

Direct Pyrolysis Mass Spectrometry of Chlorine-Containing Polymers Using Capillary GC / MS

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Synopsis

A direct pyrolysis mass spectrometric technique has been developed and applied to several chlorine-containing polymers. The capillary column in the gas chromatograph has been replaced by uncoated fused silica tubing to avoid the problem of column degradation induced by the polymer pyrolyzates. Under appropriate conditions, the pyrolysis mass spectra were found to be highly reproducible and to serve as "fingerprints." The technique can be readily applied to carbon-black-filled, crosslinked elastomers, as well as polyblends and composites. The quantitative aspects of the technique have also been addressed.

INTRODUCTION

The determination of the identity and composition of carbon-black-filled, crosslinked elastomers is a difficult problem. The most common techniques employed are pyrolysis gas chromatography (Py-GC) and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). However, when chlorine-containing polymers are pyrolyzed, hydrochloric acid is often produced, which can degrade capillary columns. We have found that pyrolysis of poly(epichlorohydrin) and poly(epichlorohydrin-co-ethylene oxide) damages capillary columns sufficiently that aliphatic alcohols are totally adsorbed. Py-GC on such a column often yields irreproducible results.

A technique which avoids the column degradation problem is direct pyrolysis mass spectrometry (Py-MS). Through the use of rapid pyrolysis techniques, such as Curie-point or filament pyrolyzers,^{1,2} or temperature-programmed pyrolysis performed with the direct insertion probe,³⁻⁵ Py-MS offers a rapid, sensitive, and specific technique for polymer identification.

Although the original Py-MS work consisted of specially built equipment for the technique, commercial mass spectrometers suitable for Py-MS are now available from several manufacturers. The cost of these instruments may prove prohibitive for a laboratory wishing to explore the potential applications of Py-MS to their particular problems.

We have found that Py-MS can be performed on a low-cost GC/MS system using the gas chromatograph as an interface for the pyrolysis unit. By substituting a length of uncoated fused silica tubing for the fused silica capillary column normally installed in the gas chromatograph, mass pyrograms were obtained that are quite similar to those acquired using instru-

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ments with direct probe inlet systems. As far as the authors are aware of, this is the first time that this has been done on a commercial instrument. The method is rapid and reproducible, and can be employed for quantitative analysis as well as for fingerprint identification.

This approach differs from previous efforts⁶ in that no modifications of the GC/MS instrument are needed. Thus, Py-MS and GC/MS can be carried out on the same sample. Also, our technique introduces all of the sample into the source (no jet separator or open-split interface), thereby improving the sensitivity of the analysis so that small particles of unknown elastomer may be readily identified and quantitatively analyzed.

EXPERIMENTAL

A Hewlett-Packard 5970B mass selective detector (Palo Alto, CA) interfaced to a HP 5890A gas chromatograph was used to obtain the mass spectra. The mass spectrometer was scanned from m/z 20 to 800 in 1.5 s at a source temperature of 250°C, and electron impact (70 eV) spectra were acquired using the HP 59970A work station supplied with the instrument. The polymers were pyrolyzed using a Chemical Data Systems Model 120 Pyroprobe (Oxford, PA) with a coil filament, and quartz tube sample holders. The standard interface supplied with the Pyroprobe was mounted on the Hewlett-Packard GC.

A 5 m × 0.20 mm uncoated polysiloxane-deactivated fused silica capillary tube (Scientific Glass Engineering, Austin, TX), maintained at 250°C (in the GC oven) was used to couple the pyrolysis unit and the mass spectrometer through a direct interface. The helium carrier gas flow was 0.63 mL min⁻¹ with a split ratio of 40:1. Sample size varied from 0.2 to 0.3 mg. All samples were preheated in the pyrolysis unit interface for 5 min at 250°C with continuous helium flushing, to remove residual solvents and additives such as antioxidants or plasticizers. The samples were then pyrolyzed using one of two programs: (a) heating from 250 to 750°C at the fastest Pyroprobe heating rate (about 330°C/s) with a total pyrolysis time of 10 s; (b) 250–500°C at 100°C/s, and holding the final temperature (500°C) for 17.5 s.

The polymers used in this work were either experimental samples or purchased from Aldrich Chemical Co. (Milwaukee, WI). They were used without further purification.

RESULTS AND DISCUSSION

To minimize adsorption of polar pyrolysis products on the glass surface, a short (5 m) tube was inserted directly into the source of the mass spectrometer. However, the use of short tubes, which have small pressure drops, exacerbates the problem of high carrier-gas flow rate. The mass spectrometer source must be maintained at a low pressure, so it is necessary to limit the flow of gas entering the source from the tube. One method of limiting flow is to use an open-split interface. Disadvantages of an open-split interface are lower sensitivity, and the increased amount of glass surface, which enhances adsorption of polar compounds. Because we used a direct interface, a small diameter (0.20 mm) fused silica tube was selected so that the pressure controller on the gas chromatograph could maintain a sufficiently low gas flow. Smaller lengths and diameters (e.g., 2 m × 0.10 mm) could be used.

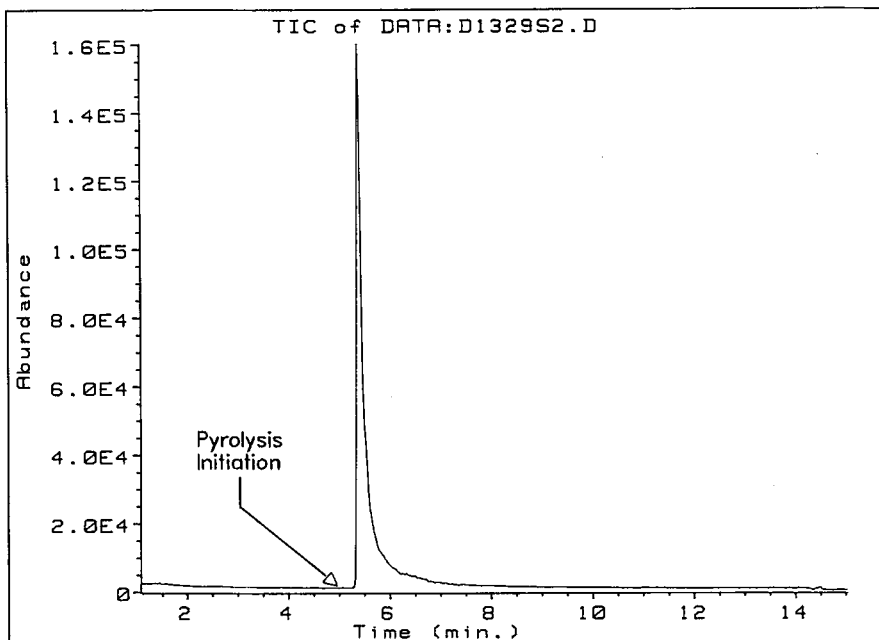


Fig. 1. Total ion current chromatogram obtained from poly(chloroprene) pyrolyzate swept through fused silica capillary tube.

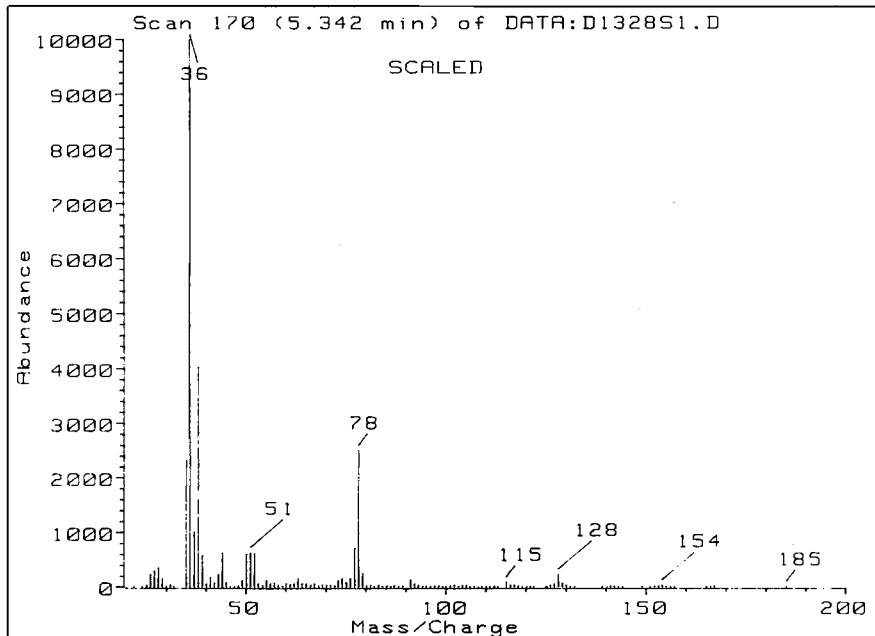


Fig. 2. Pyrolysis mass spectrum of poly(vinyl chloride).

The use of capillary tubing between the pyrolysis zone and the mass spectrometer source has the advantage of protecting the source from low volatility, tarry pyrolysis products. These products contaminate the mass spectrometer source when the direct insertion probe is used for Py-MS.⁷ Instrument modifications such as cold traps⁷ are unnecessary when a capillary tube is employed, because the tube traps the tarry products. After the Py-MS experiments in this study had been completed, the mass spectrometer source remained clean.

Owing to the absence of any coating on the 5 m capillary tube, the pyrolyzate is swept essentially unretained into the mass spectrometer. Figure 1 shows a typical trace of the total ion current obtained. Pyrolysis was performed at 5.0 min after an initial heating at 250°C. Although some tailing is evident, the majority of the effluent elutes within one minute. The mass spectra reported here were recorded at the point of maximum elution. It was found that single spectra were more reproducible than a spectrum averaged over the entire peak.

For this investigation, a number of chlorine-containing polymeric systems were analyzed:

Polymer

- Poly(chloroprene)
- Poly(vinyl chloride)
- Poly(vinyl chloride-co-vinyl acetate)
- Poly(epichlorohydrin)
- Poly(epichlorohydrin-co-ethylene oxide)

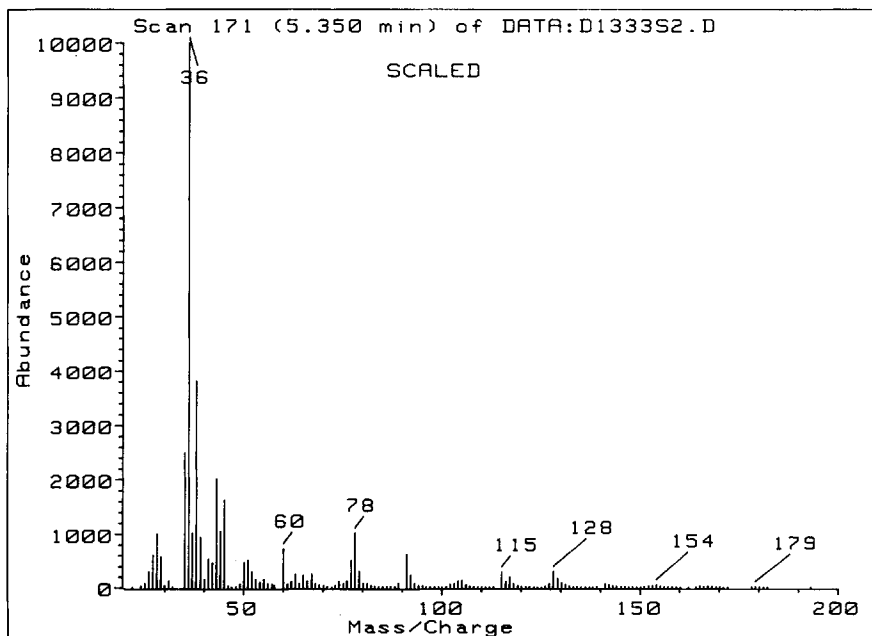
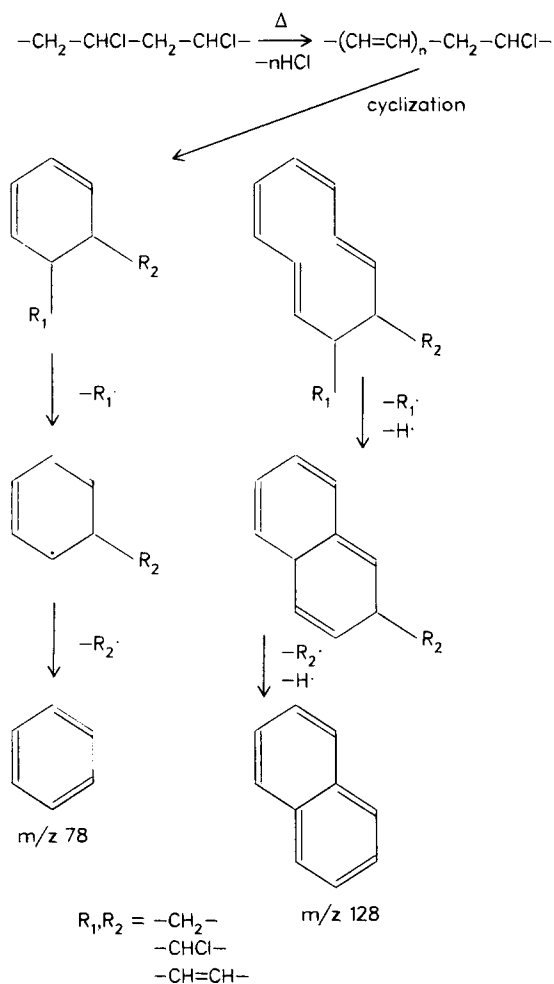


Fig. 3. Pyrolysis mass spectrum of vinyl chloride/vinyl acetate (83:17) copolymer.

Composite

- Carbon-black-filled Neoprene® rubber
- Carbon-black-filled poly(epichlorohydrin)
- Carbon-black-filled poly(epichlorohydrin-co-ethylene oxide)

Initially, samples of these elastomers were pyrolyzed at 750°C using the fastest heating rate. These pyrolysis parameters are similar to those commonly used for Py-GC/MS of polymers. However, with these parameters, the mass spectra of poly(epichlorohydrin) and poly(epichlorohydrin-co-ethylene oxide) could not be reliably distinguished, and the reproducibility of the mass spectra was poor. When the final temperature was decreased to 500°C, and the heating rate was decreased to 100°C/s, the intensity of higher mass ions increased, enhancing the difference between the mass spectra of the two polymers. In addition, the reproducibility of the mass spectra was improved.



Scheme I

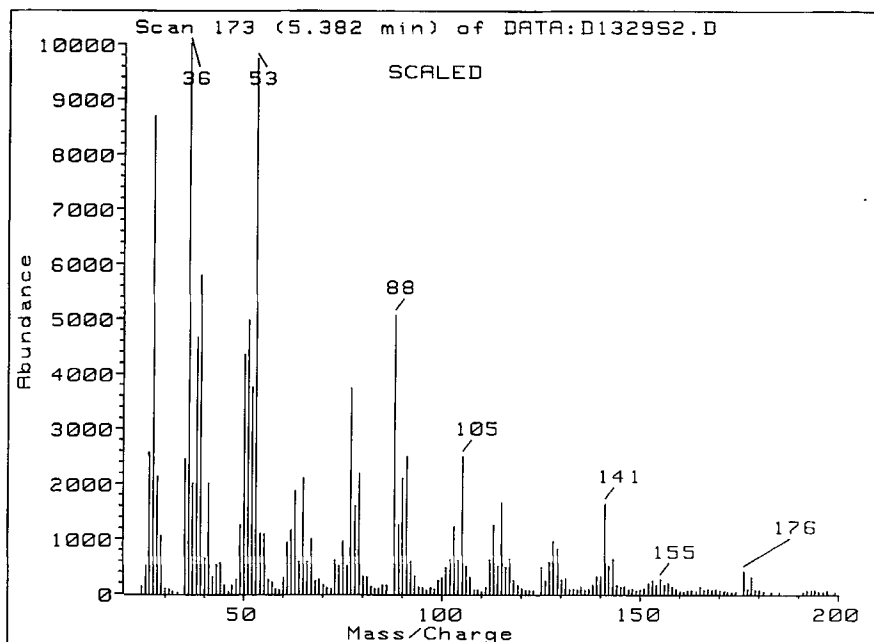


Fig. 4. Pyrolysis mass spectrum of poly(chloroprene).

All of the pyrolyses discussed below were performed using the latter pyrolysis parameters.

Typical direct pyrolysis-electron impact mass spectra for these polymers and elastomers are shown in Figures 2-9. All of the spectra have been normalized to the base peak in each spectrum. For the two vinyl polymers, poly(vinyl chloride) (PVC) and the copolymer of vinyl chloride (VC) with 17% vinyl acetate, the spectra indicate the preponderance of dehydrochlorination reaction⁸⁻¹⁰ with overwhelming amounts of HCl (m/z 36) ions (Figs. 2 and 3). Additional ions due to the coelimination of acetic acid (m/z 43, 45, 60) characterized the VC copolymers (Fig. 3) while both spectra showed evidence of aromatic hydrocarbons, particularly benzene (m/z 78) and naphthalene (m/z 128), resulting from intra- and intermolecular cyclization. These findings are consistent with the known chemistry (Scheme I) of the degradation of PVC (11-15).

Two polychloroprene samples were examined, both the resin and a carbon-black-filled Neoprene[®] vulcanizate, in an effort to define the utility of this method for examining different elastomeric materials. Ions due to chloroprene itself ($C_4H_5Cl^+$, m/z 88 and $C_4H_5^+$, m/z 53) and chloroprene dimers (m/z 77, 105, 141, and 176) were prominent in the pyrolysis mass spectrum of the resin (Fig. 4). The mass pyrogram of the carbon-black-filled Neoprene vulcanizate (Fig. 5) is identical to the resin, with the exception of the relative intensities of the chloroprene ions. These ion intensities are less (by a factor of three) in the vulcanizate, probably due to the crosslinking obtained during the curing process.

A third class of chlorine-containing polymers examined was the polyethers. Figure 6 shows the spectrum obtained from a commercial poly(epichlorohy-

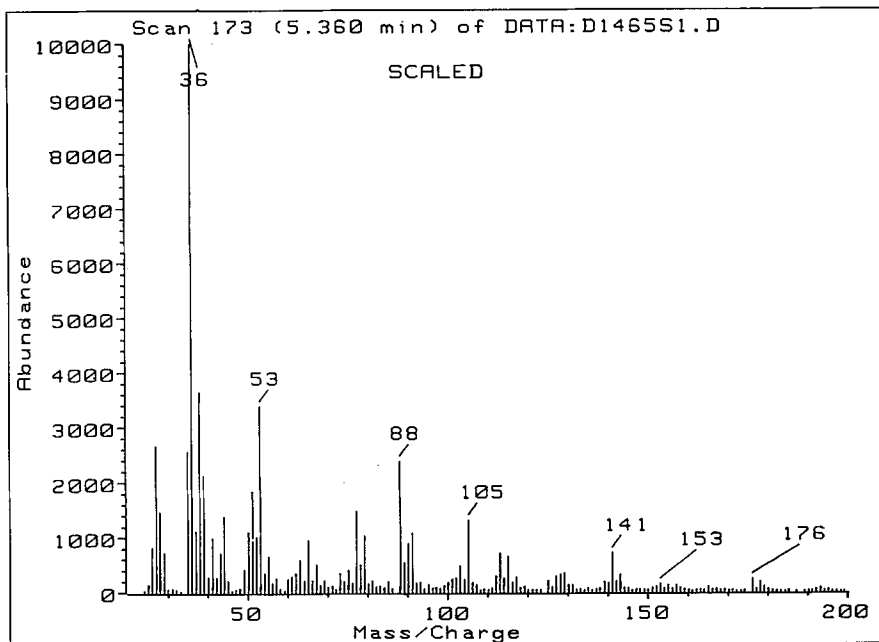


Fig. 5. Pyrolysis mass spectrum carbon-black-filled Neoprene vulcanizate.

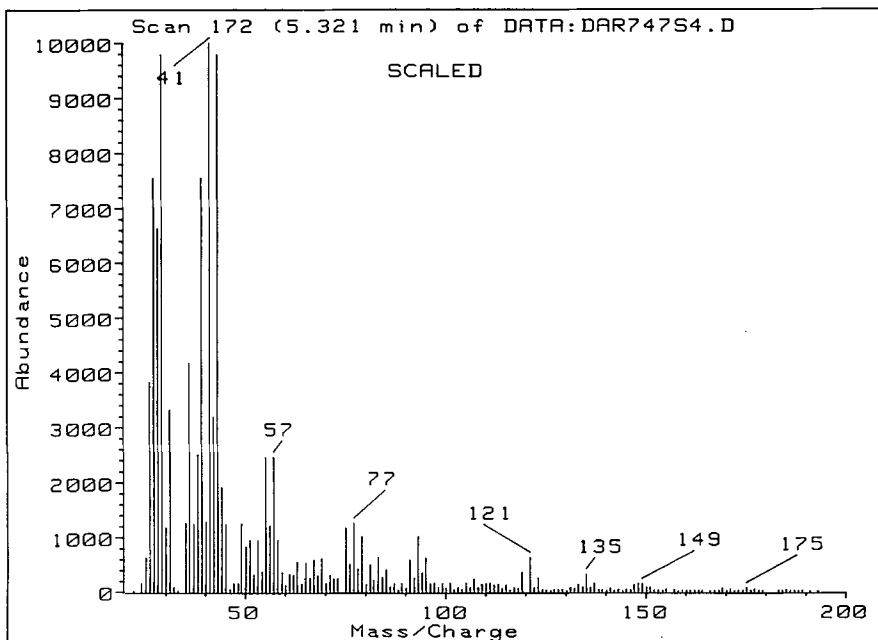
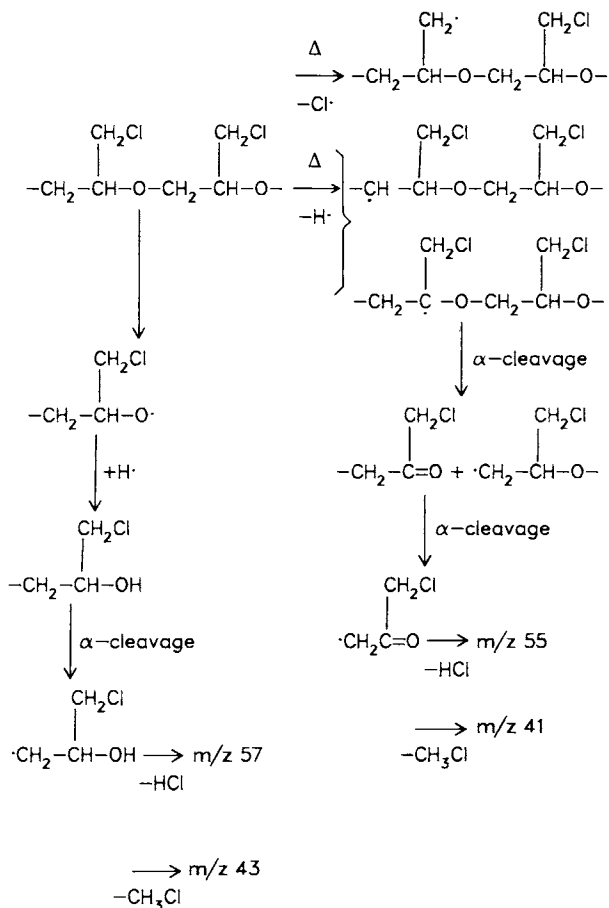


Fig. 6. Pyrolysis mass spectrum of poly(epichlorohydrin) elastomer.



Scheme II

drin) elastomer. This sample is typical of a commercial formulation containing a minor amount of stabilizer and antiozonant. Several of the major ions diagnostic of the poly(epichlorohydrin) include m/z 41 and 43, resulting from the loss of CH_3Cl , m/z 55 and 57, resulting from the loss of HCl , and m/z 93, corresponding to the protonated molecular ion of epichlorohydrin.

These ions are believed to be formed from free radical reactions which occur during the thermal degradation processes. Scheme II shows possible reaction pathways for the formation of these species. In addition, the production of higher molecular weight oligomers may yield fragment ions, such as m/z 121 and 135, due to the electron-impact-induced reactions. However, using this method of direct pyrolysis-mass spectrometry it was not possible to clearly distinguish between thermal and/or electron-impact-induced degradative mechanisms.

Further evidence for the utility of this method in examining intractable rubbers is shown in Figure 7, which is the pyrolysis mass spectrum of cured poly(epichlorohydrin) elastomer. This spectrum is essentially identical to the previous pyrolysis mass spectrum of the gum stock (Fig. 6).

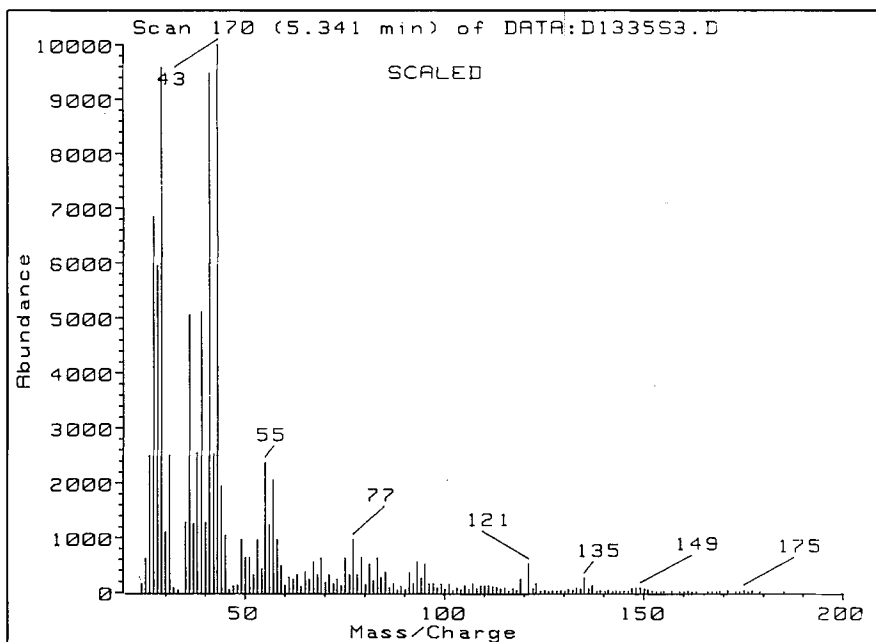


Fig. 7. Pyrolysis mass spectrum of carbon-black-filled poly(epichlorohydrin) elastomer.

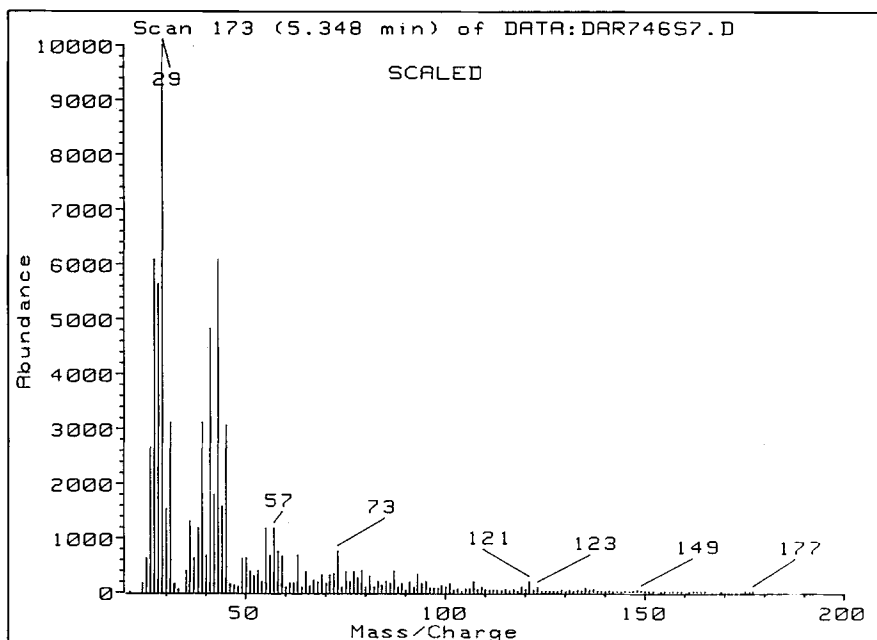


Fig. 8. Pyrolysis mass spectrum of poly(epichlorohydrin-co-ethylene oxide) elastomer.

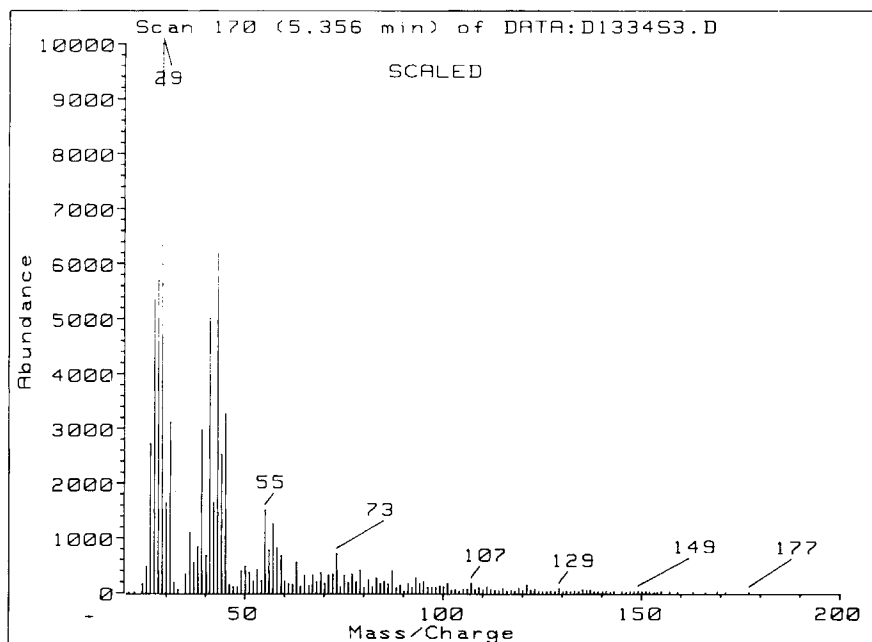


Fig. 9. Pyrolysis mass spectrum of carbon-black-filled poly(epichlorohydrin-co-ethylene oxide) elastomer.

Finally, two samples of epichlorohydrin-ethylene oxide copolymers were pyrolyzed and mass spectra obtained. The mass pyrogram of the gum stock is shown in Figure 8. This spectrum is similar to the epichlorohydrin homopolymer, except for the relative intensities of the ions at m/z 29 and 45. These ions are more intense in the spectrum of the copolymer due to the presence of the ethylene oxide. Figure 9 shows the pyrolysis mass spectrum of a cross-linked and filled sample of the copolymer, again indicating the usefulness of this method in examining intractable elastomeric materials.

The reproducibility of this method was investigated by pyrolyzing a sample of poly(vinyl chloride) over a period of several weeks. Ten different samples were used and the average of the 10 major peaks from a single scan of each pyrolysis run was recorded. These results are summarized in Table I. The precision is good for lower masses, but deteriorates at higher masses. The result is rather good, considering that during the course of this reproducibility study, the mass selective detector was being used for normal GC/MS analyses in addition to the pyrolysis work.

TABLE I
Direct Pyrolysis-Mass Spectrometry of Poly(vinyl Chloride)

Ion (m/z)	35	36	37	38	39	50	51	52	77	78
Mean intensity ^a	22.9	100	10.1	34.8	7.8	9.5	10.2	8.6	10.6	37.8
Relative standard deviation (%) ^a	2.2	—	6.5	2.8	17	14	14	17	17	16

^aFor ten mass spectra.

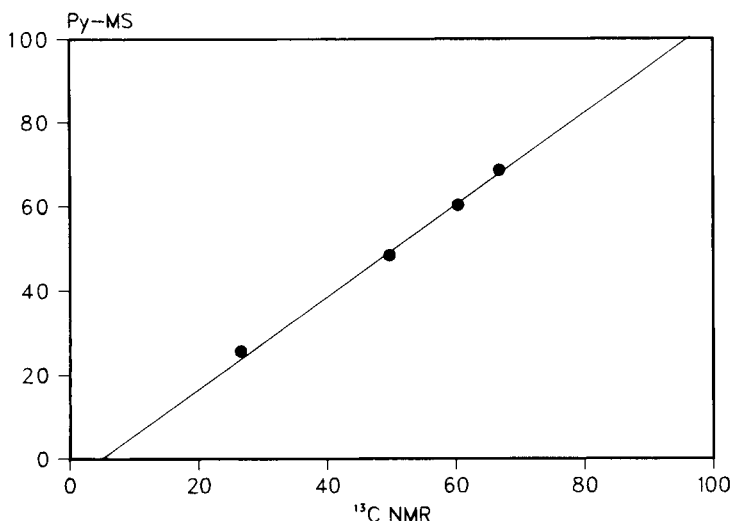


Fig. 10. Mole per cent of epichlorohydrin in poly(epichlorohydrin-co-ethylene oxide) gum stocks as determined by direct Py-MS versus ^{13}C NMR.

QUANTITATIVE ANALYSIS

The ability to perform quantitative analysis of polymers is very important in industrial laboratories. We report here the compositional analysis of carbon-black-filled elastomers by Py-MS.

Initial analyses were performed on ECO (poly(epichlorohydrin co-ethylene oxide)) gum stocks, so that ^{13}C nuclear magnetic resonance (NMR) spectrometry could be employed to confirm the composition. By the use of principal component analysis¹⁶ for several of the major peaks in the spectra, the following equation was developed to determine the mol% of epichlorohydrin present in the copolymers of epichlorohydrin (Epi) and ethylene oxide (EO):

$$\% \text{ Epi} = 50.853 + 30.352 \ln(\Sigma \text{ Epi} / \Sigma \text{ EO})$$

where $\Sigma \text{ Epi}$ = the sum of the intensities of m/z 36, 39, 41, 42, 55, and 57, and $\Sigma \text{ EO}$ = the sum of the intensities of m/z 31, 44, 45, 59, 72, and 73.

Figure 10 shows a plot of the results obtained from the analysis of four different ECO copolymer compositions using direct pyrolysis mass spectrometry and ^{13}C NMR. Each of the four points represents an average of five pyrolysis runs with a relative standard deviation of 2.3%. The correlation between the two techniques is quite good. The Py-MS technique is now used routinely for quantitative analysis of carbon-black-filled ECO elastomers.

CONCLUSIONS

The feasibility of direct pyrolysis-mass spectrometry using a low-cost mass-selective detector has been demonstrated for several chlorine-containing polymers. The technique not only allows us to perform qualitative identifications of intractable samples such as elastomer composites and polyblends, but also provides a means of performing quantitative analyses of carbon-black-filled

and crosslinked copolymers. The technique is superior to Py-GC, because capillary columns can be damaged by the pyrolyzate of some chlorinated polymers.

In addition, further detailed interpretation may yield information concerning the microstructure of copolymers. Several polymeric systems are currently under investigation by this method of direct pyrolysis-mass spectrometry for polymer sequence distribution.

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