Mechanism of thermal generation of poly(*p*-phenylene vinylene) from poly(*p*-xylene-α-dimethylsulphonium halides)

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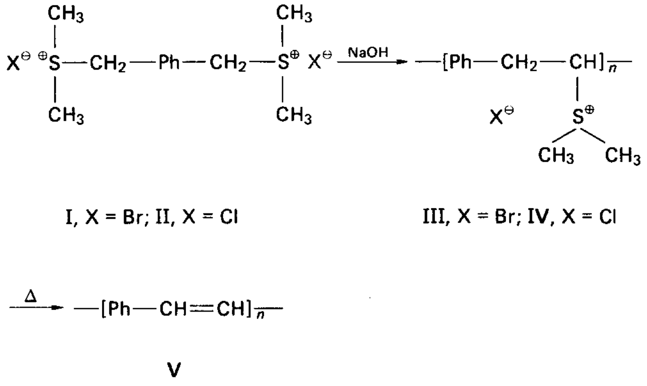
The thermal conversion of poly(*p*-xylene-α-dimethylsulphonium halides) into poly(*p*-phenylene vinylene) (PPV) can occur through two concomitant reactions. The principal reaction is an elimination of dimethyl sulphide and halogen acid, while the second reaction, an undesirable one, is the nucleophilic attack of the halide counterion on a methyl group to form the methyl halide and a methyl sulphide. The two thermal processes were observed in the pyrolysis of both poly(*p*-xylene-α-dimethylsulphonium bromide) and poly(*p*-xylene-α-dimethylsulphonium chloride). On storage at room temperature, poly(*p*-xylene-α-dimethylsulphonium halides) undergo partial decomposition to PPV, as shown by thermogravimetric experiments. The flash pyrolysis–gas chromatography–mass spectrometry of PPV obtained by the thermal conversion of poly(*p*-xylene-α-dimethylsulphonium bromide) at 400°C was also investigated.

(Keywords:

INTRODUCTION

Poly(*p*-phenylene vinylene) (PPV) on treatment with strong oxidizing agents ('doping') has been shown to be a good electrical conductor[1–3]. The synthesis of high-molecular-weight PPV (**V**) by the thermal conversion of films of an intermediate water-soluble polyelectrolyte, **III** or **IV**, in the reaction sequence shown below, has been described[4–6]:



$$X^{\ominus}\,{}^{\oplus}S(CH_3)_2-CH_2-Ph-CH_2-S^{\oplus}(CH_3)_2\,X^{\ominus} \xrightarrow{NaOH} -[Ph-CH_2-CH(S^{\oplus}(CH_3)_2\,X^{\ominus})]_n-$$

I, X = Br; II, X = Cl

III, X = Br; IV, X = Cl

$$\xrightarrow{\Delta} -[Ph-CH{=}CH]_n-$$

V

For this sequence, the bis(sulphonium salt) monomer, **I** or **II**, was polymerized in an aqueous sodium hydroxide solution to obtain a soluble poly(*p*-xylene-α-dimethylsulphonium halide), **III** or **IV**, in high molecular weight. Simple heating of the latter polymers in film form resulted in the formation of PPV[4–6]. Dimethyl sulphide and hydrochloric or hydrobromic acid were reported to be evolved from **III** or **IV** on heating, but the reaction was not studied in detail[4–6].

Since the process of thermal generation of PPV from its precursor might influence the structure of the final polymer, it is important to study in some detail the reaction products and the mechanism by which they are found. In the present investigation, the synthesis of poly(*p*-xylene-α-dimethylsulphonium bromide), **I**, was also undertaken in order to compare the effect of the counterion on the distribution of the thermal reaction products.

EXPERIMENTAL

p-Xylene-bis(dimethylsulphonium bromide), I

For the preparation of this monomer, **I**, 5 g (0.0189 mol) of α,α'-dibromo-*p*-xylene (Aldrich) was dissolved in 200 ml of methanol and 50 ml of water was added with stirring at 50°C. To this solution was added 9.3 g (0.151 mol; 4 times the stoichiometric amount) of dimethyl sulphide, and a rapid reaction began immediately. After 1 h the solution was concentrated by evaporation and poured in 500 ml of acetone to obtain white crystals of **I**. The crude product was crystallized from boiling methanol; m.p., 192–193°C, with decomposition. A sample of this product was placed in the probe of a mass spectrometer and heated to 200°C to yield the mass spectrum shown in *Figure 1*.

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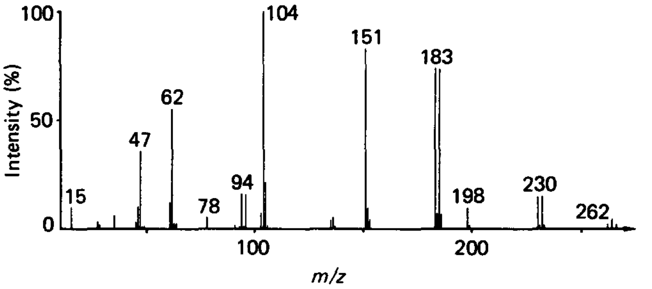


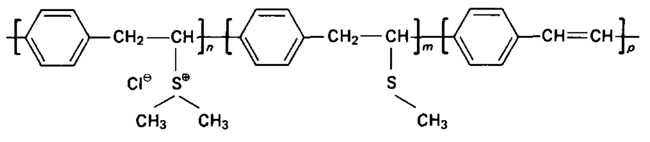
Figure 1 Electron impact mass spectrum of monomer **I** recorded at 18 eV and a probe temperature of 200°C

Poly(p-xylene-α-dimethylsulphonium bromide), **III**

Polymer **III** was synthesized by mixing equal volumes of a 0.5 M aqueous solution of monomer **I** with a 0.5 M aqueous solution of NaOH at −2°C under nitrogen with stirring. After 1 h a white, spongy precipitate was formed. The solution was neutralized with dilute hydrochloric acid, and the polymer was recovered by filtration, washed with ice water, then with acetone, and dried under vacuum at 0°C. The product was stored in a freezer under nitrogen. The colour of this polymer as formed was slightly pale yellow, and it was readily soluble in water.

Poly(p-xylene-α-dimethylsulphonium chloride), **IV**

This polymer was synthesized according to the procedure described in ref. 4, but the sample used had been stored for an extended period of time, and it was found to be yellow in colour and partially insoluble in water. Undoubtedly during the storage period the original sample was transformed into a polymer that contained both vinylene, **V**, and methyl sulphide, **VI**, units as shown below and as discussed in the following section:



IV VI V

For comparison, polymer **III** was also partially converted to these units by maintaining a sample of **III** at 50°C in air. Small amounts of these treated samples were analysed by both thermogravimetric (t.g.) and mass spectrometric (m.s.) analyses after 3 h, after 7 h and after 20 h at this temperature; these samples are designated **IIIa**, **IIIb** and **IIIc**, respectively.

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 nitrogen at a flow rate of 60 ml min^{-1} and at a furnace heating rate of 10°C min^{-1} over the temperature range from 50 to 800°C.

Mass spectrometry

Mass spectra were obtained with a Kratos MS 50S double-focusing mass spectrometer equipped with an Eclipse/120 data system from Data General with DS 55 Kratos software. M.s. analyses were carried out by use of a direct insertion probe for solid monomers and polymers, which were heated from 20 to 400°C at a heating rate of 10°C min^{-1} by the method described elsewhere[7]. Electron impact (EI) mass spectra were obtained at 18 eV.

Flash pyrolysis–gas chromatography–mass spectrometry

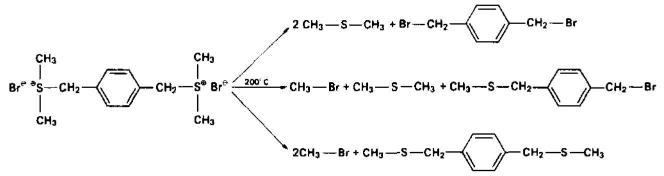
Flash pyrolysis experiments were carried out on a Curie Point Pyrolyzer model 310 from Fisher at a heating rate of either 400°C or 800°C per 7 s under He. The weight of the samples analysed was about 0.5 mg. Analyses of the pyrolysis products were performed on a Carlo Erba 4200 Gas Chromatograph combined with a Kratos MS 50 S double-focusing mass spectrometer. Gas chromatographic separation was accomplished on a WCOT silica capillary column (30 m × 0.22 mm i.d.), coated with polar stationary-phase 'Superox' (Alltech). The oven temperature programme was the following: an initial temperature of 30°C, and an initial time of 5 min, then a heating rate of 4°C min^{-1} until a final temperature of 250°C was reached. Helium was used as the carrier gas. Mass spectra were acquired by Data General Eclipse/120 data system with Kratos DS 55 software. The mass spectrometer was scanned repetitively from $m/z = 17$ to $m/z = 400$ at a scan rate of 0.7 s/decade; the ionizing conditions were 18 eV. The spectra were stored on a disc and manipulated by the data system in several ways, including display in real time. The analysis of g.c.–m.s. data and the structural assignments of each compound were made by the inspection of EI fragmentation pathways in the mass spectra. Furthermore, some assignments were confirmed by comparison of the pyrolysis–g.c.–m.s. spectra with those of the corresponding compounds present in the Kratos DS 55 library.

RESULTS AND DISCUSSION

Thermal decomposition of p-xylene-bis(dimethylsulphonium bromide, **I**

Monomer **I** was pyrolysed by the direct pyrolysis–mass spectrometry (d.p.–m.s.) technique at 200°C. Decomposition was observed to begin at about 190°C. The pyrolysis mass spectrum obtained at the probe temperature of 200°C at 18 eV is shown in *Figure 1*. Because **I** is not volatile, the molecular ion is missing, of course, but a triplet is seen at $m/z = 262$, 264, 266 corresponding to α,α′-dibromo-*p*-xylene. A successive EI bromine loss from the latter ion generated a doublet at $m/z = 183$, 185 and a singlet at $m/z = 104$. The doublet at $m/z = 230$, 232 in *Figure 1* is presumably for another pyrolysis product, α-bromo-α-methylthio-*p*-xylene, and the EI bromine loss from this ion generated a peak at $m/z = 151$. The peak at $m/z = 198$ in *Figure 1* is believed to correspond to the bis-sulphide derivative, α,α′-bis(methylthio)-*p*-xylene. Dimethyl sulphide ($m/z = 62$) and methyl bromide ($m/z = 94$, 96) are also present among pyrolysis products in *Figure 1*.

Based on the m.s. identification of these compounds, the mechanism of thermal decomposition of **I** can be represented by the three parallel reactions shown below:



Two different reactions are involved in these processes. The first reaction, as expected, is the nucleophilic dissociation of **I** into the starting reactants, dimethyl sulphide and α,α′-dibromo-*p*-xylene. The second reaction is the generation of methyl bromide by the alternative nucleophilic attack of the bromide ion on a methyl group. It would also be expected that, in the thermal decomposition of polymer **III** obtained from **I**, these two thermal reactions should be observed too.

Thermal conversion of poly(p-xylene-α-dimethylsulphonium halides), III *and* IV*, to poly(p-phenylene vinylene),* V

In *Table 1* is reported the mass balance for the transformation of four samples of poly(*p*-xylene-α-dimethylsulphonium bromide), **III**, three of which had been subject to thermal ageing at 50°C, and of one sample of poly(*p*-xylene-α-dimethylsulphonium chloride), **IV**, which had undergone extended storage before analysis. The corresponding t.g. analyses for each of these samples are shown in *Figure 2*.

The data in *Table 1* and *Figure 2* suggest that the sample of polymer **III**, which had been stored at low temperature to prevent decomposition, was cleanly converted to poly(*p*-phenylene vinylene) (PPV) by gradual heating up to 450°C with the loss of the theoretical amount by weight, 58%, of by-products, presumably HBr and $(CH_3)_2S$. The pretreated samples, **IIIa–IIIc**, which had been treated for 3, 7 and 20 h, respectively, lost less weight than **III**, indicating that a certain amount of dimethyl sulphide, hydrobromic acid and possibly methyl bromide had been eliminated during the treatment process. Similarly, polymer **IV** lost about two-thirds of the theoretical weight amount, thus indicating that, as expected, some degree of conversion of this sample to PPV occurred during the extended storage period at room temperature.

Table 1 Mass balance for the transformation of poly(*p*-xylene-α-dimethylsulphonium chloride), **IV**, and poly(*p*-xylene-α-dimethylsulphonium bromide), **III**, on heating, as measured by t.g.

	Weight loss (%)			
	First step[a]	Second step[b]	Calculated[c]	PPV (%)[d]
III	53	58	58	0
IIIa (3 h at 50°C)	46	52	58	10
IIIb (7 h at 50°C)	35	43	58	26
IIIc (20 h at 50°C)	17	26	58	55
IV	28	31	48	35

[a] Weight loss (%) between 50 and 300°C in t.g. experiments under N_2 flow

[b] Weight loss (%) between 50 and 450°C in t.g. experiments under N_2 flow

[c] Calculated content of halogen plus dimethyl sulphide (wt %) in each polymer, based on structural formula

[d] PPV generated on ageing (%) =

$$\frac{\text{Calculated weight loss }(\%) - \text{Weight loss at second step }(\%)}{58} \times 100$$

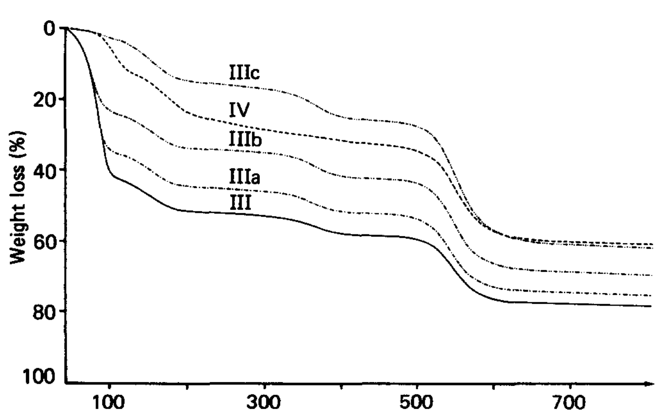
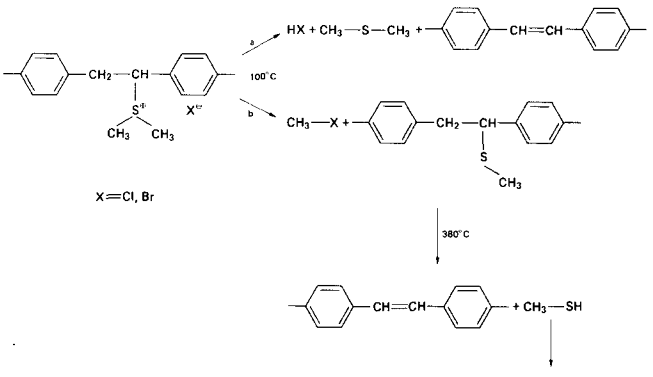


Figure 2 T.g. weight-loss plots for polymer samples: **III**, poly(*p*-xylene-α-dimethylsulphonium bromide) stored at low temperature; **IIIa–IIIc**, treated for 3, 7 and 20 h, respectively, at 50°C in air; **IV**, poly(*p*-xylene-α-dimethylsulphonium chloride) after extended storage at room temperature

Direct pyrolysis–mass spectrometry (d.p.–m.s.) was applied to study the conversions of polymers **III** and **IV** to **V** to determine the chemical structures of the evolving compounds[7]. Samples of either polymer **III** or **IV** were introduced into the ion source of the mass spectrometer through the direct insertion probe for solid samples, and the probe temperature was increased at a rate of 10°C min^{-1} from 20 up to 400°C. The volatile compounds that evolved were monitored as a function of time, and the single ion currents of the five most abundant pyrolysis products are reported in *Figures 3a* and *3b* for polymers **III** and **IV**, respectively. Similar compounds were evolved in the thermal conversion of both polymers **III** and **IV** as shown in these figures.

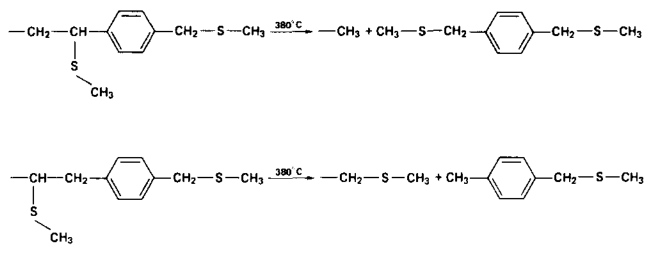
Two concomitant elimination reactions are apparently responsible for the conversion of polymers **III** and **IV** to PPV, as shown below:



The first reaction proceeds by the elimination of either hydrobromic or hydrochloric acid and dimethyl sulphide at a relatively low temperature, while the second reaction proceeds at an intermediate temperature through a nucleophilic attack of the halide counterion on a methyl group of the sulphonium functional to form either methyl bromide or methyl chloride and, at still higher temperatures, to form first methyl mercaptan and then dimethyl disulphide, as shown.

In addition to the gradual pyrolysis experiments, just described, the thermal conversion to PPV was also investigated by fast pyrolysis, Py–g.c.–m.s.[8]. The total ion current (*TIC*) chromatogram of the pyrolysis of polymer **III** at 400°C is shown in *Figure 4*, and peak structural assignments are reported in *Table 2*.

With the exception of hydrobromic acid, which was retained in the g.c. column, the first four peaks are identical to those detected by d.p.–m.s. However, the intensity of the methyl bromide and methyl mercaptan peaks appear to be noticeably reduced with respect to the results from the d.p.–m.s. experiments. The sulphur compounds 5 and 6 appear to be generated by further thermal reactions of methyl mercaptan and/or dimethyl disulphide. The formation of compounds 7 and 8 can be attributed to some type of hydrogen transfer reaction following polymer chain cleavage, as shown below in the form of the net reaction:



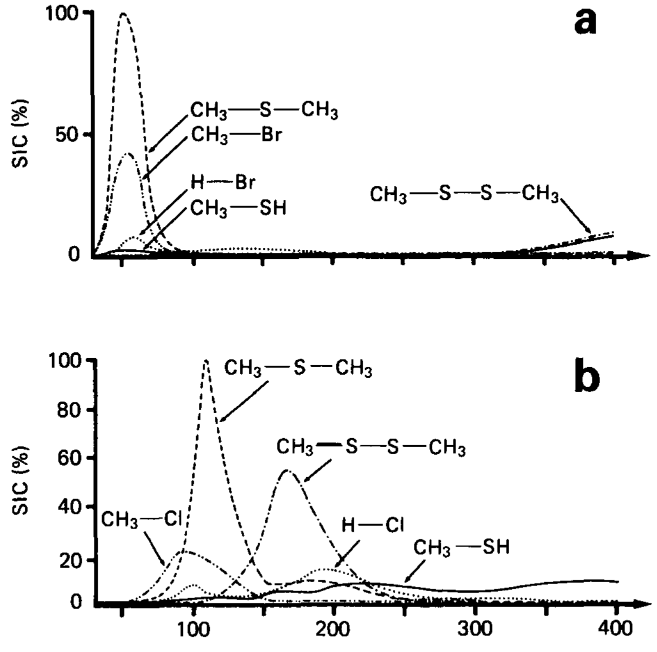


Figure 3 Single ion current (*SIC*) plots of the most abundant products generated in the pyrolysis of: (a) polymer IV and (b) polymer III

Flash pyrolysis–g.c.–m.s. of poly(p-phenylene vinylene), PPV

The polymer residue obtained by flash pyrolysis at 400°C of polymer III should consist of essentially pure PPV, and no additional sulphur-containing compounds were detected in the Py–g.c.–m.s. experiments carried out at 800°C on samples that had been pyrolysed at 400°C. The *TIC* chromatogram obtained from the pyrolysis products of PPV at 800°C is shown in *Figure 5* and the peak assignments are reported in *Table 3*.

Toluene and xylene, peaks 2 and 4 in *Figure 5*, were, as expected, the most abundant products. The remaining pyrolysis products were also aromatic compounds with the structure shown in *Figure 6*. The origins of these compounds could be rationalized by a variety of high-temperature, free-radical pathways involving cyclization and dehydrogenation reactions.

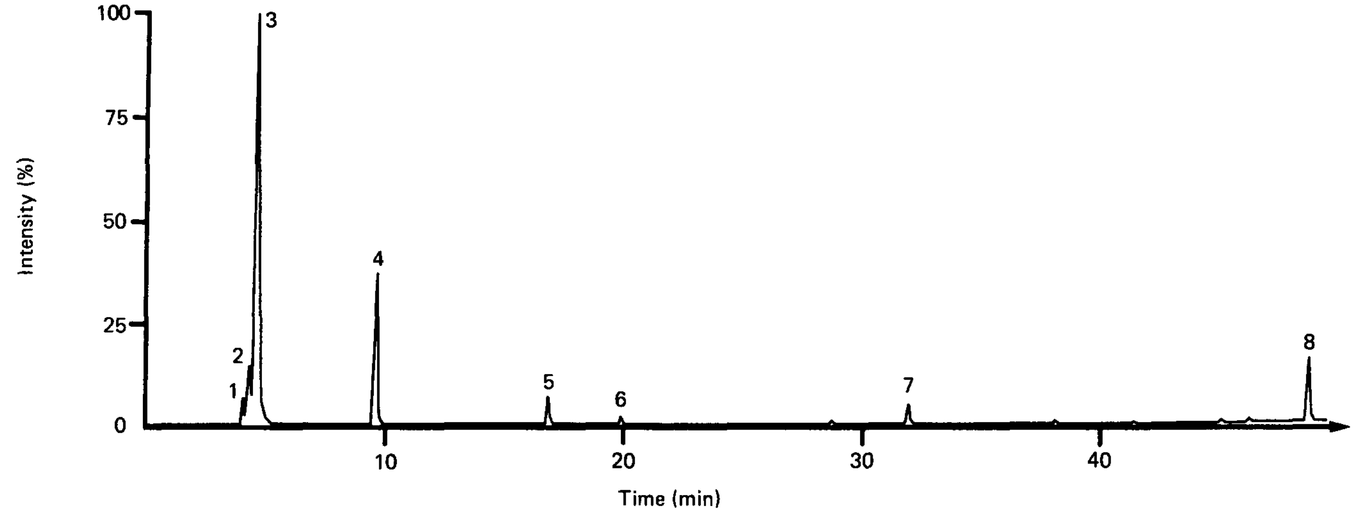


Figure 4 Total ion current (*TIC*) chromatogram of the on-line flash pyrolysis–g.c.–m.s. analysis of polymer III at 400°C per 7 s (see *Table 2*)

Table 2 Mass spectrometric data of polymer III as obtained by Py–g.c.–m.s. at 400°C

Peak[a]	Molecular ion[b]	Major EI fragments[c]	Structural assignment[d]
1	94 (100)	96 (98), 79 (11), 81 (10), 95 (3), 93 (2)	CH_3-Br
2	48 (100)	47 (69), 45 (11), 46 (8), 49 (6), 50 (4)	CH_3-SH
3	62 (100)	47 (48), 61 (18), 45 (10), 35 (6), 46 (5)	CH_3-S-CH_3
4	94 (100)	79 (24), 96 (8), 95 (5), 61 (4), 46 (4)	CH_3-S-S-CH_3
5	108 (100)	61 (72), 109 (8), 110 (6), 45 (5), 62 (4)	CH_3-S-CH_2-S-CH_3*
6	94 (100)	79 (15), 95 (8), 96 (7), 61 (6), 48 (4)	CH_3-S-CH_2-SH*
7	152 (65)	105 (100), 153 (9), 106 (6), 104 (3), 154 (2)	CH_3-Ph-CH_2-S-CH_3*
8	198 (73)	151 (100), 104 (25), 105 (10), 152 (9), 199 (9)	CH_3-S-CH_2-Ph-CH_2-S-CH_3*

[a] Peak numbers in *Figure 4* and also compound numbers in text
[b] Molecular ion in the corresponding EI spectrum; the relative intensities are given in parentheses
[c] The relative abundances of the EI fragments are given in parentheses
[d] The assignments are made by comparison of the Py–g.c.–m.s. spectra with those of the corresponding compounds present in the computer library, except for peaks marked by asterisk, which are our assignments

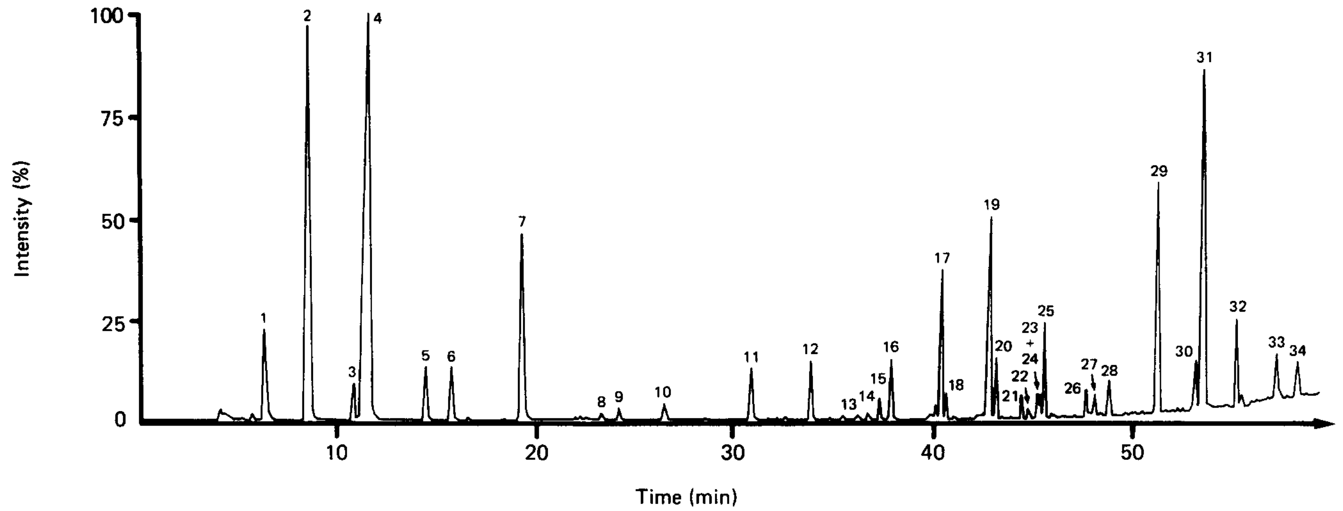
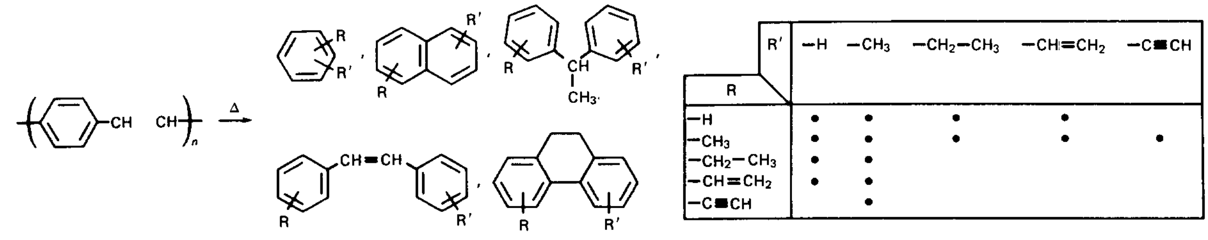


Figure 5 Total ion current (*TIC*) chromatogram of the on-line flash pyrolysis–g.c.–m.s. analysis of polymer V at 800°C per 7 s (see *Table 3*)

Table 3 Mass spectrometric data of polymer III as obtained by Py–g.c.–m.s. at 800°C

Peak[a]	Molecular ion[b]	Major EI fragments[c]	Structural assignment[d]
1	78 (100)	79 (6), 77 (5), 52 (4), 63 (2), 75 (1)	benzene
2	92 (100)	91 (70), 93 (8), 90 (5), 65 (2), 77 (1)	methylbenzene
3	106 (95)	91 (100), 78 (7), 92 (4), 105 (4), 107 (3)	ethylbenzene
4	106 (100)	91 (56), 105 (19), 107 (8), 92 (5), 78 (3)	dimethylbenzene
5	120 (77)	105 (100), 106 (12), 121 (11), 91 (4), 77 (2)	methylethylbenzene
6	104 (100)	103 (24), 78 (8), 105 (5), 79 (2), 77 (1)	ethylenebenzene
7	118 (100)	117 (57), 116 (9), 91 (8), 119 (8), 103 (4)	methylethylenebenzene
8	116 (100)	115 (36), 117 (7), 89 (1)	methylethynebenzene
9	132 (100)	117 (35), 131 (6), 133 (5), 118 (4), 104 (4)	tetrahydronaphthalene
10	130 (100)	129 (62), 115 (21), 131 (19), 102 (4), 77 (2)	dihydronaphthalene
11	128 (100)	129 (12), 127 (3), 102 (2), 126 (2)	naphthalene
12	142 (100)	141 (35), 143 (14), 140 (5), 89 (1), 144 (1)	methylnaphthalene
13	156 (62)	141 (100), 128 (43), 115 (41), 157 (17), 142 (8)	ethylnaphthalene
14	156 (100)	141 (17), 155 (15), 157 (13), 128 (5), 115 (3)	dimethylnaphthalene
15	154 (100)	153 (16), 155 (12), 152 (3), 151 (2), 128 (1)	ethylenenaphthalene
16	168 (100)	167 (53), 169 (15), 153 (8), 166 (5), 165 (4)	methylethylenenaphthalene*
17	182 (100)	167 (55), 183 (13), 181 (11), 152 (8), 105 (6)	1,1-diphenylethane
18	180 (100)	179 (53), 165 (13), 178 (11), 181 (8), 152 (5)	1,2-diphenylethylene
19	196 (100)	181 (77), 182 (22), 197 (16), 195 (9), 166 (6)	1-phenyl-1-methylphenylethane*
20	194 (100)	179 (37), 193 (17), 178 (14), 195 (13), 177 (5)	1-phenyl-2-methylphenylethylene
21	210 (55)	105 (100), 211 (12), 106 (10), 77 (4), 104 (3)	1,2-dimethylphenylethane
22	210 (90)	181 (100), 195 (53), 89 (17), 117 (13), 105 (9)	1-phenyl-1-ethylphenylethane
23	208 (100)	193 (33), 209 (17), 178 (11), 207 (8), 165 (4)	1-phenyl-1-ethylenephenylethane*
24	166 (100)	165 (28), 167 (17), 142 (2)	methylethynenaphthalene*
25	208 (100)	193 (22), 179 (20), 209 (15), 207 (11), 192 (8)	1-phenyl-2-ethylphenylethylene*
26	180 (100)	165 (48), 179 (35), 181 (14), 89 (11), 166 (6)	1,1-diphenylethylene*
27	208 (100)	193 (58), 207 (28), 209 (13), 165 (9), 178 (4)	1,2-dimethylphenylethylene
28	180 (100)	179 (48), 178 (18), 165 (15), 181 (11), 89 (5)	9,10-dihydrophenanthrene
29	194 (100)	179 (39), 193 (17), 195 (14), 178 (14), 165 (8)	methyl-9,10-dihydrophenanthrene*
30	178 (100)	179 (13), 89 (5), 176 (4), 177 (3), 151 (2)	phenanthrene
31	208 (100)	193 (20), 209 (18), 178 (10), 180 (8), 165 (4)	ethyl-9,10-dihydrophenanthrene*
32	222 (24)	192 (100), 191 (20), 193 (19), 223 (11), 207 (8)	methylethyl-9,10-dihydrophenanthrene*
33	206 (100)	207 (17), 205 (15), 191 (9), 133 (5), 119 (3)	ethylene-9,10-dihydrophenanthrene*
34	220 (100)	221 (17), 205 (14), 191 (9), 175 (5), 163 (4)	methylethylene-9,10-dihydrophenanthrene*

[a,b,c,d] See *Table 2*



R \ R'	$-H$	$-CH_3$	$-CH_2-CH_3$	$-CH=CH_2$	$-C\equiv CH$
$-H$	●	●	●	●	
$-CH_3$	●	●	●	●	●
$-CH_2-CH_3$	●	●			
$-CH=CH_2$	●	●			
$-C\equiv CH$		●			

Figure 6 Aromatic compounds formed in the flash pyrolysis of polymer III present in *Figure 5*

ACKNOWLEDGEMENTS

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REFERENCES

1 Murase, I., Ohnishi, T., Noguchi, T., Hirooka, M. and Murakami, S. ICSM Abstract, Abano Terme, Italy, 1984, p. 56

2 Kahlert, H. and Leising, G. ICSM Abstract, Abano Terme, Italy, 1984, p. 21

3 Gagnon, D. R., Capistran, J. D., Karasz, F. E. and Lenz, R. W. *ACS Polym. Prepr.* 1984, **25**(2), 284

4 Karasz, F. E., Capistran, J. D., Gagnon, D. R. and Lenz, R. W. *Mol. Cryst. Liq. Cryst.* 1985, **118**, 327

5 Antoun, S., Gagnon, D. R., Karasz, F. E. and Lenz, R. W. *Polym. Bull.* 1986, **15**, 181

6 Wessling, R. A. and Zimmermann, R. G. US Patents 3 401 152, 1968, and 3 706 677, 1972

7 Foti, S. and Montaudo, G. in 'Analysis of Polymer Systems', (Eds. L. S. Bark and N. S. Allen), Applied Science, London, 1982, Chap. 5, p. 103

8 Montaudo, G., Puglisi, C., Scamporrino, E. and Vitalini, D. *Macromolecules* 1986, **19**, 882