

# Evaluation of Cure Conditions for Polyimide Thin Films by Pyrolysis–Mass Spectrometry

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## SYNOPSIS

Films of a BTDA–mPDA–ODA polyimide copolymer (DuPont Pyralin PI-2555) were spin-coated onto silicon wafers and cured at either 300 or 350°C. Films cured at each temperature were then analyzed by various pyrolysis mass spectrometric methods. Low-temperature pyrolysis mass spectrometry showed that polyimide films cured at the lower temperature contained more residual water and *N*-methyl pyrrolidone solvent than did the films cured at the higher temperature. High-temperature pyrolysis mass spectrometry of the two samples showed subtle differences in the mass spectrum of the polyimide pyrolysate under electron impact (EI) ionization conditions. Principal components analysis was used to differentiate between the EI mass spectra of the high- and low-temperature cured films. Several pyrolysis products, primarily aromatic hydrocarbon and heterocyclic fragments, were separated and identified by gas chromatography/mass spectrometry.

## INTRODUCTION

Polyimide films are widely used in the microelectronics industry for a variety of applications. One of the most important functions of polyimide films is as an interlayer dielectric in multichip packaging. The chemical, mechanical, and electrical properties of these materials are an important factor in their performance in these applications, and it is well known that these properties are determined in part by the polymer curing procedure. Excessive levels of water remaining in the cured film can lead to hydrolytic degradation of the film, in addition to being detrimental to the electrical properties. Also, the presence of volatile residues in the film can limit their applicability in microelectronic packaging applications.

Pyrolysis mass spectrometry (MS) has been used to study the properties and degradation mechanisms of many common polymeric systems, including several types of polyimides. Dussel et al.<sup>1</sup> and Hummel et al.<sup>2</sup> used pyrolysis field-ionization MS to identify characteristic fragments of several polyamides and polyimides and proposed mechanisms for their deg-

radation. Hu et al.<sup>3</sup> monitored the degradation of specific functional groups as a function of temperature and found that between 500 and 650°C thermal degradation sets in and the polymer becomes more carbon-rich, eventually resulting in an amorphous carbon film. Price et al.<sup>4</sup> used pyrolysis MS in conjunction with principal components analysis to differentiate between several structurally similar propylene polymers.

Several other analytical techniques, including thermal analysis and infrared spectrometry, have been used to study the curing process in polyimides. Simoff et al.<sup>5</sup> used TGA to quantify the degree of cure in polyimide thin films cured at various temperatures. Pryde<sup>6</sup> used infrared spectroscopy to measure the degree of imidization as a function of cure temperature for polyimide films. Douglas and Smeby<sup>7</sup> used MS and TGA to study the outgassing of partially and fully cured polyimide films and reported the presence of water and solvent residues in films cured up to 390°C.

In the current investigation, pyrolysis MS and pyrolysis GC/MS are used to characterize the differences between polyimide films produced by two different curing procedures, 300°C under vacuum and 350°C in a nitrogen atmosphere. Films made by both methods show satisfactory performance in microelectronic applications, but it is necessary to

determine the effects of the curing process on the physicochemical properties of the films, particularly on the level of volatile components and the thermal stability.

## EXPERIMENTAL

A commercially available polyamic acid solution, DuPont Pyralin PI-2555, was used to prepare the films for these experiments. The polyamic acid solution is approximately 19% solid by weight, dissolved in a mixture of 80% *N*-methyl pyrrolidone (NMP) and 20% aromatic hydrocarbons. The polyamic acid consists of a copolymer of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), *meta*-phenylenediamine (*m*-PDA), and oxydianiline (ODA), which is converted into a polyimide by thermal cure. The polymerization is a condensation reaction between the BTDA acid groups and the amine groups on the *m*-PDA and ODA, forming a cyclic amide and eliminating water.

Polyimide film samples were prepared by spin coating silicon wafers with DuPont PI-2555 polyamic acid and curing the films in an oven at either 300°C under vacuum or at 350°C in a nitrogen atmosphere. Films prepared by this method are extremely uniform in thickness and composition, and the film thickness can be controlled by varying the spin speed of the wafer. Films used in this study were typically 5  $\mu\text{m}$  thick. No adhesion promoters were used on the wafers prior to film deposition. Coated wafers were stored in individual "flat-pack" wafer holders (Fluoroware H22-40) under ambient atmospheric conditions. Samples prepared by each procedure were stored together at all times between cure and analysis. Samples of the films were removed from the wafer by scraping with a razor blade. Prior to sampling, the razor blade was cleaned sequentially with acetone and hexane to minimize the potential for contamination of the film. Typical sample size was approximately 0.7 mg, and all samples were run at least in triplicate. Samples were analyzed from several different areas of each wafer, and no significant intrawafer differences were seen.

The data presented here were obtained using a Hewlett-Packard 5988A gas chromatograph/mass spectrometer, either as a GC/MS system or as a stand-alone mass spectrometer. The mass analyzer in this system is a quadrupole with mass range of 4–1000 amu. Ionization was by 70 eV electron-impact; the ion-source temperature was 200°C for the chromatographic and low-temperature probe experiments and 300°C for the high-temperature pyrolysis probe work.

Chromatographic separations were done on a 25 m  $\times$  0.2 mm Ultra-1 (Hewlett-Packard) capillary column, with helium as the carrier gas. Low-temperature mass spectra were obtained using the HP direct insertion probe, which is temperature programmable up to 350°C.

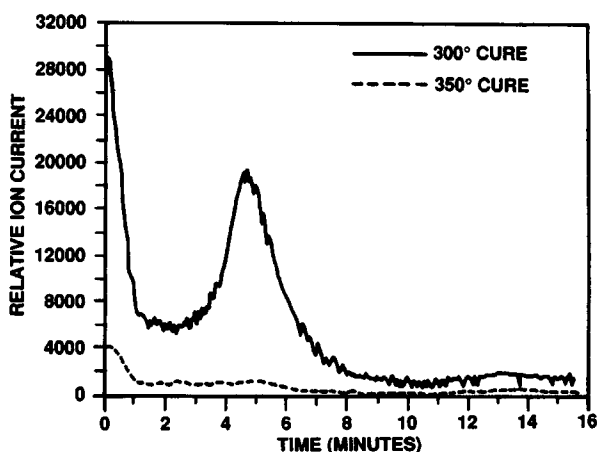
Polyimide samples were pyrolyzed using a Chemical Data Systems (Bellefonte, PA) Model 122 Extended Pyroprobe. Two pyrolysis probes were used for these experiments. The first was a heated coil probe for use in the injection port of the gas chromatograph to allow chromatographic separation of the pyrolysis products; the second was a heated coil probe that was inserted directly into the mass spectrometer ion source. Both probes used the same temperature control unit, which allowed the selection of pyrolysis temperatures up to 1400°C. The heating rate and duration of pyrolysis could also be controlled to suit the requirements of each particular analysis.

Statistical analysis of the data was done using Lotus 1-2-3 (Lotus Development Corp.) on an AT&T 6386WGS computer and the S Statistical Package (AT&T Software Sales, Greensboro, NC), running on an IBM 3081K computer.

## RESULTS AND DISCUSSION

### Low-Temperature Experiments

Mass spectral results from the low-temperature direct insertion probe experiments are shown in Figure 1. The figure shows the total ion current (TIC) as a function of time while the probe temperature is ramped from ambient to 350°C for a typical sample



**Figure 1** Total mass spectrometer ion current for (a) 300 and (b) 350°C cured polyimide films. Sample temperature ramped from ambient to 350°C in 15 min.

from each set of cure conditions. The corresponding temperatures are shown on the upper axis of each plot.

From the TIC it can be seen that there is significantly more outgassing from the film cured at 300°C than from the film cured at 350°C. Figure 2 shows the extracted ion current profiles for  $m/z = 18$  and 99, the parent ions for water and NMP, respectively. Summation of these two EICPs gives a curve virtually identical to the TIC for the 300°C film, confirming that water and NMP are the major volatile species present. The small initial peak in the TIC plot for the 350°C film is due primarily to water, either trapped in the polyimide film or adsorbed onto the surface of the film prior to analysis.

Direct measurement of the sample weight loss during pyrolysis was not feasible since the measurement required measuring a change in mass that was smaller than the measurement precision of the available balance. An estimate of the amount of water and NMP lost from the 300°C film was made by integrating the ion currents for masses 18 and 99 and comparing them to the integrated ion currents

from the introduction of known quantities of water and NMP into the mass spectrometer through the gas chromatograph. By this method, the NMP loss from the 300°C film is 0.1% and the water loss is 0.08%. These estimates may be subject to errors arising from the loss of volatile components from the film as the sample is introduced to the heated ion source in the vacuum chamber of the mass spectrometer.

Bachman et al.<sup>8</sup> reported TGA measurements on identical polyimide samples in which it was shown that the 300°C cured film loses approximately 0.3% of its weight upon heating to 400°C, as compared to 0.1% total weight loss for the 350°C cured film. The TGA experiment, using 10 mg samples and done at atmospheric pressure under a nitrogen atmosphere would give the more accurate measure of sample weight loss for each of the films. The TGA and MS measurements are thus complementary in that the MS can accurately identify the volatile components lost during the heating cycle, while the TGA gives a more accurate measure of total weight loss.

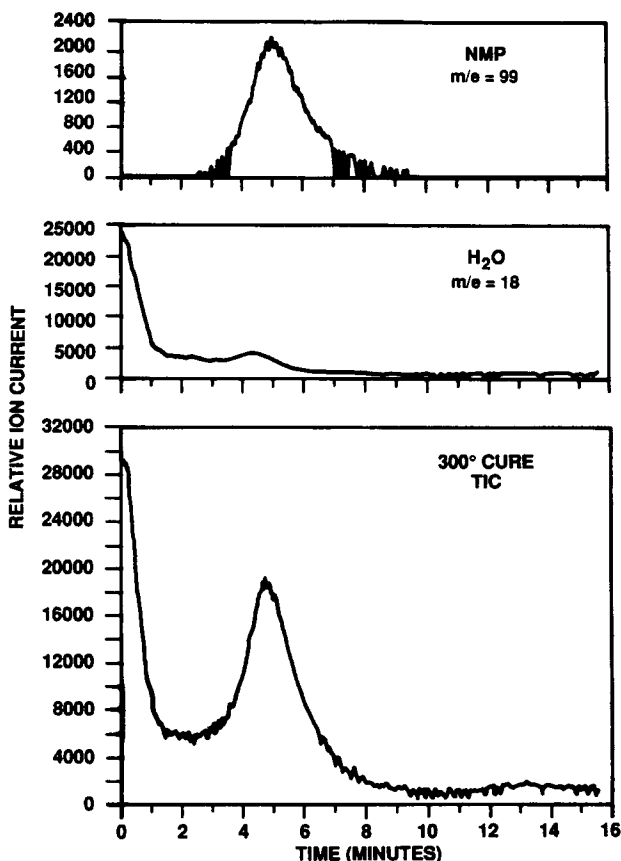
In these low-temperature experiments, there is no evidence of decomposition of the sample, making this a useful and rapid screening method for volatile residues in the film.

### Stepwise Pyrolysis

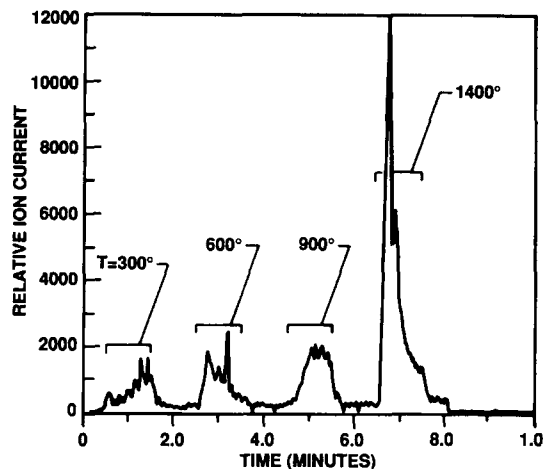
Stepwise pyrolysis-MS was used as a way of determining the thermal stability of the polyimide films. Polyimide film samples were placed in a quartz tube in the direct-insertion pyrolysis probe. The sample was heated sequentially in the mass spectrometer ion source to 350, 600, 900, and 1400°C. Each temperature was held for 1.0 min, with a 1.0 min dwell time between each heating cycle in which the probe was not heated.

Since it was not feasible to monitor the probe temperature during heating, a stepwise pyrolysis program was used, rather than a programmed temperature ramp. With a 1 min hold at each selected temperature, one could be reasonably confident of the probe temperatures without concern for thermal lag from heat losses in the probe and ion source. No attempt was made to measure or control the probe temperature during the dwell times.

Samples prepared by each cure procedure gave similar results in the stepwise pyrolysis experiment. Figure 3 shows the results of the stepwise pyrolysis temperature program for a sample of the 300°C polyimide film. As in the previous example, the figure shows a plot of total ion current vs. time.



**Figure 2** Extracted ion current profile for characteristic masses of water ( $m/z = 18$ ) and NMP ( $m/z = 99$ ) and total ion current from low-temperature MS experiment.



**Figure 3** Total MS ion current for stepwise pyrolysis of 300°C cured polyimide film. Increases in ion current correspond to heating cycles of 1.0 min duration at (a) 350, (b) 600, (c) 900, and (d) 1200°C.

Examination of the mass spectra taken at various times during the analysis allow the identification of the various components as they are evolved from the sample. Figure 4 shows mass spectra taken from each of the four pyrolysis temperatures. In Figure 4(a), the mass spectrum at 350°C shows the evolution of water and NMP, as seen in the low-temperature pyrolysis experiments. As in the low-temperature experiments described in the previous section, the 350°C cured film contained less NMP and water. The mass spectra in Figure 4(b) and (c) (600 and 900°C) show few features not seen at lower temperature, indicating that the film is relatively stable at these temperatures within the time frame of the heating cycles. The 1400°C pyrolysis [Figure 4(d)] shows severe breakdown of the polymer film, with several characteristic fragments of the polyimide structure appearing in the mass spectrum.

### High-Temperature Pyrolysis

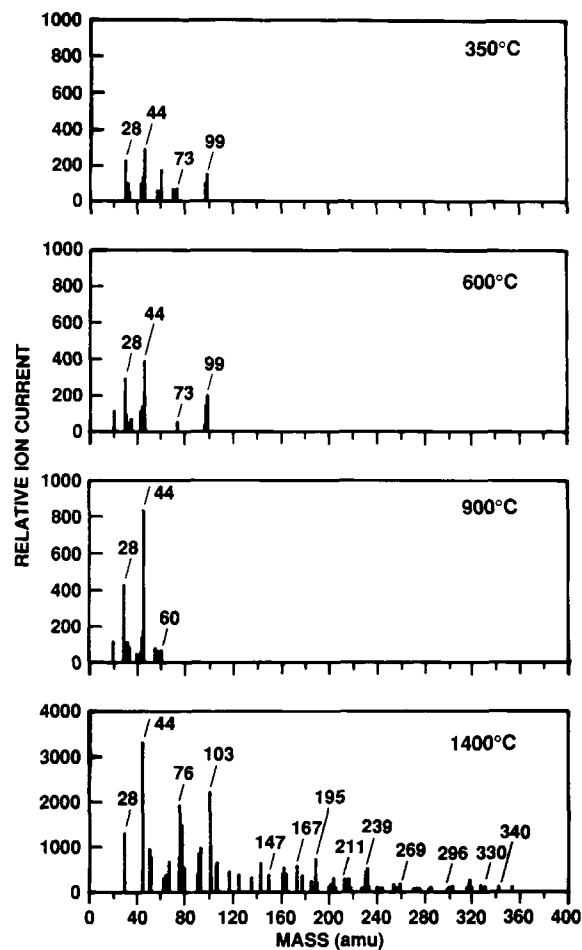
Ballistically heated high-temperature pyrolysis was done on the samples to obtain a pyrolysis mass spectrum of the polyimide films that could be used for structural elucidation and comparisons between samples. Using the same experimental setup as in the stepwise pyrolysis experiments, the temperature program was changed to heat the probe to 1400°C in approximately 5 s, holding at that temperature for 2.0 min.

Figure 5 shows spectra of polyimide film samples cured at 300 and 350°C. In each spectrum there are

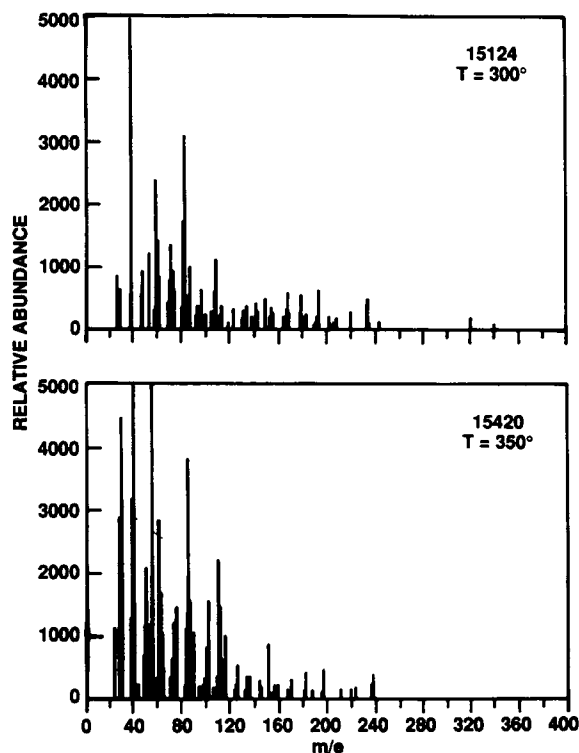
many prominent characteristic peaks, similar to the 1400°C mass spectrum of the stepwise pyrolysis runs [Fig. 4(d)]. A pyrolysis temperature of 1400°C maximizes the fragment ion abundance at the expense of preserving the higher molecular weight fragments, such as the BTDA-ODA monomer at  $m/z = 460$ .

Pyrolysis mass spectra of polyimides cured at 300°C are very similar to spectra from the 350°C material. The interpretation of the polyimide mass spectra is complicated by the considerable structural rearrangement evident in these spectra, which is attributable in part to the large population of radical species generated in the ion source by the electron impact ionization of polyimide molecules. Principal components analysis was used to reduce the dimensionality of the data set and aid in differentiation between the spectra of the two groups.

Five mass spectra from three samples of the



**Figure 4** Mass spectra taken during stepwise pyrolysis of 300°C cured polyimide.  $T =$  (a) 350, (b) 600, (c) 900, and (d) 1200°C.



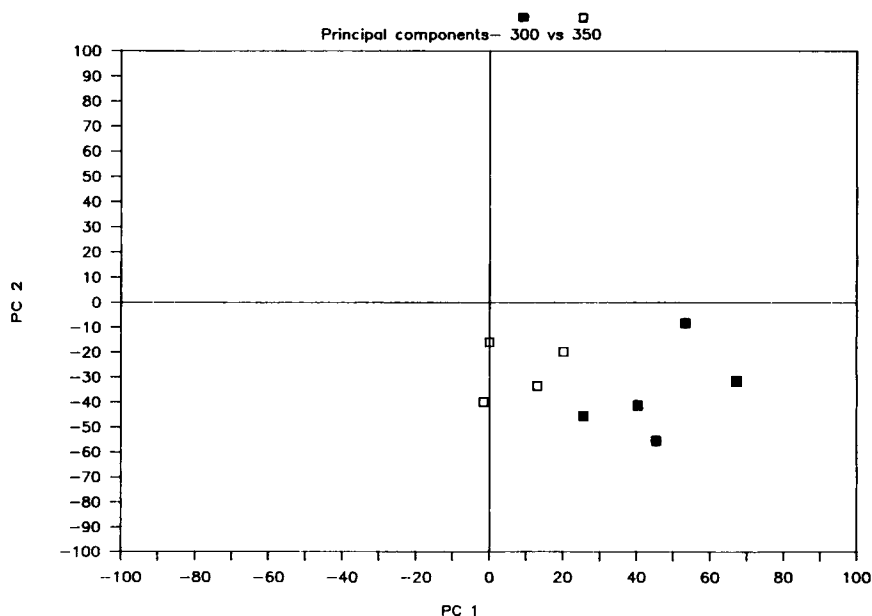
**Figure 5** Pyrolysis mass spectra of (a) 300 and (b) 350°C polyimide films. Pyrolyzed at 1400°C for 2.0 min.

300°C cure polyimide were compared to four spectra from three samples of 350°C cure material. For each spectrum, ion abundances were normalized to mass 76 and the spectra were plotted in tabular form.

Twelve prominent peaks common to all of the sample spectra were identified and used as the basis set for the principal components analysis.

Figure 6 is a plot of the first two principal components for the mass spectral data, which account for 70% of the total variance in the data. All nine data points are clustered in the same quadrant of the scatter plot, indicating a close similarity among all of the spectra; however, segregation of the cluster into two distinct groups representing the 300 and 350°C spectra shows that there are consistent differences between the mass spectra for these two groups of samples.

Analysis of the principal components analysis data shows that the largest variances occur in the high-mass ion abundances. The lower abundance of high-mass ions in the pyrolysis mass spectra of the 350°C cure samples may be indicative of differences in the degree of cure between the groups of samples. This is consistent with measurement of the degree of cure on similar samples by thermal methods,<sup>5,8</sup> in which it was determined that although both the 300 and 350°C films are more than 99% cured, imidization is still more complete in the 350°C cure film. It is reasonable to postulate that an incompletely cured film would contain more marginally volatile oligomeric species, which could account for the greater abundance of high-mass ions in the lower-temperature film, although accurate measurements of the molecular weight distribution in the films would be necessary to verify this.



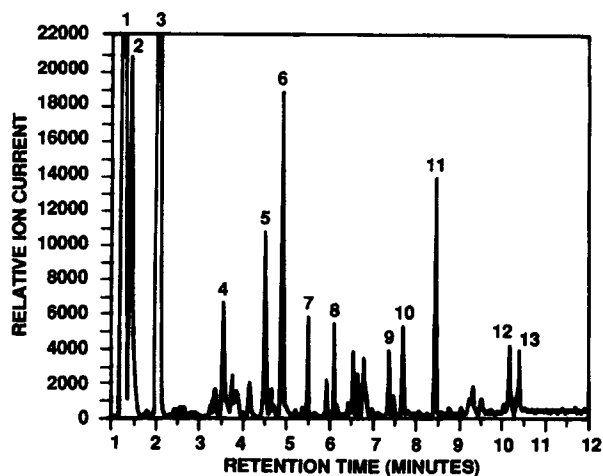
**Figure 6** Plot of first and second principal components for pyrolysis mass spectra of 300°C (solid squares) and 350°C (open squares).

### Pyrolysis GC/MS

To separate and identify the stable polyimide pyrolysis fragments, samples of each type were pyrolyzed in the GC injection port of the HP 5988A GC/MS. The sample was ballistically heated to 1400°C for 2 min; the injection port was in the split-injection mode, with a split ratio of 60:1. The GC oven temperature was ramped from 125°C to 290°C at 20°C/min and held at 290°C for 10 min. The mass spectrometer was scanned from  $m/z$  10 to 500.

Figure 7 shows the total ion current chromatogram for the 350°C polyimide. The structure of each major pyrolysis component as determined from the mass spectrum is shown in Table I. The most significant difference between the chromatograms is the presence of the NMP peak in the 300°C cure sample, which is shown in detail in Figure 8.

Most of the pyrolysis fragments identified in this experiment are simple fragments of the polyimide structure, although several show some degree of rearrangement. Comparison of the mass spectra of pyrolysis fragments found in the Py-GC/MS experiment with spectra from the Py-MS runs show similar features, although the pyrolysis products obtained in the atmospheric pressure injection port of the GC must necessarily be rearranged to stable species, whereas radical species formed in the pyrolysis MS experiment will be more stable under the high-vacuum conditions of the MS ion source.



**Figure 7** Gas chromatograms of pyrolysis products for 350°C polyimide film pyrolyzed in the GC injection port at 1400°C for 2.0 min. Column: HP Ultra-1, 25 m × 0.2 mm. Temperature program: 125°C (1.0 min), 20°C/min to 290°C (10.0 min). Mass scan range: 10–550 amu.

**Table I** Pyrolysis Fragments of PI-2555 (T [pyrolysis] = 1400°C)

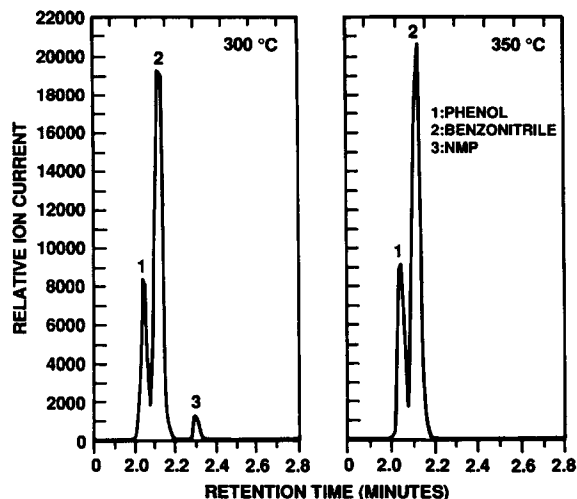
1	CO, CO <sub>2</sub>	8	
2		9	
3		10	
4		11	
5		12	
6		13	
7			

### CONCLUSIONS

The experiments reported here have demonstrated the use of pyrolysis-MS techniques to differentiate between polyimide films prepared under two different cure regimes. Residual solvent and volatile polymerization products were effectively and rapidly measured by low temperature, direct-insertion probe, mass spectrometric methods, and pyrolysis GC/MS. These experiments complement previous TGA studies by identifying the volatile components lost upon heating.

The higher-temperature pyrolysis methods, stepwise and ballistic, were useful for determining thermal stability of the films by measuring the increase in MS ion current as the film is pyrolyzed.

The composition and pyrolysis properties of polyimide films has been shown in these and other experiments to vary significantly with relatively small changes in the cure temperature used during



**Figure 8** Detail of pyrolysis chromatograms of 300 and 350°C polyimides showing peak for NMP in 300°C sample.

preparation of the film. Differences in the MS fragmentation pattern are seen when comparing the pyrolysis mass spectra from low- and high-temperature cured polyimide samples. Films cured at the lower temperature contain more residual volatile components than do higher-temperature cured films. Mass spectra of high-temperature cured films show lower high-mass abundance, possibly indicating a more complete cure.

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## REFERENCES

1. H.-J. Dussel, H. Rosen, and D. O. Hummel, *Makromol. Chem.*, **177**, 2343 (1976).
2. D. O. Hummel, I. Holland-Moritz, J. Kolb, and H.-J. Dussel, *Acta Polym.*, **32**, 512 (1981).
3. C. Hu, J. Andrade, and P. Dryden, *J. Appl. Polym. Sci.*, **35**, 1149 (1988).
4. D. Price, G. Milnes, P. Tayler, J. Scrivens, and T. Blease, *Polym. Degradation Stability*, **25**, 307 (1989).
5. D. Simoff, M. Robinson, C. Pryde, and E. Johnson, in *Proceedings of the 34th ANTEC Conference, Society of Plastics Engineers*, 1990, pp. 435-438.
6. C. Pryde, in *Proceedings of the 34th ANTEC Conference, Society of Plastics Engineers*, 1990, pp. 439-442.
7. R. B. Douglas and J. M. Smeby, *IEEE Proc. Electron. Comp. Conf. 37th*, 197-201 (1987).
8. B. J. Bachman, C. A. Pryde, E. T. Johnson, D. A. Simoff, V. W. Ryan, and M. B. Robinson, Evaluation of polyimide as a dielectric for multichip packaging. Presented at the Annual Meeting, International Society for Hybrid Microelectronics, Baltimore, MD, October 1989.

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