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Solubilization of Poly(phenylene sulfilde) via Sulfonium Formation by Alkylation

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ABSTRACT: Poly(phenylene sulfide) was solubilized to poly(arylenesulfonium) salts **5** by the acidified reaction with aliphatic esters (methyl formate, methyl triflate, ethyl formate, and ethyl acetate). The reaction quantitatively proceeds in sulfuric acid or triflic acid to give the corresponding alkylated polymers, which were well-characterized by various spectroscopic methods. The effects of the acidity, the esters, and the reaction temperatures on the alkylation were investigated. Polymers **5** are soluble in acids and polar organic solvents depending upon the alkyl substituents and counteranions. Poly(phenylene sulfide) could be regenerated by the dealkylation of **5** with refluxing pyridine without structural changes and decomposition.

Introduction

Aromatic polymers have been extensively investigated for decades due to their excellent thermal stability, semicrystallinity, extended π-delocalized structure, and promising industrial applications. Poly(phenylene sulfide) (PPS, poly(thiophenylene)) is one of these polymers with increasing commercial production as the sixth engineering plastic.[1] PPS has a T_g of 85 °C, T_m of 285 °C, and T_d above 420 °C[2] and shows electrical conductivity greater than 10 S cm^{-1} when doped with AsF_5.[3] The polymer is hardly soluble in solvents at moderate temperatures, a serious drawback for the structural characterization and the processing of the polymer. Several attempts have been made to solubilize PPS; strong oxidants such as SO_3, AsF_5, and $AlCl_3$ oxidize the polymer to the polymeric cation which dissolves in acids or aromatic hydrocarbon solvents.[4] However, these are deemed unsatisfactory since such oxidation is irreversible and is accompanied by some chemical reactions (sulfonation or cross-linking) or decomposition, and hence, the polymer loses its conspicuous properties.

We have found that high-molecular-weight novel poly(arylenesulfonium) salts could be obtained by the facile electrophilic[5] or oxidative[6] polymerization of thioanisole derivatives. The polysulfonium salts are very soluble in polar organic solvents such as methanol, acetone, acetonitrile, and DMF and are converted into PPS by reaction with a nucleophile (pyridine or halide ion). Our preliminary communication reports that the reverse reaction is also possible—PPS is methylated to the polysulfonium salt by the reaction with methyl triflate.[7] In this paper, we describe our extended results on the solubilization of PPS via sulfonium formation. Model experiments with oligomers (2−4-mers) and the alkylation behavior of PPS using several kinds of esters are also discussed.

Results and Discussion

Synthesis of Oligomers of Sulfoniophenylene Triflates. We have found that the superacidified reaction of sulfides and esters gives sulfonium salts in high yield.[8] The reaction proceeds well for phenylene sulfide oligomers to give the corresponding oligomers of sulfoniophenylene salts (Scheme 1). Diphenyl sulfide (dimer) was methylated by the reaction with 2 equiv of methyl formate in triflic acid at 25 °C for 10 h to form diphenylmethylsulfonium triflate (**1**) in 85% yield (Table 1). When methyl triflate was used as an ester, the product was obtained almost quantitatively (99% yield). On the basis of the experiments with 1,4-bis(phenylthio)benzene (trimer), it was found that the degree of methylation could be controlled with the feed amount of the ester used. The reaction of the trimer with an equimolar amount of methyl triflate gives 4-(phenylthio)diphenylmethylsulfonium triflate (**2**) in 74% yield.[9] 1,4-Bis(methylphenylsulfonio)benzene bis(triflate) (**3**) is obtained in 98% yield when 2 equiv of methyl triflate was used. The tetramer could also be methylated to bis(4-methylphenylsulfoniophenyl)methylsulfonium tris(triflate) (**4**) in the reaction with 3 equiv of the ester.

The obtained oligomers of sulfoniophenylene triflates were white powders characterized by IR, ^{1}H NMR, and ^{13}C NMR spectra and elemental analyses. In Figure 1 is shown the ^{1}H and ^{13}C NMR spectra of **4**, where two methyl groups bound to sulfonio groups are observed at 4.06, 4.13 ppm (^{1}H) and at 28.1, 28.2 ppm (^{13}C). The eight peaks of aromatic carbons in the ^{13}C NMR could be well-assigned to the structure on the basis of the substituent parameters of sulfonio groups of compound **3**. The existence of the counteranion (triflate) was confirmed by the vibration peaks at 1092, 1272 cm^{-1} (ν_{SO}) and at 1260, 1159, 639 cm^{-1} (ν_{CF}) in the IR spectrum. The solubility of oligomers **1**−**4** depends on the content of sulfonio groups. Oligomers **1** and **2** with one sulfonio group are very soluble in dichloromethane, acetone, and tetrahydrofuran, while oligomers **3** and **4** are only soluble in polar solvents such as acetone, DMF, and DMSO. Oligomers **1**−**4** are also soluble in pyridine; however, the demethylation reaction immediately takes place in solution to afford the starting phenylene sulfide oligomers. HPLC and NMR analyses have only shown the formation of sulfides. As a consequence, we demonstrated the recycling of the material from the dealkylation of the sulfonium salts.

Solubilization of PPS by the Alkylation. The methylation reaction of PPS was carried out using methyl triflate in triflic acid at 110 °C (Scheme 2). During the reaction, the polymer was gradually dis-

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Scheme 1

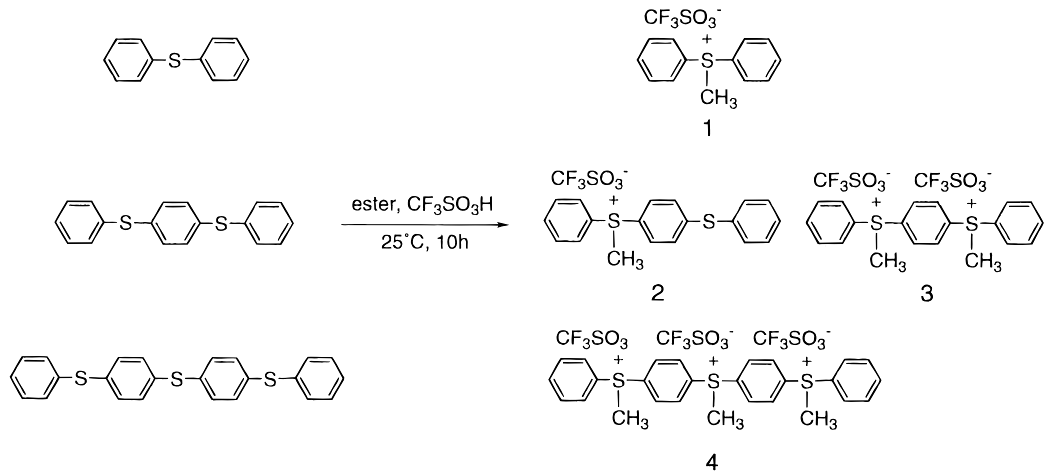


Table 1. Methylation of Phenylene Sulfide Oligomers

product[a]	ester	yield (%)[b]
1	$HCOOCH_3$	85
	$CF_3SO_3CH_3$	99
2	$CF_3SO_3CH_3$	74
3	$CF_3SO_3CH_3$	98
4	$CF_3SO_3CH_3$	96

[a] As triflate. [b] Isolated yields.

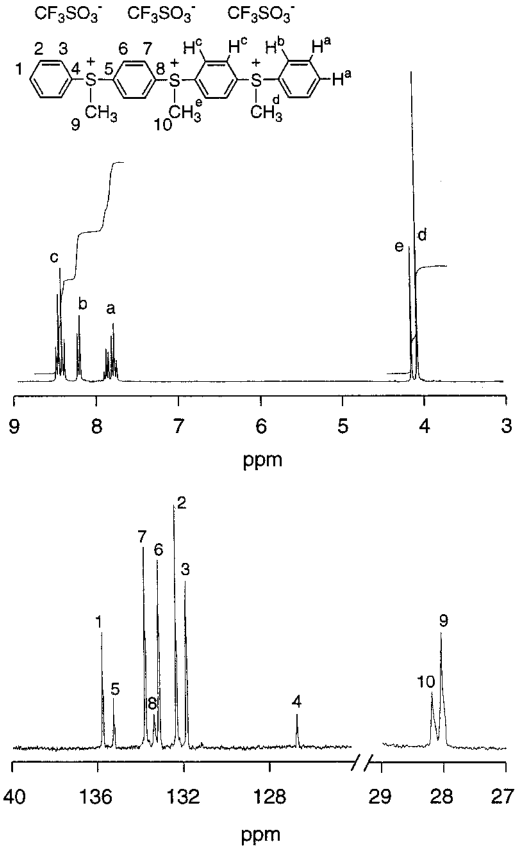
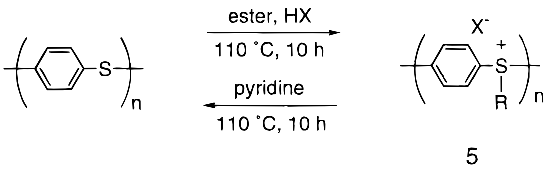


Figure 1. ^1H and ^{13}C NMR spectra of bis(4-methylphenylsulfoniophenyl)methylsulfonium tris(triflate) (**4**) in acetone-d_6.

solved in triflic acid to give a homogeneous red solution. The precipitation from excess diethyl ether afforded the fully methylated polymer **5a** in 100% yield. The NMR spectra of the product in D_2SO_4 showed two singlet peaks at 3.38 (CH_3) and 7.82 (Ar) ppm (^1H) and three peaks at 48.3 (CH_3), 119.2, and 120.8 (Ar) ppm together with the four characteristic peaks (101.8, 104.9, 108.1, 111.2 ppm) of the triflate anions (^{13}C) (Figure 2). These results are in good agreement with those of poly(methylsulfonio-1,4-phenylene triflate) prepared by the electrophilic polycondensation of benzene with sodium methanesulfinate in triflic acid.[5b] The IR spectrum and elemental analyses also support the structure.

Scheme 2



a: R = CH_3, X = CF_3SO_3
b: R = CH_2CH_3, X = CF_3SO_3
c: R = CH_3, X = HSO_4
d: R = CH_2CH_3, X = HSO_4

The methylation reaction depends on the acid and the ester applied. To first examine the effect of acidity, the methylation reaction of PPS was carried out at 25 °C for 10 h in several acids of H_0 (0 to -15) with methyl triflate, methyl formate, and ethyl acetate (Figure 3). During the reaction of PPS with methyl triflate, the methylation degree[10] increases with the acidity: 0% in formic acid ($H_0 = 0$), 56% in methanesulfonic acid (-8.0), 72% in sulfuric acid (-10.4), and 76% in triflic acid (-15.0). Since the active species is supposed to be the protonated ester (oxonium cation),[8] a stronger acid generating more oxonium cations favors the kinetics. When methyl formate was used, the methylation reaction did not take place in acids of $H_0 > -10$ and proceeded only in triflic acid with a 44% conversion. Ethyl acetate was inactive under the given reaction conditions (25 °C, 10 h). The higher conversions with triflates instead of formates and acetates probably reflect the reactivity of the oxonium cations, where those from triflates are more reactive in an S_N2 reaction by sulfide due to the inductive effects of a CF_3SO_2 group.

The methylation reaction of PPS proceeds faster at elevated temperatures. In Figure 4 is shown the time course of the conversion of the methylation reaction of PPS with methyl triflate in triflic acid and with methyl formate in sulfuric acid at 110 °C. In both cases, the reaction is completed within 1 h to give the fully

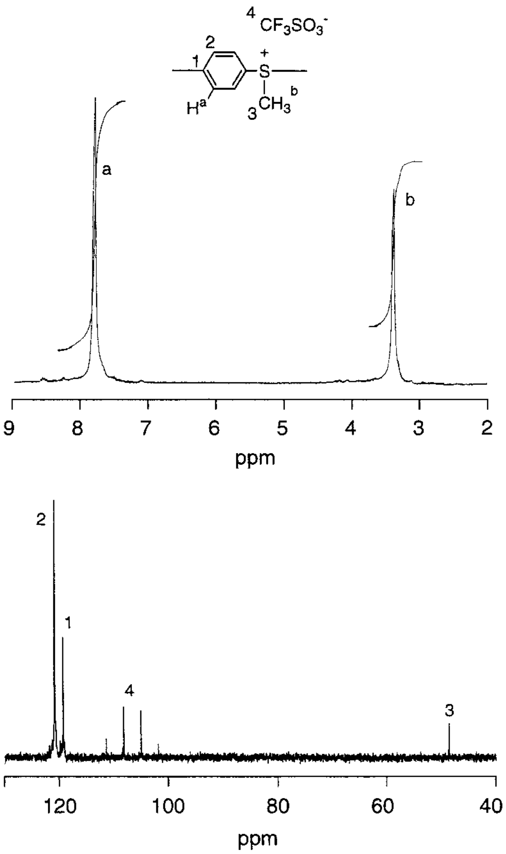


Figure 2. ^{1}H and ^{13}C NMR spectra of poly(methylsulfonio-1,4-phenylene triflate) (**5**) in D_2SO_4.

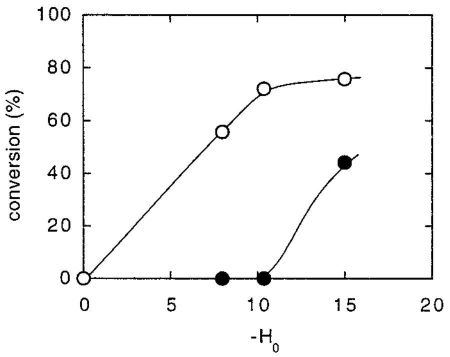


Figure 3. Acidity effect on the methylation of PPS with methyl triflate (○) and methyl formate (●) in triflic acid at 25 °C for 10 h.

methylated PPS (polysulfonium salts **5a** and **5b**, respectively), although the rate is slightly faster in triflic acid.

The temperature effect on the methylation of PPS was investigated with three esters (methyl formate, ethyl formate, and ethyl acetate) in triflic acid (Figure 5) and in sulfuric acid (Figure 6). In triflic acid with methyl formate, the conversion increases with the temperature from 44% at 25 °C to 100% at 110 °C. With the ethyl esters, the reaction does not proceed below 60 °C since the polymer is hardly soluble in the mixture. The polymer is dissolved and reacts with the oxonium species above 65 °C; however, the conversion is 59%. The conversion with ethyl esters is lower than with the methyl ester because ethyl groups on the oxonium cations are less easily attacked in an S_N2 reaction due to the steric effects. Besides, diphenylethylsulfonium cations are less stable on heating than diphenylmethylsulfonium cations, because the former with β-hydrogen atoms undergo Hofmann degradation to form sulfides and alkenes.[11] In sulfuric acid with methyl formate, although the methylation does not occur at 25 °C, the conversion increases with the temperature up to 100% at 110 °C as well as the case in triflic acid. The ethylation conversions in sulfuric acid are higher than in triflic acid, probably because the hydrogen sulfate, being a less nucleophilic anion than the triflate,[12] stabilizes the resulting poly(arylenesulfonium) salts. In contrast to the methyl and ethyl esters, the butyl ester (butyl formate) is inactive, and butylated PPS could not be obtained even at elevated temperatures. In the series of alkylation reactions, poly(arylenesulfonium) salts with methyl groups and triflate anions (**5a**, 100% conversion), with ethyl groups and triflate anions (**5b**, 59%), with methyl groups and hydrogen sulfate anions

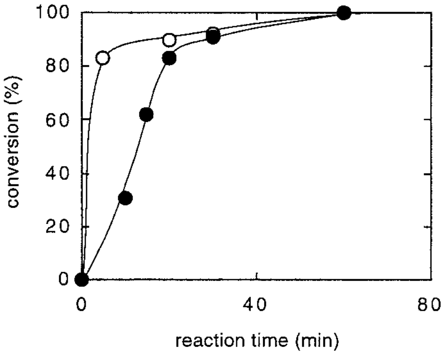


Figure 4. Methylation of PPS with methyl triflate in triflic acid (○) and with methyl formate in sulfuric acid (●) at 110 °C.

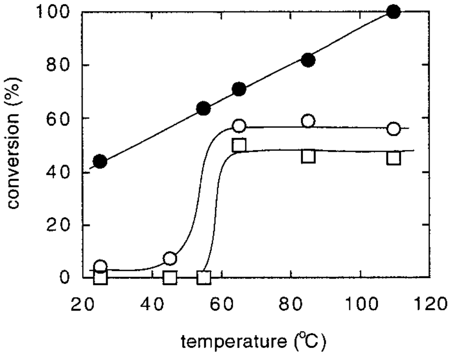


Figure 5. Temperature effect on the methylation of PPS with methyl formate (●), with ethyl formate (○), and with ethyl acetate (□) in triflic acid for 10 h.

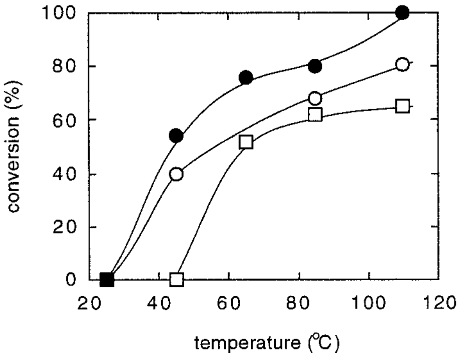


Figure 6. Temperature effect on the methylation of PPS with methyl formate (●), with ethyl formate (○), and with ethyl acetate (□) in sulfuric acid for 10 h.

Table 2. Solubility of Polysulfonium Salts[a]

solvent	**5a**	**5b**	**5c**	**5b**
H_2SO_4	+	+	+	+
HCOOH	+	+	+	+
CH_3COOH	−	−	−	−
H_2O	−	−	+	+
DMSO	+	+	+	+
DMF	+	+	+	+
NMP	+	+	+	+
acetone	−	+	−	−
MeOH	−	+	−	+

[a] + = soluble at 25 °C; − = insoluble at 25 °C.

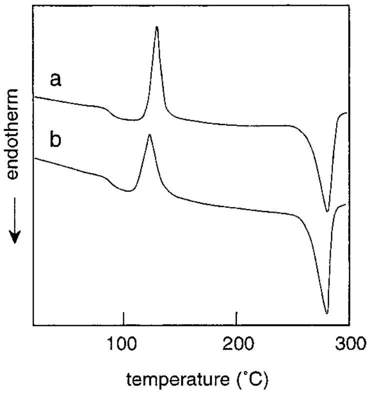


Figure 7. DSC thermograms of PPS: pristine (a) and regenerated from **5a** (b).

(**5c**, 100%), and with ethyl groups and hydrogen sulfate anions (**5d**, 81%) were obtained.

The solubilities of the polysulfonium salts **5** are summarized in Table 2. While the starting PPS is insoluble in solvents at moderate temperatures and only soluble in NMP and 1-chloronaphthalene above 200 °C, the resulting polysulfonium salts show good solubility in polar organic solvents at 25 °C. The polymers are also soluble in sulfuric acid and formic acid, but not in acetic acid. Polymers **5c** and **5d** with hydrogen sulfate anions are hygroscopic and even soluble in water. However, the dealkylation of the polymers gradually takes place in aqueous solution, which was confirmed by ^1H NMR experiments. The ethylated polymers **5b** and **5d** with increased lypophilicity are soluble in methanol and acetone (**5b** only). Polymers are insoluble in nonpolar organic solvents, such as benzene, hexane, and chloroform.

As well as oligomers **1**−**4**, polymers **5** could be dealkylated to PPS by the reaction in refluxing pyridine for 10 h (Scheme 2). A pale brown powder of PPS was regenerated in quantitative yield after the treatment. The molecular weight of the polymers was measured by GPC (eluent: 1-chloronaphthalene, at 210 °C), in which the PPS regenerated from **5a** had almost same molecular weight (M_w = 19 900, M_n = 6370) as the pristine polymer (M_w = 18 700, M_n = 6760). These results indicate that the regeneration or recycling of PPS is available by the dealkylation without decomposition or side reactions. The IR spectra of the pristine and the regenerated polymers are identical. No peaks assigned to the counteranions ($CF_3SO_3^-$, HSO_4^-) could be observed for the regenerated polymers, indicating that the dealkylation is complete. DSC measurements show that both polymers have the same glass transition temperature at 90 °C and melting temperature at 282 °C (Figure 7). The differences in T_c between the polymers (129 °C for pristine and 123 °C for regenerated) would be due to the crystallinity. The regenerated PPS is less crystalline than the commercial product because the dealkylation process was carried out at the lower temperature of 120 °C than Phillip's method.[13] After annealing above its T_g, the regenerated polymer shows the same T_c as the pristine PPS.

Conclusions

We have found that poly(phenylene sulfide) could be converted into the soluble polysulfonium salts by the reaction with esters in strong acids. The model reactions of the dimer, trimer, and tetramer with methyl triflate in triflic acid revealed that the methylation selectively takes place on the sulfur atoms to give the oligomers of sulfoniophenylene triflates in quantitative yields. The reaction proceeded well for the polymer, and the poly(methylsulfonio-1,4-phenylene salt) was obtained as the triflate or hydrogen sulfate. Ethylation is also possible; however, the conversion is lower (81%) than the case of the methylation due to less liability of ethyloxonium cations to nucleophilic attack by sulfides and the lower stability of the product. The polymers are soluble in sulfuric acid, formic acid, DMF, and DMSO and in water with hydrogen sulfate counteranions. The polysulfonium salts could be converted back to the poly(phenylene sulfide) by dealkylation with pyridine. The regenerated polymer has nearly the same molecular weight and thermal properties (T_g = 90 °C, T_c = 129 °C, T_m = 282 °C).

Experimental Section

Measurement. The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500 (500 MHz ^1H, 125 MHz ^{13}C) spectrometer system with chemical shifts (δ) downfield from tetramethylsilane as the internal standard. Infrared analyses were performed as a KBr pellet using a Jasco FT-IR 5300 spectrometer. 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 UV/vis spectra were recorded using a Shimazu UV-2100 spectrometer.

Gas chromatography (GC) was performed using a Shimazu GC-17A equipped with a silicone SE-30 column ($\Phi \times L$ = 3.2 mm × 2.1 m). High-pressure liquid chromatography (HPLC) analysis was taken on a Shimazu LC-9A system equipped with a Shodex Hikarisil column, in which the operating temperature was regulated at 25 °C. Methanol was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight measurement was carried out by gel permeation chromatography (GPC) at 210 °C using a Senshu Kagaku model VHT-GPC SSC-7000 with a Soma Optics S3750 UV/vis absorption detector. 1-Chloronaphthalene was used as an eluent at a flow rate of 1.0 mL/min. Narrow dispersed polystyrene standards were made for calibration.

Differential scanning calorimetry (DSC) was carried out on a Seiko DSC 220C thermal analyzer at a heating rate of 20 °C/min under nitrogen at a flow rate of 150 mL/min. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a Seiko TG/DTA 220 instrument at a heating rate of 20 °C/min under nitrogen at a flow rate of 300 mL/min. A 10 mg sample was used for each thermal analysis.

Materials. Methyl formate, ethyl formate, ethyl acetate, methyl triflate, triflic acid, and sulfuric acid were purified by distillation before use. Bis(4-phenylthio)benzene and bis(4-phenylthiophenyl) sulfide were prepared by a previously reported method.[14] Commercial products of diphenyl sulfide and poly(phenylene sulfide) were purchased from Aldrich Co. Inc., and used as received.

Methylation of Phenylene Sulfide Oligomers. The typical procedure is as follows. To a solution of methyl triflate (3.28 g, 20 mmol) in triflic acid (5 mL) was added dropwise diphenyl sulfide (1.86 g, 20 mmol) over a period of 30 min in an ice bath. The mixture was stirred for 10 h at 25 °C. After the reaction, the mixture was poured into 100 mL of water. The solution was extracted with three portions of 100 mL of dichloromethane. The combined organic layer was evaporated to 10 mL and then poured into 200 mL of diethyl ether to precipitate the white powdered product. The precipitate was washed with diethyl ether and dried in a vacuum to obtain diphenylmethylsulfonium triflate (**1**) in 99% yield.

Diphenylmethylsulfonium Triflate (1). IR (KBr, cm^{-1}): 3098, 2936 (ν_{C-H}), 1636, 1480, 1449 ($\nu_{C=C}$), 1258, 1159, 637 (ν_{C-F}), 1271, 1159, 1092 ($\nu_{S=O}$), 1030, 814 (δ_{C-H}). ^{1}H NMR (acetone-d_6, ppm): 3.99 (CH_3, s, 3H), 7.78−8.16 (Ar, m, 10H). ^{13}C NMR (acetone-d_6, ppm): 28.0, 128.0, 130.9, 132.0, 135.1. Anal. Calcd for $C_{14}H_{13}F_3O_3S_2$: C, 47.99; H, 3.74; S, 18.30. Found: C, 48.06; H, 3.98; S, 18.13.

4-Phenylthiodiphenylmethylsulfonium Triflate (2). IR (KBr, cm^{-1}): 3080, 3027, 2936 (ν_{C-H}), 1640, 1476, 1449 ($\nu_{C=C}$), 1275, 1088 ($\nu_{S=O}$), 1260, 1163, 639 (ν_{C-F}), 1032, 812 (δ_{C-H}). ^{1}H NMR (acetone-d_6, ppm): 3.94 (CH_3, s, 3H), 7.39−8.13 (Ar, m, 14H). ^{13}C NMR (acetone-d_6, ppm): 28.2, 123.8, 128.2, 129.3, 130.7, 130.8, 130.9, 131.2, 131.7, 132.1, 135.0, 135.8, 148.5. Anal. Calcd for $C_{20}H_{17}F_3O_3S_3$: C, 52.39; H, 3.74; S, 20.98. Found: C, 52.22; H, 3.50; S, 21.30.

1,4-Bis(methylphenylsulfonio)benzene Bis(triflate) (3). IR (KBr, cm^{-1}): 3090, 3029, 2938 (ν_{C-H}), 1632, 1574, 1480, 1451 ($\nu_{C=C}$), 1271, 1090 ($\nu_{S=O}$), 1260, 1161, 637 (ν_{C-F}), 1030, 833 (δ_{C-H}). ^{1}H NMR (acetone-d_6, ppm): 4.07 (CH_3, s, 3H), 7.79−8.45 (Ar, m, 14H). ^{13}C NMR (acetone-d_6, ppm): 28.1, 126.7, 131.7, 132.3, 133.0, 134.7, 135.7. Anal. Calcd for $C_{22}H_{20}F_6O_6S_4$: C, 42.44; H, 3.24; S, 20.60. Found: C, 42.70; H, 3.37; S, 20.85.

Bis(4-methylphenylsulfoniophenyl)methylsulfonium Tris(triflate) (4). IR (KBr, cm^{-1}): 3094, 3030, 2938 (ν_{C-H}), 1638, 1572, 1478, 1449 ($\nu_{C=C}$), 1272, 1092 ($\nu_{S=O}$), 1260, 1159, 639 (ν_{C-F}), 1032, 820 (δ_{C-H}). ^{1}H NMR (acetone-d_6, ppm): 4.06 (CH_3, s, 6H), 4.13 (CH_3, s, 3H), 7.79−8.50 (Ar, m, 18H). ^{13}C NMR (acetone-d_6, ppm): 28.1, 28.2, 126.6, 131.8, 132.3, 133.1, 133.3, 133.7, 135.2, 135.7. Anal. Calcd for $C_{30}H_{27}F_9O_9S_6$: C, 40.26; H, 3.04; S, 21.50. Found: C, 40.20; H, 3.30; S, 21.69.

Alkylation of Poly(phenylene sulfide). The typical procedure is as follows. Into an autoclave were placed poly(phenylene sulfide) (1.00 g, 9.25 mmol), methyl triflate (3.04 g, 18.5 mmol), and triflic acid (5 mL). The mixture was stirred at 110 °C for 10 h. After the reaction, the mixture was poured into 100 mL of diethyl ether to precipitate the white powdered product. The precipitate was washed with diethyl ether and dried in a vacuum for 12 h to obtain poly(methylsulfonio-1,4-phenylene triflate) (**5a**) in 100% yield.

Poly(methylsulfonio-1,4-phenylene triflate) (5a). Conversion 100%. IR (KBr, cm^{-1}): 3094, 3030, 2938 (ν_{C-H}), 1636, 1572, 1478 ($\nu_{C=C}$), 1272, 1092 ($\nu_{S=O}$), 1260, 1167, 638 (ν_{C-F}), 1032, 818 (δ_{C-H}). ^{1}H NMR (D_2SO_4, ppm): 3.38 (CH_3, s, 3H), 7.82 (Ar, s, 4H). ^{13}C NMR (D_2SO_4, ppm): 48.3, 119.2, 120.8. Anal. Calcd for $C_8H_7F_3O_3S_2$: C, 35.29; H, 2.59; S, 23.55. Found: C, 35.02; H, 2.54; S, 23.76.

Poly(ethylsulfonio-1,4-phenylene triflate) (5b). Conversion 59%. IR (KBr, cm^{-1}): 3092, 2951 (ν_{C-H}), 1638, 1570, 1478 ($\nu_{C=C}$), 1270, 1071 ($\nu_{S=O}$), 1260, 1165, 639 (ν_{C-F}), 1032, 822 (δ_{C-H}). ^{1}H NMR (acetone-d_6, ppm): 1.52, 1.55, 1.57 (CH_3, t, 1.8H), 4.56, 4.58, 4.60, 4.62 (CH_2, q, 1.2H), 7.74, 7.77, 8.20, 8.23 (Ar, q, 1.6H), 8.44, 8.49 (Ar, d, 2.4H). ^{13}C NMR (acetone-d_6, ppm): 9.9, 41.5, 114.8, 119.2, 123.8, 128.2, 133.0, 133.8.

Poly(methylsulfonio-1,4-phenylene hydrogen sulfate) (5c). Conversion 100%. IR (KBr, cm^{-1}): 3081, 2926 (ν_{C-H}), 1647, 1572, 1474 ($\nu_{C=C}$), 1329, 1186, 1071 ($\nu_{S=O}$), 853 (δ_{C-H}). ^{1}H NMR (D_2SO_4, ppm): 3.16 (CH_3, s, 3H), 7.59 (Ar, s, 4H). ^{13}C NMR (D_2SO_4, ppm): 48.0, 119.2, 120.7.

Poly(ethylsulfonio-1,4-phenylene hydrogen sulfate) (5d). Conversion 81%. IR (KBr, cm^{-1}): 3079, 2940 (ν_{C-H}), 1636, 1570, 1474 ($\nu_{C=C}$), 1323, 1181, 1071 ($\nu_{S=O}$), 853 (δ_{C-H}). ^{1}H NMR (D_2SO_4, ppm): 0.89 (CH_3, br, 2.4H), 3.83 (CH_2, br, 1.6H), 7.09 (Ar, br, 0.8H), 7.49 (Ar, br, 3.2H).

Dealkylation of 5. Polymer **5** (1.00 g) was dissolved in pyridine (20 mL). The solution was stirred at 25 °C for 30 min and at 120 °C for 10 h. The reaction mixture was poured into methanol (500 mL) containing 5 wt % hydrochloric acid. The precipitate was washed with methanol and chloroform several times. After drying in a vacuum, poly(phenylene sulfide) was obtained as a pale brown powder in 100% yield.

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