Thermal decomposition processes in aliphatic–aromatic polysulphides investigated by electron impact and chemical ionization mass spectrometry

G. Montaudo and E. Scamporrino
Dipartimento di Scienze Chimiche, Università di Catania, Viale Andrea Doria 6, 95125 Catania, Italy

and C. Puglisi and D. Vitalini
Istituto per la Chimica e la Tecnologia dei Materiali Polimerici, Consiglio Nazionale delle Ricerche, Viale Andrea Doria 6, 95125 Catania, Italy

(*Received 12 May 1986*)

The thermal degradation of four aliphatic–aromatic polysulphides was investigated by direct pyrolysis in the ion source of a mass spectrometer operating both in electron impact and chemical ionization modes. The overall evidence indicates that the primary thermal decomposition processes of these polysulphides yield cyclic sulphides or disulphides according to a backbiting process initiated at the SH ends. A β-CH hydrogen transfer process occurring in parallel with the former produces compounds with both olefin and SH end-groups.

(Keywords: thermal decomposition; aliphatic–aromatic polysulphides; mass spectrometry)

INTRODUCTION

The study of thermal degradation of polymers by direct pyrolysis mass spectrometry (DPMS) yields important information[1–4]. The pyrolysis is achieved very close to the ion source and no problem of transport exists; fragments of high mass, which are often essential for the structural characterization of the polymer, can be detected, whereas they are often lost using other techniques. The main problem connected with this technique is, however, the identification of the products in the spectrum of the multicomponent mixture produced by thermal degradation. In fact, in the mass spectrum of a polymer, the molecular ions of the pyrolysis compounds will appear mixed with the fragment ions formed in the ionizing step. In some instances, identification of thermal degradation products can be achieved by using soft ionization methods, exact mass measurements or by matching spectra of authentic samples[4]. In other cases, MS/MS analysis has been applied with success[5].

In previous studies we have investigated several classes of polymers by the DPMS method[4]. Here we report a similar study, for some aliphatic–aromatic polysulphides (*Table 1*), designed to characterize the primary thermal degradation processes occurring in these polymers. A linked scan MS technique has been used to confirm the identity of some thermal degradation compounds.

The results reported in this work indicate that the mechanism of primary thermal degradation of polysulphides I–IV (*Table 1*) involves a backbiting process, most likely initiated at the chain ends, which leads to the formation of cyclic compounds. A β-CH hydrogen transfer reaction from the methylene group to the sulphur atom also occurs in polysulphides II–IV and produces compounds with thiol and olefin end-groups.

EXPERIMENTAL

Materials

Basic materials were commercial products appropriately purified before use.

Polymer synthesis

Polymers I–IV were synthesized starting from 1,3-benzenedithiol and the appropriate dibromoalkane or diiodomethane (polymer I). In a typical procedure 0.648 g of sodium (0.028 mol) was dissolved in 20 ml of anhydrous ethanol and 1.97 g of 1,3-benzenedithiol (0.0141 mol) was added. The solution was refluxed with stirring while 2.85 g of 1,3-dibromopropane (0.0141 mol) in 35 ml of benzene was added. When the vigorous reaction subsided, another 35 ml of benzene was added and the mixture was refluxed for 5 h. The hot mixture was filtered to remove NaBr and the solution was cooled in a freezer. Polymer is recovered as a white powder and dried under vacuum at room temperature. The solution was dried using a rotary evaporator and analysed by MS and g.p.c.: it consisted mainly of cyclic oligomers[6].

Mass spectrometry

Mass spectra were obtained using an LKB 9000 mass spectrometer and a Kratos MS 50 S double focusing mass

0032–3861/87/030477–07$03.00

spectrometer equipped with an Eclipse/120 data system from Data General using DS 55 Kratos software. MS analysis was carried out using the direct insertion probe for solid materials heated from 30 to 400°C at a heating rate of 10°C min^{-1} by the method described elsewhere[1]. Electron impact (EI) mass spectra were obtained at 18 eV. Chemical ionization (CI) was performed using ammonia (99.998 %) as reagent gas, purchased from Matheson Gas Products.

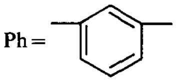
Viscometry

Inherent viscosities of the polymers investigated ($\eta_{\text{inh}} = \ln \eta_r / c$; $c = 0.5\ \text{g dl}^{-1}$) were measured in a Desreux–Bishoff suspended level viscometer that contained a coarse sintered-glass filter attached just below the reservoir through which the solution passes as it rises into the capillary. The measurements were performed on purified polymers in *N*-methylpyrrolidone (NMP) at 50°C.

Table 1 Structure, thermal stability and inherent viscosity of polysulphides I–IV

Polysulphide	Structure	*PDT* (°C)[a]	η_{inh}
I	$-\!\left[S-Ph-S-CH_2\right]_n$	350	0.10
II	$-\!\left[S-Ph-S-(CH_2)_2\right]_n$	355	0.11
III	$-\!\left[S-Ph-S-(CH_2)_3\right]_n$	390	0.10
IV	$-\!\left[S-Ph-S-(CH_2)_6\right]_n$	390	0.16

[a] Temperature of maximum rate of polymer degradation from t.g. experiments (10°C min^{-1}); nitrogen flow rate 60 ml min^{-1}

Ph =


Thermogravimetry

A Perkin–Elmer TGS-2 thermal analyser was used to determine the thermal stability of the polymers. Experiments were carried out on samples of about 2 mg under a nitrogen flow rate of 60 ml min^{-1} at a furnace heating rate of 10°C min^{-1} up to 800°C. Temperatures of maximum rate of polymer degradation (*PDT*) are collected in *Table 1*.

RESULTS AND DISCUSSION

Polysulphide I

Figure 1a shows the EI mass spectrum of polysulphide I recorded at a temperature of 350°C. The structural assignments for the most intense peaks are reported in *Table 2*.

Table 2 Molecular ions of the thermal degradation products and EI fragments as detected in the DPMS of polysulphide I

Structural assignments	*m/z*(*n*)
$\underline{\left[S-Ph-S-CH_2\right]_n S-Ph-S}$	294(1), 448(2), 602(3)
$\underline{\left[S-Ph-S-CH_2\right]_n}$	308(2), 462(3), 616(4)
$\underline{\left[S-Ph-S-CH_2\right]_n S-Ph}$	416(2), 570(3)
$\underline{\left[S-Ph-S-CH_2\right]_n S-Ph-S-S-Ph}$	402(1), 556(2)
$HS-Ph-S\left[CH_2-S-Ph-S\right]_n CH_3$	156(0), 310(1), 464(2), 618(3)
$HS-CH_2\left[S-Ph-S-CH_2\right]_n S-Ph-S-CH_3$	356(1), 510(2)
$CH_3-S-Ph-S\left[CH_2-S-Ph-S\right]_n CH_2$[a]	169(1), 323(2)

[a] EI fragments

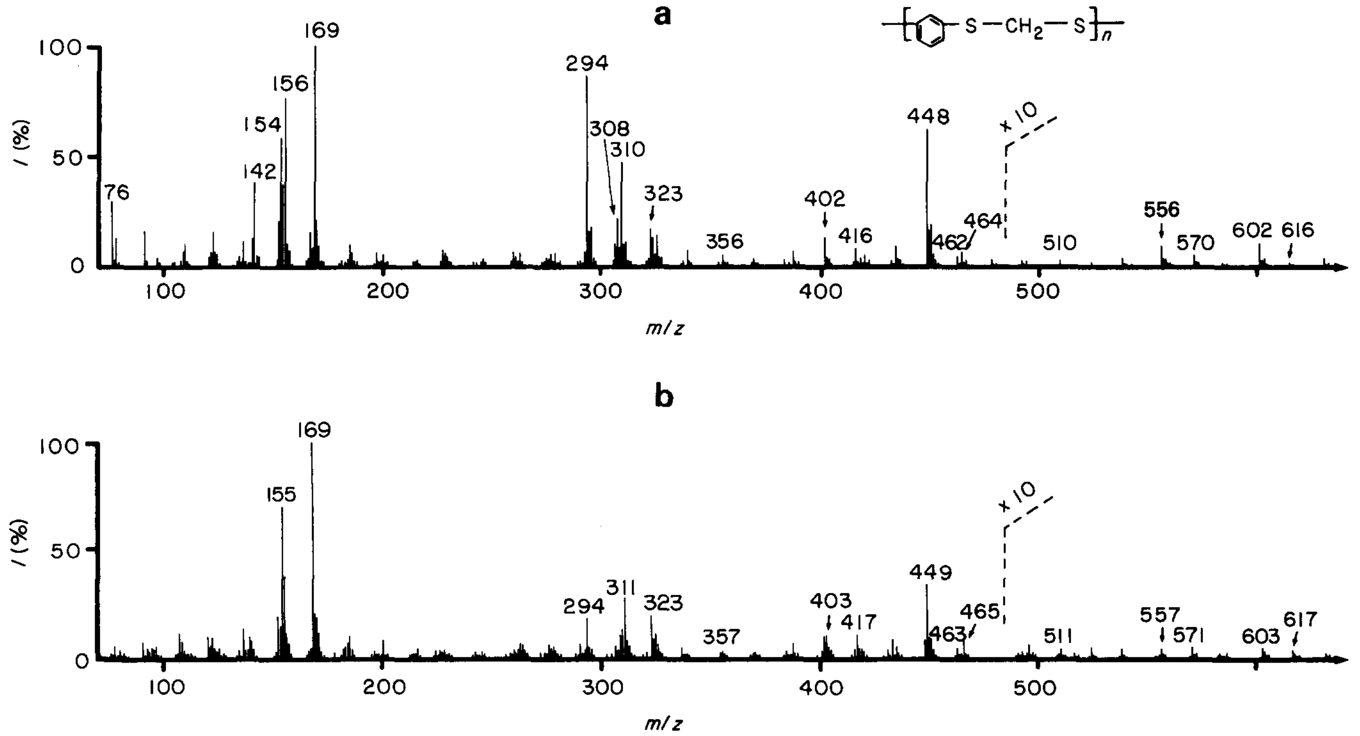


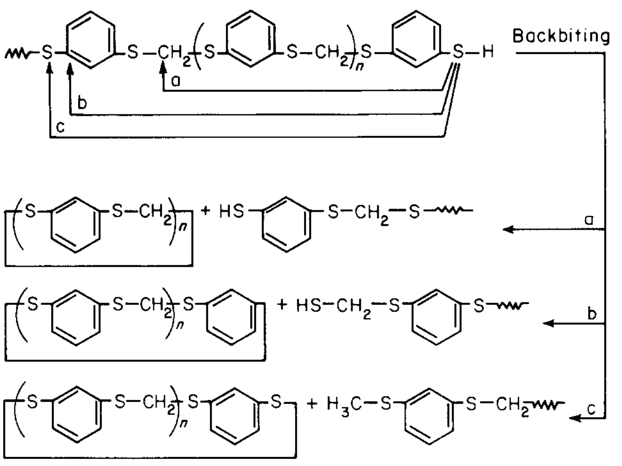
Figure 1 Mass spectra of polysulphide I at 350°C: (a) EI and (b) ammonia CI

In the spectrum appear peaks at $m/z = 294 + n154$ which are assigned to cyclic compounds with a disulphide bridge (*Table 2*). The corresponding peaks of the protonated molecular ions at $m/z = 449$ and $m/z = 603$ are present in the ammonia CI mass spectrum in *Figure 1b*. However, the intense peak at $m/z = 294$ might originate by EI fragmentation since the corresponding $(MH)^+$ peak is absent from the ammonia CI mass spectrum in *Figure 1b* and it appears with lower intensity.

Another series of peaks at $m/z = 308 + n154$, corresponding to cyclic oligomers of polysulphide I, is present in the spectrum in *Figure 1a*. The structural assignment of the peak at $m/z = 308$ to cyclic dimer was confirmed by the comparison of the collision activated decomposition daughter ion (CAD-*B*/*E*) mass spectrum of an authentic cyclic dimer sample with the CAD-*B*/*E* spectrum of the pyrolysis compound corresponding to the peak at $m/z = 308$ (*Figure 1a*)[7].

The series of peaks at $m/z = 416 + n154$ and $m/z = 402 + n154$ in *Figure 1a*, corresponding to cyclic structures in *Table 2*, and the peaks at $m/z = 156 + n154$ and $m/z = 356 + n154$ (*Figure 1a*) corresponding to compounds with methyl and thiol end-groups (*Table 2*), are assigned to molecular ions of pyrolysis compounds by the appearance of the $(MH)^+$ ions in the ammonia CI spectrum in *Figure 1b*.

These results suggest that the primary thermal degradation mechanism of polysulphide I involves a backbiting process initiated by –SH end-groups according to equation (1), which shows the origin of different species of cyclic sulphides whose structure depends on the exchange sites (equation (1), *Table 2*).



(1)

Polysulphide II

Figure 2a shows the EI mass spectrum of polysulphide II taken at 355°C. Two intense peaks at $m/z = 336$ and $m/z = 504$ corresponding to molecular ions of compounds with olefin and SH end-groups are present (*Table 3*). The assignment to open chain fragments instead of cyclic oligomers has been confirmed by the comparison of the CAD-*B*/*E* mass spectrum of the authentic cyclic dimer sample (*MW 336*) with the CAD-*B*/*E* spectrum of the compounds ($m/z = 336$, *Figure 2a*) contained in the mixture of pyrolysis compounds obtained by DPMS of polysulphide II[7]. The peaks at $m/z = 362 + n168$ corresponding to compounds with olefin end-groups at both chain ends (*Table 3*) are also present in the spectrum

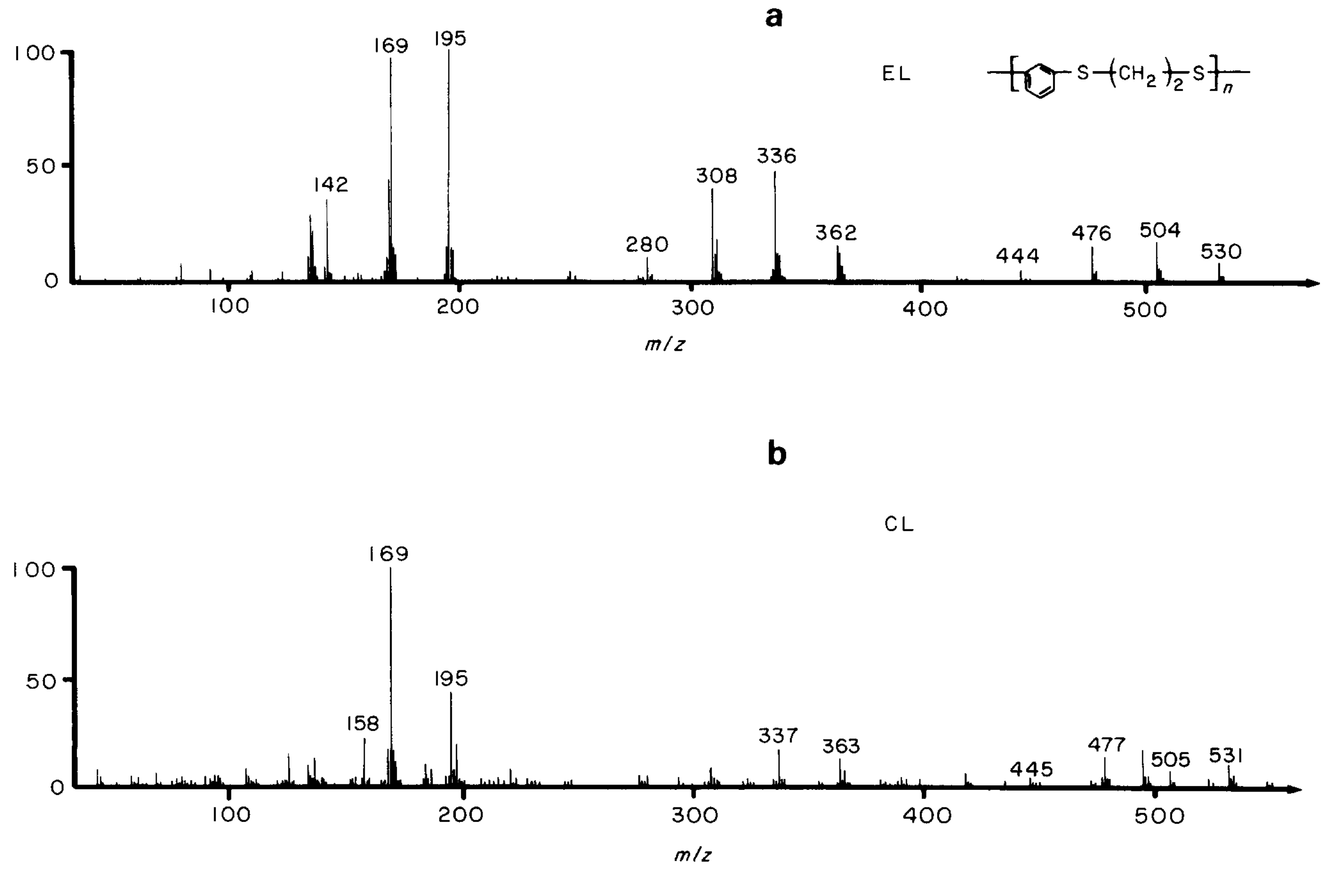
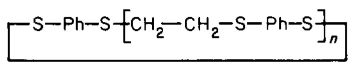
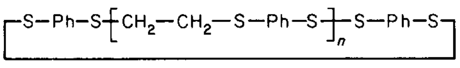


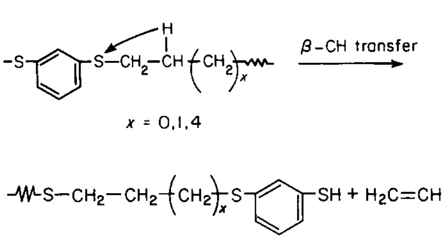
Figure 2 Mass spectra of polysulphide II at 355°C: (a) EI and (b) ammonia CI

Table 3 Molecular ions of the thermal degradation products and EI fragments as detected in the DPMS of polysulphide II

Structural assignments	*m*/*z*(*n*)
$HS{-}Ph{-}S{+}[CH_2{-}CH_2{-}S{-}Ph{-}S]_n{+}CH{=}CH_2$	336(1), 504(2)
$CH_2{=}CH{-}S{-}Ph{-}S{+}[CH_2{-}CH_2{-}S{-}Ph{-}S]_n{+}CH{=}CH_2$	362(1), 530(2)
$CH_2{=}CH{-}S{-}Ph{-}S{+}[CH_2{-}CH_2{-}S{-}Ph{-}S]_n{+}CH_2{-}CH_3$	196(0), 364(1), 532(2)
 $-S{-}Ph{-}S{+}[CH_2{-}CH_2{-}S{-}Ph{-}S]_n{-}$	308(1), 476(2)
$HS{-}Ph{+}[S{-}CH_2{-}CH_2{-}S{-}Ph]_n{+}SH$	142(0), 310(1), 478(2)
 $-S{-}Ph{-}S{+}[CH_2{-}CH_2{-}S{-}Ph{-}S]_n{+}S{-}Ph{-}S{-}$ [a]	280(0), 444(2)
$CH_2{=}CH{-}S{-}Ph{-}S{-}CH_2{-}CH_2$ [a]	195
$HS{-}Ph{-}S{-}CH_2{-}CH_2$ [a]	169

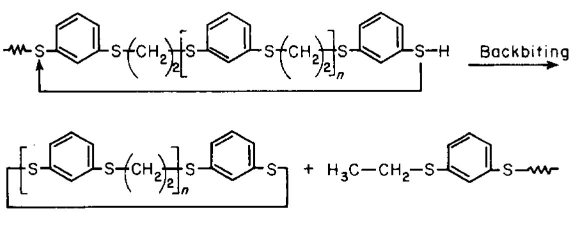
[a] EI fragments

in *Figure 2a*. Therefore, the formation of compounds with olefin end-groups takes place through a primary thermal degradation mechanism which involves a β-CH hydrogen transfer process as depicted in equation (2).



(2)

The peaks at $m/z = 308$ and 476, corresponding to molecular ions of cyclic compounds with a disulphide bridge in *Table 3*, are also present in the spectrum in *Figure 2a*. These peaks may be originated by EI fragmentation of higher molecular weight compounds, since they have been found in the EI spectra of pure samples of cyclic oligomers ($m/z = 336$, 504)[6]. However, the peak at $m/z = 308$, contained in the multicomponent EI spectrum of pyrolysis compounds (*Figure 2a*), does not arise from any parent ion, as shown by the linked scan parent ion (B^2/E) spectrum[7]. This suggests that the peak at $m/z = 308$ and, by analogy, its higher homologues are due to molecular ions originated by thermal degradation of polysulphide II through a backbiting mechanism as illustrated in equation (3).



(3)

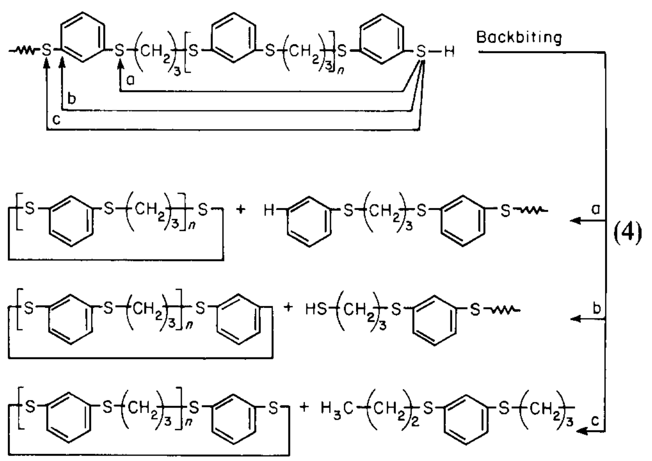
This process also produces compounds with methyl end-groups ($m/z = 196 + n168$, *Table 3*) which are missing in the EI spectrum (*Figure 2a*) but are present in the ammonia CI mass spectrum in *Figure 2b* as protonated molecular ions $(MH)^+$ at $m/z = 197 + n168$, accompanied by their ammonia adducts $(M{-}NH_4)^+$ at $m/z = 382$ and 550.

The peaks at $m/z = 142 + n168$ (*Figure 2a*) may be tentatively assigned to thermally formed 1,3-benzenedithiol and its higher homologues, but they may originate by EI fragmentation since they appear with low intensity or are missing from the ammonia CI spectrum (*Figure 2b*).

Polysulphide III

Figure 3a shows the EI mass spectrum of polysulphide III taken at 390°C. The structural assignments for the most intense peaks are reported in *Table 4*. In the spectrum appear a series of intense peaks at $m/z = 182 + n182$ probably corresponding to molecular ions of compounds with olefin and SH end-groups (*Table 4*), which are isomeric with cyclic oligomers of polysulphide III. The presence in the spectrum of other compounds showing diolefin ($m/z = 222 + n182$), propyl-olefin ($m/z = 224 + n182$) and phenyl-olefin ($m/z = 332 + n182$, $m/z = 285 + n182$) end-groups (*Table 4*) supports the formation of open chain fragments through a β-CH hydrogen transfer process as primary thermal degradation mechanism (equation (2)).

The presence in the spectrum of peaks at $m/z = 214 + n182$, $m/z = 322 + n182$ assigned to cyclic compounds with a disulphide bridge and the peaks at $m/z = 290 + n182$ assigned to cyclic sulphides (*Table 4*) also suggests the occurrence of a backbiting process, depicted in equation (4), which produces compounds with methyl, thiol and phenyl end-groups (*Table 4*).



(4)

The peak assignments reported in *Table 4* are related to pyrolysis products by the appearance of the corresponding protonated molecular ions $(MH)^+$ in the ammonia CI mass spectrum shown in *Figure 3b*. The peak at $m/z = 142$ (base peak in the EI spectrum in *Figure 3a*) is assigned to 1,3-benzenedithiol (*Table 4*). It appears with lower intensity in the CI spectrum while its higher homologues are completely missing from this spectrum (see above, polysulphide II).

Polysulphide IV

The EI mass spectrum recorded at 390°C of polysulphide IV illustrated in *Figure 4a* is dominated by a series of peaks at $m/z = 224 + n224$ corresponding to compounds with olefin and SH end-groups (*Table 5*). The assignments to pyrolysis compounds are confirmed by the ammonia CI mass spectrum (*Figure 4b*) in which the corresponding protonated molecular ions $(MH)^+$ are very intense (the peak at $m/z = 449$ is the base peak in this spectrum).

The presence in the spectrum (*Figure 4a*) of other peaks at $m/z = 306 + n224$, $m/z = 340 + n224$ and $m/z = 308 + n224$ corresponding to compounds with olefin end-groups (*Table 5*) suggests a primary thermal

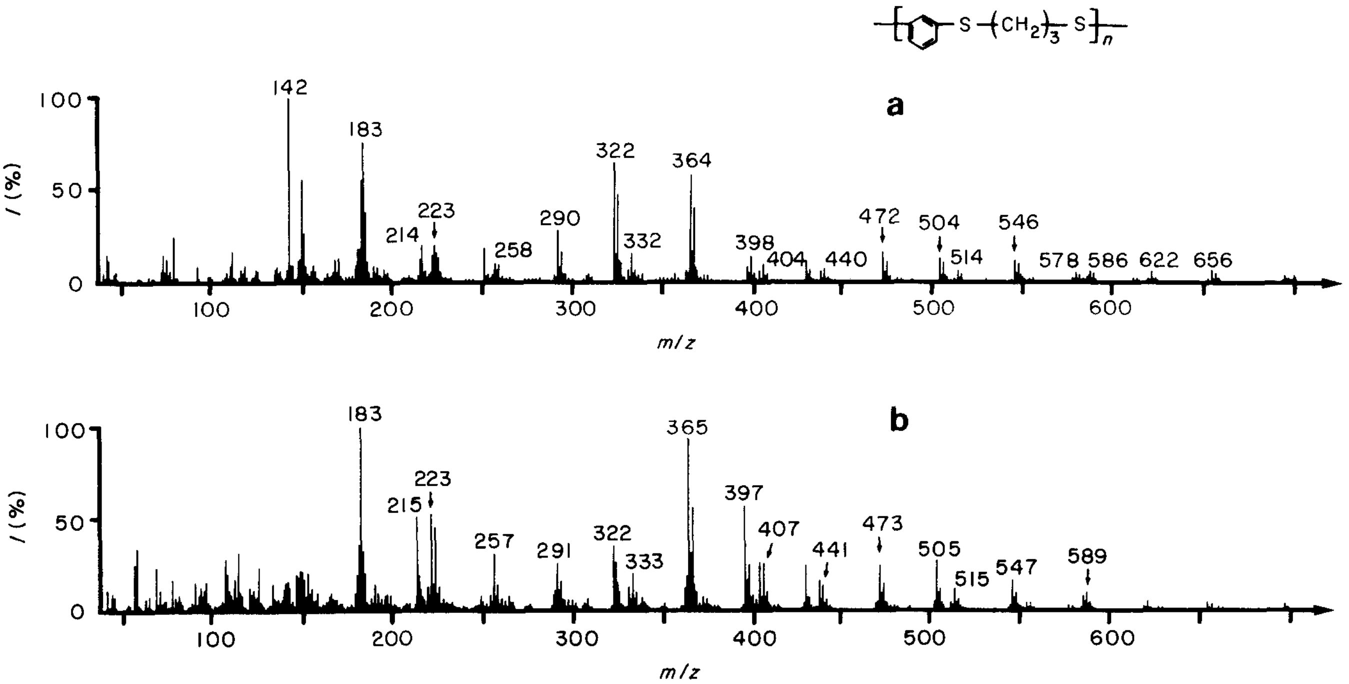


Figure 3 Mass spectra of polysulphide III at 390°C: (a) EI and (b) ammonia CI

Table 4 Molecular ions of the thermal degradation products as detected in the DPMS of polysulphide III

Structural assignments	m/z(n)
$\mathrm{HS{-}Ph{-}S{-}[(CH_2)_3{-}S{-}Ph{-}S]_n{-}CH_2{-}CH{=}CH_2}$	182(0), 364(1), 546(2)
$\mathrm{CH_2{=}CH{-}CH_2{-}S{-}Ph{-}S{-}[(CH_2)_3{-}S{-}Ph{-}S]_n{-}CH_2{-}CH{=}CH_2}$	222(0), 404(1), 586(2)
$\mathrm{CH_3{-}CH_2{-}CH_2{-}S{-}Ph{-}S{-}[(CH_2)_3{-}S{-}Ph{-}S]_n{-}CH_2{-}CH{=}CH_2}$	224(0), 406(1), 588(2)
$\mathrm{CH_3{-}CH_2{-}CH_2{-}[S{-}Ph{-}S{-}(CH_2)_3]_n{-}S{-}Ph{-}SH}$	366(1), 548(2)
$\mathrm{HS{-}Ph{-}S{-}[(CH_2)_3{-}S{-}Ph{-}S]_n{-}(CH_2)_3{-}SH}$	398(1), 580(2)
$\mathrm{[S{-}Ph{-}S{-}(CH_2)_3]_n{-}S}$	214(1), 396(2), 578(3)
$\mathrm{S{-}Ph{-}S{-}[(CH_2)_3{-}S{-}Ph{-}S]_n}$	322(1), 504(2)
$\mathrm{S{-}Ph{-}S{-}[(CH_2)_3{-}S{-}Ph{-}S]_n{-}Ph}$	290(1), 472(2), 656(3)
$\mathrm{HS{-}[Ph{-}S{-}(CH_2)_3{-}S]_n{-}Ph{-}H}$	292(1), 474(2), 658(3)
$\mathrm{CH_2{=}CH{-}CH_2{-}[S{-}Ph{-}S{-}(CH_2)_3]_n{-}S{-}Ph{-}H}$	332(1), 514(2)
$\mathrm{CH_2{=}CH{-}CH_2{-}[S{-}Ph{-}S{-}(CH_2)_3{-}S]_n{-}S{-}Ph{-}S{-}Ph{-}H}$	258(0), 440(1), 622(2)
$\mathrm{HS{-}Ph{-}[S{-}(CH_2)_3{-}S{-}Ph]_n{-}SH}$	142(0), 324(1), 506(3)

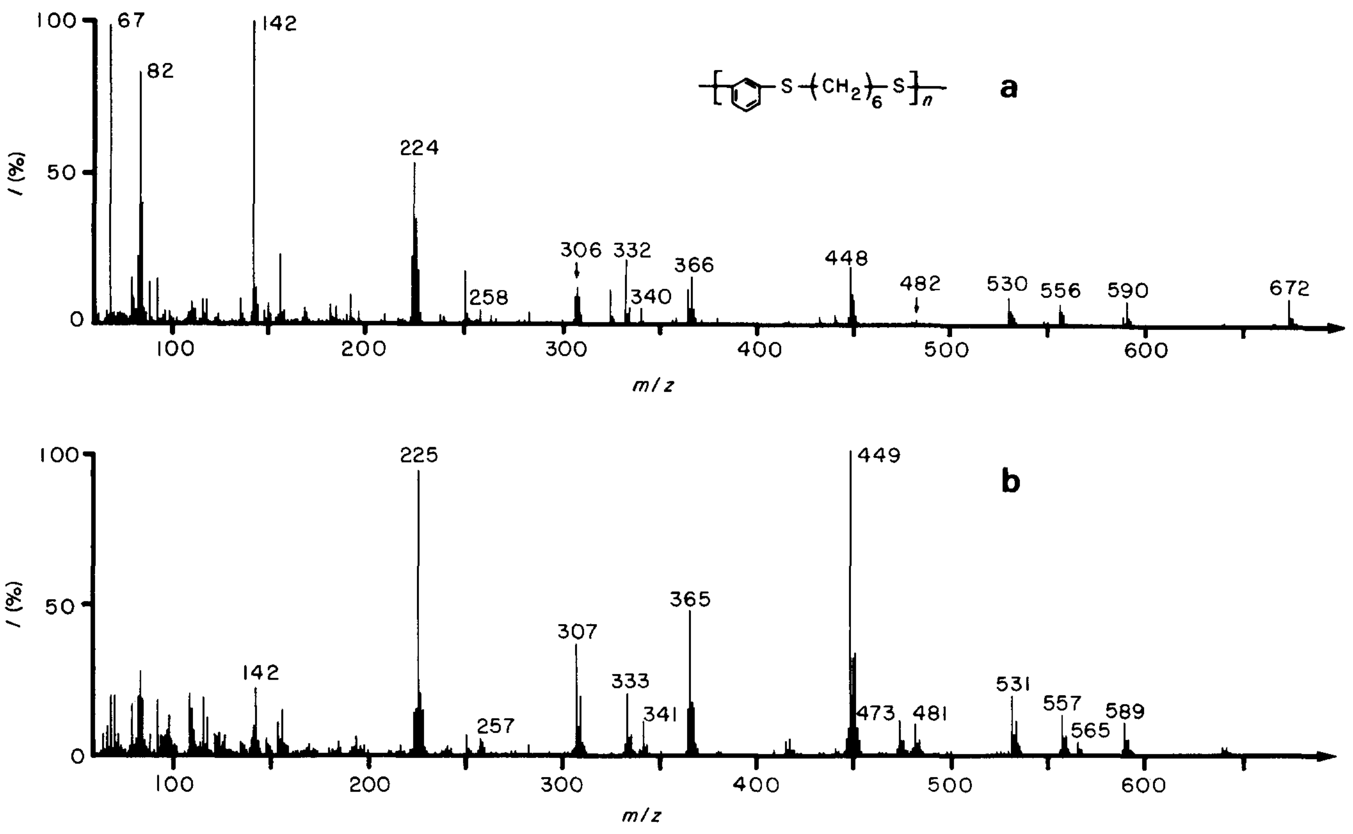
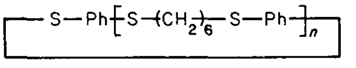


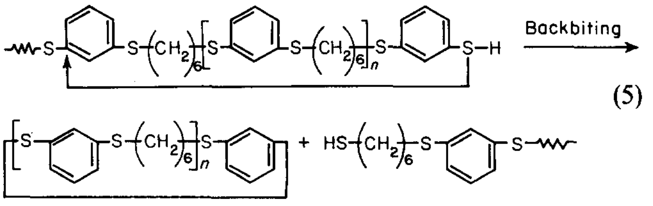
Figure 4 Mass spectra of polysulphide IV at 390°C: (a) EI and (b) ammonia CI

Table 5 Molecular ions of the thermal degradation products as detected in the DPMS of polysulphide IV

Structural assignments	*m/z*(*n*)
$HS{-}Ph{-}S[(CH_2)_6{-}S{-}Ph{-}S]_n(CH_2)_4CH{=}CH_2$	224(0), 448(1), 672(2)
$CH_2{=}CH(CH_2)_4S{-}Ph{-}S[(CH_2)_6{-}S{-}Ph{-}S]_n(CH_2)_4CH{=}CH_2$	306(0), 530(1)
$HS(CH_2)_6S{-}Ph{-}S[(CH_2)_6{-}S{-}Ph{-}S]_n(CH_2)_4CH{=}CH_2$	340(0), 564(1)
$CH_2{=}CH(CH_2)_4S{-}Ph{-}S[(CH_2)_6{-}S{-}Ph{-}S]_n(CH_2)_5CH_3$	308(0), 532(1)
$HS{-}Ph[S(CH_2)_6S{-}Ph]_nSH$	142(0), 366(1), 590(2)
$HS{-}Ph{-}S[(CH_2)_6S{-}Ph{-}S]_n(CH_2)_6SH$	258(0), 482(1)
	332(1), 556(2)

degradation mechanism involving a β-CH hydrogen transfer process (equation (2)).

The presence in the spectrum of peaks at $m/z=332$ and $m/z=556$ corresponding to cyclic compounds also in this case suggests a parallel thermal degradation mechanism through a backbiting process (equation (5)) which may generate compounds with thiol end-groups ($m/z=258$ and $m/z=482$, *Table 5*).



(5)

The assignments to thermal degradation products are confirmed by the appearance in the CI spectrum (*Figure 4b*) of the corresponding protonated molecular ions $(MH)^+$ at $m/z=259$ and $m/z=483$. The peak at $m/z=142$ (1,3-benzenedithiol) appears to have the same EI origin as in the cases of polysulphides II and III.

ACKNOWLEDGEMENT

The work was carried out under partial financial support of the Ministry of Public Education and Consiglio Nazionale delle Ricerche, Roma, Italy.

REFERENCES

1 Foti, S. and Montaudo, G. in 'Analysis of Polymer Systems' (Eds. L. S. Bark and N. S. Allen), Applied Science, London, 1982, p. 103, and references therein
2 Schulten, H. R. and Lattimer, R. P. *Mass Spectrom. Rev.* 1984, **3**, 231
3 Montaudo, G., *Br. Polym. J.*, 1986, **18**, 231
4 Montaudo, G. and Puglisi, C. in 'Developments in Polymer Degradation', Vol. 7 (Ed. N. Grassie), Applied Science, London, 1986, and references therein
5 Foti, S., Maravigna, P., Montaudo, G. and Liguori, A., *Anal. Chem.* 1982, **54**, 674
6 Montaudo, G., Puglisi, C., Scamporrino, E. and Vitalini, D., *J. Polym. Sci., Polym. Chem. Edn.* 1986, in press
7 Montaudo, G., Puglisi, C., Scamporrino, E. and Vitalini, D., *J. Anal. Appl. Pyrol.* 1987, in press