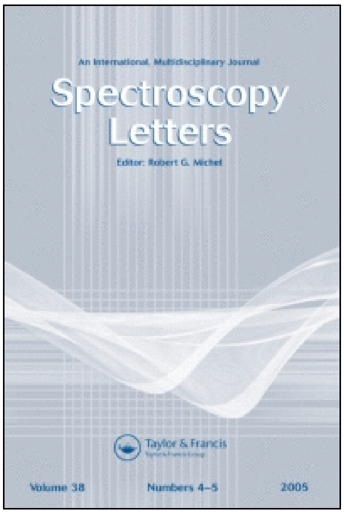

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Mass Spectrometry of Molecular Solids: Laser Microprobe Mass Analysis (LAMMA) of Selected Polymers

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MASS SPECTROMETRY OF MOLECULAR SOLIDS:
Laser Microprobe Mass Analysis (LAMMA) of Selected Polymers

Key Words: Laser Microprobe Mass Analysis, LAMMA, Polymer Mass Spectra

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ABSTRACT

Positive and negative ion mass spectra of organic polymers were recorded using the Laser Microprobe Mass Analysis (LAMMA) technique. The mass spectra are characteristic of both the hydrocarbon backbone of simple straight-chain polymers [polyethylene, poly(vinyl chloride), and poly(tetrafluoroethylene)] and of slight changes in side chain functionality [poly (phenyl methacrylate) and poly (benzyl methacrylate)]. The spectra show ion clusters having masses up to and beyond the monomer unit. This study indicates the power of the LAMMA technique for organic polymer materials analysis. Preliminary analysis of the mass patterns is given for the most probable positive and negative molecular cluster ions formed.

INTRODUCTION

The problem of obtaining direct mass spectra of solids has attracted a large amount of attention, and has involved development of several elaborate techniques. The problems inherent in the methods is the ionization/vaporization step, which must be done while maintaining chemical integrity. Techniques such as Field Desorption (FD), ^{252} Cf - Plasma Desorption (^{252}Cf PD), and Secondary Ion Mass Spectrometry (SIMS) have been developed specifically for solids.

There remains a large gap in the application of these techniques to organic polymer materials. Matsuo, Matsuda and Katakuse[1] recently have applied FD to polymers, for use as mass references up to 10,000 a.m.u. The pattern of the spectra reflected the molecular weight distribution, but no attempt has been made to use FD as a method for investigating chemical structure and reactive effects. Macfarlane, McNeal and Hunt[2] have recently developed ^{252} Cf PD as an ionization/vaporization method, and applied it to large biopolymer molecules with success. No commercial polymers have been analyzed as yet by this method. SIMS has been used, with great success, on large organic molecules for sometime. By using "static" conditions (low primary ion beam energy and current density), surface integrity is maintained, and formation of large molecular cluster ions is maximized. Work continuing in this laboratory[3] has utilized static SIMS for analyzing polymer chemical structure and reactive effects on surfaces. All of the methods listed above have drawbacks, if considering ideal direct analysis conditions for a mass spectrum of organic polymers. FD requires a very high electromagnetic field, focused to a point. Maintenance of the field and the reactive effects that could be induced by such a field make its use for structural analysis in a routine manner questionable. ^{252}Cf PD takes long data aquisition time, because of the low intensity of high mass ions generated. Static SIMS is a surface sensitive technique and thus can be used with bulk results to examine the very important differences between surface and bulk composition and structure. In order to increase sampling depth to achieve bulk results with SIMS, there must be an increase in primary ion beam energy and current density (so-called dynamic conditions). It has been shown for organic materials analyzed at even moderate primary ion beam conditions, there can be significant selective sputtering of the surface,[4] making the resultant mass spectrum somewhat questionable as to the relationship to the structure of the polymer.

We have become interested recently in the application of a new technique Laser Microprobe Mass Analysis[5] (LAMMA) to the study of organic materials. The method uses a laser pulse from a Nd-YAG laser (frequency quadrupled $\lambda = 265$ nm) to ionize/vaporize the sample ($\sim 10^{-13}$ gram) into a time of flight mass spectrometer. It is capable of focusing the laser excitation to 0.5 μm and thus offers microprobe capabilities. The feasibility of using the LAMMA technique to probe differences in chemical structure of organic materials has been suggested by Hillenkamp et. al.[6] who used LAMMA to examine the methodological parameters such as laser power density levels and trace detection capabilities on doped organic resin samples. Spectra showed differences between varied resin samples, but no structural analysis was attempted.

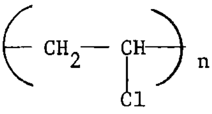
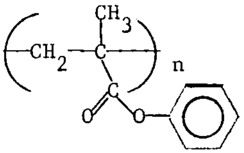
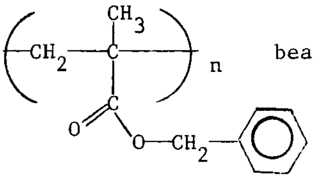
In the present paper five polymers are examined by the LAMMA technique, which illustrate the utility of the method for organic materials. Results show typical mass patterns expected from the backbone and the side chains of the polymers, and the ability to differentiate between small changes in polymer structure.

EXPERIMENTAL

Polymers used in this study are shown in Table 1 and are commercially available from Scientific Polymer Products (Ontario, NY 14519). The polymers were mounted on quartz glass cover slides for analysis as received. The spectra were recorded using a Leybold-Heraeus, Inc. LAMMA 500 spectrometer having a frequency quadrupled ($\lambda = 265$ nm) Nd YAG laser as the

Table 1

Polymers Analyzed

Sample Name	Polymer Name	Structure	Characteristics
PET	Polyethylene	$(-CH_2-CH_2-)_n$	high density beads
Teflon	Poly(tetrafluoroethylene)	$(-CF_2-CF_2-)_n$	powder
PVC	Poly(vinyl chloride)	 $(-CH_2-\underset{Cl}{CH}-)_n$	Low MW powder
PPMA	Poly(phenyl methacrylate)		beads
PBzMA	Poly(benzyl methacrylate)		beads

ionization/vaporization source. Laser power density was in the range of 1-10 x 10^{10} watts/cm^2. The laser was pulsed for ca. 20 nanoseconds. Each spectrum shown is the analogue output from a single pulse, but is representative of the 5 to 10 pulses averaged for each sample for positive and negative ion spectra.

Spectra were recorded over several mass ranges. The 0-100 mass range was used to calibrate the spectra. The 20-200 a.m.u. range was chosen as the most illustrative of molecular clusters and their relative intensities.

RESULTS AND DISCUSSION

The positive and negative ion spectra of each polymer are shown in Figures 1-5. The mass range of each spectrum is 20-200 a.m.u., the abcissa being time of flight, which is related to $\sqrt{\text{mass}}$. We will discuss the results in two sections. We have studied backbone polymers by examing straight chain polymers: polyethylene (PET), poly(tetrafluoroethylene) (Teflon) and poly (vinyl chloride) (PVC). We also examined the effects of minor modifications of side chain functionality by examining poly (phenyl methacrylate) (PPMA) and poly(benzyl methacrylate) (PBzMA).

Backbone Polymers

Polyethylene shows typical straight chain polymer patterns in both the positive and negative ion spectra (Figure 1). The positive ion spectrum shows "clusters" of ions, each approximately 12 a.m.u. apart. Each of these mass groupings can be assigned to 3-6 different ions, ususally C_n^+, C_nH^+, $C_nH_2^+$, $C_nH_3^+$, etc. Besides the peaks assignable to the carbon chain, peaks are assigned to common processing contaminants: Na^+ (23), Al^+ (27), K^+ (39, 41) and Co^+ (59). Small peaks are noted at higher laser powers, intermediate to each $C_nH_m^+$ cluster. These, most likely, are due to ions present from rearrangement during the ionization

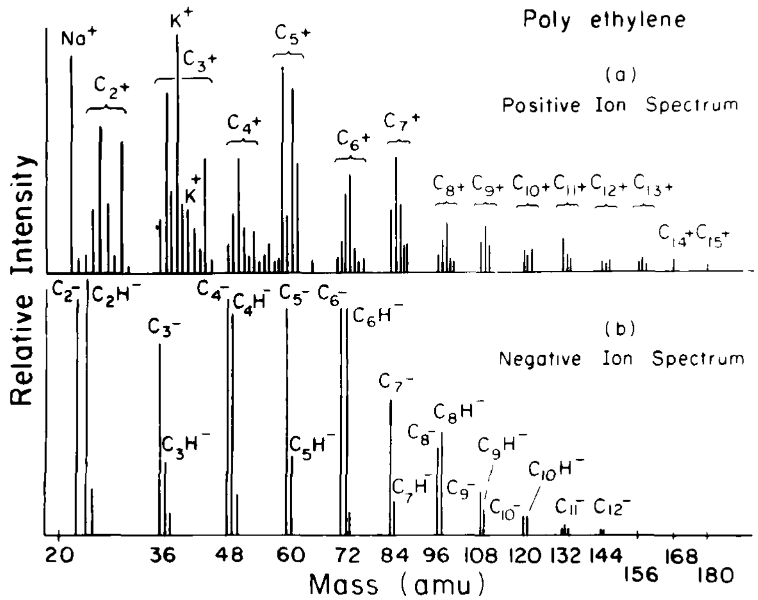


FIG. 1.

LAMMA positive (a) and negative (b) ion spectra of Polyethylene. Scale 20-200 amu.

process, where a laser induced plasma exists for a short time. Thus, rearrangement would be expected, but these events are minor compared to ejection and ionization of molecular fragments directly related to the structure. The maximum mass ion that was detected was a C_{14} group at 168 a.m.u.

The negative ion spectrum of PET shows unusual intensity, as most techniques (outside of chemical ionization) do not produce negative ion spectra of equal intensity to the positive ion spectra. The major peaks parallel the positive ion pattern but show a pattern of C_n^- molecular clusters, where only the C_n^-, C_nH^- and $C_nH_2^-$ appear. The $C_nH_2^-$ peak usually is only seen under extreme ionization conditions. A further pattern is observed where for C_n^- where n is an odd number, the peak assignable to C_nH^- is of much lower intensity, relative to the C_n^-. The even n cluster has C_nH^- intensity nearly equal to or greater than the C_n^- intensity. In general, for the polymers studied, the backbone pattern reactive intensities of $C_nH_m^{+,-}$ clusters increase to n = 3, 4, 5 or 6 after which there is a general sloping decrease in intensity. In the case of PET, where the monomer is a C_2 group, C_2H^- is the most intense peak in the negative spectrum. The maximum mass negative ion detected was at 144 a.m.u.

Poly(tetrafluoroethylene), Teflon, shown in Figure 2 offers a check of the conclusions drawn from PET. Besides the common contaminants mentioned above, the positive spectrum exhibits very few fragments, but those seen are very characteristic. The peaks assignable to C_n^+ fragments have much lower intensity than the $C_nF_m^+$ fragments. In particular, the $C_3F_m^-$ series is the most intense series, showing C_3^+, C_3F^+, $C_3F_2^+$, $C_3F_3^+$ and $C_3F_5^+$ at 36, 55, 74, 93, and 131 a.m.u. respectively. Besides the base peak, CF^+ (31 a.m.u.), the second highest relative intensity is 69 a.m.u. corresponding to CF_3^+ which is due to branching and/or rearrangement in the plasma. All of these positive molecular ions are characteristic due to the atomic mass of 19 a.m.u. for fluorine.

The negative ion spectrum exhibits much the same patterns as polyethylene, F^- at 19 a.m.u. is the base peak for the negative ion spectrum. The next most intense peaks are assignable to C_n^-

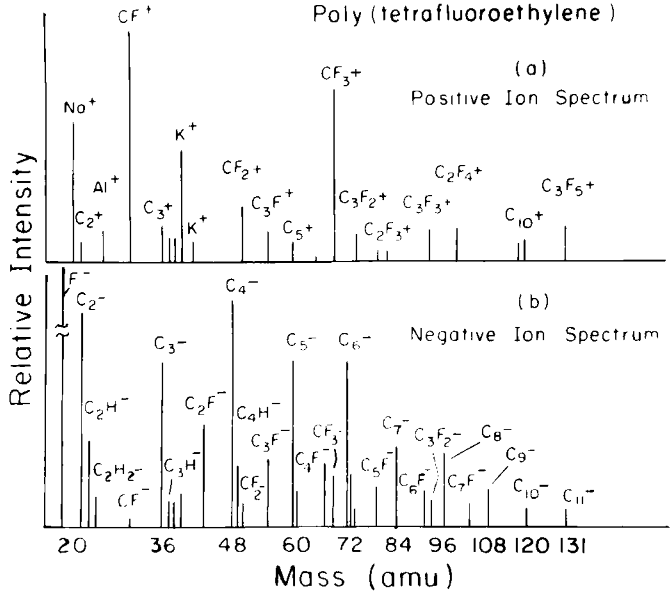


FIG. 2.

LAMMA positive (a) and negative (b) ion spectra of Poly(tetrafluroethylene). Scale 19-200 amu.

ion series (12, 24, 36, etc. a.m.u.). The C_nF^- molecular ions can be assigned to peaks at 31, 43, 55, 67, 79, 91 and 103 a.m.u. respectively. However, the pattern of alternating intensities for odd and even n's is not seen for C_nF^-. These intensities follow the pattern of a general sloping decrease. Some organic contaminants present are seen as masses assignable to C_nH^- peaks, but they have low relative intensity. Again the odd mass of F(19 a.m.u.) leads to unique fingerprint for Teflon. In both positive and negative spectra, the highest mass fragment detected is at 131 a.m.u.

Figure 3 shows spectral results for poly(vinyl chloride)

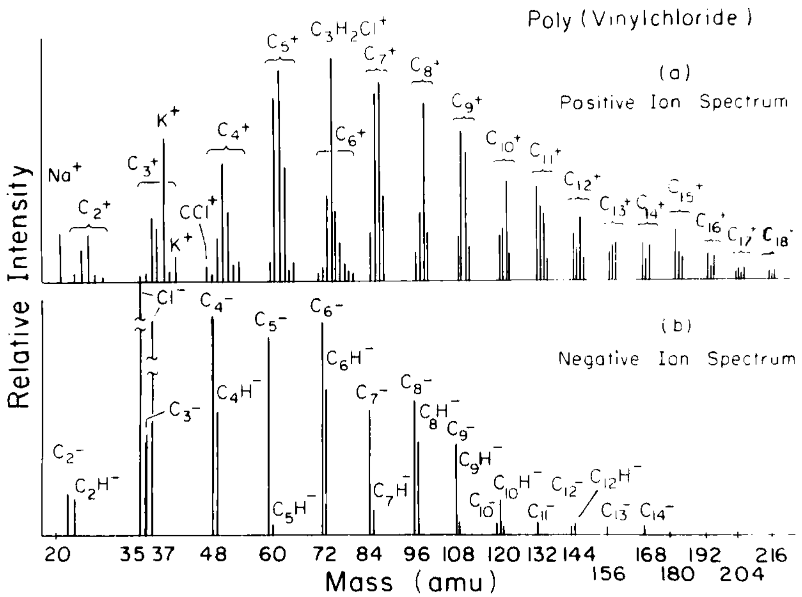


FIG. 3.

LAMMA positive (a) and negative (b) ion spectra of Poly(vinyl chloride). Scale 20-200 amu.

(PVC). The positive ion spectrum shows a molecular fragment ion cluster pattern similar to PET, i.e., the groups based on each $C_nH_m^+$, with increasing relative intensity until C_3 to C_5 and then gradual decrease to a C_{22} fragment at 264 a.m.u. A characteristic peak assignable to a Cl containing molecular ion at 73 a.m.u. can be assigned to $C_3H_2Cl^+$. No other Cl containing positive ions were detected. Matched with the negative ion results, the C_n^-, C_nH^- peaks with alternating C_nH^- intensities up to C_{17} at 204 a.m.u. and Cl^- at 35 and 37 a.m.u. we are provided with a rational fingerprint for PVC.

Side Chain Functionality

The test of the LAMMA technique's ability to differentiate between small changes in chemical structure can be shown by comparing results for poly(phenyl methacrylate) (PPMA) and poly (benzyl methacrylate) (PBzMA), shown in Figures 4 and 5. The positive spectrum for PPMA exhibits the typical backbone characteristics for the methacrylate series, groupings of $C_nH_m^+$ ions up to C_{18} at 216 a.m.u. The peak at 77 a.m.u. characteristic of the phenyl positive ion is prominant, but there

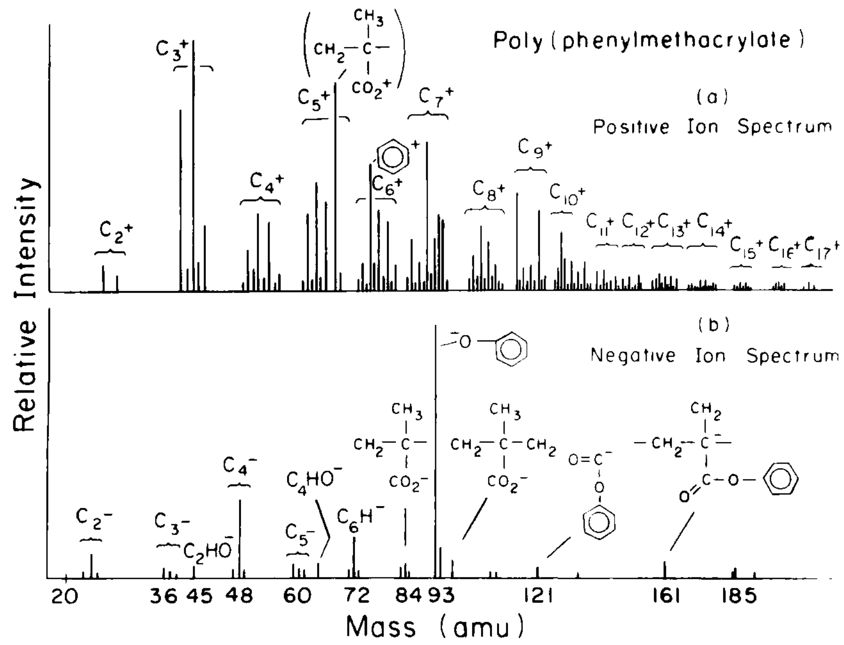


FIG. 4.

LAMMA positive (a) and negative (b) ion spectra of Poly(phenyl methacrylate). Scale 20-200 amu.

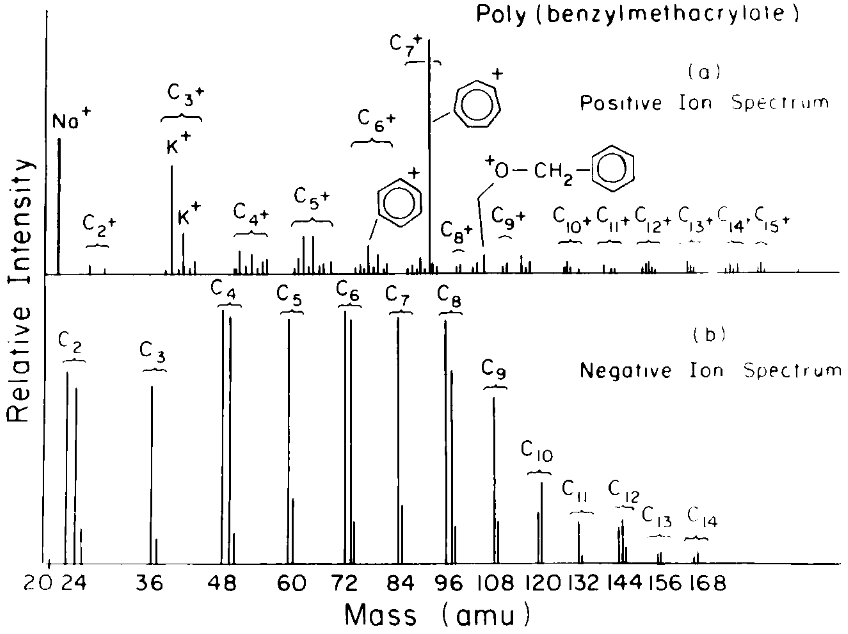


FIG. 5.

LAMMA positive (a) and negative (b) ion spectra of Poly(benzyl methacrylate). Scale 20-200 amu.

remains no dominant feature due to the side chain. This type of feature is present in the negative spectrum, where the 93 a.m.u. peak due to phenoxy negative ion dominates the typical backbone C_n^-, C_nH^- feature. Other characteristic negative ions are labeled for 85, 121, 161, and 185 a.m.u. which are fragments of the monomer unit. The highest mass seen is the monomer plus another CH_2 group at 185 a.m.u.

Figure 5 shows the opposite effect for PBzMA. The positive ion spectrum is dominated by peaks at masses assignable to common stable ions, in particular the 77, 91 a.m.u. peaks assigned to the phenyl positive ion, and the tropyllium ion, a favored rearrangement commonly seen for benzyl moeities. The negative ion spectra shows only the familiar backbone C_n^-, C_nH^- odd even in intensity pattern up to C_{14}.

These results clearly show that small differences in chemical structure lead to radically different spectra, which shows the utility of the method, for obtaining fast direct characteristic mass spectra of molecular solids.

CONCLUSIONS

Typical positive and negative ion mass spectra generated by the LAMMA technique on polymers were analyzed. Contributions due to the backbone of the polymer were seen as molecular ion clusters based on $C_nH_m^+$ groups in the positive spectrum and C_n^-, C_nH^- groups in the negative spectrum. The negative C_nH^- intensity was large, where n was odd the relative intensity was small. Stable ions generated from the sidechain could be used as characteristic fingerprints, small changes in structure (from phenyl to benzyl sidechain) produced effects in spectrum which reflect typical ion stability, and can be rationally explained.

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