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Sulfide Bond Formation for the Synthesis of Poly(thioarylene) through Oxidation of Sulfur Chloride with Aromatics

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ABSTRACT: A new homogeneous series of hydrocarbon polymers having phenoxy and thiophenoxy units in the main chain were prepared by oxidative polymerization of α,ω-diphenoxyalkanes (m = 2–8, 10) with S_2Cl_2. Polymers with weight-average molecular weights in the range of 4800–33 500 have been obtained in high yields (>94%). The effect of the chain length of the methylene units on the thermal properties of the polymers is discussed. Increasing the length of the methylene units results in a decrease in the glass transition temperature (T_g) of the polymers. An alternating odd–even effect in melting temperatures (T_m) and molecular weights is observed. The resulting polymers having even numbers of methylene units possess a higher melting temperature and lower molecular weight than those of the odd numbered ones. Polymerization of S_2Cl_2 with other aromatic compounds, such as p-xylene, durene, and diphenyl ether, is also demonstrated to yield the corresponding poly(thioarylene)s. The polymerization proceeds via a cationic mechanism through the oxidation of the disulfide bond.

Introduction

Several synthetic methods for the preparation of the sulfide bond are known; e.g. the nucleophilic displacement of aryl halides with metal alkanethiolates or with thiophenols catalyzed by a nickel complex,[1,2] the reaction between thiophenols or alkyl mercaptans with organic halides using tricaprylmethylammonium chloride (TCMAC) as a phase-transfer catalyst,[3–5] and the thermolysis of diaryl disulfides in the presence of aryl iodides[6,7] have been reported. These reactions proceed under severe conditions. Since an electron-donating substituent such as ether and thioether suppresses the nucleophilic displacement for synthesis of the oxyarylene or thioarylene chain, poly(oxyarylene) derivatives are generally synthesized through the activation of aryl halides. It has been demonstrated that electron-withdrawing groups such as sulfone and ketone are effective in activating aryl halides toward nucleophilic displacement.[8–10]

Poly(thio-1,4-phenylene) (PPS) which is an excellent engineering plastic is synthesized by the polycondensation of p-dichlorobenzene and sodium sulfide.[11] The obtained polymer subsequently had to be cured or re-reacted in order to increase the molecular weight for upgrading to useful properties even if cross-linking occurs. Recently, new synthetic methods for the preparation of a high molecular weight linear PPS have been developed by several groups.[12–15] The Friedel–Crafts reaction has also been demonstrated for the synthesis of poly(thioarylene)s with electron-donating groups through an electrophilic reaction;[16,17] however, the electrophilic reaction is accompanied by many side reactions and the formed polymer contains disulfide or thianthrene bonds. We have preliminarily reported that preferential sulfide bond formation occurs and linear poly(thio-2,5-dimethyl-1,4-phenylene) is prepared in the reaction of p-xylene with sulfur monochloride (S_2Cl_2) in the presence of an equimolar amount of an oxidizing agent, such as 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), or of a catalytic amount of vanadyl compounds.[18]

The aryl sulfide bond formation should be applicable to the synthesis of alternating copolymers of phenylene units and hydrocarbon ones by binding α,ω-diphenoxyalkane units with the sulfide bond in order not only to produce a new type of PPS but also to improve the toughness of PPS. The introduction of flexibility could give rise to a new elastic poly(thioarylene) with a desirable glass transition temperature (T_g) and melting temperature (T_m) similar to the thermotropic liquid crystalline polymers, such as poly(biphenylene-α,ω-alkylene)s.[19]

As a remarkable characteristic of the sulfur atom, the sulfide bond is easily oxidized and converted to the sulfone one by using oxidants.[20] The polyaromatic sulfones show high T_g's which mean upgrading the thermal properties. The alternating copolymer of an alkane segment and a phenylene is easily converted to the corresponding sulfone polymer because of the solvent solubility. In this paper, we describe the synthesis and characterization of a new series of hydrocarbon polymers having phenoxy and thiophenoxy units in the main chain, which were prepared by oxidative polymerization of α,ω-diphenoxyalkanes with S_2Cl_2 under ambient atmosphere at room temperature. Polymerization of simple aromatic compounds such as p-xylene and diphenyl sulfide and a discussion of the polymerization mechanism are also included.

Experimental Section

Materials. Guaranteed reagents of α,ω-dibromoalkane and phenol were used without further purification. p-Xylene, diphenyl sulfide, diphenyl ether, anisole, thioanisole, and 4-bromodiphenyl ether were purified by distillation under reduced pressure in a usual manner. Durene was purified by recrystallization twice from ethanol. All the solvents, such as dichloromethane, chloroform, carbon tetrachloride, N-methyl-2-pyrrolidone, N,N-dimethylformamide, and tetrahydrofuran were purified by distillation. Sulfur monochloride (S_2Cl_2), trifluoroacetic acid, trifluoroacetic anhydride, and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) were used without further purification.

Synthesis of α,ω-Diphenoxyalkanes. α,ω-Diphenoxyalkanes were synthesized from α,ω-dibromoalkanes and phenol according to a literature method.[21] In a typical preparation, α,ω-dibromoalkane (0.3 mol) was added dropwise to a stirred solution of phenol (1.4 mol) and NaOH (1.4 mol) in 200 mL of water. The mixture was refluxed for 3 h and then cooled while being stirred. The product was filtered off and washed with 3% NaOH aqueous

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solution and with water several times. Recrystallization twice from ethanol gave white needles of α,ω-diphenoxyalkane.

1,2-Diphenoxyethane: IR (KBr, cm^{-1}) 2940, 2870 (ν_{C-H}), 1506 ($\nu_{C=C}$), 1253 (ν_{C-O-C}), 755, 698 (δ_{C-H}); ^{1}H NMR (CDCl$_3$, ppm) 4.18 (t, –OCH$_2$–, 4H), 6.98 (m, phenyl, 10H); mass (*m/z*) 214, 121; mp = 98 °C; yield 88%.

1,3-Diphenoxypropane: IR (KBr, cm^{-1}) 2937, 2870 (ν_{C-H}), 1500 ($\nu_{C=C}$), 1247 (ν_{C-O-C}), 750, 692(δ_{C-H}); ^{1}H NMR (CDCl$_3$, ppm) 2.21 (m, –CH$_2$–, 2H), 4.18 (t, –OCH$_2$–, 4H), 7.00 (m, phenyl, 10H); mass (*m/z*) 228, 135; mp = 60 °C; yield 78%.

1,4-Diphenoxybutane: IR (KBr, cm^{-1}) 2938, 2875 (ν_{C-H}), 1502 ($\nu_{C=C}$), 1251 (ν_{C-O-C}), 754, 692 (δ_{C-H}); ^{1}H NMR (CDCl$_3$, ppm) 1.95 (m, –CH$_2$–, 4H), 4.04 (t, –OCH$_2$–, 4H), 7.10 (m, phenyl, 10H); mass (*m/z*) 242, 149; mp = 101 °C; yield 90%.

1,5-Diphenoxypentane: IR (KBr, cm^{-1}) 2940, 2859 (ν_{C-H}), 1502 ($\nu_{C=C}$), 1245 (ν_{C-O-C}), 756, 692 (δ_{C-H}); ^{1}H NMR (CDCl$_3$, ppm) 1.77 (m, –CH$_2$–, 6H), 3.92 (t, –OCH$_2$–, 4H), 6.93 (m, phenyl, 10H); mass (*m/z*) 256, 163; mp = 46 °C; yield 69%.

1,6-Diphenoxyhexane: IR (KBr, cm^{-1}) 2940, 2860 (ν_{C-H}), 1498 ($\nu_{C=C}$), 1244 (ν_{C-O-C}), 750, 698 (δ_{C-H}); ^{1}H NMR (CDCl$_3$, ppm) 1.64 (m, –CH$_2$–, 8H), 3.93 (t, –OCH$_2$–, 4H), 6.96 (m, phenyl, 10H); mass (*m/z*) 270, 177; mp = 83 °C; yield 85%.

1,7-Diphenoxyheptane: IR (KBr, cm^{-1}) 2938, 2849 (ν_{C-H}), 1501 ($\nu_{C=C}$), 1246 (ν_{C-O-C}), 750, 693 (δ_{C-H}); ^{1}H NMR (CDCl$_3$, ppm) 1.53 (m, –CH$_2$–, 10H), 3.94 (t, –OCH$_2$–, 4H), 6.93 (m, phenyl, 10H); mass (*m/z*) 284, 191; mp = 51 °C; yield 67%.

1,8-Diphenoxyoctane: IR (KBr, cm^{-1}) 2948, 2865 (ν_{C-H}), 1500 ($\nu_{C=C}$), 1255 (ν_{C-O-C}), 754, 700 (δ_{C-H}); ^{1}H NMR (CDCl$_3$, ppm) 1.55 (m, –CH$_2$–, 12H), 3.94 (t, –OCH$_2$–, 4H), 6.95 (m, phenyl, 10H); mass (*m/z*) 298, 205; mp = 83 °C; yield 83%.

1,10-Diphenoxydecane: IR (KBr, cm^{-1}) 2952, 2840 (ν_{C-H}), 1498 ($\nu_{C=C}$), 1250 (ν_{C-O-C}), 748, 698 (δ_{C-H}); ^{1}H NMR (CDCl$_3$, ppm) 1.55 (m, –CH$_2$–, 16H), 3.94 (t, –OCH$_2$–, 4H), 6.93 (m, phenyl, 10H); mass (*m/z*) 326, 233; mp = 86 °C; yield 72%.

Polymerization. The typical procedure is as follows. A solution of α,ω-diphenoxyalkane (0.04 mol) and sulfur monochloride (0.02 mol) in dichloromethane (100 mL) was added to a solution of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (0.02 mol), trifluoroacetic acid (0.2 mol), and trifluoroacetic anhydride (0.04 mol) in dichloromethane (100 mL). The deep green color of the mixture turned to pale yellow with time. After the reaction for 40 h at room temperature, the mixture was dropwise added in 1000 mL of methanol acidified with hydrochloric acid to precipitate a white polymer, which was washed with 5% NaOH aqueous solution and with methanol, respectively, and dried in vacuo for 12 h to obtain poly(thio-1,4-phenyleneoxy-α,ω-alkyleneoxy-1,4-phenylene).

Poly(thio-1,4-phenyleneoxy-1,2-ethyleneoxy-1,4-phenylene): IR (KBr, cm^{-1}) 2925 (ν_{C-H}), 1491 ($\nu_{C=C}$), 1238 (ν_{C-O-C}), 825 (δ_{C-H}). Anal. Calcd for ($C_{14}H_{12}O_2S$): C, 68.83; H, 4.95. Found: C, 68.41; H, 4.91.

Poly(thio-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene): IR (KBr, cm^{-1}) 2932 (ν_{C-H}), 1491 ($\nu_{C=C}$), 1240 (ν_{C-O-C}), 824 (δ_{C-H}); ^{1}H NMR (CDCl$_3$, ppm) 2.20 (m, –CH$_2$–, 2H), 4.13 (t, –OCH$_2$–, 4H), 6.75, 6.82, 7.17, 7.24 (AB q, phenyl, 8H); ^{13}C NMR (CDCl$_3$, ppm) 29.2, 64.5 (methylene C), 115.5, 127.8, 132.8, 158.3 (phenyl C). Anal. Calcd for ($C_{15}H_{14}O_2S$): C, 69.74; H, 5.46; S, 12.41. Found: C, 69.49; H, 5.72; S, 12.77.

Poly(thio-1,4-phenyleneoxy-1,4-butyleneoxy-1,4-phenylene): IR (KBr, cm^{-1}) 2928 (ν_{C-H}), 1491 ($\nu_{C=C}$), 1240 (ν_{C-O-C}), 824 (δ_{C-H}). Anal. Calcd for ($C_{16}H_{16}O_2S$): C, 70.56; H, 5.92. Found: C, 70.12; H, 5.54.

Poly(thio-1,4-phenyleneoxy-1,5-pentyleneoxy-1,4-phenylene): IR (KBr, cm^{-1}) 2932 (ν_{C-H}), 1491 ($\nu_{C=C}$), 1242 (ν_{C-O-C}), 825 (δ_{C-H}). Anal. Calcd for ($C_{17}H_{18}O_2S$): C, 71.30; H, 6.34. Found: C, 70.73; H, 6.16.

Poly(thio-1,4-phenyleneoxy-1,6-hexyleneoxy-1,4-phenylene): IR (KBr, cm^{-1}) 2936 (ν_{C-H}), 1492 ($\nu_{C=C}$), 1242 (ν_{C-O-C}), 825 (δ_{C-H}). Anal. Calcd for ($C_{18}H_{20}O_2S$): C, 71.97; H, 6.71. Found: C, 71.79; H, 6.56.

Poly(thio-1,4-phenyleneoxy-1,7-heptyleneoxy-1,4-phenylene): IR (KBr, cm^{-1}) 2930 (ν_{C-H}), 1494 ($\nu_{C=C}$), 1242 (ν_{C-O-C}), 822 (δ_{C-H}). Anal. Calcd for ($C_{19}H_{22}O_2S$): C, 72.58; H, 7.05. Found: C, 71.99; H, 6.98.

Poly(thio-1,4-phenyleneoxy-1,8-octyleneoxy-1,4-phenylene): IR (KBr, cm^{-1}): 2932 (ν_{C-H}), 1496 ($\nu_{C=C}$), 1243 (ν_{C-O-C}), 825 (δ_{C-H}). Anal. Calcd for ($C_{20}H_{24}O_2S$): C, 73.13; H, 7.37. Found: C, 72.87; H, 7.22.

Poly(thio-1,4-phenyleneoxy-1,10-decyleneoxy-1,4-phenylene): IR (KBr, cm^{-1}) 2934 (ν_{C-H}), 1491 ($\nu_{C=C}$), 1243 (ν_{C-O-C}), 826 (δ_{C-H}). Anal. Calcd for ($C_{22}H_{28}O_2S$): C, 74.12; H, 7.92. Found: C, 74.00; H, 7.95.

Poly(thio-2,5-dimethyl-1,4-phenylene): IR (KBr, cm^{-1}) 2918 (ν_{C-H}), 1591, 1470, 1452 ($\nu_{C=C}$), 883 (δ_{C-H}); CP-MAS ^{13}C NMR (ppm) 20 (methyl C), 124, 132, 141 (phenyl C); mass (*m/z*) 544, 408. Anal. Calcd for (C_8H_8S): C, 70.54; H, 5.92; S, 23.54. Found: C, 69.86; H, 5.95; S, 23.77.

Poly(thio-1,4-phenylene): IR (KBr, cm^{-1}) 3100 (ν_{C-H}), 1571, 1473, 1389 ($\nu_{C=C}$), 819 (δ_{C-H}); mass (*m/z*) 618, 434. Anal. Calcd for (C_6H_4S): C, 66.63; H, 3.73; S, 29.64. Found: C, 66.72; H, 3.63; S, 29.65.

Poly(thio-1,4-phenyleneoxy-1,4-phenylene): IR (KBr, cm^{-1}) 3035 (ν_{C-H}) 1580, 1481 ($\nu_{C=C}$), 1236 (ν_{C-O-C}), 826 (δ_{C-H}). Anal. Calcd for ($C_{12}H_8OS$): C, 71.97; H, 4.03; S, 15.36. Found: C, 71.77; H, 3.83; S, 15.51.

Poly(thio-2,3,5,6-tetramethyl-1,4-phenylene): IR (KBr, cm^{-1}) 2919 (ν_{C-H}), 1470 ($\nu_{C=C}$); mass (*m/z*) 656, 494, 330. Anal. Calcd for ($C_{10}H_{12}S$): C, 73.12; H, 7.36; S, 19.52. Found: C, 72.96; H, 7.24; S, 19.79.

Oxidation of Poly(thio-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene). Trifluoroacetic acid (10 mL) and 30% hydrogen peroxide (1.0 g) were added to a solution of poly(thio-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene) (1.0 g) in chloroform (10 mL). The solution was stirred at room temperature for 10 min followed by heating at 60 °C for 6 h. After the reaction, the mixture was poured dropwise into 300 mL of methanol to precipitate a polymer. The resulting polymer was washed with water and methanol several times, and dried in vacuo for 12 h to obtain a white powder of poly(sulfonyl-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene).

Poly(sulfonyl-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene): IR (KBr, cm^{-1}) 2946 (ν_{C-H}), 1495 ($\nu_{C=C}$), 1296, 1152 (ν_{SO2}), 1256 (ν_{C-O-C}), 833 (δ_{C-H}); ^{1}H NMR (CDCl$_3$, ppm) 2.30 (m, –CH$_2$–, 2H), 4.21 (t, –OCH$_2$–, 4H), 6.98, 7.02, 7.81, 7.84 (AB q, phenyl, 8H); ^{13}C NMR (CDCl$_3$, ppm) 29.0, 65.1 (methylene C), 115.8, 129.9, 132.0, 163.6 (phenyl C). Anal. Calcd for ($C_{15}H_{14}O_4S$): C, 62.05; H, 4.86; S, 11.04. Found: C, 61.83; H, 4.99; S, 11.33.

Isolation of 2,3-Dichloro-5,6-dicyano-*p*-hydroquinone (DDH). The polymerization of *p*-xylene and sulfur monochloride was carried out in the presence of an equimolar amount of DDQ, as well as that of α,ω-diphenoxyalkane with S_2Cl_2. During the polymerization, DDH which is the reduced form of DDQ precipitated out with time. The precipitate was filtered out and extracted with ethyl acetate to remove the polymer. The ethyl acetate layer was evaporated to dryness under reduced pressure to obtain DDH as a white powder.

Determination of Rate Constants (k_1 and k_2). The typical procedure is as follows. S_2Cl_2 (0.1 mol) was added into a solution of anisole (1 mmol), trifluoroacetic acid (0.05 mol), and trifluoroacetic anhydride (0.01 mol) in 50 mL of dichloromethane. The color of the mixture turned gradually from yellow to dark green, which was traced by UV/vis measurement at 800 nm. The rate constant, k_1 of the reaction of anisole with S_2Cl_2 was determined by means of the pseudo-first-order reaction method.

A solution of 4-methoxybenzenethiosulfenyl chloride (0.05 mol) was prepared by mixing anisole (0.05 mol) and S_2Cl_2 in 150 mL of dichloromethane. Benzene (0.05 mol) was added to the solution, whose color change was traced at 800 nm. The rate constant k_2 of the reaction of 4-methoxybenzenethiosulfenyl chloride with benzene was determined by means of the initial rate method.

Reaction of S_2Cl_2 with 4-Bromodiphenyl Ether. S_2Cl_2 (0.025 mol) was added to a solution of 4-bromodiphenyl ether (0.05 mol) in 25 mL of hexane containing trifluoroacetic acid (0.025 mol). After stirring for 20 h, the mixture was poured into 100 mL of dichloromethane and washed with water several times in order to deactivate the residual S_2Cl_2 and remove trifluoroacetic acid. The dichloromethane layer was evaporated to dryness under reduced pressure to obtain the crude product. The product was analyzed by HPLC: conversion 74%; [bis[4-[(4-bromophenyl)-oxy]phenyl] disulfide]/[product] = 88%; [bis[4-[(4-bromo-

Scheme 1

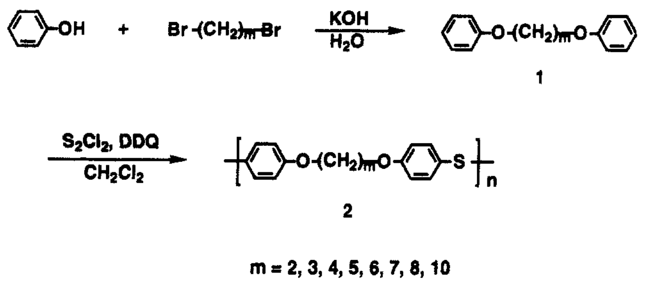


Table 1. Synthesis of Hydrocarbon Polymers 2

m	yield (%)	M_n[a]	M_w[a]	M_w/M_n[a]	D_p[b]
2	100	2100	4 800	2.3	9
3	100	8200	33 500	4.1	32
4	100	3700	15 600	4.2	14
5	100	5600	25 400	4.5	20
6	100	6400	19 000	3.0	21
7	95	7200	25 000	3.5	23
8	94	5600	21 800	3.9	17
10	100	5300	12 600	2.4	15

[a] Measured by GPC calibrated with polystyrene standards. [b] Based on M_n in the third column.

phenyl)oxy]phenyl] sulfide]/[product] = 11%. Bis[4-[(4-bromophenyl)oxy]phenyl] disulfide (7.93 g) was isolated according to the previously reported method[22] and characterized as follows: IR (KBr, cm^{-1}) 3084, 3057 (ν_{C-H}), 1582, 1481, 1400 ($\nu_{C=C}$), 1240 (ν_{C-O-C}), 868, 845, 824 (δ_{C-H}), 1273, 1198, 1167, 1098, 1071, 1009, 652; ^{13}C NMR (CDCl$_3$, ppm) 156.9, 155.7, 132.8, 131.4, 131.0, 120.8, 119.2, 116.3 (phenyl); mass (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.

Measurement. ^{1}H and ^{13}C NMR spectra were recorded using CDCl$_3$ as a solvent and tetramethylsilane as the internal standard on a JEOL GSX-400 spectrometer. IR spectra were obtained as KBr pellets on a JASCO FT/IR-5300 spectrometer. Mass spectra were obtained on a JEOL JMS-DX300 spectrometer using an ionization energy of 70 eV. Differential scanning calorimetry (DSC) was carried out with a SEIKO DSC220C thermal analyzer with a heating rate of 20 °C/min. HPLC analysis was done using a Shiseido CAPCELL PAK C_{18} column. The operating temperature was 25 °C using acetonitrile as an eluent with a flow rate of 1.0 mL/min. The molecular weight was determined by GPC measurement on a Shimadzu LC-9A system and Asahipac (GS510H and 310H) columns calibrated with polystyrene standards. Distilled NMP was used as an eluent at 25 °C with a flow rate of 1.0 mL/min. The detector was a UV/vis spectrophotometer (Shimadzu SPD-6A, 265 nm). The UV/vis spectrum was measured on a Shimadzu UV 2100 spectrometer.

Results and Discussion

Polymerization of α,ω-Diphenoxyalkanes with Sulfur Monochloride. The hydrocarbon polymers with the general structure 2 were synthesized as shown in Scheme 1. The polymerization of α,ω-diphenoxyalkanes with S_2Cl_2 proceeds under ambient atmosphere at room temperature in the presence of an equimolar amount of oxidizing agent, DDQ, and the corresponding polymers with methylene spacers (m = 2–8, 10) having a thiophenylene moiety in the main chain are obtained in >95% yields (Table 1). The weight-average molecular weight (M_w) of the polymers is in the range 4800–33 500, which was determined by GPC measurement calibrated with polystyrene. The polymers are soluble in common organic solvents, such as dichloromethane, chloroform, THF (tetrahydrofuran), and NMP (N-methyl-2-pyrrolidone), even at room temperature. It is well-known that poly(thiophenylene) and poly(oxyphenylene) are insoluble at room temperature. Incorporation of the hydrocarbon moiety into the main chain increases solubility, which results in the formation of an easily processible polymer with a relatively high molecular weight. The polymers with an odd number methylene units have better solubilities and form films by casting from a chloroform solution. The resulting films of about 0.1 mm in thicknesses are transparent, self-supporting, and flexible.[23]

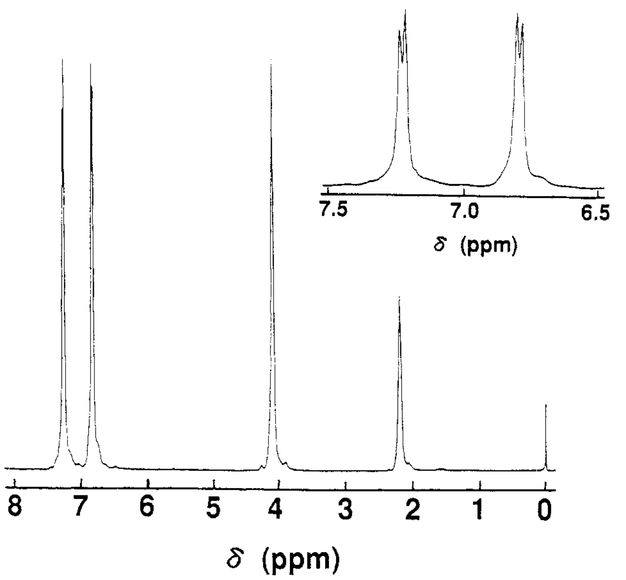


Figure 1. ^{1}H NMR spectrum of poly(thio-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene).

The chemical structures of the polymers were confirmed by NMR, IR, mass, and elemental analyses. Mass and elemental analyses reveal that polymers are constructed of monomer units formed by a sulfide bond. The resulting polymers do not contain the disulfide bond as a main structure. It is reported[16,17] that the reaction of S_2Cl_2 with aromatic compounds results in the formation of disulfide bond as well as a sulfide bond; however the disulfide bond when it forms is rapidly oxidized to form the sulfide one through electrophilic substitution of the sulfonium cation, whose chemistry has been previously described in the study on the oxidative polymerization of diphenyl disulfides.[24-26]

IR spectra of the polymers in the region of 800–900 cm^{-1} show only one absorption at ca. 825 cm^{-1} which is attributed to the C–H out-of-plane vibration of a 1,4-disubstituted benzene. The large absorption attributed to the C–H stretching vibration of methylene is also observed at ca. 2930 cm^{-1}. NMR spectra also support the formation of these polymers. The ^{1}H NMR spectrum of poly(thio-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene) is shown in Figure 1. Phenyl protons (7.24, 7.17, 6.82, 6.75 ppm: AB q) and two kinds of methylene protons (4.13, 2.20 ppm) are observed, where the AB quartet peaks actually indicate a 1,4-disubstituted phenylene ring binding different groups. The integration ratio is consistent with the proton numbers for a structure of the thio-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene unit. In the ^{13}C NMR spectrum, four kinds of phenyl carbons (158.3, 132.8, 127.8, 115.5 ppm) and two kinds of methylene carbons (64.5, 29.2 ppm) are confirmed, which are assigned as shown in Figure 2a. The combination of IR and NMR spectra reveals the formation of a linear polymer. The structure of the other resulting polymers is also confirmed by spectroscopic measurements.

The thermal properties of the polymers have been studied by differential scanning calorimetry (DSC). All the polymers exhibit a single melting transition on DSC analysis. A representative DSC thermogram, for poly(thio-1,4-phenylene-1,2-ethyleneoxy-1,4-phenylene), is

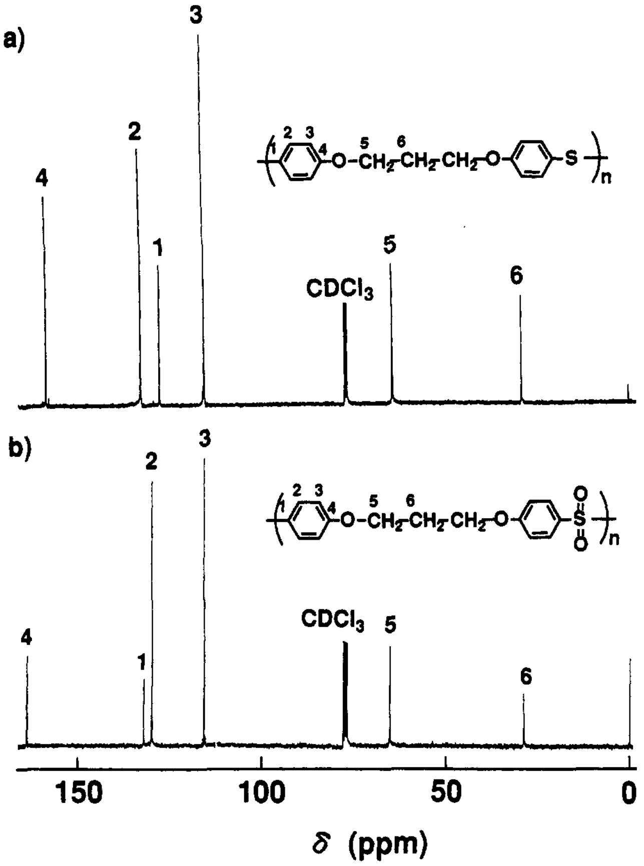


Figure 2. ^{13}C NMR spectrum of (a) poly(thio-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene) and (b) poly(sulfonyl-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene).

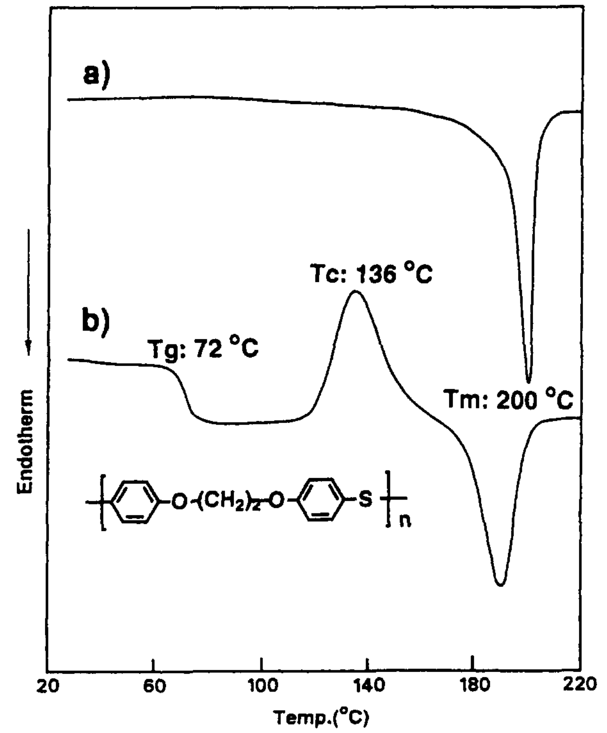


Figure 3. DSC thermograms of poly(thio-1,4-phenyleneoxy-1,2-ethyleneoxy-1,4-phenylene): (a) annealed; (b) quenched.

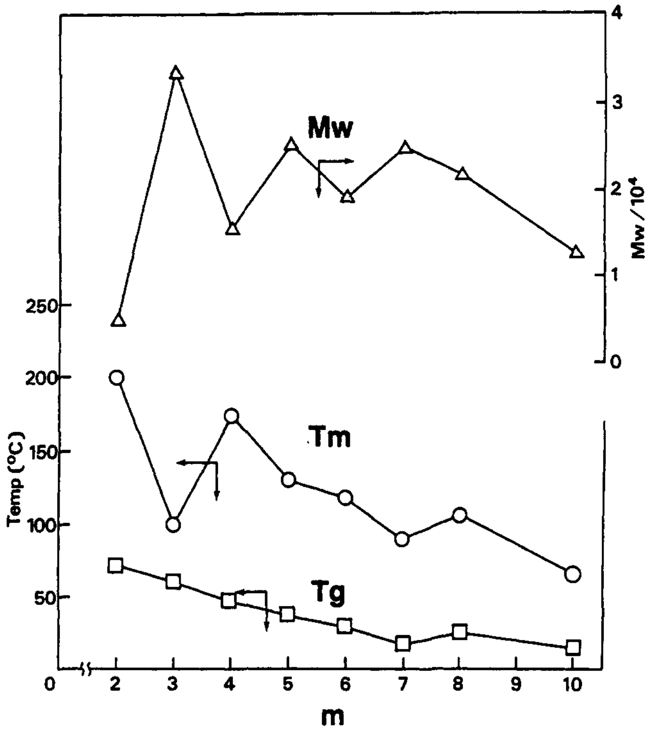


Figure 4. Thermal properties and molecular weight of poly(thio-1,4-phenyleneoxy-α,ω-alkyleneoxy-1,4-phenylene).

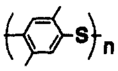
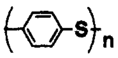
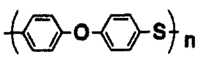
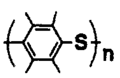
shown in Figure 3. Clear evidence of a melting temperature (T_m = 200 °C) is observed in the first heating scan after annealing, and the DSC thermogram after quenching shows a glass transition temperature (T_g) at 72 °C and a crystallization temperature (T_c) at 136 °C. The variation of the methylene units affects on the thermal properties of the polymers as shown in Figure 4. Increasing the length of the methylene units results in a decrease in T_g. Polymers with $m > 5$ show elasticity since the T_g's are below room temperature. It is believed that phenylene rings in the polymer chain play a role as a virtual cross-linking point.

An alternating odd–even effect is observed in the melting temperatures, where the even members show higher melting temperatures due to their higher crystallinity. The latter have a center of symmetry which may promote easier crystallization. The odd–even effect tends to reflect in the molecular weight on the resulting polymers. Even members aggregate and precipitate during the polymerization because of the higher crystallinity.

The T_g of the polymer can be increased by further oxidation to convert the sulfide bond to a sulfone one. Poly(thio-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene) was easily oxidized with 30% hydrogen peroxide to obtain the corresponding hydrocarbon polysulfone in 100% yield. The linear structure of the resulting polymer was confirmed by spectroscopies. In the ^{1}H NMR spectrum, two peaks attributed to the methylene protons (4.21, 2.30 ppm) and AB quartet peaks attributed to the phenyl protons (7.84, 7.81, 7.02. 6.98 ppm) are observed. The AB quartet peaks are shifted to a lower magnetic field than those of the original sulfide polymer due to the electron-withdrawing sulfone group. The ^{13}C NMR spectrum shows four kinds of phenyl carbon (163.6, 132.0, 129.9, 115.8 ppm) and two kinds of methylene carbon (65.1, 29.0 ppm), which are different from those of the original polymer (Figure 2b). Poly(sulfonyl-1,4-phenyleneoxy-1,3-propyleneoxy-1,4-phenylene) is soluble in chloroform, THF, and NMR and shows a T_g at 154 °C 93 deg higher than that of the sulfide polymer.

Polymerization of Aromatic Compounds with Sulfur Monochloride. This polymerization with S_2Cl_2 is applicable to various aromatic compounds, such as *p*-xylene, diphenyl sulfide, diphenyl ether, and 1,2,4,5-tetramethylbenzene (durene) (Table 2).[27] Aromatic compounds having electron-donating substituents are suitable for this polymerization because the reaction is classified

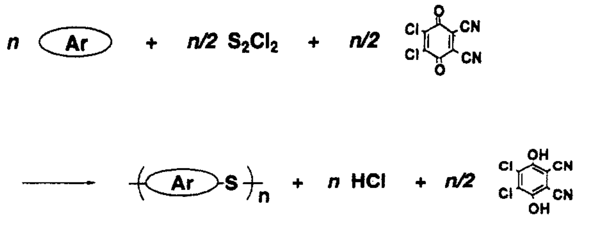
Table 2. Oxidative Polymerization of Aromatics with S_2Cl_2

aromatics	polymer	yield (%)	T_m (°C)
p-xylene		95	306
diphenyl sulfide		98	183
diphenyl ether		100	184
durene		92	275

as an electrophilic substitution. Diphenyl ether provides the corresponding polymer in 100% yield. However, benzene and *p*-dichlorobenzene were not polymerized due to their low π-electron density. A white powder of poly(thio-2,5-dimethyl-1,4-phenylene) which has a high melting temperature at 306 °C can be obtained from the polymerization of *p*-xylene with S_2Cl_2, with the same conditions as those for α,ω-diphenoxyalkanes. The structure of the 1,4-phenylene binding sulfide bond was confirmed by spectroscopic measurements. The IR spectrum of the resulting polymer is consistent with that of poly(thio-2,5-dimethyl-1,4-phenylene) prepared by conventional polycondensation of 2,5-dimethyl-*p*-dibromobenzene and sodium sulfide.

Polymerization Mechanism. The polymerization proceeds efficiently in low basicity solvents, such as dichloromethane, chloroform, and carbon tetrachloride. In particular, dichloromethane is the most suitable solvent for the polymerization. Basic solvents, such as THF, *N*-methyl-2-pyrrolidone (NMP), and *N*,*N*-dimethylformamide (DMF), which have a larger donor number, retard the polymerization. This result suggests that the polymerization proceeds via a cationic mechanism. The basic solvents deactivate the cationic species and suppress the polymerization.

The effect of the oxidizing agent has been investigated in the polymerization of *p*-xylene and S_2Cl_2. Evolution of hydrogen chloride and formation of a reductant of DDQ, 2,3-dichloro-5,6-dicyano-*p*-hydroquinone (DDH), are observed during the polymerization. DDH is quantitatively isolated after the polymerization proceeds to 100%. This result indicates that the polymerization proceeds through oxidation by DDQ, and the stoichiometry is assumed as in eq 1.



(1)

It has already been reported that sulfenyl chloride and thiosulfenyl chloride would electrophilically substitute with aromatic compounds as active species.[28] This electrophilic reaction of S_2Cl_2 was demonstrated by using anisole as a nonpolymerizable model compound to confirm the formation of arenethiosulfenyl chloride. When S_2Cl_2 is added to the acidic dichloromethane solution containing anisole under the same condition as that for polymerization, the mixture turns gradually from pale yellow to dark green (λ = 700–900 nm), due to presumably the formation of 4-methoxybenzenethiosulfenyl chloride

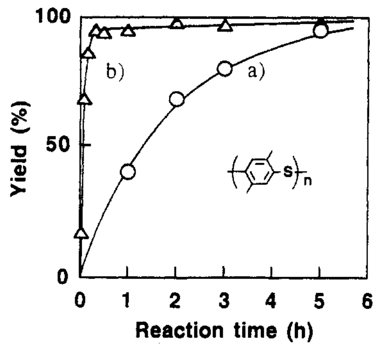
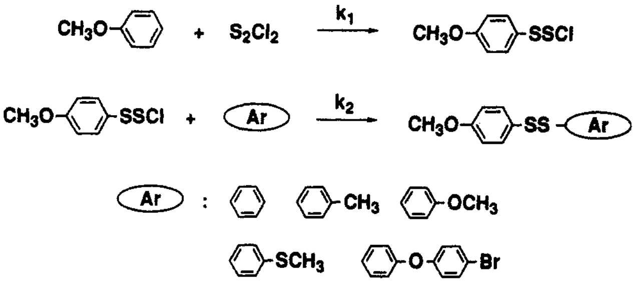


Figure 5. Oxidative polymerization of (a) *p*-xylene with S_2Cl_2 and (b) bis(2,5-dimethylphenyl)disulfide.

Scheme 2

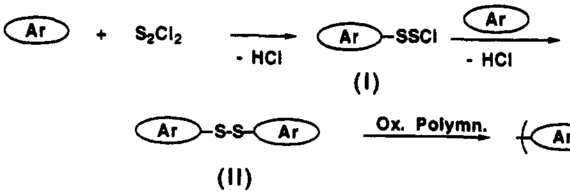


(Scheme 2). The product was also confirmed by the ^1H NMR spectrum. Phenyl protons (7.61, 7.52, 6.99, 6.90 ppm: AB q, 4H) and the methyl proton (3.88 ppm: s, 3H) were detected, which are different from those of anisole.[29] The AB quartet peaks support the structure of the 1,4-disubstituted phenylene ring binding different groups, i.e. 4-methoxybenzenethiosulfenyl chloride. The formation obeys the pseudo-first-order reaction on the basis of the kinetic analysis. The rate constant k_1 of the reaction of S_2Cl_2 with anisole is determined to be 4.6×10^{-5} $dm^3\ mol^{-1}\ s^{-1}$ by means of the UV/vis spectroscopic measurement.

The saturated absorption of 4-methoxybenzenethiosulfenyl chloride at λ = 800 nm (ε = 15.3 $m^2\ mol^{-1}$) gradually decreased by adding aromatic compounds such as benzene and toluene. This is believed to be caused by the following reaction, i.e. the coupling of 4-methoxybenzenethiosulfenyl chloride with the aromatic compound. The rate constant k_2 of the reaction of 4-methoxybenzenethiosulfenyl chloride with benzene, toluene, 4-bromodiphenyl ether, thioanisole, and anisole is determined to be 1.5×10^{-3}, 2.8×10^{-3}, 3.4×10^{-3}, 8.8×10^{-3}, and 8.8×10^{-2} $dm^3\ mol^{-1}\ s^{-1}$, respectively. Aromatics with higher π-electron densities react faster with 4-methoxybenzenethiosulfenyl chloride, since the reaction proceeds through an electrophilic reaction of 4-methoxybenzenethiosulfenyl chloride. In the earlier stages of the polymerization, arenethiosulfenyl chloride is formed, accommpanied by the elimination of hydrogen chloride, followed by electrophilic attack or arenethiosulfenyl chloride on the phenyl ring. Then, the resulting disulfide compound is oxidatively polymerized to poly(thioarylene).

In comparison with oxidative polymerization of bis(2,5-dimethylphenyl) disulfide, the polymerization of *p*-xylene with S_2Cl_2 proceeds much slower in spite of yielding the same product, poly(thio-2,5-dimethyl-1,4-phenylene) (Figure 5). This result supports the idea that the formation of disulfide compounds is the rate-determining step in this polymerization. The formation of the disulfide compound is confirmed as the main product in the controlled reaction of 4-bromodiphenyl ether with S_2Cl_2 in a poor solvent. Under the same conditions as for the polymerization except for the solvent, the corresponding

Scheme 3



disulfide compound forms as the main product ([disulfide]/[product] = 88%). The product is precipitated in hexane once 4-bromodiphenyl ether is coupled, which can be excluded from the other side and following reactions of the resulting disulfide. In the classical Friedel–Crafts reaction of S_2Cl_2 with an aromatic catalyzed by a Lewis acid, many side products such as polysulfide and thianthrene could be given which are formed through the exchange and/or electrophilic reactions of disulfide with S_2Cl_2 proceeding homogeneously. In this polymerization, the following oxidation suppresses these side reactions and provides a selective formation of poly(thioarylene). The disulfide once-formed by the electrophilic reaction of S_2Cl_2 is rapidly oxidized without reacting S_2Cl_2.

As a conclusion, the polymerization mechanism is assumed to be that in Scheme 3. S_2Cl_2 attacks the aromtic compound electrophilically to form arenethiosulfenyl chloride (I). I is coupled with another aromatic to yield the corresponding disulfide compound (II). II is oxidatively polymerized to poly(thioarylene) as in the previously reported mechanism for diphenyl disulfide.[24-26]

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