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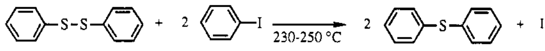
Synthesis of Poly(*p*-phenylene sulfide) by Thermolysis of Bis(4-halophenyl) Disulfides

Poly(*p*-phenylene sulfide) (PPS) is an important high-temperature engineering thermoplastic with good mechanical strength, thermal stability, excellent chemical resistance, flame resistance, and good electrical characteristics.[1] PPS was first commercialized on the basis of the method of Edmonds and Hill,[2] involving polycondensation of *p*-dichlorobenzene with sodium sulfide in *N*-methylpyrrolidone at 240–260 °C under high pressure, and a large number of modifications of this process have appeared subsequently, principally in the Patent literature.[3] PPS has also been synthesized by Lenz[4] by the self-condensation of *p*-halobenzenethiolates in pyridine or/and quinoline at high temperatures. Recently copoly(phenylene sulfide–disulfide) containing only very small amounts of disulfide linkages has been reported by the direct reaction of sulfur with *p*-diiodobenzene.[5] Other synthetic routes that have investigated include (1) the electrophilic substitution of benzene with elemental sulfur in the presence of aluminum chloride,[6] (2) the $S_{RN}1$-type polymerization of *p*-bromobenzenethiolate initiated by a diazonium salt in DMSO at room temperature,[7] and (3) the oxidative polymerization of diphenyl disulfide with antimony pentachloride or quinones or vanadyl acetylacetonate under air atmosphere at room temperature.[8] However, polymers prepared by these methods either contain variable amounts of cyclic and cross-linked species,[6] are obtained in very low yields (3.9–28%),[7] or are low in molecular weight (ca. 10^3) and have low melting points (113–191 °C).[8]

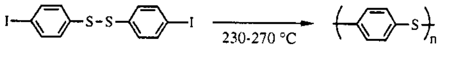
Recently, we have found that heating diphenyl disulfide with iodobenzene at 230–250 °C resulted in a nearly quantitative conversion of iodobenzene and the formation of diphenyl sulfide and iodine (eq 1).[9] The corresponding phenyl aryl sulfides and bis(phenylthio)arenes were also obtained in good yields from reaction of diphenyl disulfide with iodo- and diiodoarenes. It should be pointed out that in this reaction we have been able to detect only the unsymmetrically substituted sulfides as products. If extrusion of sulfur from the disulfide were to occur initially, as has been described in the literature for the thermolysis of diphenyl disulfide,[10] then the reaction described by Rule[11] between sulfur and an iodoarene would occur and a mixture of three sulfides would be formed. Since this reaction proceeds cleanly in high yield, we thought that it could be used for polymer formation (eq 2).



(1)

$$\text{I—Ar–S—S–Ar–I} \xrightarrow{\Delta} \left(\text{Ar–S}\right)_n + I_2 \qquad (2)$$

We report here the synthesis of linear, high molecular weight poly(*p*-phenylene sulfide) from bis(4-iodophenyl) disulfide in high yield (eq 3). Bis(4-iodophenyl) disulfide (mp 120–122 °C; lit.[12] mp 124.5–125.5 °C) was prepared by the reaction of potassium iodide with the diazonium salt generated from 4-aminophenyl disulfide with sodium nitrite. Polymerizations were carried out in diphenyl ether at temperatures of 220–270 °C, and polymers were obtained in high yields as off-white or pale yellow solids with melting points ranging from 270 to 282 °C. A typical polymerization procedure is as follows: Bis(4-iodophenyl) disulfide (940 mg, 2.0 mmol) and diphenyl ether (1.8 g) were placed in a Pyrex test tube (1.5 × 15 cm). The tube was immersed in a heated sand bath to a depth of about 2 cm to cover the contents inside. The reaction temperature was controlled at 250–260 °C and held at that temperature for 18 h while a stream of nitrogen was bubbled into the solution through a pipette. The reaction mixture was diluted with 1-chloronaphthalene (4 mL), and the solution was allowed to cool to ambient temperature. The resulting solids were triturated with methanol and poured into methanol (200 mL), and the polymer was collected by filtration and dried in air. The solids were then dissolved in 1-chloronaphthalene, and the solution was cooled to room temperature. The polymer was filtered with suction and stirred in hot methanol, hot chloroform, and then methanol, respectively. After drying in air and then in a vacuum oven at 120 °C overnight, PPS was obtained as a pale yellow powder (398 mg, 92%). The analytical data are presented in Table I (sample 3).



(3)

Polymerization takes place readily at about 230 °C, as evidenced by the formation of iodine, and the completion of the polymerization is indicated by the cessation of iodine evolution. The degree of polymerization is very temperature dependent. At 220–230 °C it took nearly 2 days to complete the polymerization, and PPS with a low molecular weight (DP ~ 50, sample 1) was obtained, which contains a high percentage of iodine. As the reaction temperature rises, the required reaction time shortens dramatically and the degree of polymerization increases significantly. Polymerization at 260–270 °C took place in 8 h to yield polymer that had a number-average molecular weight of approximately 20 000 (DP ~ 180, sample 4) and that could be fabricated into a flexible film by compression molding. The polymers synthesized were examined by differential scanning calorimetry (Table II). In the first scan T_g's are not observed for the commercial sample as well as for our samples. After quenching the samples, in a second scan, the glass transition temperatures are now observed. The T_g's of these polymers range from 85.8 to 91.7 °C and the melting points from 270 to 282 °C corresponding to DP's of 50–183 estimated from the end-group analysis. In comparison a commercial PPS[13] has a T_g of 88.5 °C and a T_m of 282 °C and a number-average molecular weight of 10 000, which corresponds to a DP of 92. The thermal data then corroborate the molecular weight estimates made from the analysis of the iodo end groups. The FTIR spectrum of PPS agrees with that of the commercial PPS (Figure 1). The absorption attributed to 1,4-substituted phenylene at 814 cm^{-1} confirms a linear, 1,4-phenylene sulfide structure.

The structure of PPS was further characterized by solid-state ^{13}C NMR spectroscopy. The NMR spectrum shows two peaks at 131.6 and 133.6 ppm, which match those from the commercial sample (Figure 2). No other peaks of significance can be seen in the spectrum. By a dipole dephasing experiment the signal at 133.6 ppm is clearly assigned to the nonprotonated carbons or the carbons adjacent to the sulfurs in PPS.

Heitz[14] has proposed a single-electron-transfer mechanism for the reaction of sodium sulfide with *p*-dichlorobenzene to produce PPS in which the propagation step in the polymerization reaction involves the attack of sulfenyl radicals on the chloro aromatic to give a reactive intermediate that then loses chloride ion (eq 4). Further reaction with HS^- then regenerates the next higher oligomeric sulfenyl radical. In the present case, as in the reaction of elemental sulfur with 1,4-diiodobenzene,

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Table I
Analysis of PPS

sample	reaction temp, °C	time, h	yield, %	expl. formula	elem anal., % C	H	S	I	DP[a]
1	220–230	48	96	$C_{6.0}H_{4.1}S_{1.0}$	63.90	3.61	28.40	4.3	50
2	240–250	30	94	$C_{6.5}H_{4.7}S_{1.0}$	66.03	3.96	27.10	2.6	86
3	250–260	18	92	$C_{6.6}H_{4.5}S_{1.0}$	64.63	3.72	26.30	2.3	100
4	260–270	8	95	$C_{6.3}H_{4.3}S_{1.0}$	65.92	3.70	27.80	1.3	183

[a] The degree of polymerization (DP) is calculated from the elemental analyses, assuming that both ends of PPS are iodo groups. Analyses were performed by Guelph Chemical Laboratories. Iodine results are ±0.2; therefore, the DP ranges are as follows: 1, 48–53; 2, 80–94; 3, 91–110; 4, 157–218.

Table II
Thermal Analysis of PPS[a]

sample	T_m, °C	T_c, °C	T_g, °C	DP
1	270	123	85.8	50
2	270	130.8	90.6	86
3	280	128.5	88.5	100
4	282	133.5	91.7	183
5[b]	282	125.2	88.5	92

[a] DSC analyses were performed on a Seiko 220 instrument at 10 °C/min. The results are for the second scan after quenching of the sample. In the first scan no T_g or T_c is observed. [b] Sample obtained from Aldrich Chemical Co.: M_n = 10 000; calcd DP = 92.

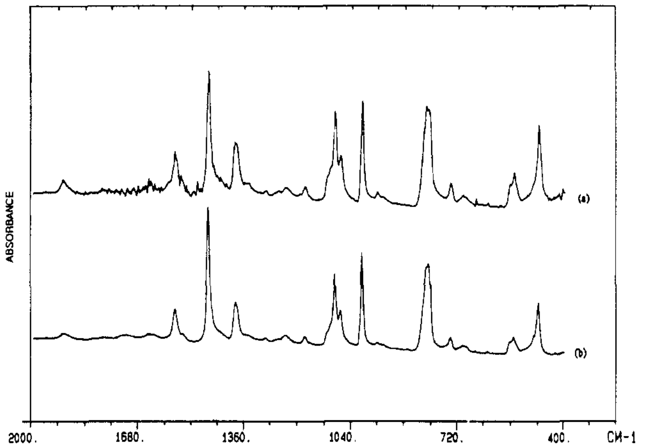
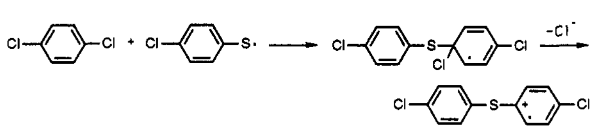


Figure 1. FTIR spectra (KBr): (a) commercial PPS; (b) PPS sample 3.



(4)

elemental iodine is released. We have found that PPS is also formed from the thermolysis of bis(4-bromophenyl) disulfide and bis(4-chlorophenyl) disulfide if an equivalent amount of iodide ion is present, in which case elemental iodine is also evolved. Polymers with T_m's of 275 and 175 °C, respectively, are isolated. If instead of iodide ion a reactive substrate such as diphenyl ether is present, polymers are also formed and the diphenyl ether is brominated during the reaction. In the latter case some diphenyl ether moieties are also incorporated into the polymer, presumably by the reaction of the sulfenyl radical intermediates with bromodiphenyl ether. We have not been able to detect T_g's in quenched samples. Bromine analysis corresponds to a DP of about 60. The infrared spectrum now contains a strong C–O stretching absorption at 1236.1 cm^{-1}, and the solid-state ^{13}C NMR spectrum shows an additional minor peak at 157.99 ppm. Bis(4-fluorophenyl) disulfide is recovered unchanged when heated to 260 °C and then cooled. We therefore can infer that Br$^-$ is not released in this reaction and that instead bromine or a bromine radical is generated in the reaction.

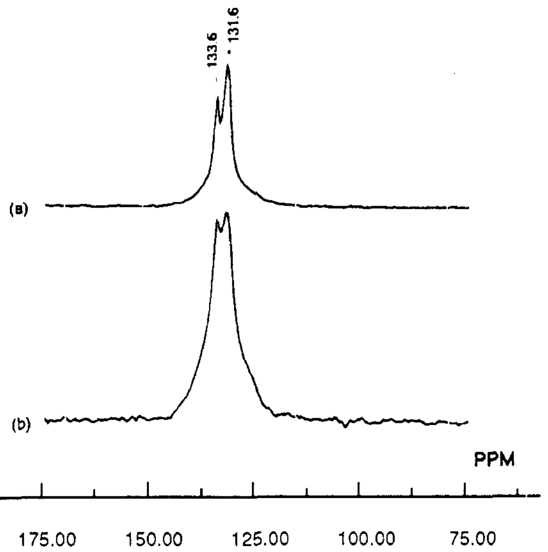
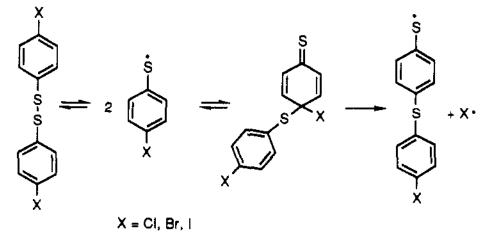


Figure 2. Solid-state ^{13}C NMR spectra: (a) commercial PPS; (b) PPS sample 3.

Heitz[15] has also proposed a single-electron-transfer mechanism for the polymerization of 4-bromo-2,6-dimethylphenol.[16] In this case also the elimination of bromide ion is a key step in the reaction, which is performed under basic conditions. The quinone–ketal rearrangement and dissociation mechanisms proposed for the polymerization of 2,6-dimethylphenol, however, involve radical intermediates and can take place under neutral conditions. This reaction has also been demonstrated on unsubstituted phenoxyphenols.[18] The polymerization of bis(4-iodophenyl) disulfide would be expected to proceed initially by thermal homolysis of the disulfide bond to the corresponding thiophenoxy radical. By analogy with the quinone–ketal mechanisms the thiophenoxy radical could then dimerize to give a dithioquinone ketal, which could subsequently rearrange to a dimeric thiophenoxy radical with the release of iodine radical (eq 5) which could then give iodine. In the case of bis(4-bromophenyl) disulfide, the bromine radical could be reduced by iodide to also give iodine or brominate the diphenyl ether. The removal of unreactive iodine is the driving force for the polymerization as in the case for the direct reaction of sulfur with iodoarenes.



(5)

We have also synthesized poly(naphthylene sulfide)s, the 1,4-, 1,5-, and 1,6-isomers, from the corresponding bis(iodonaphthyl) disulfides by this method. In conclusion, a new, general route for the synthesis of poly(arylene sulfide)s from bis(4-halophenyl) disulfides has been developed. Poly(phenylene sulfide) of high molecular weight (ca. 20 000) was obtained by the thermolysis of bis(4-iodophenyl) disulfide.

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Zhi Yuan Wang and Allan S. Hay*

Department of Chemistry, McGill University
801 Sherbrooke St. W., Montreal, Quebec, Canada H3A 2K6

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