AN INTEGRATED SYSTEM USING TEMPERATURE BASED SAMPLING FOR POLYMER CHARACTERIZATION

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ABSTRACT

The full characterization of a polymeric system may include the analysis of retained volatiles such as solvents and monomers, semi-volatile additives such as plasticizers and the identification of the polymer itself, or quantitation of monomers in copolymers. Gas chromatography and mass spectrometry have been used successfully for these various analyses by combining solvent extractions, headspace sampling, pyrolysis and other sample preparation techniques.

This paper presents a simple approach to polymer characterization using sample temperature as the only preparation technique. Accurate temperature control permits the selection of different fractions of organics based on volatility. Low temperatures are employed for the removal of small molecules, moderate temperatures for semi-volatiles and very high temperatures for thermolysis of the polymer, so that all constituents may be volatilized and studied, either by GC-MS or directly to the mass spectrometer.

The system described includes a temperature based sample preparation station and a mass spectrometer, which may be used with or without GC separation. Modes of operation include low temperature thermal desorption with trapping and analysis by GC, pyrolysis with GC-MS for detailed macromolecular structure analysis, pyrolysis direct to MS for rapid polymer identification and programmed heating for thermal resolution direct to the mass spec. In the last case, the sample is heated at a controlled rate by the pyrolysis coil, with the evolved products transferred directly to the mass spectrometer for analysis through fused silica tubing.

Examples show the analysis of real world samples such as tire rubber, vinyl film, textile fibers, treated papers and adhesives.

INTRODUCTION

A finished polymer product is comprised of many components, both intentional, such as the various monomers used for a copolymer, antioxidants, plasticisers, and unintentional, including residual monomers, solvents and contamination. Low molecular weight components, volatiles like solvents and monomers, may be extracted with various degrees of effectiveness, depending on the polymer matrix (crosslinking, etc.). Once extracted, the assay depends at least in part on how the presence of a solvent peak interferes with the compounds of interest, themselves frequently solvents. This problem may be alleviated by performing headspace - either static or dynamic - as one step in the polymer analysis.

Thermal sampling such as pulse pyrolysis provides much information about polymers, including copolymers and semivolatiles like plasticisers and lubricants. Figure 1, for example, shows analytical results from a sample of a clear packaging material, in which may be seen peaks for the monomers used to formulate the polymer (including styrene, methyl methacrylate and PVC) as well as for the semivolatile plasticizer added to the product.

A more complete picture of such complex polymers may be produced by the careful selection of a series of temperatures which transfer various fractions of the material to the GC for analysis, without the use of solvent extraction, dilution or additional sample manipulation.

EXPERIMENTAL

ANALYTICAL CONDITIONS - PYROLYSIS

Pyrolyzer: CDS Analytical Pyroprobe 5000
Filament: Coil, Platinum
Interface: Model 1500

ANALYTICAL CONDITIONS - GAS CHROMATOGRAPHY

Instrument: Agilent 6890
Column: 30 m x 0.25 mm HP-5
Program: Initial 40°C for 2 minutes
Ramp 10°C/minute
Final 300°C
Carrier: Helium
Split: 50:1

ANALYTICAL CONDITIONS - MASS SPECTROMETER

Instrument: Agilent 5973 MSD
Range: 20 - 600 AMU

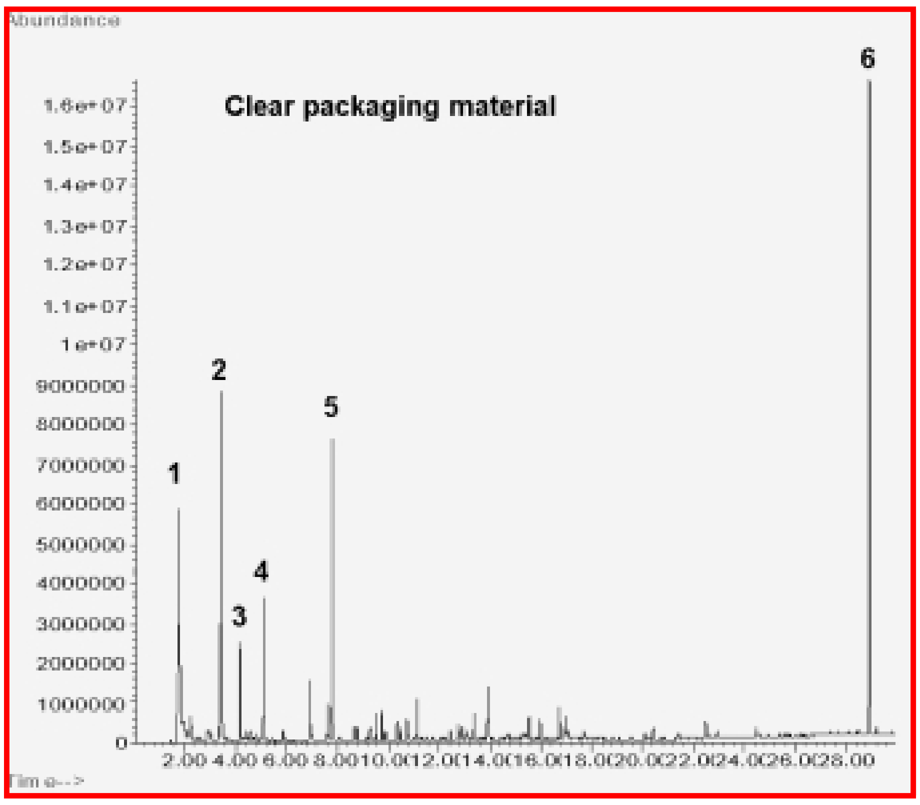

FIGURE 1. Pyrolysis at 700°C of a molded packaging product made from polystyrene, polymethyl methacrylate and polyvinyl chloride. The HCl, Benzene and Toluene are pyrolysis products of PVC.

1. HCl
2. Benzene
3. Methyl methacrylate
4. Toluene
5. Styrene
6. Bis 2-ethylhexyl phthalate (DOP)

RESULTS

A simple pyrolysis, coupled with gas chromatography or GC/MS is frequently enough to identify or differentiate polymeric materials. Sample preparation generally consists of merely taking a piece that is about 50 µG and placing it into the pyrolyzer. The sample is then heated very quickly to a high temperature at the beginning of the GC run. The volatile compounds produced from the sample are delivered directly to the GC column, and the chromatography proceeds as it would for any other sample introduction technique.

In Figure 2, a sample of material formed into a small bead used in jewelry was pyrolyzed at 650°C. True amber is a fossilized tree resin, which forms complex terpenoid structures. The sample in this case produced only a series of phenols when pyrolyzed, and none of the typical fragments seen in a true amber, indicating that it is not a sample of amber, or even a natural product, but a synthetic resin.

In Figure 3, a sample of real amber from Lebanon was pyrolyzed under the same conditions. The complex pyrogram which results contains many hydrocarbons, saturated and unsaturated, including cyclic compounds. The large peak just after 5 minutes, for example, is dimethyl cyclohexene.

For Figure 4, the adhesive from a sample of clear packaging tape was removed from the polymer film that made the tape. The adhesive by itself was then pyrolyzed for the chromatogram. The results show a fairly wide distribution of compounds, including alcohols, hydrocarbons and esters. Some of the peaks identified include:

Retention time	Compound
2.6 min	Acetic acid
3.1	Butanol
4.1	3-methylene Heptane
5.8	Butyl acetate
7.7	Butyl acrylate
10.2	2-ethyl Hexanol

along with longer chain acrylic compounds. When acrylic polymers with long chain ester groups are pyrolyzed, they usually from some of the monomer (as in the butyl acrylate) as well as some of the corresponding alcohol (here, butanol). The adhesive then is made from a mixture of acrylic compounds, including butyl and octyl esters. The two sets of peaks at about 22 minutes and at 26 minutes may be dimers, and will be seen again in a stepwise analysis of the whole tape.

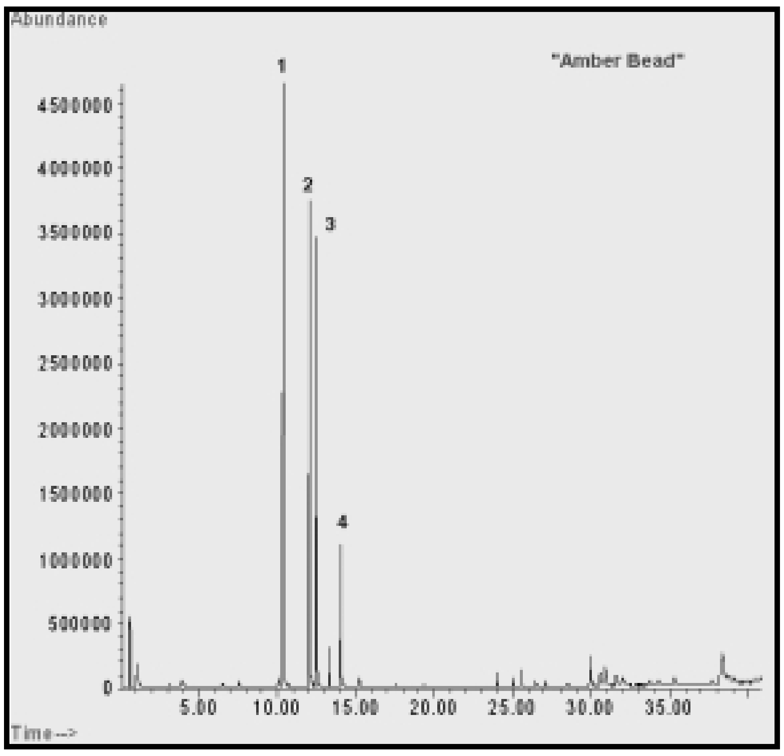

FIGURE 2. Pyrolysis of amber colored bead.
1. Phenol
2. 2-methyl phenol
3. 4-methyl phenol
4. 2,4-dimethyl phenol

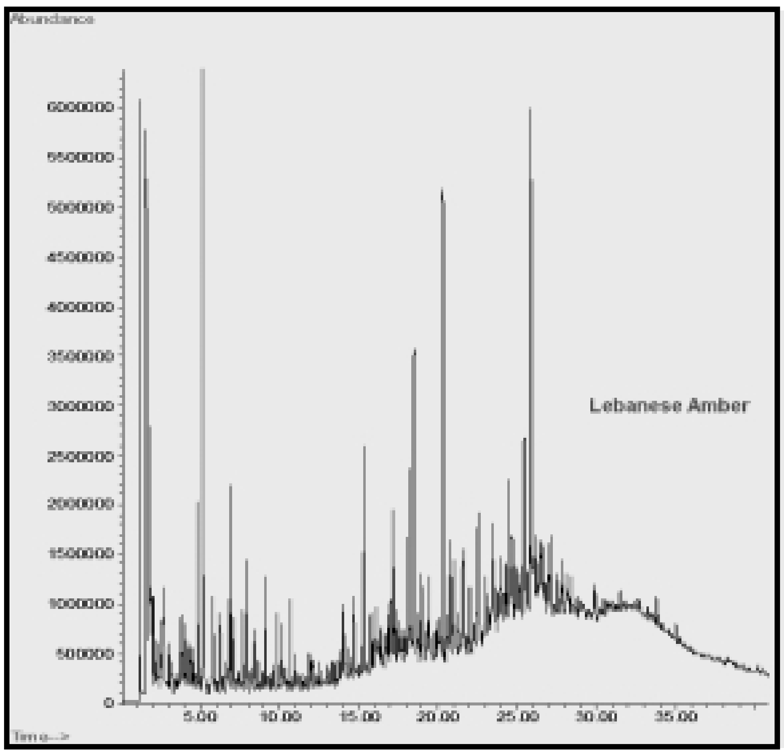

FIGURE 3. Pyrolysis of true amber from Lebanon.

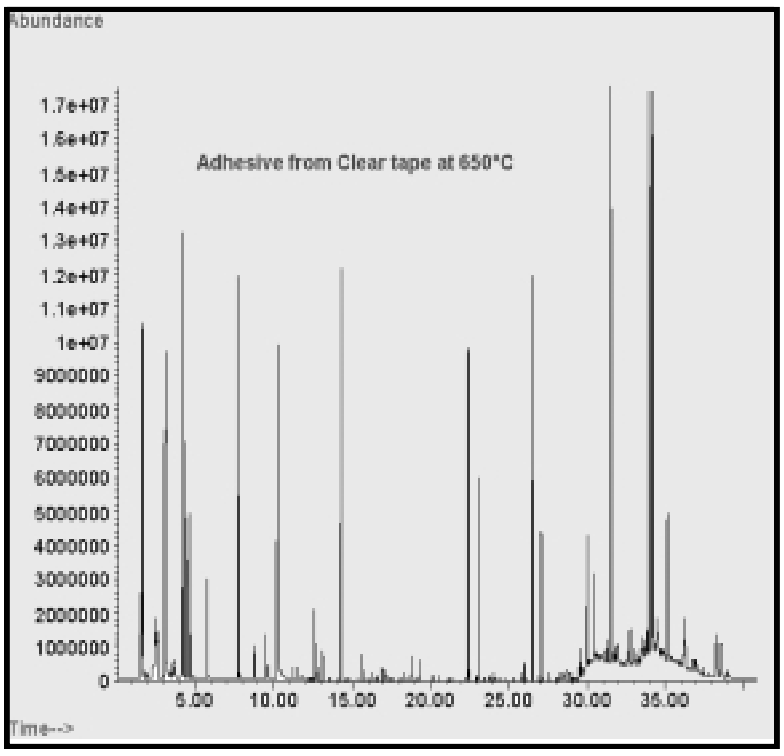

FIGURE 4. Pyrolysis of adhesive from clear tape.

MULTI-STEP ANALYSIS

A single run of the whole tape, from which the adhesive was taken for Figure 4, would include peaks for pyrolysis products from the adhesive, plus the polymer film, in addition to volatile and semi-volatile compounds like residual solvents, monomers and additives. A multi-step approach, taking the sample material stepwise to increasingly higher temperatures, may help separate some of the compounds and simplify the analysis.

In this series, a 1.25 mm circle of the tape was heated sequentially to 100°, 200°, 400° and finally 650°C, for a few seconds each time. At 100°C, only a few very small peaks are seen from the sample.

Figure 6 shows that at 200°, some compounds are beginning to be released from the tape and adhesive matrix, including a phthalate plasticizer at 23 minutes and another at 28 minutes.

At 400°C, the largest peak is for 2-ethyl hexanol, which was also seen in the analysis of the adhesive in Figure 4. This is a breakdown product from one of the acrylics used to in the adhesive. Beyond that, there are the two sets of peaks at about 23 and 26 minutes, also prominent in the single step analysis of the adhesive. Earlier eluters include acetic acid, butanol, 3-methylene heptane and butyl acetate. So most of the compounds released from the sample at 400°C may be associated with the adhesive and not with the polymer film used for the tape itself.

It isn't until the run at 650° that evidence of the tape polymer is seen. Now, in addition to many of the peaks seen earlier, there is a series of hydrocarbons, starting with the dimethyl heptene indicated in Figure 8. This compound is the trimer of propene and always the largest peak in a pyrogram of polypropylene. Other oligomers of propylene may be seen at about 10 minutes (the tetramer) and 15 minutes (the pentamer). From this series, then, the tape may be deformulated and shown to be comprised of a polypropylene film with an acrylic adhesive and phthalate plasticizers.

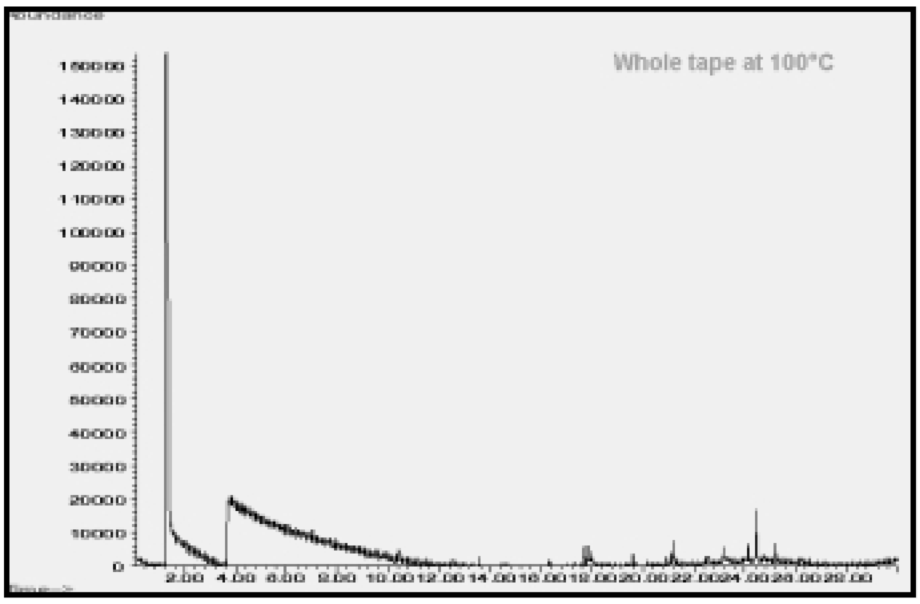

FIGURE 5. Whole tape at 100°C.

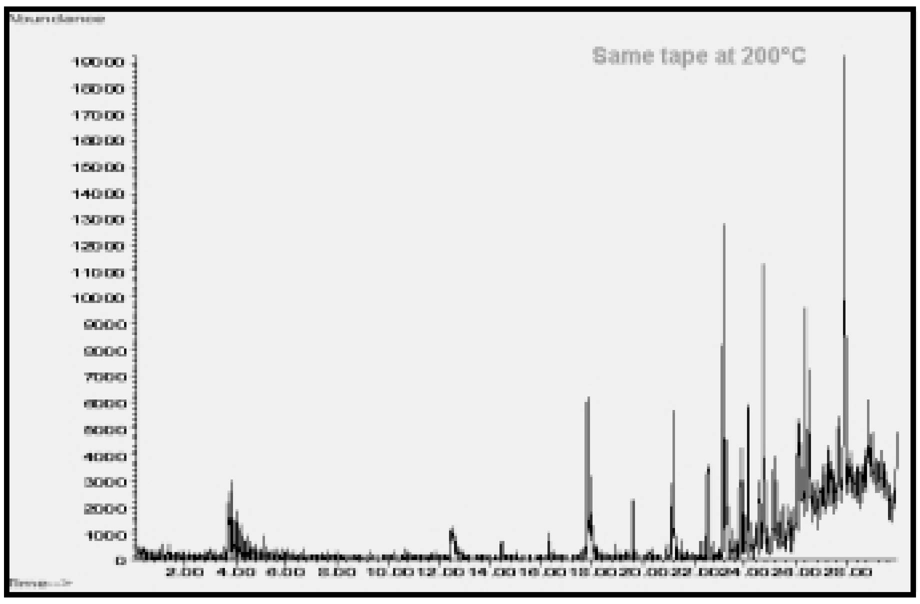

FIGURE 6. Whole tape at 200°C.

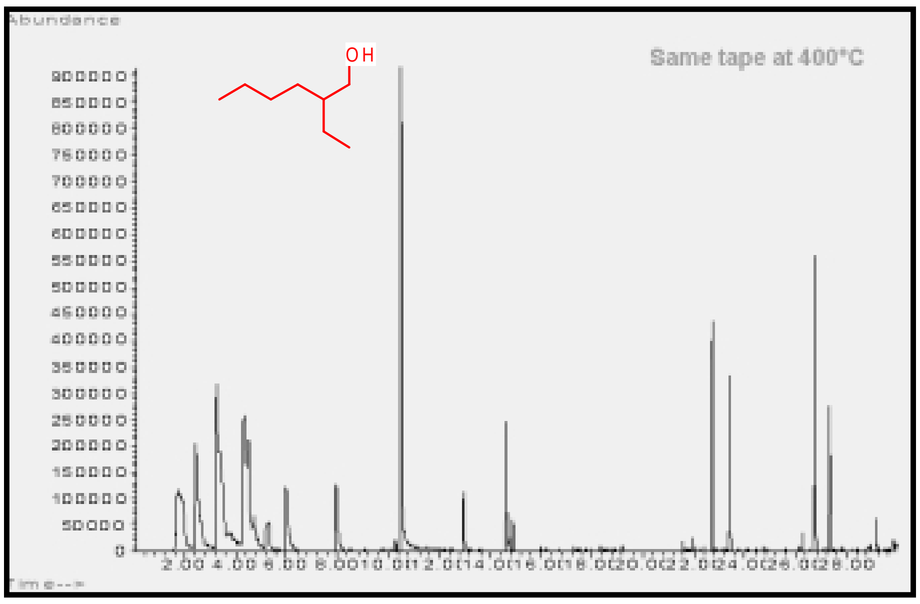

FIGURE 7. Whole tape at 400°C.

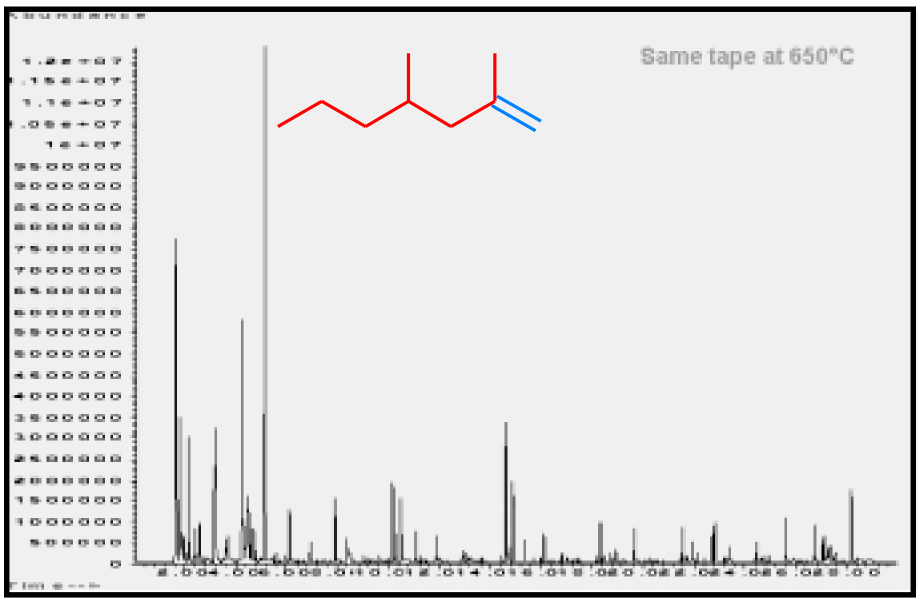

FIGURE 8. Whole tape at 650°C.

DIRECT TO MS
PULSE AND PROGRAMMED

An alternative to stepwise chromatographic analysis is to interface the pyrolyzer directly to the mass spectrometer and perform either pulse or programmed heating of the sample. The results are obtained faster, and reveal the relative temperatures at which some products are formed, but the mass spectra may be complex when dealing with a multi-component system, and may rely on chromatographic runs to help sort things out.

In these runs, the GC column was removed and replaced with a 1 m long piece of 0.1 mm fused silica. The injection port, split ratio and pyrolysis interface were left the same as for the chromatographic runs. The GC oven was set to 200°C isothermal.

Figure 9 shows a pulse pyrolysis at 650°C of poly butyl methacrylate, with data collected for a total of one minute. Like other methacrylates, PBMA mostly unzips to form monomer, and the mass spectrum obtained throughout the peak is identified as butyl methacrylate. If the same polymer is heated through a range of temperatures, as in Figure 10, more information is obtained. In this case, there is an early, small peak, then a large peak as the sample is pyrolyzed. Both peaks have the same mass spectrum, and the first peak represents the residual butyl methacrylate (and other volatiles) being released from the polymer before pyrolysis.

For Figure 11 a small piece of glossy coated paper was heated, again at 100°/minute. The main peak at about 4.5 minutes consists of heavily oxygenated compounds resulting from the cellulose used to make the paper. After this peak, there is a smaller peak at about 6.5 minutes. The mass spectra in this area contain masses seen in the paper pyrolysis, plus a large peak for mass 104, which comes from the styrene used in the coating of the paper.

When a piece of clear vinyl film is heated under these conditions, several peaks are produced, as shown in Figure 12. Phthalic anhydride, from a plasticizer, is seen in the early region labeled A in the figure. As poly vinyl chloride is heated, it degrades by a two-step process, First, at relatively low temperatures, the chlorine is removed from the polymer as HCl. This leaves behind a highly unsaturated backbone, which, upon further heating produces cyclic compounds, including benzene, toluene, xlyenes and naphthalene. In Figure 12, the peak labeled B consists mainly of mass 36, showing the evolution of HCl from the PVC. Finally, the peak marked C contains, among other things, mass spectra with a large peak at mass 91, showing the production of toluene.

CONCLUSIONS

Careful selection and control of sample temperature may be used to replace many time consuming steps in the characterization of polymeric materials. The sample may be heated to a series of temperatures to separate volatile and semi-volatile components from the polymer matrix, then pyrolyzed to reveal the structure of the polymer itself. As an alternative, the sample may be heated directly to the mass spectrometer to obtain temperature resolved data. For complex samples, chromatographic analysis first may indicate specific compounds or masses are significant in the faster direct or programmed runs.

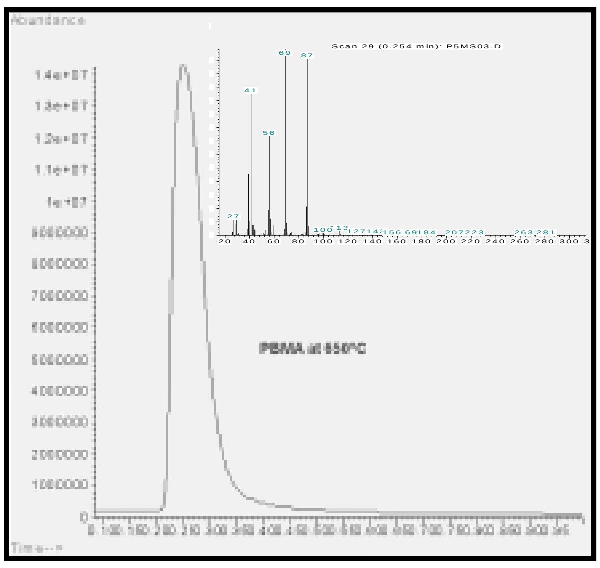

FIGURE 9. Pyrolysis of Poly butyl methacrylate at 650°C.

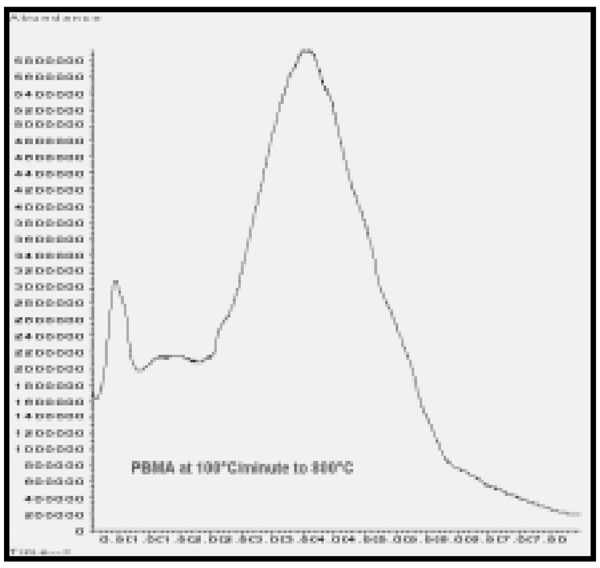

Figure 10. PBMA heated at 100°C/minute.

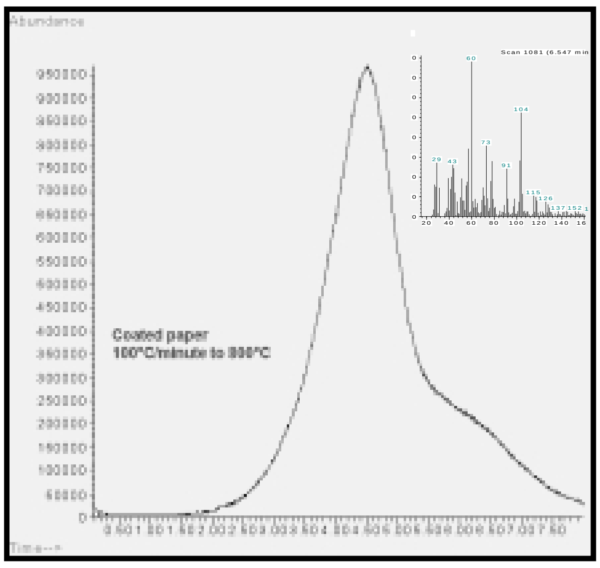

Figure 11. Coated Paper heated at 100°C/minute.

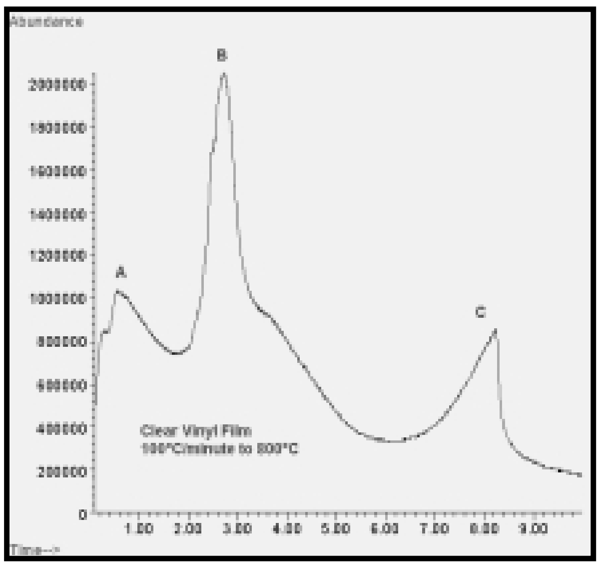

Figure 12. Clear vinyl film heated at 100°C/minute.