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Polymerization of 4-Bromobenzenethiol to Poly(1,4-phenylene sulfide) with a Free Radical Initiator

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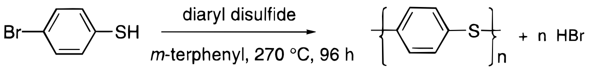
Poly(1,4-phenylene sulfide) (PPS) is commercially manufactured by a condensation reaction between 1,4-dichlorobenzene and sodium sulfide in a polar solvent, such as *N*-methylpyrrolidinone at 200−280 °C under high pressure.[1,2] Numerous other syntheses have been reported. Preparations of PPS prior to 1988 have been covered in a review,[2] and we have briefly reviewed recent advances in the synthesis of PPS.[3] Among all of these methods, to the best of our knowledge, there are only two reports for preparation of PPS in the presence of an initiator or a catalyst. The first one, reported in 1986,[4] was polymerization of 4-bromobenzenethiolate achieved in DMSO by the use of catalytic amounts of a diazonium salt *via* a radical-anion chain pathway. However, only oligomeric PPS was obtained with repeating units around 9 based on the elemental analyses. Another catalytic process was reported by Tsuchida *et al.*in 1994.[5] High molecular weight PPS was obtained via a soluble precursor by catalytic oxidative polymerization of methyl phenyl sulfide in the presence of ceric ammonium nitrate (CAN) catalyst and in the presence of a strong acid. The use of large amounts of strong acid and the necessity for maintaining anhydrous conditions are major drawbacks of this process.

One of the earliest methods for preparation of PPS was by the polymerization of a salt of 4-bromobenzenethiol.[6,7] The attempted polymerization of bis(4-bromophenyl) disulfide itself gave either no polymerization or low molecular weight products.[8,9] When a stoichiometric amount of copper, or an excess amount of potassium iodide, was present in the reaction mixture, high molecular weight PPS polymers were obtained.[8−10] We have previously reported that bis(4-iodophenyl) disulfide on heating to 270 °C yields linear high molecular weight PPS along with elemental iodine.[9] When bis(4-bromophenyl) disulfide is heated, bromination of the solvent or oligomers occurs. However, high molecular weight polymers are formed if iodide ion is added to reduce the bromine radicals. On the basis of these results we hypothesized that 4-bromobenzenethiol could be directly polymerized in a free radical chain reaction by the addition of an initiator, such as a disulfide, since the bromine radicals formed could be efficiently reduced by the 4-bromobenzenethiol. Herein, we report our preliminary results for the polymerization of 4-bromobenzenethiol in the presence of a radical initiator, which leads to high molecular weight PPS with the evolution of HBr.

In the presence of a small amount of a diaryl disulfide initiator at 270 °C, the polymerization of 4-bromobenzenethiol was achieved (eq 1). Since the boiling point of 4-bromobenzenethiol is only 230 °C, a high-boiling point solvent, *m*-terphenyl (bp 365 °C), which is unreactive to the thiyl radical, was used to hold the substrate in solution. We have used several diaryl disulfides to initiate the polymerization reaction, e.g. bis(4-bromophenyl) disulfide, cyclic disulfide oligomer **1**,[11] and 2,2′-dithiobis(benzothiazole). Elemental sulfur itself can also serve as a initiator. The thermal properties of PPS polymers obtained in the presence of 1 mol % of these different catalysts are listed in Table 1. With 1 mol % of disulfide or elemental sulfur, linear high molecular weight PPS polymers were obtained after 96 h at 270 °C. The high glass transition temperatures (T_g) indicate that the polymers are high molecular weight. In all cases, flexible PPS films were obtained by the following simple technique. PPS powder (200 mg) was put on a piece of aluminum foil, and the foil was folded into a square around 1 × 2.5 cm. The square was put on the surface of a hot plate preheated to 330 °C for 5 min, pressed with a piece of glass, and then queched immediately by dipping into cold water. After the aluminum foil was removed, a flexible PPS film was obtained.



(1)

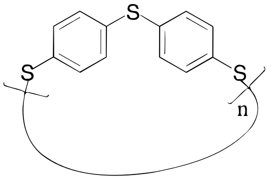


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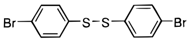
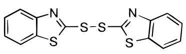
Table 1. Thermal Properties of PPS Polymers Obtained by Polymerization of 4-Bromobenzenethiol[a]

Catalyst	Yield (%)	T_g (°C)	T_c (°C)	T_m (°C)
	95	92	145	285
1	95	87	133	284
	89	89	142	278
S_8	89	87	137	280

[a] Thermal properties were obtained using a Seiko 220 DSC instrument at a heating rate of 20 °C in a nitrogen atmosphere. The samples were quenched from 350 °C on a cold metal block. The amounts of catalysts used were 1 mol %.

The high molecular weight properties of PPS obtained by the present process have been confirmed by high-temperature GPC analysis.[12] The GPC chart of PPS obtained from 4-bromobenzenethiol initiated by bis(4-bromophenyl) disulfide is shown in Figure 2. The PPS has a weight average molecular weight (M_w) of 19 600 and a number average molecular weight (M_n) of 6900 compared to polystyrene standards. In comparison, a commercial PPS polymer sample obtained from Aldrich Chemical Inc. has a M_w of 17 100 and a M_n of 5600. From the GPC there is no indication of branching or cross-linking.

The FT-IR (KBr) spectra of PPS polymers obtained in the presence of bis(4-bromophenyl) disulfide and **1** are shown in Figure 1. The IR spectra are identical to those of PPS polymers obtained by other methods.[13,14] The strong peak at 813 cm^{-1} is attributed to 1,4-substituted phenylene, which confirms that they have a linear, 1,4-phenylene sulfide structure.

The proposed mechanism for the polymerization is shown in Scheme 1 using bis(4-bromophenyl) disulfide

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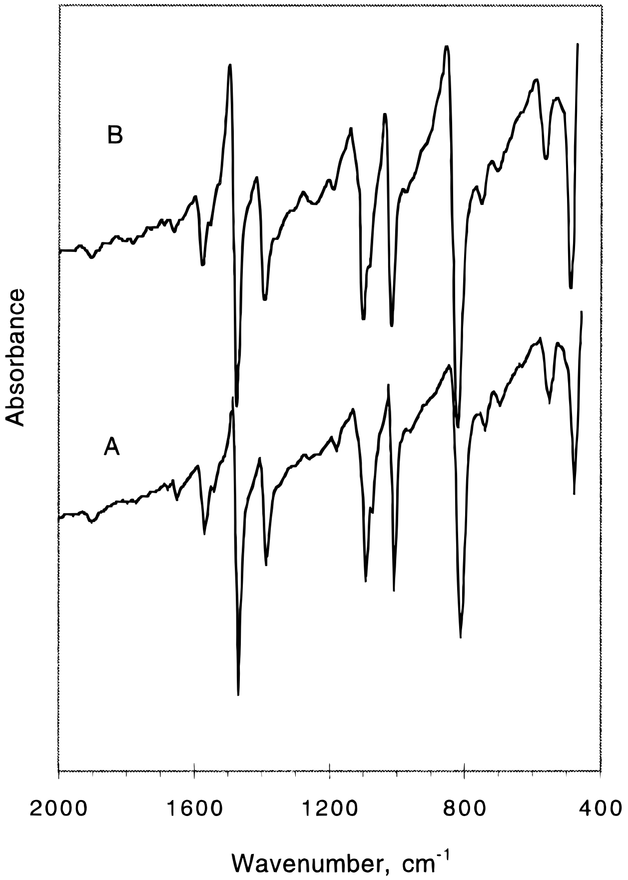


Figure 1. FT-IR spectra of PPS polymers obtained by polymerization of 4-bromobenzenethiol: (A) initiated by cyclic disulfide oligomers, 1 mol %; (B) initiated by bis(4-bromophenyl) disulfide, 1 mol %.

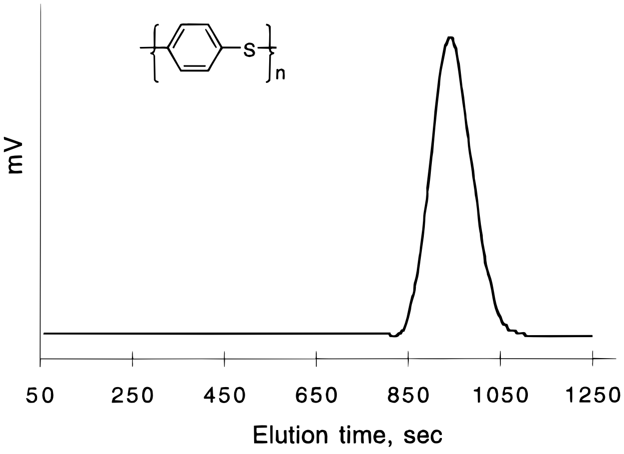
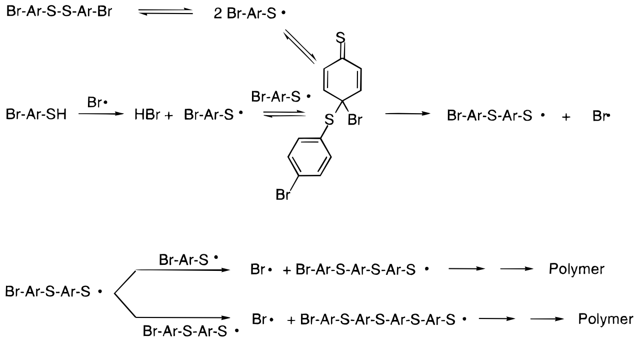


Figure 2. High-temperature GPC of PPS obtained by polymerization of 4-bromobenzenethiol in the presence of bis(4-bromophenyl) disulfide.

as initiator. The bromine radicals here play a key role which carry on the chain reaction by reacting with the thiol group to generate HBr and the thiophenoxy radical. The oligomeric radicals formed can then react further to give PPS. If a different disulfide is used as initiator, the organic moiety would be expected to be present as a chain end.

Scheme 1. Proposed Mechanism for the Polymerization of 4-Bromobenzenethiol



The polymerization reaction (eq 1) was conducted in a Pyrex test tube (1.5 × 15 cm). 4-Bromobenzenethiol was purchased from Lancaster Synthesis Inc. and recrystallized from chloroform under a nitrogen atmosphere. A typical experimental procedure is as follows. 4-Bromobenzenethiol (1.0 g, 5.29 mmol), bis(4-bromophenyl) disulfide (0.0199 g, 0.0529 mmol), and *m*-terphenyl (1.0 g) were mixed and charged into a test tube, which was placed in a salt bath preheated to 270 °C so that the contents were immersed to a depth of around 2 cm. The test tube was capped with a septum, and a slow flow of nitrogen was passed through. After the reaction was conducted for 96 h, 3 mL of 1-chloronaphthalene was added to dilute the reaction mixture. The contents were poured into 200 mL of methanol to precipitate the polymer. The methanol solution was heated to boiling under stirring and filtered. The solid was washed again, consecutively, with 30 mL of hot chloroform and 30 mL of hot methanol and dried at 100 °C under vacuum for 24 h. A white powder product (0.54 g) was obtained.

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References and Notes

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