Novel Synthesis of Linear Perfluorinated Poly(phenylene sulfide) from Aryl Sulfoxide

Kenji Miyatake, Kimihisa Yamamoto,[†] Yoshihiro Yokoi, and Eishun Tsuchida*,[§]

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

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ABSTRACT: The linear perfluorinated poly(phenylene sulfide) [poly(thio-2,3,5,6-tetrafluoro-1,4-phenylene)] has been successfully prepared by polycondensation of 4-(methylsulfinyl)-2,3,5,6-tetrafluorophenyl 2,3,5,6-tetrafluorophenyl sulfide in an electrophilic reaction via the polysulfonium salt as a precursor. The polymerization proceeds efficiently in trifluoromethanesulfonic acid with the addition of phosphorus pentoxide as a dehydrating agent to produce the polymer in 100% yield. The polymer obtained is only partly soluble in 1-chloronaphthalene at 210 °C. The molecular weight (M_w) of the soluble part of the polymer is ~4000 as determined by high-temperature gel permeation chromatography. The polymer has a melting temperature of 373 °C, which is 88 °C higher than that of the unfluorinated analog (285 °C). The contact angle measurements show that the surface energy of the polymer ($\sigma_s = 41$ mN/m) is comparable to those of poly(ethylene terephthalate) and polystyrene.

Introduction

Fluorinated polymers represented by poly(tetrafluoroethylene) (PTFE) exhibit some remarkable properties including thermal and chemical stability; low refractive index, frictional resistance, and wettability, and toughness.[1] Recent interest in this area has been directed toward the synthesis of fluorinated aromatic polymers to develop a new class of high-performance polymers. Among the fluorinated aromatic polymers being prepared, the polyethers, esters, carbonates, amides, and imides containing hexafluoroisopropylidene (hexafluoroacetone) units have been studied extensively in the last decade.[2] These polymers show promise as film formers, gas separation membranes, seals, soluble polymers, and coatings and in other applications. In contrast to the CF_3-containing polymers, polymers containing perfluorophenylene moieties have not been studied much because of the limited synthetic methods available to prepare the polymers. Perfluorophenylene groups would also contribute to increasing the crystallinity and, hence, the thermal stability and mechanical strength of polymers. Some recent examples of perfluorophenylene-containing polymers are polyketones,[3] polysulfides,[4] and polydisilanes.[5]

As a semicrystalline polymer with a high melting temperature (T_m) of 285 °C and a decomposition temperature (T_d) of >400 °C, poly(phenylene sulfide) [PPS, poly(thio-1,4-phenylene)] is of significant interest for perfluorination. A previous study revealed that perfluorinated oligo(phenylene sulfide) shows photocatalytic activities for the reduction of water and olefins through the formation of polymeric radical salts.[6] The preparative methods reported for perfluorinated PPS are based on the nucleophilic aromatic substitution at high temperature (> 200 °C); that is, polycondensation of hexafluorobenzene with sodium sulfide or self-condensation of pentafluorothiophenolate alkaline salt.[7] The polymerization is activated by the fluorine substituents, and the resulting polymer might suffer some branching and/or intra- and intercross-linking.[8] The synthesis of perfluorinated PPS by electrophilic reaction under moderate conditions has never been reported.

During the course of our study to synthesize poly(arylene sulfide) by oxidative polymerization, we found[9] that aryl sulfides and sulfoxides are sufficiently activated by a strong acid to polymerize electrophilically in the Swern reaction.[10] The polycondensation proceeds efficiently under atmospheric conditions to give a high molecular weight poly(arylenesulfonium salt), which is useful as a soluble precursor of poly(arylene sulfide). In this paper, we report our first successful preparation of linear perfluorinated PPS by the polycondensation of the corresponding fluorinated aryl sulfoxide via the poly(arylenesulfonium salt). The fluorinated aryl sulfoxide could react electrophilically with thioanisole in the presence of excess trifluoromethanesulfonic acid. The successive aromatic electrophilic substitution of the perfluorinated aryl sulfonium cation gives a polymer composed of the thio-2,3,5,6-tetrafluoro-1,4-phenylene unit after demethylation. Thermal and surface properties of the perfluorinated PPS are also discussed.

Results and Discussion

Coupling Reaction of Fluorinated Thioanisole and Aryl Sulfoxide. To confirm the formation of the sulfonium compound by the electrophilic reaction of a fluorinated aryl sulfoxide, the coupling reaction of tetrafluorothioanisole (**1**) and (methylsulfinyl)tetrafluorobenzene (**2**) was carried out under acidic conditions (Scheme 1). Although thioanisole and methyl phenyl sulfoxide react in strong acid, with an H_0 (Hammett acidity function) of < -8.0, giving the quantitative formation of the dimeric sulfonium cation,[11] the coupling reaction of **1** and **2** does not proceed efficiently under the same conditions; sulfuric acid ($H_0 = -11.9$) and methanesulfonic acid ($H_0 = -7.9$) are not effective during the 1-h reaction, and the fluorinated dimeric sulfonium product (**3**) was formed in only 2% yield in trifluoromethanesulfonic acid ($H_0 = -14.1$). The yield of the product gradually increased with the reaction

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[†] Present address: Department of Chemistry, Keio University.

[§] CREST JST Investigator, Research Development Corporation of Japan.

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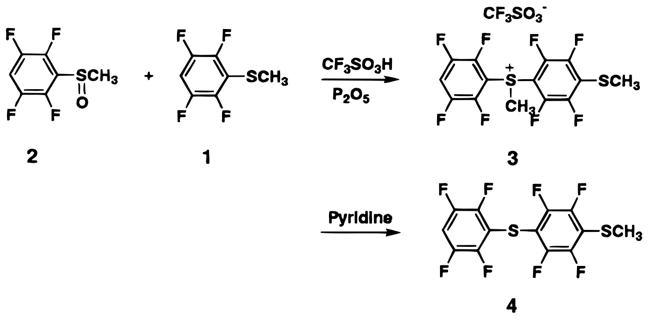
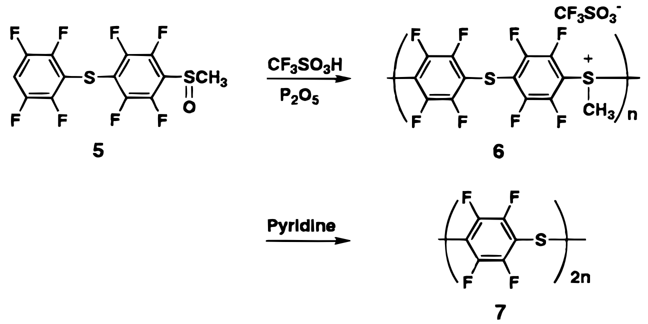
Scheme 1



Scheme 2



time up to 60% after 2 days. The four fluorine substituents of each substrate deactivate the electrophilic coupling reaction of **1** and **2** compared with the case of thioanisole and methyl phenyl sulfoxide. In attempts to promote the reaction, the addition of dehydrating agents was found to be useful for the formation of **3**. Among the several kinds of organic and inorganic dehydrating agents studied, the organic ones, which produce by dehydration a strong enough acid for the reaction, showed good activity. The most effective dehydrating agent was phosphorus pentoxide, which gave the product in 100% yield. Phosphorus pentoxide removed the water as a byproduct of the coupling reaction and kept the acidity high enough for further reaction.

The resulting fluorinated dimeric sulfonium compound, 4-(methylsulfenyl)-2,3,5,6-tetraoctafluorophenyl (2,3,5,6-tetrafluorophenyl)methylsulfonium triflate (**3**), was demethylated with pyridine to 4-(methylsulfenyl)-2,3,5,6-tetrafluorophenyl 2,3,5,6-tetrafluorophenyl sulfide (**4**), which was characterized by its IR, MS, and ^{1}H and ^{19}F NMR spectra. Satisfactory elemental analysis was also obtained.

Acid-Promoted Polycondensation of Fluorinated Aryl Sulfoxide. (4-(Methylsulfinyl)-2,3,5,6-tetrafluorophenyl) 2,3,5,6-tetrafluorophenyl sulfide (**5**) as a monomer was prepared by the oxidation of **4** with 70% nitric acid. The polymerization of **5** was carried out in trifluoromethanesulfonic acid under the same conditions as for the model reaction (Scheme 2). During the polymerization, the mixture gradually became a dark brown viscous solution due to the formation of the polysulfonium cation. A white powder of the polysulfonium cation as the triflate salt (**6a**) was isolated in 55% yield after polymerization for 2 days. The polymerization is promoted by the addition of phosphorus pentoxide (Table 1). The polymer yield increased to 97% with the addition of four equivalent amounts of phosphorus pentoxide (**6d**). A 100% yield could be also attained by extending the polymerization time for 7 days (**6e**).

Table 1. Polymerization of 5

step	P_2O_5 (M)	time (d)	yield (%)	M_n[a]	M_w[a]	M_w/M_n
a	0	2	55	970	1640	1.7
b	0.31	2	69	1030	1580	1.5
c	0.62	2	76	790	2430	3.1
d	1.25	2	97	1340[b]	4070[b]	3.0
e	1.25	7	100	2070[b]	3800[b]	1.8

[a] Molecular weight was measured by GPC as perfluorinated PPS (7) after demethylation. [b] Soluble part in 1-chloronaphthalene at 210 °C.

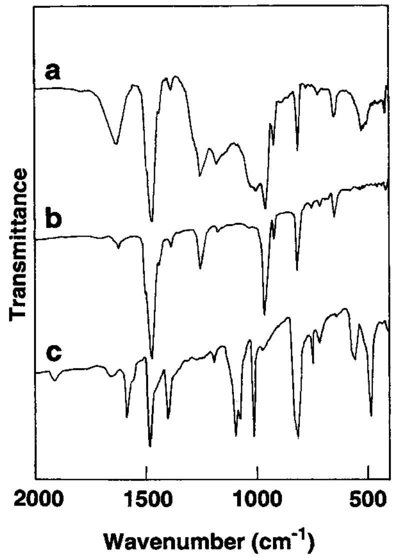


Figure 1. IR spectra of (a) **6e**, (b) **7e**, and (c) the unfluorinated poly(thio-1,4-phenylene) (PPS).

Polymer **6** is insoluble in most organic solvents and only slightly soluble in *N,N'*-dimethylformamide and sulfuric acid. In the IR spectrum of polymer **6e** (Figure 1a), a peak typical for the hexa-substituted benzene ring is observed at 1628 cm^{-1}. A strong peak at 1470 cm^{-1} is assigned to the aromatic C=C stretching vibration. Aromatic C—F stretching could also be confirmed by the peak at 812 cm^{-1}. The existence of the triflate group as the counter anion is confirmed by the peaks at 1256 (ν_{CF}), 1179 (ν_{SOasym}), 1020 (ν_{SOsym}), and 640 (ν_{CF}) cm^{-1}. In the ^{1}H NMR spectrum, only a singlet peak attributable to the sulfoniomethyl proton was observed at 3.90 ppm. Elemental analysis corresponds to the empirical formula $C_{14}H_3O_3S_3F_{11}$. The aforementioned results suggest that the resulting polymer consists of a (((methylsulfonio)-2,3,5,6-tetrafluoro-1,4-phenylene)thio)-2,3,5,6-tetrafluoro-1,4-phenylene structure with the triflate group as the counter anion.

The effect of perfluorination on the electronic structure of the poly(arylenesulfonium salt) was demonstrated by comparison of the UV spectra for polymer **6e** and its unfluorinated derivative (Figure 2). Poly((((methylsulfonio)-1,4-phenylene)thio)-1,4-phenylene triflate) has its λ_{max} at 317 nm, which is shifted to 286 nm for polymer **6e**. The hypsochromic shift due to the electron-withdrawing fluorine groups would be expected in view of our previous results on the bathochromic shift by electron-donating groups in a similar polymer system.[9d]

Polymer **6** was reacted with pyridine in excess for conversion to poly(thio-2,3,5,6-tetrafluoro-1,4-phenylene) (**7**) by demethylation. The demethylation reaction efficiently proceeds at reflux temperature to obtain the

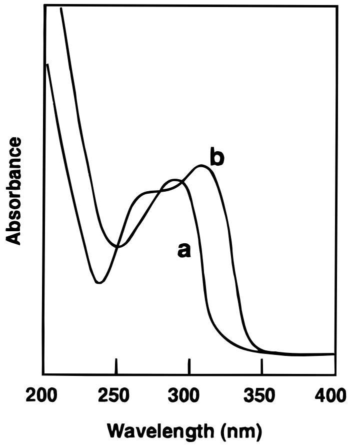


Figure 2. UV spectra of (a) **6e** and (b) poly((((methylsulfonio)-1,4-phenylene)thio)-1,4-phenylene triflate).

product as a white powder in 100% yield. The resulting polymers **7a**−**c** are insoluble at room temperature and soluble in some halogenated aromatic solvents such as 1,2,4-trichlorobenzene and 1-chloronaphthalene above 200 °C. However, only <20 wt% of **7d** and **7e** is soluble in 1-chloronaphthalene at 210 °C. In the IR spectrum of polymer **7e** (Figure 1b), the peak at 1470 cm^{-1} (attributable to the aromatic C═C stretching vibration) is a sharp singlet like that of the unfluorinated linear PPS (Figure 1c). The IR spectrum of polymer **7e** is almost consistent with that of the perfluorinated PPS prepared by the polycondensation of potassium pentafluorothiolate in a nucleophilic reaction at 240 °C,[12] except for a minor peak observed at 1410 cm^{-1} for the latter polymer. These results suggest that polymer **7** has a linear structure.[13] The demethylation was complete because the peaks assigned to the triflate counter anion disappeared. The existence of the end methylsulfinyl groups has not been confirmed.

The molecular weight of the soluble part of polymers **7a**−**e** in hot 1-chloronaphthalene was measured by high-temperature gel permeation chromatography (GPC) at 210 °C. A number-average molecular weight (M_n) of 2070 and a weight-average molecular weight (M_w) of 3800 for the soluble part of **7e** were determined relative to polystyrene standards. From these values, the degree of polymerization (P_n) is ∼11−20. The insoluble part of the polymer could not be characterized, but is expected to have a molecular weight higher than the soluble part.[14]

Thermal and Surface Properties of Perfluorinated PPS. Polymer **7e** is crystalline and shows a high T_m at 373 °C with a heat of fusion (ΔH) of 68 J/g, which was determined by differential scanning calorimetry (DSC, Figure 3). The melting temperature is 88 °C higher than that of the unfluorinated PPS, because perfluorination of PPS contributes to a lower entropy of fusion (ΔS) and hence, increases the T_m. Because **7e** consists of a strictly linear structure and probably has a high molecular weight, the T_m is 51 °C higher than the reported value (T_m = 322 °C) for the previous perfluorinated PPS.[15] In the second DSC scan after quenching from the melt, a clear glass transition temperature (T_g) could not be observed. Thermogravimetric analysis (TGA) shows that polymer **7e** begins to decompose above the T_m in a nitrogen atmosphere. The T_g of polymer **7e** is lower than that of the unfluorinated PPS (T_d = 420 °C). It is thought that the perfluorination would weaken the C_{Ph}—S—C_{Ph} linkage in the main chain. After heating to 600 °C, 23% of its original weight remains as a black solid.

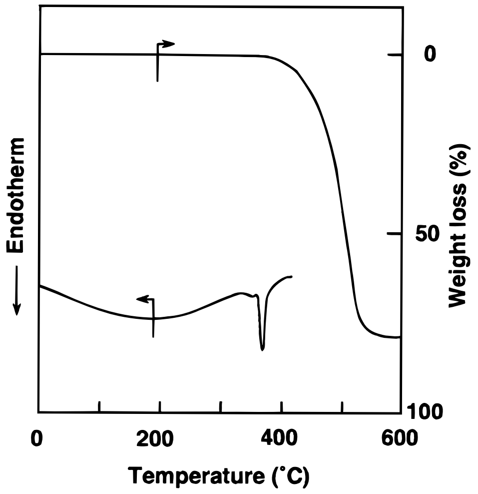


Figure 3. DSC and TGA thermograms of **7e**.

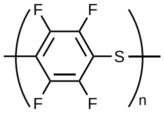
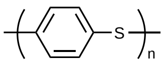
The surface energies for polymer **7e** and the unfluorinated PPS as melt pressed samples placed onto glass slides were obtained from contact angle measurements with water, methylene iodide, ethylene glycol, and formaldehyde on the sample surfaces (Table 2). Polymer **7e** has a total surface tension of 41 mN/m, a value that is comparable to those of other aromatic-containing polymers [poly(ethylene terephthalate) = 44 mN/m; polystyrene = 41 mN/m] but higher than that of PTFE (22 mN/m). Fluorine substituents in general contribute to lowering the dispersive surface tension of hydrocarbon polymer solids; however, the dispersive force component (σ_s^d) of polymer **7e** is higher than that of the unfluorinated PPS (37 mN/m). Although there have been no systematic reports about the effect of perfluorination on aromatic polymers, it appears that aromatic fluorine groups, unlike the -CF_2- and -CF_3 groups, would not have much effect on the solid surface tension.

Conclusions. It has been found that fluorinated aryl sulfoxide is activated enough by strong acid in excess trifluoromethanesulfonic acid/P_2O_5 to electrophilically react with fluorinated thioanisole. The acid-promoted reaction of the sulfoxide could be applied to the polymerization to obtain a poly(arylenesulfonium salt) composed of perfluorophenylene and methylsulfonio groups. The demethylation of the polysulfonium salt gave a perfluorinated poly(phenylene sulfide) with a strict 1,4-linkage. Perfluorination of PPS results in the hypsochromic shift of the $\pi-\pi^*$ transition and an increased T_m. The solid surface tension of the polymer (41 mN/m) is slightly lower than that of the unfluorinated PPS (43 mN/m).

Experimental Section

Measurement. The IR spectra were obtained as KBr pellets with a JASCO FT/IR-5300 spectrometer. The band resolution was maintained at 2 cm^{-1} for all measurements. The UV-vis spectra were obtained with a Shimazu UV-2100 spectrophotometer. A quartz glass cell with a 0.2-cm optical path length was employed. The ^{1}H and ^{19}F NMR spectra were recorded on a JEOL JNM-LA500 (500 MHz ^{1}H, 470 MHz ^{19}F) spectrometer. The ^{1}H NMR chemical shifts were calibrated with tetramethylsilane (0 ppm) as the internal standard. The ^{19}F NMR chemical shifts were calibrated with trifluoroacetic acid (76.5 ppm) as the internal standard. Elemental analysis was performed on a Perkin Elmer PE-2400 II and a Metrohm 645 Multi-DOSIMAT. Two parallel analyses were performed

Table 2. Surface Tension Data of Perfluorinated PPS (7e) and PPS

	contact angle (degree)				solid surface tension (mN/m)		
polymer	H_2O	CH_2I_2	ethylene glycol	formamide	σ_s^d	σ_s^p	σ_s
	95	44	64	71	41	0	41
	84	34	58	63	37	6	43

for each sample. Gas chromatography (GC) was carried out on a Shimazu GC14B system. The GC mass spectra were recorded on a Shimazu GCMS-QP5050 instrument with an ionization energy of 70 eV. 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. The molecular weight of the polymer was determined by high-temperature GPC (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. Contact angle measurements were done using a Kyowa Interface Science CA-X goniometer with distilled solvent at 25 °C. Five measurements were made on each sample at different locations. The combined Owens-Wendt/Young equation used is:

$$\frac{\sigma_l(1+\cos\theta)}{2(\sigma_l^d)^{1/2}} = (\sigma_s^d)^{1/2} + (\sigma_s^p)^{1/2}\left(\frac{\sigma_l^p}{\sigma_l^d}\right)^{1/2} \qquad (1)$$

where θ is the contact angle and σ is the surface tension. Subscript l refers to the contact angle test liquids and subscript s refers to the solid. Superscript d refers to the dispersion force component of the surface tension and superscript p refers to the polar component. The values used for these components come from the literature.[16] The solid surface tension can be obtained from the intercept and slope of eq 1.

Materials. Commercially guaranteed reagents of 2,3,5,6-tetrafluorothiophenol, iodomethane, trifluoromethanesulfonic acid, dichloromethane, 70% nitric acid, phosphorus pentoxide, pyridine, and potassium hydroxide were obtained from the Kanto Chemical Company, Inc. or Aldrich Chemical Company, Inc. and used without further purification.

Synthesis of 4-(Methylsulfinyl)-2,3,5,6-tetrafluorophenyl 2,3,5,6-Tetrafluorophenyl Sulfide (5). A typical procedure for the synthesis of **5** was as follows. 2,3,5,6-Tetrafluorothiophenol (10.93 g, 0.06 mol) and potassium hydroxide (4.49 g, 0.08 mol) were dissolved in 120 mL of water. Iodomethane (11.36 g, 0.08 mol) was added to the solution, and the mixture was stirred for 30 min at 20 °C and for 3 h at 50 °C. The progress of the reaction was followed by thin layer chromatography (TLC) and GC. The resulting solution was extracted with three 100-mL portions of dichloromethane. The combined dichloromethane extracts were dried over anhydrous sodium sulfate and evaporated to obtain a colorless oil of 2,3,5,6-tetrafluorothioanisole (**1**, 11.42 g, yield 97%).

To a 40-mL dichloromethane solution of **1** (9.81 g, 0.05 mol), 85 mL of 70% nitric acid was added. The mixture was vigorously stirred using a magnetic stirrer for 3 h. The mixture turned from colorless to pale yellow accompanied by the evolution of nitric dioxide. The usual workup gave the white powder of 1-methylsulfinyl-2,3,5,6-tetrafluorobenzene (**2**, 9.76 g, yield 92%).

To the mixture of **1** (7.84 g, 0.04 mol), **2** (8.48 g, 0.04 mol), and phosphorus pentoxide (7.10 g, 0.05 mol), 30 mL of trifluoromethanesulfonic acid was added in a dropwise manner over a period of 1 h with stirring. The reaction was continued for another 8 h until the solution became reddish-brown. The mixture was diluted with 50 mL of water and then neutralized with 50 mL of pyridine followed by refluxing at 100 °C for 10 h. The usual workup gave 14.85 g of crude product. Simple vacuum distillation afforded a colorless oil of pure **4** (13.99 g, yield 93%). Compound **4** was oxidized with 70% nitric acid by the method just described to produce **5** (yield 88%).

2,3,5,6-Tetrafluorothioanisole (1). IR (KBr, cm^{-1}): 3034, 2934, 1501, 1236, 1194, 918, 712. ^{1}H NMR ($CDCl_3$, ppm): 2.50 (s, 3H), 6.99 (m, 1H). ^{19}F NMR ($CDCl_3$, ppm): −135.6 (m), −139.2 (m). Anal. calcd for $C_7H_4SF_4$: C, 42.86; H, 2.06; F, 38.74. Found: C, 42.81; H, 1.88; F, 38.59. MS (*m*/*z*): 196 (M^+), 181 ($M^+ - CH_3$).

1-Methylsulfinyl-2,3,5,6-tetrafluorobenzene (2). IR (KBr, cm^{-1}): 3034, 2931, 1501, 1236, 1194, 1061, 918, 889, 710. ^{1}H NMR ($CDCl_3$, ppm): 3.12 (s, 3H), 7.26 (m, 1H). ^{19}F NMR ($CDCl_3$, ppm): −135.5 (m), −139.8 (m). Anal. calcd for $C_7H_4OSF_4$: C, 39.83; H, 1.90; F, 35.82. Found: C, 39.97; H, 1.68; F, 35.61. MS (*m*/*z*): 212 (M^+), 197 ($M^+ - CH_3$), 149 ($M^+ - SOCH_3$).

4-(Methylsulfenyl)-2,3,5,6-tetrafluorophenyl 2,3,5,6-Tetrafluorophenyl Sulfide (4). IR (KBr, cm^{-1}): 3034, 2920, 2854, 1493, 1470, 1233, 1179, 918, 712. ^{1}H NMR ($CDCl_3$, ppm): 2.51 (s, 3H), 7.01 (m, 1H). ^{19}F NMR ($CDCl_3$, ppm): −133.0 (m), −139.5 (m). Anal. calcd for $C_{13}H_4S_2F_8$: C, 41.49; H, 1.07; F, 40.39. Found: C, 41.25; H, 0.92; F, 40.40. MS (*m*/*z*) 376 (M^+), 351 ($M^+ - CH_3$).

4-(Methylsulfinyl)-2,3,5,6-tetrafluorophenyl 2,3,5,6-Tetrafluorophenyl Sulfide (5). IR (KBr, cm^{-1}): 3034, 2920, 1493, 1466, 1254, 1236, 1082, 957, 916, 716. ^{1}H NMR ($CDCl_3$, ppm): 3.17 (s, 3H), 7.17 (m, 1H). ^{19}F NMR ($CDCl_3$, ppm): −131.9 (m), −140.1 (m). Anal. calcd for $C_{13}H_4OS_2F_8$: C, 39.80; H, 1.03; F, 38.74. Found: C, 40.03; H, 0.99; F, 38.54. MS (*m*/*z*) 392 (M^+), 377 ($M^+ - CH_3$), 329 ($M^+ - SOCH_3$).

Polymerization. A typical procedure for the polymerization of **5** was as follows. Compound **5** (1.02 g, 2.6 mmol) and phosphorus pentoxide (1.77 g, 12.5 mmol) were placed in a 100-mL three-necked round-bottom flask equipped with a mechanical stirrer to which 10 mL of trifluoromethanesulfonic acid was added in a dropwise manner over a period of 30 min. The solution changed from colorless to bright blue in 20 min and finally to dark brown. After running the reaction for 7 d at 20 °C, the viscous mixture was poured into 200 mL of diethyl ether to precipitate a powder, which was successively washed with diethyl ether and dried under a vacuum for 8 h. The white powder of poly((((methylsulfonio)-2,3,5,6-tetrafluoro-1,4-phenylene)thio)-2,3,5,6-tetrafluoro-1,4-phenylene triflate) (**6e**) was obtained in 100% yield.

The resulting polymer **6e** (1.00 g) was dissolved in 20 mL of pyridine and heated at 100 °C. A white powder of the product precipitated during the reaction. The white suspension was heated to reflux and stirred for another 10 h to complete the demethylation. The mixture was poured into 200 mL of 10% hydrochloric methanol to obtain the crude product. The usual work-up gave poly(thio-2,3,5,6-tetrafluoro-1,4-phenylene) (**7e**) in 100% yield.

Poly((((methylsulfonio)-2,3,5,6-tetrafluoro-1,4-phenylene)thio)-2,3,5,6-tetrafluoro-1,4-phenylene triflate) (6e). IR (KBr, cm^{-1}): 2918, 1628, 1470, 1256, 1179, 999, 961, 812, 640. ^{1}H NMR (D_2SO_4, ppm): 3.90 (s, 3H). Anal. calcd for

($C_{14}H_3O_3S_3F_{11}$): C, 32.07; H, 0.58; S, 18.35; F, 39.86. Found: C, 32.18; H, 0.66; S, 18.06; F, 39.66.

Poly(thio-2,3,5,6-tetrafluoro-1,4-phenylene) (7e). IR (KBr, cm^{-1}): 2940, 1468, 1258, 959, 920, 812, 644. Anal. calcd for (C_6SF_4): C, 40.01; S, 17.80; F, 42.19. Found: C, 40.25; S, 17.77; F, 41.98. $T_m = 373$ °C.

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References and Notes

(1) For reveiws, see: (a) *Fluoropolymers*; Wall, L. A., Ed.; John Wiley & Sons: New York, 1972. (b) Mark, H. F.; Bikales, N. M.; Overberger, G. G. In *Encyclopedia of Polymer Science and Engineering, 2nd ed.*; Menzes, G., Ed.; John Wiley & Sons: New York, 1987; Vol. 7, pp 256−257; Vol. 16, pp 577−600. (c) Feiring, A. E. In *Organofluorine Chemistry Principles and Commercial Applications*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum: New York, 1994; Chapter 15, p 339.

(2) Cassidy, P. E.; Aminabhavi, T. M.; Farley, J. M. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29 (2, 3)*, 365.

(3) Goodwin, A. A.; Mercer, F. W.; McKenzie, M. T. *Macromolecules* **1997**, *30*, 2767.

(4) (a) Ding, Y.; Hay, A. S. *Macromolecules* **1996**, *29*, 6386. (b) Ding, Y.; Hay, A. S. *Macromolecules* **1997**, *30*, 2527.

(5) Kira, M.; Tokura, S. *Organometallics* **1997**, *16*, 1100.

(6) (a) Murano, K.; Kawazura, H.; Inokuchi, H.; Ohmori, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3230. (b) Kawazura, H.; Yamamoto, Y.; Ohmori, T.; Murano, K.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 829. (c) Maruo, K.; Yamada, K.; Wada, Y.; Yanagida, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1053.

(7) Robson, P.; Stacey, M.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc.* **1960**, 4754.

(8) Aromatic nucleophilic substitution of hexafluorobenzene and 4-(*t*-butyl)thiophenol as a model reaction gives bis(4-(*t*-butyl)-phenylsulfenyl)tetrafluorobenzene with isomer distribution of 96% *para*, 3% *meta*, and 0.5% *ortho*. See: Kellman, R.; McPheeters, J. C.; Gerbi, D. J.; Williams, R. F. *Polym. Prepr.* **1981**, *22*, 383.

(9) (a) Yamamoto, K.; Shouji, E.; Nishide, H.; Tsuchida, E. *J. Am. Chem. Soc.* **1993**, *115*, 5819. (b) Tsuchida, E.; Suzuki, F.; Shouji, E.; Yamamoto, K. *Macromolecules* **1994**, *27*, 1057. (c) Yamamoto, K.; Shouji, E.; Suzuki, F.; Kobayashi, S.; Tsuchida, E. *J. Org. Chem.* **1995**, *60*, 452. (d) Tsuchida, E.; Yamamoto, K.; Miyatake, K.; Nishimura, Y. *Angew, Chem. Int. Ed. Engl.* **1996**, *35*, 2843.

(10) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.

(11) Tsuchida, E.; Shouji, E.; Yamamoto, K. *Macromolecules* **1993**, *26*, 7144.

(12) Christopher, N. S. J.; Cotter, J. L.; Knight, G. J.; Wright, W. W. *J. Appl. Polym. Sci.* **1968**, *12*, 863.

(13) Aromatic C=C stretching vibration in this area is sensitive to structural defects (tri-thio substitution) of polymers composed of thio-1,4-phenylene structure. The peak at 1410 cm^{-1} has also been observed in the IR spectrum of unfluorinated poly(phenylene sulfide) containing a small amount of branching structure. See: Lenz, R. W.; Handlovitz, C. E. *J. Polym. Sci.* **1960**, *43*, 167.

(14) High molecular weight PPS ($M_w > 2 \times 10^5$) without detectable structural defects is obtained by the polycondensation of the unfluorinated monomer by a similar method.

(15) Elsenbaumer, R. L.; Shacklette, L. W.; Sowa, J. W.; Baughman, R. H. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 229.

(16) (a) Kaelble, D. H. *J. Adhesion* **1970**, *2*, 66. (b) Kaelble, D. H.; Dynes, P. J.; Cirlin, E. H. *J. Adhesion* **1974**, *6*, 23.

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