Homopolycondensation of thiophenol

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A homopolycondensation of thiophenol in a medium of concentrated sulphuric acid has been investigated. As a result, two types of poly(phenylene sulphide), melting at 130°–135°C and 310°–330°C have been obtained. Linear and branched structures and a mechanism for the reaction are proposed. The thermal properties of the polymers were studied by thermal gravimetric analysis (t.g.a.).

INTRODUCTION

Much attention has been paid in the literature to the homopolycondensation of aromatic derivatives containing active protons, in presence of protonic catalysts. These data indicate that the mechanisms of these reactions are complex. In particular, mercapto derivatives of benzene have been studied.

Hilditch[1] prepared an amorphous, cream coloured powder (m.p. 290°–295°C), insoluble in boiling alcohol, by reaction of thiophenol with concentrated sulphuric acid. The structure of this substance was not determined. Interest in this reaction has increased because of the unusual thermal stability and potential utility of new polymers, such as poly(phenylene sulphide), synthesized by Macallum[2]. Several grades of poly(phenylene sulphide) are produced under the trademark Ryton by the Philips Petroleum Company, and are prepared by the reaction of *p*-dichlorobenzene and sodium sulphide in polar solvents.

The present study was undertaken to investigate the conditions of homopolycondensation of thiophenol in concentrated sulphuric acid, to determine properties of the products obtained and to discuss the mechanism of reaction.

EXPERIMENTAL

Homopolycondensation of thiophenol was carried out in a medium of concentrated sulphuric acid according to the method of Hilditch[1].

Concentrated sulphuric acid (500.0 g) was added to thiophenol (30.0 g) and the reaction mixture was stirred for 1 h. After 24 h at room temperature the reaction mixture was poured into water (600 cm^3). The precipitate was filtered, washed with water until neutral and dried. The crude product (20.0 g) was obtained and extracted for 8 h with boiling toluene. After evaporation of the toluene extract diphenylene *o*-disulphide-thiantrene (2.6 g, m.p. 156°–159°C) was collected. The product was then extracted with methanol. A glassy, yellow substance (3.4 g, m.p. 125°–130°C) was separated from the methanol extract. The i.r. spectrum is given in *Figure 1*. The residue, after extractions, was a yellow powder (m.p. 310°–330°C) weighing 24.0 g; the i.r. spectrum is given in *Figure 1*. I.r. spectra in this study were taken using a Specord IR 71 Zeiss infra-red spectrophotometer.

Thermal analysis were obtained using a MOM OD 103 thermogravimetric analyser.

X-ray diffraction powder photographs of the polymers were taken using Ni-filtered CuKα radiation and Zeiss apparatus, model TUR–M 62.

A Bothius microscopic melting point of the polymers was determined on model HMK 69/2554 (F. Kustner Nachf. KG, Dresden).

The sulphur content was analysed by the Schöniger micromethod. The solubility was determined by treating samples of the polymers with solvents for 6 weeks at room temperature.

RESULTS AND DISCUSSION

As a result of homopolycondensation of thiophenol in a concentrated sulphuric acid medium two types of

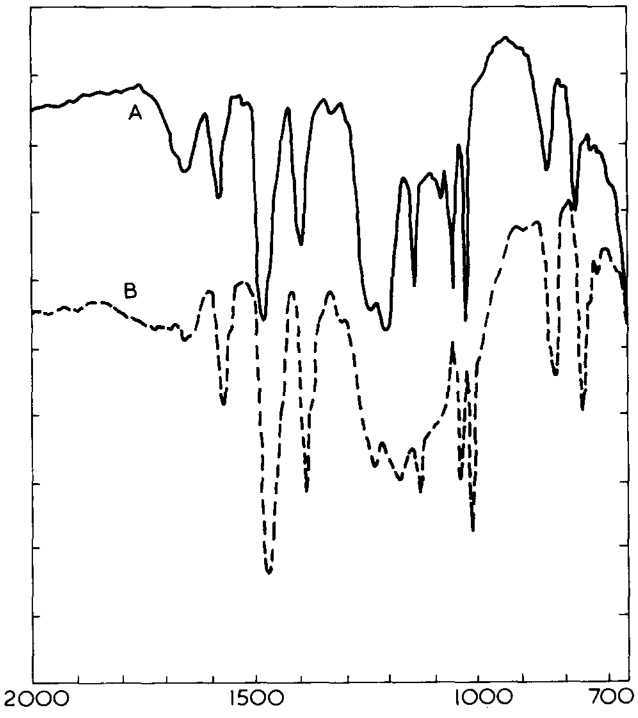


Figure 1 I.r. spectrum of poly(phenylene sulphide) obtained from thiophenol (nujol). A, Polymer melting at 310°–330°C; B, polymer melting at 125°–130°C

Table 1 Properties of poly(phenylene sulphides) obtained from thiophenol in a medium of sulphuric acid

	Property				
Polymer	Melting point (°C)	Sulphur content (%)	Density (g/cm^3)	Crystallinity (%)	Yield (%)
I	310°–330°	29.21*	1.25	0	80.8
II	125°–130°	27.66	1.33	0	11.4

* Theoretical content of sulphur in linear poly(phenylene sulphide) is 29.37%

Table 2 Solubility of poly(phenylene sulphides) obtained from thiophenol

Solubility	Polymer	
m (%)	I	II
Acetone	+2.6	+20.6
Methanol	−3.9	−100.0
Ethyl acetate	+2.7	+13.1
Benzene	+2.6	+14.5
Toluene	−0.7	−1.2
Dioxane	+1.7	+3.7
HMPT	−0.6	−100
DMF	+1.5	−100
Carbon tetrachloride	+1.9	−10.8
H_2SO_4 (30%)	+0.3	+6.8
HCl (35%)	+0.2	+7.1
CH_3COOH (100%)	+0.7	+2.1

poly(phenylene sulphide) were obtained. These polymers differed in melting point because of the differences in their molecular weights.

I.r. spectra of the polymers obtained are nearly identical. Slight differences are observed in the range 1225–1130 cm^{-1}. Physical data of synthesized polymers are shown in the *Tables 1* and *2*.

Because of low solubility, only the n.m.r. spectrum of the polymer melting at 130°–135°C was taken. The spectrum showed only one multiplet at $\tau = 2.5$ attributed to the protons of the benzene ring. The presence of the protons of the SH group was not detected in the n.m.r. spectrum. This fact can be explained by a low absorption of the SH group proton and the small number of these groups in the polymer.

I.r. spectra of the polymers were compared with the spectrum of linear poly(phenylene sulphide) obtained by Lenz and Handlovits[3], in which there are characteristic bands at 750, 820, 1010, 1090 and 1580 cm^{-1}; with the spectrum of Ryton P–3 (*Figure 2*) and with the data of Price and Tsunawaki[4], who attributed the following bands to poly(phenylene sulphide): 800, 1000, 1060, 1080, 1170, 1380 and 1460 cm^{-1}.

A comparison of the quoted spectra with the spectrum of poly(phenylene sulphide) obtained from thiophenol (*Figure 1*) indicates a large similarity of the polymers. Particularly important is the range at around 900–700 cm^{-1}. Bands in this range indicate a type of aromatic substitution and a polymer structure. I.r. spectra of the synthesized polymers revealed bands at 750 and 820 cm^{-1} within this range. They are attributable to a 1,2,4- and 1,4-substituted benzene ring.

In the case of linear poly(phenylene sulphide)[3] and Ryton P–3 the band at around 820 cm^{-1} has a higher intensity in comparison with the band at 750 cm^{-1}, denoting a predominance of 1,4 structure. Similar intensity absorptions at around 820 and 750 cm^{-1} in the i.r. spectrum of polymers synthesized from thiophenol indicates approximately equal participation of 1,2,4, and 1,4 structures.

This interpretation is consistent with spectra of model compounds at $(C_6H_5)_2S$ (dimer) and $(C_6H_5)_3S_2$ (trimer) (*Figure 3*). In the spectrum of $(C_6H_5)_3S_2$ a band at around

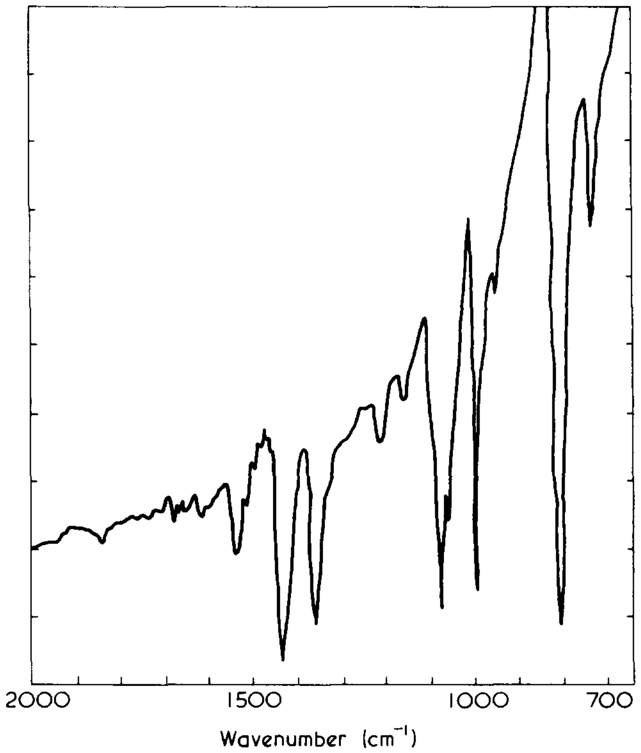


Figure 2 I.r. spectrum of Ryton P–3 (nujol)

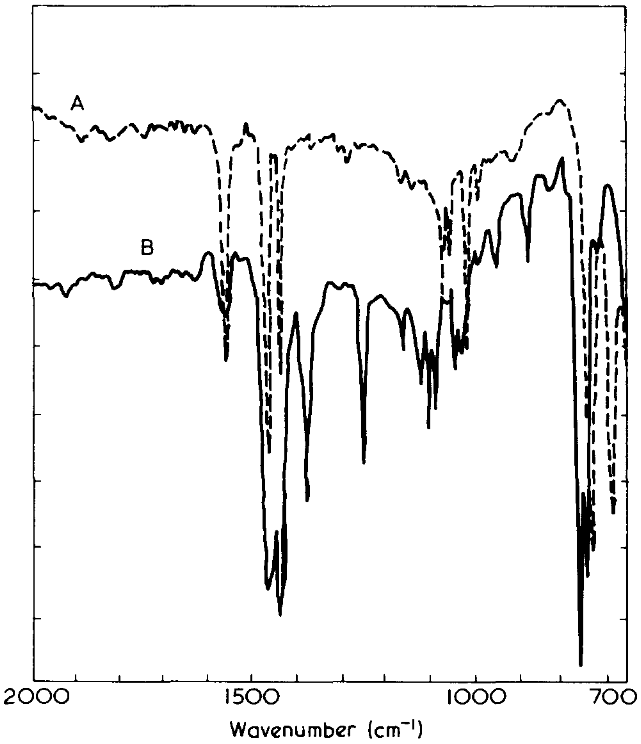


Figure 3 I.r. spectra of $(C_6H_5)_2S$ (film) (A), and $(C_6H_5)_3S_2$ (nujol), (B)

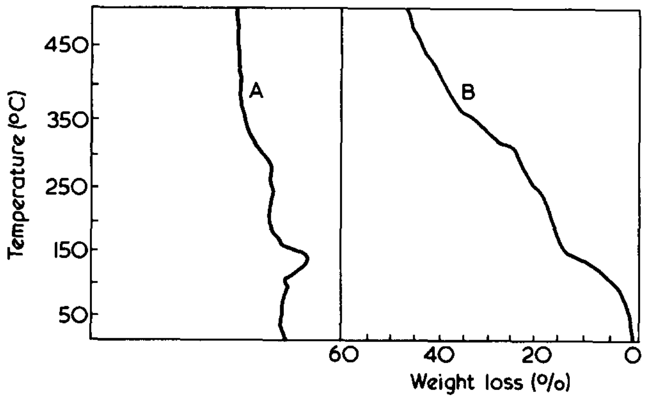
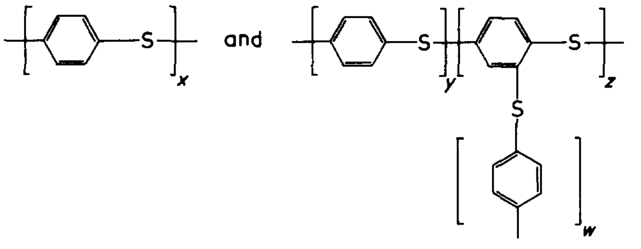


Figure 4 T.g. (B) and d.t. (A) analysis of polymer II (m.p. 130°–135°C), in air atmosphere, at ΔT = 5°C/min

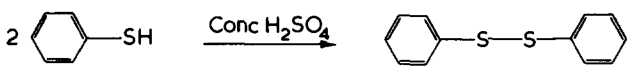
820 cm^{-1} is assigned to a 1,4-substituted benzene ring. This band appears also in spectra of polymers but is absent in the spectrum of diphenyl disulphide.

In the spectra of polymers there are bands at around 730 and 690 cm^{-1} characteristic of diphenyl disulphide which indicates the presence of a 1-substituted benzene ring.

Sulphur content determination revealed that there is ~1 sulphur atom per repeat unit. The sulphur content in polymer II is slightly lower than in polymer I. This confirms a lower molecular weight of polymer II. It is possible to suggest the following structures for polymers obtained from thiophenol in a medium of concentrated sulphuric acid:

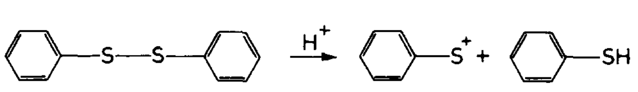


These structures correspond with the proposed mechanism of homopolycondensation. In the first stage diphenyl disulphide was isolated:



(1)

In the second stage, as a result of proton charge, a heterolytic dissociation of diphenyl disulphide into sulphenyl ion and mercaptan follows:



(2)

In the following stage *p*-substitution (or *o*-substitution) and elimination of a proton in each step occurs. Thiantrene is formed as a by-product.

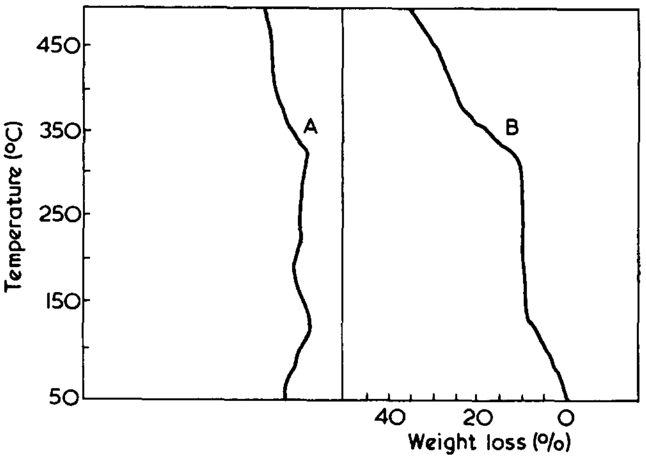
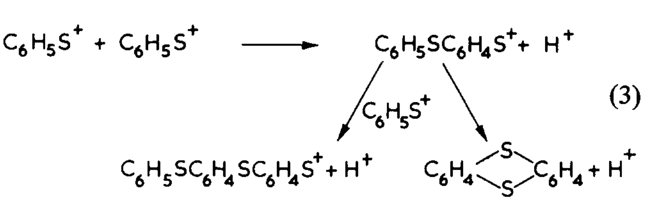


Figure 5 T.g. (B) and d.t. (A) analysis of polymer I (m.p. 310°–330°C), in air atmosphere, at ΔT = 5°C/min



$$C_6H_5S^+ + C_6H_5S^+ \longrightarrow C_6H_5SC_6H_4S^+ + H^+$$
$$C_6H_5SC_6H_4SC_6H_4S^+ + H^+ \qquad C_6H_4\langle S_2 \rangle C_6H_4 + H^+$$

(3)

Linear poly(phenylene sulphides) are known as materials with unusual thermal stability. Because of the potential utility of the new polymer, thermal gravimetric analysis was carried out.

D.t.a. of the low molecular polymer (II) (*Figure 4*) revealed two endothermic peaks at 130° and 255°C. A strong peak at 130°C is assigned to the phase transition in the range of the melting point. This peak corresponds to weight loss amounting to ~15%. Then up to a temperature of 500°C a further weight loss, amounting to ~30%, is observed.

D.t.a. of the polymer melting in the range 310°–330°C (I) (*Figure 5*) exhibits two endothermic peaks, at 130° and 330°C. The peak at 130°C is attributable to phase transition (melting of the residue of the low molecular polymer in the sample). The second peak corresponds to melting of high molecular polymer. The t.g.a. curve shows a weight loss of ~8% in the range 60°–130°C and a further weight loss amounting to ~14%, in the range of 330°–400°C.

Low molecular poly(phenylene sulphide) obtained from thiophenol possesses a lower thermal stability than the high molecular poly(phenylene sulphide).

A comparison of these results with data of Lenz and Handlovits[3] indicates a lower thermal stability of poly(phenylene sulphide) synthesized from thiophenol compared with linear poly(phenylene sulphide) produced by polycondensation of *p*-halogenothiophenolates, which possesses a higher stability.

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