

## Synthesis of Polyphenylene Polysulfur

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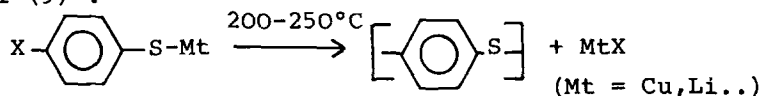
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### Summary

Polymers with conjugated double bonds are both of theoretical and practical interest. Poly(thio-1,4 phenylene), which is called poly(phenylene sulfide) (or PPS), is an original class of polymers capable of displaying conductive properties. Usually, PPS are prepared by Friedel-Crafts reaction or by Macallum synthesis. In this paper we describe another way to obtain poly(phenylene polysulfane). They are prepared in a one-pot reaction with alkali metal,  $S_8$  and p-dichlorobenzene. The reaction is studied on model molecules.

### Introduction

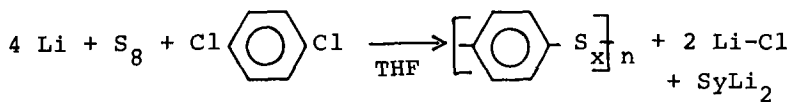
The literature describes few ways to obtain poly(phenylene polysulfanes). The poly(phenylene sulfides) were obtained by Friedel-Crafts reaction of sulfur with benzene (1), or by reaction of dichlorobenzene with sodium sulfide (2,3). The Macallum (4-8) synthesis was of great interest, but it gives branched and cross-linked products with 1 or 1.3 sulfur atoms per base unit. Research efforts led to a new synthesis, namely the self-condensation of metal salts of p-halothio-phenol (9) :



In our case, we have studied the synthesis of dialkyl sulfides by the reaction of sulfur with carbanionic oligomers (10-13). We have extended this reaction to carbanion formation in situ. The method chosen offers two advantages :

- . carbanion formation and condensation reactions occur in a one-shot process.
- . the reaction is exothermic and easy to control.

The reaction proceeds schematically as follows :



to give the poly(phenylene polysulfanes) with  $\bar{x} + \bar{y} = 8$ .

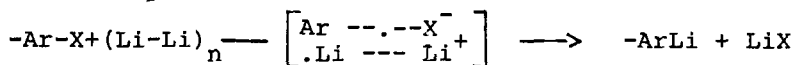
### Results and discussion

This paper concerns an exploration of this reaction type which is very exothermic and must be cooled to control it. We have studied in THF solution the reaction of sulfur  $\text{S}_8$  and alkali metal (Li) in the presence of monochlorobenzene (MCB). The compounds have been analyzed by VPC coupled with mass spectrometry. For the ratios  $K_1 = [\text{Li}] / [\text{S}_8] = 2$  and  $K_2 = [\text{Li}] / [\text{MCB}] = 1$  we have detected different arylpolysulfides with  $x = 1$  :  $\phi\text{-S-}\phi$  at  $m/e = 186$  ; and  $x = 2$  :  $\phi\text{-S-S-}\phi$  at  $m/e = 218$ . The other polysulfides with  $x = 2$  are not detected under our chromatographic experimental conditions, probably due to thermal degradation. Besides these diarylpolsulfides we have detected a small amount of diphenyl at  $m/e = 154$ .

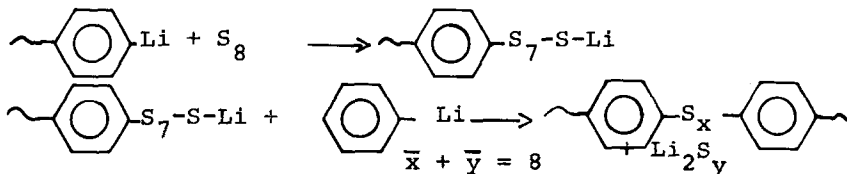
When the same reaction is carried out with dichlorobenzene with sulfur  $\text{S}_8$  and alkali metal, we isolate polymers the formulae<sup>8</sup> of which correspond to :

$\left[ \text{C}_6\text{H}_4 \text{---} \text{S}_{\bar{x}} \right]_n$  with  $2 < \bar{x} < 3$ . ( $\bar{M}_n = 12\ 000$ ). The  $^1\text{H-NMR}$  analysis only shows the existence of aromatic protons at 7.15 ppm (broad singlet).

The mechanism of the reaction between an organic halide and lithium metal is not well understood. The fact that by-products in the model reaction include hydrocarbons derived from coupling suggests that radicals may be involved. The type of mechanism which is currently felt to be most likely is one involving a one-electron transfer to the halide at the metal surface as the first step :



The aryl carbanions can attack either  $\text{S}_8$  to give poly(phenylene polysulfide) or another arylchloride to give diphenyl that we have not observed in the polymer: there is one single peak for the aromatic protons.



### Experimental

- The solvent is purified by refluxing over and distillation from sodium wire and distilled from living anions before use.
- At first p-dichlorobenzene (0.1 M) and sulfur  $S_8$  (0.1 M) are introduced in dry THF (100 cm<sup>3</sup>) under argon.

When p-dichlorobenzene is dissolved, 0.2 M of lithium sand (kept under argon) is directly added to the solution. The solution is cooled to control the reaction.

After two hours, isopropyl alcohol (10 cm<sup>3</sup>) and water (20 cm<sup>3</sup>) are added. The solvent is evaporated. The polymer is dissolved in benzene, washed several times with water. After final decantation, the benzenic solution is dried over  $MgSO_4$ , filtrated and the solvent is evaporated. The polymer is isolated and freeze dried in benzene.

### Analytical methods :

- Molecular weights have been determined by gel permeation chromatography (GPC : Waters apparatus) using styragel columns and THF as a solvent.
- Spectral measurements : <sup>1</sup>H-NMR spectra of polymers have been carried out with either a Bruker (90 MHz) or a Hitachi Perkin Elmer (60 MHz) spectrometer.
- Mass spectrometer Riber R 10.10

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