

# Analysis of an Acrylic Copolymer Using Pyrolysis-GC/MS

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## Introduction

Analytical pyrolysis<sup>1</sup> is a means of extending the utility of gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS), to the analysis of non-volatile samples like paint, rubber and plastic. The sample is heated to a high temperature up-stream of the GC column to cause rapid fragmentation into compounds which are both characteristic of the polymer and amenable to analysis by gas chromatography. Polymers fragment in a reproducible way, producing specific molecules which help identify not only the nature of the original polymer, but much about the structure, purity and bonding within the macromolecule. In the case of copolymers, information is provided on the nature and relative amounts of the various monomers used to make the original material.

This Field Application Report describes the analysis of an acrylic copolymer which includes methyl methacrylate (MMA), butyl acrylate (BA) and butyl methacrylate (BMA). The analytical system consists of a PerkinElmer<sup>®</sup> Clarus<sup>®</sup> 500 GC/MS interfaced with a CDS Analytical Pyroprobe 2500 Pyrolysis Autosampler\*. Samples are rapidly pyrolyzed, automatically introduced into the GC carrier stream and transferred to the GC column for analysis.

Like many polymers, acrylic and methacrylic homopolymers and copolymers degrade to provide significant amounts of the original monomers used in the polymerization.<sup>2</sup> Comparing peak-area ratios for these major products provides an indication of the repeatability of the Pyrolysis-GC/MS system (Py-GC/MS).

## Experimental

The analytical parameters used are listed in Table 1 (Page 2). Since the polymeric sample is introduced as a solid, no solvent peak is generated, and all peaks in the chromatogram are the result of constituents of the sample material. To be consistent with the sample capacity of the analytical column, typical samples are approximately 100 µg. Replicate samples need not be of identical mass, however, since the peak-area ratios are used to show reproducibility. Sample preparation consists of placing the polymer material into a small quartz tube, which is introduced from a carousel into the pyrolysis coil of the pyrolyzer. An on-line/off-line valve permits the venting of air from the system before it is connected in-line to the GC, equilibration with the GC carrier before the run is started and removal of the sample after pyrolysis.

\*Available for purchase directly from CDS Analytical Inc., 1-800-541-6593, [www.cdsanalytical.com](http://www.cdsanalytical.com)

## Results

The total ion chromatogram of the Py-GC/MS run (the pyrogram) is shown in Figure 1. Once the pyrolysis products have been generated and transferred to the GC column, the peaks they produce may be analyzed using the same methods as those used for any other GC application, including mass spectrometry. Polymers frequently degrade to produce monomer, and spectra for these compounds are generally found in libraries for comparison. Figure 2 shows the mass spectra for the three largest peaks in the pyrogram, which, when searched as in Figure 3, identify these peaks as the monomers methyl methacrylate (MMA, Peak 1), butyl acrylate (BA, Peak 3) and butyl methacrylate (BMA, Peak 4). Other peaks were identified as well, including butanol and methacrylic acid (Peak 2).

Many polymers produce larger fragments in addition to the monomers, including dimers and higher oligomers. The mass spectra of these peaks helps elucidate the structure of the compounds involved, even if spectra for such complex molecules may not be found in mass spec libraries. Analysis of homopolymers and model compounds also helps in identifying specific oligomers. In this analysis, the peaks at 27 minutes are mixed dimers of the copolymer, and the peaks at 37 minutes are trimers (Figure 1).

To evaluate the reproducibility of the Py-GC/MS system, four samples were pyrolyzed and the area data for the monomer peaks recorded. Figure 4 shows three replicate analyses of this copolymer. Table 2 shows the area for each of the peaks in the four runs, plus the peak-area ratios comparing MMA to BA, MMA to BMA and BA to BMA. Relative standard deviations of approximately 2% were found for all of the monomer-area comparisons.

## Conclusions

Analytical pyrolysis is a simple technique which extends the use of GC and GC/MS to the analysis of polymeric materials. Interfacing a CDS Model 2500 Pyrolysis Autosampler to a PerkinElmer Clarus 500 GC/MS produces a system capable of providing detailed analysis of up to 36 samples automatically. Frequently, the products generated by pyrolysis are simple molecules, such as the monomers of the original polymer, and may be identified readily by mass spectrometry. Sample preparation is minimal and the reproducibility is excellent with an RSD (monomer-area ratios) of just over 2%. The data provided may be used in product identification and deformation, quality-control assays of monomer content, forensic analysis, including the identification of paint fragments from crime scenes and polymer microstructure analysis.

Table 1. Instrument Parameters.

<b>Clarus 500 GC</b>		<b>Clarus 500 MS</b>	
Injector Temperature:	300 °C	Mass Range:	30-550 u
Oven Initial Temperature:	40 °C for 2 min	Scan Time:	0.39 second
Ramp:	6 °C/min	InterScan Delay:	0.01 second
Oven Final Temperature:	295 °C for 10 min	Transfer Line:	250 °C
Column:	Elite-5* 30 m, 0.25 mm I.D., 1.0 µm film	Solvent Delay Time:	NA
Carrier Gas:	He (split ratio 50:1)	Source Temperature:	280 °C
		Multiplier Voltage:	350 V
		Trap Emmission:	100 mA
		Ion Energy:	70 eV
<b>Model 2500 Pyrolyzer</b>			
Oven:	300 °C		
Transfer Line:	300 °C		
Pyrolysis Temperature:	750 °C		
Pyrolysis Time:	15 seconds		
Heating Rate:	10 °C/ms		

\* PerkinElmer part number N9316077

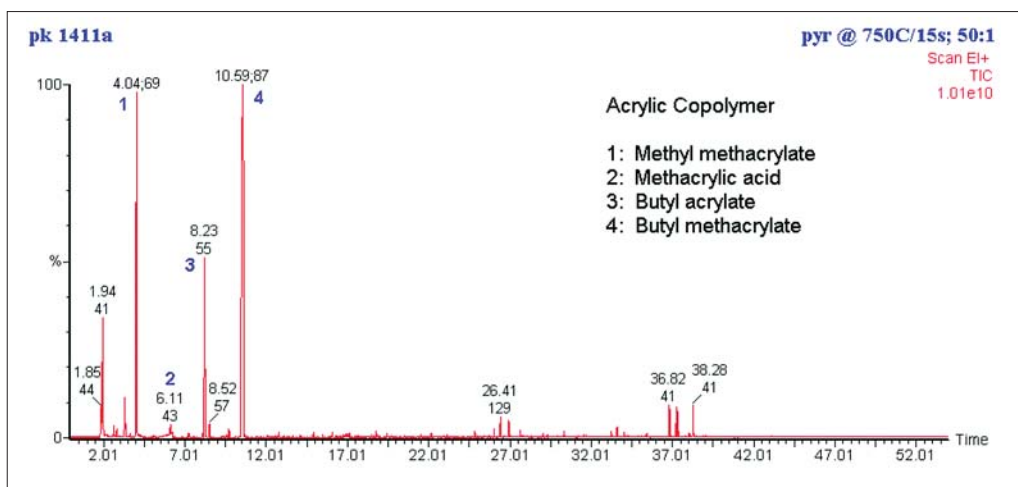


Figure 1. Total ion chromatogram resulting from pyrolyzing the copolymer at 750 °C for 5 seconds.

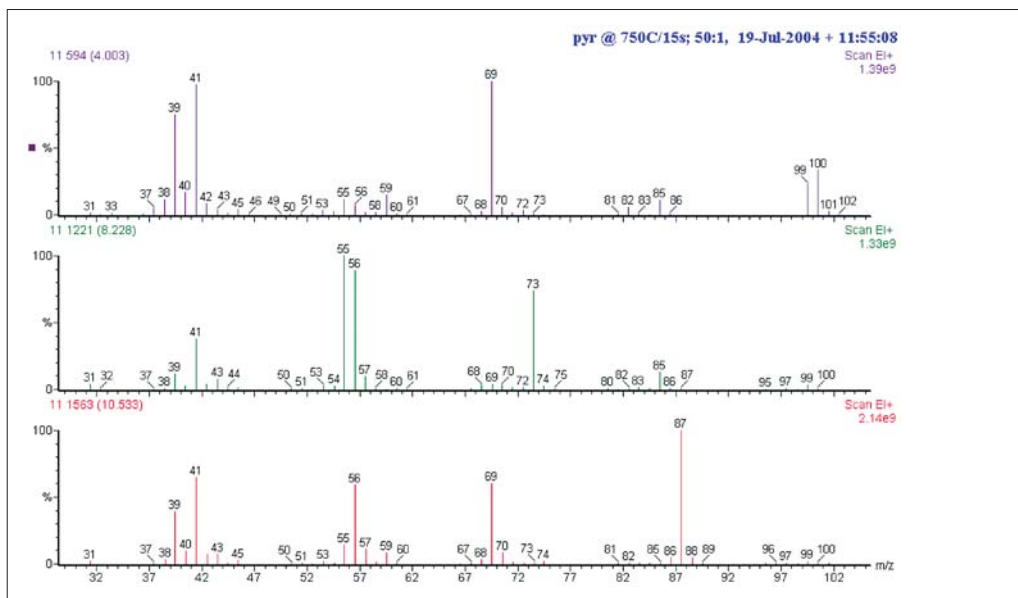


Figure 2. Mass spectra of Peaks 1, 3 and 4 from the pyrogram shown in Figure 1.

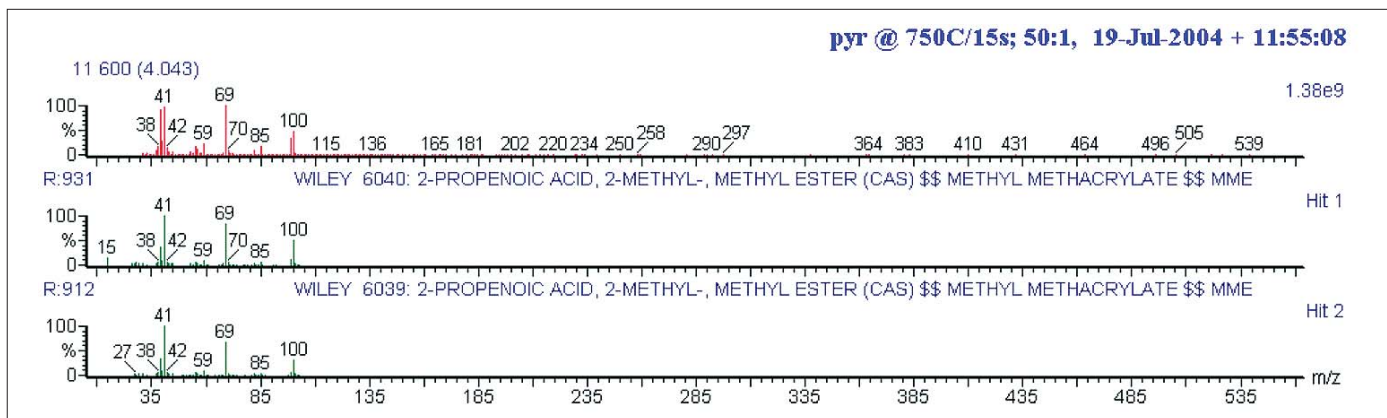


Figure 3. Mass spectrum from Peak 1 identified using the Wiley 7 database as methyl methacrylate.

Table 2. Instrument Parameters.

Run #	MMA Area	BA Area	BMA Area	Ratios		
				MMA/BA	MMA/BMA	BA/BMA
1	619283264	326181184	1298866432	1.899	0.477	0.251
2	521646016	285819680	1162512000	1.825	0.449	0.246
3	633592740	338938912	1357293312	1.869	0.467	0.250
4	837413888	464536064	1800524416	1.803	0.465	0.258
<b>Average</b>				1.849	0.465	0.251
<b>S</b>				0.043	0.012	0.005
<b>RSD</b>				2.33%	2.50%	2.01%

## References

1. Applied Pyrolysis Handbook, T.P. Wampler (Ed.) Marcel Dekker, New York (1995).
2. F.C.-Y. Wang, The Microstructure Exploration of Thermoplastic Copolymers by Pyrolysis-Gas Chromatography, J. Anal. Appl. Pyrolysis, 71 (2004) 83-106.

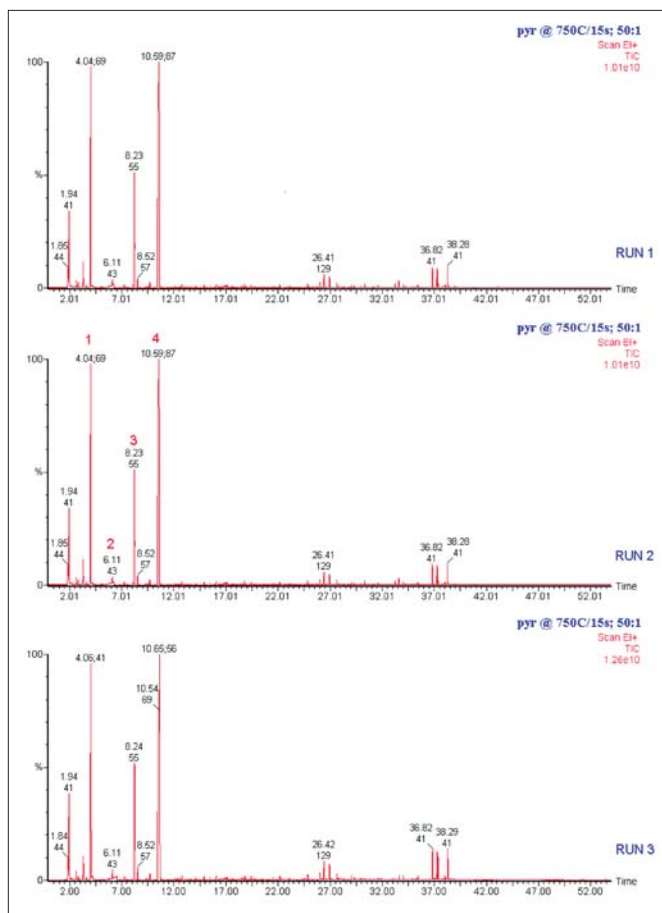


Figure 4. Three consecutive runs of the copolymer. Peak identifications are listed in Figure 1.

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