Thermal Polymerization of Diaryl Disulfides To Yield Poly(arylene sulfide)s

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ABSTRACT: The reaction of aromatic compounds and sulfur monochloride is investigated as a convenient route to prepare disulfides. Bis[4-[(4-bromophenyl)oxy]phenyl] disulfide (**I**), bis[4-[(4-bromophenyl)thio]-phenyl] disulfide (**II**), and bis[4-[[[(4-bromophenyl)sulfonyl]phenyl]oxy]phenyl] disulfide (**III**) were prepared through the electrophilic reaction of sulfur monochloride with aromatic compounds catalyzed by SiO_2. The thermal polymerization of the disulfide **I** results in the formation of high molecular weight poly(thio-1,4-phenyleneoxy-1,4-phenylene) (PPOS; M_w = 141 000) which is a high crystalline polymer with high stability after melting. The crystallographic data reveal that the resulting PPOS and poly(phenylene sulfide) both possess an orthorhombic unit cell.

Introduction

Aryl disulfides are valuable compounds as initiators for radical polymerization and as monomers for thermal polymerization and oxidative polymerization. For example, at 260 °C bis(4-iodophenyl) disulfide[1-5] is polymerized to poly(*p*-phenylene sulfide) (PPS) as a high-performance engineering plastic.[6] The poly(arylene sulfide)s have also been synthesized through the oxidative polymerization of diphenyl disulfide.[7,8]

A convenient and efficient disulfide formation is effected by the oxidation of thiols. However, disulfides having a more complicated structure have been synthesized by the Leuckart method from anilines as the starting material.[9] In contrast, Friedel–Crafts reactions of aromatic compounds and sulfur or sulfur monochloride (S_2Cl_2) with Lewis acids result in the formation of aryl sulfide compounds through an electrophilic reaction. However, these reactions are not suitable for the quantitative formation of the disulfide. We have reported the synthesis of poly(arylene sulfide)s through the oxidative polymerization of aromatic compounds with S_2Cl_2.[10] The predominant formation of the sulfide bond provides a low-cost process.

Our present work reveals the halosubstituted diaryl disulfides can be prepared through the electrophilic reaction of aromatics with S_2Cl_2 using silica gel as a catalyst. The resulting disulfides were allowed to polymerize to poly(arylene sulfide)s in the presence of KI at 230–280 °C. The structures and thermal properties of the resulting poly(arylene sulfide)s are described in this paper.

Experimental Section

Materials. 4-Bromodiphenyl ether (Aldrich; >99%), 1-bromonaphthalene (Kantoh Chem.; >98%), 4-bromobiphenyl (Tokyo Kasei; >96%), and bromobenzene (Kantoh Chem.; >95%) were used without further purification. 4-Bromodiphenyl sulfide was prepared from diphenyl sulfide and bromine in CCl_4 at room temperature in the presence of a catalytic amount of Fe powder [yield, 70%; 138 °C (1.6 mm Hg)]. S_2Cl_2 (Wako Chem.; >90%) was also used without further purification. Silica gel (Merck; >230 mesh) was dried in vacuo at 100 °C for 24 h.

Bis[4-[(4-bromophenyl)oxy]phenyl] Disulfide (I). 4-Bromodiphenyl ether (0.1 mol) and S_2Cl_2 (0.05 mol) were dissolved in dichloromethane (50 mL). Silica gel (2.70 g) as a catalyst was added to the yellow solution. After continual stirring for 70 h, the solution was filtered to remove the silica gel. The filtrate was poured into the aqueous methanol solution (10 vol %, 1 L) in order to deactivate the residual S_2Cl_2. The mixture was evaporated and dried in vacuo for 10 h at 100 °C. The crude product was dissolved in THF (170 mL), and the solution was added dropwise to THF (40 mL) containing $LiAlH_4$ (0.075 mol) in an ice bath. After 12 h at 20 °C, an aqueous H_2SO_4 solution (70 vol %) was added dropwise with cooling until the evolution of hydrogen stopped. 4-Bromo-4′-mercaptodiphenyl ether was extracted with chloroform as a crude product. The thiol was purified by distillation [149 °C (0.5 mmHg)].

4-Bromo-4′-mercaptodiphenyl ether was oxidized with I_2 in ethanol. The product was purified by recrystallization twice from ethanol to yield bis[4-[(4-bromophenyl)oxy]phenyl] disulfide (**I**; yield, 46%; T_m = 88 °C).

Bis[4-[(4-bromophenyl)thio]phenyl] disulfide (**II**) and bis-[4-[[[(4-bromophenyl)sulfonyl]phenyl]oxy]phenyl] disulfide (**III**) were prepared in the same manner (yield: 8% for **II** and 16% for **III**).

Thermal Polymerization. The typical procedure is as follows. Monomer **I** (1 mmol) and KI (5 mmol) were ground together to form a fine powder and then placed in a test tube, followed by the addition of 0.5 mL of diphenyl ether. The mixture was heated at 250 °C for 40 h under a N_2 atmosphere. After addition of 1-chloronaphthalene (3.0 mL) to dissolve the formed polymer, the solution was poured into 300 mL of methanol to precipitate the polymer. The polymer was isolated by filtration and washed with hot water, hot methanol, and hot chloroform.[11] After drying in vacuo for 12 h, poly(thio-1,4-phenyleneoxy-1,4-phenylene) (PPOS) was obtained as a white powder.

Spectroscopic Data. Bis[4-[(4-bromophenyl)oxy]phenyl] Disulfide (I). IR (KBr): 3084, 3057 (ν_{CH}), 1582, 1481, 1400 ($\nu_{C=C}$), 1240 (ν_{COC}), 868, 845, 824 (δ_{CH}), 1273, 1198, 1167, 1098, 1071, 1009, 652 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 156.9, 155.7, 132.8, 131.4, 131.0, 120.8, 119.2, 116.3 (phenyl). MS (*m*/*z*): 560, 280. Anal. Calcd for ($C_{24}H_{16}O_2Br_2S_2$): C, 51.44; H, 2.88; Br, 28.52; S, 11.45. Found: C, 51.23; H, 2.70; Br, 28.88; S, 11.50.

Bis[4-[(4-bromophenyl)thio]phenyl] Disulfide (II). IR (KBr): 3075 (ν_{CH}), 1570, 1472 ($\nu_{C=C}$), 814 (δ_{CH}), 1386, 1086, 1071, 1009, 527, 488 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 136.0, 134.9, 134.3, 132.8, 132.4, 131.3, 128.5, 121.6 (phenyl). Anal. Calcd for ($C_{24}H_{16}Br_2S_4$): C, 48.65; H, 2.72. Found: C, 48.76; H, 2.78.

Bis[4-[[[(4-bromophenyl)sulfonyl]phenyl]oxy]phenyl] Disulfide (III).[12] IR (KBr): 3045 (ν_{CH}), 1576, 1483 ($\nu_{C=C}$), 1298, 1105 (ν_{SO_2}), 829 (δ_{CH}). Anal. Calcd for ($C_{36}H_{24}O_6Br_2S_4$): C, 51.44; H, 2.88. Found: C, 49.24; H, 2.80.

Poly(thio-1,4-phenyleneoxy-1,4-phenylene) (PPOS). IR (KBr): 3032 (ν_{CH}), 1580, 1481 ($\nu_{C=C}$), 1236, 1082 (ν_{COC}), 826 (δ_{CH}). ^1H NMR ($(CD_3)_2SO$, at 140 °C): δ 7.0, 7.3. CP-MAS ^{13}C NMR: 156.8, 131.7, 129.6, 121.4 (phenyl). Anal. Calcd for ($C_{12}H_8OS$):

† PRESTO, JRDC, Investigator 1992–1994.

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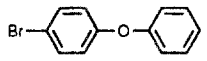
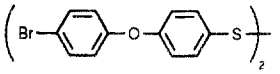
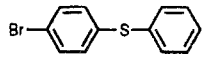
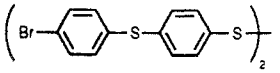
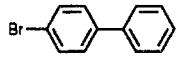
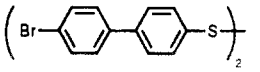
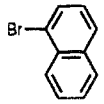
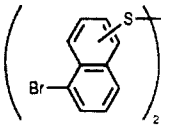
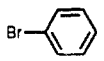
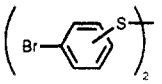
Table I. Synthesis of New Arylene Disulfides

aromatics	disulfides	cat.	convn (%)	yield (%)
		Fe	85	5
		$FeCl_3$	91	8
		$AlCl_3$	87	3
		Al_2O_3	98	53
		SiO_2	98	71
		SiO_2	92	21
		SiO_2	0	0
		SiO_2	0	0
		SiO_2	0	0

C, 71.97; H, 4.03; S, 15.36. Found: C, 71.29; H, 3.88; S, 15.23; Br, 0.48; K, 8 (ppm). T_g = 88 °C, T_m = 191 °C, T_d(10%) = 535 °C.

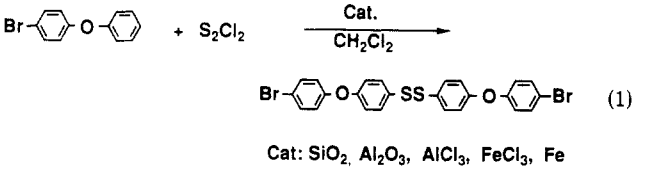
Poly(thio-1,4-phenylene) (PPS). IR (KBr): 3065 (ν_{CH}), 1572, 1470 ($\nu_{C=C}$), 812 (δ_{CH}), 1092, 1074, 1009, 552, 478. Anal. Calcd for (C_6H_4S): C, 66.63; H, 3.73; S, 29.64. Found: C, 65.34; H, 3.62; S, 28.59; Br, 0.95. T_g = 91 °C, T_m = 282 °C, T_d(10%) = 524 °C.

Poly(thio-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) [Poly(thioether-ether-sulfone)].[12] IR (KBr): 3063 (ν_{CH}), 1578, 1483 ($\nu_{C=C}$), 1298, 1107 (ν_{SO_2}), 829 (δ_{CH}). Anal. Calcd for ($C_{18}H_{12}O_3S_2$): C, 63.51; H, 3.55. Found: C, 57.64; H, 3.01. T_g = 128 °C, T_d(10%) = 475 °C.

Measurements. IR spectroscopy was carried out with a Jasco FT/IR 5300 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL GSX-400. Mass spectra were measured using an ionization energy of 20 eV on a JMS-DX300 spectrometer. A SHISEIDO CAPCELL PAK C_{18} was used for HPLC analysis. The operating temperature was 25 °C with a flow rate of 1.0 mL/min of the acetonitrile solution. The molecular weight of the polymer was determined by GPC using a Senshu Kagaku Model VHT-GPC SSC-7000 with a Soma Optics S-3750 UV/vis absorption detector.[13] Two Shodex AT80M/A columns and an AT-800P column from Showa Denko were used. 1-Chloronaphthalene was used as the carrier solvent. To obtain a homogeneous polymer slurry, 6 mg of polymer samples in 3 mL of 1-chloronaphthalene were mixed under stirring at 250 °C for 4 min and quenched to room temperature. On each run 500 μL of polymer slurry was injected at room temperature and redissolved at 250 °C through the capillary ($\phi \times L$ = 0.5 mm × 1 m) in the preheater. The temperatures of the column oven, the transfer line, and the flow cell were regulated at 210 °C. A flow rate of 1.0 mL/min was adopted. The eluent was monitored at 360 nm by a UV/vis spectrophotometer. The GPC was calibrated by a polystyrene standards substituted pyrene group as a fluorescence. Differential scanning calorimetry (DSC) was carried out with a Seiko DSC220C thermal analyzer at a heating rate of 20 °C/min. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out simultaneously with a Seiko TG/DTA220 thermal analyzer at a heating rate of 20 °C/min. Wide-angle X-ray scattering (WAXS) patterns were obtained on a powder sample employing a Rigaku RAD-C diffractometer with a curved crystal, graphite monochromator and counting equipment. Measurements were made with Ni-filtered Cu Kα radiation. With the generator operated at 35 kV and 20 mA, an intensity of 1-s counts taken every 0.01° (2θ) over the angular range 10–60° was recorded.

Results and Discussion

Preparation of Bis(4-haloaryl) Disulfides. The Friedel–Crafts type reaction of an aromatic halide was carried out in order to prepare halosubstituted diaryl disulfides as monomers which are available for thermal polymerization yielding poly(arylene sulfide)s (eq 1).



4-Bromodiphenyl ether (Br-DPE) is allowed to react with S_2Cl_2 in the presence of Friedel–Crafts catalysts (Table I). The catalysts such as $FeCl_3$, Fe, and $AlCl_3$ gave a low yield of disulfide since the reaction resulted in high conversion to a mixture of sulfide and polysulfide compounds. The catalysts cause extensive decomposition of substrates or products. In contrast, the reaction with silica gel gave bis[4-[(4-bromophenyl)oxy]phenyl] disulfide (I) in high yield. Silica gel as a catalyst suppresses the formation of sulfide and polysulfide bonds and promotes the predominant formation of disulfide (Figure 1). This reaction system provides not only efficient disulfide formation but also a simple work-up process to remove the acid catalyst.

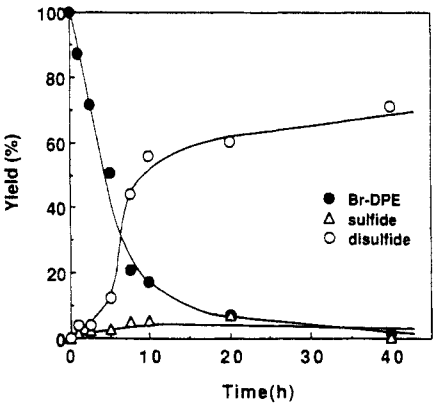
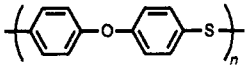
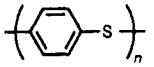
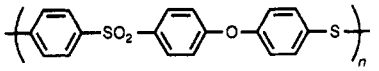


Figure 1. Preparation of bis[4-[(4-bromophenyl)oxy]phenyl] disulfide (I).

4-Bromodiphenyl ether shows high reactivity and selectivity to yield the corresponding disulfide. However, the reaction of 4-bromodiphenyl sulfide results in a low yield of the disulfide because of the formation of byproducts such as sulfide and polysulfide compounds. Biphenyl, naphthalene, and benzene derivatives, which possess a

Table II. Synthesis of Poly(arylene sulfide)s through Thermal Polymerization

polymer	temp (°C)	time (h)	yield (%)	T_m (°C)	T_d(10%)[a] (°C)	M_w[b]	M_n[b]	M_w/M_n
	250	20	100	191	530	42 100	14 600	2.9
	250	40	100	191	535	141 000	34 300	4.1
	230	20	95	157	520	1 600	800	2.0
	280	10	97	192	530	41 200	18 700	2.2
	250	20	91	280	518	22 000	8 000	2.8
	280	20	97	282	524	33 000	9 200	3.5
	250	40	71		467	4 500	2 400	1.9
	250	120	100		475	6 600	2 400	2.8

[a] Temperature for 10% weight loss. [b] Measured by GPC calibrated with polystyrene standards.

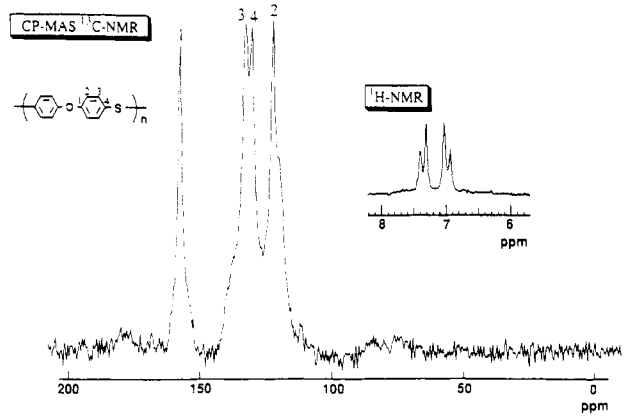
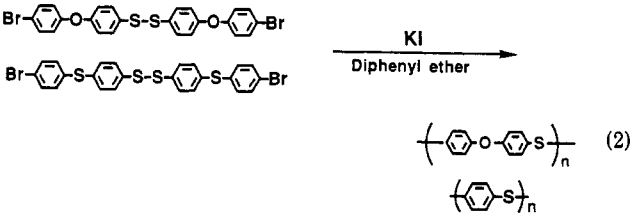


Figure 2. ^1H and ^{13}C NMR spectra of PPOS.

lower π-electron density than 4-bromodiphenyl ether or 4-bromodiphenyl sulfide, do not react with S_2Cl_2 under the same conditions.

Isolation of high-purity disulfide is essential to obtain polymers of high molecular weight by thermal polymerization. Therefore, the crude product was reduced to the thiol by $LiAlH_4$ to remove the sulfide compound, and then the thiol was purified by distillation. After the oxidation of the thiol, high-purity (>99.7%; yield, 46%) white needles of bis[4-[(4-bromophenyl)oxy]phenyl] disulfide (**I**) are obtained after recrystallization twice in ethanol.

Synthesis of Poly(thio-1,4-phenyleneoxy-1,4-phenylene) through Thermal Polymerization. Thermal polymerization of **I** was carried out in diphenyl ether in the presence of excess KI (eq 2). Polymerization proceeds



(2)

with the evolution of I_2. PPOS (M_w = 141 000) is obtained in high yield from polymerization at 250 °C for 40 h (Table II). Since the melting point of PPOS is below 200 °C, the polymer formed is always melted during the thermal polymerization at 250 °C in the reaction mixture. A high reaction temperature accelerates the polymerization to give a polymer of M_w = 41 200 at 280 °C for 10 h.

Elemental analysis of the product is consistent with the calculated values for PPOS. Four peaks attributed to the phenyl carbons were observed in the CP-MAS ^{13}C NMR spectrum (Figure 2). The AB quartet peaks attributed to phenyl protons were detected in the ^1H NMR spectrum measured at 140 °C (in DMSO-d_6). These results indicate

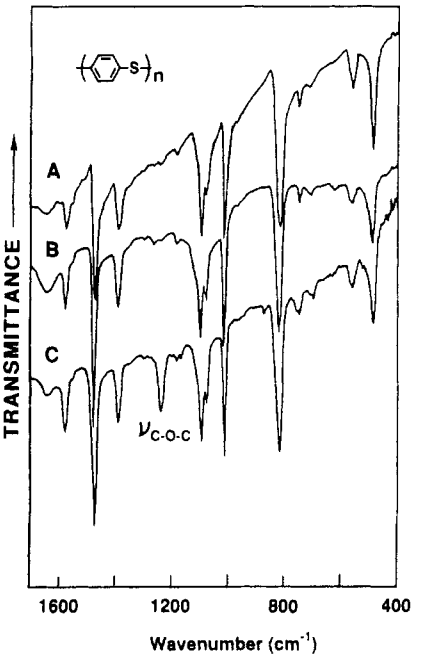


Figure 3. IR spectra of PPS: Ryton (A); obtained through the thermal polymerization with KI (10 mol/L) (B) and with KI (5 mol/L) (C).

that the resulting polymer has a linear structure without detectable branching or cross-linking.[14]

The polymerization proceeds through the formation of KBr as a byproduct. The potassium salt content is determined to be 8 ppm after washing with hot water. A highly pure PPOS is easily obtained through the thermal polymerization.

Thermal Polymerization of Diaryl Disulfides. The disulfide **II** was allowed to polymerize upon heating in the same manner as PPOS (eq 2). A polymer of M_w = 33 000 was obtained from the polymerization of **II** at 280 °C for 20 h (Table II). The structure of the product from **II** is confirmed as a linear poly(thio-1,4-phenylene) by spectroscopic measurements. The IR spectrum agrees with that of the commercially available PPS (Figure 3A,B). KI as a reductant is required for the formation of high molecular weight PPS. The concentration of KI affects the structure of the polymer. A low concentration of KI results in the introduction of diphenyl ether moieties used as solvent during the polymerization (Figure 3C). No ether bond is detected in the polymer when the thermal polymerization is carried out in the presence of a large amount of KI (10 mol/L). The side reaction retards the formation of the high molecular weight polymer.

A disulfide having a sulfone group (**III**) was also polymerized upon heating in the same manner as PPOS and PPS. Poly(thioether–ether–sulfone) is obtained as a white powder. The polymerization proceeds much slower

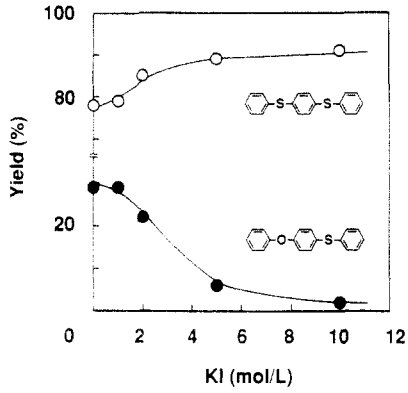
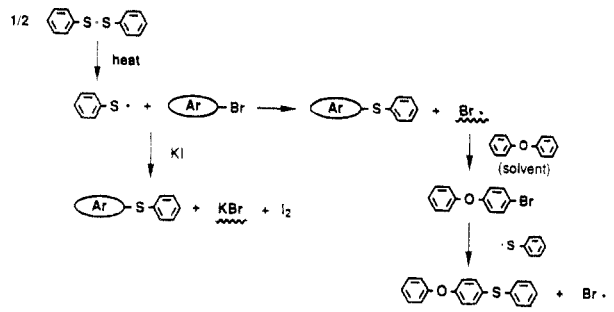


Figure 4. Effect of KI concentration on the formation of sulfide bond through thermolysis of diphenyl disulfide. [4-Bromodiphenyl sulfide] = 2.0 (mol/L), [diphenyl disulfide] = 1.0 (mol/L).

Scheme I



than that for PPOS and PPS. The polymer is not a high molecular weight even though the yield reaches 100% from the polymerization at 250 °C for 120 h. This result supports the idea that introduction of an electron-attracting group yields a low-reactive monomer for thermal polymerization, which might mean the formed thiyl radical has an electrophilic property.

Polymerization Mechanism. The thermal reaction of 4-bromodiphenyl sulfide and diphenyl disulfide was carried out as a control experiment in the presence of various KI concentrations in order to elucidate the effect of KI on the thermal polymerization (Figure 4). The presence of a large amount of KI (10 mol/L) results in the predominant formation of 1,4-bis(phenylthio)benzene. 1-Phenoxy-4-(phenylthio)benzene was produced when the KI concentration was decreased, which explains that the introduction of diphenyl ether used as a solvent occurs during the polymerization with a low KI concentration. The controlled reaction of diphenyl disulfide with diphenyl ether reveals that the introduction of an ether bond does not occur without 4-bromodiphenyl ether.[15] Therefore, 1-phenoxy-4-(phenylthio)benzene forms via 4-bromodiphenyl ether generated by the bromination of diphenyl ether. The thermal reaction of diphenyl disulfide with KI demonstrated that the formed thiophenoxy radical did not oxidize iodide anion (I^-) under the same conditions[16] because the redox potential of the thiophenoxy radical (0.2 V vs Ag/AgCl) is less cathodic than that of I^- (0.6 V vs Ag/AgCl).

The polymerization mechanism is summarized in Scheme I. First, the disulfide bond is cleaved by thermolysis to yield the thiophenoxy radical. The radical attacks the aromatic bromide to form the sulfide bond with elimination of the bromine atom. The bromine atom oxidizes I^- to yield a bromide anion in the presence of an excess amount of KI. I_2 is evolved through oxidation by the bromine atom during the reaction. In the absence of KI, the bromine atom attacks the diphenyl ether to yield 4-bromodiphenyl ether. The formed 4-bromodiphenyl ether reacts with a thiophenoxy radical to form 1-phenoxy-4-(phenylthio)benzene. It is confirmed that KI acts as a reductant for the bromine atom to suppress the side reaction during the thermal polymerization.

Table III. Crystallographic Data of PPOS and PPS

polymer	lattice param a (Å)	b (Å)	c (Å)
PPOS	8.46	5.58	9.64
PPS	8.67	5.63	10.25
PPS (Ryton)	8.67	5.61	10.26

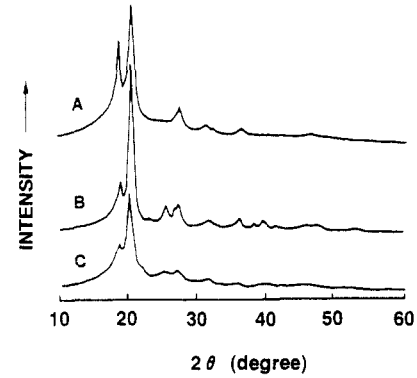


Figure 5. X-ray spectra of obtained PPOS (A), PPS through thermal polymerization (B), Ryton (C).

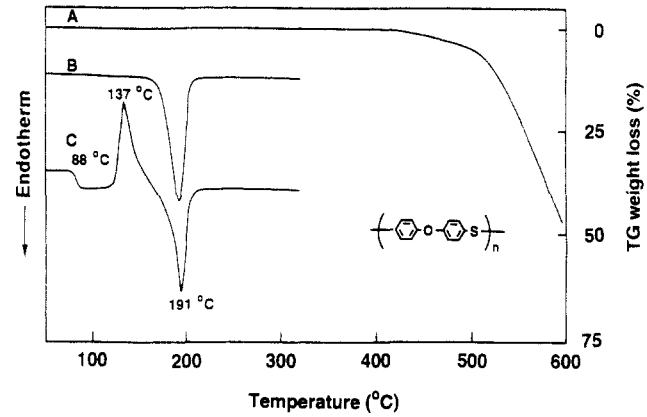


Figure 6. Thermal properties of PPOS: TG curve (A); DSC curve of the initial scan (B); DSC curve after quenching (C).

Physical Properties. Crystallographic data were calculated by WAXS analysis. The unit cell of PPOS is orthorhombic, similar to that of PPS.[17-19] The lattice parameters of PPOS are in agreement with that of PPS except for the *c*-axis (Table III). The X-ray spectrum of the resulting PPS was compared with commercially available PPS (Figure 5). The high intensity indicates a high crystallinity of the resulting polymer. The lattice parameters of the unit cell for the resulting PPS are consistent with the values reported by Tabor et al.[19] That is, the formed PPS has a high crystallinity with the same unit cell of commercially available PPS.

PPOS is soluble in hot 1-chloronaphthalene and hot *N*-methyl-2-pyrrolidone. PPOS is also a crystalline polymer whose T_m (191 °C), T_g (88 °C), and T_c (137 °C) were determined by DSC measurements (Figure 6). The T_m of PPOS is ca. 90 °C lower than that of PPS. An increase in ΔS causes a decrease in T_m since T_m is represented by the ratio of ΔH and ΔS. The length of the C–S bond (1.74 Å) is longer than that of the C–O bond (1.36 Å), and the angle of C–S–C (110°) is narrower than that of C–O–C (124°).[19] It is considered that the symmetry of PPOS is

lower than that of PPS because of the difference between the C–O and C–S bonds, and, therefore, T_m of PPOS decreases to 191 °C. Moreover, PPOS shows a high stability over a wide range of temperatures between T_m and T_d(10%), which means PPOS is applicable to melt-molding. The T_d(10%) of PPOS (535 °C) is higher than that of PPS. The thermal properties are caused by the higher binding energy of the ether bond as compared to the thioether bond. Introduction of a sulfone group makes the polymer amorphous with a higher T_g (128 °C) than that of PPS (91 °C).

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(11) Hot water, hot methanol, and hot chloroform were used to remove monomer, diphenyl ether, 1-chloronaphthalene, KI, and KBr completely. In the case that the polymer is obtained in 100% yield, a large amount of the residual oligomer in the solvent was not confirmed through the treatment after evaporation. A small amount of the monomer and the oligomer is detected in the case of the polymer yield below 100%. But the molecular weight distribution does not change after washing treatment.
(12) Purification of monomer **III** was quite difficult, because the contaminants such as polysulfide and sulfide compounds could not be removed completely. Therefore, elemental values of monomer **III** and the formed polymer are not in fair agreement with theoretical ones. Also it may be possible that some reaction occurs at the elevated temperatures between the sulfone groups and the thiophenoxy radicals. However, the ^{13}C NMR spectrum suggests that the resulting polymer mainly consists of a thio-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene unit.
(13) This GPC system includes viscosity, FID, and UV/vis detectors. The viscosity detector is so insensitive to low molecular weight polymers that the molecular weight distribution may be estimated narrower. FID and UV detectors also suffer the same fate, but to a much lesser extent. We used the UV/vis detector. See: (a) Stacy, C. J. *J. Appl. Polym. Sci.* **1986**, *32*, 3959. (b) Housaki, T.; Satoh, K. *Polym. J.* **1988**, *20*, 1163.
(14) Radical polymerization would result in the formation of PPS or PPOS containing slightly nonlinear structure. A combination of IR and ^1H and ^{13}C NMR spectra does not reveal detectable branching or cross-linking structure. On the basis of the previous report, the resulting PPS contains branching structure less than 1% by IR spectra. But these analytical methods to detect very small amounts of branching are difficult. Nonetheless, one technique stands out in looking for branching in PPS. Flow activation energy for linear and branched polymers is very different and highly sensitive to small amounts of branching. In the case of linear PPS, the flow activation energy is approximately 15 kcal/mol. Incorporation of a fraction of a mole percent trifunctional comonomers raises the reproducibility. We will measure the flow activation energies of the resulting polymers and report them in the near future. See: (a) Kraus, G.; Whitte, W. M. *Proc., IUPAC, Macromol. Symp.* **1982**, *28*, 558. (b) Rule, M.; Fagerburg, D. R.; Watkins, J. J.; Lawrence, P. B.; Zimmerman, R. L.; Cloyd, J. D. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 233.
(15) Diphenyl disulfide was allowed to react with diphenyl ether at 250 °C for 20 h. 1-Phenoxy-4-(phenylthio)benzene was not obtained from the reaction mixtures.
(16) Thermolysis of diphenyl disulfide was carried out in the presence of an excess amount of KI. Thiophenol was not detected in the reaction mixture. Therefore, reduction of the thiophenoxy radical by KI does not occur in such reaction conditions.
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