

## One-pot Synthesis of Poly(thioarylene)s: Predominant Sulphide Bond Formation through Oxidative and Electrophilic Reaction

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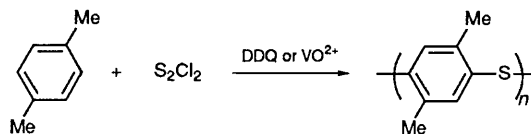
Poly(thioarylene)s are conveniently prepared in high yield at room temperature and atmospheric pressure through oxidative and electrophilic reaction of disulphur dichloride ( $S_2Cl_2$ ) and aromatic compounds.

Sulphide chains are generally constructed through a nucleophilic reaction of a metal sulphide with an aromatic halide at high temperature. Poly(thioarylene)s are commercially produced by this polycondensation reaction in a high temperature and pressure process.<sup>1,2</sup> Freidel-Crafts reaction of sulphur and aromatic compounds has been used in attempts to prepare poly(thioarylene)s conveniently, but the electrophilic reaction proceeds accompanied by many side reactions, and the polymer formed contains thianthrene bonds.<sup>3,4</sup>

The present work shows that preferential sulphide bond formation occurs and linear poly(thioarylene)s may be prepared in the reaction of xylene with disulphur dichloride ( $S_2Cl_2$ ) 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.

To  $S_2Cl_2$  (0.2 mol  $dm^{-3}$ ) and *p*-xylene (0.5 mol  $dm^{-3}$ ) in tetrachloroethane (20  $cm^3$ ) were added DDQ (0.2 mol  $dm^{-3}$ ) and trifluoroacetic acid (1.0 mol  $dm^{-3}$ ). After reaction for 20 h at 20 °C, the mixture was poured into HCl-methanol. The precipitate was washed with carbon disulphide to remove elemental sulphur. The polymer was isolated in >95% yield (based on sulphur)<sup>†</sup> and was identified as poly(thio-2,5-dimethyl-1,4-phenylene). The polymer formed does not contain disulphide bonds as the main structural component on the basis of its high thermal stability and elemental analytical

data.<sup>‡</sup> Spectroscopic data are consistent with those of linear poly(thio-2,5-dimethyl-1,4-phenylene) prepared by the Phillips method from dichloro-*p*-xylene. The oxidative polymerization also proceeded in the presence of catalytic amounts of 2,4-pentane-dionato(oxo)vanadium (10 mmol  $dm^{-3}$ ) and trifluoroacetic anhydride (0.2 mol  $dm^{-3}$ ) as an alternative to oxidation with DDQ at room temperature.



<sup>‡</sup> Poly(thio-2,5-dimethyl-1,4-phenylene): Found: C, 69.8; H, 5.95; S, 23.4. Calc. for  $C_8H_8S$  C, 70.5; H, 5.9; S, 23.5%; IR (KBr,  $\nu/cm^{-1}$ ) 2920 ( $\nu_{C-H}$ ); 1590, 1455, 1475 ( $\nu_{C=C}$ ); 890 ( $\delta_{C-H}$ ); CP-MAS NMR  $\delta$  20 (methyl C);  $\delta$  124, 132, 141 (phenyl C);  $m/z$  408 and 544. This suggests monomer units of  $M_r$  136.  $T_{d10\%}$  (temperature for 10% weight loss of polymer) 400 °C. The weight averaged molecular weight of the *N*-methylpyrrolidone-soluble part is ca. 1000.

Poly(thio-2,3,5,6-tetramethyl-1,4-phenylene): Found: C, 73.1; H, 7.35; S, 19.5. Calc. for  $C_{10}H_{12}S$  C, 73.1; H, 7.4; S, 19.5%; IR (KBr,  $\nu/cm^{-1}$ ) 2920 ( $\nu_{C-H}$ ); 1470 ( $\nu_{C=C}$ );  $m/z$  330, 494 and 656.

Poly(thio-1,4-phenyleneoxy): Found: C, 71.8; H, 3.8; S, 15.5. Calc. for  $C_{12}H_8OS$  C, 72.0; H, 3.70; S, 16.0%; IR (KBr,  $\nu/cm^{-1}$ ) 3050 ( $\nu_{C-H}$ ); 1580, 1480 ( $\nu_{C=C}$ ); 1240 ( $\nu_{C-O-C}$ ); 830 ( $\delta_{C-H}$ ).

Poly(thio-1,4-phenylene): Found: C, 66.6; H, 3.7; S, 29.6. Calc. for  $C_6H_4S$  C, 66.7; H, 3.7; S, 29.65%; IR (KBr,  $\nu/cm^{-1}$ ) 3100 ( $\nu_{C-H}$ ); 1580, 1480, 1400 ( $\nu_{C=C}$ ); 820 ( $\delta_{C-H}$ ), m.p. 186 °C. The degree of polymerization is ca. 6–10 because PPS is precipitated during the polymerization owing to its insolubility.

<sup>†</sup> Yield = (product wt.)/{ $[S_2Cl_2] \times 2 \times$  (monomer unit of mol wt.)}  $\times$  100. 100% yield implies 100% consumption of  $S_2Cl_2$  in the polymerization.

Table 1

Aromatic compound	Polymer <sup>a</sup> yield (wt %)	M.p., <sup>b</sup> t/°C	$\nu_{\text{C-H}}$ / cm <sup>-1</sup>
Xylene	95	306	890
Durene	87	275	—
Ph <sub>2</sub> O	100	170	830
Ph <sub>2</sub> S	100	183	820

<sup>a</sup> Based on S. <sup>b</sup> Melting point of polymer. <sup>c</sup> C-H out-of-plane deformation.

The sulphur species used affects the polymerization, S<sub>2</sub>Cl<sub>2</sub> being most effective. Sulphur dichloride may also be used, but the use of other sulphur compounds such as thionyl chloride and sulphuryl chloride does not lead to reactions with aromatic compounds. Elemental sulphur shows low reactivity in the polymerization because of its lower solubility.

This polymerization only proceeds in an acidic environment. Strong basic solvents such as *N,N*-dimethylformamide and dimethyl sulphoxide suppress the polymerization. This result indicates that a cationic species is active in the polymerization. The polymerization is promoted by an equimolar amount of oxidizing agent. Control experiments show that the electrophilic reaction of S<sub>2</sub>Cl<sub>2</sub> with aromatic compounds gives aromatic sulphides in high yield in the presence of a Freidel-Crafts catalyst having oxidizing ability, e.g. AlCuCl<sub>4</sub>.

These results support the idea that the polymerization proceeds through an oxidation and an electrophilic reaction. The electrophilic substitution of S<sub>2</sub>Cl<sub>2</sub> on the aromatic ring to yield poly(thioarylene)s is promoted in the oxidative and acidic atmosphere, as in the cationic oxidative polymerization of benzene.<sup>5</sup> In this polymerization S-S bond formation is possible; however, once formed S-S bonds are cleaved to form sulphide bonds by oxidation through the previously reported mechanism.<sup>6</sup>

This polymerization not only leads to efficient formation of poly(thio-2,5-dimethyl-1,4-phenylene) at room temperature but is also applicable to other poly(thioarylene)s. For example, durene, dimethoxybenzene, diphenyl ether and diphenyl sulphide form the corresponding polymers<sup>‡</sup> in high yields. E.g. the reaction of diphenyl sulphide with S<sub>2</sub>Cl<sub>2</sub> yields poly(thio-1,4-phenylene) (PPS). The IR spectrum of the PPS thus formed agrees with that of the commercially available material. The absorption at 820 cm<sup>-1</sup> attributed to the C-H out-of-plane vibration of a 1,4-substituted benzene and the absence of absorptions at 850 and 880 cm<sup>-1</sup> ascribed to tri- and tetra-substituted benzene units indicate a 1,4-conjugated thiophenylene structure. The IR spectrum in the 1000–1150 cm<sup>-1</sup> region also shows that the PPS does not contain detectable sulphoxide or sulphone structures.

The reaction is particularly applicable to aromatic compounds with high frontier  $\pi$ -electron density, and provides an efficient and convenient synthesis of aromatic polymers, and enables sulphide bonded compounds to be designed.

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