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Synthesis of Reactive Functionalized Oligo(*p*-phenylene sulfide)s

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ABSTRACT: Modification of the oligo(phenylene sulfide) chain at the ends with reactive groups such as chloro, bromo, iodo, and carboxyl to enhance its reactivtiy was performed. α,ω-Dihalooligo(*p*-phenylene sulfide) was synthesized through the oxidative polymerization of diphenyl disulfide in the presence of bis(4-halophenyl)disulfide. Linear oligo(*p*-phenylene sulfide) (OPS) terminated by Cl or Br with a high degree of functionality was obtained by a one-pot process. α-Carboxy-OPS was synthesized by the thermolysis of the disulfide bond of the OPS in the presence of an aromatic iodide having a carboxyl group. The carboxy-terminated OPS was used for the synthesis of polyamide-*graft*-OPS copolymers.

I. Introduction

Poly(*p*-phenylene sulfide) (PPS) exhibits good thermal stability, moldability, and chemical resistance.[1] Such properties make PPS an attractive engineering plastic. Much effort has been consumed on the development of modifications of PPS to expand the use. For example, reinforcement of PPS with short glass or carbon fibers is effective in improving mechanical properties.[2] However, no polymers are miscible with PPS completely due to its high crystallinity. Some attempts to improve properties by preparing copolymers using α,ω-disubstituted PPS have been described in recent years. Daccord and Sillion have reported the preparation of PPS with a functional end group.[3] Heitz has also demonstrated a process for the synthesis of PPS-*block*-polyamide using α,ω-dicarboxy-PPS.[4]

Recently, it has been reported that oligo(*p*-phenylene sulfide) (OPS) containing one disulfide bond can be prepared by the oxidiative polymerization of diphenyl disulfide (DPS).[5] Disulfide bonds act as reactive groups which condense with aryl iodides to form a sulfide bond with evolution of elemental iodine.[6] Therefore, functionalized OPS containing a disulfide bond should be obtained by reaction of OPS with iodides. This paper describes a one-pot synthesis of OPS having a terminal halogen and attempts at its thermal polymerization. An OPS having carboxylic acid groups was also synthesized, which was used for the synthesis of a polyamide-*graft*-OPS copolymer by polycondensation with *m*-phenylene diisocyanate and for the synthesis of an analogous copolymer through the amide exchange reaction with a polyamide.

II. Experimental Section

Materials. Diphenyl disulfide (99%, Kantoh Chem. Co.) was purified by recrystallization from ethanol (mp: 59 °C). Bis(2,4-pentanedionato) oxovanadium(IV) (vanadyl acetylacetonate) was obtained from Tokyo Kasei Co. and recrystallized from benzene. Trifluoromethanesulfonic acid was obtained from 3M Co. with 97% purity and was used under a dry argon atmosphere without further purification. Trifluoroacetic acid and its anhydride (reagent grade) were obtained from Kantoh Chem. Co. and were used without further purification. Dichloromethane, methanol, pyridine, and benzene were purified by distillation in the usual manner. Thionyl chloride, triethylamine, and sodium methoxide were obtained from Wako Chem. Co. and used as received. 4-Bromothiophenol, 4-chlorothiophenol, 4-aminothiophenol, 4-hydroxythiophenol, 4-biphenylcarboxylic acid, 3-methyl-1-phenyl-3-phospholene 1-oxide, and *m*-phenylene diisocyanate were obtained from Aldrich Chemical Co. as reagent grade and were used as received. *p*-Diiodobenzene and *n*-dodecylamine were obtained from Tokyo Kasei Co. and used as received. 5-Hydroxyisophthalic acid was obtained from Kantoh Chem. Co. and purified by recrystallization from water. Nylon-11 was obtained from Aldrich Chemical Co. and was used as received.

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Measurements. ^{1}H and ^{13}C-NMR spectra were obtained on a JEOL 270-MHz FT-NMR JMN-EX270. A ^{13}C CP/MAS spectrum was obtained on a JEOL 400-MHz FT-NMR GXS400. Infrared spectra were obtained on a Jasco FT-IR 5300 as a potassium bromide pellet. Melting points were determined on a SEIKO thermal analyzer SSC/550 with a heating rate of 10 °C/min. Molecular weights of polymers were measured by using a GPC SSC-7000 instrument (Senshu Kagaku Co.) at 210 °C with 1-chloronaphthalene and polystyrene as the eluent and standard, respectively.

Preparation of Oligo(*p*-phenylene sulfide) (OPS). Oligo(*p*-phenylene sulfide) was prepared by the oxidative polymerization of diphenyl disulfide using vanadyl acetylacetonate as a catalyst.[7] A typical procedure is as follows. Diphenyl disulfide (5 mol) and vanadyl acetylacetonate (0.25 mol) were dissolved in 50 L of dichloromethane. Trifluoroacetic acid (50 mol) and trifluoroacetic anhydride (10 mol) were added to the solution. The reaction was carried out for 20 h under an oxygen atmosphere with constant stirring at 25 °C. During the polymerization white powder precipitated from the solution. The mixture was poured into 250 L of methanol. The precipitate was collected and washed with methanol and water. The low molecular weight component of the polymer was removed by extraction, twice, with hot chloroform to yield >90 wt % OPS as a powder. IR (KBr, cm^{-1}): 3050 (ν_{C-H}), 1393, 1470, 1570 ($\nu_{C=C}$), 818 (δ_{C-H}), 480, 550, 690, 740, 1010, 1070, 1090. For other analytical data, see Results and Discussion section.

Preparation of Diaryl Disulfides (1a,b,d,e). Bis(4-bromophenyl) disulfide (**1b**) was prepared by the use of the corresponding thiophenol as follows. To the ethanol (100 mL) solution of 4-bromothiophenol (15 g, 0.079 mol) was added iodine (0.042 mol, 10.7 g) in ethanol (100 mL). After stirring for 12 h excess iodine was reduced with Na_2SO_3 and thin white plates were collected by filtration. Recrystallization from ethanol gave pure product as white crystals. Total yield: 14 g (95%). Mp: 94–95 °C (lit.[8] mp 91–92 °C). Anal. Calcd for $C_{12}H_8S_2Br_2$: C, 38.3; H, 2.1. Found: C, 38.2; H, 1.9. IR (KBr, cm^{-1}): 1471 ($\nu_{C=C}$), 813 (δ_{C-H}). ^{1}H-NMR ($CDCl_3$, TMS, ppm): 7.35 (m). ^{13}C-NMR ($CDCl_3$, TMS, ppm): 132.3, 129.6. UV (λ_{max}, nm): 250.8. Bis(4-chlorophenyl) disulfide was prepared analogously and recrystallized from ethanol to give yellow plate crystals (**1a**). Mp: 71–72 °C. Anal. Calcd for $C_{12}H_8Cl_2S_2$: C, 50.2; H, 2.8. Found: C, 50.1; H, 2.6. IR (KBr, cm^{-1}): 1477 ($\nu_{C=C}$), 818 (δ_{C-H}). ^{1}H-NMR ($CDCl_3$, TMS, ppm): 7.29 (m). ^{13}C-NMR ($CDCl_3$, TMS, ppm): 129.3. UV (λ_{max}, nm): 248.6. Bis(4-aminophenyl) disulfide (**1d**) was prepared analogously from the corresponding 4-aminothiophenol and was recrystallized from ethanol to give yellow needles. Mp: 75–76 °C. Anal. Calcd for $C_{12}H_{10}N_2S_2$: C, 58.0; H, 4.9. Found: C, 58.0; H, 4.6. IR (KBr, cm^{-1}): 1492 ($\nu_{C=C}$), 822 (δ_{C-H}). ^{1}H-NMR ($CDCl_3$, TMS, ppm): 7.20, 6.49, 3.73. ^{13}C-NMR ($CDCl_3$, TMS, ppm): 147.2, 133.7, 115.4. UV (λ_{max}, nm): 260.2. Bis(4-hydroxyphenyl) disulfide (**1e**) was prepared analogously and was recrystallized from benzene–hexane to give yellow needles. Mp: 150–152 °C. Anal. Calcd for $C_{12}H_{10}O_2S_2$: C, 57.8; H, 4.0. Found: C, 57.6; H, 3.8. IR (KBr, cm^{-1}): 1493 ($\nu_{C=C}$), 828 (δ_{C-H}). ^{1}H-NMR ($CDCl_3$, TMS, ppm): 7.33, 6.75, 4.80. ^{13}C-NMR ($CDCl_3$, TMS, ppm): 132.9, 116.3. UV (λ_{max}, nm): 243.0.

Preparation of Bis(4-iodophenyl) Disulfide (1c). Bis(4-aminophenyl) disulfide (0.05 mol, 12.4 g) and 96% sulfuric acid (12 g) were dissolved in hot H_2O, and the resulting solution was cooled to 0 °C to give a white suspension. To this suspension was added $NaNO_2$ (0.1 mol, 6.9 g) in H_2O (20 mL) for 1 h. After stirring for 30 min, 3.7 g of sulfuric acid and KI (0.12 mol, 19.9 g) in H_2O (20 mL) was added at 0 °C, and the mixture was stirred for 5 min. With constant stirring, the solution was heated slowly to 80 °C. After evolution of N_2 ceased, the solution was cooled and extracted with $CHCl_3$. The extract was washed with the solution of Na_2SO_3, NaOH, HCl, NaOH, and water successively and dehydrated with anhydrous Na_2SO_4. Evaporation of the solvent and recrystallization from dichloromethane–acetone gave a yellow amorphous solid. Yield: 9.14 g (39%). Mp: 120 °C (lit.[9] mp 124.5–125.5 °C). Anal. Calcd for $C_{12}H_8S_2I_2$: C, 30.7; H, 1.7. Found: 31.8; H, 1.9. IR (KBr, cm^{-1}): 1462 ($\delta_{C=C}$), 804 (δ_{C-H}). ^{1}H-NMR ($CDCl_3$, TMS, ppm): 7.39 (m). ^{13}C-NMR ($CDCl_3$, TMS, ppm): 138.3, 129.8. UV (λ_{max}, nm): 253.6.

Preparation of α,ω-Dihalogenated Phenylene Sulfide Pentamer (3b,c). Step 1: Thiophenol (0.085 mol, 9.37 g), KOH (0.085 mol, 4.77 g), and dimethylacetamide (35 mL) were mixed in a flask at room temperature. After the reaction mixture became a homogeneous solution, the solvent was evaporated under vacuum to give potassium thiophenolate. Then it was mixed with *p*-dichlorobenzene (0.035 mol, 5.15 g) in *N*-methylpyrrolidinone at 190 °C for 15 h. The reaction was carried out under a nitrogen atmosphere. Then, after the solvent was evaporated, the mixture was poured into water, and the product was extracted with chloroform which was washed with water repeatedly. Recrystallization from ethanol gave 1,4-dithiophenoxybenzene (phenylene sulfide trimer) (**2**) as pale brown crystals (3.04 g). Yield: 29.5%. Mp: 83 °C. Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79. Found: C, 73.40; H, 4.61. IR (KBr, cm^{-1}): 820, 740, 680 (δ_{C-H}). The purity was confirmed by gas chromatography (99%). Step 2: Phenylene sulfide trimer (**2**) (0.05 mol/L) and bis(4-bromophenyl) disulfide (**1b**) (0.15 mol/L) were dissolved in dichloromethane (50 mL). To this solution was added trifluoroacetic acid (1.0 mol/L), trifluoroacetic anhydride (0.2 mol/L), and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (0.15 mol/L). The mixture was stirred for 15 h at room temperature. The mixture was then poured into methanol (500 mL) containing hydrochloric acid (5%) to precipitate the crude product which was washed with an aqueous KOH solution, H_2O, methanol, and dichloromethane. The insoluble part was collected and dried under vacuum to give α,ω-dibrominated phenylene sulfide pentamer as a white powder (**3b**). Yield: 1.56 g (94%). Mp: 204 °C. Anal. Calcd for $C_{30}H_{20}Br_2S_4$: C, 53.90; H, 3.02. Found: C, 53.98; H, 3.10. IR (KBr, cm^{-1}): 820 (δ_{C-H}). When bis(4-iodophenyl) disulfide (**1c**) was used, the corresponding α,ω-diiodinated phenylene sulfide pentamer was obtained as a yellow powder (**3c**). Yield: 100%. Mp: 203 °C. Anal. Calcd for $C_{30}H_{20}I_2S_4$: C, 47.25; H, 2.64. Found: C, 46.99; H, 2.60. IR (KBr, cm^{-1}): 820 (δ_{C-H}).

Preparation of α,ω-Disubstituted Oligo(*p*-phenylene sulfide) (4a-c). 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (2.5 mmol, 0.57 g), trifluoroacetic acid (25 mmol, 2.85 g), and trifluoroacetic anhydride (5 mmol, 1.05 g) were dissolved in CH_2Cl_2 (25 mL). To this solution were added diphenyl disulfide (1.25 mmol, 0.27 g) and **1a** (1.25 mmol). After stirring for 20 h at room temperature, the solution was poured into 200 mL of MeOH containing 5% HCl. The precipitate was filtered, washed with an aqueous solution of KOH (5%) and acetone, and dried for 10 h *in vacuo* at room temperature to give **4a** as a pale yellow powder. Yield: 0.33 g (52%).

The other halo-terminated oligo(*p*-phenylene sulfide)s (**4b,c**) were prepared analogously. Yield: **4b**, 0.24 g (32%); **4c**, 0.45 g (52%) (melting points and elemental analyses; see Table 2).

Bromination of Oligo(*p*-phenylene sulfide) with Br_2. Bromine (3.20 g, 20 mmol) was added to OPS (1.09 g), and the mixture was stirred for 20 min at room temperature. Then, excess bromine was reduced with Na_2SO_3; the precipitate was collected by filtration, washed with MeOH, and dried for 10 h *in vacuo* at room temperature to give a yellow powder as a product (1.5 g). IR (KBr, cm^{-1}): 870, 818 (δ_{C-H}).

Preparation of 4′-Iodo-4-biphenylcarboxylic Acid (5). 4-Biphenylcarboxylic acid (9.91 g, 0.05 mol), iodine (5.08 g, 0.02 mol), and $HIO_4 \cdot 2H_2O$ (2.28 g, 0.01 mol) were dissolved in 80% acetic acid. The iodine color faded after stirring for 8 h at 80 °C. Then the solution was diluted with water, and unreacted iodine was reduced with Na_2SO_3. The precipitate was collected by filtration and washed with water. Recrystallization from acetic acid and 2-methoxyethanol gave white needle crystals. Yield: 11.86 g (73%). Mp: 321–322 °C (lit.[10] mp 312–313 °C). IR (KBr, cm^{-1}): 1684 ($\delta_{C=C}$), 1300 (ν_{C-O}), 820 (δ_{C-H}). MS (*m*/*z*): 327 (M), 307 (M − OH), 197 (M − I), 152 (M − I − COOH). ^{1}H NMR ($(CD_3)_2SO$, TMS, ppm): 7.5–8.1 (m). ^{13}C NMR ($(CD_3)_2SO$, TMS, ppm): 167.0, 143.1, 138.4, 137.7, 129.9, 129.0, 126.6, 94.8.

Preparation of α-Carboxyoligo(*p*-phenylene sulfide) (6). OPS (0.32 g, 0.3 mmol) and **5** (0.24 g, 0.75 mmol) were suspended in diphenyl ether (0.3 mL). The mixture was stirred for 20 h at 260 °C with evolution of iodine. Then it was diluted with 1-chloronaphthalene (5 mL). After being allowed to cool, the mixture was poured into MeOH. The precipitate was filtered, washed with 2-methoxyethanol, $CHCl_3$, and MeOH successively, and dried for 10 h *in vacuo* at 50 °C to give a pale brown powder. Yield: 0.28 g. Mp: 225, 247 °C. IR (KBr, cm^{-1}): 1687 ($\delta_{C=O}$), 818 (δ_{C-H}).

Preparation of Dimethyl 5-(4-Iodophenoxy)isophthalate (7). 5-Hydroxyisophthalic acid (10.93 g, 0.06 mol) and anhydrous pyridine (1 mL) were dissolved in hot thionyl chloride (57.1 g, 0.48 mol). The mixture was refluxed for 22 h. After the removal of residual $SOCl_2$ under vaccum, methanol (40 mL) and triethylamine (12.13 g, 0.12 mol) were added. The solution was stirred for 96 h and acidified with hydrochloric acid. The product was extracted with chloroform and recrystallized from chloroform, twice, to give dimethyl 5-hydroxyisophthalate as white needles. Mp: 160−162 °C (lit.[11] mp 159−160 °C). Yield: 9.5 g (85 wt %). **7** was prepared by the Ullmann reaction as follows.[12] Dimethyl 5-hydroxyisophthalate (2.98 g, 16 mmol) was dissolved in anhydrous benzene (32 mL). The solution was flushed with nitrogen. Then a methanol solution of sodium methoxide (2.93 g, 28%) was added. After the removal of benzene and methanol by distillation, the corresponding sodium salt was obtained as a yellow powder. *p*-Diiodobenzene (26.4 g, 80 mmol) and copper(I) chloride were dissolved in anhydrous pyridine (250 mL) under nitrogen. To this solution was added a slurry of the sodium salt in pyridine (100 mL). The mixture was refluxed for 20 h. Then the solution was cooled, poured into water (900 mL), and acidified with hydrochloric acid. The precipitated brown powder was collected, dissolved in chloroform, and dehydrated with anhydrous $MgSO_4$. Additional product was also extracted from the filtrate with chloroform and treated in the same manner. The product was isolated by column chromatography on silica gel with chloroform as eluent. Yield: 36 wt %. Mp: 87 °C. R_f: 0.51. ^{1}H-NMR ($CDCl_3$, TMS, ppm): 8.45 (t, 1H), 7.83 (d, 2H), 7.23 (q, 4H), 3.93 (s, 6H). IR (KBr, cm^{-1}): 2954, 1724, 820, 757. Anal. Calcd for $C_{16}H_{13}O_5I$: C, 46.62; H, 3.18. Found: C, 46.59; H, 3.35.

Preparation of 5-(4-Iodophenoxy)isophthalic Acid (8). **7** (0.49 g, 1.2 mmol) was dissolved in methanol (12 mL), and an aqueous solution of NaOH (0.2 N, 13.2 mL) was added. After the mixture was stirred for 14 h at 50 °C, a small amount of the remaining orange precipitate was filtered off. The product (**8**) was isolated as a white powder by filtration after acidification of the filtrate by hydrochloric acid, which was washed with water repeatedly. Yield: 0.45 g (98%). Anal. Calcd for $C_{14}H_9O_5I$: C, 43.77; H, 2.36. Found: C, 42.96; H, 2.49. ^{1}H-NMR ($(CD_3)_2SO$, TMS, ppm): 8.25 (1H), 7.77 (d, 2H), 6.96 (d, 2H). IR (KBr, cm^{-1}): 1694 ($\nu_{C=O}$), 836, 762, 693 (δ_{C-H}).

Preparation of Dicarboxyoligo(*p*-phenylene sulfide) (9). The condensation of **8** with OPS was carried out as follows. **8** (5.76 g, 15 mmol) and OPS (5.25 g, 5 mmol) were suspended in diphenyl ether (30 mL). Then the mixture was stirred for 20 h at 260−270 °C under nitrogen. The evolution of iodine was observed during the reaction. Then 30 mL of 1-chloronaphthalene was added to the vessel. After cooling, the mixture was poured into methanol. The precipitate was collected, washed with aqueous NaOH, HCl, H_2O, MeOH, and hot $CHCl_3$, and dried *in vacuo*. The product (**9**) was a pale brown powder. Yield: 4 g (71%). Mp: 240 °C. IR (KBr, cm^{-1}): 1696 ($\nu_{C=O}$), 1235 (ν_{COC}), 811 (δ_{C-H}). ^{1}H-NMR ($(CD_3)_2SO$, TMS, 120 °C, ppm): 7.28−7.36 (m, ca. 40H), 7.70 (s, 2H), 8.24 (s, 1H).

Preparation of Diamido-OPS (10). To an α-chloronaphthalene solution (10 mL) of the dicarboxy-OPS (**9**) (0.0561 g) was added *n*-dodecylamine (0.2 mol, 0.037 g). The mixture was stirred for 1 day at 140 °C. After cooling, the mixture was poured into 500 mL of methanol containing 5% HCl to precipitate the product which was washed repeatedly with methanol and H_2O and dried in vacuum. The product (**10**) was a pale brown powder. Yield: 0.062 g (97%). IR (KBr, cm^{-1}): 2926, 2852 (ν_{C-H}), 1636 ($\nu_{C=O}$), 814 (δ_{C-H}). ^{1}H-NMR ($(CD_3)_2SO$, TMS, ppm, 60 °C): 0.87 (6H), 1.2−1.3 (50H), 2.18 (4H), 7.2−7.4 (*ca.* 40H).

Preparation of Poly(*m*-phenyleneisophthalamide)-*graft*-OPS (11). Dicarboxy-OPS (**9**) (0.30 g) and 3-methyl-1-phenyl-3-phospholene 1-oxide (4.8 mg, 0.025 mmol) were added into sulfolane (1.25 mL). By heating to 200 °C under a N_2 atmosphere, the mixture turned to a brown slurry. To this was added *m*-phenylene diisocyanate (0.04 g); the mixture was stirred for 4 h at 200 °C. After cooling, it was poured into 200 mL of MeOH containing 5% HCl. The precipitate was collected and dissolved in 200 mL of a *N,N*-dimethylacetamide solution containing 1% LiCl. The insoluble part was removed by filtration. The solution was poured into MeOH. The precipitated product was filtered, washed with hot MeOH, and dried for 10 h *in vacuo* at 50 °C to give **11** as a brown powder (0.09 g, 26 wt %). IR (KBr, cm^{-1}): 3316 (ν_{N-H}), 1644 ($\nu_{C=O}$), 868, 813 (δ_{C-H}). ^{13}C CPMAS NMR (TMS, ppm): ca. 158−152, ca. 137, 134.5, 131.9.

Preparation of Nylon-11-*graft*-OPS (12). Dicarboxy-OPS (**9**) (0.0312 g) and Nylon-11 (0.0471 g) were heated in α-chloronaphthalene (30 mL) at 180 °C for 10 h with constant stirring under nitrogen. Then the mixture was cooled and poured into 500 mL of methanol to isolate the crude product. The precipitated powder was collected, washed with methanol, and dried *in vacuo* for 10 h. The product was suspended in 20 mL of DMF and stirred for 48 h. The insoluble part was collected by filtration washed with DMF and methanol, and dried *in vacuo* for 20 h to give the product **12** as a pale brown powder. Yield: 0.03 g (38 wt %). IR (KBr, cm^{-1}): 3308 (ν_{N-H}) 1644 ($\nu_{C=O}$), 814 (δ_{C-H}). ^{1}H-NMR ($(CD_3)_2SO$, TMS, ppm, 80 °C): 7.2−7.4 (m), 1.9−2.2 (m), 1.2−1.6 (m), 0.8−0.9 (m).

III. Results and Discussion

Structure of OPS. OPS was isolated in high yield (>90%) as a white powder with high purity by the oxidative polymerization of diphenyl disulfide (DPS) and was soluble in hot *N*-methylpyrrolidinone and α-chloronaphthalene. We have previously discussed our conclusions that this reaction proceeds *via* a cationic mechanism through the oxidation of DPS.[13] Bis(phenylthio)phenylsulfonium cation that is formed by the oxidation acts as the active species in the polymerization.[14] The sulfonium cation electrophilically reacts with the benzene ring at the end of the chain.

The structure of the 1,4-disubstituted phenylene unit was confirmed by its IR spectrum. The strong absorption at 820 cm^{-1}, attributed to the C−H out-of-plane vibration of 1,4-phenylene, was observed in the IR spectrum of the OPS (Figure 1a). A weak absorption of a C−H out-of-plane vibration of a monosubstituted terminal phenyl ring was also detected at 740 and 690 cm^{-1} which supports the formation of an oligomer.

The molecular weight of the OPS was determined to be $M_n = 1050$ and $M_w/M_n = 5.2$ by high-temperature GPC at 210 °C with α-chloronaphthalene as an eluent. The degree of polymerization was estimated to be *ca.* 9. The DSC curve of the oligomer showed a single endothermic peak at 197 °C. This result agrees with the melting point of a nonamer on the basis of the relationship between the melting point and the molecular weight of PPS oligomers reported by Heitz et al.[15]

The existence of a disulfide bond at the OPS chain is predicted from the polymerization mechanism.[14] We have previously confirmed the existence of a disulfide bond at the end of a chain in soluble poly(2,6-dimethylphenylene sulfide) in the early stage of the polymerization.[16] This suggests that the unsubstituted oligomer also has a disulfide bond at the end of the chain. In the case of unsubstituted OPS, the low-molecular-weight part extracted with dichlorobenzene from the crude product of polymerization has also been shown to have one disulfide bond.[14] The elemental analysis also indicated that the OPS has a disulfide bond because

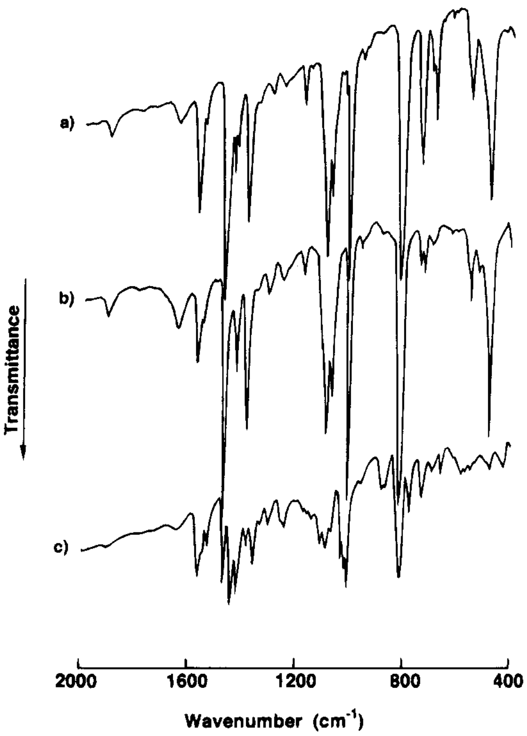


Figure 1. IR spectra of OPS (a), **4b** (b), and OPS brominated with Br_2 (c).

the content of C, H, and S is more closely in agreement with an empirical formula of $C_{60}H_{42}S_{10}$ rather than $C_{60}H_{42}S_9$ as shown in Table 1.

Synthesis of α,ω-Dihalosubstituted OPS. Although the oxidation of bis(4-bromophenyl) disulfide yields a (4-bromophenyl)bis[(4-bromophenyl)thio]sulfonium cation, polymerization does not proceed because halosubstituents at the *para* position of the phenyl ring suppress the electrophilic substitution by the cation. However, in the presence of thiophenylene trimer (**2**), the sulfonium cation acted as an electrophile to give α,ω-disubstituted thiophenylene pentamers (**3b**,**c**) in high yield (Scheme 1).

One-pot syntheses of α,ω-disubstituted OPS (**4a**–**c**) from disulfides were achieved by the oxidative polymerization of DPS in the presence of an equimolar amount of 4,4′-disubstituted DPS (Scheme 2). The telomerization proceeds efficiently because halosubstituted DPS is oxidized more slowly than the nonsubstituted one. Terminal groups are introduced through an electrophilic reaction by the para-substituted sulfonium cation to the end phenyl ring of OPS. The exchange reaction between the disulfide bond at the end of the OPS and the para-substituted sulfonium cation is responsible for introducing terminal groups as described in Scheme 2.[14,17] When the substituents were Br, Cl, and I, the corresponding substituted OPSs were obtained. The introduction of amino (**1d**), hydroxy (**1e**), or carboxy groups by this method was not successful because of the side reaction. The melting points of the oligomers ranged from 170 to 190 °C, which indicates that the degrees of the polymerization were ca. 5–6.

The linear structures of the substituted OPSs were confirmed by IR spectroscopy. The C–H out-of-plane vibration of the 1,4-phenylene unit was observed at 820 cm^{-1}. The α,ω-disubstituted OPS showed no peak attributed to an isolated ring hydrogen. These indicate that the oligomers are comprised of only 1,4-disubstituted phenylene units. A decrease in the absorption intensity of the monosubstituted phenyl ring hydrogen at 740 and 690 cm^{-1} supports the introduction of substituents at the α and ω positions (Figure 1b).

A quantification of the halogen groups introduced was obtained by IR spectroscopy. The absorption intensity of the α,ω-disubstituted oligomer at 740 and 690 cm^{-1} against that of the unsubstituted one (mp 191 °C) was calculated by using the intensity of absorption at 820 cm^{-1} in each spectrum as a standard. The decrease in the intensity of the absorption at 740 and 690 cm^{-1} corresponds to the percentage of the substituted OPS.

Thus, the functionality (f) is given by eq 1 using the absorption intensity at 740 cm^{-1} (I_1) and at 820 cm^{-1} (I_2)

$$f = [1 - (I_1/I_2)_s/(I_1/I_2)_u] \times 2 \qquad (1)$$

where the subscripts of s and u represent the *substituted* OPS and the *unsubstituted* OPS, respectively. When the substituents are Cl and Br, high functionality (>1.7) was achieved.

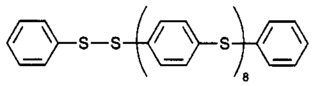
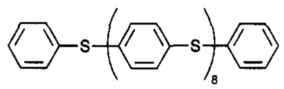
Elemental analysis also supported the efficient introduction of the halogen into OPS. The degree of polymerization (**4a** = 5; **4b**,**c** = 6) could be assumed from the melting points (170–180 °C). The content of C, H, S, and halogen was in agreement with the calculated value based on each functionality and the degree of polymerization (Table 2).

A comparative reaction of OPS with Br_2[18] was carried out to introduce bromine into OPS. The resulting polymer contained trisubstituted benzene units as indicated by IR absorption at 860–870 cm^{-1} (Figure 1c). Even at low temperature (0 °C), the bromination of OPS with Br_2 showed a much lower α,ω-selecivity than the oxidative polymerization method. While this may be due in part to the fact that the active species in the oxidative polymerization, the sulfonium cation, is more bulky than the bromo cation, it is not clear at this stage that reactivity plays a role. Nevertheless this oxidative polymerization procedure is a convenient method for the quantitative preparation of α,ω-disubstituted OPS with a high degree of functionality.

Thermal polymerization of bis(4-bromophenyl) disulfide in the presence of copper to produce poly(*p*-phenylene sulfide) has been reported.[8] Since **4b** has a disulfide bond in its chain, thermolysis of the oligomer with copper powder also proceeded in quinoline–pyridine at 250 °C as expected. The obtained polymer (off-white powder) was confirmed to be a linear poly(*p*-phenylene sulfide) by its IR spectrum and elemental analysis which showed the melting point at 270–290 °C and the onset temperature for weight loss above 500 °C.

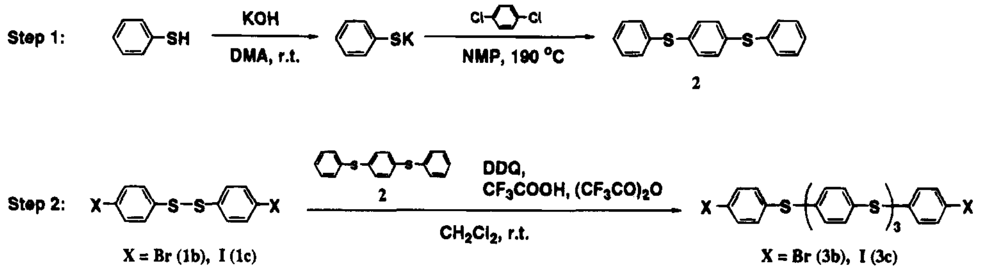
Synthesis of Carboxy-Terminated OPS. The introduction of the carboxyl group into the OPS was achieved by the thermolysis of the disulfide with a carboxyl-containing aromatic iodide. Aromatic iodides are usually prepared by the Sandmeyer reaction in which the corresponding aromatic amine is transformed to a diazonium salt followed by decomposition with I_2. However, aromatic iodides containing carboxyl groups could not be prepared by this method. Direct iodination of 4-biphenylcarboxylic acid was achieved by the reaction with iodine and periodic acid as described in Scheme 3 to give 4′-iodo-4-biphenylcarboxylic acid (**5**). The disulfide bond at the end of the OPS was allowed to react with **5** above 220 °C because the disulfide bond can be cleaved above that temperature. I_2 evolution occurs which confirms that the reaction proceeds. The

Table 1. Elemental Analysis of OPS

oligomer	formula	$\bar{M}_n$	elem anal.			
				C	H	S
OPS		1050	found	66.81	3.65	29.12
	$C_{60}H_{42}S_{10}$	1083.54[a]	calcd	66.50	3.91	29.59
	$C_{60}H_{42}S_9$	1051.48[b]	calcd	68.53	4.03	27.44

[a,b] Calculated from the formula.

Scheme 1



Scheme 2

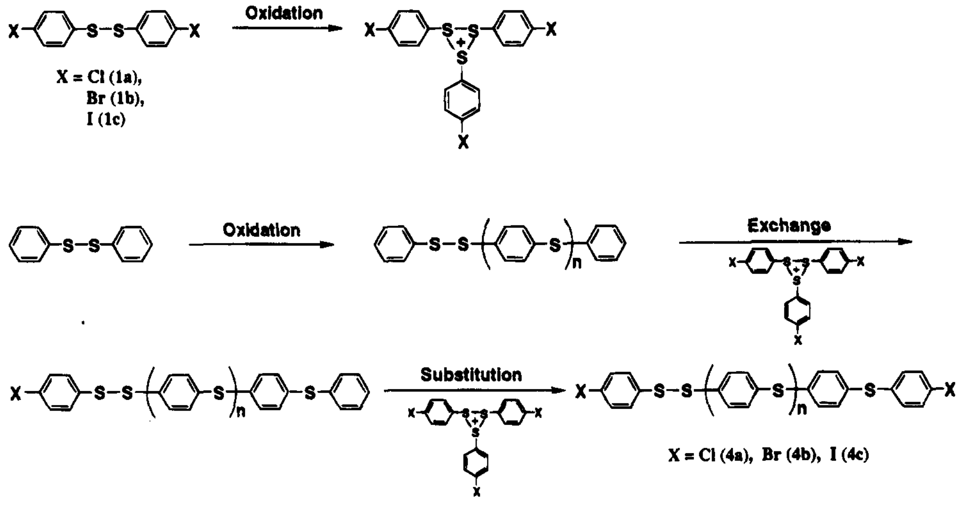


Table 2. Elemental Analysis of Halogenated OPS (4a–c)

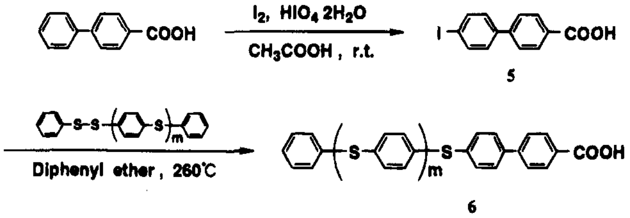
oligomer	mp (°C)	f^a	formula		elem anal.			
					C	H	S	X
4a	174	1.8	$C_{30}H_{20.2}Cl_{1.8}S_5$	calcd	59.6	3.4	26.5	10.6
				found	59.4	3.0	26.3	10.8
4b	184	1.7	$C_{36}H_{24.3}Br_{1.7}S_6$	calcd	55.1	3.1	24.5	17.3
				found	55.2	2.9	24.2	17.7
4c	188	1.2	$C_{36}H_{24.8}I_{1.2}S_6$	calcd	53.9	3.1	24.0	19.0
				found	53.7	2.9	23.7	19.6

[a] Functionality obtained by IR spectra.

absorption at 1686 cm^{-1} ($\nu_{C=O}$) in the IR spectrum of the product indicates the introduction of a carboxyl group.

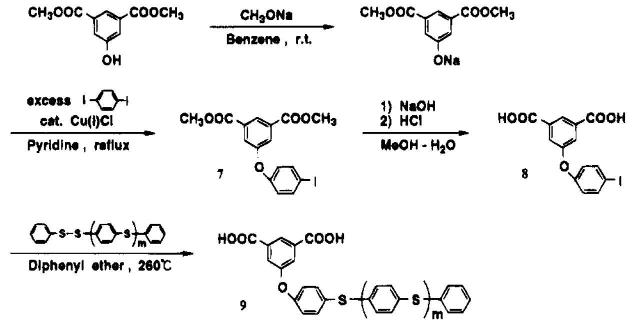
Since the oligomers are insoluble in common solvents, separation of the product from the unreacted OPS was difficult. The crude product exhibited two endothermic peaks at 225 and 247 °C in DSC. The peak at 247 °C moved to 282 °C by treating the product with KOH–H_2O and moved back to 251 °C by treating again with HCl–methanol, while the peak at 227 °C (unsubstituted OPS) was independent of these treatments. These results indicate that the peak at 247 °C could be ascribed to the melting point of the COOH-terminated OPS and the 282 °C peak to that of the COOK-terminated OPS. On the basis of a comparison of each endothermic peak area in the DSC thermogram, the content of unreacted OPS in the crude product is estimated to be *ca* 50% on the assumption that their heats of fusion are approximately identical.

Scheme 3



Dicarboxy-terminated OPS (**9**) was synthesized by a similar process (Scheme 4). The direct iodination used for the synthesis of **5** was not applicable to the synthesis of aromatics having two carboxylic acids. 5-Hydroxyisophthalic acid was used as a starting material for the synthesis of **9**. The iodophenyl group was introduced by the Ullmann reaction. The carboxylic acid group was protected by esterification prior to condensation with diiodobenzene. The product was carefully purified in

Scheme 4



order to exclude acidic groups completely. Then the product was transformed to the sodium phenolate salt and reacted with diiodobenzene under completely anhydrous conditions to give **7** as a yellow solid. A large excess of diiodobenzene was used in order to minimize the yield of disubstituted byproduct. Hydrolysis of the methyl ester **7** was achieved by treating it with an alkali solution to give 5-(4-iodophenoxy)isophthalic acid (**8**).

The iodide **8** was allowed to react with OPS in diphenyl ether at 250–260 °C. The product was isolated as a pale brown powder (**9**) in 71% yield. Since **9** was soluble in a mixture of a tetrabutylammonium hydroxide solution and *N*-methylpyrrolidone at room temperature, separation from the unreacted OPS was successfully achieved. The existence of the carboxyl groups was confirmed by the IR spectrum (Figure 3a) in which $\nu_{C=O}$ was observed at 1696 cm^{-1}.

The ^1H-NMR spectrum of the dicarboxy-OPS (**9**) in $(CD_3)_2SO$ (120 °C) exhibited three signals (Figure 2b). The peaks at 7.70 and 8.24 ppm are attributed to the ring protons of the isophthalic acid group because of the coincidence with the ^1H-NMR spectrum of 5-(4-iodophenoxy)isophthalic acid (**8**) (Figure 2a). The broad peak at 7.3 ppm is attributed to the ring protons of the phenylene sulfide chain attached to the isophthalic acid group. The peak at 7.3 ppm corresponds to *ca.* 40 protons. The degree of the polymerization of the phenylene sulfide chain is estimated to be m = *ca.* 7 (Scheme 4), which is in good agreement with the results of Table 1.

The dicarboxy-OPS (**9**) reacted with *n*-dodecylamine in hot α-chloronaphthalene to produce the corresponding diamido OPS (**10**) (Scheme 5). The increase in the weight of the product and its ^1H-NMR spectrum (Figure 2c) confirmed the stoichiometric amide formation (yield: 97%).

Synthesis and Characterization of Polyamide-*graft*-OPS Copolymer. Synthesis of polyamide-*graft*-OPS copolymer was attempted using the dicarboxy-OPS (**9**) as shown in Scheme 6. High-temperature solution polycondensation of **9** with *m*-phenylene diisocyanate was carried out in sulfolane at 200 °C with phospholene oxide derivative as a catalyst.[19] The graft copolymer (**11**) obtained as a brown powder (Scheme 6) was partly soluble in dimethylformamide or dimethylacetamide containing LiCl at 70 °C. The absorption of the carboxyl group at 1696 cm^{-1} in the IR spectrum disappeared (Figure 3b); absorption due to the amide bond was observed at 1644 cm^{-1} ($\nu_{C=O}$). The IR spectrum indicated that **11** is comprised of both OPS and a polyamide unit.[20]

Figure 4 shows the ^{13}C CP/MAS spectrum of **11**. The two signals at 131.9 and 134.5 ppm are attributed to OPS carbons. These sharp signals indicate that the OPS unit is partly crystalline.[21] There are also signals at 137.0 and *ca.* 155 ppm attributed to the polyamide carbon.

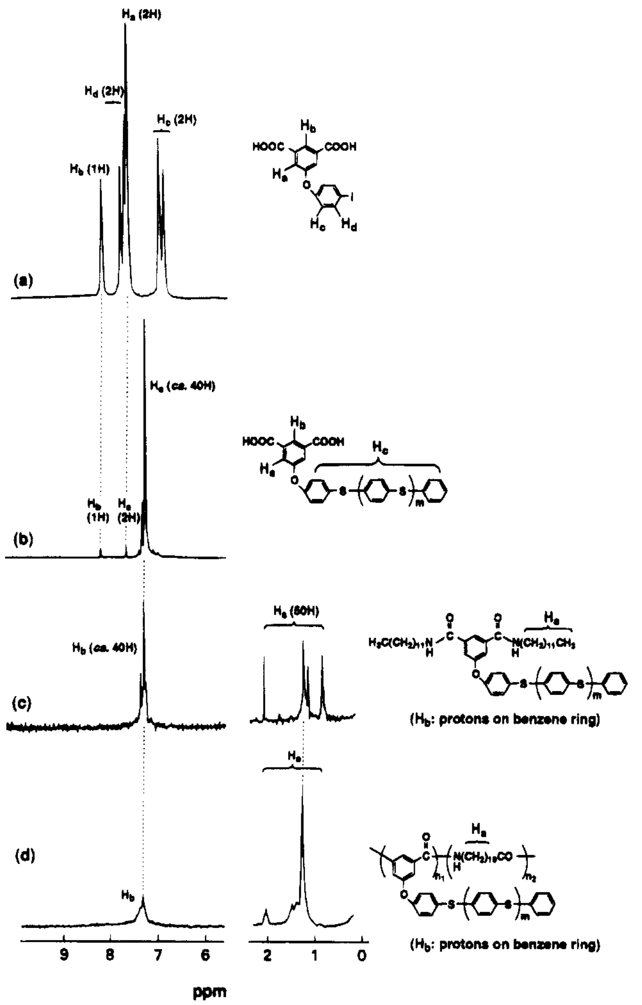
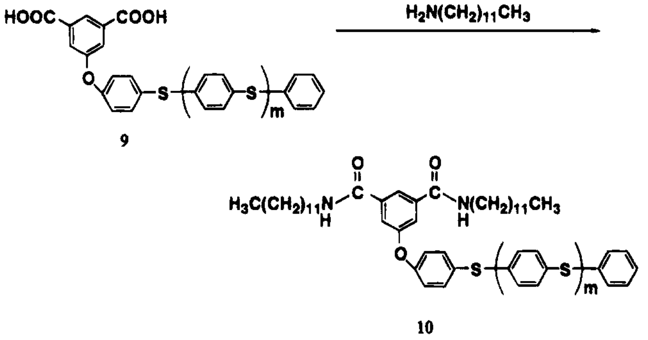


Figure 2. ^1H-NMR spectrum of 5-(4-iodophenoxy)isophthalic acid (a), dicarboxy-OPS (**9**) (b), diamido-OPS (**10**) (c), and Nylon-11-*graft*-OPS (**12**) (d) in $(CD_3)_2SO$. Temp: (a) 20 °C; (b) 120 °C; (c) 60 °C; (d) 80 °C.

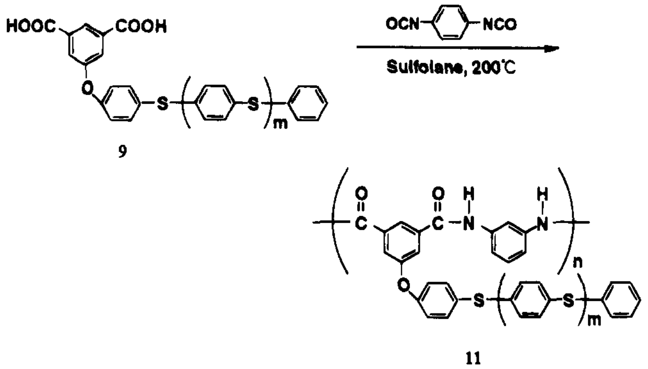
Scheme 5



The DSC curve of **11** showed two endothermic peaks at 207 and 356 °C which corresponded to the melting points of OPS and poly(*m*-phenyleneisophthalamide), respectively. This result indicates that microphase separation occurs in the graft copolymer.

Synthesis and Characterization of Nylon-11-*graft*-OPS Copolymer. The synthesis of Nylon-*graft*-OPS copolymer was achieved by an amide exchange reaction at high temperature using dicarboxy-OPS (**9**) (Scheme 7). Nylon-11 was used since it is soluble in DMF and could be separated from the crude copolymer easily by washing with hot DMF.

Scheme 6



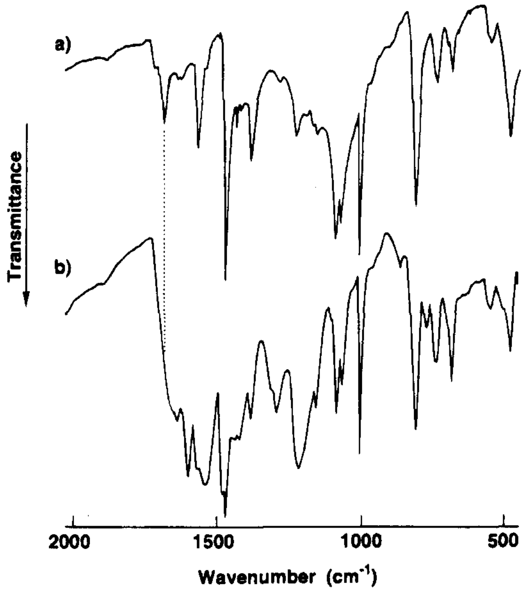


Figure 3. IR spectra of dicarboxy-OPS (**9**) (a) and polyamide-*graft*-OPS copolymer (**11**) (b).

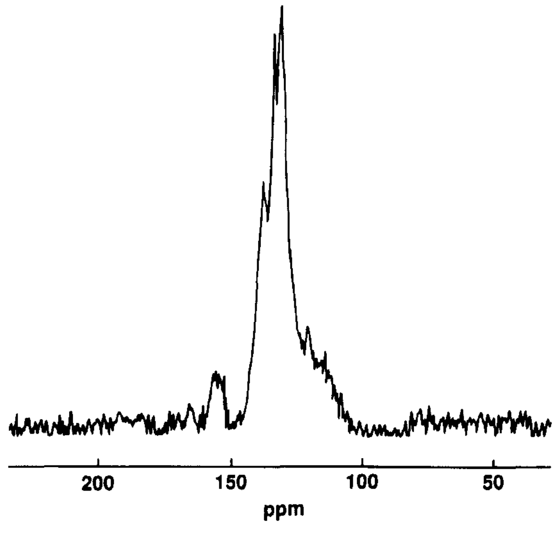
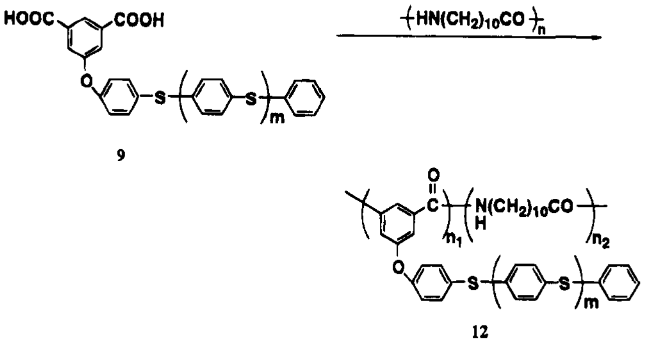


Figure 4. ^{13}C CP/MAS spectrum of polyamide-*graft*-OPS copolymer (**11**).

Taking account of the polymerization degree of the dicarboxy-OPS (**9**), it was mixed with 10-fold mole units of Nylon-11 in α-chloronaphthalene and heated. The copolymer obtained after extraction of unreacted Nylon-11 (**12**) (yield: 38 wt %) exhibited no absorption near 1695 cm^{-1} which suggested that all the COOH groups were consumed to form amide bonds. The C=O stretching absorption of the formed amide bonds overlapped that of Nylon-11. The IR spectrum confirmed that the product contained both OPS and Nylon chains.

Scheme 7



The copolymer **12** was soluble in DMSO above 80 °C. In the ^{1}H-NMR spectrum of **12** in hot $(CD_3)_2SO$ (Figure 2d), the broad peak near 7.4 ppm is attributed to the ring protons of the *graft*-OPS chain. The broad peaks near 0.8–2.2 ppm are ascribed to the Nylon protons. Introduction of the OPS into the Nylon chain was confirmed by the disappearance of the ^{1}H-NMR signals at 7.70 and 8.24 ppm that were observed in the spectrum of the dicarboxy-OPS (**9**). These signals shift to higher field and overlap with those of the phenylene chain. The high-field shift of the signal due to the amide formation of **9** was also confirmed by the model compound **10** (Figure 2c).[22] From the integration of the signals of the peaks near 7.4 and 0.8–2.2 ppm ($H_a/H_b = 3$), it is estimated that, for **12**, OPS is introduced for every 6 monomer units of Nylon-11 on average (n_2/n_1 = *ca.* 6 in Scheme 7). When larger amounts of the dicarboxy-OPS (**9**) were reacted with Nylon-11, the ratio of *graft*-OPS versus the mole of Nylon-11 increased. However, increasing the amount of OPS in the graft chain reduced the solubility of the obtained copolymer.

The copolymer **12** was characterized by DSC. Nylon-11 and the dicarboxy-OPS (**9**) homopolymer exhibited melting points near 192 and 240 °C, respectively. The graft copolymer exhibited two endothermic peaks near 190 and 240 °c, which indicate a microphase separation and the presence of the crystal phase of an OPS chain in the copolymer.

IV. Conclusions

Oxidative polymerization of diphenyl disulfide provides oligo(*p*-phenylene sulfide) with a number-average molecular weight of *ca.* 1000. Phenylbis(phenylthio)-sulfonium cation, produced by the oxidation of the disulfide in acidic media, is the active species in the polymerization. Oxidation of bis(4-halophenyl) disulfides in acidic medium produces (4-halophenyl)bis[(4-halophenyl)thio]sulfonium cation which reacts with phenylene sulfide chains to produce α,ω-disubstituted oligo(*p*-phenylene sulfide)s. Oxidation of both species together enabled a convenient one-pot synthesis of the halogenated OPS.

Since OPS produced by the oxidative polymerization of disulfide contains one disulfide bond at the end of the chain, thermolysis of the disulfide bond in the presence of an iodo compound is also an effective way to modify OPS. Introduction of the carboxyl group was achieved by the thermolysis of the OPS with the aromatic iodides 4′-iodo-4-biphenylcarboxylic acid and 5-(4-iodophenoxy)isophthalic acid. The obtained carboxy-OPS reacted with *m*-phenylene diisocyanate to produce a graft copolymer of polyaromatic amide and

OPS. The amide exchange reaction offered another synthetic route to a graft copolymer of polyamide and OPS. Nylon-11–OPS copolymer was synthesized by heating Nylon-11 and the dicarboxy-OPS.

The DSC curves of these polyamides exhibited two endothermic peaks which were attributed to the melting points of the OPS and polyamide, respectively. The DSC results suggest that microphase separation of the obtained graft copolymer occurs due to the high crystallinity of the graft OPS chain.

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