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Novel Synthesis of Poly(*p*-phenylene sulfide) from Cyclic Disulfide Oligomers

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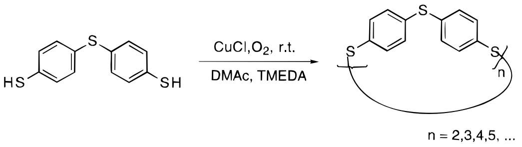
Poly(*p*-phenylene sulfide) (PPS) is manufactured commercially by the polycondensation of *p*-dichlorobenzene with sodium sulfide in *N*-methylpyrrolidinone at 200−280 °C under high pressure.[1,2] Recently, there have been new efforts directed toward alternative syntheses of PPS.[3−7] In one example, high molecular weight PPS was prepared by heating bis(4-iodophenyl) disulfide in phenyl ether at 270 °C.[7] This method can also give rise to highly crystalline PPS (T_m = 313 °C).[8] Herein, we report the novel synthesis of PPS starting from a cyclic aromatic disulfide oligomer and a dihalo-substituted aromatic compound.

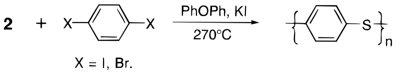
Although several cyclic aromatic disulfides have been prepared,[9] little attention has been given to their applications. Most of the reported cyclic aromatic disulfides were synthesized from dithiols by using iodine as oxidizing agent,[9d,f] although DMSO was also used as an oxidizing agent to prepare a cyclic tetramer from *p*-tetrafluorobenzenedithiol.[9c] In 1966, Hay reported that dithiol compounds can be oxidized to form polydisulfides with oxygen using copper−amine catalysts.[10] In this paper, we have succeeded in preparing the cyclic aromatic disulfide oligomer **2** starting from 4,4′-thiobis(benzenethiol)[11] under high dilution conditions using this method (eq 1). DMAc was found to be the best solvent for the synthesis of the cyclic oligomers, since both reactant and resulting products remain soluble. Cuprous chloride and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were used as copper salt and amine ligand, respectively. The reactants were added to the reaction mixture via a dropping funnel over a 4 h period. The final concentration of the reactants in the mixture was 0.05 M. The resulting reaction mixture was filtered through a layer of alumina, and the filtrate was then poured into 500 mL of water to precipitate the products. The copper catalyst remaining in the mixture was easily removed by stirring in 5% HCl solution three times. Linear gradient HPLC clearly showed the distribution of cyclic oligomers with repeating units starting from 2 to 9 (Figure 1).[12] ^{1}H NMR ($CDCl_3$) showed there is no detectable thiol (SH) signal in the range of δ 3−4 ppm. GPC analysis of the products shows the cyclic oligomers have a number-average molecular weight M_n of 380 and weight-average molecular weight M_w of 570 (using polystyrene standards).[13]



(1)

1 **2**

The thermal polymerization reactions of cyclic disulfide **2** with the *p*-dihalobenzene (eq 2A) were carried out in a Pyrex test tube (1.5 × 15 cm) in which **2** (0.2478 g, 1 mmol), *p*-diiodobenzene, and phenyl ether (0.5 mL) were charged. The test tube was immersed in a salt bath preheated to 270 °C to a depth of about 2 cm to cover the contents inside for 10 h under an atmosphere of nitrogen. The polymer was worked up according to the procedure previously described[7a] to give 95% of a white to pale yellow product. PPS was also prepared by reacting **2** with *p*-dibromobenzene in the presence of potassium iodide (KI/**2** = 5.0/1.0). A poly(ether thioether) **3** was obtained in 96% yield by reacting **2** with bis(4-bromophenyl) ether (molar ratio 1.0:1.0) in the presence of potassium iodide (KI/**2** = 5.0/1.0) at 270 °C for 24 h (eq 2B).



(2A)

X = I, Br.

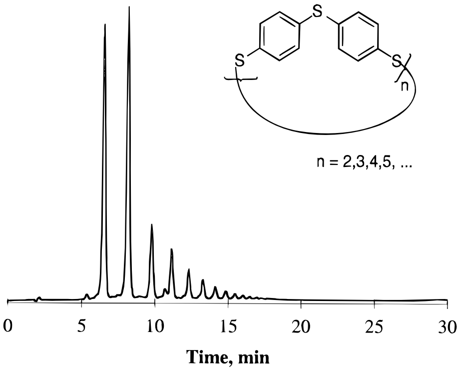
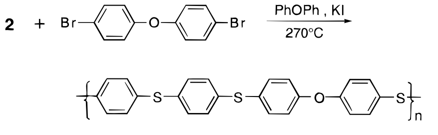


Figure 1. Gradient HPLC of cyclic aromatic disulfide oligomers **2**.[12]

Table 1. Effect of Molar Ratio of Reactants on Thermal Properties of PPS

no.	diiodobenzene/**2**	T_g (°C)	T_c (°C)	T_m (°C)
1	1.00	85	123	284
2	1.01	85	125	286
3	1.02	88	127	287
4	1.04	88	132	286
5	1.06	82	125	286



(2B)

3

The polymers formed were examined by differential scanning calorimetry.[14] As expected, a glass transition temperature T_g was not observed for any of the polymers during the first scan. After quenching the sample, a T_g, a crystallization temperature T_c, and a melting point T_m were observed. We found that an excess amount of diiodobenzene was required to obtain PPS with the highest glass transition temperatures (Table 1). Although the glass transition temperature should be a monotonic function of molecular weight, we had difficulty in choosing the better condition between entry 3 and entry 4 in Table 1 since they gave almost the same glass transition temperatures. Fagerburg *et al.* have correlated the thermal properties with the molecular weight of PPS.[15] They found that the higher the T_c detected by DSC, the higher the molecular weight. The molar ratio of the cyclic disulfide oligomer **2** to *p*-diiodobenzene has significant influence on the T_c of the product (Table 1). *p*-Diiodobenzene has to be used in ~4% excess to obtain PPS with the highest T_c, which we assume represents the highest molecular weight. This is due to the decomposition of the diiodo compound

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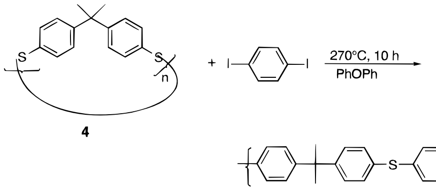
at high temperature. The need for additional diiodo compound has been rationalized by other researchers in other polymerization reactions.[16] However, when *p*-dibromobenzene was used, the molar ratio of 1:1 of the reactants was found to be ideal. The PPS obtained after 24 h under these conditions has a T_c of 150 °C, a T_g of 92 °C, and a T_m of 275 °C. Copolymer **3** is also crystalline with a T_g of 84 °C, a T_c of 139 °C, and a T_m of 238 °C.

The FT-IR spectra (KBr) of PPS synthesized from *p*-diiodobenzene and *p*-dibromobenzene as well as of **3** were measured on an Analect instrument. The strong absorptions at 814 cm^{-1} attributed to 1,4-substituted phenylene confirmed that they have linear, 1,4-phenylene sulfide structures. Polymer **3** shows a strong absorption peak at 1234 cm^{-1} ($-$C$-$O$-$C$-$) compared to PPS. The structures of all PPS polymers obtained were also characterized by solid-state ^{13}C NMR. The NMR spectra show two peaks at 134.6 and 132.2 ppm, which are in accordance with reported results.[7a]

To further substantiate that we can get high molecular weight PPS by the present method, the novel cyclic aromatic disulfide oligomer **4** was also synthesized by catalytic oxidation of the respective dithiol compounds. Cyclic oligomer **4** produces a novel soluble poly(aryl sulfide) **5** by reacting with *p*-diiodobenzene (diiodobenzene/**4** = 1.04/1.00) under the same conditions illustrated above for preparing PPS (eq 2C). GPC shows this polymer has a number-average molecular weight M_n of 15 000 and a weight-averge molecular weight of 42 000 (n = 125) using a polystyrene calibration. However, when dibromo compounds were used, highly cross-linked and insoluble products were obtained even in the presence of potassium iodide. This is due to the fact that the bromo radical is much more reactive than the iodo radical, and presumably some of the bromo radicals react with methyl groups first instead of reacting with potassium iodide. Therefore, dibromo compounds are not suitable for the preparation of polysulfides by reacting with **4**.



4

5

(2C)

In conclusion, a cyclic aromatic disulfide oligomer has been prepared from 4,4′-thiobis(benzenethiol) by catalytic oxidation. The cyclic disulfide oligomer undergoes polymerization with dihalobenzenes to give PPS. By reacting with oxybis(4-bromobenene), a copolymer with a T_m of 238 °C was also obtained. This method can be extended to the synthesis of other polysulfides. This work is ongoing in our laboratory.

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(11) 4,4′-Thiobis(benzenedithiol) was purchased from Aldrich.

(12) Linear gradient HPLC was performed on a Milton Roy CM4000 multiple solvent delivery system with a C8 Prime Sphere 4.6 × 250 mm column, THF and water as eluent solvents, and a UV detector at 300 nm. The total running time for each injection was 30 min. The gradient condition was as follows: at 0 min, THF 70%; at 20 min, THF 90%; at 25 min, THF 100%; at 27 min, THF 70%; at 30 min (end), THF 70%.

(13) GPC analyses was performed on a Waters 510 HPLC equipped with 5 μm Phenogel columns (linear, 3 × 500 Å) arranged in series and a UV detector at 254 nm. Chloroform was used as eluent.

(14) DSC scans were obtained using a Seiko 220 DSC instrument at a heating rate of 20 °C/min in N_2 (160 mL/min).

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