Epoxy resin analysis by Fourier transform mass spectrometry: a comparison of pyrolysis and laser ablation

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The pyrolysis or decomposition products of cured, fire retardant epoxy resin (diglycidyl ether of tetrabrominated bisphenol A) were compared under several different conditions: thermal pyrolysis, laser ablation and cw laser pyrolysis. Volatile neutral products were ionized by electron impact, except in the case of direct laser ionization, and detected by Fourier transform mass spectrometry. Pyrolysis gave high molecular weight fragments and a considerable amount of information about the monomer composition. Detection of directly ionized, laser-ablated products gave some molecular fragments from microprobe sample sizes, although the spectra are complex. Laser ablation/electron impact ionization produced mostly low molecular weight fragments that gave limited information about the material. Laser pyrolysis using a cw argon ion laser provided some large fragments and consumed small amounts of sample. The relationships and analytical value of these techniques are discussed.

(Keywords: laser microprobe mass spectrometry; pyrolysis mass spectrometry; Fourier transform mass spectrometry; epoxy resin; laser pyrolysis)

INTRODUCTION

Identification of polymer resins after cure can be a difficult analytical problem. Pyrolysis mass spectrometry is often used for identification of volatile degradation products of epoxy resins in order to provide molecular information about the resin[1–8]. Direct pyrolysis in a mass spectrometer combined with soft ionization techniques such as low energy electron impact[1,8] or field ionization[2,9] can be used to detect fairly high molecular weight pyrolysis products. These products can give information on the degradation mechanism of the polymer at high temperatures and can also be used to identify unknown polymers and their additives[6]. Alternatively, gas chromatography–mass spectrometry (g.c.–m.s.) on the pyrolysis products[3–5,7,8] allows separation and identification of volatile compounds.

Another commonly used technique for polymer analysis is laser microprobe mass spectrometry (l.m.m.s.)[10–14]. This type of analysis uses a focused, pulsed laser to ablate and ionize material from the surface. A mass spectrum is obtained that is characteristic of the polymer. Neutral species can also be detected with a secondary ionization method such as electron impact[15,16]. Microprobe analysis has the advantage over pyrolysis measurements in that samples as small as nanograms of material are required, while pyrolysis requires larger sample sizes on the order of 0.1–5 mg[6,8]. Pyrolysis can also require careful sample preparation[6]. Therefore, it is advantageous to determine whether laser microprobe analysis of a resin can provide comparable information to pyrolysis.

The process of laser ablation used in l.m.m.s. may be similar in some ways to rapid thermal heating of the polymer, depending on the laser wavelength. If this is the case, the pyrolysis spectrum should resemble the laser ablation/electron impact (l.a./e.i.) spectrum, in which neutral species formed by laser ablation are subsequently ionized by electron impact. Lum[15] has suggested that l.a./e.i. spectra are comparable to pyrolysis spectra for some simple polymers including polyvinyl chloride. Pyrolysis and l.a./e.i. analysis of polystyrene also gives similar products, predominantly the monomer[16,17]. On the other hand, Montaudo *et al.*[18] reported that flash pyrolysis, using high heating rates, gives very different results to pyrolysis with slow heating rates for aliphatic-aromatic polyethers similar to epoxy resins.

Fire retardant epoxy resin is a type of resin used in applications such as printed circuit boards. The principal component (*Structure 1*) is the diglycidyl ether of tetrabrominated bisphenol-A. Pyrolysis g.c.–m.s. has been reported to produce some low molecular weight products such as HBr[7]. High molecular weight pyrolysis products have been reported for related unbrominated aromatic-aliphatic polyethers[1]. The products are fragments of the polymer chain, and can be used to identify the polymer.

Since high mass fragments that can be analytically useful are observed using pyrolysis, a resin is a promising candidate for comparison of l.m.m.s. methods. The goal of this study is comparison of pyrolysis and laser ablation mass spectra of an epoxy resin under a variety of conditions and with different laser wavelengths in order to determine whether a method can be found for observing the same types of pyrolysis or degradation products from the different methods. The laser wavelengths used are 266 nm and 1.06 μm from a pulsed

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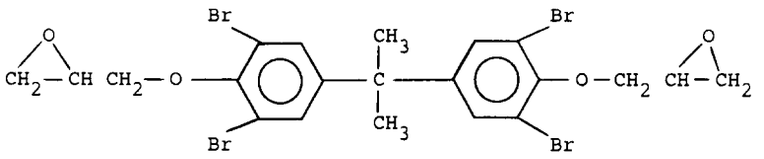


Structure 1 Monomer of the principal component of fire retardant epoxy resin, diglycidyl ether of tetrabrominated bisphenol-A

Nd:YAG laser and all lines from a cw argon ion laser. Using these spectra, the degradation mechanisms can be compared.

EXPERIMENTAL

All measurements were taken with an Extrel FTMS/2000 Fourier transform mass spectrometer (Extrel FTMS, Madison, WI, USA). The technique of Fourier transform mass spectrometry (*FT*m.s.) has been discussed previously[19–21]. The Fourier transform mass spectrometer has a 3.0 T superconducting magnet and an aluminium, 4.6 cm cubic cell. The cell can be easily disassembled for cleaning, which is advantageous for pyrolysis studies. Ions are formed by direct laser ionization (d.l.i.) with one laser pulse, or by electron impact on pyrolysed or laser-ablated neutrals. The ions are trapped in the mass spectrometer cell by the parallel magnetic (3 T) and electric (2 V) fields. They are detected by exciting them into large cyclotron orbits and then detecting the image current induced on the cell plates by the orbiting ions. The amplified signal is then Fourier transformed to obtain a frequency spectrum, which is converted to a mass spectrum with the appropriate calibration equation. In this way, all the ions in the cell are detected simultaneously, and the peak heights are proportional to the number of ions in the cell.

In order to excite the ions, a swept rf frequency (chirp) excite pulse is used, which follows the ion formation by only a short delay (typically 3 ms). For the pyrolysis studies, a bandwidth of 1.33 MHz and 64 K data points were collected and transformed in the broadband spectrum. This gave a mass spectral calibration accuracy of 10–20 ppm, or 0.007 amu at mass 200 (less at higher masses). Results from eight independently calibrated mass spectra were averaged to obtain accurate mass measurements. For the d.l.i. or l.a./e.i. studies, only 16K data points were used. Signal averaging of 10 to 1000 spectra was done to improve the signal-to-noise ratio, depending on the signal intensity.

Pyrolysis mass spectra were taken by heating a sample of resin on the end of the standard Extrel FTMS solids probe to a temperature of 350–370°C. Pyrolysis products were ionized by 15 eV electron impact. The pressure increase during pyrolysis is less than 1×10^{-7} torr (1.333×10^{-5} Pa).

L.m.m.s. spectra were taken using the IBM-Endicott laser microprobe system[22]. The laser ablation/electron impact technique was reported previously[16]. In both cases, the output of a Nd:YAG laser is focused onto the sample using a 60 mm lens and mirror in the mass spectrometer vacuum chamber. For d.l.i., the laser power density is increased until ions are generated, usually due to the formation of a plasma in the ablated material. The peak power is on the order of 10^8 W cm^{-2} with a spot size of 10–25 μm. For l.a./e.i. ionization, the laser pulse is timed to coincide with an electron beam pulse of either 15 or 70 eV electrons, which ionize the neutral ablated material. The laser fluence is decreased to prevent d.l.i. The electron beam pulse is 0.1–1 ms in length. In cases of weak signals, the background e.i. spectrum is subtracted.

Pulsed laser spectra were taken using a Continuum YG660 Nd:YAG laser (Continuum, Santa Clara, CA, USA). The wavelengths used were 266 nm (fourth harmonic) and a mixture of 1.06 μm and 532 nm (unseparated fundamental and second harmonic). For 1.06 μm, both Q-switched and free lasing (un-Q-switched) operations were used. For the Q-switched mode, the pulse width was 10 ns; for the free lasing operation it was 400–500 μs. The additional 532 nm wavelength, which facilitated alignment of the laser beam, had about 10–20% of the power of the fundamental for Q-switched operation but much less for free lasing operation. In each case, the total power per pulse was 1 mJ or less, although it is difficult to measure the power density at the sample.

For cw laser pyrolysis, the output from a Spectra-Physics Series 2000 argon ion laser (Spectra Physics, Mountain View, CA, USA) was focused on the sample, using the same microprobe optics as the YAG laser.

Two samples of epoxy resin were used. The first was a colourless, single ply, resin-impregnated glass cloth of 70 μm thickness. The second was a section from a completed circuit board, which was chemically identical to the first sample except for additional green dyes. The dark colour and the thickness of the board (about 1 mm) made the sample much more optically absorbant. The principal component is the diglycidyl ether of tetrabrominated bisphenol A, but the resin also contains 10% novolac resin, which is known to decompose at a higher temperature[5]. It was cured using diamine curing agents. The same two samples of material were used for all analyses to avoid comparison of dissimilar samples.

RESULTS

Pyrolysis

A detailed study of all the pyrolysis products of brominated resin has not been reported previously. Using *FT*m.s., the mass spectral peaks were measured accurately in order to determine the elemental composition of each peak. The pyrolysis mass spectrum is shown in *Figure 1*. *Table 1* lists the accurate masses of the pyrolysis ions from the mass spectrum. The mass of each peak is compared to a calculated mass for the assigned molecular formulas. Reasonable structures are derived from stable molecules or electron impact fragments related to the monomer structure, although in some cases other isomers are possible.

The most abundant low-molecular-weight products are hydrogen bromide (HBr), methyl bromide (CH_3Br) and phenol (C_6H_5OH). The higher molecular weight species can be assigned to fragments or derivatives of the

Table 1 Pyrolysis products of FR4 epoxy as ionized by low energy electron impact

Nominal mass	Accurate mass	Calculated mass	Proposed structure
80, 82	79.9256 81.9250	79.9262 81.9242	HBr
94, 96	93.9414 95.9396	93.9419 95.9399	CH_3Br
94	94.0419	94.0418	PhOH[a]
172, 174	171.9573 173.9546	171.9524 173.9504	Br–Ph–OH
250–254	249.8614 251.8627 253.8611	249.8629 251.8610 253.8590	Br_2–Ph–OH
119	119.0535	119.0496	CH≡C–Ph–OH
121	121.0653	121.0652	CH_2=CH–Ph–OH
134	134.0758	134.0731	CH_2=C(CH_3)–Ph–OH
212, 214	211.9883 213.9828	211.9837 213.9817	CH_2=C(CH_3)–PhBr–OH
290–294	289.8955 291.8916 293.8878	289.8943 291.8923 293.8903	CH_2=C(CH_3)–PhBr_2–OH
170	170.0767	170.0731	Ph–O–Ph
190	190.1022	190.0993	$CH_2C(CH_3)$–Ph–OC_2H_4CHO
270, 272	270.0285 272.0257	270.0255 272.0235	$CH_2C(CH_3)$–PhBr–$OC_2H_4CH_2O$
			$X \quad + \quad X$ HO–Ph–C–Ph–OH $X \quad CH_3 \quad X$
213	213.0949	213.0915	$X = 4H$
369–373	370.9056	370.9106	$X = 2H, {}^{79}Br, {}^{81}Br$
447–453	448.8257	448.8212	$X = H, 2{}^{79}Br, {}^{81}Br$
525–533	528.7388	528.7298	$X = 2{}^{79}Br, 2{}^{81}Br$
			$X \quad CH_3 \quad X$ HO–Ph–C–PhO $X \quad CH_3 \quad X$
228	228.1166	228.1149	$X = 4H$
462–468	465.8363	465.8427	$X = H, {}^{79}Br, 2{}^{81}Br$
540–548	543.7525	543.7533	$X = 2{}^{79}Br, 2{}^{81}Br$
251	251.1073	251.1071	HCC–O–Ph–$C(CH_3)_2$–Ph–O
266	266.1312	266.1306	H_2C=CH–O–Ph–CH(CH_3)–Ph–O–CH=CH_2
269	269.1227	269.1176	HO–Ph–$C(CH_3)_2$–Ph–O–C_2H_2–O
349, 351	349.0464 351.0463	349.0432 351.0418	HO–Ph–$C(CH_3)_2$–PhBr–O–C_2H_4–O

[a]Ph, phenyl group

monomer unit. Most consist of substituted phenols with alcohol or ether end groups replacing the epoxy functionality. In general, the products agree well with those from the pyrolysis of a similar aromatic aliphatic polyether, also using 15 eV e.i. ionization[1]. However, no ions are observed that are more massive than the epoxy monomer unit, in contrast to the polyether, for which products up to the trimer are found.

Each phenyl group in the resin has a maximum of two bromine atoms. There are several series of ions which demonstrate that all possible combinations of 0–2 Br atoms per phenyl group can be present. The bromine substitution can be observed in the mass spectrum by the characteristic isotope peaks, since ^{79}Br and ^{81}Br have nearly equal natural abundances. However, the accurate masses shown in *Table 1* are better indicators of bromine substitution than the isotope ratios alone. In *FT*m.s., extensive signal averaging is sometimes necessary to obtain accurate isotope ratios[23]. *Figure 2*, which is an expansion of a section of *Figure 1*, shows that at the nominal mass of 94 amu $CH_3{}^{79}Br$ and C_6H_5OH can be easily resolved, even in a broadband spectrum. The isotope peaks for $CH_3{}^{81}Br$ at mass 96 and for $^{13}CC_5H_5OH$ at mass 95 are also shown.

The series of ions containing 0–2 or 0–4 bromine atoms, listed in *Table 1*, are not electron impact fragments. In all cases, increase in the number of bromine atoms corresponds to a decrease in the number of H atoms on the phenyl ring, so the ring is completely substituted. An example is the series including phenol (C_6H_5OH, mass 94), bromophenol (C_6H_4BrOH, mass 172 and 174), and dibromophenol ($C_6H_3Br_2OH$, mass 250, 252 and 254). Fragments of dibromophenol such as C_6H_3BrOH and C_6H_3OH are not observed. This effect is also observed for the series beginning at mass 134, mass 213 and mass 228.

On the other hand, several of the series are possibly associated by e.i. fragmentation. The mass 213 ion and

its brominated series may be formed by fragmentation of corresponding ions in the mass 228 series, or both may be fragments of the same neutral precursor. Some ions are not radical ions corresponding to stable neutrals and could be e.i. fragments, such as the mass 270 and 272 ions. Finally, the mass 170 ion is difficult to relate to the monomer structure and may be formed from rearrangement of a product ion or from degradation of an additive in the resin.

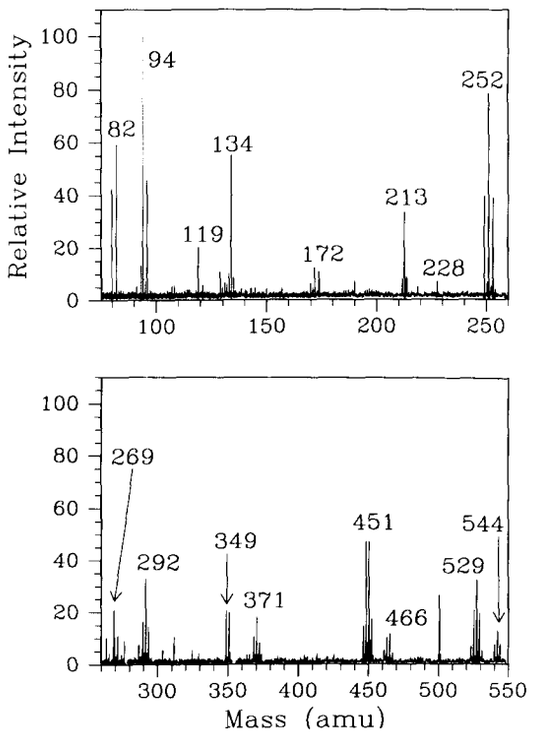


Figure 1 Pyrolysis mass spectrum of the resin sample heated to 350–370°C, using 15 eV electron impact ionization

The large relative intensity of phenol and 2-allyl phenol (mass 134) suggests a degradation of the bisphenol group shown in *Scheme 1*, which was suggested previously[1]. The formation of CH_3Br may involve a complex mechanism. Some of the products in *Table 1* suggest that the isopropyl group of the bisphenol A can lose a methyl group to form an ethylene ($CHCH_2$) group, such as products at mass 121 and mass 266. The methyl group can then add a free bromine atom to form methyl bromide. Nara and Matsuyama[7] suggested that the formation of Br atoms is an important step in the degradation of brominated epoxy. This mechanism may be related to the formation of ethyl bromide in the pyrolysis of Nylon-66, another fire retardant material[24].

These mechanisms suggest that the formation of phenol and methyl bromide involve a complex, sequential series of reactions which result in the formation of stable products. This could also be the case for the formation of higher mass products. However, the observation of high mass products shows that pyrolysis of this resin can give analytically useful information.

Laser ablation spectra

Next, it is interesting to compare the d.l.i. and l.a./e.i. laser microprobe mass spectra. A positive ion mass spectrum using d.l.i. is shown in *Figure 3*. Intense peaks at 134 and 213 amu correspond to stable fragments observed in the pyrolysis spectrum. However, the spectrum contains a large number of peaks, with a peak at nearly every mass unit between 100 and 400 amu. Many of these ions are likely to be formed by gas phase reactions in the laser-generated plasma and do not necessarily provide direct information about the polymer. These types of product have been observed in previous *FT*m.s. studies of polymer ablation[13].

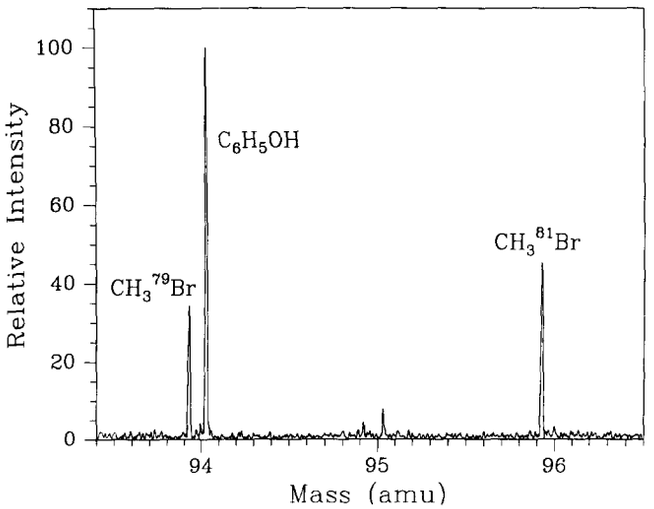


Figure 2 Expanded scale plot of *Figure 1* in the region of 94–96 amu. The two peaks at 94 amu are well resolved

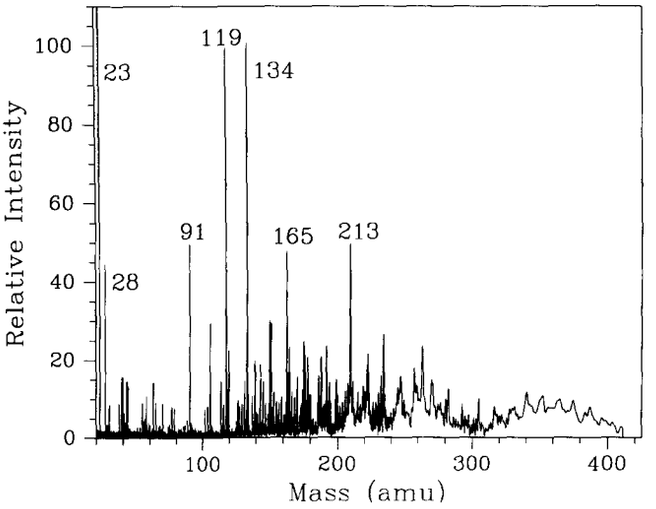
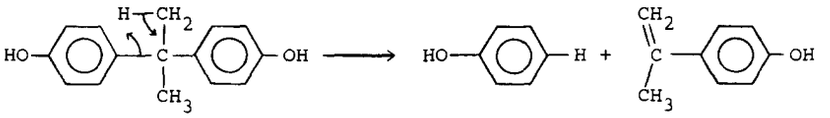


Figure 3 D.l.i. positive ion mass spectrum of resin using 266 nm radiation from a Nd:YAG laser



Scheme 1

A negative ion mass spectrum can also be obtained using d.l.i. The spectrum is much simpler, and it is not shown. The most intense peaks are due to Br^-, with weaker peaks at mass 93 ($C_6H_5O^-$) and mass 117 ($C_8H_5O^-$). This result is in contrast to negative ion spectra for some other polymers, for which structural ions are observed[13].

A mass spectrum using l.a./e.i. with 266 nm radiation is shown in *Figure 4*. Ionization was done using 70 eV electron impact ionization. Electron impact with 15 eV ionization gives a very similar spectrum, but with poorer signal. The base peak of the spectrum is due to HBr. The species at mass 43 (C_2H_3O) may correspond to the epoxy group, but other structural ions are not present.

A spectrum taken using Q-switched 1.06 μm radiation and l.a./e.i. is shown in *Figure 5*. The mass spectrum contains a large number of hydrocarbon fragments of the type C_xH_y in the range of $x = 2$–8 and $y = 2$–7, although not all combinations are present. There are also species of the type C_xH_yO, for $x = 1$–2 and $y = 0$–4. HBr is observed, but CH_3Br is not. The spectrum also includes some metal ions, such as Na^+, Mg^+, Al^+, Si^+ and K^+, which are observed even at threshold laser powers.

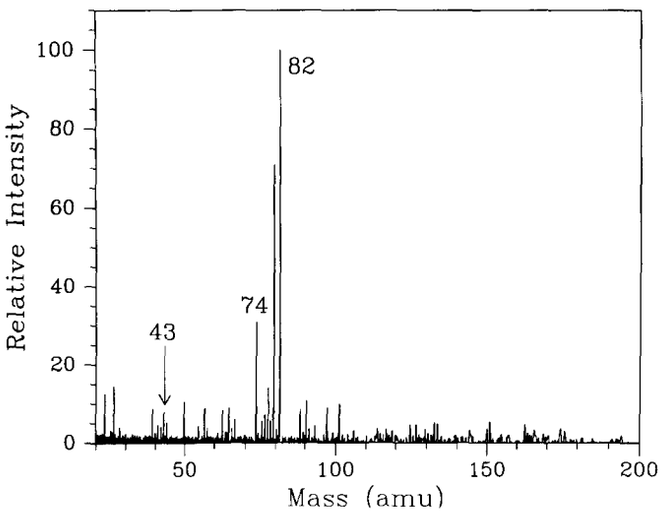


Figure 4 L.a./e.i. mass spectrum using 266 nm radiation for ablation of neutral species

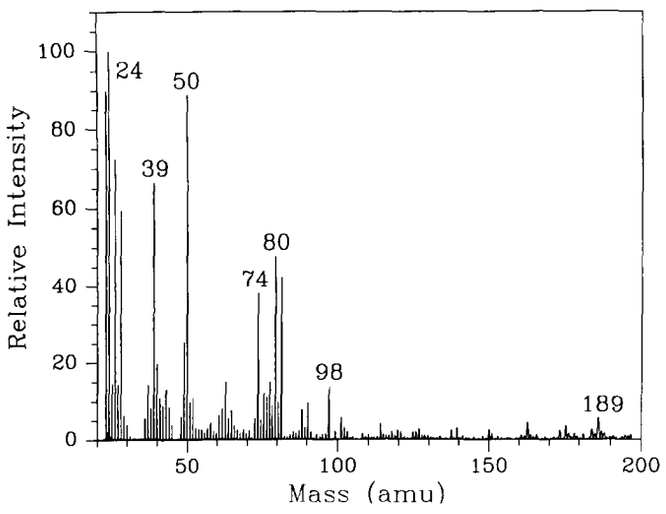


Figure 5 L.a./e.i. mass spectrum using 1.06 μm radiation from a Q-switched laser (10 ns pulse width)

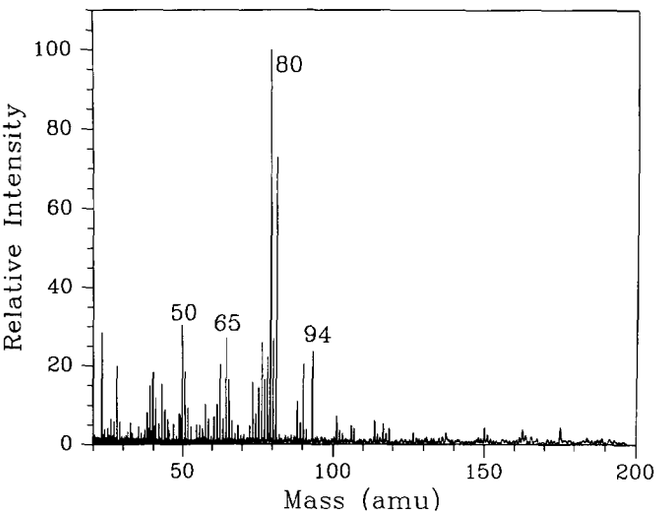


Figure 6 L.a./e.i. mass spectrum using 1.06 μm radiation from a free running laser (400–500 μs pulse width)

For free lasing operation with 1.06 μm radiation, the laser pulse width is longer by a factor of 10^4, resulting in a slower heating rate. The mass spectrum using these conditions is shown in *Figure 6*. It is similar to *Figure 5*, and includes similar C_xH_y and C_xH_yO species as well as HBr. A peak for phenol is observed, in common with the pyrolysis spectrum, but no high mass substituted phenols are detected. These products are similar to those reported by Lincoln[25] for a graphite/epoxy composite, although the type of epoxy was not specified.

Comparing these l.a./e.i. spectra, the effects of laser wavelength and pulse width do not make a large difference. In all cases, only small hydrocarbon ions (with or without oxygen), and some Br or HBr are observed. No fragments of the epoxy monomer unit or large organic ions are detected. The spectra are not similar to the pyrolysis spectrum. The d.l.i. spectrum with 266 nm radiation gives a more useful fingerprint mass spectrum, and a few peaks are present which can be assigned to the epoxy structure. However, even in this case, the spectrum does not provide enough information to identify the resin without a known reference spectrum.

Although the l.a./e.i. spectra using 1.06 μm radiation are similar for the short and long laser pulses, the laser ablation has different characteristics. For ablation with free lasing operation, a high mass carbon cluster ion (fullerene) distribution is formed by d.l.i. This type of distribution is not observed for Q-switched pulses of either 266 nm or 1.06 μm. The ions are formed directly by the laser pulse, and no electron beam pulse is necessary for ionization. The distribution is shown in *Figure 7*. It is possible that several laser pulses are required on the same spot before the distribution is observed, since signal averaging of >50 laser pulses on the same spot was required to observe the signal.

Similar fullerene distributions have been observed previously from ablation of polyimide, graphite and other polymers using 266 nm or 532 nm Q-switched pulses[26,27]. The clusters were attributed to gas phase condensation of polymer fragments in the high density plume of neutrals formed by the ablation[28]. In the present case, however, the free lasing pulse causes a much longer neutral gas pulse which is therefore likely to be correspondingly less dense. This observation implies that

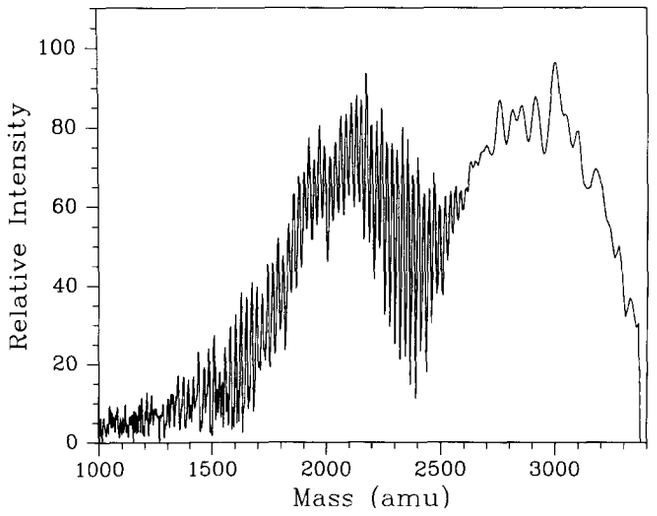


Figure 7 D.l.i. mass spectrum using 1.06 μm radiation from a free running laser, showing the high mass carbon cluster distribution

the formation mechanism may be different in this case. Recent experiments have shown that C_{60} and other fullerenes can be formed in large quantities by vaporization of graphite[29]. Formation of these fullerenes is also believed to occur in the gas phase, however. A peak for C_{60}^+ can sometimes be observed by this method, but it is not the most intense fullerene peak.

Visual inspection of the sample shows that there are morphological differences on the craters formed by the laser for the different pulse lengths. For long laser pulses the surface is blackened, while for the short pulses the sample has a grayish residue on the surface around the crater. Therefore, the blackening of the surface may be related to the fullerene formation similar to that observed for ETFE (ethylene–tetrafluoroethylene copolymer) polymer films[27]. However, ablation of the blackened craters using an independent 266 nm laser pulse did not produce fullerenes, suggesting that they are not present on the resin surface but are formed in the gas phase.

cw Laser pyrolysis

Since the pulsed laser techniques did not give detailed analytical information about the resin, another method was needed for vaporizing small areas. A focused continuous (cw) laser provides a method of heating the polymer more slowly than with a pulsed laser but is still localized to a small spot. *Figure 8* shows the laser pyrolysis of a sample of green-coloured resin. A laser power of about 100 mW is focused on a spot of 150–200 μm in diameter, and 15 eV electron impact ionization is used.

This spectrum has many peaks in common with the pyrolysis spectrum in *Figure 1*. The base peak in the spectrum is due to mass 94 (phenol), and other peaks correspond to mass 94–96 (CH_3Br), 134, 170–174, 212–214, 228 and 250–254, which were assigned in *Table 1* as substituted phenols. Unlike the pyrolysis spectrum, no multiply brominated ions higher than 300 amu are observed. However, the peaks that are observed show that the cw laser pyrolysis can provide useful information about this resin which is related to the thermal pyrolysis results.

The cw laser pyrolysis is very dependent on the optical properties of the material. A laser pyrolysis measurement was done with the thin sample of colourless epoxy glass resin, which has less absorption of the visible argon ion laser radiation than the dark green material. For laser power up to about 700 mW, no pyrolysis was observed for a free-standing film. Therefore, this method may be less general than pulsed laser ablation. However, it may be possible to use a different laser wavelength which is more strongly absorbed by the film, such as a CO_2 laser wavelength. This may allow laser pyrolysis of films with a wider range of thicknesses[30].

DISCUSSION

These results demonstrate that very different mass spectra are obtained from brominated resin with the methods of pyrolysis, laser ablation with a pulsed laser, or laser heating with a cw laser. A major difference between these methods is the heating rate. Montaudo *et al.*[1] and Lum[15] have shown that flash pyrolysis of a sample can give different products to slow pyrolysis. Faster heating gives smaller fragments that are less closely related to the polymer structure.

The present results are consistent with this observation. For the pulsed laser, even the free lasing pulse gives a heating rate on the order of $10^{6\circ}C\ s^{-1}$, higher than that for flash pyrolysis[15]. In both cases, a range of small fragments of the polymer are observed. On the other hand, slow pyrolysis with a heater or a cw laser produces larger, structural molecules rather than small fragments, and stable molecules as opposed to radicals.

The detailed mechanism of the degradation is complex. However, a major effect is likely to be the formation of enthalpy-favoured products at low heating rates, and of entropically favoured products for high heating rates. The entropically favoured products tend to be lower mass, less stable fragments which form in processes that are less constrained kinetically. On the other hand, the slower thermal pyrolysis allows more complex kinetic mechanisms that lead to more stable products. This is consistent with the mass spectra that are observed.

Chemical reactions between the pyrolysis products and the polymer may also be significant. For slow heating of

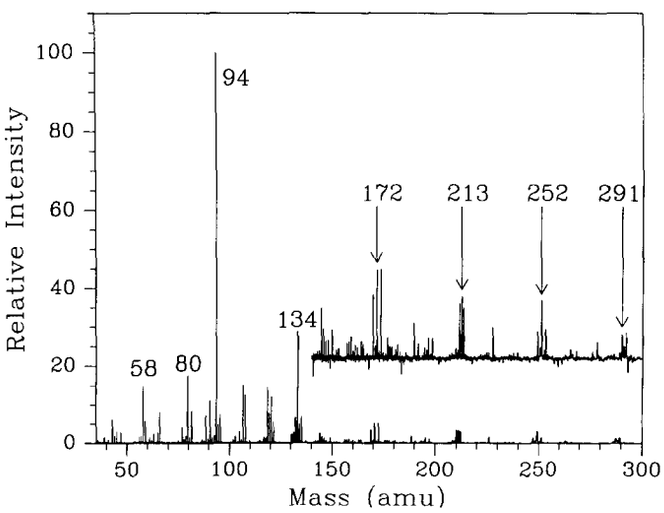


Figure 8 Laser pyrolysis mass spectrum of resin using 100 mW cw output from an argon ion laser on a green-coloured sample

the polymer, the products which are formed must diffuse out of the polymer on a slow time scale. In some simple cases, it is possible to use kinetics to separate effects due to diffusion from decomposition[31]. The slow diffusion allows greater interaction of the gaseous species with the remaining polymer, allowing the reactive species to chemically decompose the polymer chain into the most chemically stable fragments. On the other hand, rapid heating or ablation of the polymer causes ejection of the fragments from the surface before they can react with the remaining polymer, allowing reactive radical species to be observed. These interactions can cause complex effects, and make the chemical interpretation or optimization of the polymer degradation more difficult.

For analytical applications the differences between these techniques can give different information about the material. Heating with a cw laser is a promising method for obtaining molecular information from small sample volumes. However, it depends strongly on the thermal and optical absorption properties of the sample. In fact, the only difference that was observed between the thin clear resin sample and the thick green sample for all of these techniques was for the cw laser heating. Alternatively, laser ablation gives some information about the elemental composition and functional groups of the polymer on small spots, but less structural information. Direct laser ionization may give some molecular information, but there are interferences from ions formed in reactions in the plasma which complicate the interpretation of the spectrum. The spectra can be very useful for analysis of small spots if reference spectra can be obtained from known compounds. Pyrolysis gives detailed information on temperature dependence and degradation mechanisms, but requires a larger, uniform sample and may be sensitive to sample preparation.

Although some polymers, such as polystyrene, give similar spectra for both laser ablation and pyrolysis, this study illustrates that for complex polymers and resins this need not be the case. The analysis of complex polymers or mixtures that are typically used in industrial applications requires careful consideration of the conditions used for analysis and the type of information that is desired.

All of these laser or pyrolysis methods work well with Fourier transform mass spectrometry. *FT*m.s. operates in a pulsed mode consistent with a pulsed laser. However, since ions are trapped for long times in a cell by magnetic and electric fields, they can be accumulated and detected from a low-yield continuous source. A number of different ionization methods can also be used with *FT*m.s., including electron impact, laser ionization, or chemical ionization. The high mass resolution capability of *FT*m.s. is useful for obtaining accurate mass measurements of ions in order to assign the elemental composition. These varied capabilities allow flexibility in designing experiments for polymer analysis.

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