Laser-Induced Decomposition of PVC

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Synopsis

A laser probe–molecular beam experimental technique devised to investigate the dynamic characteristics of polymer decomposition processes is described. Results are presented from application of the technique to the laser vaporization of pure poly(vinyl chloride) (PVC). Vaporization products are sampled directly from the source cell using modulated molecular beam mass spectrometry. Only signals arising from the PVC species in the molecular beam appear in the modulated mass spectra; background species from the residual gas are automatically rejected. Time-resolved spectra provide information on the relative evolution characteristics of the PVC decomposition products. Hydrogen chloride, benzene, and toluene are found to evolve concurrently from the irradiated PVC sample. PVC monomer species are not detected in the laser-vaporized products. The presence of loosely bound water in the sample is distinguished from the evolution of volatile decomposition products by its burst-like release mode. The effect of plasticizer and flame retardant additives on the evolution characteristics of the laser-vaporized species from PVC are also presented.

INTRODUCTION

A cw argon-ion laser (λ = 5145 Å) has been used to vaporize samples of unplasticized poly(vinyl chloride) (PVC) directly in the source cell of a mass spectrometer system. The experimental technique of this paper offers a number of advantages in the study of the decomposition processes of polymeric materials. Trace species (e.g., additives, etc.) in the laser-vaporized products can be detected with sensitivities on the order of 10 ppm or better. Precise areas of the sample can be investigated with a focused laser beam. Laser probing can be performed in a vacuum environment or with the sample in atmospheres of different gases. Various stages of evolution of a given product can be observed, and it is possible to distinguish between separate products that are evolved concurrently. Release of loosely bound species (e.g., water) can be differentiated from volatile decomposition products.

Measurements are obtained on the overall course of the laser vaporization process of PVC, the composition of the volatile products, and the evolution history of each product. Such information is important in the study of flame inhibition mechanisms since (1) identification of the actual volatile flame retardant species is possible, and (2) it is generally sought to match the vapor release rate of the inhibitor with the fuel release properties of the flammable substrate.[1] In addition, these studies have an immediate practical application to the recently developed laser bonding technique[2] for polymeric materials.

The results of this paper represent the first utilization of low-power (1-W output) gas lasers in material vaporization studies. Although the interactions of laser radiation with a large number of substances have been investigated, relatively little work has been done with organic materials. Of the various types of lasers used to study laser–solid interactions, the argon and krypton ion lasers offer the advantage that a number of output wavelengths can be selected over a relatively wide spectral region (3500–7500 Å). Application of Ar/Kr ion lasers to the irradiation of polymeric materials at low power densities can thus provide information regarding polymer stability to thermal- and photo-decomposition processes.

Detection of the vaporization products is accomplished by using modulated molecular beam mass spectrometry. Beam modulation is normally accomplished by using a mechanical chopper, although periodic irradiation with a laser beam[3] and pulsed electrical discharges[4] have also been employed. Only signals arising from the PVC species in the molecular beam appear in the modulated mass spectra; signals from background gases present in the spectrometer chamber are rejected. Identification of the parent neutral precursors of the various fragment ions created in the ion source is obtained from phase measurements of the modulated ion signals at the beam chopping frequency. These initial experiments with PVC represent the first application of the "phase spectrometry" technique to investigations of the thermal degradation of organic materials. The experimental results demonstrate the capabilities of the phase measurement technique and serve to illustrate its potential for studies of more complex polymer systems.

EXPERIMENTAL

System Description

A schematic of the experimental arrangement is shown in Figure 1. The laser beam enters the source chamber through a quartz window and irradiates a disc-shaped PVC sample at normal incidence to its surface. The laser-vaporized species effuse through a thin-walled orifice in the source chamber and pass as a molecular beam into the first of two differentially pumped vacuum chambers. After collimation by the skimmer cone at the entrance of the second chamber, the molecular beam is modulated by a mechanical chopper. The modulated beam then travels a distance of 5 cm before being ionized. Ions having the selected m/e value travel the length of the quadrupole mass filter ($\sim$22 cm) and are deflected into an electron multiplier which is offset from the mass filter axis. Ion signals from the electron multiplier are fed into an electrometer where the a.c. (molecular beam) and d.c. (residual gas) signal components are separated. The a.c. component is sent to a lock-in amplifier where the phase of the modulated signal is determined with respect to a reference signal from the mechanical chopper.

Laser target samples of pure, unplasticized PVC are obtained by hot pressing the resin powder at 180°C to form clear sheets with a thickness of 0.5 mm. Typical sample weights prior to irradiation range from 30 to 50 mg. Measurements are reported for source aperture diameters of 0.2 and 2 mm. Maximum pressures attained in the source during laser vaporization of the sample
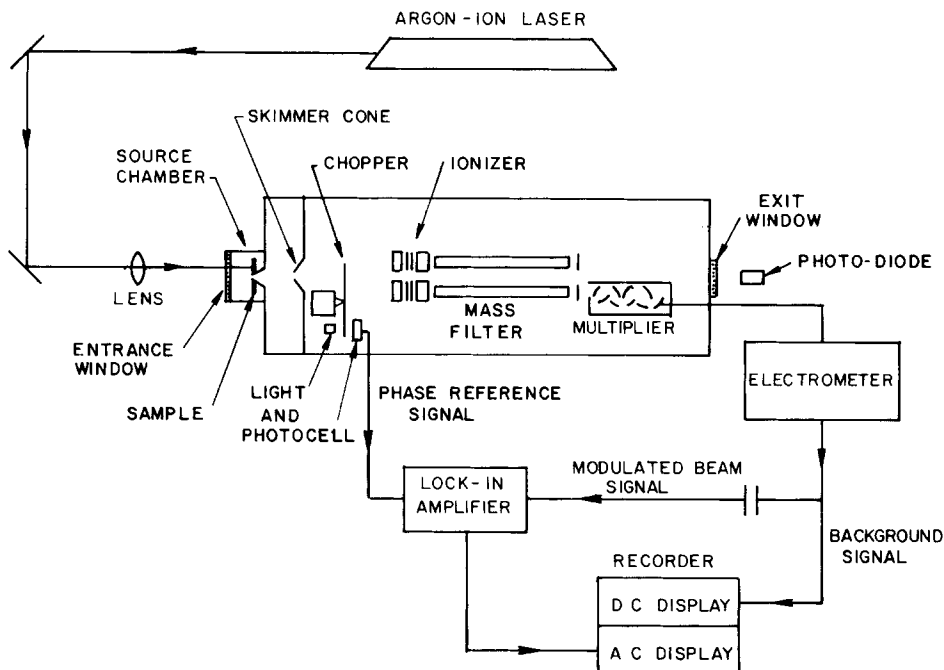
Fig. 1. Schematic of laser/molecular beam apparatus. Two source designs are used. Distances from the laser entrance window to the source aperture at the vertex of the conical nozzle are 1 mm and 7 mm, respectively, for orifice diameters of 2 mm and 0.2 mm.

are approximately 1 torr for the 0.2-mm orifice and 10^{-2} torr for the 2-mm orifice. The maximum resulting pressure in the first chamber under these gas loads is less than 10^{-4} torr, which ensures that the molecules forming the beam do not suffer collisions between the source aperture and the collimating cone (1-mm orifice diam.). A background pressure of 1×10^{-7} torr is usually maintained in the second chamber.

Laser Source

The argon ion laser is capable of delivering a 1.4-W output power when tuned to the strongest individual laser emission at 5145 Å. A dispersive prism situated within the optical cavity is used to tune through the various lines in the argon laser spectrum between 4579 Å and 5287 Å. With specially coated mirrors, laser operation is possible in the near-UV at about 3500 Å. The output beam has a Gaussian shape and a beam divergence of 0.6 mrad. At the sample surface, the $1/e^2$ beam diameter is approximately 2 mm. A lens is located ahead of the entrance window, and the intensity of the laser radiation at the sample surface is varied by changing the lens-to-sample distance thereby slightly defocusing the laser beam.

Laser-heating of solid samples offers a number of advantages over conventional heat sources. Only the sample itself is heated thus eliminating interfering reactions of the vapor species that could occur at hot surfaces of the sample chamber or with contaminant species liberated by various chamber components at elevated temperatures. Remote location of the laser heat

source from both the sample and sample chamber simplifies source design and permits vaporization studies to be performed in various gas atmospheres at various pressures. Precise areas of the sample can be probed by focusing the laser radiation to a small spot. However, a major difficulty is that surface temperatures resulting from laser–solid interactions are not easily determined. This is especially true in the case of organic materials. Previous work on laser irradiation of solids has been reviewed by Honig[5] and Knox[6] and is characterized by the use of relatively high-power pulsed lasers with power densities ranging from 10^6 to 10^{13} W/cm^2, as contrasted with values of approximately 10 to 10^3 W/cm^2 (3–300 cal/cm^2/sec) used in this work.

PHASE MEASUREMENT TECHNIQUE

Modulated molecular beam mass spectrometry was originally developed to discriminate between the weak signals associated with a molecular beam and the usually larger background signals due to ionization of the residual gas in the mass analyzer vacuum chamber.[7,8] The mass spectrometer signal then consists of two components: an a.c. signal due to the molecules in the modulated beam, which appears at the modulation frequency with a specific phase, and a d.c. component resulting from ionization of the background gas. Signal phases are measured by tuning the mass filter to a single mass and using signal integration time constants of from 1 to 10 sec to improve the signal-to-noise ratio. A beam shutter located in the first chamber is used to verify that the detected signals originate from the source. The phase of the laser signal, obtained by transmitting the laser beam down the axis of the apparatus, is used as the zero reference for all other measurements.

The lock-in amplifier detects the fundamental Fourier component of the modulated ion signal which is proportional to $\sin(\omega t - \phi)$. Here, ω is the modulation frequency and ϕ is the phase lag introduced by the finite transit time of the beam species between the chopper and detector. This phase lag consists of two separate contributions: $\phi_n = \omega t_n$ arising from the flight time of the neutral molecule from the chopper to the ionizer, and $\phi_i = \omega t_i$ due to the ion flight time through the mass filter. Since the ion transit times are relatively rapid, the contribution of ϕ_i to the observed phase lag is negligible at the lower modulation frequencies and

$$\phi = \phi_n = \frac{\omega L}{v_n} \tag{1}$$

where ω = modulation frequency, L = chopper-to-ionizer distance, and v_n = neutral particle velocity. For square-modulated Maxwellian beams, Harrison et al.[9] have accounted for velocity dispersion and have computed values for the averaged phase lag, $\bar{\phi}_n$.

At higher modulation frequencies, the phase shift due to ion transit times can become significant:

$$\phi_i = \omega L_i (m_i/2E_i)^{1/2} \tag{2}$$

where L_i = length of the mass filter, m_i = ion mass, and E_i = ion energy.

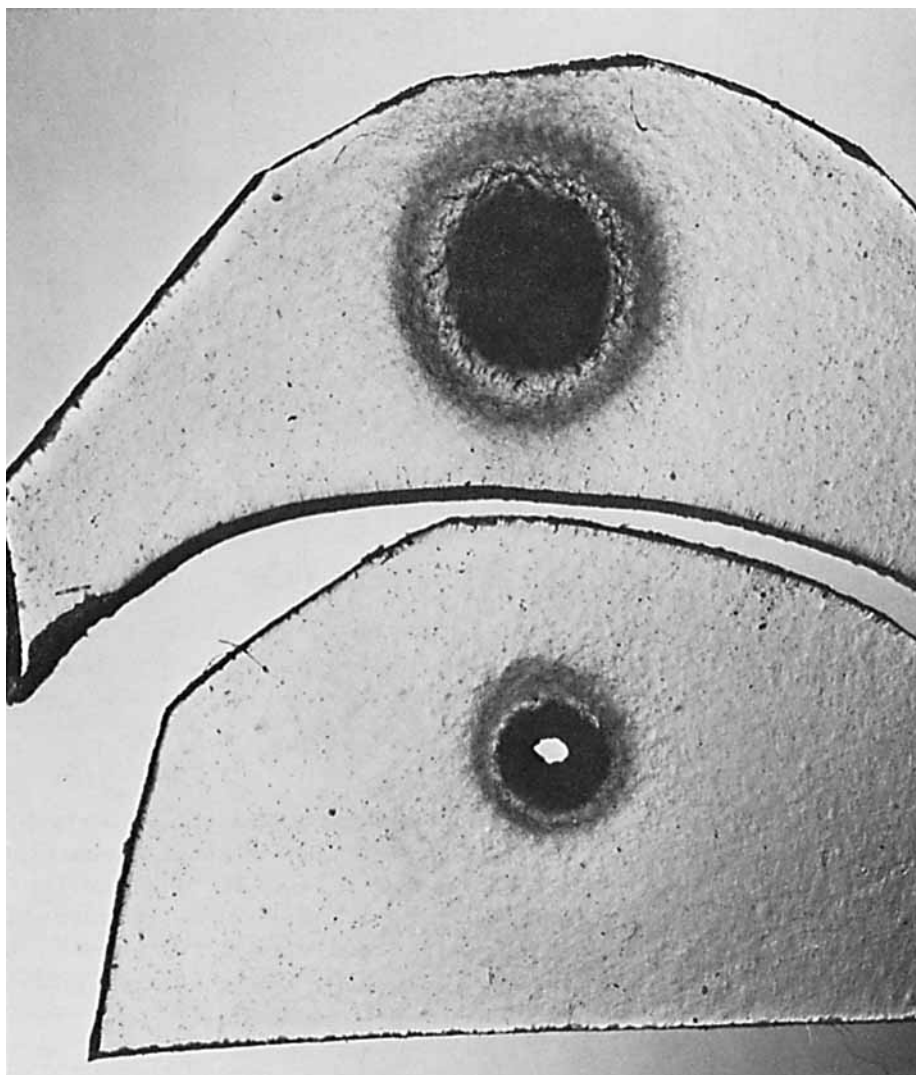The total phase lag is then given by

Fig. 2. Laser-induced thermal degradation of a PVC sample. Upper sample irradiated with an unfocused laser beam (flux density ~ 10 W/cm^2), bottom sample with a focused laser beam (flux density ~ 1000 W/cm^2).

$$\phi = \phi_n + Cm_i^{1/2} \qquad (3)$$

where C is a constant containing the remaining parameters of eq. (2).

In the present experimental arrangement, both the modulation frequency ω and the chopper-to-ionizer distance L can be varied. It is then possible from phase measurements to determine whether a given observed ion is the primary ion of a light molecule or a fragment ion resulting from dissociative ionization of a heavier molecule. In addition, it is possible to determine whether a given spectrum of fragment ions arises from a single parent molecule or from several,[10] since the signal phases of ions from the same neutral
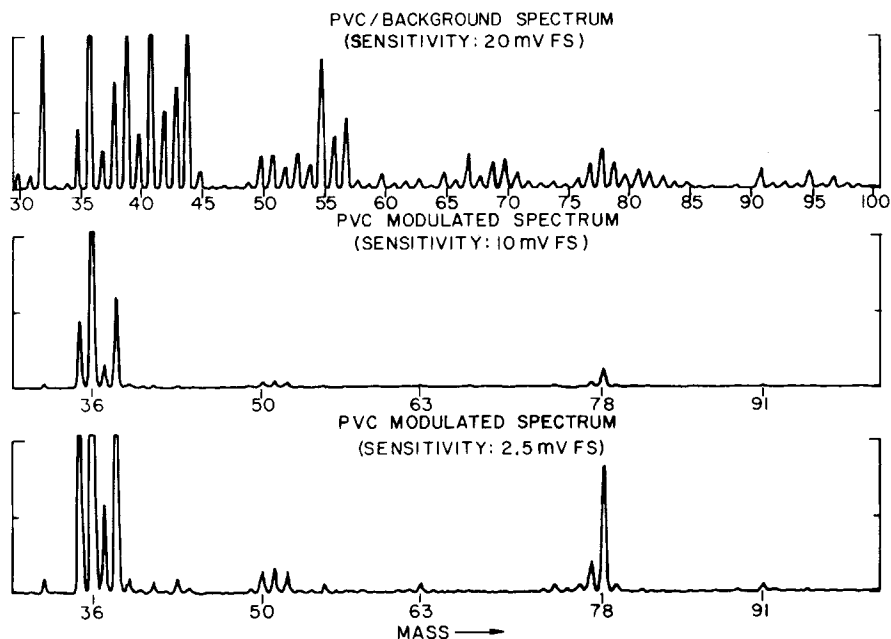
Fig. 3. Simultaneous d.c. and modulated mass spectra of laser-irradiated PVC. During the mass scan the pressure in the first chamber is constant at 3×10^{-6} torr; 2-mm-diameter source aperture used; modulation frequency = 407 Hz.

molecule are proportional to $m_i^{1/2}$. In a plot of the observed phases versus $m_i^{1/2}$, all ions having phases lying on the straight line with slope C possess the same ϕ_n and hence come from the same neutral molecule. The constant C can be determined by introducing a known gas into the source chamber and plotting the observed phases of the parent and fragment ions as a function of $m_i^{1/2}$. In the experiments reported here, C_6H_6 ($C_6H_6^+$, $C_5H_3^+$, $C_4H_3^+$, $C_3H_3^+$, $C_2H_2^+$) and Kr (Kr^+, Kr^{++}) are used.

RESULTS AND DISCUSSION

Laser Thermal Degradation of PVC

PVC samples illustrating the effects of irradiation with an unfocused and focused laser beam are shown in the photograph of Figure 2. Total irradiation time in both cases is approximately 3 min. An "induction" period of about 150 sec is observed prior to the detection of any vaporization products from the sample. Induction times are somewhat longer when an unfocused laser beam is used. Discoloration of the samples due to thermal degradation is readily apparent. With the unfocused beam, extensive char formation occurs throughout the sample thickness over an area approximately equal to that of the laser beam. Focusing the laser beam results in complete penetration of the sample as shown in the bottom sample. The hole diameter is about equal to the diameter of the focused beam. In both cases, the laser is
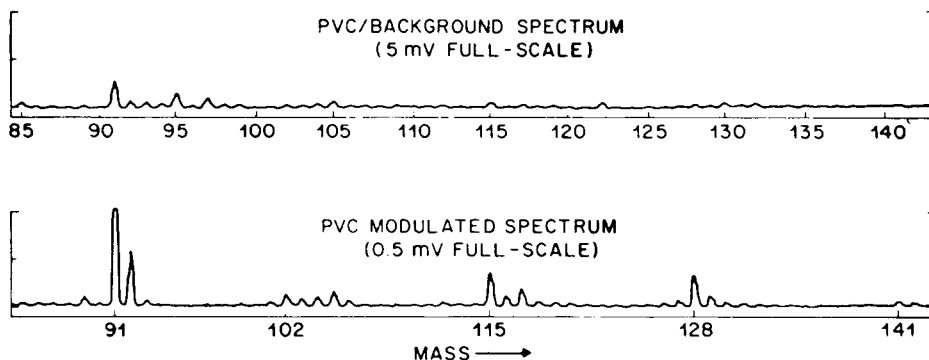
Fig. 4. d.c./modulated PVC mass spectra from m/e = 85 to 150. Pressure in first chamber is approximately constant at 1×10^{-5} torr; 2-mm-diameter source aperture used; modulation frequency = 407 Hz.

turned off after a vaporization interval of about 23 sec. Sample weight losses of 0.2 mg and 0.3 mg are incurred with the unfocused and focused beams, respectively. Reirradiation of a charred sample area results in immediate vaporization and detection of evolved gases.

PVC-Modulated Mass Spectra

Simultaneous d.c. and modulated mass spectra obtained during prolonged irradiation of a PVC sample with an unfocused laser beam are shown in Figure 3. During the scan from mass 30 to 100, the pressure in the first chamber remained constant at approximately 3×10^{-6} torr, indicating a pressure in the source of a few millitorr. The upper trace of Figure 3 is the combined spectrum of the laser-vaporized species from the sample and of the background due to the residual gas. However, only the vaporized PVC products which form the modulated molecular beam appear in the spectra of the lower two traces. Rejection of the d.c. signals from the residual gas is clearly evident. Weak beam signals appearing at masses which have large concentrations in the residual gas are easily discriminated and detected. The possible introduction of inaccuracies resulting from background subtraction involving two relatively large numbers is thus eliminated. The modulated spectrum due to the products from PVC is relatively simple, and identification of the vaporized species in this case can be obtained directly from known fragmentation patterns.

The major peaks observed in the modulated spectrum appear at m/e values of 35–38 and are due to the evolution of hydrogen chloride (HCl^{35} and HCl^{37}) from the PVC sample since the intensity of alternate peaks exhibits the proper 3:1 isotopic ratio. Peaks at masses 50–52 and 73–79 form the characteristic fragmentation spectrum of benzene and indicate its presence in the laser vaporized plume. A small amount of toluene ($C_6H_5CH_3$) in the molecular beam can be identified by the peaks at masses 91 and 92. Species at higher m/e values are also observed, but at much lower intensities than even the mass 91 peak, as shown in the modulated spectra of Figure 4.

Phase Measurements

Identification of the neutral beam species based on the ion signal phase measurements confirms the above assignments. The measured signal phases of the major ions observed in the PVC-modulated mass spectrum are plotted in Figure 5 as a function of $m_i^{1/2}$ for three different chopping frequencies. The solid lines represent the phase values determined from measurements when benzene vapor alone is admitted to the source. At the lowest modulation frequency (166 Hz), the phases of all the ions, except that at mass 128, lie near the solid line. As the frequency is increased, larger phase lags are observed for all the ions in accordance with eq. (1). For the ions at masses 26, 39, 51, 63, and 78, the $m_i^{1/2}$ relationship of eq. (3) continues to hold, indicating that these ions all have the same ϕ_n. However, the phase of the ion at mass 91 definitely lies above the solid line at the higher frequencies, indicating that it has a different ϕ_n and that its neutral parent is thus a heavier molecule. Similarly, the mass 36 ion lies progressively below the $m_i^{1/2}$ line as the frequency is increased, indicating that it comes from a lighter molecule. The phase measurements thus establish that the $C_2H_2^+$, $C_3H_3^+$, $C_4H_3^+$, and $C_5H_3^+$ ions all arise from dissociative ionization of the same neutral molecule, viz., benzene.

There is no evidence for the presence of PVC monomer species in the laser-vaporized products. Phase measurements for the ion signals at $m/e = 62$ and 64 indicate that these species arise from fragmentation of C_6H_6 and not from direct ionization of the lighter C_2H_3Cl molecule. Minor peaks due to dissociative ionization of C_6H_6 are observed at these m/e values when benzene vapor alone is admitted to the source. In addition, the peak amplitudes do not exhibit the characteristic 3:1 isotopic ratio of chlorine products.

Phase values characteristic of the laser-vaporized PVC species are compared in Table I with measurements obtained when hydrogen chloride, benzene, and krypton are separately admitted to the source chamber. The hot species liberated from the laser-irradiated PVC sample possess essentially the same absolute phase values as the corresponding gaseous species leaked into the source at room temperature. This indicates that the PVC products are rapidly equilibrated in the source prior to beam formation. Equivalent results are obtained with both source apertures.

Evolution Profiles of Laser-Vaporized Species

Initiation of species evolution from the irradiated PVC sample can be detected independently from the mass filter signal by simply monitoring the output of the ionization gauge in the first vacuum chamber. This gauge acts as a total pressure sensor and provides information on the overall evolution rate of the thermal decomposition products from the source. The mass filter acts as a partial pressure sensor and, when tuned to a single ionic mass, it provides information on the evolution history of a given product. By simultaneously recording the ionization gauge signal and the mass filter output (modulated beam signal), it is possible to differentiate between different modes of decomposition. For example, as the temperature of the sample is increased, it can be determined whether different products are released se-
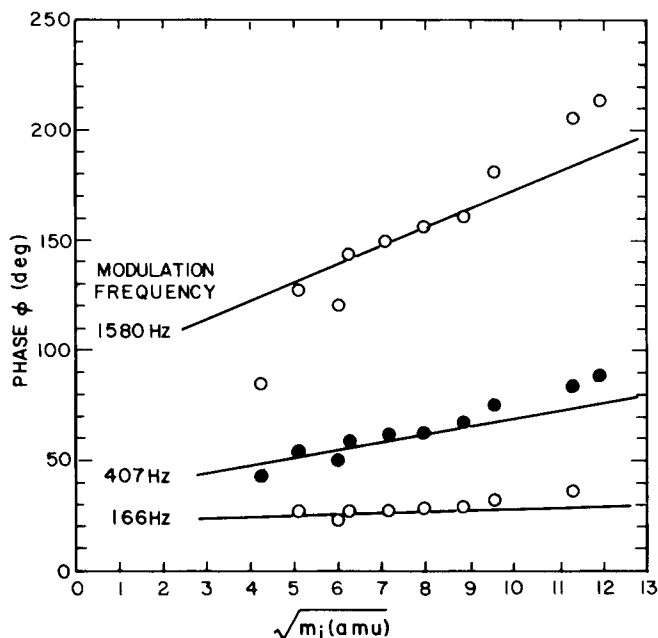
Fig. 5. Modulated ion signal phases observed for PVC species at three different chopping frequencies as a function of $m_i^{1/2}$. Sample irradiated with an unfocused laser beam.

quentially or concurrently. This information is of basic importance for understanding the detailed operating mechanism of various flame retardant additives incorporated into polymers.

In Figure 6, the evolution profiles for the three major products released from PVC are presented. Evolution of water absorbed by the sample is also shown (Fig. 6d). For each profile, a different portion of the sample is irradiated by the unfocused laser beam. The upper trace in Figures 6a–d is the variation observed in the ionization gauge signal from the first chamber, p_1, as a function of time. This represents the combined evolution of all the products and is similar in all four cases. In the lower trace, the modulated signal at a given mass is recorded (note different sensitivities in a–d). Since the partial pressures of hydrogen chloride, benzene, and toluene all track the total pressure pulse, it is evident that these products are evolved concurrently from the laser-heated sample. A similar behavior is exhibited in the evolu-

TABLE I
Comparison of Phase Values

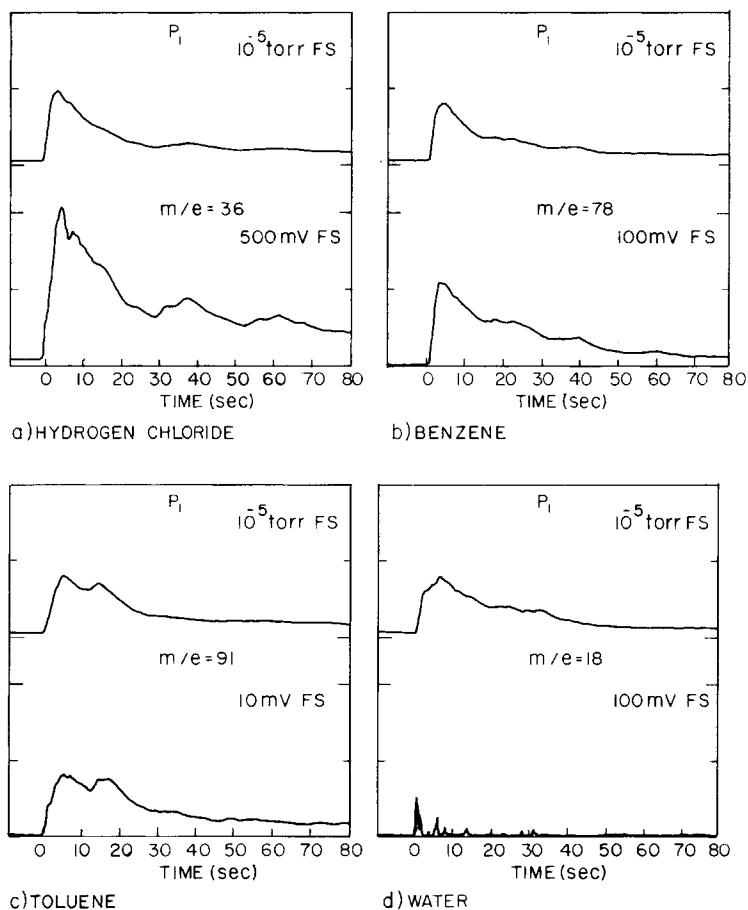|	$f = 166$ Hz				$f = 407$ Hz				$f = 1580$ Hz			
m/e	$\phi(PVC)$	$\phi(C_6H_6)$	$\phi(Kr)$	$\phi(HCl)$	$\phi(PVC)$	$\phi(C_6H_6)$	$\phi(Kr)$	$\phi(HCl)$	$\phi(PVC)$	$\phi(C_6H_6)$	$\phi(Kr)$	$\phi(HCl)$
84							67.0				163.0	
78	27.5	27.0			66.5	65.0			160.5	163.0		
63	27.0	26.5			62.5	60.5			157.5	158.0		
51	26.0	26.5			61.0	59.5			149.0	147.5		
42							62.0				146.0	
39	25.5	26.0			58.5	56.0			143.0	141.0		
36	22.5				49.5			47.0	120.0			115.0

Fig. 6. Evolution profiles for laser-vaporized species from PVC: (a) hydrogen chloride; (b) benzene; (c) toluene; (d) water. Sample irradiated with an unfocused laser beam; modulation frequency = 407 Hz. Initial detection of an increase in the P_1 signal is arbitrarily taken as the zero reference time.

tion profiles of the heavier hydrocarbon products at m/e values of 105, 115, and 128.

Several degradation reactions thus occur simultaneously with the liberation of HCl from PVC, in contrast to conclusions drawn from experiments employing differential condensation techniques.[11] Measurements by Kleineberg et al.,[12] using combined thermogravimetric–mass spectrometric methods, and by Chang and Salovey,[13] using a gas chromatography–mass spectrometric technique, confirm the concurrent evolution of HCl and benzene from PVC in the temperature interval of ~250–400°C. The data of Figures 6a–c clearly demonstrate that the occurrence of similar evolution profiles at several m/e peaks cannot be taken as evidence that these signals arise solely from fragmentation of a given parent peak as has been suggested.[14]

Previous data on PVC pyrolysis have been obtained at discrete sample temperatures, and detailed evolution profiles are unavailable. Studies employing both static[13,15] and dynamic[16] analytical techniques indicate that
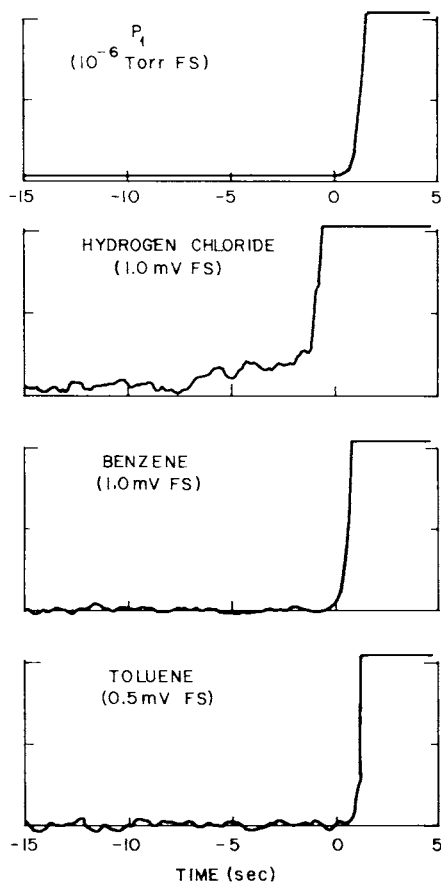
Fig. 7. Initial evolution characteristics for hydrogen chloride, benzene, and toluene from PVC irradiated with an unfocused laser beam; modulation frequency = 407 Hz. Initial detection of an increase in the P_1 signal is arbitrarily taken as the zero reference time.

the relative intensities of heavier hydrocarbon products increase as the sample temperature exceeds approximately 300°C. An order of magnitude indication of the relative signal intensities of the PVC decomposition products is given in Table II. These relative values do not vary significantly with irradiation time.

TABLE II
Approximate Relative Intensities of PVC Decomposition Products

Product	m/e	I_{rel}
Hydrogen chloride	36	100
Benzene	78	10
Toluene	91	1.0
a	128	0.1
a	141	0.001

a Detailed identification of the neutral parents associated with the relatively low signals at the higher ion masses was not made.
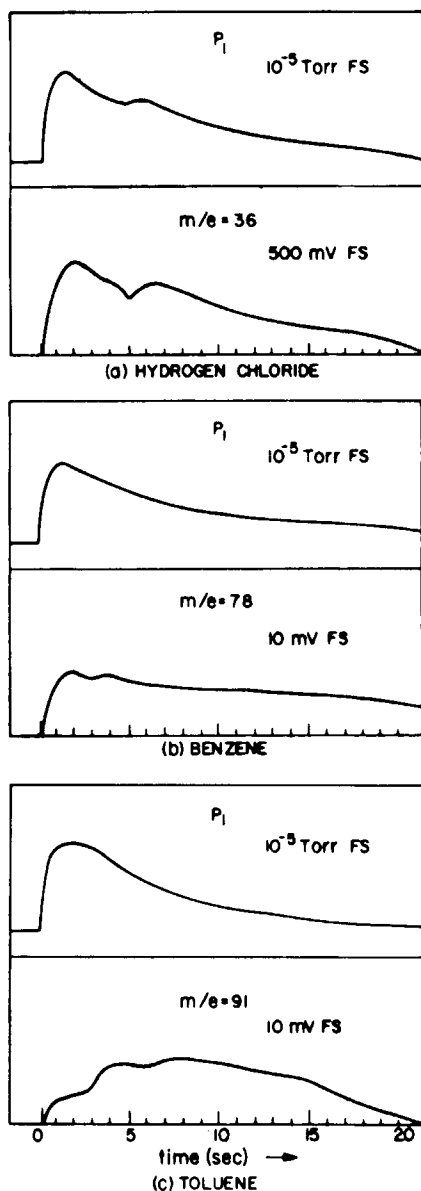
Fig. 8. Evolution profiles for laser vaporized species from plasticized PVC (35 phr DOP): (a) hydrogen chloride; (b) benzene; (c) toluene. Sample irradiated with an unfocused laser beam; modulation frequency = 407 Hz. Initial detection of an increase in the P_1 signal is arbitrarily taken as the zero reference time.

Evolution of water vapor from the PVC sample exhibits a markedly different behavior, as shown in Figure 6d. A large burst of water is initially observed with subsequent sporadic increases occurring as the sample volume is heated, possibly due to water occlusions. Preheating the PVC sample in an oven at 110°C for ½ hr and then storing in a desiccator prior to sample use removes most of the water. This oven treatment procedure does not result in
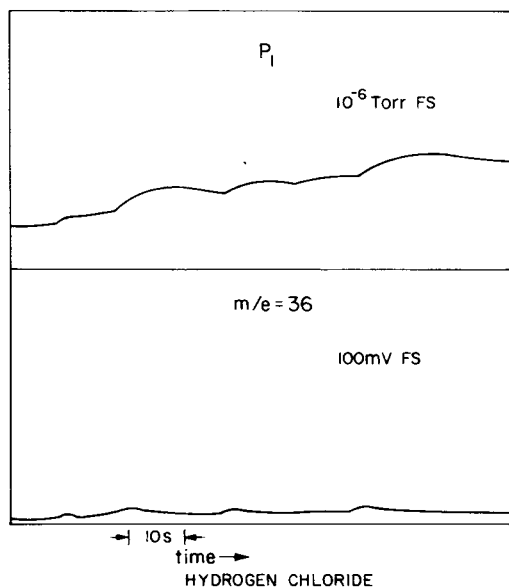
Fig. 9. HCl evolution profile resulting from the laser irradiation of PVC in the presence of Sb$_2$O$_3$. Modulation frequency = 407 Hz. Initial detection of an increase in the P_1 signal is arbitrarily taken as the zero reference time.

any observable sample weight loss. Irradiation of the treated sample results in a reduction of over a factor of 10 in the evolved water signal (1.5 mV max). Detection of laser-induced evaporation of water from the sample demonstrates the extreme sensitivity afforded by the beam modulation technique even in the presence of a large background signal. Modulation signals three orders of magnitude below the $m/e = 18$ background signal are easily discriminated and detected.

A series of experiments performed at increased detection sensitivities reveals differences in the initial evolution of HCl, benzene, and toluene upon irradiation with an unfocused laser beam, as shown in Figure 7. When HCl is monitored with a full-scale sensitivity of 1 mV, an increase is observed in the modulation signal approximately 7 sec prior to initial detection of an increase in the ionization gauge signal. During this interval the $m/e = 36$ signal gradually increases from 0.1 to 0.5 mV (i.e., approximately 0.1% of its ultimate maximum value). On the other hand, evolution of toluene is not detected until about 1 sec after an initial increase in the total pressure is observed. Increases in the modulated benzene signal appear to be coincident with the observed pressure rise. These results are supported by the measurements of Chang and Salovey[13] which indicate that as the pyrolysis temperature is increased, first HCl, then benzene, and finally toluene is formed.

Irradiation with a focused laser beam increases the power density at the sample surface by a factor of ~100. Under the resultant higher heating rate, the various stages of sample pyrolysis are not resolved and initial detection of all three products is coincident with the chamber 1 pressure rise. With both the focused and unfocused laser beam, however, all three species reach their maximum evolution rate at the same time, indicating that after initial dehy-

drochlorination at lower temperatures, several pyrolysis reactions occur simultaneously.

Effect of Additives on Laser Vaporization of PVC

Incorporation of a plasticizer into PVC significantly affects the vaporization of various organic products. Results from laser irradiation of a standard wire insulation material formulated from 100 phr PVC resin and 35 phr of di-2-ethylhexyl phthalate (DOP) are shown in Figure 8. Evolution of HCl and benzene track the total pressure, as was the case in pure PVC. However, the character of the toluene evolution profile is radically changed. In addition, the benzene:toluene signal ratio is reduced in qualitative agreement with results obtained by O'Mara[17] in the high-temperature pyrolysis of plasticized PVC. Stabilizing additives also alter the evolution characteristics of the volatile decomposition products from PVC. Irradiation of PVC in the presence of antimony oxide (Sb_2O_3) results in a greatly moderated release of HCl as depicted in Figure 9. An overall step-like character is observed in the total pressure profile which is dominated by the formation of gaseous $SbCl_3$.[18]

CONCLUSIONS

Thermal degradation of PVC in a vacuum environment is observed upon irradiation with an argon ion laser (λ = 5145 Å) at power densities of $10–10^3$ W/cm^2. A number of different gaseous products are evolved during decomposition of the sample. Identification of these products is based upon the modulated mass spectra of PVC. The major decomposition products, hydrogen chloride, benzene, and toluene, as well as heavier hydrocarbons, are found to evolve concurrently from the degrading polymer. There is no apparent change in the relative intensities of the predominant volatile species with continued irradiation of the sample ($HCl:C_6H_6:C_6H_5CH_3 \approx 100:10:1$). PVC monomer species are not detected in the laser-vaporized products. The presence of water in the sample is distinguished from the evolution of decomposition products by its burst-like release mode. Incorporation of DOP plasticizer into the PVC affects both the relative intensity and release rate of toluene. The presence of Sb_2O_3, a flame retardant additive, completely alters the overall course of the decomposition process and results in a greatly moderated release of HCl.

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