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Mass Spectrometric Evaluation of Thermal Oxidation Processes in Poly(Vinyl Alcohol)

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Thermal oxidation is one of the primary causes of degradation leading to failure in polymers. Because of this, a thorough understanding of thermal oxidation processes is very helpful in determining polymer applications and in predicting their useful lifetimes. Using an integrated approach, we have analyzed the thermal oxidation products of poly(vinyl alcohol) in all phases. Interpretation of the laser desorption mass spectrometry of the solid residues indicates that oxidation causes more extensive fragmentation of the polymer backbone than found in samples produced by non-oxidative thermal degradation. Gas chromatography of the liquid oxidation products also sheds light on the oxidation mechanisms and allows distinction from pyrolytically produced materials.

Keywords: Thermal degradation, thermal oxidation, GC-MS, mass spectrometry, vinyl polymers, poly(vinyl alcohol)

INTRODUCTION

Recently, we reported on the use of the off-line pyrolysis-gas chromatography mass spectrometry (Py-GCMS) for investigating the pyrolysis pathways of poly(vinyl alcohol).^[1] The newly applied method was compared with traditional benchmark techniques such as thermogravimetric analysis, and differential scanning calorimetry in order to determine how this

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method might provide new information concerning pyrolysis processes. Py-GCMS confirms the existing information and brings to light new pathways for consideration. In this investigation, we have applied Py-GCMS to the evaluation of thermal oxidation processes in poly(vinyl alcohol). In addition, we report on the use of laser desorption mass spectrometry (LD-MS) for analyzing solid thermal oxidation products.

Thermal oxidation is an important consideration in determining the useful lifetime of a polymer. It is believed that thermal oxidation in synthetic polymers requires a radical chain reaction involving the formation of peroxide radicals as part of the initiation process.^[2-4] Low temperature oxidation (up to 150°C), known as autoxidation, is said to be autocatalytic. At higher temperatures, initiation occurs when radical fragments are formed due to heat or light.^[3] Norling and Tobolsky^[4] have indicated several polymer characteristics with effect the oxidation process. Among the characteristics studied are morphology, viscosity, and tacticity, as well as the presence of trace impurities. An indication of the importance of tacticity is the work of Tanigami *et al.*^[5] which illustrated the effects of blending two types of poly(vinyl alcohol) (PVA) with different tacticities. Their results show that the presence of atactic PVA causes a melting point depression in syndiotactic PVA. No information was given, however, concerning the effects of this blending on high temperature degradation. Day and co-workers^[6] discussed the activation energy of thermal degradation of polypropylene (PP) in inert atmospheres. They indicated that atactic PP and isotactic PP have very similar activation energies under He and N₂. In addition, they have shown that processing also has an important effect on properties involved in oxidation processes. Several early investigations of the oxidation processes of vinyl polymers have been review by Conley and Malloy.^[7] It is important to note, from their review, that the majority of this early work involving PVA did not include thermal oxidation, but rather acid oxidation in solution. Other studies involving poly(vinyl chloride) (PVC) have indicated that the presence of oxygen introduces oxygenated structures into the PVC char. These oxygenated structures, peroxides, hydroxyls, and/or carbonyls, lead to destruction of the polyacetylene backbone.^[7]

In order to further evaluate the thermal oxidation pathways of poly(vinyl alcohol), we have chosen to use pyrolysis-gas chromatography mass spectrometry (Py-GCMS) and laser desorption mass spectrometry (LD-MS). By applying Py-GCMS to the liquid oxidation products it is possible to identify the moderate molecular weight components which are volatile at elevated tempe-

ratures. LD-MS, however, provides information for evaluation of the extent of backbone cleavage of the solid polyacetylene residue. With the use of these methods, as well as common thermal analysis techniques such as thermogravimetric analysis-mass spectrometry and differential scanning calorimetry, it is possible to obtain a comprehensive picture of the thermal oxidation processes.

EXPERIMENTAL

Instrumental

GC-MS analysis of the thermal oxidation products was carried out using a Hewlett Packard 5890 (Palo Alto, CA) Series II+ GC equipped with a 5972 mass selective detector. A 30-m Hewlett Packard (Palo Alto, CA) HP-5MS capillary column with 0.25-mm ID, and 0.25- μm film thickness was employed for separation of the semi-volatile products. Thermal analysis studies were performed on a TA Instruments (New Castle, DE) 2950 high resolution thermogravimetric analyzer as well as a TA instruments 2920 differential scanning calorimeter. TGA was completed using a platinum sampling pan. DSC was accomplished using hermetically sealed aluminum pans. Mass selective detection for TGA-MS was carried out using a quadrupole mass analyzer controlled through software written, in house, using ASYST 4.0 (Asyst Software Technologies, Inc., Rochester, NY).

Time-of flight mass spectrometry was accomplished using a linear time-of flight mass analyzer designed and built at the University of Kentucky; it consists of a 1.3 m flight tube typically held at 5×10^{-6} Torr. The repeller voltage was maintained at 7.5 kV and the microchannel plate detector (Model 3025 Galileo Electro-Optics Corp., Sturbridge, MA) was biased at -2.5 kV. The signal was digitized using a Lecroy 8013A digitizer (Lecroy, Chesnut Ridge, NY) and transferred to an IBM-PC using software written with Asyst 3.0 (Asyst Software Technologies, Rochester, NY). Each laser pulse yielded a complete mass spectrum, and twenty individual spectra were co-added in order to obtain the mass profiles.

Materials

Poly(vinyl alcohol) was purchased from Scientific Polymer Products Inc. (Ontario, NY) (2×10^3 and 3×10^3 g/mol M_w) and samples were used without further purification. Char samples were prepared by placing a known

amount of PVA into a ceramic crucible. The crucible was then placed into a preheated ceramic furnace and allowed to undergo thermal oxidation. For GC-MS analysis, samples were obtained by placing a glass tube bent into a "cold-finger" configuration into a hole in the furnace door. The tube was packed with glass wool prior to usage. The tubing was then cooled to 0°C by placing the cold finger into an ice bath. Oxidation products were drawn into the tube using an aspirator and extracted from the glass wool using HPLC grade methanol. Solid thermal oxidation residues for LD analysis were homogenized, placed into a toluene solution and sonicated for 1 h. The suspended material was then deposited onto a sampling platform and allowed to evaporate. Following evaporation, the sampling platform was affixed to the repeller plate in the sampling chamber of the TOF system. Samples for ex-situ studies were prepared by placing a thin film of 5% PVA in deionized water onto a sampling flat. The samples were then dried and placed into a preheated furnace. After thermal oxidation, the samples were cooled and transferred to the time-of-flight mass spectrometer for analysis.

RESULTS AND DISCUSSION

Thermogravimetric analysis has been applied, in this investigation, as the primary method for determining experimental parameters. The TGA trace shown in Figure 1 indicates that poly(vinyl alcohol) undergoes a two step decomposition process with maximum rates of decomposition at approximately 300°C and 440°C. According to TGA-MS results these transitions are characterized by the loss of several low-molecular-weight species including fragments with $m/z = 31$ (possibly $\text{H}_2\text{C-OH}^+$) and $m/z = 44$ (acetaldehyde). DSC of poly(vinyl alcohol) with $M_w = 2000$ g/mol produces the curve shown in Figure 2. Clearly discernable, from this figure, are the glass transition and melting temperatures. The endothermic event found at approximately 310°C corresponds to the first weight loss transition found in Figure 1 and is indicative of a degradation process. Following this event, the DSC trace becomes increasingly exothermic. We believe that this may be due to the cyclization and aromatization of the thermal oxidation products (as supported by data presented below). Cyclization and aromatization would lead to a decrease in energy of the remaining species, clearly in agreement with DSC results.

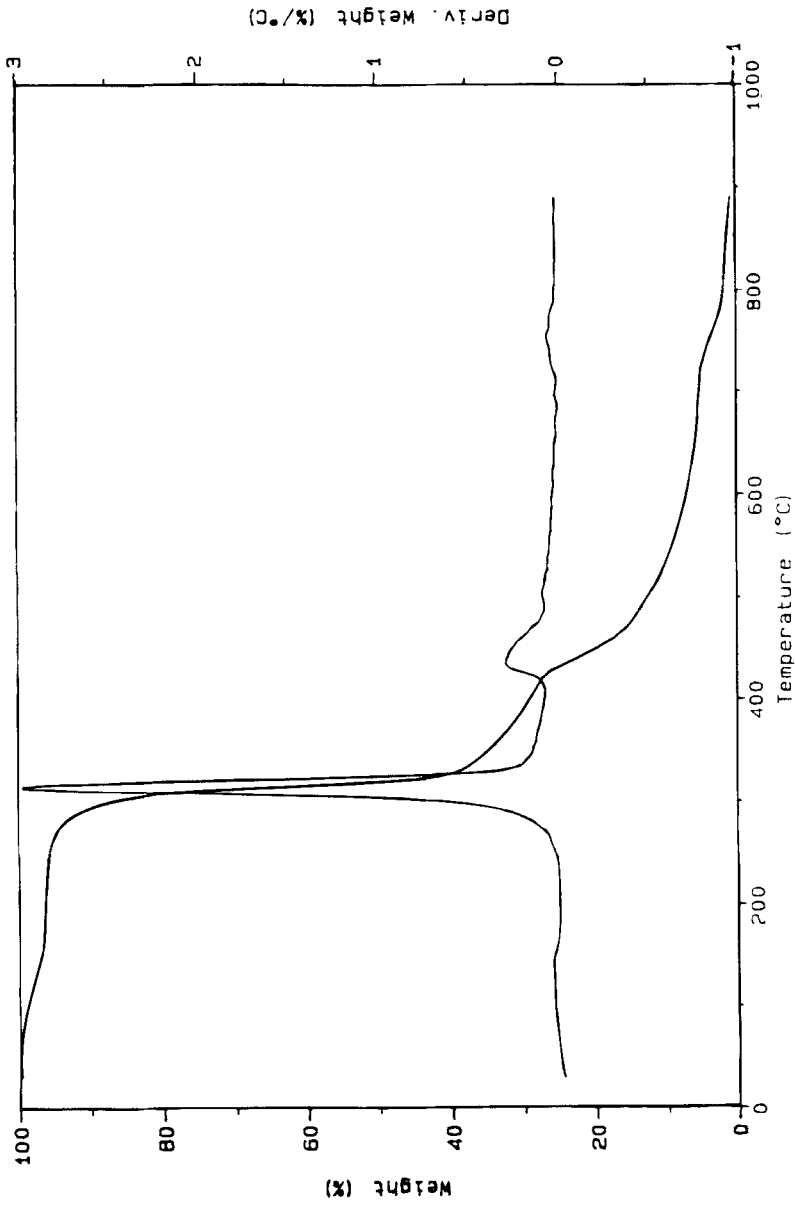


FIGURE 1 High resolution thermogravimetric analysis results obtained from poly(vinyl alcohol) with $M_w = 2 \times 10^5$ g/mol under O_2 .

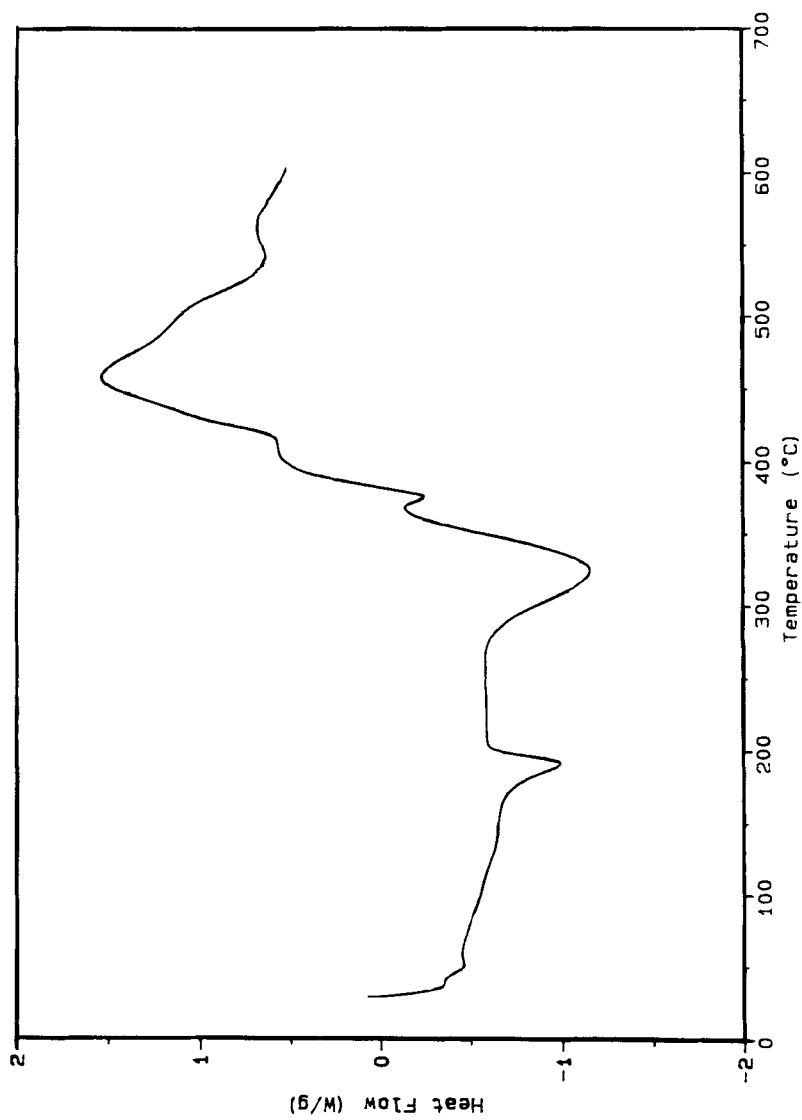


FIGURE 2 Differential scanning calorimetry results obtained from poly(vinyl alcohol), 10°C/min temperature ramp using hermetically sealed Al sampling pans;

Py-GCMS studies of thermal oxidation products

Following thermal analysis by TGA and DSC, the liquid thermal oxidation products were collected as described above. From the TGA results it was determined that samples would be collected at 325°C (first weight loss transition), 400°C (between transitions), and 480°C (following final weight loss transition). Volatile components could not be obtained at temperatures lower than 300°C, and at temperatures greater than 480°C, the identifiable components did not change significantly from those collected at 480°C. The resulting chromatogram obtained from pyrolysis products collected at 325°C (Fig. 3) indicates the presence of aromatic compounds. As described above, the presence of these products can be predicted from the exothermic events visible in the DSC trace. We believe that such products may occur via Diels-Alder type thermal cycloaddition reactions of the polyalkenes, followed by an oxidation event leading to aromatic stabilization. Many of the products are of similar size and nature as those found during pyrolysis studies.^[1]

At 400°C the chromatogram (Fig. 4) becomes more complex. In contrast to previous results,^[1] the sample taken between the two TGA weight loss transitions does not appear to be similar to the sample taken at the first transition. Again, these results are consistent with those predicted by DSC. In contrast with the known oxidation pathway, several of these species do not contain oxygen. The high temperatures of the furnace may explain the lack of the expected oxygenated products. It is well known that thermal oxidation produces peroxides which are known to decompose, often violently, at high temperatures. At this temperature, derivatives of the higher polycyclic aromatics are also clearly present in high abundance which may be explained by considering the thermal cycloaddition reaction discussed previously.

Evaluation of the chromatogram of the products collected at 480°C (Fig. 5) indicates the presence of moderate molecular weight aromatic and highly conjugated compounds. Species present in this sample include aromatic ketones as well as polycyclic aromatic hydrocarbons and their derivatives. The relative abundances of species present in Figure 4 changes dramatically with respect to those same species found in Figure 5. This may indicate that certain pathways or cleavage points are favored at one temperature and are less favorable at a different temperature. Furthermore, the appearance of many small, unidentifiable peaks indicates additional backbone fragmentation at elevated temperatures.

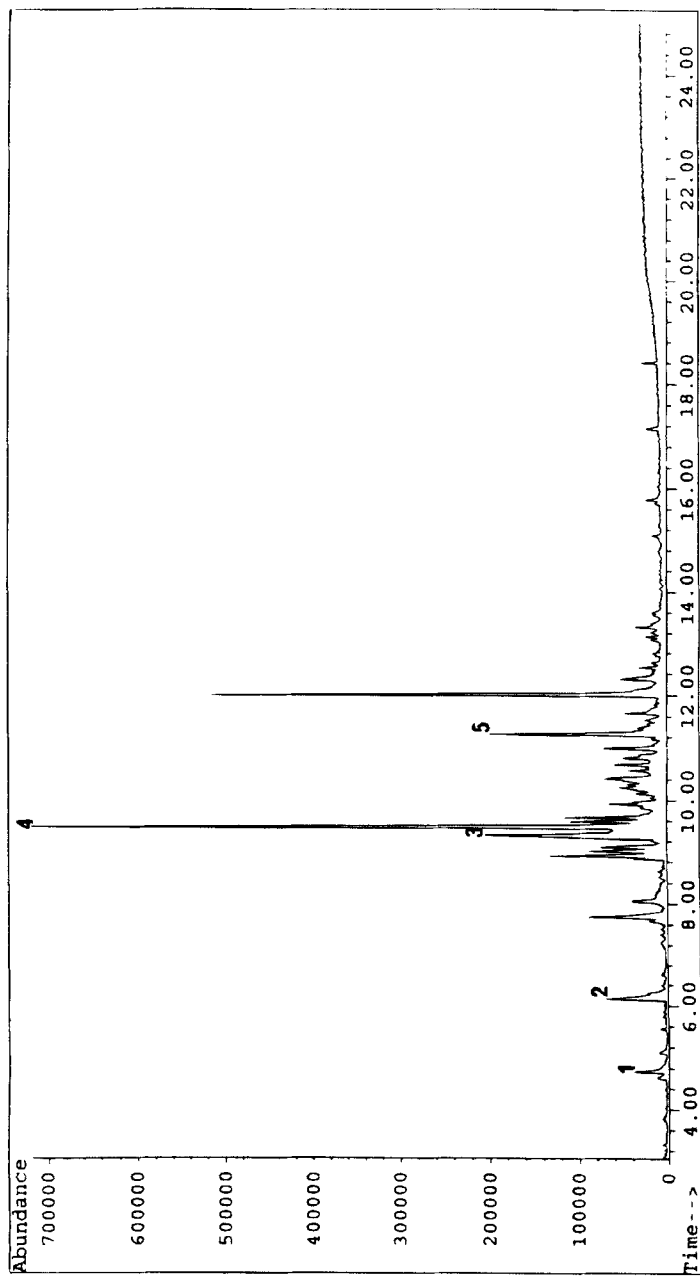


FIGURE 3 Total ion chromatogram of semi-volatile materials obtained from thermal oxidation of PVA at 325°C; temperature program 100°C (1 min) to 280°C at 10°C/min; (1) 4-phenyl-2-butanone, (2) 4-phenyl-3-buten-2-one, (3) 1-naphthalenyl ethanone, (4) di-phenyl methanone, (5) anthracene, unlabeled peaks have not been unambiguously identified.

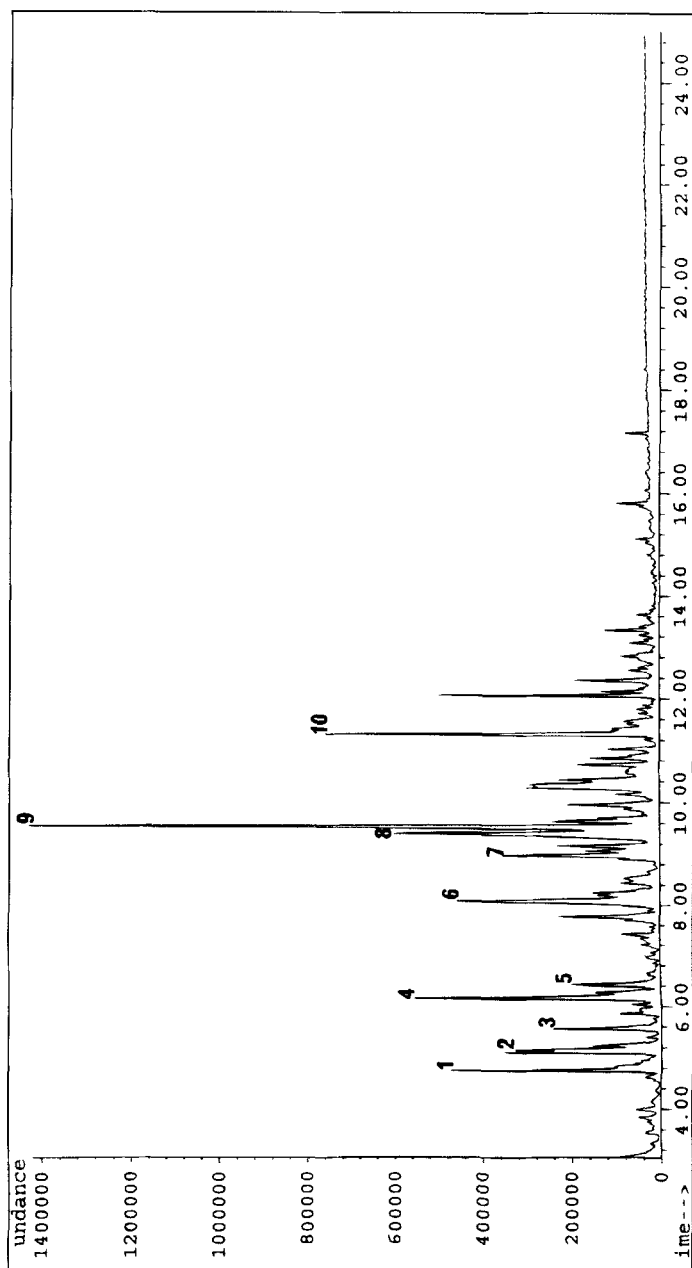


FIGURE 4 Total ion chromatogram of semi-volatile materials obtained from thermal oxidation of PVA at 400°C; temperature program 100°C (1 min) to 280°C at 10°C/min; (1) 4-phenyl-2-butanone, (2) 3-phenyl-2-propanal, (3) methyl naphthalene, (4) 4-phenyl-3-buten-2-one, (5) 1,1'-biphenyl, (6) naphthalenecarboxaldehyde, (7) naphthalenyl ethanone, (8) naphthalenyl ethanone, (9) diphenyl methanone, (10) anthracene.

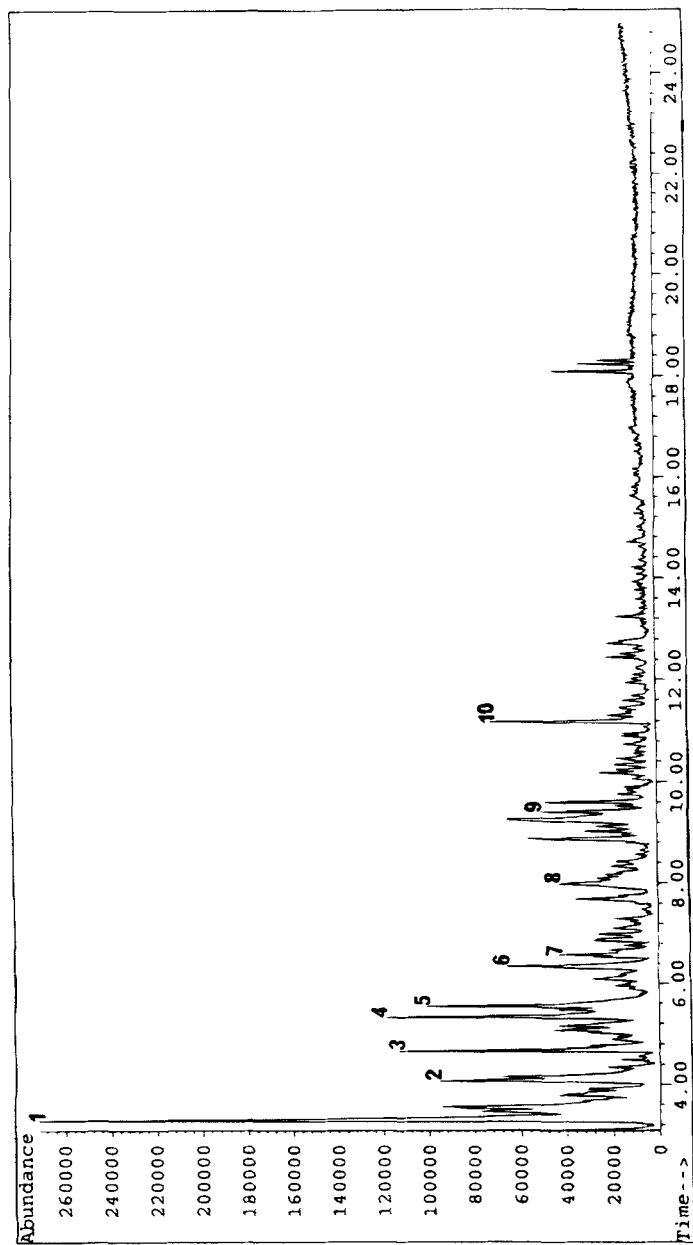


FIGURE 5 Total ion chromatogram of semi-volatile materials obtained from thermal oxidation of PVA at 480°C; temperature program 100°C (1 min) to 280°C at 10°C/min; (1) dimethyl acetal benzaldehyde, (2) naphthalene, (3) 4-phenyl-2-butanone, (4) 2-methyl naphthalene, (5) methyl naphthalene, (6) 1, 1'-biphenyl, (7) ethyl naphthalene, (8) naphthalene-carboxaldehyde, (9) diphenyl methanone, (10) anthracene.

Laser Desorption Mass Spectrometry

Mass profiles resulting from the laser desorption mass spectrometry of solid thermal oxidation residues are displayed in Figure 6. The difference in the background between these mass profiles and those found in Figure 7 indicates a major difference between these two sets of data. The data found in Figure 7 are collected from samples prepared under pyrolytic conditions. It is clear, from this data, that thermal oxidation causes increased degradation of the polymer backbone. Because of this increased degradation, a broad range of masses is produced which cannot be resolved with this instrument. These components cause peaks in Figure 6A to be completely indistinguishable from the background. At 400°C the signal-to-noise ratio (S/N) begins to increase and mass-to-charge ratios can be assigned to the peaks. It is important to note that the low molecular weight ions observed in the LD-MS profiles are most likely fragments of larger molecules produced during thermal oxidation. These fragments, however, can give information concerning the nature of the actual products. The base peak at $m/z = 149$ is believed to be caused by phthalate plasticizer and is assigned as $C_6H_4C_2O_3H$. Also present, in this profile is a strong peak at $m/z = 69$. As the temperature is increased to 480°C, the background is further diminished. Present in this TOF profile are the base peak at $m/z = 69$ and a strong peak at $m/z = 142$. It is also interesting to note that of the peaks with appropriate S/N to assign masses, pyrolysis residues contain several high molecular weight species which cannot be discerned from the thermal oxidation residues. Increases in S/N at high temperatures may be due to a rise in the fractions of singular components or to increased loss of small neutral species during the oxidation procedure. The latter explanation is in agreement with Py-GCMS data, discussed above, which indicated the increased presence of unidentifiable components in samples collected at higher temperatures. Also important in Figure 6A and B, is the presence of a strong peak at $m/z = 77$, which is indicative of aromatic species.

In sharp contrast to the data given in Figure 6, are the profiles displayed in Figure 8. These mass profiles were collected as "ex-situ" samples whereby thermal oxidation was conducted on PVA samples previously evaporated onto the time-of-flight sampling platforms. In this way a thin sample film could be analyzed rather than an inhomogeneous group of char particles. Of primary importance here is the dramatic improvement in S/N . Examination of Figure 8A indicates a very simple spectrum containing a

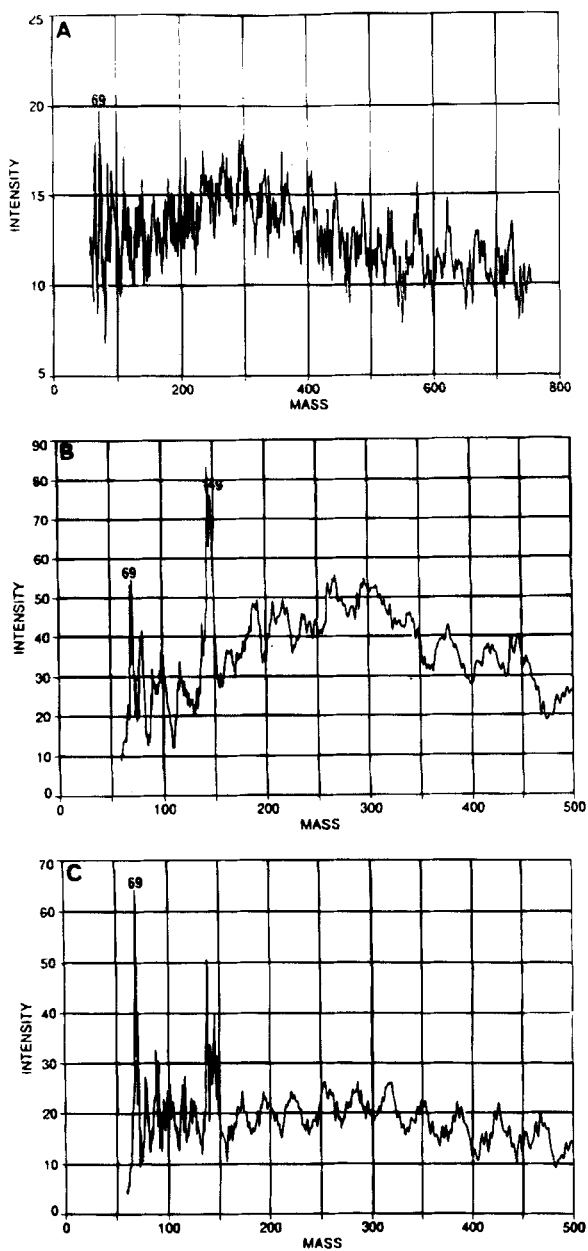


FIGURE 6 Laser desorption time-of-flight mass profiles of solid thermal oxidation residues collected at (A) 325°C; (B) 400°C; (C) 480°C.

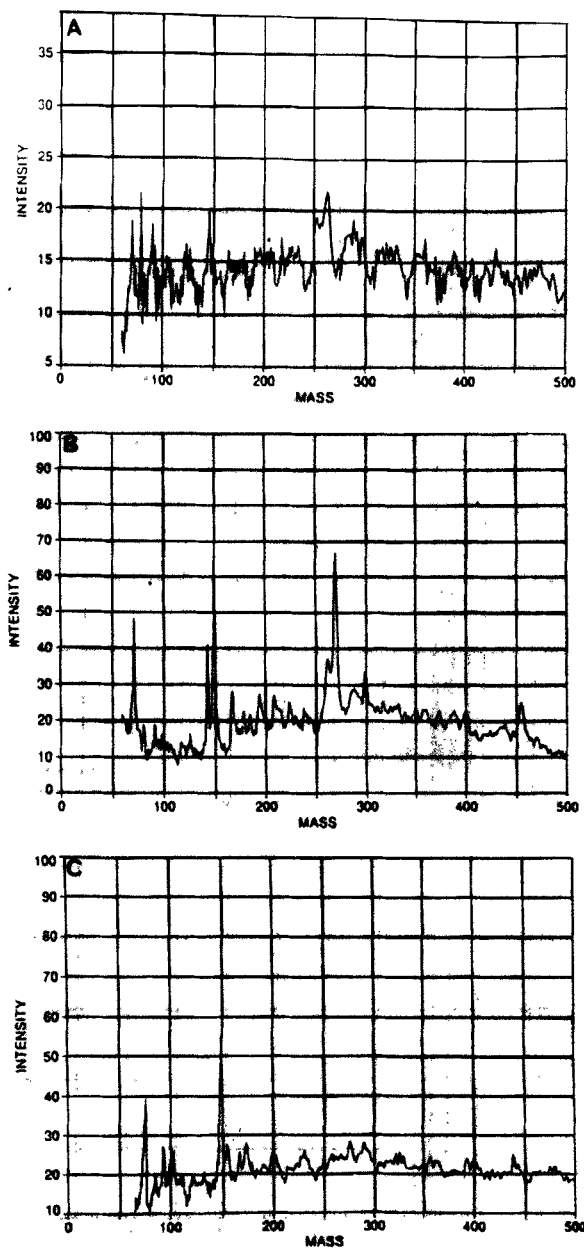


FIGURE 7 Laser desorption time-of-flight mass profiles of solid pyrolysis residues collected at (A) 325°C; (B) 400°C; (C) 480°C

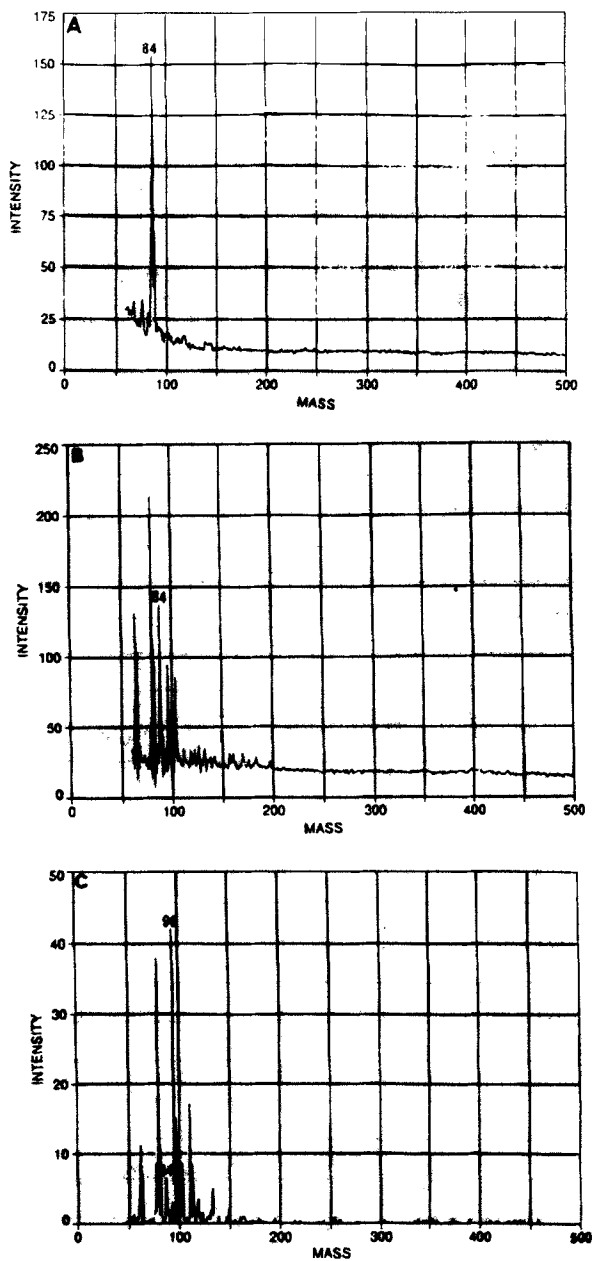


FIGURE 8 Laser desorption time-of-flight mass profiles of ex-situ thermal oxidation residues collected at (A) 325°C; (B) 400°C; (C) 480°C

single peak at $m/z = 84$. The profile given as Figure 8B contains a much larger abundance of peaks than found in 8A. In addition, there is evidence of several masses of higher molecular weight ($m/z > 150$). The presence of peaks at $m/z = 84$ as well as other multiples of 12 amu present in Figures 8B and 8C may indicate that the oxidation process produces carbon clusters as well as organic hydrocarbons. Again, it is important to remember that the observed ions are most likely fragments of larger molecules present in the sample. The distribution of ions in the oxidation products is in sharp contrast to pyrolysis residues which appear to contain aromatic compounds. As the oxidation temperature is increased to 480°C (Fig. 8C), the high molecular weight species are noticeably absent and those ions which are present may again be due to carbon clusters and organic hydrocarbons. Furthermore, there is a significant reduction in overall intensity which may be attributed to increased loss of material on the sampling platform.

CONCLUSIONS

Mass spectrometric analysis of thermal oxidation residues is best accomplished using an integrated approach. Through the use of techniques that are suitable for oxidation products, in all phases, a comprehensive picture of the thermal oxidation pathways is given, that cannot be obtained using one individual method. Results indicate that while the gaseous products of thermal oxidation are similar to those observed during pyrolysis, liquid and solid phase residues differ significantly. Observation of the liquid (semi-volatile) components indicates that the predicted polyacetylene residues undergo thermal cyclization and oxidation to produce aromatic and polycyclic aromatic hydrocarbons. In contrast, solid residues contained carbon clusters as opposed to identifiable organic fragments.

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