Mass spectral analysis of poly (*p*-phenylene sulphide)

W. D. Reents, Jr. and M. L. Kaplan
Bell Laboratories, 600 *Mountain Avenue, Murray Hill, New Jersey* 07974, *USA*

(*Received* 26 *August* 1981)

Low molecular weight and high molecular weight samples of poly(*p*-phenylene sulphide) were extracted exhaustively with methylene chloride. The extracts were examined by h.p.l.c. and by solid probe mass spectroscopy. Four families of compounds have been identified in these extracts: (1) cyclic (*p*-phenylene sulphide) oligomers; (2) chlorine terminated linear (*p*-phenylene sulphide); (3) single chlorine terminated linear (*p*-phenylene sulphide); and (4) linear (*p*-phenylene sulphides). The fully extracted polymer did not exhibit any mass spectrum. In addition to the compounds specified above, dibenzothiophene was found in all samples while phenyl biphenyl ether was found only in the extract of the high molecular weight material.

Keywords Spectral analysis; chromatographic analysis; liquid chromatography; poly(*p*-phenylene sulphide); oligomers; ether formation

INTRODUCTION

Poly(*p*-phenylene sulphide) (PPS) is a thermoplastic resin which is finding increasing use in electronics applications. PPS is also interesting because, when it is doped with AsF_5, it becomes conducting[1,2]. However, not a great deal of information is available about the impurities found in commercial preparations nor of the products formed on thermal treatment of the polymer[3,4]. It was our intention to examine both these points using chromatographic and mass spectroscopic techniques.

Pyrolysis g.c. and pyrolysis g.c./m.s. are commonly used methods for the identification and quantification of polymers. However, by its very nature pyrolysis results in the destruction of the organic material present. The identification of non-polymeric species, especially those chemically similar to the polymer, may be defeated by the destructive pyrolysis. Even if these non-polymeric species should remain intact, their low volatility may preclude analysis by gas chromatography. To circumvent these problems we utilized a direct insertion probe for sample introduction into a mass spectrometer. This resulted in increased sensitivity and, more importantly, enabled us to detect less volatile components in the polymer and in polymer extracts. Soluble fractions were also subjected to liquid chromatographic separation to aid in identification.

EXPERIMENTAL

The poly (*p*-phenylene sulphide) (PPS) was obtained from Phillips Petroleum. Our samples were a low molecular weight formulation (Ryton® VI powder) and a higher molecular weight formulation (Ryton® R6 pellets), both without additives. The higher molecular weight of the R6 is obtained by the manufacturer by a thermal cure in air.

A Varian MAT 112 mass spectrometer with a solids probe was utilized for polymer analysis. The solids probe was rapidly heated to a specified temperature after which a mass spectrum was recorded. Each sample was examined over the full temperature range available (ambient to 400°C). The probe temperature was maintained at each step until a significant decrease in the total ion current occurred. This treatment effectively reduced the amount of more volatile material for the next higher temperature run. Both 70 eV and 20 eV electron energies were used, the latter for molecular weight information with reduced fragmentation and the former for higher sensitivity.

The VI polymer is divided into two categories: the resin as received commercially, and the resin subjected to heat treatment (VIPT). This heat treatment was utilized to observe if heating, e.g. under processing and moulding conditions, altered the polymer. The heat-treatment consisted of heating in air at 100°C for one hour, at 150°C for one hour, and at 235°C for 16 h. Low molecular weight material was removed by Soxhlet extraction with methylene chloride. The VI extract contained 3% by weight of the total polymer. The VIPT contained somewhat less. The methylene chloride was then concentrated by a factor of 100. A 5.0 μl aliquot of this extract was applied to an aluminium crucible on the solid probe for mass spectral analysis. The R6 polymer was extracted with methylene chloride in the same manner. Complete extraction of the R6 material was difficult due to its pelletized form.

Methylene chloride was freshly distilled from $CaCl_2$ and was found to contain no detectable impurities by g.c./m.s. The liquid chromatographic analyses were performed on a DuPont Zorbax® column, 4.5 mm × 25 cm; lml min^{-1} solvent flow; 7:2:1 acetronitrile: methylene chloride: isopropyl alcohol solvent; u.v. detection at 254 nm.

RESULTS AND DISCUSSION

Poly (*p*-phenylene sulphide) is prepared commercially by reaction of Na_2S and *p*-dichlorobenzene, as follows:

$$Na_2S + Cl{-}C_6H_4{-}Cl{-}> NaCl + ClC_6H_4{-}(S{-}C_6H_4)_x{-}S{-}C_6H_4Cl$$

The resulting polymer has many desirable properties including excellent thermal stability. However, at the moulding temperature (300°C), low molecular weight material may diffuse through the melt into contact with sensitive eletrical components. At the same time these low molecular weight substances may have insufficient volatility to be analysed by gas chromatography. Thus, instead of a g.c./m.s. system we chose to use a solid probe for direct sample introduction into a mass spectrometer.

The spectral data shown in *Tables 1–4* were obtained from the methylene chloride extracts of the polymer samples. The ions due to the major sulphur- and chlorine-containing species are presented. At each temperature, the signal of greatest intensity is normalized to 100.

0032–3861/82/020310–04$03.00

Table 1 Intensity of ions vs. solid probe temperature for various mass numbers for VI polymer extract at 22 eV

	1	2			3a					3b						4			5				6
Temperature (°C)	184	186	294	402	216	324	432	540	648	270	270.5	324	324.5	378	378.5	254	362	470	220	328	436	544	246
95	100	26			14											48			41				
150	100	12	29		21		71									50	58		36	71			
210	44				15		100	59													7	3.7	
265			2		3		13	100										4		2	6		
300	4				5	1		100	3	2	1	1						1					

1 = dibenzothiophene
2 = C_6H_5-(S-C_6H_4-)$_x$-S-C_6H_5 $x = 0, 1, 2 \ldots$
3 = Cyclic (-S-C_6H_4-)$_x$ (a) singly charged ions $x = 4, 5, 6 \ldots$ (b) doubly charged ions $x = 5, 6, 7 \ldots$
4 = ClC_6H_4(-S-C_6H_4-)$_x$-S-C_6H_4Cl $x = 0, 1, 2 \ldots$
5 = C_6H_5-(S-C_6H_4-)$_x$-S-C_6H_4Cl $x = 0, 1, 2 \ldots$
6 = $C_6H_5C_6H_4OC_6H_5$

Table 2 Intensity of ions vs. solid probe temperature for various mass numbers for VIPT polymer extract at 70 eV

	1	2			3a					3b						4			5				6
Temperature (°C)	184	186	294	402	216	324	432	540	648	270	270.5	324	324.5	378	378.5	254	362	470	220	328	436	544	246
50	100	25														65			80				
95	100	24	34				2									100	31		20	66			
150	82	29	34	4			76										100		16	86	5		
210			3	8			100	23		8	2						12	6		7	13		
265			5	9			100	48		53	17						3	8		11	23		
320	35	2	2	1	16	14	4	100	38	32	10	14	4	12	5			1				5	

Legend as for *Table 1*

Table 3 Intensity of ions vs. solid probe temperature for various mass numbers for VIPT polymer extract at 22 eV

	1	2			3a					3b						4			5				6
Temperature (°C)	184	186	294	402	216	324	432	540	648	270	270.5	324	324.5	378	378.5	254	362	470	220	328	436	544	246
95	100	18	9													55			27	27			
150	88	2	2				48										100		2	100			
210	15			6			100	8												1			
265	9	1	1		5		7	100										5			4		

Legend as for *Table 1*

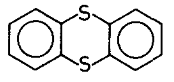
Table 4 Intensity of ions vs. solid probe temperature for various mass numbers for R6 polymer extract at 70 eV

	1	2			3a					3b						4			5				6
Temperature (°C)	184	186	294	402	216	324	432	540	648	270	270.5	324	324.5	378	378.5	254	362	470	220	328	436	544	246
RT	27	22			8														5				100
50	11	15	2		4														2				100
95	13	9	12		5														2				100
150	55	10	75		6														1	10			100
210	100	10	33	25	18		59	6									4		2	14			33
265	65	5	9	14	16		33	100		21	8												13
320	15	1			6	1	3	100	3	21	8	1											

Legend as for *Table 1*

It is evident from the spectra that a considerable amount of low molecular weight material (i.e. mass < 1000) is present. That this material does not arise from the thermal degradation of higher molecular weight material is shown by the following experiment. A sample of VI polymer, after methylene chloride extraction, was introduced into the mass spectrometer *via* the solids probe, heated to 380°C, and maintained at that temperature for several minutes. No mass spectrum above background was observed.

There are several families of chemically related ions in the VI and VIPT extract samples (*Tables 1–3*). Within each family, the next higher homologue has an additional C_6H_4S (mass 108) unit. The simplest series, consisting of masses 432, 540, 648, etc., represents the first identification of cyclic (*p*-phenylene sulphides), a class of molecules not previously known. Previous workers[5] apparently incorrectly, interpreted these ions as being open chain diradicals derived from pyrolytic fragmentation of the polymer itself. Our explanation follows from the observation of the molecular ions, even at low electron energy (≈20eV), and the doubly charged ions (m/e 270, 270.5, 324, 324.5, 378, 378.5) at high electron energy (≈70 eV). Mass 324 is present in negligible amounts and may be a fragment ion of a higher mass species. Mass 216 may be a fragment ion or it may be a side product, e.g.:



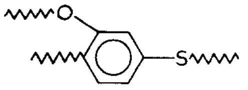
A second series, with masses 254, 362, 470, etc., is representative of the set of chlorine-terminated linear *p*-phenylene sulphides:

$$ClC_6H_4(\text{-}S\text{-}C_6H_4\text{-})_xS\text{-}C_6H_4Cl$$

$$x = 0, 1, 2, \text{etc.}$$

Also present are the series with masses 186, 294, 402, etc. and the series with masses 220, 328, 436, 544, etc., which we interpret as being due to linear *p*-phenylene sulphides with no chlorine termination and one chlorine termination, respectively. These latter two series are unexpected, perhaps resulting from monochlorobenzene impurities in the dichlorobenzene reactant or free radical side reactions. The corresponding initial members of these series have been observed for PPS prepared from *p*-dibromobenzene[6]. Mass 184, which may be dibenzothiophene, is also observed in the pyrolysis of PPS[6,7].

There is no appreciable difference between the VI and VIPT samples. However, the R6 formulation (*Table 4*) has two striking differences. First, mass 246 is the dominant ion from R6 whereas it is absent from VI and VIPT. This ion may be attributed to phenyl biphenyl ether ($C_6H_5C_6H_4OC_6H_5$). The formation of ether linkages in Ryton after commercial heat treatment in air has been observed previously by Hawkins[8]. However, he assumed the ether linkages were substituted aryl ethers; e.g.



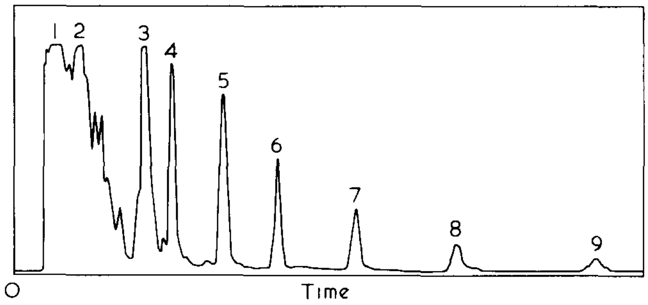


Figure 1 Trace of HPLC analysis of Ryton®VI extract. A DuPont Zorbax®column was used with acetonitrile: methylene chloride: isopropyl alcohol (7 : 2 : 1) at a flow rate of 1 ml min^{-1}. Time for analysis was 1 hour

Table 5 Mass spectral results on selected liquid chromatographic fractions[a]

Peak[b]	Results
1	Very low mass material
2	Chlorine terminated phenylene sulphide up to 4 units long; cyclic tetramer and pentamer
3	Cyclic hexamer (weak) and cyclic heptamer
4	Cyclic octamer
5	Cyclic nonamer (?)
6	Cyclic decamer

[a] Results are presented for the first six chromatographic peaks only due to the upper mass limit (1000 a.m.u.) of our mass spectrometer
[b] Peak corresponds to numbered peaks on the chromatogram in *Figure 1*

whereas we find that at least some of the ether linkages are due to phenyl biphenyl ether. We are unable to observe the higher weight material to determine the presence of the trisubstituted aryl ethers.

The second difference is the marked decrease in the amount of chlorine-terminated phenylene sulphides (masses 254, 362, 470, etc. and masses 220, 328, 436, etc.). This is expected of a heat treatment designed to increase the polymer's molecular weight.

Analysis of the methylene chloride extract of the VI polymer yielded the liquid chromatogram shown in *Figure 1*. Several fractions were collected and examined by solids probe mass spectrometry and the results are presented in *Table 5*. Cyclic pentamer purified by gradient sublimation (mass 540)[9] was used to verify its retention time in the liquid chromatograph.

CONCLUSIONS

We have found numerous species present in the methylene chloride extract of poly(*p*-phenylene sulphide) before and after thermal curing. These consist of four main groups: cyclic (*p*-phenylene sulphide) oligimers as well as linear (*p*-phenylene sulphides) with no chlorine terminations, with one chlorine termination, and with two chlorine terminations. Also, the presence of dibenzothiophene in significant quantities is noted. The poly(*p*-phenylene sulphide) which is commercially heat treated exhibits a reduction in the amounts of chlorine-terminated linear chains observed and the appearance of a species (phenyl biphenyl ether) not observed in the other samples.

The low molecular weight species in the thermoplastic polymer may have sufficient mobility at moulding temperatures to come into contact with electrical components which are being encapsulated. The final products may, therefore, exhibit electrical malfunctions. Also, the same low molecular weight species may be reducing the conductivity in doped PPS[1,2]. We suggest the removal of low molecular weight substances, prior to use, may result in more desirable properties.

ACKNOWLEDGEMENT

We wish to thank P. G. Kelleher for his helpful discussions and Ilene Heyward for her assistance with the liquid chromatographic experiments.

REFERENCES

1 Rabolt, J. F., Clarke, T. C., Kanazawa, K. K., Reynolds, J. R. and Street, G. B. *J. Chem. Soc., Chem. Commun.* 1980, 347
2 Chance, R. R., Shacklette, L. W., Miller, G. G., Ivory, D. M., Sowa, J. M., Elsenbaumer, R. L. and Baughman, R. H. *J. Chem. Soc., Chem. Commun* 1980, 348
3 Ehlers, G. F. L., Frisch, K. R. and Powell, W R. *J Polym. Sci., A-1* 1969, **1**, 2955
4 Hortling, B. *Mackromol. Chem.* 1977, **178**, 2185
5 Bruno, G., Foti, S., Maravigna, P., Montaudo, G. and Przybylski, M. *Polymer* 1977, **18**, 1149
6 Christopher, N. S. J., Cotter, J. L., Knight, G. J and Wright, W W. *J. Appl. Polym Sci.* 1968, **12**, 863
7 Munier, G. B. and Weschler, C. J, private communications
8 Hawkins, R. T *Macromolecules* 1979, **9**, 189
9 The isolation and characterization of the cyclic oligomers will be reported in a separate communication