Thermal degradation of bridged polyaromatic sulphides investigated by direct pyrolysis in the mass spectrometer

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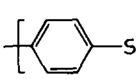
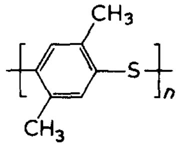
The thermal degradation of three bridged polyaromatic sulphides (I–III) was investigated in the ion source of a mass spectrometer. The reactions were followed by detecting the thermal and electron impact induced fragments. The electron impact induced fragmentation reactions of the pyrolytic fragments are influenced by *ortho*-methyl substitution, and the mechanisms of these processes are discussed. The results indicate also that the disulphide bridge content in the methyl substituted polymers considerably lowers the thermal stability of these materials with respect to poly(phenylene sulphide).

INTRODUCTION

We have been interested in the synthesis of bridged polyaromatic polymers containing methylene, oxygen and sulphur bridges[1,2], and in the study of the thermal degradation products of these materials by means of direct pyrolysis in the mass spectrometer[3,4]. This technique has proved to be an excellent method for the characterization of polycondensates, and furthermore the data obtained provide details on the mechanisms of thermal degradation[4,5].

We have now investigated the thermal stability and the electron impact induced fragmentation of three bridged polyaromatic sulphides (I–III) by direct pyrolysis in the ion source of a mass spectrometer.


(I)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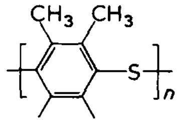

(III)

Polymers II and III were prepared by iron catalysed sulphuration directly from the aromatic monomers and SCl$_2$. This reaction, although yielding linear, crystalline polysulphides, is known[6] to produce a certain number of disulphide bridge inclusions in the polymer chain. The disulphide bridge content for polymers II and III was estimated[2] to be about 10%; this raises the question of whether the presence of this amount of disulphide linkage influences the thermal stability of these polymers. It is in fact known[4] that the thermal stability of poly(phenylene disulphide)(IV) is much lower than that of poly(phenylene sulphide)(I), due to the weakness of the disulphide bridges which results in the extrusion of sulphur (*m/e* 64) from the polymer at ~300°C.

EXPERIMENTAL

Materials

The synthesis and characteristics of polymer samples I–III have been described elsewhere[2].

Mass spectrometry

Pyrolyses were carried out in gold probes using the direct insertion inlet of an electron impact mass spectrometer (Varian CH 711).

To increase the possibility of a selective thermal degradation, pyrolyses were carried out under relatively mild conditions; in a typical run, the sample was temperature programmed with a heating rate of about 40°C/min and several spectra (up to 20) were recorded during the pyrolysis.

At low temperatures, when the degradation of the polymers did not take place, negligible total ion current (*TIC*) was detected. At higher temperatures, as soon as the thermal degradation initiated, total ion current progressively increased and mass spectra were repetitively scanned. A digital computer (Varian SP 100), directly connected to the mass spectrometer with an opportune software, was used for the storage of the spectra scanned at different temperatures. The total ion current of each spectrum at each recorded temperature was then reported *versus* the temperature (*Figure 2*). Curves in this diagram are of the same type as the differential thermogravimetric curves, so that their maxima characterize the maximum decomposition rate of each polymer under batch conditions.

The polymers were investigated with a reduced electron energy of 15 eV; it could be shown that under these conditions only a few selective fragmentation steps take place.

RESULTS AND DISCUSSION

Although the polymers investigated remain unvolatilized at

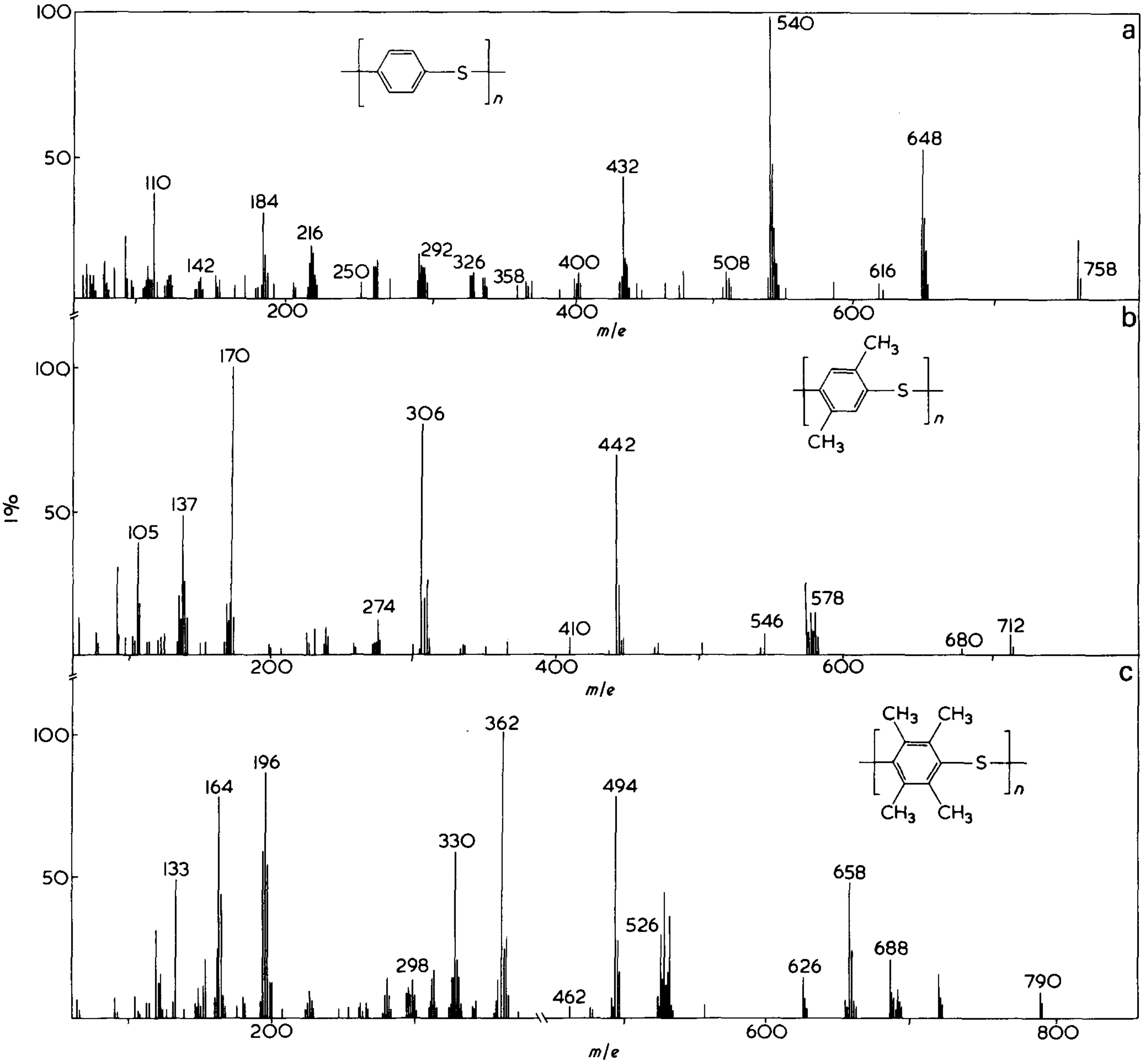
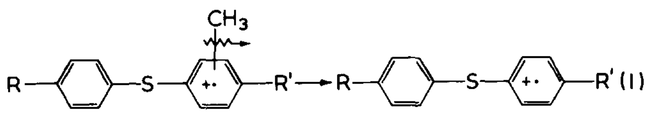


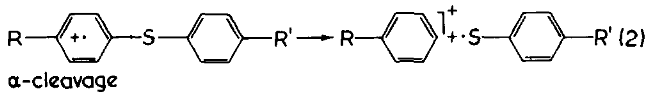
Figure 1 (a) Mass spectrum (15 eV) of the products of thermal degradation at 435°C of polymer I. (b) Mass spectrum (15 eV) of the products of thermal degradation at 290°C of polymer II. (c) Mass spectrum (15 eV) of the products of thermal degradation at 290°C of polymer III.

room temperature, in the mass spectrometer ion source, when the temperature is sufficiently high, the thermal cleavage generates volatile fragments which undergo electron impact fragmentation before detection by the spectrometer analyser.

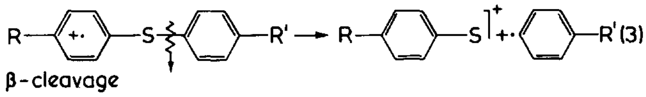
Accordingly, in order to account for the mass spectra relative to the pyrolysates of polymers I–III (*Figure 1*), one must consider the most likely fragmentation reactions.



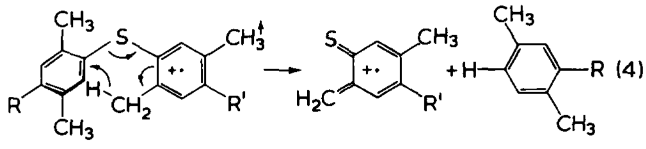
Alkyl-cleavage



α-cleavage



β-cleavage



Ortho-rearrangement

Only two fragmentation processes (2 and 3) are possible in the case of the unsubstituted polymer I. For this polymer, thermal fragments corresponding to oligomers with α-phenyl-ω-thio sequences are preferentially generated. From these fragments, through hydrogen uptake in the ion source of the spectrometer, phenyl and mercapto end-groups are formed, but they correspond to low intensity peaks in the spectrum in *Figure 1a* (*m/e*: 110, 326). Instead, peaks corresponding to fragments with formal radical end-groups are found to

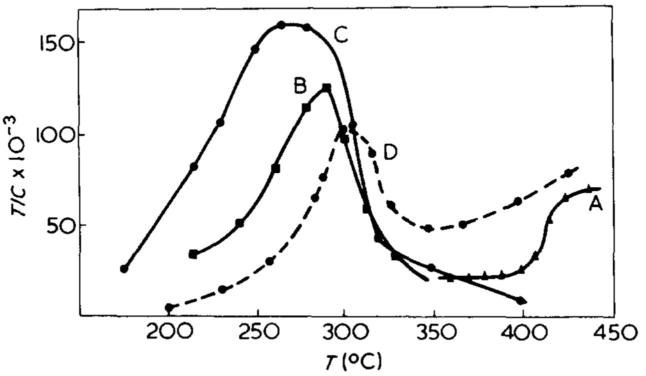


Figure 2 Volatilization rate profiles (total ion current against temperature) relative to polymers I–III. Total ion current expressed as the sum of absolute ion intensities. A, polymer I, intensity X 10; B, polymer II; C, polymer III; D, polymer IV, intensity X 10^{-1}

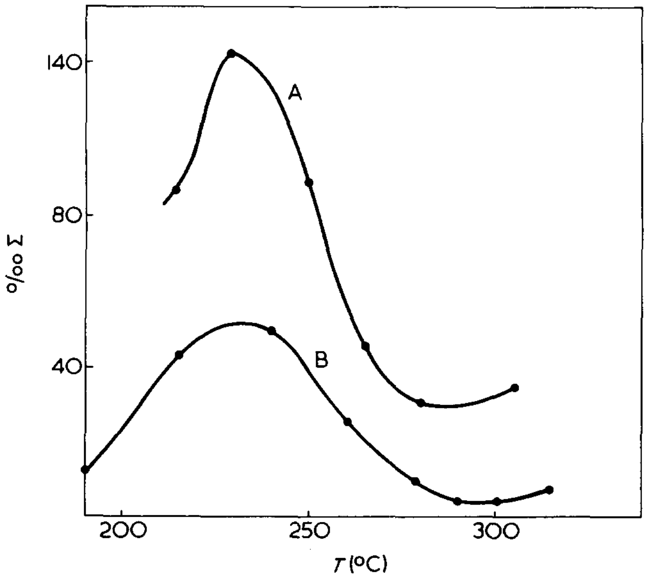


Figure 3 Intensity of the sulphur peak at *m/e* 64 as a function of temperature for polymers II and III. A, polymer III, *m/e* 64, intensity X 10; B, polymer II, *m/e* 64

have higher intensity (*m/e*:216, 432, 540, 648, 758). This may be interpreted by considering the possibility of a resonance stabilization of the diradical structures within the phenyl sulphide chain. Furthermore, inspection of *Figure 1a* reveals very weak fragments with two mercapto end-groups (*m/e*: 142; 250; 358), generated by hydrogenation of the corresponding dithio radicals, and also reveals the presence of weak fragments with two phenyl radical end-groups (*m/e*: 184; 292; 400; 508; 616).

Coming now to the *ortho*-methyl substituted polymers II and III, the relative intensity of the various classes of fragments seen above changes dramatically. In fact, for polymer II the fragments with two mercapto end-groups are the most intense peaks in the spectrum (*Figure 1b*: *m/e*: 170; 306; 442; 578; 712). In our opinion, these fragments result mainly from the hydrogenation of fragments generated by the *ortho*-rearrangement (reaction 4); the latter rearrangement clearly cannot take place in polymer I. An alternative interpretation would be that the methyl substitution induces a higher frequency of β-cleavages (reaction 3) with respect to α-cleavages (reaction 2) which are instead dominant in the unsubstituted polymer I. Although a contribution of this kind cannot be excluded, evidence exists that the intramolecular *ortho*-rearrangement is the predominant electron impact induced process in *ortho*-methyl substituted molecules[3]. Besides, a contribution due to cleavage of the disulphide linkages present in polymer II must be taken in account.

Also for polymer III the α-duryl-ω-thio fragments with formal radical end-groups appear with negligible intensity (*Figure 1c*). The peak at *m/e* 164, formally belonging to this family, is instead originated by an *ortho*-rearrangement on the terminal sequence of a thermally formed oligomer. This is also true for the peak at *m/e* 196, which appears with high abundance in the spectrum. The peaks at *m/e* 330; 494 and 658 have also high abundance corresponding to hydrogenated α-duryl-ω-thio fragments, and the peaks at *m/e* 362 and 526 corresponding to fragments with two mercapto end-groups. The latter are formed as seen previously for the corresponding fragments in polymer II.

In *Figure 2* the intensities of the total ion current (*TIC*) against the pyrolysis temperatures are given for polymers I–III together with the total ion current curve for the poly(*p*-phenylene disulphide) (IV).

A remarkable difference exists in the relative thermal stabilities of the unsubstituted polymer I and the two *ortho*-methyl substituted polymers II and III. The comparison of *TIC* curves clearly reveals that the different thermal stability can be attributed to the disulphide bridges content of the methyl substituted polymers. In fact, *TIC* curves indicate that thermal degradation for polymers II and III occurs in about the same range of temperature as for poly(*p*-phenylene disulphide) (IV). The intensity of the peak at *m/e* 64 as a function of temperature for polymers II and III (*Figure 3*) indicates loss of sulphur at about 200°–250°C, confirming that the thermal degradation process for the substituted polymers is similar to that of poly(*p*-phenylene sulphide).

ACKNOWLEDGEMENT

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