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## Characterization of Polymers by Direct Pyrolysis/Chemical Ionization Mass Spectrometry

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### ABSTRACT

The characterization of polymers by pyrolysis directly in the ion source of a double focusing magnetic sector mass spectrometer, operating in the chemical ionization mode, is described. Pyrolysis is achieved by two different probe techniques. A low temperature, slow heating rate direct insertion probe (DIP) is used at 400°C, and a specifically constructed high temperature, fast heating rate, high temperature pyrolysis (HTP) probe is used at 1000°C. This probe is capable of achieving pyrolysis temperatures of 1200°C at controlled heating rates up to 20,000°C/s. The mass spectrometric analysis of the pyrolysis products was achieved under chemical ionization (CI) conditions utilizing methane, isobutane, and ammonia as reagent gases. Under CI conditions the molecular ions formed in the mass spectrometer show little tendency to fragment. The CI mass pyrograms are very simple, with each peak in the spectra ascribable to a particular component in the pyrolysis product mixture. The results of the two probe pyrolysis techniques are compared and the utility of each technique for the characterization of polymers is demonstrated using the vinyl polymers polymethyl methacrylate, polyvinyl chloride, and polystyrene.

## INTRODUCTION

The need for the characterization of materials is a classic problem in all areas of chemistry and materials science. In the case of polymers, these materials are most commonly characterized by their bulk physical properties. These techniques are quite adequate when the composition of the polymer is known; however, these techniques alone are often inadequate when information concerning polymer composition and structure is desired. In addition, many of these techniques require that the polymer be soluble, thus precluding the possibility of studying crosslinked and other insoluble polymers. The characterization and elucidation of the structure of polymeric materials or molecules in a high molecular weight matrix is complicated due to the high molecular weight of these materials. The classic approach to the problem of polymer characterization has been to fragment the polymer chain followed by analysis of the degradation products [1, 2]. Typically, the fragmentation is carried out thermally and the analysis by chemical means, or in the modern laboratory by gas chromatography (GC) or by combined gas chromatography-mass spectrometry (GC/MS).

The fragmentation of polymers by pyrolytic means has, over the last 40 years, developed from a crude, ill-defined technique to a well specified, if still varied one [1]. The analysis techniques of gas chromatography and combined gas chromatography-mass spectrometry have been applied to pyrolysis products since it was first recognized that pyrolysis gave a complex mixture of products [1]. At first, peak identification was not attempted but rather it was found that the overall pyrogram was sufficiently unique for each system that it could provide a "fingerprint" of the material [2, 3]. Later, investigators began to attempt to identify individual peaks [4]. Pyrolysis GC (PY-GC) and pyrolysis GC/MS (PY-GC/MS) have the distinct disadvantage in that the pyrolysis fragments must be volatile enough to be analyzed by GC. The large molecular weight fragments are not analyzed and tend to condense in the injection port, on the column, or in the transfer lines. In addition, the process of PY-GC and PY-GC/MS involves the collection of the pyrolysis products before or during analysis, thus the products being analyzed are the stable, rearranged equilibrium products of the pyrolysis mixture and not the highly energetic primary products of the pyrolysis. A third factor contributing to the disadvantages of PY-GC and PY-GC/MS is the time required for each analysis and the large amount of data generated [2].

Mass spectrometry has long been recognized as a powerful tool for both identification of chemical substances and for investigations into the mechanisms of chemical reactions. MS has not been found useful in the analysis of polymeric material directly due to the very high molecular weight and extremely low vapor pressure exhibited by these materials. On the other hand, mass spectrometry has been shown to have the potential of being a very powerful method for the analysis of the degradation products of polymers [5-7].

The degradation of the polymer may be performed separate from the mass spectrometer, the products collected and then introduced into the mass spectrometer for analysis. This approach suffers from many of the same disadvantages of the PY-GC and PY-GC/MS techniques. Ideally, the pyrolysis should be carried out by a pyrolysis probe that is specially interfaced to the ion source of the mass spectrometer. Thus the pyrolysis is performed directly within the ion source of the mass spectrometer and the products analyzed directly. By this approach the degradation products enter the ion source as they are evolved and the analysis is immediate. In the case where the degradation is conducted isothermally, it is possible to monitor the evolution of the degradation products with time. In the case where a temperature programmed heating mode is employed, the analysis yields a relationship between the evolved products and temperature of degradation. This type of direct pyrolysis-mass spectrometry was proposed as early as 1948 as a method of studying polymers [1].

Early work was conducted in this area using a normal electron impact mass spectrometer. Electron impact mass spectrometry (EI-MS) uses high energy electrons to bombard the sample molecule, thus causing its ionization. The highly energetic radical anion produced will then undergo fragmentation to give a mass spectra unique to the compound (Fig. 1). When the pyrolysis is performed directly in the ion source of an electron impact mass spectrometer, the large number of chemical species produced by the pyrolysis will simultaneously undergo electron impact mass spectral fragmentation. This yields an extremely complex spectrum composed of the mass spectrum of each of the thermal degradation products superimposed upon one another. Pyrolysis electron impact mass spectrometry (PY-EI/MS) studies have been reported in the literature for a number of samples, but the interpretation of the resulting spectra has been very difficult. The utility of much of this published work is in the area of "fingerprinting" of materials. Only in the cases where one or more peaks can be definitely ascribed to a specific component in the pyrolysis mixture has this technique found utility [5, 8].

Chemical ionization (CI) is a relatively new technique of mass spectral ionization that has been developed to allow the analysis of compounds that do not show stable molecular ions under electron impact conditions. It accomplishes this by avoiding the high energy ionization of EI-MS, and thus minimizes the mass spectral fragmentation.

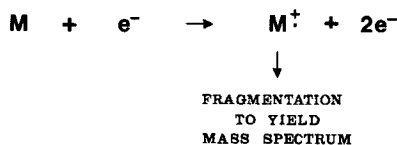


FIG. 1. Electron impact mass spectrometry.

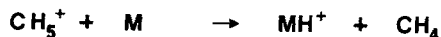


FIG. 2. Chemical ionization mass spectrometry.

Chemical ionization is essentially a gas-phase acid-base reaction, with the sample molecule being ionized through the gain of a proton, thus forming a quasi-molecular ion. Figure 2 depicts a greatly simplified reaction scheme for the ionization of a molecule by a chemical ionization using methane as the reagent gas. This process can be controlled such that little excess energy is imparted to the quasi-molecular ion and thus under ideal conditions no fragmentation will occur [9, 10]. The CI mass spectrum of a sample should give a single peak at a one mass unit higher than the molecular weight of the compound. Thus, in the analysis of a mixture, each peak in the spectra may be ascribed to a particular component in the mixture [10-12]. An additional factor in chemical ionization is the ability to employ reagent gases other than methane. The common reagent gases, methane, isobutane, and ammonia, each offer differing degrees of selectivity based on the acidic character of the reagent ion formed [10].

The application of chemical ionization mass spectrometry to the analysis of pyrolysis products has the distinct advantage of simplifying the mass spectrum (mass pyrogram) of the pyrolysis mixture and of insuring that each peak in the mass pyrogram has a direct and interpretable correlation to the individual products of the thermal degradation. This approach has been demonstrated for the pyrolysis of pure polymers with the pyrolysis conducted using a low temperature direct insertion probe [11, 12], and also in our laboratory by a specially constructed high temperature, fast heating rate probe [12, 13].

In this report we describe a series of PY-CI/MS studies conducted on pure polymers using both a low temperature, ballistically heated direct insertion probe and a specially constructed high temperature pyrolysis probe.

## EXPERIMENTAL

### Instrumentation

#### High Temperature Pyrolysis Probe

A high temperature, fast heating rate pyrolysis probe (HTP probe) was designed in this laboratory and its construction was accomplished in our machine shop and at the machine shop of Chemical Data Systems (Oxford, Pennsylvania). The probe is shown in Fig. 3. The probe is configured with a pyrolysis nosepiece on the end of a 9.0-mm o.d. stainless steel shaft. The nosepiece consists of a platinum coil with its frame support. The nosepiece with coil is shown in Fig. 4. A ceramic

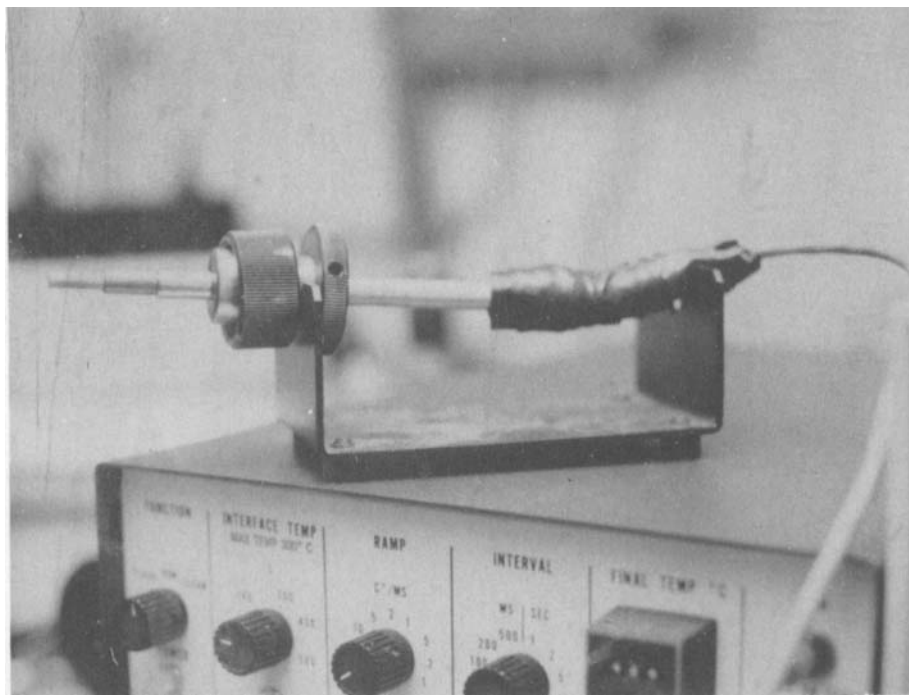


FIG. 3. High temperature, fast heating rate pyrolysis probe (HTP probe).

insulator fits over this frame and is secured to the base of the nose-piece by means of a threaded stainless steel collar. The purpose of this ceramic insulator is threefold. It must electrically isolate the probe from the ionization box; it must reflect the heat back toward the quartz sample tube, thus promoting a more uniform temperature profile; and it must make a pressure-tight seal against the CI box in the ion source. A vacuum-tight collar is provided to mate with the direct insertion probe inlet of the MS so as to allow the introduction and withdrawal of the probe from the ionization box using the inlet's vacuum lock system.

The probe is controlled by a CDS Pyroprobe 120 Control Unit (Chemical Data Systems, Oxford, Pennsylvania) which allows control of pyrolysis temperatures to 1200°C at controlled heating rates in excess of 20,000°C/s.

#### Mass Spectrometer

All determinations were made using a Varian Model 112S Double Focusing Magnetic Sector Mass Spectrometer with a combined electron

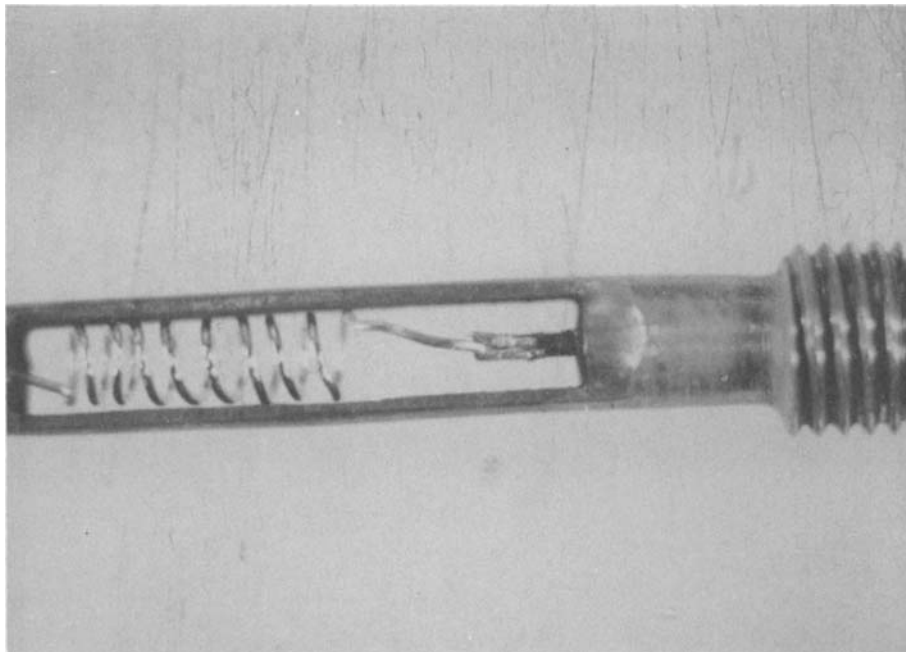


FIG. 4. HTP probe nosepiece.

impact/chemical ionization ion source. Methane, isobutane, and ammonia were utilized as chemical ionization reagent gases. The MS is interfaced to a Varian Model V-76 Computer for data acquisition and reduction.

### Materials

#### Polystyrene

Polystyrene, MW =  $2.7 \times 10^6$ , Waters Associates Inc., Milford, Massachusetts.

#### Poly(Methyl Methacrylate)

Poly(methyl methacrylate), Perspex CQ clinical quality sheets.

#### Poly(Vinyl Chloride)

Poly(vinyl chloride), B. F. Goodrich Chemical Co.

## Pyrolysis

### Low Temperature Pyrolysis

Low temperature pyrolysis was achieved by means of a ballistically heated direct insertion probe (DIP) supplied by Varian MAT, the manufacturer of the mass spectrometer. The sample was placed into a quartz tube (sealed at one end) of 1.91 mm outside diameter and 10 mm in length. A typical sample size was about 1  $\mu\text{g}$ . The sample tube was placed in the DIP and the probe inserted into the mass spectrometer through the vacuum lock. Mass spectral scanning and data acquisition was begun. After one minute the probe was ballistically heated to 400°C. This probe was capable of being heated reproducibly to 400°C at an average rate of approximately 20°C/min. Data acquisition was terminated when the sample was exhausted.

### High Temperature Pyrolysis

High temperature, fast heating rate pyrolysis was achieved by means of the previously described specially constructed high temperature pyrolysis (HTP) probe. The sample was placed into a quartz tube (sealed at one end) of 1.9 mm o.d. and 17.5 mm in length. A typical sample size was about 1  $\mu\text{g}$ . The sample tube was placed within the platinum coil of the HTP probe. The ceramic insulator was then placed over the sample tube and frame, and was then secured to the base of the nosepiece by the stainless steel collar. The probe was then inserted into the mass spectrometer through the vacuum lock. Mass spectral scanning and data acquisition was begun, and after 1 min the probe was fired. A typical pyrolysis would be carried out to a final temperature of 1000°C at the maximum heating rate (in excess of 20,000°C/s). Typically, the temperature would be maintained at the final temperature for 3 s. Data acquisition was continued until the sample was exhausted.

## RESULTS AND DISCUSSION

A series of characterization studies was conducted to demonstrate the utility of this pyrolysis technique and to determine the differences between, and applicability of, the low temperature DIP probe and the high temperature HTP probe techniques. The systems of interest in this study were the pure polymers polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), and polystyrene.

In the study of these pure polymers, each system was pyrolyzed at 400°C using the DIP probe and at 1000°C using the HTP probe. In the



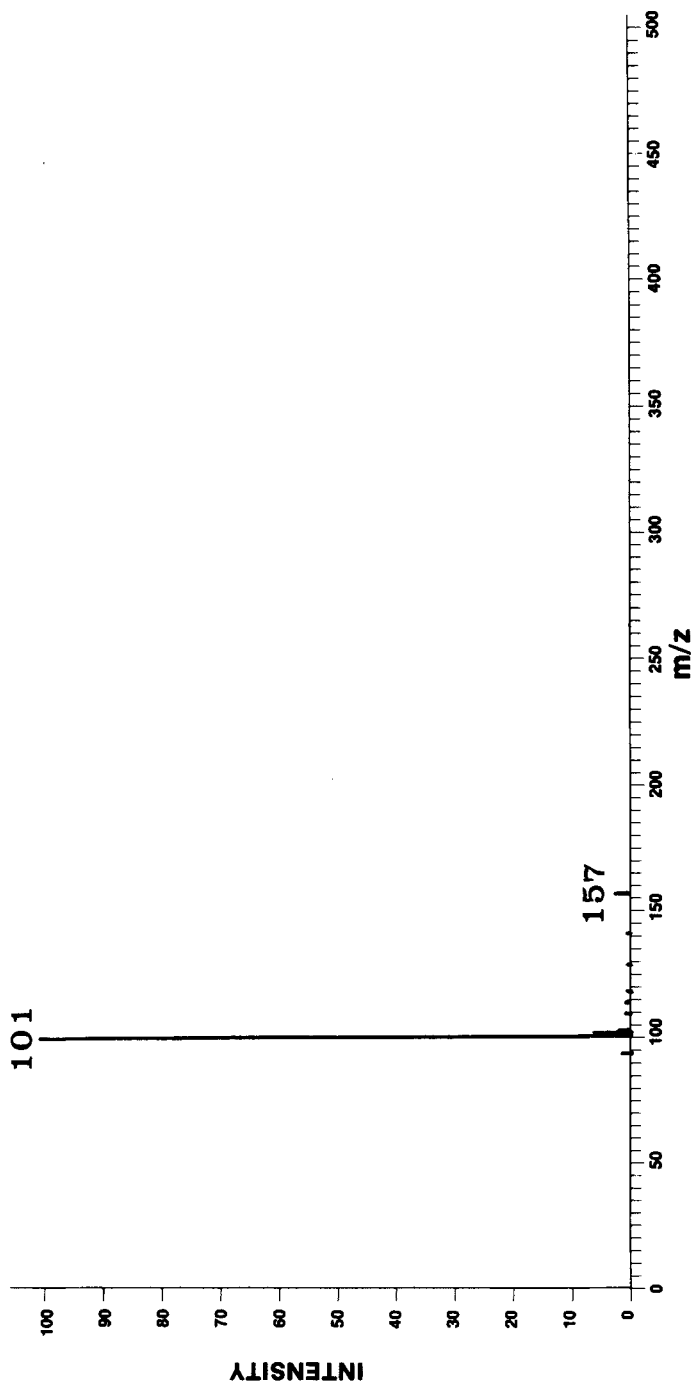


FIG. 5. Isobutane-chemical ionization mass pyrogram of the DIP probe pyrolysis of poly(methyl methacrylate) at 400°C.

case of the DIP studies, CI/MS analysis was performed using isobutane as the reagent gas. In the case of the HTP studies, the analysis was carried out using methane, isobutane, and ammonia as reagent gases. Degradation proceeded at both the low and high temperature conditions for all systems under study.

### Poly(Methyl Methacrylate)

The isobutane-CI mass pyrogram obtained for the 400°C DIP pyrolysis of PMMA is shown in Fig. 5. The major peak is found at  $m/z = 101$ , and its associated isotope peaks at 102 and 103. This peak cluster can be attributed to the protonated monomer. The only other peak of significance in the spectra is at  $m/z = 157$ . This is attributed to the addition of the protonated isobutane reagent ion to the monomer. Thus this mass pyrogram indicates only one species formed during the degradation process, and this species can be identified as the MMA monomer. A few very small peaks, of less than 1%, can be seen in the pyrogram, and these may be attributed to impurities in the polymer; i.e.,  $m/z = 115$  and 117 may be due to ethyl methacrylate and ethyl butanoate, respectively.

The isobutane-CI mass pyrogram obtained for the 1000°C HTP pyrolysis of PMMA is shown in Fig. 6. The major peak is again found at  $m/z = 101$ . As was the case for the DIP pyrolysis, the peaks at 101 and 157 can be attributed to the monomer. A second major peak is observed in this pyrogram at  $m/z = 201$ . This peak is ascribable to the protonated dimer of MMA, and it appears that there is a trace peak at 301 due to the trimer. The other trace peaks in the pyrogram are similar to those observed in the DIP pyrogram.

Figures 7 and 8 show the mass pyrograms for the HTP pyrolysis of PMMA under CI-methane and CI-ammonia, respectively. Both of these pyrograms yield essentially the same information as the CI-isobutane pyrogram, except that with methane and ammonia we see evidence for the monomer, dimer, trimer, and tetramer. In the case of the CI-methane pyrogram we observe the protonated species ( $m/z = 101, 201, 301, 401$ ) as well as the  $C_2H_5^+$  ( $m/z = 129$ ) and the  $C_3H_5^+$  ( $m/z = 141$ ) adducts. The adduct peaks in the CI spectra allow us to distinguish between those species that arise from the pyrolysis and those species that arise due to mass spectral fragmentation. In the case of the CI-ammonia pyrogram we do not observe the expected molecular ion, but we observe very strong peaks for the ammonium ion adducts ( $m/z = 118, 218, 318, 418$ ) as well as weaker peaks for the  $NH_3NH_4^+$  adduct ( $m/z = 135, 235$ ). The peak at  $m/z = 35$  is due to the  $NH_3NH_4^+$  species in the reagent gas.

It appears that for the pyrolysis of PMMA there is a distinct difference between the DIP and HTP pyrolysis processes. PMMA is known to undergo thermal degradation by unzipping, yielding essentially monomer [14]. This is what is observed for the DIP pyrolysis, and it may be argued that with slow heating the sample is at equilib-

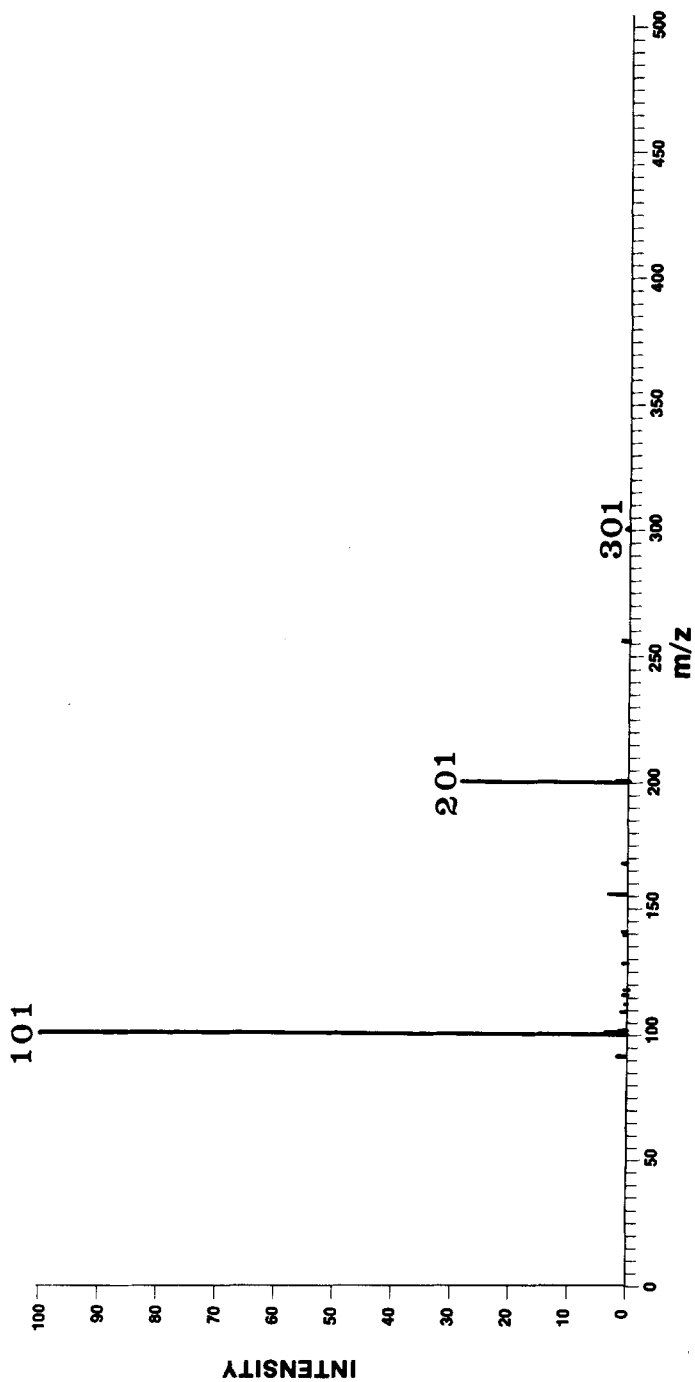


FIG. 6. Isobutane-chemical ionization mass pyrogram of the HTP probe pyrolysis of poly(methyl methacrylate) at 1000°C.

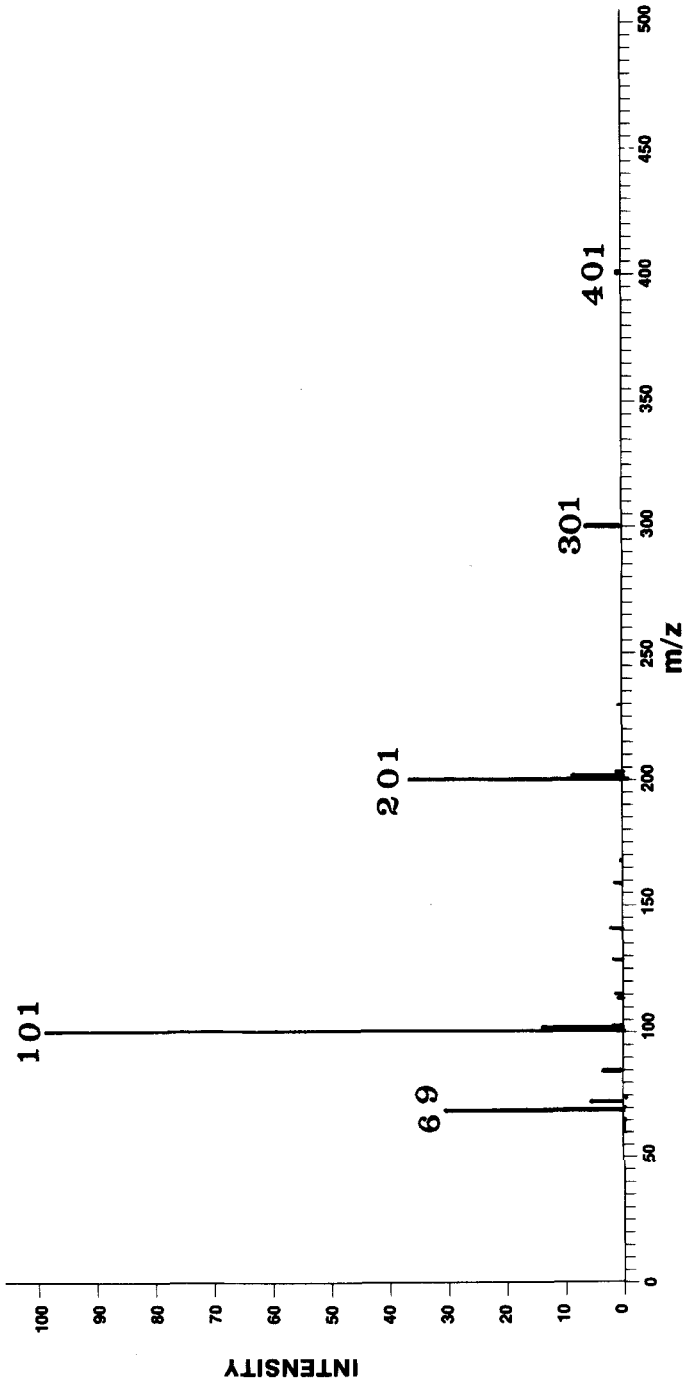


FIG. 7. Methane-chemical ionization mass pyrogram of the HTP probe pyrolysis of poly(methyl methacrylate) at 1000°C.

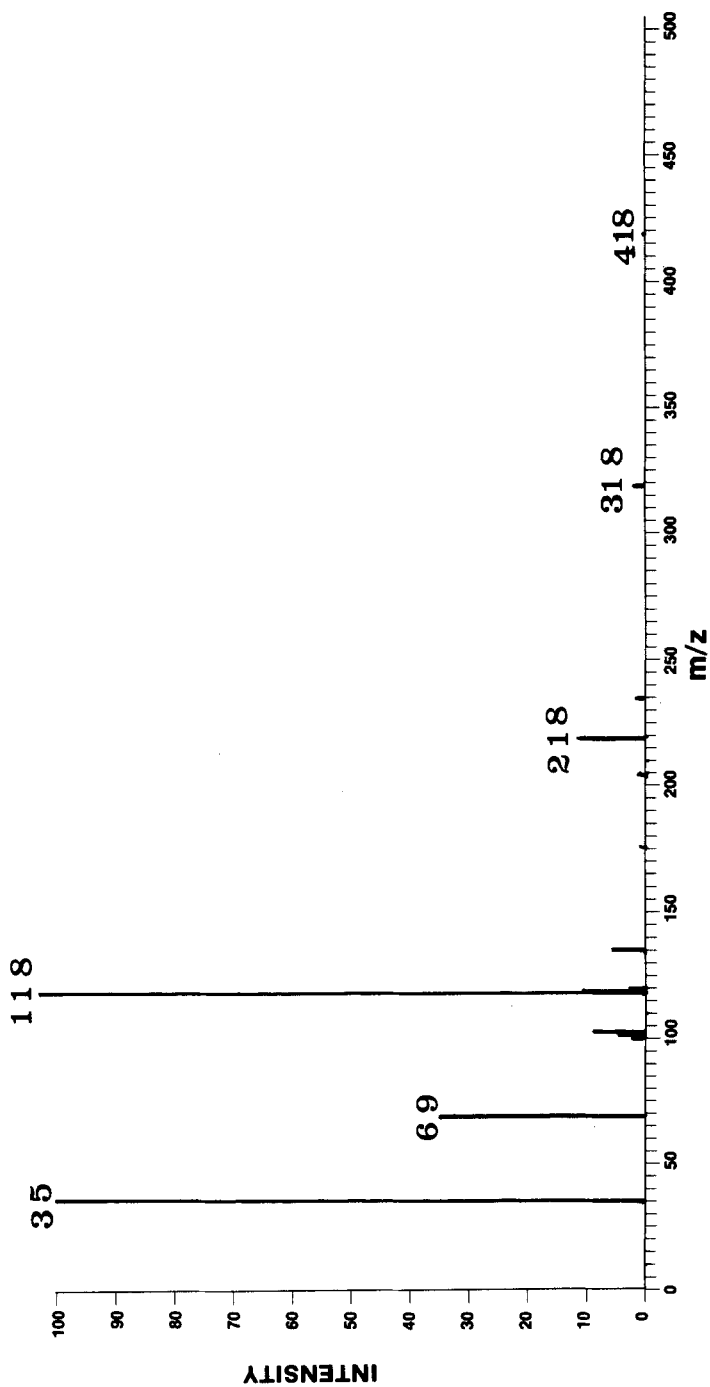


FIG. 8. Ammonia-chemical ionization mass pyrogram of the HTP probe pyrolysis of poly(methyl methacrylate) at 1000°C.

rium and thus there is complete unzipping to monomer. In contrast, HTP pyrolysis is a very rapid process to a very high temperature. The argument can then be made that the appearance of chain fragments larger than monomer is due to nonequilibrium cleavage along the polymer chain.

### Polystyrene

The isobutane-CI mass pyrogram obtained for the 400°C DIP pyrolysis of PS is shown in Fig. 9. The major peak is found at  $m/z = 105$ , and its associated isotope peaks are at 106 and 107. This peak cluster can be attributed to the protonated monomer. The protonated isobutane adduct to the monomer is found in the spectra at  $m/z = 161$ . A small amount of protonated dimer is detected ( $m/z = 209$ ). The pair of peaks at  $m/z = 117$  and 173 appears to be due to a methyl-styrene-like chain fragment formed during the pyrolysis. This mass pyrogram indicates that the main species formed during the degradation process can be identified as styrene monomer with a small amount of dimer.

The isobutane-CI mass pyrogram obtained for the 1000°C HTP pyrolysis of PS is shown in Fig. 10. The major peak is again found at  $m/z = 105$ . As was the case for the DIP pyrolysis, the peaks at 105 and 161 can be attributed to the monomer. A second major pair of peaks is observed in this pyrogram at  $m/z = 209$  and 265. These peaks are ascribable to the protonated dimer of styrene. The protonated trimer is found at  $m/z = 313$ , and it appears that there is a trace peak at 416, probably due to the tetramer. A number of the remaining peaks in the pyrogram may be ascribed to the saturated and unsaturated chain fragments that would arise from random chain scission along the polymer backbone.

Figures 11 and 12 show the mass pyrograms for the HTP pyrolysis of PS under CI-methane and CI-ammonia, respectively. Both of these pyrograms yield essentially the same information as the CI-isobutane pyrogram, except that with methane and ammonia we see evidence for the monomer, dimer, trimer, and tetramer. In the case of the CI-methane pyrogram we observe the protonated species ( $m/z = 105, 209, 313, 417$ ) as well as the  $C_2H_5^+$  ( $m/z = 133$ ) and the  $C_3H_5^+$  ( $m/z = 145$ ) adducts. In the case of the CI-ammonia pyrogram we observe the expected molecular ion as well as strong peaks for the ammonium ion adducts ( $m/z = 122, 226, 330, 434$ ) and weaker peaks for the  $NH_3NH_4^+$  adduct ( $m/z = 139, 243$ ). The peak at  $m/z = 35$  is due to the  $NH_3NH_4^+$  species in the reagent gas. As in the case of the HTP CI-isobutane, both the CI-methane and the CI-ammonia contain peaks that can be ascribed to the saturated and unsaturated chain fragments that would arise from random chain scission. This is particularly true in the case of the CI-methane, where these peaks are more prominent than in the CI-ammonia pyrogram. The lower intensity of these peaks in the CI-ammonia pyrogram may be attributed to the greater selectivity of ammonia as a reagent gas.

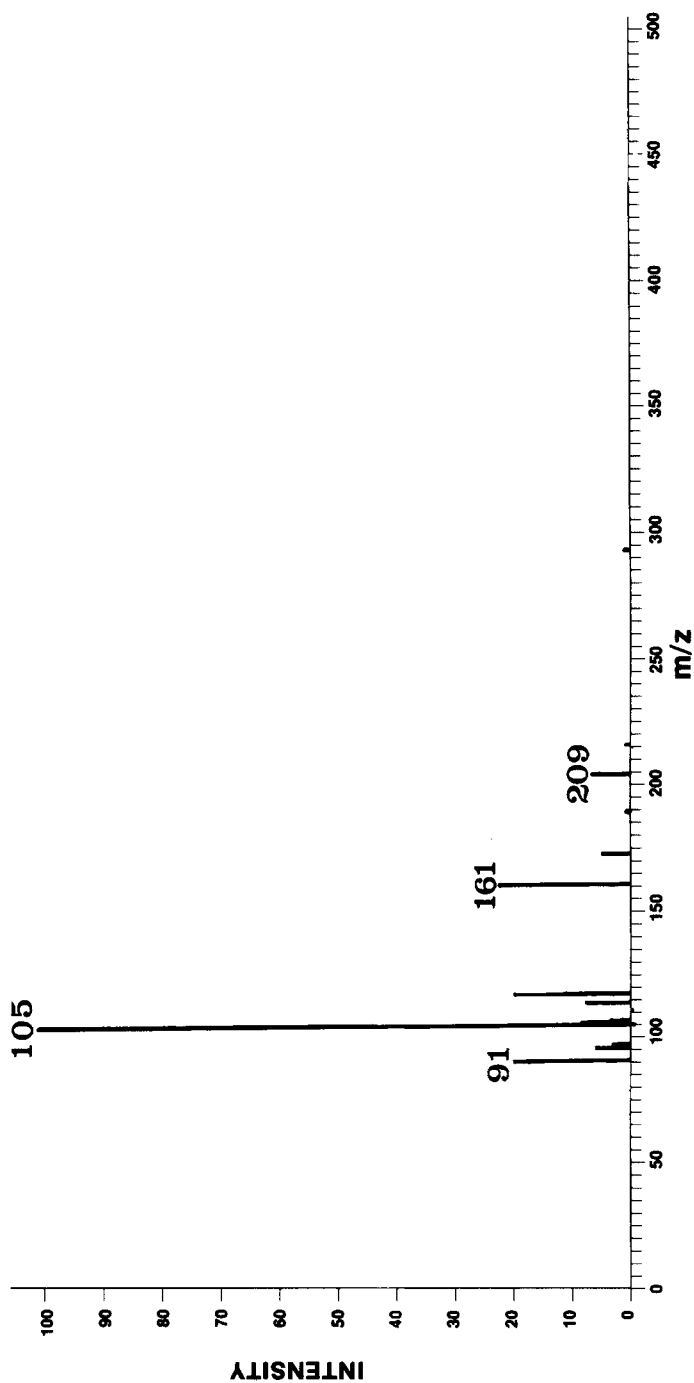


FIG. 9. Isobutane-chemical ionization mass pyrogram of the DIP probe pyrolysis of polystyrene at 400°C.

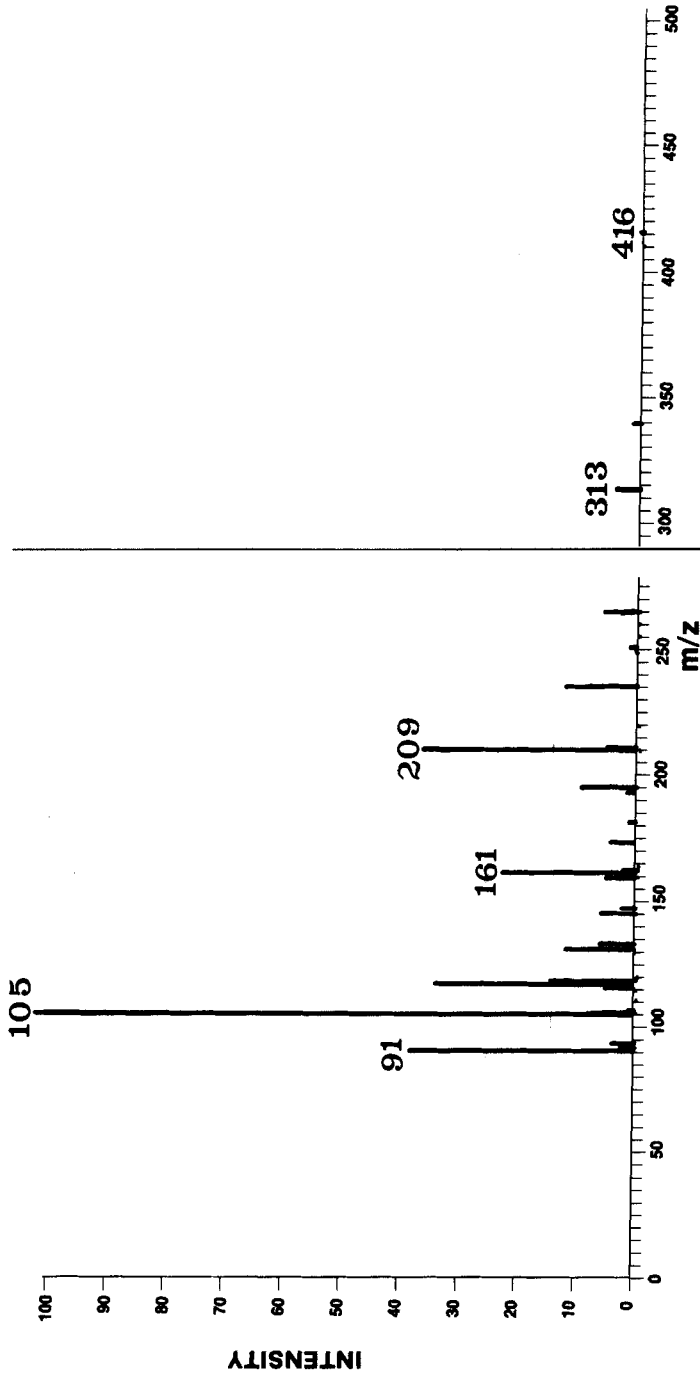


FIG. 10. Isobutane-chemical ionization mass pyrogram of the P probe pyrolysis of polystyrene at 1000°C.



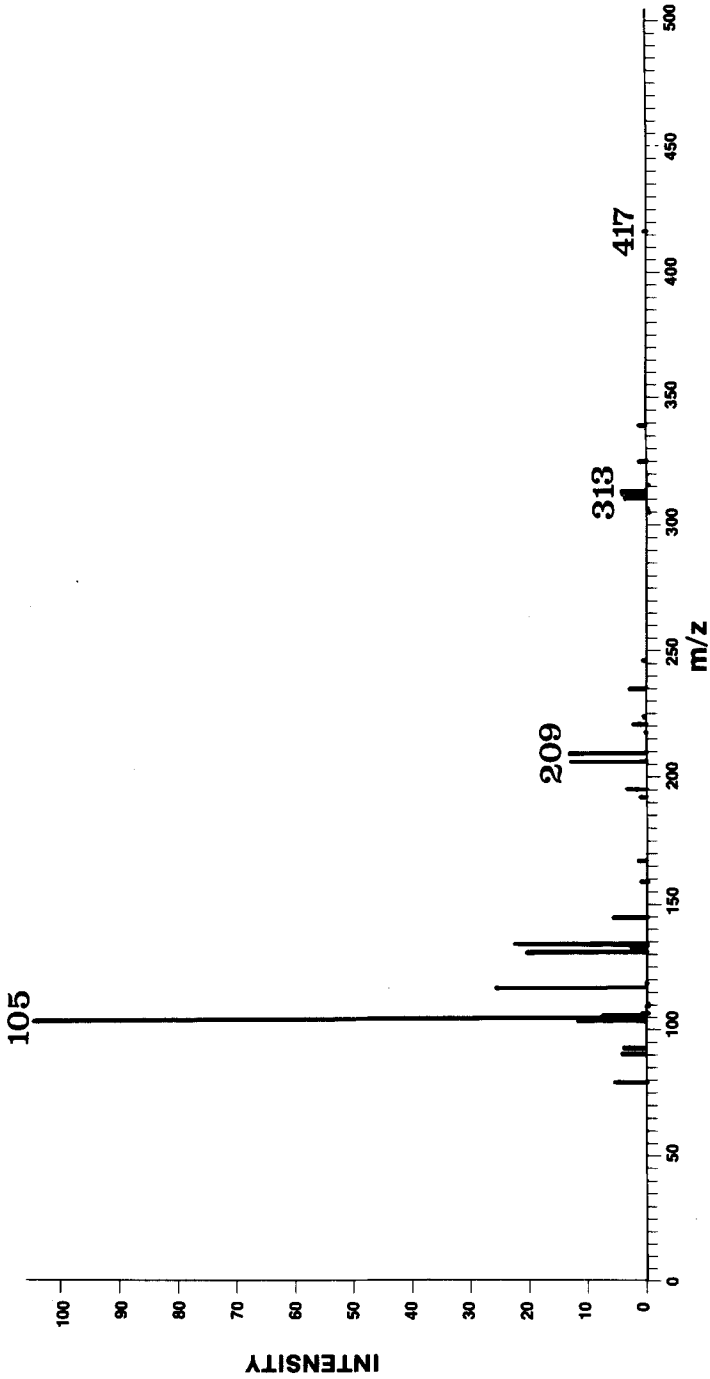


FIG. 11. Methane-chemical ionization mass pyrogram of the HTP probe pyrolysis of polystyrene at 1000°C.

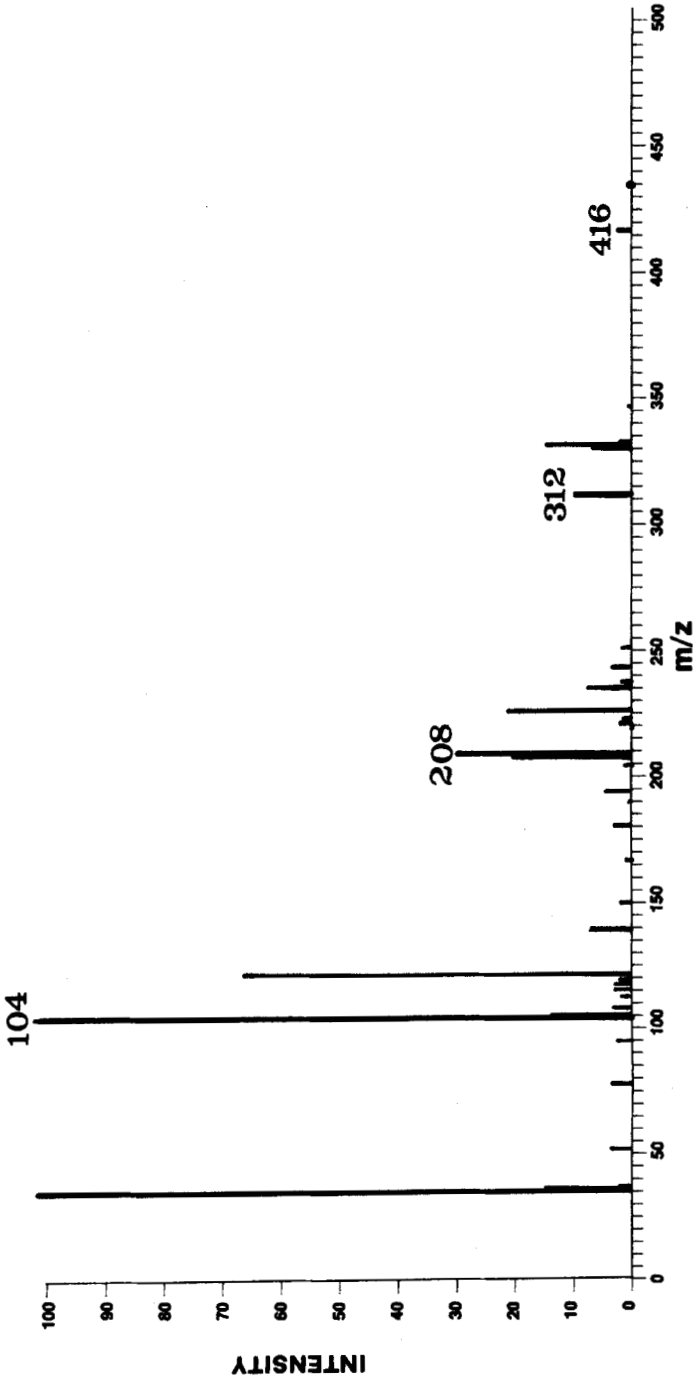


FIG. 12. Ammonia-chemical ionization mass pyrogram of the HTP probe pyrolysis of polystyrene at 1000°C.

As in the case of PMMA, it appears that there is a distinct difference between the DIP and HTP pyrolysis processes. The pyrolysis of PS with the DIP probe favors monomer while the HTP probe causes random chain cleavages as well as producing monomer.

### Poly(Vinyl Chloride)

The isobutane-CI mass pyrogram obtained for the 400°C DIP pyrolysis of PVC is shown in Fig. 13. From this pyrogram it is immediately obvious that, unlike PMMA and PVC, the pyrolysis of PVC proceeds by a mechanism other than simple depolymerization. Numerous degradation product peaks are observed in the pyrogram. This is in agreement with the reported degradation mechanism for PVC [14]. It has been reported that the major degradation products are HCl and benzene. In our analysis we did not scan to low enough mass to detect HCl. This is necessary so as not to scan over the reagent gas peaks. Benzene is detected at  $m/z = 79$  and 135.

Figures 14, 15, and 16 show the HTP pyrolysis of PVC under CI-isobutane, CI-methane, and CI-ammonia conditions, respectively. These three pyrograms appear to be quite different from one another even though it is the same degradation product mixture that is being analyzed in each case. The differences in these three pyrograms may be directly attributable to the differences in selectivity of the three reagent gases. These selectivity differences result in vastly different peak heights for the species under analysis. The use of these selectivity differences can be a very powerful aid in the interpretation of the pyrograms. This interpretation is beyond the scope of this report and will be addressed in a later publication. It should be noted that we may identify in the pyrograms many of the substituted aromatic and polynuclear aromatic compounds that have been reported to be produced in the degradation of PVC. It should also be noted that the pyrograms indicate the presence of chlorine isotope peaks in some of the higher molecular weight species.

As in the case of PMMA and PS, there appears to be a difference in the pyrolysis process produced by the DIP probe and the HTP probe. The HTP probe pyrolysis yields a different product mixture containing species at much higher mass than does the DIP probe pyrolysis.

## CONCLUSION

It has been demonstrated that the application of probe pyrolysis directly in the ion source of a mass spectrometer is an extremely useful technique for the analysis of polymers. The application of chemical ionization mass spectrometry for the analysis of the pyrolysis products has the advantage of greatly simplifying the mass pyrogram such that each peak in the pyrogram has a direct and interpretable correlation to the individual products generated by the pyrolysis. The ability to

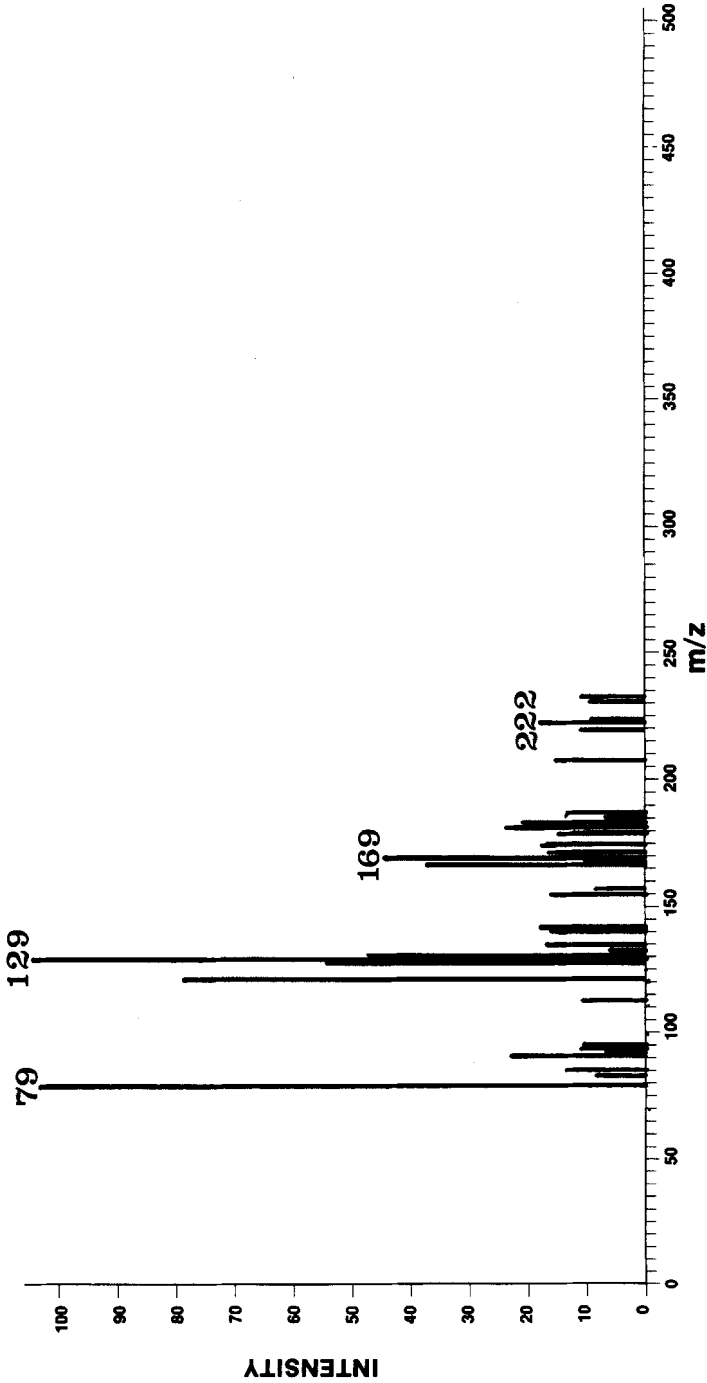


FIG. 13. Isobutane-chemical ionization mass pyrogram of the DIP probe pyrolysis of poly(vinyl chloride) at 400°C.

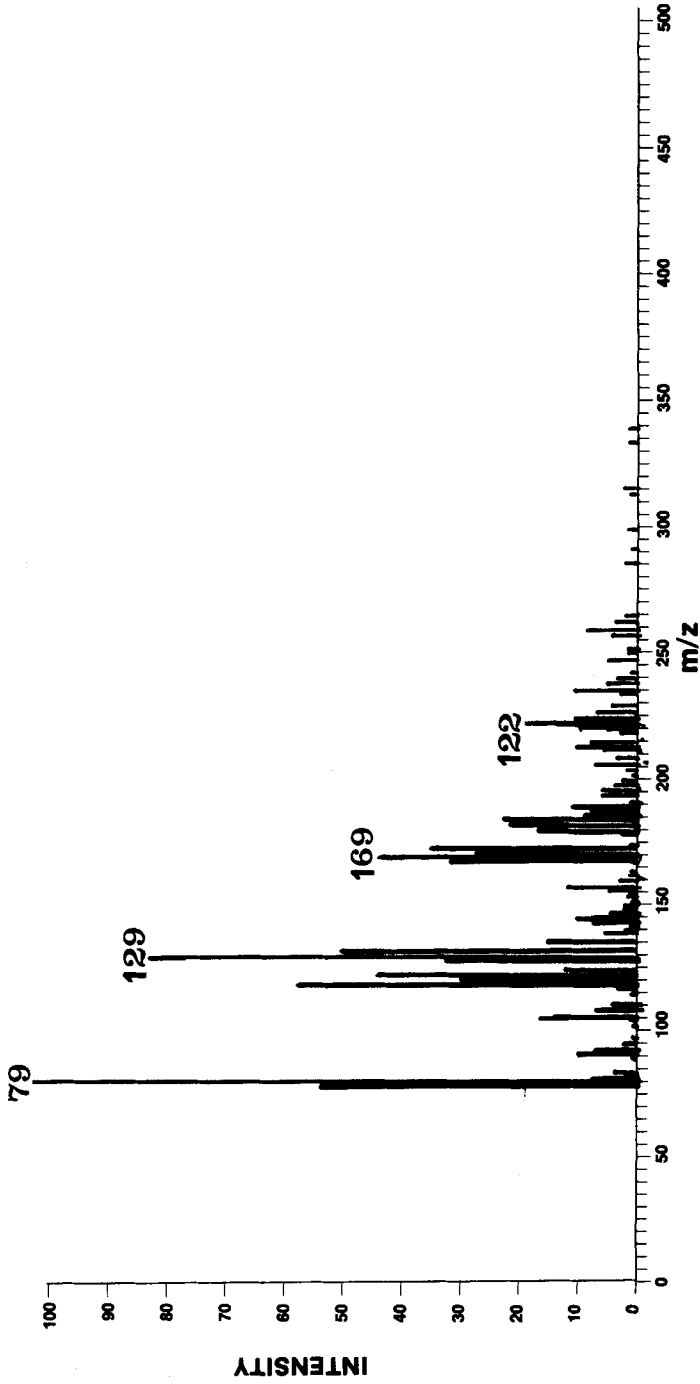


FIG. 14. Isobutane-chemical ionization mass pyrogram of the HTP probe pyrolysis of poly(vinyl chloride) at 1000°C.

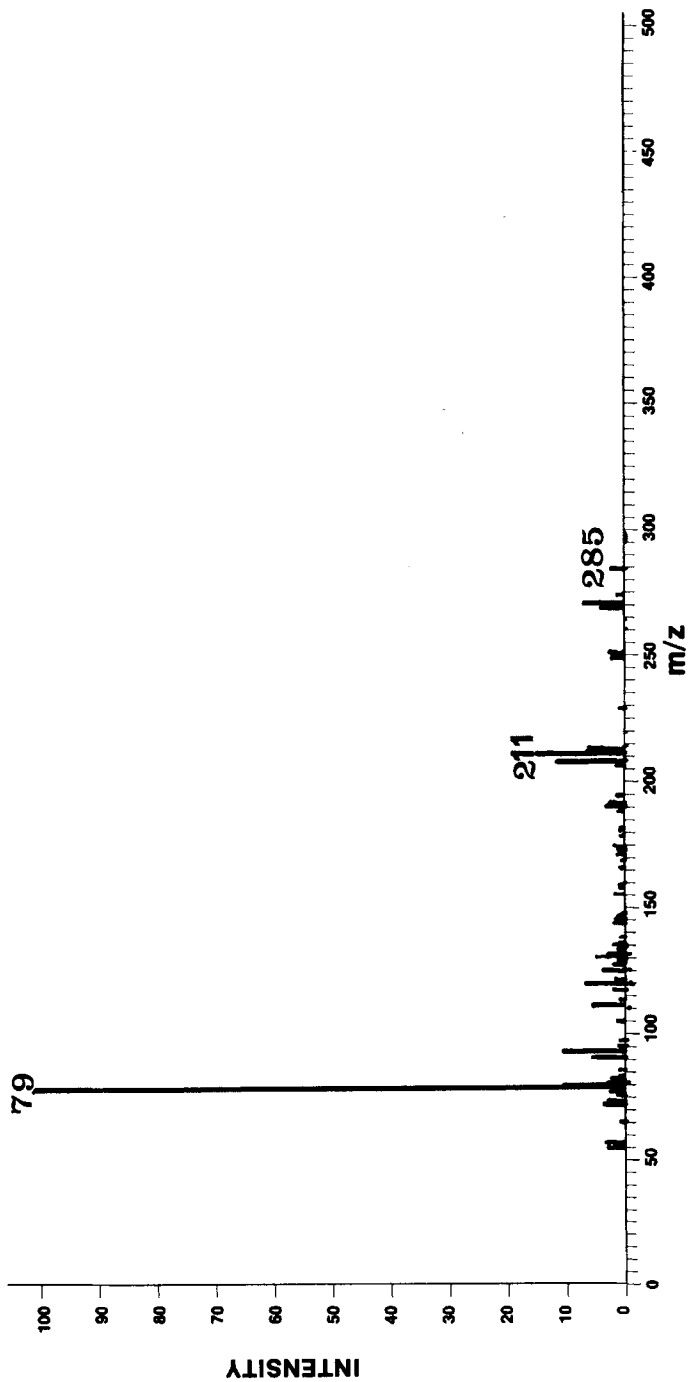


FIG. 15. Methane-chemical ionization mass pyrogram of the HTP probe pyrolysis of poly(vinyl chloride) at 1000°C.

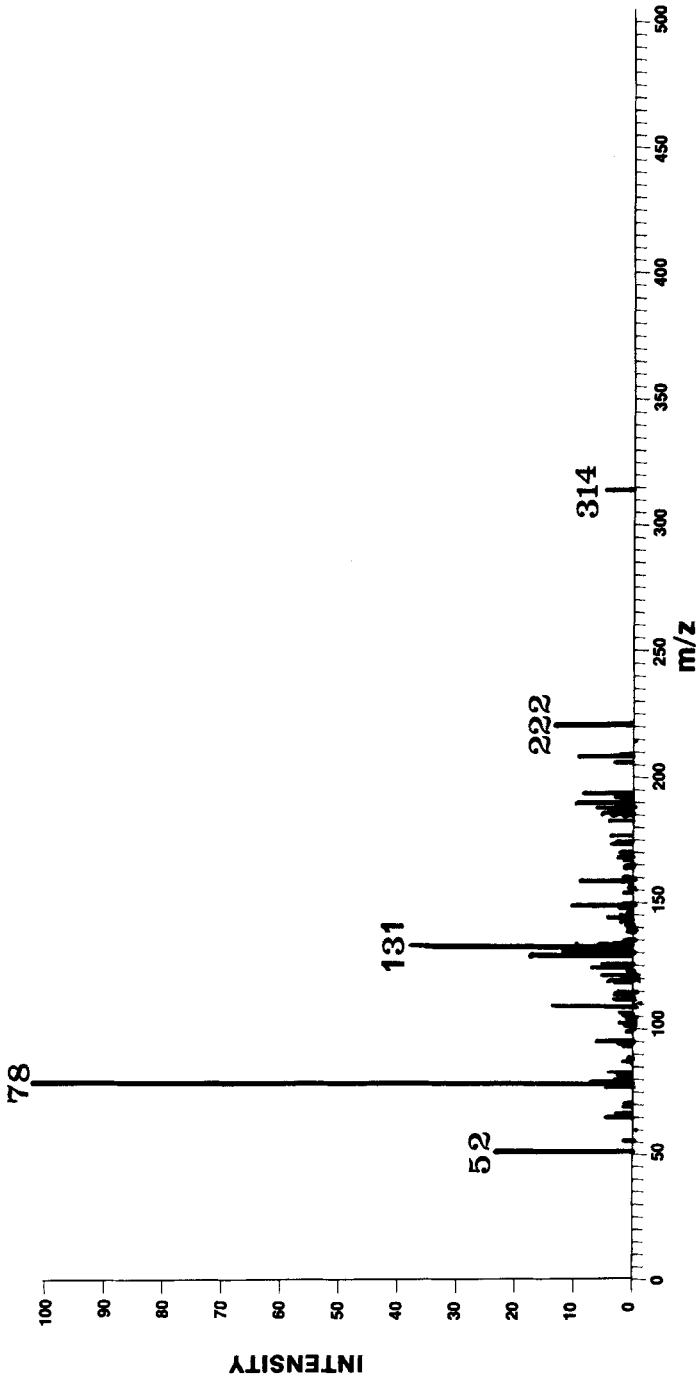


FIG. 16. Ammonia-chemical ionization mass pyrogram of the HTP probe pyrolysis of poly(vinyl chloride) at 1000°C.

use selective reagent gases was also shown to be helpful in the interpretation of the pyrogram.

The low temperature DIP probe was found to be an effective tool for following the equilibrium degradation of the material and has great utility in the analysis of degradation products generated under temperature profiles matching those used in other standard thermal analysis techniques. The high temperature HTP probe yields a highly reproducible pyrogram that allows for the elucidation of the polymer structure.

#### ACKNOWLEDGMENTS

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