

The thermal degradation of poly(phenylene sulphide)—Part 1

Olufemi A. Peters

Chemistry Department, Ahmadu Bello University, Zaria, Nigeria

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Richard H. Still

Manchester Materials Science Centre, UMIST, Grosvenor Street, Manchester, UK M1 7HS

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The thermal degradation of poly(phenylene sulphide) (PPS) has been studied *in vacuo* at temperatures between 300 and 550°C. Results indicate extensive cross-linking reactions with few degradation products at temperatures below 450°C. The products formed at higher temperatures were analysed using thermal analysis, infrared spectroscopy, mass spectrometry and gas-liquid chromatography. The major products were cyclic oligomers, dibenzothiophene and thiophenol. Mechanisms which account for these products have been suggested and discussed.

INTRODUCTION

Degradation studies on poly(phenylene sulphide) (PPS) have mainly involved curing of the resinous material coupled with weight loss measurements in air and nitrogen. Lenz *et al.*,¹ Black *et al.*² and Christopher *et al.*³ have assessed and compared the thermal stabilities of poly(arylene sulphide)s using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) and have reported no appreciable degradation at temperatures below 500°C. At temperatures higher than 500°C, the initiation reaction was suggested to involve breaking of the C—S bond in the PPS structure to give low molar mass sulphur compounds and a cross-linked residue.

More detailed studies using elemental analysis, mass spectroscopy (MS) and infrared spectroscopy (IR), carried out by Ehlers *et al.*⁴ and by Kaplan,⁵ provided further evidence of C—S bond rupture followed by intermolecular abstraction of hydrogen atoms to give fragments having substituted aryl and arylthiyl chain end groups. The formation of these groups and the

cross-linked residue has been suggested by Hawkins⁶ to involve simultaneous reactions of chain extension, thermal cross-linking and, in appropriate environment, oxidative cross-linking.

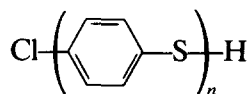
Analysis of the more readily condensed volatiles indicated the presence of such components as dibenzothiophene, thianthrene and higher oligomeric components. Hydrogen and hydrogen sulphide are also observed.⁴ However, little quantitative assessment of the products of pyrolysis has been made mainly due to the limitations of the experimental technique. Thermal degradation using a molecular still^{7,8} is a well developed method of pyrolysis that allows for separation of degradation products into fractions, based on volatility. The fractions are: (i) a gaseous fraction volatile at all experimental temperatures; (ii) a liquid monomeric fraction, V_{25} , volatile at both pyrolysis and ambient temperatures but involatile at liquid nitrogen temperature, -196°C ; (iii) an oligomeric fraction, V_{pyz} , volatile at pyrolysis temperature but involatile at ambient temperature; and (iv) a residue involatile at all experimental temperatures.

This paper reports on the products of pyrolysis obtained from the vacuum pyrolysis of PPS.

EXPERIMENTAL

Materials

Ryton® P-3 was obtained from Phillips Petroleum Company, U.S.A. It was stripped of its low molar mass components via Soxhlet extraction to give a toluene-insoluble fraction (98.0 wt%) referred to herein as PPS. It was dried to constant weight at 100–110°C/0.04 mmHg prior to characterisation. $Mn(Cl)$ was found to be 8875 assuming the structure:



Infrared spectroscopy (IR)

Spectra were recorded on a Nicolet Fourier-transform infrared spectrophotometer in the mid-infrared range (4000–400 cm^{-1}). Typical spectrometer conditions were 20 scans at a resolution of 4 cm^{-1} . Samples were run as 1–2% dispersions in KBr.

Gas-liquid chromatography (GLC)

This was performed on a Hewlett-Packard 5830A gas chromatograph equipped with a Pyrex glass column (2 m \times 2 mm), packed with Silicon SE 30(10%) on Chromosorb G-AW-DMCS (80–100 mesh). The liquid (1 μl) was injected on to the column and the separated components detected using a flame-ionisation detector. The separation temperature profile was: initial temperature, 140°C for 1 min; final temperature, 220°C for 10 min at a heating rate of 5°C min^{-1} ; injection temperature, 250°C; and detector temperature and maximum oven temperature were both maintained at 300°C.

Mass spectrometry (MS)

Spectra were recorded using a Kratos MS 45 instrument at isothermal temperatures between ambient and 300°C.

Melting point (mp)

Melting points were determined on a Reichert polarising hot stage microscope (HSM) at a heating rate of 2–4°C per minute.

Thermal analysis

Thermal analyses were performed on a DuPont 990 differential thermal analyser using the facility for differential scanning calorimetry (DSC). Samples (5–15 mg) were heated at a nominal heating rate of 20°C per minute in a crimped aluminium pan with a similar pan as reference. The glass transition temperatures (T_g)—was taken as the temperature at the intersection of an extension of the original baseline with a tangent drawn at the point of steepest slope in the baseline step. Melting temperatures (T_m) were taken at the peak of the endotherm.

Elemental analysis

Elemental analyses were carried out by the micro-analysis section of the Chemistry Department, UMIST to the following limits of accuracy: C \pm 0.3%, H \pm 0.2%, S \pm 0.5%, Cl \pm 0.3%.

Vacuum pyrolysis apparatus and procedure

The pyrolysis apparatus was similar to that described previously.⁸ A dried sample of about 100 mg of polymer was weighed into a dry specimen tube and placed at the end of the quartz pyrolysis tube which was then connected to a vacuum system. When the pressure was reduced to 2.5×10^{-3} mmHg, the furnace, preheated to the required temperature (300–550°C), was wheeled into position such that the polymer samples were within the 'hot spot'⁸ of the furnace. The furnace was removed after 45 min and the system allowed to cool and equilibrate for 60 min. Nitrogen was leaked into the system to atmospheric pressure. The various cooling devices along the rig were then removed. The pyrolysis tube was removed from the quartz tube and the procedures for the isolation of the fractions were as described in the text.

RESULTS AND DISCUSSION

Gaseous and residue fractions

A gaseous fraction was inferred by the pressure increases observed within the degradation system at all temperatures. H_2S was detected at all pyrolysis temperatures from its odour and

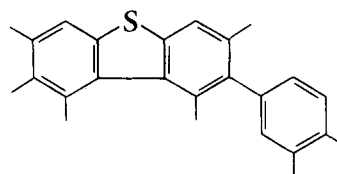
Table 1. Characterisation of the residues from PPS

Temperature (°C)	Physical appearance	T_g (°C)	T_m (°C)	Elemental analysis (%)			
				C	H	S	Cl
Ambient	Brown powder	85	276	66.5	3.8	27.8	0.4
300	Tough dark brown solid	90	271	66.9	3.8	27.6	0.3
350	Tough dark brown solid	90	262	66.6	3.5	27.3	—
400	Ductile black solid	95	248	66.3	3.3	28.7	0.4
450	Ductile black solid	106	—	67.9	2.5	27.1	0.5
500	Brittle black pellets	—	—	66.5	2.4	23.3	—
550	Brittle black pellets	—	—	66.0	—	23.1	—

confirmed by the discoloration of lead acetate paper placed in one of the cold traps.

The residues obtained below 450°C were observed as a tough swollen mass which, when pierced with a sharp object, revealed a chambered cavity as H_2S gas was given off. At temperatures higher than 450°C the residues were obtained as brittle black pellets. All the residues were found to be insoluble in solvents for undegraded polymer. Table 1 shows the appearance, T_g , T_m and the elemental analysis of the residues. T_g was observed to increase with pyrolysis temperature up to 450°C. However a decrease in T_m was observed up to 450°C with increase in pyrolysis temperature. These trends in transition temperatures can be ascribed to an increasing degree of cross-linking in the residues. Cross-linking reduces chain mobility and hence increases T_g . Decreasing T_m values therefore arise from the reduction in the ability of the chains to pack within the matrix due to branching and cross-linking. At temperatures higher than 450°C, where no T_g and T_m transitions were observed, the cross-linking density had increased such that there was a significant reduction in molecular motions in the residues. The observed decrease in sulphur and hydrogen contents and the increase in the carbon content of the residues with increased pyrolysis temperature supports this progressive formation of infusible residue through increased proportions of carbon-carbon linkages. The resinification of the residues was also evident from the IR spectra which became progressively ill-defined with increase in pyrolysis temperature.

Elemental analysis also revealed that about 83% of the original sulphur was still retained in the residues at 550°C, and a similar percentage of residual sulphur (79%) reported by Ehlers *et al.*⁴ prompted them to suggest a structure,



for the residue, involving one sulphur atom per three benzene rings.

Oligomeric fraction

The oligomeric fraction was obtained as a multilayered condensate in the pyrolysis tube at the opened end of the furnace (Fig. 1). Only layers A, B and D were observed at pyrolysis temperatures lower than 500°C. Figure 2 shows the IR spectra of the bulk fractions obtained at 300, 400 and 450°C, respectively. The main differences between the spectra occurred in the range 800–1200 cm^{-1} . At 800 cm^{-1} , the band which is indicative of a disubstituted aromatic ring is singlet and sharp for the fraction obtained at 300°C but doublet for the other fractions. In addition, only the 300 and 350°C fractions (not shown) showed a prominent absorption at 870 cm^{-1} which is ascribed to 1,2,4-trisubstitution in an aromatic ring. This observation suggests that the fraction obtained at 300°C contains some branched components and is an early indication of cross-linking reactions. Finally, the band at 1100–1000 cm^{-1} , which has been used⁹ to differentiate between cyclic and linear forms of PPS, was observed to be doublet for all fractions, thus implying cyclic structural dispositions. However, the doublet was broad for the fraction obtained at 300°C and narrow in the spectra of the other fractions. The narrowness of the peak is interpreted as indicating the diluting effect of linear components in these fractions.

Isolation of the components was performed for

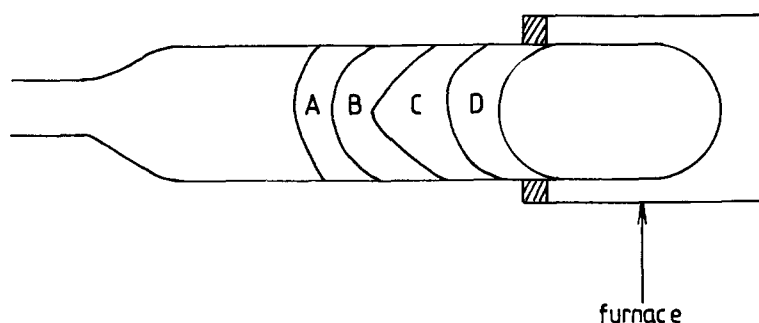


Fig. 1. Diagrammatic representation of the oligomeric fraction obtained at 500°C. (A) White layer with yellow tint; (B) light brown crystalline layer; (C) white layer with brown tint; (D) white layer appearing as a mixture of liquid condensate and particles.

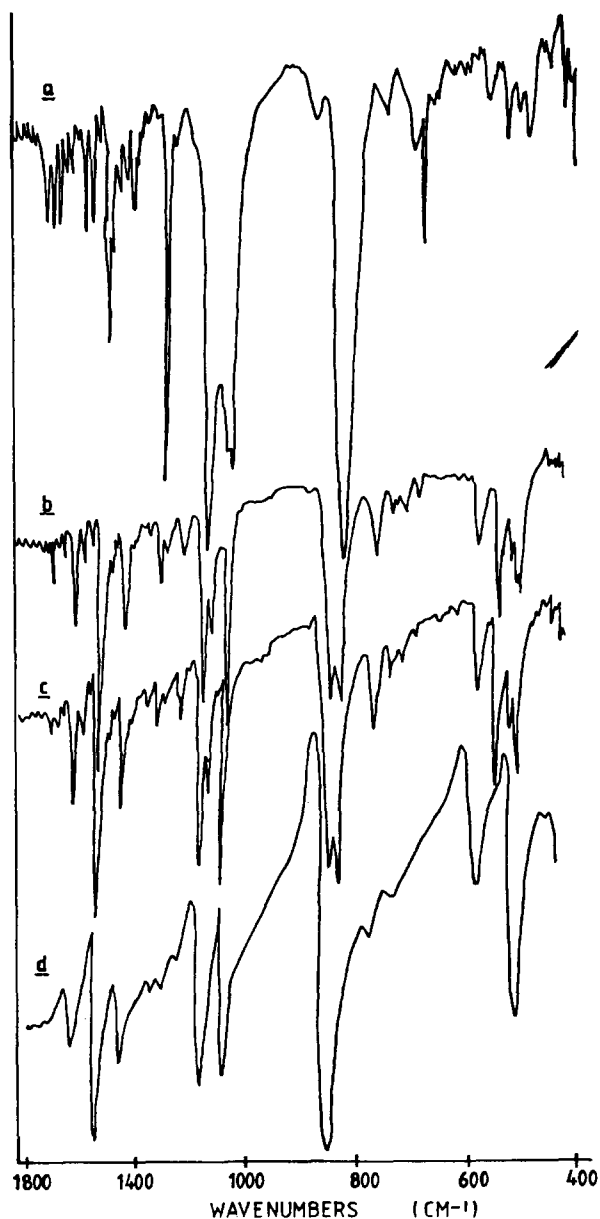
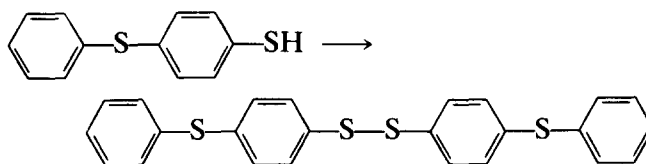


Fig. 2. IR spectra of oligomeric fraction obtained at: (a) 300°C, (b) 400°C, (c) 450°C, and (d) undegraded polymer.

the fraction obtained at 500°C. CHCl_3 was used to wash out the fraction to give a light yellow suspension. Filtration and drying at the pump gave a mixture of a cream powder and white crystals which amounted to 6.8 wt% of the total amount volatilised. The white crystals were recrystallised in ethanol. IR and an MS peak at m/e 184 both indicated dibenzothiophene, mp 100–101°C (Ref. 10: 97–99°C). The cream powder (component A) was shown by MS to be a tetramer with m/e 432 (Fig. 3(a)). Thereafter, a fraction referred to as Apet was obtained by scraping off layer A and extracting with pet ether 80/100°C. Filtration and drying at the pump gave an off-white solid and a liquid component observed as a coating on the walls of the test tube. MS of the white solid showed a base peak at m/e 218. It was suspected to be 4-(benzenethio)thiophenol and was recrystallised from pet ether (60/80°C) to give white crystals with mp 44–46°C (Ref. 11: 46°C). It is suggested that the yellow coating on the test tube wall was bis (-4-benzene thiophenyl) disulphide,



obtained as a result of possible oxidation of 4-(benzene thio) thiophenol in air after a similar observation reported by Koch *et al.*¹²

Layer B was an off-white powder sparingly soluble in hot chloroform. It had an mp of 214–218°C. Figure 3(b) shows the MS of layer B with major m/e peaks at 432(95), 215(15) and 184(25), respectively. With the most abundant

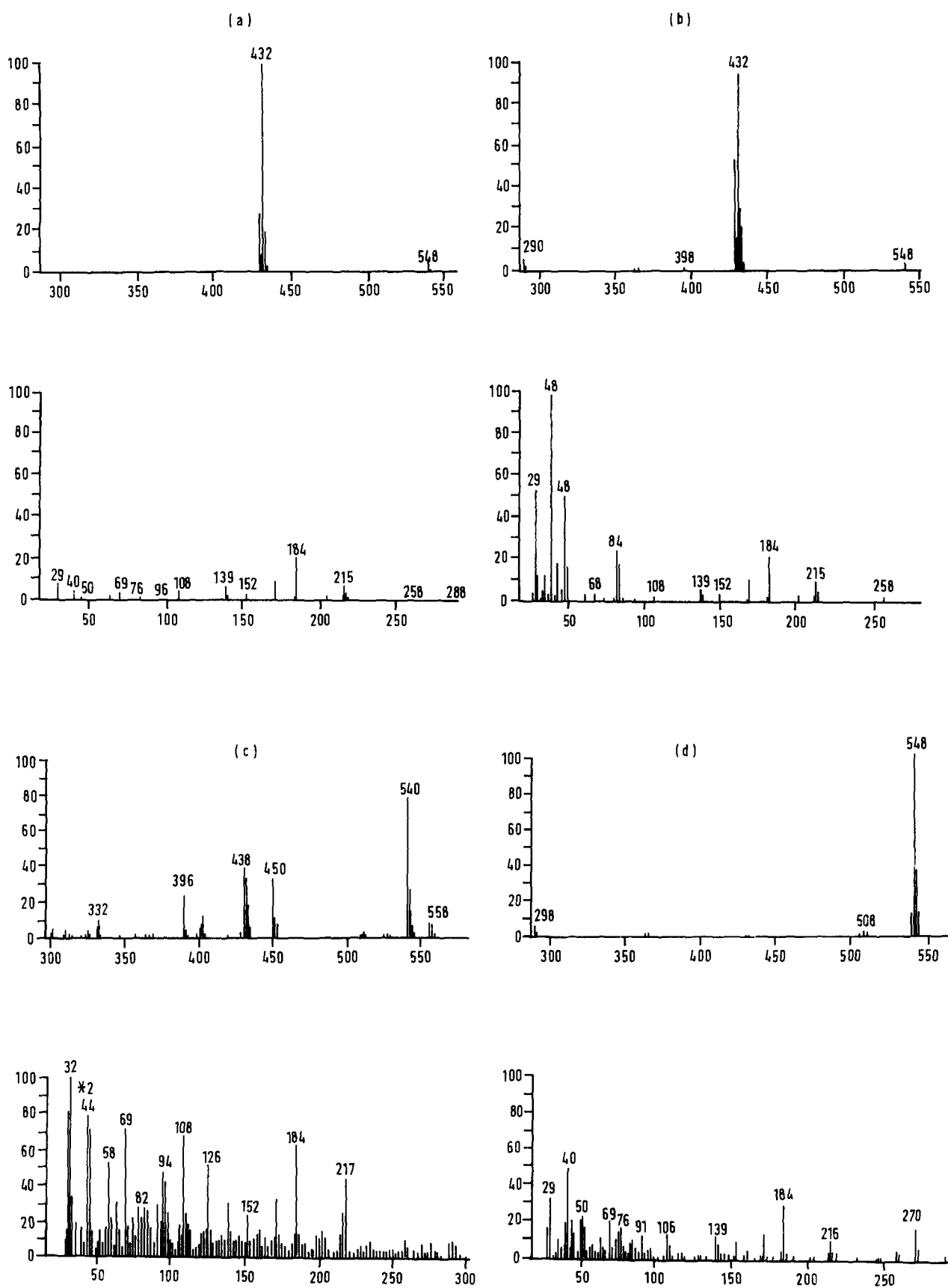


Fig. 3. Mass spectra of oligomeric components isolated from the fraction obtained at the pyrolysis temperature of 500°C: (a) component A, (b) layer B, (c) layer C, and (d) layer D.

peak at m/e 432, the layer is suggested to be a tetramer.

Layer C was a cream-coloured granular material (mp 224–228°C) soluble in hot benzene. Figure 3(c) shows an MS base peak at m/e 540, indicating a pentamer. Other prominent peaks were at 450(35), 432(42), 217(45), 184(65), 152(35), 126(55) and 108(70), all of which might be due to fragmented ions, and hence the probable presence of linear structural components. Layer D was extracted using toluene, to give an off-white material with an mp of 254–258°C. The MS, in Fig. 3(d) shows a base peak at m/e 540, indicating a pentamer. Other prominent peaks were at 270(22), 216(14), 184(35), 139(14) and 108(15).

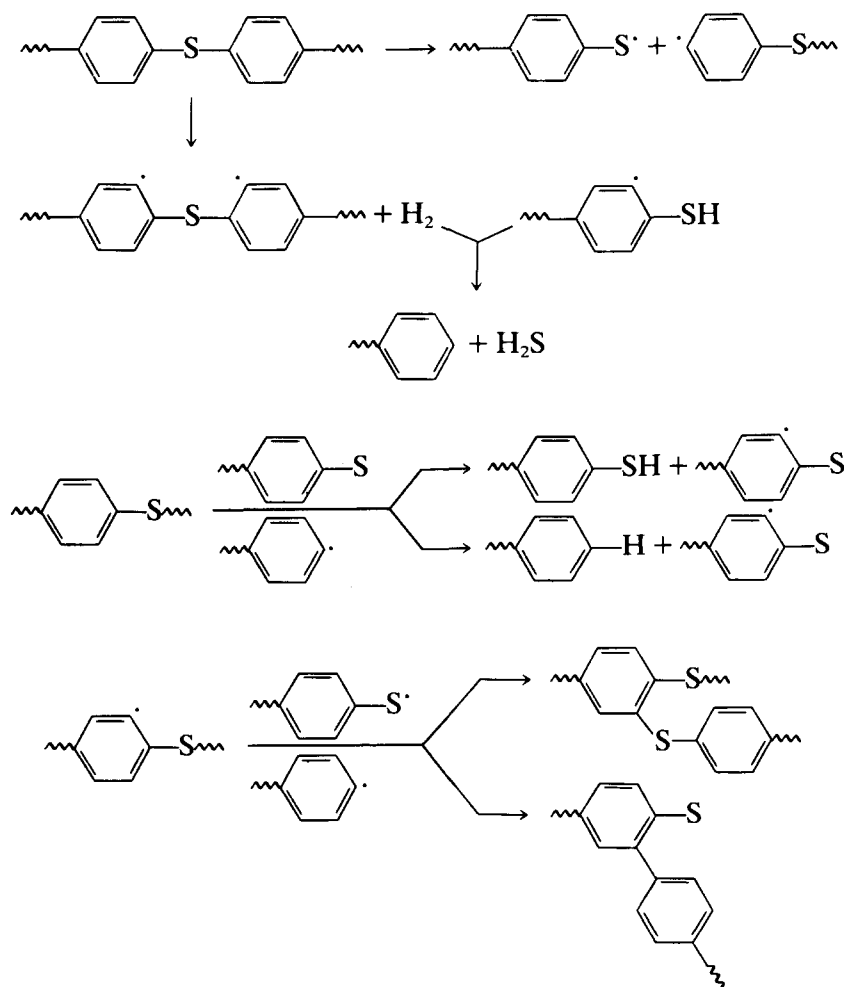
Monomeric V_{25} fraction

No significant amount of the V_{25} fraction was produced below 450°C. At 500 and 550°C, the fraction constituted only 2.5 and 2.2 wt%, respectively, of the total mass degraded and

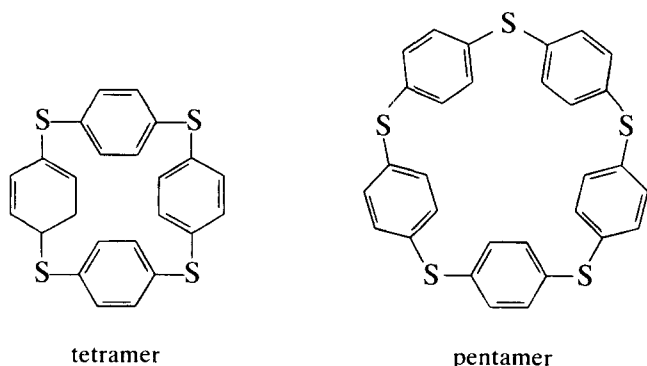
3.2 wt% of the total amount volatilised. The IR of the neat fraction obtained at 500°C was characterised by strong bands at: (i) 1600 and 900 cm^{-1} , indicating monosubstitution of the aromatic ring; (ii) 2550 cm^{-1} , the stretching mode of the S—H bond; and (iii) 700 cm^{-1} , indicating vibrations of a C—S bond attached to an aromatic ring. GLC showed five main components, three of which were identified as thiophenol, phenylsulphide and benzene, using retention times of reference compounds.

Mechanism of degradation

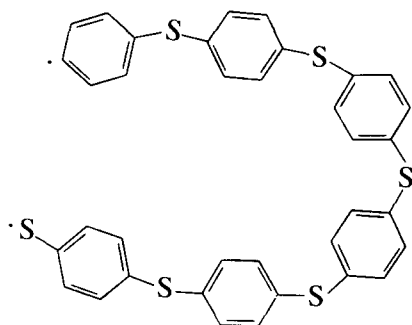
The simultaneous evolution of H_2S gas and the formation of a cross-linked residue during PPS pyrolysis has long been established⁴ and reactions leading to their formation suggested.⁴ The degradation is believed to start with thermal scission of a C—S bond. The macroradicals thus produced abstract hydrogen atoms from nearby polymer chains. These reactions may be represented thus:



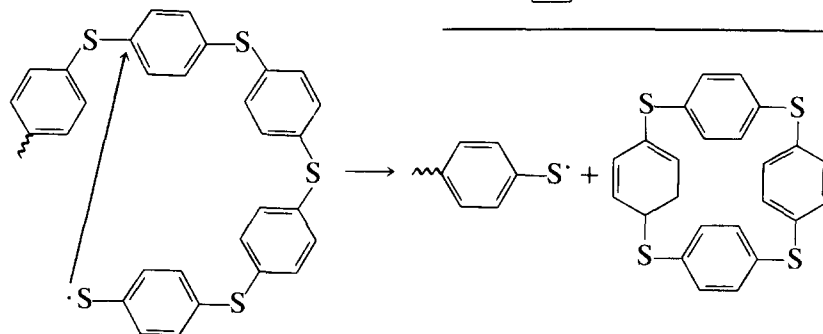
The results from the oligomeric fraction suggest that at low pyrolysis temperatures only branched and cyclic oligomers were formed, whilst at high temperatures low molecular mass compounds, such as dibenzothiophene and 4-(benzenethio)-thiophenol, together with linear oligometric components were also produced. Cyclic oligomers have been isolated previously⁵ from undegraded PPS although it has been suggested that such structures are formed^{13,14} during its pyrolysis. Kaplan and Reents⁵ suggested structures for the tetramer and pentamer:



Although the calculated molar masses fit the MS data for the V_{pyz} fractions, the route of formation remains unclear. One such route could be an open chain diradical molecule which can react with itself;

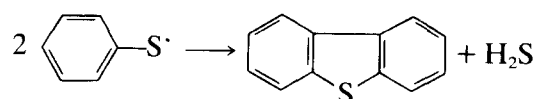


Another possible route might involve incestuous attack of a macromolecule with an arylthiyl radical end group:

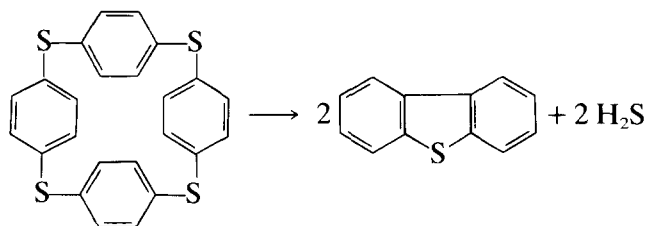


The problem arises as to what determines the number of units involved in cyclisation and the ratio of the amounts of one oligomer to the other. It would appear from structural models constructed from the orbit molecular building system of molecular models that the tetramer would be the most abundant because ring stability was found to increase from the trimer to tetramer and decrease to hexamer. Indeed, the MS of the bulk fractions indicate the significant presence of the tetramer at all pyrolysis temperatures.

It has been suggested that dibenzothiophene is formed in a condensation reaction of two arylthiyl radicals with the elimination of H_2S :



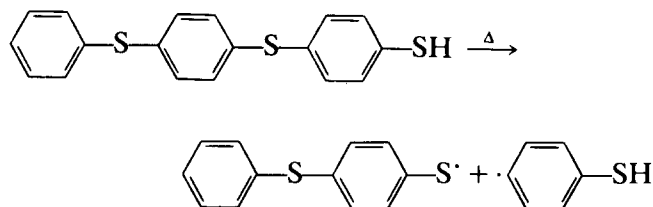
Whilst not ruling out this reaction, it is to be expected that thiophenol and phenylsulphide, both likely products from arylthiyl radicals, could have been produced at temperatures below $450^\circ C$ because the abstraction of a hydrogen atom by the radical to form thiophenol should be more probable than the condensation of two arylthiyl radicals. However, since thiophenol and phenylsulphide were detected at $500^\circ C$ and above whilst dibenzothiophene was produced at $450^\circ C$ and below, there must be another possible route of dibenzothiophene production which must account for its higher amount relative to thiophenol at all pyrolysis temperatures. Thus, it is suggested that formation of dibenzothiophene could also occur by intramolecular hydrogen transfer and rearrangement involving cyclic precursor molecules:



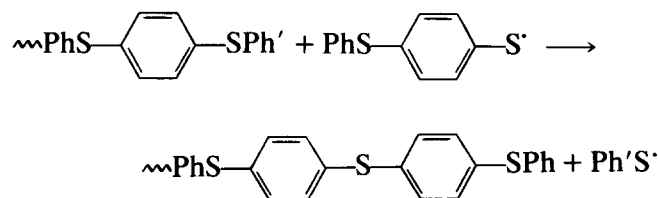
Although an adequate mechanistic explanation for this reaction cannot be proposed at the moment, evidence for this suggestion comes from: (i) the higher amount of dibenzothiophene obtained¹⁵ from the pyrolysis of a low molar mass PPS relative to PPS which was conformationally found to be cyclic; and (ii) the observation that MS of these cyclic oligomeric components only give a spectral peak corresponding to dibenzothiophene apart from that due to the parent ion.

The formation of 4-(benzenethio)thiophenol is suggested to have occurred through linear oligomeric precursors made possible only at high temperatures as a result of increased random scission before cross-linking, branching and/or cyclisation occurs.

Finally, the results indicate that the monomeric fraction was produced in detectable quantities only at high pyrolysis temperatures which coincided with the appearance of linear oligomeric components. The predominance of thiophenol (90%) over other components in the fraction suggests that arylthiyl radicals were present at a higher concentration than phenyl radicals. The arylthiyl radicals must therefore have been formed from increased random bond scission within the polymer matrix. The formation of arylthiyl radicals and thus thiophenol could also proceed via two routes: (i) direct scission of a macromolecule with a thiol end group:

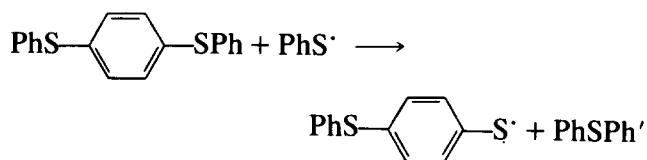


and (ii) from a reaction analogous to the chain extension reaction proposed by Hawkins:⁶

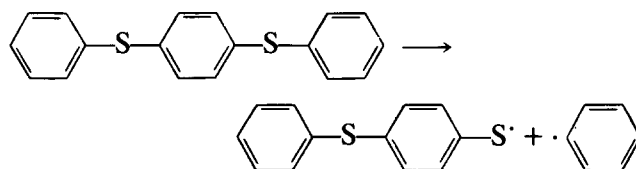


In a similar manner, phenylsulphide can also be

formed by attack of an arylthiyl radical on a polymer molecule with a phenyl end group:



It is suggested that benzene is formed either from random scission with the polymer matrix or from linear oligomeric component precursors with phenyl end groups:



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