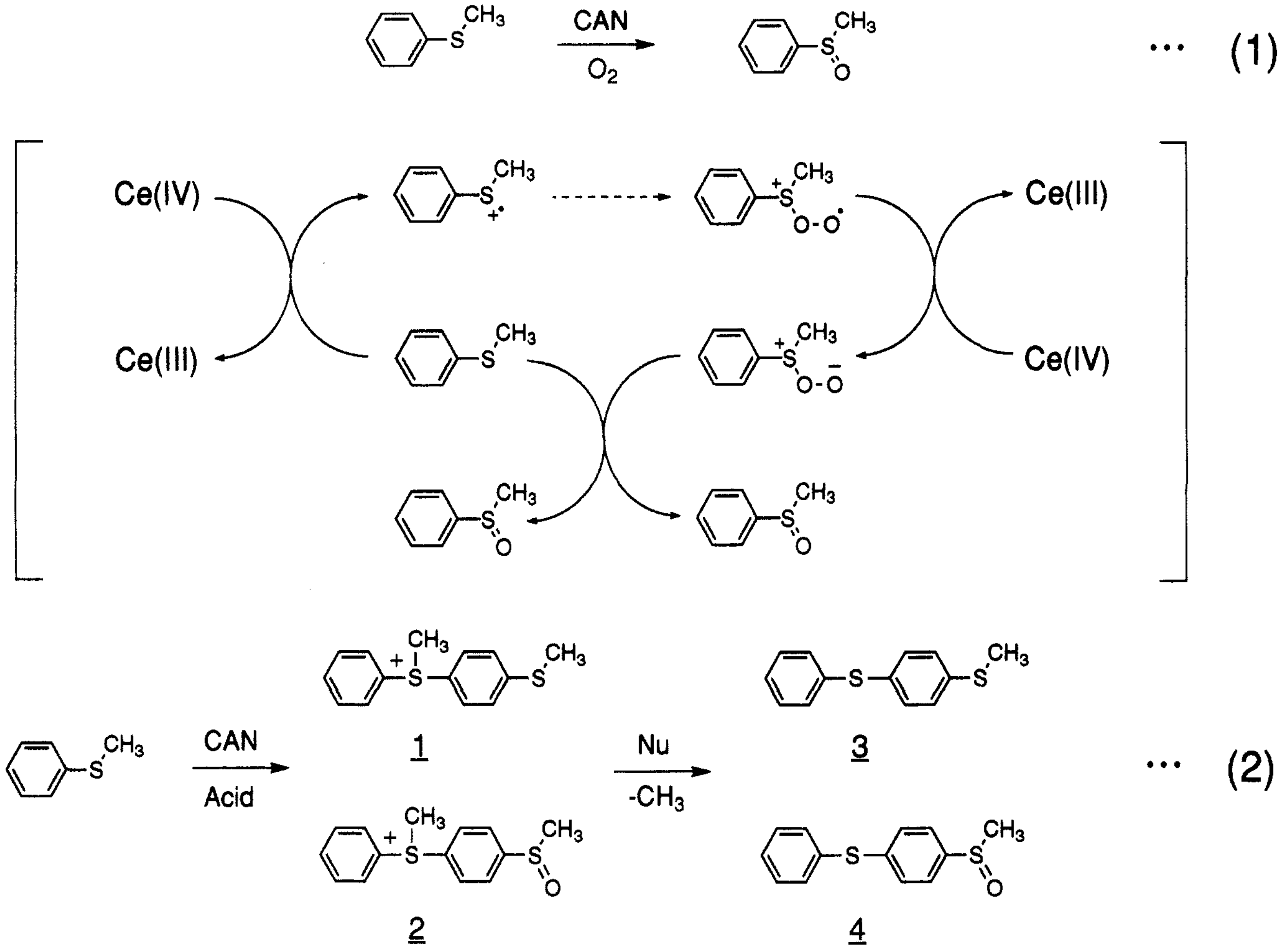
Scheme 1



131.9 (phenyl C). Anal. Calcd for C_6H_4S: C, 66.63; H, 3.73; S, 29.64. Found: C, 66.70; H, 3.59; S, 30.32.

Results and Discussion

Oxidation of Thioanisole in Acid in the Presence of O_2. Thioanisole is oxidized quantitatively to yield methyl phenyl sulfoxide (Scheme 1) with oxygen in the presence of a catalytic amount of $Ce(NH_4)_2(NO_3)_6$ (CAN) under high pressure.[9,10] In the presence of methanesulfonic acid, the Ce-catalyzed oxidation of thioanisole in an oxygen atmosphere at ambient pressure for 20 h at 25 °C yields 22% of MPS (3) and 78% of methyl 4-phenylthiophenyl sulfoxide (4) after refluxing with pyridine as the nucleophile (Nu; Scheme 1).

Control experiments reveal that, under acidic conditions, methyl phenyl sulfoxide couples with thioanisole to yield the methyl-(4-methylthiophenyl)phenylsulfonium cation quantitatively via formation of methyl phenyl sulfoxide in the Ce-catalyzed oxidation. MPS is produced by demethylation of the methyl-(4-methylthiophenyl)phenylsulfonium cation (1) and methyl 4-phenylthiophenyl sulfoxide is produced by demethylation of the methyl-[4-(methylsulfinyl)phenyl]phenylsulfonium cation (2) which is formed by the O_2 oxidation of the methyl-(4-methylthiophenyl)phenylsulfonium cation in the reaction mixture (Scheme 1, eq 2). The O_2 oxidation is influenced by the acid strength. In a weak acid such as acetic acid, the coupling reaction does not proceed because the formed sulfoxide is not activated through the protonation on the oxygen atom. The predominant formation of the dimer (1 and 2) supports the fact that Ce(IV) acts as a catalyst for oxidation of the sulfide in acid and the resulting sulfoxide is allowed to electrophilicity react with thioanisole to form the sulfonium cation in high yield.

Oxidative Polymerization. On the basis of the model reactions, the polymerization of MPS was carried out in methanesulfonic acid in an oxygen atmosphere in the presence of a catalytic amount of CAN. In the reaction, water was formed in an amount equivalent to MPS and suppressed the polymerization because of the decreasing acidity of the mixture. P_2O_5 was added to the reaction mixture to remove the water. The polymerization proceeded rapidly with a quantitative O_2 uptake of oxygen to give the poly(sulfonium cation) (PPSP, 5) using methanesulfonic acid (10 mL). The polymerization mechanism of methyl 4-phenylthiophenyl sulfide is believed to follow Scheme 2. Methyl 4-phenylthiophenyl sulfoxide which was formed by oxidation of methyl 4-phenylthiophenyl sulfide is protonated by methanesulfonic acid. The (hydroxymethyl)phenylsulfonium cation electrophilically attacks the phenyl ring of the monomer. The coupling reaction provides PPSP. The oxidation of 1 mol of sulfide consumed $^1/_2$ mol of O_2 to give 1 mol of the sulfoxide. Oxygen is essential for the polymerization. The polymer was isolated by precipitation in perchloric acid (60%) as a white resin having the empirical formula $C_{13}H_{11}S_2ClO_4$.

The absorption peak of the resulting polymer at 2925 cm^{-1} is attributed to the ν_{C-H} of the methyl group, and the absorption peaks at 1100 and 625 cm^{-1} indicate the counteranion ClO_4^- in the IR spectrum. The peaks at 3.8 ppm in the ^{1}H-NMR spectrum and 27.5 ppm in the ^{13}C-NMR spectrum reveal the existence of the S^+-CH_3 group. An absorption band attributed to a C–H out-of-plane vibration of the benzene ring was observed at 810 cm^{-1} in the IR spectrum. ^{1}H NMR of 5 shows AB-quartet peaks

Scheme 2

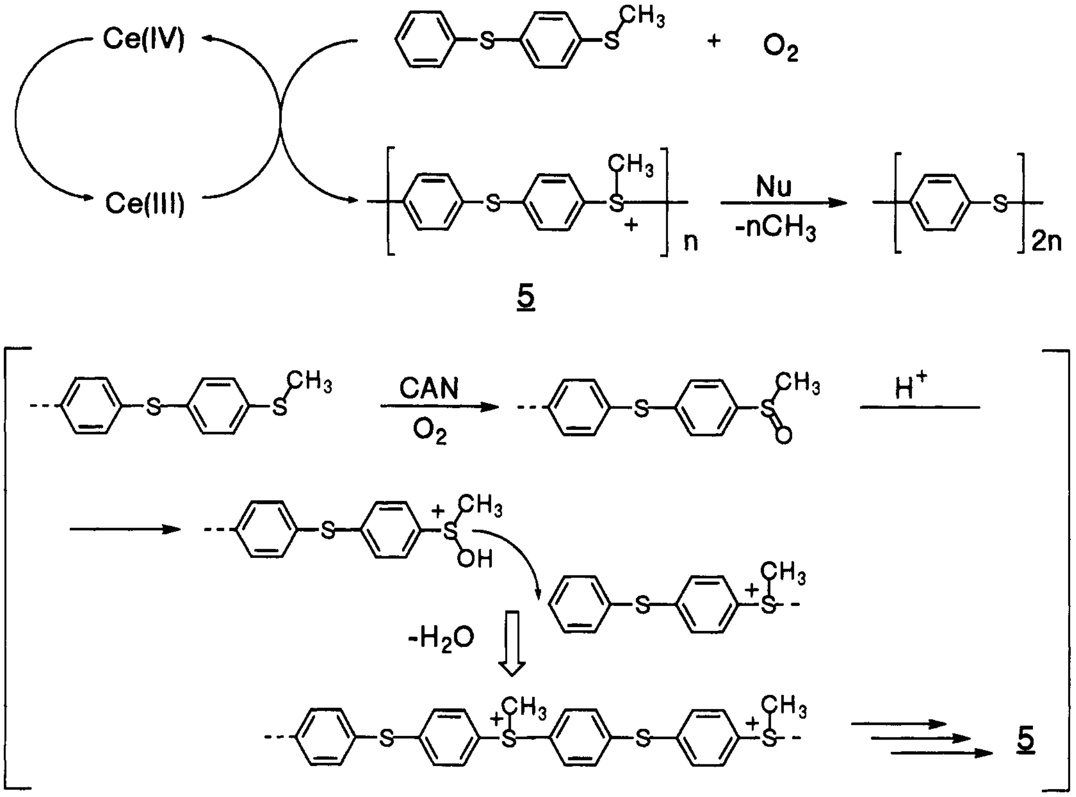


Table 1. Oxidative Polymerization of Methyl 4-Phenylthiophenyl Sulfide Using CAN under Acidic Conditions[a]

temp (°C)	time (h)	M (mol/L)[b]	M_w	T_m (°C)
25	20	0.5	33 000	261
25	20	1.0	204 000	259
70	20	0.5	104 000	260
70	3	1.0	41 000	260

[a] In CH_3SO_3H/P_2O_5. [b] Monomer (PSO) concentration.

attributed to phenyl protons at 7.7–7.9 ppm. These results clearly indicate the formation of a linear chain of a poly(sulfonium cation).

After the demethylation of PPSP by refluxing in pyridine as a nucleophile, PPS is isolated as a white powder having the empirical formula C_6H_4S. In the IR spectrum, the demethylated polymer has an absorption peak at 810 cm^{-1} attributed to a C–H out-of-plane vibration of the benzene ring. The IR spectrum of the resulting PPS was consistent with that of commercially available PPS (Ryton). The ν_{C-H} absorption peaks of the methyl group and peaks of ClO_4^- disappear in the IR spectrum. The demethylation proceeds through a *trans*-methylation-mechanism from the sulfonium cation to pyridine, and the *N*-methylpyridinium cation can be isolated. Two peaks at 131.9 and 134.4 ppm were observed in the CP/MAS ^{13}C-NMR spectrum for the resulting PPS. The molecular weight of the resulting PPS was determined as 204 000 (Table 1). DSC measurement shows T_m = 260 °C, T_g = 93 °C, and T_c = 158 °C. T_m did not change upon annealing at 200 °C, which indicates the absence of acid contamination. Even though T_m was lower than that of the Ryton V-1 grade (280 °C), detectable differences in structure between the resulting polymer and Ryton were not indicated by the IR and NMR spectra. It cannot be denied that the lower melting point[11] may be caused by the presence of a small amount of the sulfonium cation unit or ortho substitution of the sulfide bond in the main chain of the PPS.

The molecular weight of the resulting PPS is influenced by the reaction temperature. A higher temperature reaction temperature of 70 °C results in a lower molecular weight product. We propose that the polymerization proceeds via a cationic mechanism. MPS is oxidized to methyl 4-phenylthiophenyl sulfoxide with oxygen. Methyl 4-phenylthiophenyl sulfoxide is protonated to form the (hydroxymethyl)(4-phenylthiophenyl)sulfonium cation which is the active species in the polymerization. The cation electrophilically attacks[13] the benzene ring of MPS at the *para* position, yielding the dimer sulfonium cation accompanied by water elimination. The oxidation and the electrophilic reactions are continually repeated to yield the poly(sulfonium cation).

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(11) In the model coupling reaction with thioanisole only the para-substituted dimer was isolated. ^1H and ^{13}C NMR of the resulting poly(sulfonium cation) did not show any detectable ortho-linking or branching structure. Fagerburg[12] has reported an extensive study that the melting point of PPS decreases with increase of molecular weight (above DP > 50; for DP = 183, T_m = 266 °C). The molecular weight distributions (MWD) of the obtained PPS are over 3.1, and with the increase of the M_w, MWD tend to increase. It is difficult to conclude whether the lower melting point is caused by structural defects, high molecular weight, or wide MWD. A study of melt rheology is designed to elucidate the properties.

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(13) The electrophilic reaction proceeds through the formation of a cation radical after elimination of an OH radical. The ESR signal of the cation radical was observed.