Synthesis of Block Copolymers Containing Perfluoroalkane and Tetrafluoroethylene–Perfluoro(propyl vinyl ether) Block Copolymer with Sulfide Bonds

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ABSTRACT: Poly[thio-1,4-(phenylenethio)perfluoroalkane], poly[thio-1,4-phenyleneoxy-1,4-(phenylenethio)perfluoroalkane], and poly(phenylene sulfide)-*block*-[poly(tetrafluoroethylene-*co*-perfluoro(propyl vinyl ether)])-*block*-poly(phenylene sulfide) are synthesized by oxidative cationic polymerization. Poly[thio-1,4-phenyleneoxy-1,4-(phenylenethio)perfluorohexane] (T_g, 34 °C; T_m, 144 °C; $T_{d10\%}$, 394 °C; M_w, 57 000) is completely oxidized to poly[sulfonyl-1,4-phenyleneoxy-1,4-(phenylenesulfonyl)perfluorohexane] (T_g, 147 °C; $T_{d10\%}$, 395 °C; M_w, 48 500) using H_2O_2/CF_3COOH (1/1 = v/v). Poly(TFE-*co*-PVE) copolymer (M_w, 6000) linking poly[methyl 4-[(phenylthio)phenyl]sulfonium trifluoromethanesulfonate](polysulfonium cation) at both sides is synthesized through the copolymerization with methyl 4-(phenylthio)phenyl sulfoxide. The block prepolymer is converted to poly(phenylene sulfide)-*block*-[poly(tetrafluoroethylene-*co*-perfluoro(propyl vinyl ether)]-*block*-poly(phenylene sulfide) (T_g, 90 °C; T_c, 138 °C; T_m, 276 °C; $T_{d10\%}$, 395 °C) by demethylation of the polycation.

Introduction

Poly(phenylene sulfide) (PPS) is a crystalline polymer possessing excellent attributes[1] such as high thermal stability, chemical resistance, and good mechanical and electrical properties, which result in it being noted as the sixth general-purpose engineering plastic. However, the structural properties make it brittle and low sliding,[2] a disadvantage in comparison with the other engineering plastics. Therefore, much effort has been directed toward improving this disadvantage, *e.g.*, increasing the toughness and decreasing the dielectric constant by blending with other polymers.[3] The properties of the polymer alloy are dominated by the dispersibility. It is difficult to make the PPS alloy with high compatibility due to the high melting point and high crystallinity,[4] which result in restricting the kind of polymer for PPS alloy.

Recently, it was reported that addition of perfluoroalkane polymer into PPS increases the toughness and high sliding.[5] The copolymer of PPS with a perfluoroalkane segment should be employed to develop the high-performance polymers. However, the copolymerization with perfluoroalkane is not achieved because the high-temperature processes for making the PPS segment, such as polycondensation of dichlorobenzene with sodium sulfide[6] or halothiophenolate salts,[7] result in the decomposition of the perfluoroalkane polymers accompanied with elimination HF or HI due to the strong nucleophilicity of the sulfide compounds.

We previously reported on the oxidative polymerization through electrophilic reaction for synthesis of PPS; *e.g.*, aromatic compounds, such as *p*-xylene, could be reacted with sulfur chloride to yield the corresponding poly(arylene sulfides),[8] and methyl 4-(phenylthio)phenyl sulfoxide is polymerized to PPS via polysulfonium [poly(methyl 4-(phenylthio)phenylsulfonium trifluoromethanesulfonate)] as the soluble precursor.[9] The polymerization proceeds through the electrophilic attack of sulfonium cation at room temperature. The compounds substituted with more than two aromatic rings with high electron density are allowed to react with the cationic active species to form the sulfide bond. Perfluoroalkane chains binding phenylene rings at the both ends are applicable to prepare PPSs containing the perfluoroalkane segment.

As a remarkable characteristic of the sulfur atom, the sulfide bond is easily oxidized and converted to the sulfone or sulfoxide bond using oxidants.[10] It is well known that the existence of the sulfone bond in a main chain provides polyaromatics with a high glass transition temperature (T_g). Poly(arylene sulfone)s such as poly(ether sulfone) and polysulfone show relatively high T_g (>200 °C) which leads to upgrade their qualities, such as toughness, solubility in common solvents, transparency, and making a film as amorphous characteristics.[11] It is useful to convert an amorphous polymer having a high T_g by the facile oxidation of a soluble poly(arylene sulfide).

This paper describes the synthesis of thiophenylene polymer containing a perfluoroalkane segment by the oxidative polymerization at room temperature.

Experimental Section

Materials. Dichloromethane and chloroform were purchased from Tokyo Kasei Co. and distilled twice in the usual manner. 2,3-Dichloro-2,6-dicyano-4-benzoquinone (DDQ) was purchased from Merck (>98%) and used without further purification. 1,6-Diiodoperfluorohexane and 1,4-diiodoperfluorobutane were purchased from the Asahi Glass Co., Ltd. 4-(Phenoxyphenyl)thiophenol was synthesized by the nucleophilic reaction of 4-bromodiphenyl ether (purchased from Tokyo Kasei Co.) and an excess of sodium sulfide (Kanto Chemical Co.). Methyl phenyl sulfide was purchased from Tokyo Kasei Co., and methyl phenyl sulfoxide was obtained by the oxidation of the methyl phenyl sulfide.

α,ω-Bis(phenylenethio)perfluorohexane (1m). A three-necked round bottom flask equipped with reflux condenser and PTFE-covered stirring bar was charged with NaH (60%) (21.8

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g, 0.545 mol) and washed with anhydrous THF. THF was removed by a syringe, and the residue was evaporated. DMF (500 mL) was charged, and thiophenol (60 g, 0.545 mol) was added via a dropping funnel over a 10 min period at −5 °C. The reaction was stirred for 30 min, and 1,6-diiodoperfluorohexane (150 g, 0.271 mol) was added via a dropping funnel over a 10 min period. The reaction temperature was raised to 60 °C, and the reaction was continued for 2 h. The reaction mixture was then poured into 2 L of ice−water, filtered, and recrystallized in ethanol (129.4 g, yield 92.1%). IR (KBr, cm^{-1}): 1482, 1582 ($\nu_{C=C}$); 1101, 1142, 1169(ν_{CF}); 692, 831, 868(ν_{CH}). Anal. Calcd for $C_{18}H_{10}F_{12}S_2$: C, 41.71; H, 1.94. Found: C, 41.83; H, 1.99.

α,ω-Bis(phenyleneoxy-1,4-phenylenethio)perfluorobutane (2m). A three-necked round bottom flask equipped with reflux condenser and PTFE-covered stirring bar was charged with NaH (60%) (21.8 g, 0.545 mol) and washed with anhydrous THF. THF was removed by a syringe, and the residue was evaporated. DMF (500 mL) was charged, and 4-phenoxythiophenol (110 g, 0.545 mol) was added via a dropping funnel over a 10 min period at −5 °C. The reaction was stirred for 30 min, and 1,4-diiodo-perfluorobutane (123 g, 0.271 mol) was added via a dropping funnel over a 10 min period. The reaction temperature was raised to 60 °C, and the reaction was continued for 2 h. The reaction mixture was then poured into 2 L of ice−water, filtered, and recrystallized in ethanol (146.8 g, yield 90.0%). Anal. Calcd for $C_{28}H_{18}F_8O_2S_2$: C, 55.81; H, 2.99; F, 25.25; S, 10.63. Found: C, 55.56; H, 2.91; F, 25.40; S, 10.60. IR (KBr, cm^{-1}): 1480, 1580 ($\nu_{C=C}$); 1240 (ν_{COC}); 1101, 1140, 1169 (ν_{CF}); 690, 830, 870 (δ_{CH}). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): 6.65−7.85 (phenyl, m). ^{19}F-NMR (400 MHz, $CDCl_3$, ppm): −111.3, −122.0. DSC: mp 63.5 °C.

α,ω-Bis(phenyleneoxy-1,4-phenylenethio)perfluorohexane (3m). A three-necked round bottom flask equipped with reflux condenser and PTFE-covered stirring bar was charged with NaH (60%) (21.8 g, 0.545 mol) and washed with THF. The THF was removed by a syringe, and the residue was evaporated. DMF (500 mL) was charged, and 4-phenoxythiophenol (110 g, 0.545 mol) was added via a dropping funnel over a 10 min period at −5 °C. The reaction was stirred for 30 min, and 1.6-diiodoperfluorohexane (150 g, 0.271 mol) was added via a dropping funnel over a 10 min period. The reaction temperature was raised to 60 °C, and the reaction was continued for 2 h. The reaction mixture was poured into 2 L of ice−water, filtered, and recrystallized in ethanol (167.3 g, yield 88.0%). IR (KBr, cm^{-1}): 1482, 1581 ($\nu_{C=C}$); 1240 (ν_{COC}); 1100, 1140, 1170 (ν_{CF}); 691, 832, 871 (δ_{CH}). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) 6.65−7.85 (phenyl, m). ^{19}F-NMR (400 MHz, $CDCl_3$, ppm): −87.5, −119.5, −122.0. Anal. Calcd for $C_{30}H_{18}F_{12}O_2S_2$: C, 51.28; H, 2.56. Found: C, 51.25; H, 2.62. DSC: mp 84.0 °C.

α,ω-Bis(phenyleneoxy-1,4-phenylenethio)poly(TFE-*co*-PVE). A three-necked round bottom flask equipped with reflux condenser and PTFE-covered stirring bar was charged with NaH (60%) (3.2 g, 0.079 mol) and washed with anhydrous THF. THF was removed by a syringe, and the residue was evaporated. DMF (500 mL) was charged, and 4-phenoxythiophenol (16 g, 0.079 mol) was added via a dropping funnel over a 10 min period at −5 °C. After the reaction was stirred for 30 min α,ω-diiodo poly(TFE-*co*-PVE) (M_w = 6000; 50 g, 7.59 × 10^{-3} mol) was added in the solution. The reaction was carried out with vigorous stirring for 24 h at 60 °C. After the reaction the mixture was poured into 2 L of ice−water, filtrated, and washed with ethanol. After being resolved in 1,1,2-trichloro-1,2,2-trifluoroethane the product was purified by using a silica gel column. The product yield: 42%, 21 g.

The substitution of oxyphenylenethiophenylene groups on α,ω-diiodo poly(TFE-*co*-PVE) was confirmed by ^{1}H and ^{19}F-NMR. The product showed no peak attributed to $-CF_2I$ (−59 ppm) of the end group but a peak attributed to $-CF_2SPhOPh$ at −87 ppm. The phenyl protons of the end group were also observed in ^{1}H-NMR. The IR spectrum of α,ω-bis(phenyleneoxy-1,4-phenylenethio)poly(TFE-*co*-PVE) is shown in Figure 5c. ^{1}H-NMR (400 MHz, hexafluorobenzene−$CDCl_3$, ppm) 6.65−7.85 (phenyl, m). ^{19}F-NMR (400 MHz, $CDCl_3$, ppm): −140 (−CF−); −117, −119, −120, −127 ($-CF_2-$); −87 ($-CF_2S$); −81 (CF_3); −79 (OCF_2-). Reference α,ω-diiodopoly(TFE-*co*-PVE): ^{19}F-NMR −59 ppm ($-CF_2I$).

Table 1. Oxidative Polymerization of Aromatics Containing a Perfluoroalkyl Chain with S_2Cl_2[a]

monomer	polymer	yield (%)	M_w[b]	M_w/M_n[b]	[η] (dL g^{-1})[c]	(°C) T_g	T_m	$T_{d_{10\%}}$
1m	**1p**	65	1700	1.6				
2m	**2p**	91	16 300	2.0	0.15	47	114	408
3m	**3p**	100	57 500	2.6	0.39	34	144	394
	4p	92	48 500	2.1		147		395

[a] Oxidizing agent: DDQ (equimolar of S_2Cl_2), 40 h. [b] Measured by GPC standard in polystyrene. [c] In $CHCl_3$ at 30 °C.

Polymerization Procedure. α,ω-Bis(phenyleneoxy-1,4-phenylenethio)perfluorohexane (**1a**) and 1,4-bis(phenyleneoxy-1,4-phenylenethio)perfluorobutane (**2a**) (2 mmol) were allowed to react with sulfur chloride (1 mmol) in the presence of DDQ (1 mmol), trifluoroacetic acid (10 mmol), and trifluoroacetic anhydride (2 mmol) in dichloromethane (90 mL) for 40 h. The polymerization proceeded homogeneously at room temperature and atmospheric pressure. The color of the reaction mixture turned from dark green to off-white. The white powder was isolated by precipitation in methanol (HCl 5%) (Table 1).

Poly)thio-1,4-phenyleneoxy-1,4-phenylenethio-1,4-perfluorobutylenethio-1,4-phenyleneoxy-1,4-phenylene) (2p). IR (KBr, cm^{-1}): 1480, 1580 ($\nu_{C=C}$); 1240 (ν_{COC}); 1100, 1140, 1168 (ν_{CF}); 690, 830, 870 (δ_{CH}). ^{13}C-NMR (400 MHz, $CDCl_3$, ppm): 116.5, 118.8, 120.6, 131.2, 132.9, 139.3, 155.2, 159.8 (phenyl C). ^{19}F-NMR (400 MHz, $CDCl_3$, ppm): −88.0, −119.0. Anal. Calcd for $C_{28}H_{16}F_8O_2S_3$: C, 53.16; H, 2.55. Found: C, 53.30; H, 2.42.

Poly(thio-1,4-phenyleneoxy-1,4-phenylenethio-1,6-perfluorohexylenethio-1,4-phenyleneoxy-1,4-phenylene) (3p). IR (KBr, cm^{-1}): 1482, 1581 ($\nu_{C=C}$); 1240 (δ_{COC}); 1100, 1140, 1170 (ν_{CF}); 690, 832, 868 (δ_{CH}). ^{13}C-NMR (400 MHz, $CDCl_3$, ppm): 116.3, 118.8, 120.7, 131.3, 132.9, 139.3, 155.1, 159.0. ^{19}F-NMR (400 MHz, $CDCl_3$, ppm): −87.0, −119.0, −122.0. Anal. Calcd for $C_{30}H_{16}F_{12}O_2S_3$: C, 49.18; H, 2.20. Found: C, 19.23; H, 2.17.

Model Reaction from Sulfide to Sulfone. A three-necked round bottom flask (100 mL) with a PTFE-covered magnetic stirring bar was charged with α,ω-bis(phenyleneoxy-1,4-phenylenethio)perfluorohexane (1 g, 1.42 mmol) and chloroform (10 mL). Trifluoroacetic acid (10 mL) and hydroxy peroxide were added to the flask and stirred at room temperature. After 10 min of stirring, the reaction mixture was refluxed by heating for 12 h. The reaction mixture was poured into water (500 mL) and washed with water. The white powder was dried under vacuum at room temperature for 20 h. Yield: 1.01 g (93.5%). IR (KBr, cm^{-1}): 3093, 1582, 1487, 1367, 1253, 1217, 1161, 867, 844, 762, 693. ^{1}H-NMR (400 MHz, ppm, $CDCl_3$): 7.10−8.05 (phenyl, m). Anal. Calcd for $C_{30}H_{18}S_2O_2F_{12}$: C, 51.29; H, 2.58. Found: C, 51.11, H, 2.51. DSC: mp 157.2 °C.

Oxidation of Poly(thio-1,4-phenyleneoxy-1,4-phenylenethio-1,6-perfluorohexane). A three-necked round bottom flask (100 mL) with a PTFE-covered magnetic stirring bar was charged with poly(thio-1,4-phenyleneoxy-1,4-phenylenethio-1,6-perfluorohexane) (**3p**) (1 g) and chloroform (10 mL). Trifluoroacetic acid (10 mL) and hydroxy peroxide were added to the flask and stirred at room temperature. After 10 min of stirring, the reaction mixture was refluxed by heating for 12 h (also 1, 3, 6 h). The reaction mixture was poured into methanol (500 mL) and washed with water and methanol. After filtration, the resulting polymer was purified by continuous extraction in a Soxhlet apparatus with methanol (500 mL) for 5 h and was dried *in vacuo* at 60 °C for 20 h. The resulting polymer was isolated as a white powder. Yield: 1.04 g (92%). IR (KBr, cm^{-1}): 1578, 1488, 1384, 1253, 1212, 1162, 874, 838, 700, 556. ^{1}H-NMR (400 MHz, ppm, $CDCl_3$): 7.20, 7.31, 7.98, 8.09 (phenyl, AB quartet). ^{19}F-NMR (400 MHz, ppm, $CDCl_3$): −121.4, −119.2, −111.8. Anal. Calcd for $C_{30}H_{16}S_3O_8F_{12}$: C, 43.49; H, 1.95. Found: C, 43.44; H, 1.96. DSC: T_g, 138 °C; $T_{d10\%}$, 395 °C.

Model Reaction of Sulfoxide with Perfluoroalkane. A 200 mL three-necked round bottom flask equipped with a

PTFE-covered magnetic stirring bar, dropping funnel, and thermometer was charged with α,ω-bis(phenyleneoxy-1,4-phenylenethio)perfluorohexane (2 g, 2.8 mmol), methyl phenyl sulfoxide (1.6 g, 11.4 mmol), and dichloromethane (10 mL). Trifluoromethanesulfonic acid (3.5 g, 22.8 mmol) in dichloromethane (10 mL) was charged into a dropping funnel and added to the reaction mixture. The mixture was stirred for 10 h at room temperature. The reaction mixture was then extracted with chloroform (100 mL) and water (100 mL), and the organic layer was washed with water, dried (Na_2SO_4), and concentrated to afford a 3.3 g crystalline product, yield 92%. IR (KBr, cm^{-1}): 3023, 2932, 1570, 1478, 1422, 1258, 1210, 638, 1161, 1066, 833, 760. ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): 7.28, 7.30, 7.38, 7.41, 7.77, 7.79, 7.81, 8.16, 8.17, 8.22, 8.24 (phenyl, 26H, m), 3.97 (methyl, 6H, s). Anal. Calcd for $C_{46}H_{32}O_8S_6F_{18}$: C, 44.3; H, 2.59. Found: C, 44.1; H, 2.55.

Model Reaction of Methyl 4-(Phenylthio)phenyl Sulfoxide with Diphenyl Sulfide. A 100 mL round bottom flask with PTFE-covered magnetic stirring bar was charged with methyl 4-(phenylthio)phenyl sulfoxide (1 g, 4 mmol) and diphenyl sulfide (15 mg, 2 mmol %). Trifluoromethanesulfonic acid (5 mL) was added at 0 °C. The reaction mixture became dark blue and was stirred for 1 h at 10 °C. The reaction temperature was increased to room temperature and stirred for 18 h. After the reaction, the reaction mixture was poured into ice–water and washed with water to remove excess trifluoromethanesulfonic acid. The precipitate was dissolved in acetone 10 mL and poured into benzene (100 mL), washed with benzene, and dried in vacuo at room temperature for 20 h. Yield: 1.47 g (96%). IR (KBr, cm^{-1}): 3086, 3023, 2932, 1570, 1478, 1422, 1258, 1161, 1067, 816, 638. ^{1}H-NMR (CDOOD, ppm) 7.7–7.9 (d, phenyl 8H), 3.8 (s, methyl 3H).

The product was quantitatively converted to polyphenylene sulfide by demethylation. Molecular weight of the resulting polyphenylene sulfide was determined by high-temperature GPC (see ref 9). M_n: 9500. M_w: 25 000.

Synthesis of Polysulfonium-*block*-poly(TFE-*co*-PVE)-*block*-polysulfonium. A 500 mL three-necked round bottom flask equipped with a mechanical stirring stick (vacuum sealing type), thermometer, and dropping funnel was charged with α,ω-bis(phenyleneoxy-1,4-phenylenethio)poly(TFE-*co*-PVE) (30.0 g, 5 mmol as M_w 6000) and 1,1,2-trichloro-1,2,2-trifluoroethane (100 mL). After the poly(TFE-*co*-PVE) had dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane, the flask was cooled to 0 °C and trifluoromethanesulfonic acid (200 mL) was added. Methyl 4-phenylthiophenyl sulfoxide (50 g, 200 mmol) was gradually added for 1 h. The reaction mixture became dark blue and was stirred for 1 h at 10 °C. The reaction temperature was increased to room temperature and stirred for 18 h. After the reaction, the reaction mixture was poured into ice–water and washed with water to remove excess trifluoromethanesulfonic acid. After being dipped in 3 L of water for 20 h, the resulting polymer was suspended in acetonitrile (600 mL), stirred for 2 h at reflux temperature, and filtered to remove the homopolymer of polysulfonium. The filtrate was washed with acetonitrile and dried in vacuo for 24 h at room temperature to give 99.1 g, yield 93%. IR (KBr, cm^{-1}): 3086, 3023, 2932, 1570, 1478, 1422, 1258, 1161, 1067, 816, 638. ^{1}H-NMR (CD_3CN, 400 MHz, ppm): 7.63, 7.66, 7.85, 7.88 (AB quartet, phenyl 8H), 7.3–7.7 (m, end phenyl H), 3.62 (s, methyl 3H). ^{19}F-NMR (CD_3CN, 400 MHz, ppm): −78 (s, $CF_3SO_3^-$), −79, −81, −117, −119, −120, −127, −140, (s, TFE/PVE).

Synthesis of Poly(phenylene sulfide)-*block*-poly(TFE-*co*-PVE)-*block*-poly(phenylene sulfide). The block copolymer can be demethylated by refluxing pyridine. A 1 L three-necked round bottom flask equipped with a mechanical stirring stick (vacuum sealing type), thermometer, and reflux condenser was charged with obtained polymer (101.4 g) and acetonitrile (600 mL). The solution was stirred at room temperature for 2 h, and pyridine (80 g, 1.01 mmol) was added to demethylate the polysulfonium. The reaction mixture was stirred at room temperature for 10 h. The pale yellow suspension changed to a white suspension. The reaction temperature was increased, and the mixture was refluxed for 20 h and then precipitated in methanol (10% HCl, 2 L) and washed with water and methanol. The obtained polymer was refluxed in ethanol (1 L) for 5 h to wash the polymer and 1,1,2-trichloro-1,2,2-trifluoroethane (1 L) to remove the poly(TFE-*co*-PPVE) homopolymer for 15 h and dried in vacuo for 15 h at 60 °C (66.8 g, yield 96.5%). IR (KBr, cm^{-1}): 3065, 1572, 1472, 1387, 1234, 1091, 1074, 1009, 812, 554, 481. CP/MAS ^{13}C-NMR (400 MHz, ppm) 133.4, 136.5 (phenyl C). ^{19}F-NMR (400 MHz, ppm) −79, −81, −117, −119, −120, −127, −140.

Measurements. ^{1}H-, ^{13}C-, and ^{19}F-NMR were recorded using a FT-NMR (GXS 400, JEOL Co.). 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 SSC/220 (Seiko Co.) thermal analyzer: sample size, 7–10 mg; heating rate, 20 °C/min. Thermogravity (TG) measurements were done in a nitrogen atmosphere on a TG/DTA 220 (Seiko Co.) thermal analyzer: sample size, 7–10 mg; heating rate 20 °C/min. The determination of the molecular weight of the resulting polymer was measured using a GPC (Shimadzu Co.: LC-9A, SPD-6AV (265 nm) column, Asahi Chemical Industry Co. Ltd., GS-510H + GS-310H) with THF (1 mL/min) as the eluent.

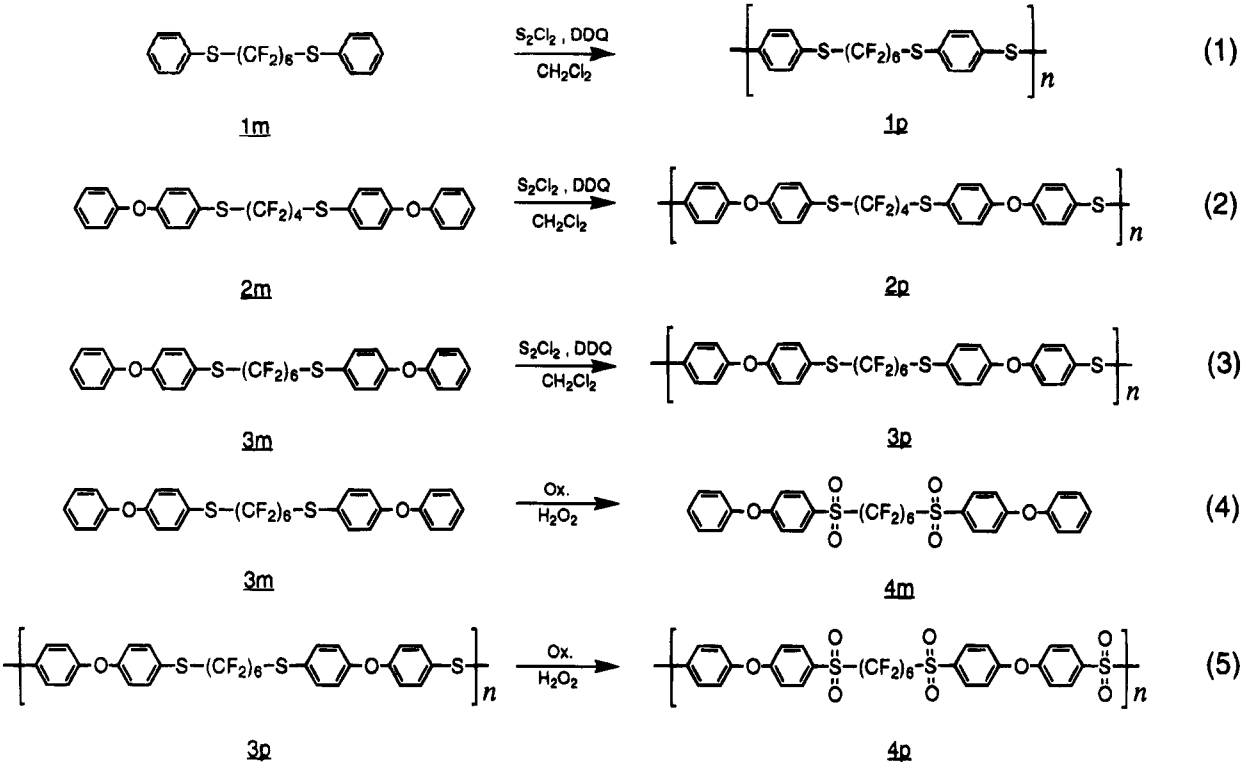
Results and Discussion

Polymerization of Perfluoroalkane with Sulfur Chloride. It has already been reported that predominant sulfide bond formation proceeds by the electrophilic substitution of aromatics with sulfur chloride through oxidation in which electron-donating substituents in the aromatics, such as ether, sulfide, and alkyl groups, accelerate the oxidative polymerization. Perfluoroalkane compounds (**1m**, **2m**, **3m**) incorporating the phenylthio or 4-(phenylthio)phenyl group at the end position were synthesized as a reactive monomer for the oxidative polymerization with sulfur chloride. α,ω-Bis(phenylthio)perfluorobutane (**1m**) and α,ω-bis(phenyleneoxy-1,4-phenylenethio)perfluorobutane (**2m**) were allowed to react with sulfur chloride in the presence of 2,3-dichloro-5,6-dicyano-4-benzenoquinone (DDQ) to yield the corresponding sulfide linked polymers (Scheme 1, eqs 2 and 3). The polymerization of **1m** does not proceed efficiently (Scheme 1, eq, 1). The perfluoroalkane binding the phenylthio groups at both sides shows lower reactivity to sulfur chloride than the (4-phenoxyphenyl)-thio one because of the lower *p*-electron density of phenyl carbon at the *p*-position due to the strong electron-withdrawing nature of the perfluoroalkane. The substituted phenoxy group in the α,ω-bis(phenyleneoxy-1,4-phenylenethio)perfluoroalkane is effective for promotion of the oxidative polymerization to keep the high *p*-electron density of the end phenyl group at the *p*-position.

The resulting polymer **3p** from the polymerization of the monomer **3m** for 40 h has a M_w = 57 500 and inherent viscosity, $[\eta]_{inh}$ 0.39 dL g^{-1}. Both resulting polymers, **2p** and **3p**, are soluble in organic solvents, such as chloroform, tetrahydrofuran, and *N*-methyl-2-pyrrolidone, which make it processible as a self-supporting film by casting from solution. However, the resulting polymers of **2m** and **3m** are precipitated in dichloromethane solution during the polymerization. The growth reaction is suppressed by the poor solvent solubility of **2p** and **3p**. The molecular weight depends on the solubility in CH_2Cl_2 because the polymer precipitated during the polymerization.

The reaction time of 20 h in the polymerization of **3m** is not enough to provide the high molecular weight polymer with high yield;[12] *i.e.*, the polymer was isolated with 58% yield and the M_w is determined to be 12 000. The reaction time over 40 h did not result in increase of the molecular weight more than M_w = 57 500. It is suggested that termination of the reaction is caused mainly on the precipitation and/or aggregation of the

Scheme 1



polymers in dichloromethane. The polymerization in the higher feed concentration (1.0 M) resulted in the decrease of the molecular weight (M_w = 5000). The polymerization was carried out at 50 °C for 4 h in an airtight reactor after the polymerization for 20 h at room temperature. **3p** with M_w = 64 000 was obtained because the phase separation was suppressed by the high temperature.

The structure of these polymers (**2p** and **3p**) was confirmed by spectroscopic measurements. AB quartet peaks at 6.97, 7.09, 7.32, 7.42 ppm that come from the neighboring protons of the phenyl ring reveal that the phenyl sulfide and phenyl ether are connected with a 1,4-linkage. The ^{13}C-NMR spectrum of the polymer **3p** shows eight carbons attributed to the aromatics. ^{19}F-NMR reveals the existence of three kinds of fluorines at −121,.4, −119.5, and −87.8 ppm (Figure 4). These results show that the resulting polymer contains a linear binding with a sulfide bond as the main structure. The formation of 1,2-linkage at the end of phenoxy ring of the monomer occurred because the smaller oxygen atom size compared to sulfur and higher electron density[13] at the *o*-position than that of thiophenylene one give rise to substitution at the *o*-position of the phenoxy group, which is supported by very small peaks in the region of the phenyl carbon in ^{13}C-NMR. The polymer **3p** was identified as poly(thio-1,4-phenyleneoxy-1,4-phenylenethio-1,6-perfluorohexane) from its spectroscopic measurements.

DSC analysis of annealed samples of **2p** and **3p** show a endothermic peak ascribed to the melting point at 114 and 144 °C, respectively, and quenched samples show a glass transition at 47 and 34 °C, respectively, in the DSC measurement. The dielectric constant of the polymer **3p** at 1000 Hz at 25 °C was 2.9, which is lower than that of PPS (ϵ:3.1).

Synthesis of Perfluoroalkane Polymer Binding Sulfone Bond. The polyalkyl sulfides are easily oxidized from the sulfide not to the sulfoxide but to the sulfone. The oxidation of the sulfide bond to sulfone was carried out by using hydrogen peroxide. As a controlled reaction, the oxidation of the aryl perfluoroalkyl sulfide was examined using 1,6-bis(phenyleneoxy-1,4-phennylenethio)perfluorohexane (**3m**) (Scheme 1, eq 4) with hydrogen peroxide as the oxidizing agent. After the oxidation for 12 h, 1,6-bis(sulfonyl-1,4-phenyleneoxy-1,4-phenylene)perfluorohexane (**4m**) was produced without detectable formation of the sulfoxide bond which was confirmed by IR (Figure 2). The thermogram of the oxidized product **4m** shows a single melting point at 157.2 °C. The oxidation from sulfide to sulfone bond using hydrogen peroxide (30%) enables it to be applicable to the oxidation of **3p** (Scheme 1, eq 5). The reaction time is enough to be over 3 h, which was confirmed by IR and ^{1}H-NMR spectra. It was obvious that the over 3 h reaction time was suitable for the complete oxidation from sulfide to sulfone. IR and ^{1}H-NMR spectra of the resulting polymer obtained after 12 h reveals the formation of **4p** (Figures 1 and 3). The ^{19}F-NMR spectrum of **3p** shows peaks at −121.4, −119.2, and −111.8 ppm (Figure 4). These chemical shifts from −87.8 to −111.8 ppm after the oxidation were attributed to the perfluoromethylene binding sulfone bond.

The ^{1}H-NMR spectrum of poly(ether sulfone) (PES) shows AB quartet peaks at 7.26, 7.39, 7.99, and 8.12 ppm. Since the unit of polymer **3p** is regarded as a similar structure of PES whose phenyl ring is alternatively bound with ether and sulfone at the 1,4-position, a couple of AB quartet peaks (7.20, 7.31, 7.98, 8.09 ppm) are ascribed to Ha, Hb and Hc, Hd. In the oxidation of **3p**, the chemical shifts of Hd, Hc are believed to agree with that of Ha, Hb. By means of DSC measurement, the T_g of **4p** was observed at 138 °C which was about 100 °C higher than that of **3p**. No melting point was observed in the region from 100 to 300 °C. The oxidation from sulfide to sulfone of **3p** makes it amorphous. The TG measurement shows $T_{d10\%}$ = 395 °C. The transport and flexible film of **3p** was obtained by casting from solution.

The molecular weight of **4p** was determined to be 48 500, which is lower than that of **4p**. The result

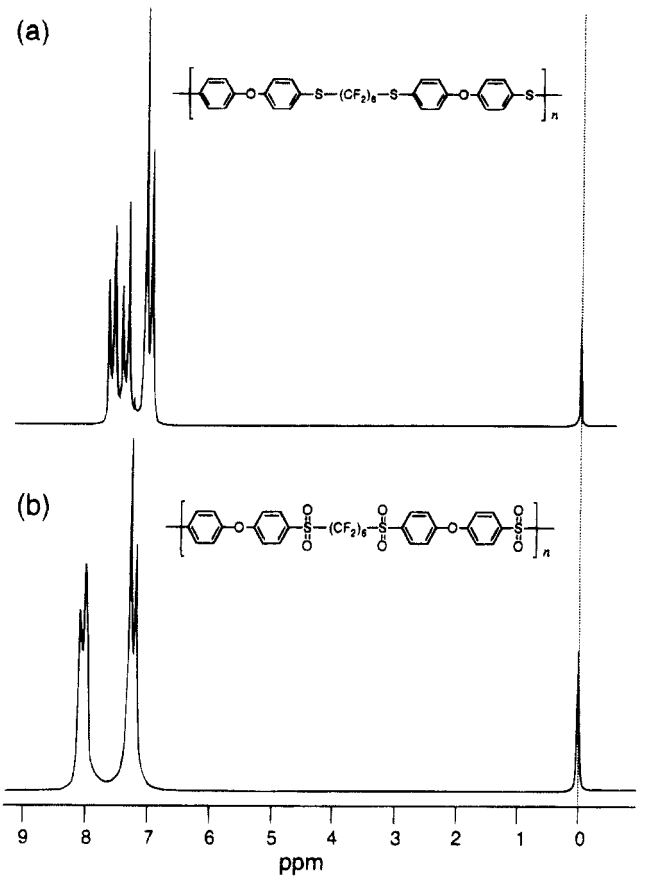


Figure 1. ^{1}H-NMR spectra of the resulting polymers **3p** (a) and **4p** (b).

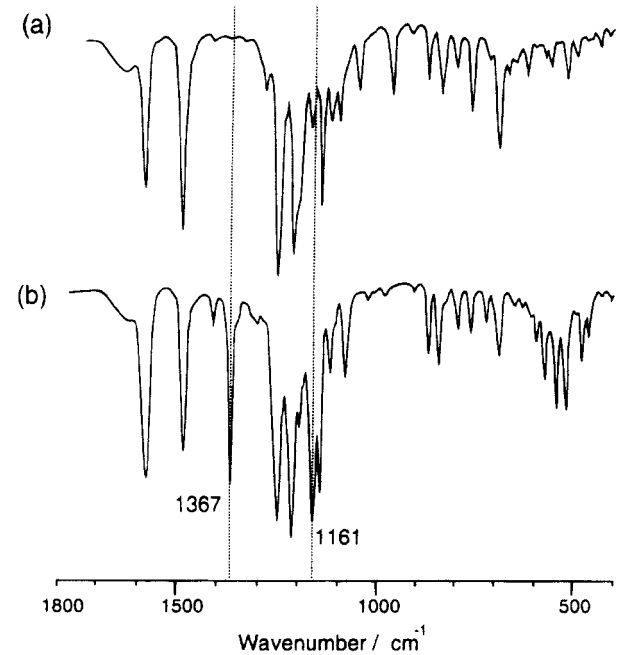


Figure 2. IR spectra of the resulting compound **3m** (a) by oxidation of **4m** (b) as the model reaction.

indicates that cleavage of the S–S bond in the main chain occurs by the oxidation with hydroxy peroxide.[14] We have already concluded[15] that the oxidative polymerization of disulfide provides poly(arylene sulfide) with a S–S bond. A disulfide bond in the resulting polymer (**3p**) is cleaved, which resulted in the formation of the lower M_w of **3p**.

Synthesis of Block Copolymer of PPS with Poly(TFE-*co*-PVE). The electrophilic reaction of methyl phenyl sulfoxide with 1,6-bis(phenyleneoxy-1,4-phenylenethio)perfluorohexane in trifluoromethanesulfonic acid (Scheme 2) was performed to examine the formation of sulfide bond as a model reaction. The sulfoxide is allowed to react with the perfluoroalkane with over 95% yield at the *p*-position of both end phenyl groups[16] to form the sulfonium bond. It is feasible to convert the sulfonium bond to the sulfide bond. The model reaction shows that the thiophenylene group is efficiently introduced to both end groups of the perfluoroalkane-substituted oxyphenylene unit.

The model reaction was performed by using diphenyl sulfide instead of poly(TFE-*co*-PVE) ([monomer]/[diphenyl sulfide] = 50) in order to examine the control of molecular weight in the polymerization. In the presence

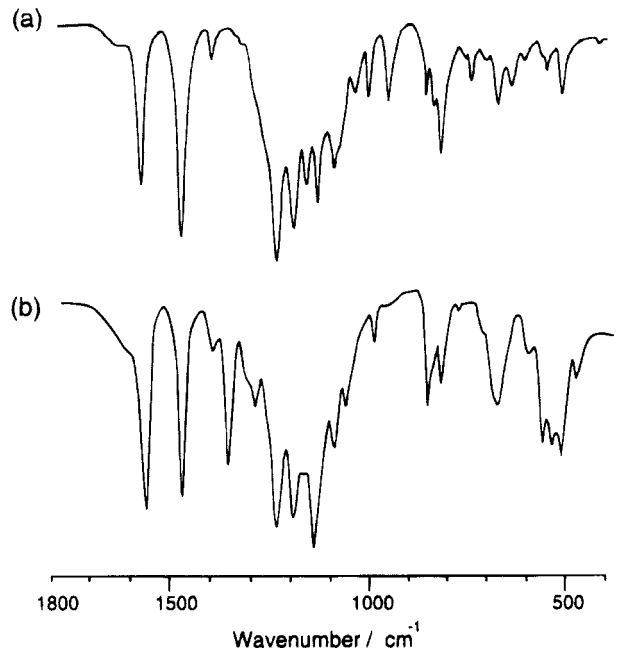


Figure 3. IR spectra of polymer **3p** before (a) and after (b, **4p**) oxidation.

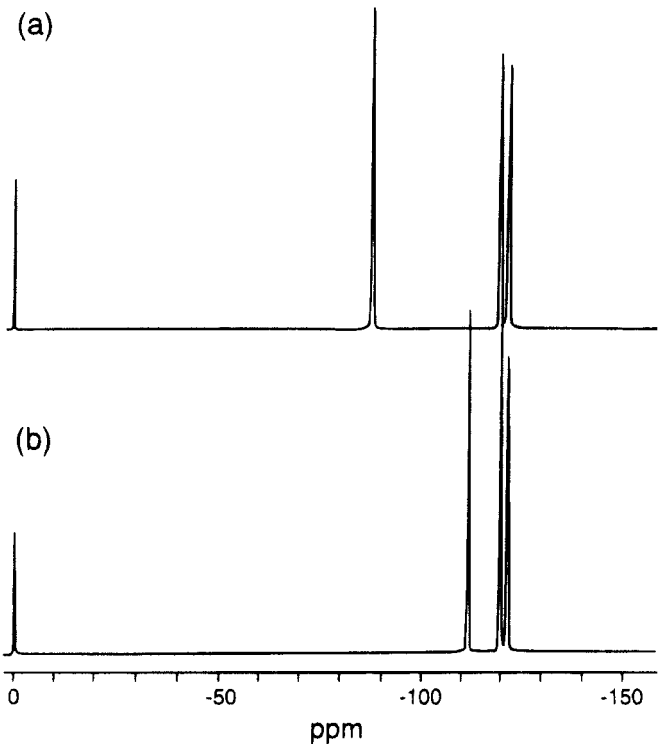
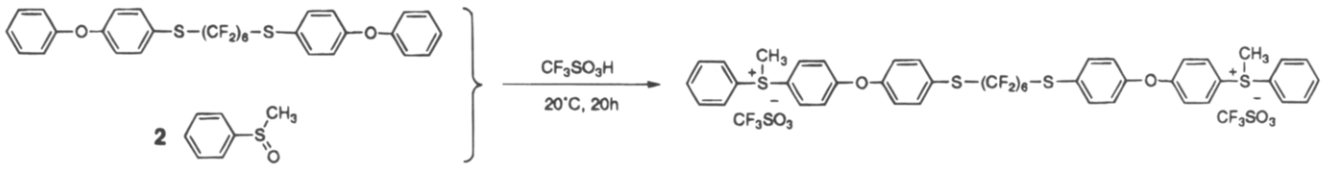
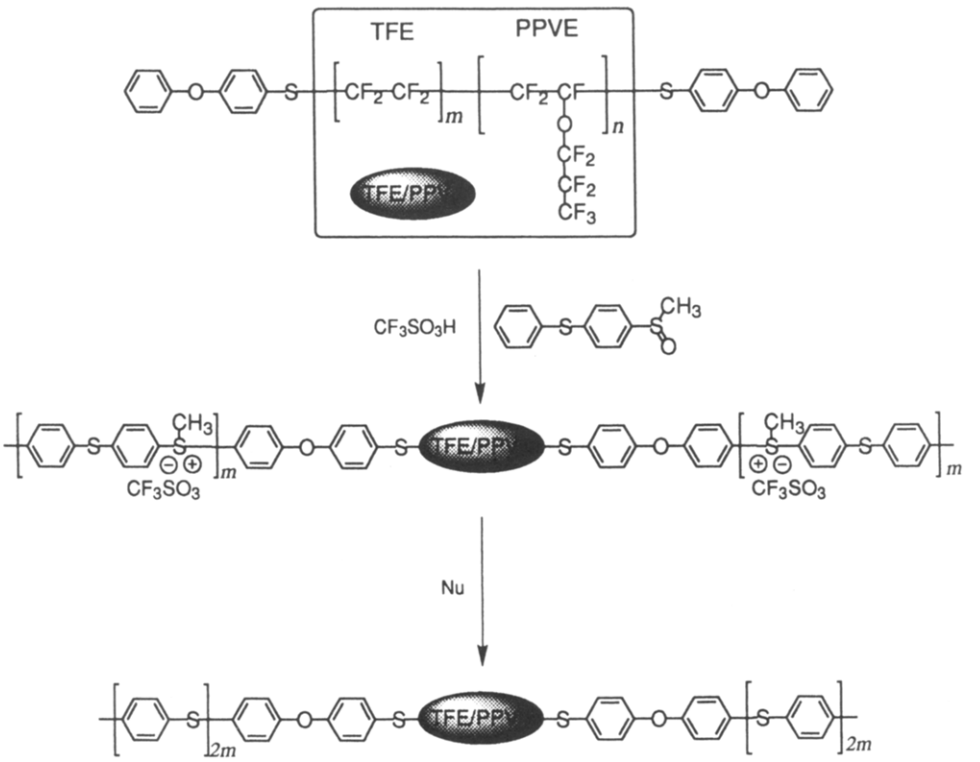


Figure 4. ^{19}F-NMR spectra of **3p** (a) and **4p** (b) in $CDCl_3$ at 25 °C.

Scheme 2



Scheme 3



of 2 mol % diphenyl sulfide polyphenylene sulfide with DP = *ca.* 90 is isolated. The result indicates molecular weight of the resulting polymer corresponds to the concentration of diphenyl sulfide in the conditions.

On the basis of the model reactions, the copolymerization of methyl 4-(phenylthio)phenyl sulfoxide with poly(TFE-*co*-PVE) was carried out a mixture of 1,1,2-trichloro-1,2,2-trifluoroethane /trifluoromethanesulfonic acid as the polymerization solvent for 10 h (Scheme 3). Polysulfonium and poly(TFE-*co*-PVE) are soluble in trifluoromethane sulfonic acid and 1,1,2-trichloro-1,2,2-trifluoroethane, respectively. The solvent viscosity increased at the end stage of the polymerization. The resulting polymer was washed with 1,1,2-trichloro-1,2,2-trifluoroethane and acetonitrile repeatedly to remove the unreacted poly(TFE-*co*-PVE) and homopolymer of polysulfonium.[17] The block copolymer was isolated with 93% yield. This means that the degree of the PPS segment is estimated to be ca. 20 as an average which depends on the feed concentration ratio of the monomers.[18]

The resulting polymer has a peak at 638 cm^{-1} in the IR spectrum, which is attributed to trifluoromethanesulfonate and at 816 cm^{-1} that corresponds to the phenylene-1,4-linkage in the polythiophenylene segment. Peaks at 7.63, 7.66, 7.85, and 7.88 ppm in the ^{1}H-NMR correspond to the aromatic 8H. Methyl 3H was observed at 3.62 ppm which is shifted to a higher magnetic field due to the positively charged sulfur atom. The presence of poly(TFE-*co*-PVE) was confirmed by IR peaks at 1258 and 1067 cm^{-1}. ^{19}F-NMR also shows peaks at −77.7 (CF_3SO_3), −78.7, −81.3, and −127.4 (perfluoroalkane chain).

These spectroscopic data indicate that it is not denied the slight possibility of the formation of diblock polymer. The poly(TFE-*co*-PVE) has two oxyphenylene groups at the end of the chain, which shows the chemical shift of the phenyl protons at 6.65−7.85 ppm similar to those of **1m** and **2m**. The ^{1}H-NMR spectrum of the resulting block polymer of polysulfonium and poly(TFE-*co*-PVE) did not show the peaks around 6.65−7.3 ppm but did show peaks around 7.3−7.9 ppm whose chemical shifts are assigned to phenyl protons at the end thiophenylene groups of the polysulfonium chain (main peaks at 7.6 and 7.8 are attributed to the polysulfonium chain).

After the demethylation with pyridine, the resulting polymer was isolated as a pale yellow powder. In the IR spectrum, the powder has an absorption peak at 812 cm^{-1} attributed to a CH out-of-plane vibration of the benzene ring and an absorption peak at 1234 cm^{-1} attributed to a CF out-of-plane vibration of the perfluoroalkane chain (Figure 5). The ν_{CH} absorption peaks of the methyl group and peaks of $CF_3SO_3^-$ disappear in the IR spectrum. The demethylation proceeds through a trans-methylation mechanism from the sulfonium cation to pyridine. Quantitative formation of the methylpyridiniuom salt was confirmed as a byproduct. ^{19}F-NMR shows peaks at −78.7, −81.3, and −127.4 ppm and CP-MAS ^{13}C-NMR show peaks at 133.4 and 136.5 ppm. These spectroscopic data indicate the presence of the poly(TFE-*co*-PVE) and PPS structure.

After a O_2 plasma etching treatment of the resulting copolymer, a three dimensional stitch is observed (di-

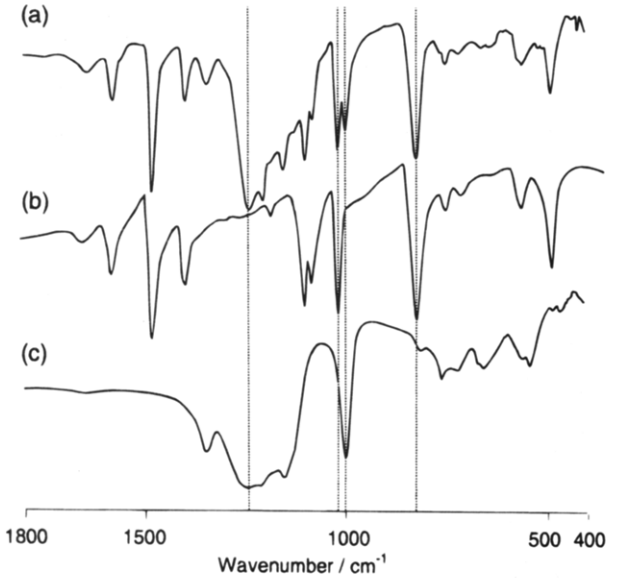


Figure 5. IR spectra of the (a) resulting PPS-poly(TFE-*co*-PVE) block copolymer, (b) PPS prepared by the precursor method,[9] and (c) poly(TFE-*co*-PVE) homopolymer.

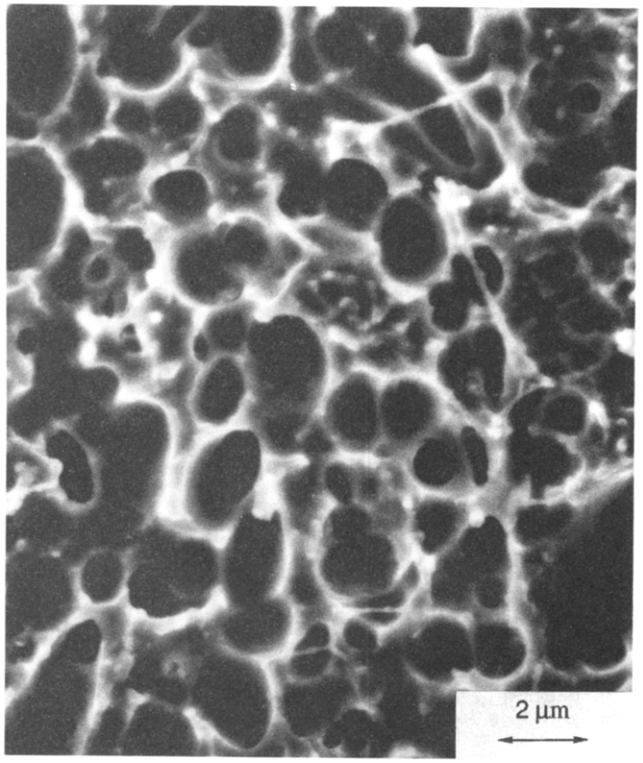


Figure 6. Scanning electron micrograph of the resulting PPS-poly(TFE-*co*-PVE) block copolymer.

ameter of one stitch is about 2 nm) by means of the SEM analysis (Figure 6), which supports a homogeneous microphase separation between PPS and poly(TFE-*co*-PVE) segment. The results mean an advantage for a new composite material of PPS and poly(TFE-*co*-PVE) for which is well-known that both polymers are not miscible as a simple blend. The DSC measurement shows peaks at $T_g = 90$ °C, $T_c = 138$ °C, and $T_m = 276$ °C which come from the PPS moieties.

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(12) The oxidative polymerization of α,ω-diaryl alkanes has been already reported. Yamamoto, K.; Jikei, M.; Miyatake, K.; Katoh, J.; Nishide, H.; Tsuchida, E. *Macromolecules* **1994**, *27*, 4312. The rate determining step is the formation of (arylthio)sulfenyl chloride (ArSSCl) as an active species. In the case of the oxyphenylene group, *e.g.*, anisole, which is similar to the end group of perfluoroalkane monomers the rate constant k of the formation of the active species has been already determined to be 4.6×10^{-5} dm^3 mol^{-1} by means of UV/vis spectroscopic measurement. It is assumed that the polymerization of α,ω-bis((phenyleneoxy)-1,4-phenylenethio)-perfluoroalkanes obeys similar kinetics.
(13) The electron density of the thiophenylene ring and oxyphenylene ring has been already confirmed by computational calculations. According to the results, the ratio of the electrophilic attack on the *o*-position of the oxyphenylene ring is higher than that of thiophenylene. Shouji, E.; Yamamoto, K.; Katoh, J.; Nishide, H.; Tsuchida, E. *Polymers Adv. Technol.* **1991**, *2*, 149.
(14) The disulfide bond is easily oxidized with an oxidant to form the sulfinate and then is converted to the sulfonic acid finally through the cleavage. In the oxidation, it is assumed that the cleavage takes place. The solubility of the resulting sulfonyl polymer increases in comparison with the sulfide polymer. The low molecular weight part in the resulting polymer is removed by the reprecipitation with methanol. The polydispersity of the resulting polymer did not increase remarkably after the sulfonation of **3m**.
(15) Sulfur chloride reacts with aromatics to form disulfenyl chloride (PhSSCl). The PhSSCl is electrophilically substituted on the phenyl ring of the monomer and the diaryl disulfide is formed as an intermediate. The once-formed disulfide is oxidatively polymerized via a cationic mechanism. We have already confirmed the existence of an interesting S−S bond polymer prepared by the oxidative polymerization of disulfide.
(16) Methylphenyl sulfoxide is not polymerized to the polysulfonium salt in the conditions. The active species which is formed by protonation of the sulfoxide in the strong acidic atmosphere could not be electrophilically substituted on the phenylene ring of the other methylphenyl sulfoxide because of low electron density due to the sulfoxide substituent. That is, methylphenyl sulfoxide is not coupled to yield the sulfonium dimer under these conditions.
(17) The solubility of the polysulfonium salt and poly(TFE-*co*-PVE) is quite different. After the polymerization, the homopolymer from the resulting block copolymer was repeatedly extracted by refluxing in the good solvents. After several extractions, the homopolymer was not contained in the solution. After the extraction of the PPS-poly(TFE-*co*-PVE) copolymer in 1-chloronaphthalene at 210 °C PPS, which is very soluble in hot 1-chloronaphthalene, was not detected in the solution.
(18) The polymerization of methyl 4-(phenylthio)phenyl sulfoxide proceeds quantiatively. Tsuchida, E.; Shouji, E.; Yamamoto, K. *Macromolecules* **1993**, *26*, 7144.