Polymer Degradation Mechanisms using Pyrolysis-GC/MS

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Introduction

The use of analytical pyrolysis[1] with gas chromatography/mass spectrometry to study the structure of polymeric material must be based on an understanding of how these large molecules behave at such elevated temperatures. The utility of the technique is based on the application of thermal energy to produce volatile fragments and products from a macromolecule – compounds capable of being analyzed using GC/MS. The production of these analytes must, of course, be reproducible and follow chemical principles which permit the interpretation of results applied to unknown polymers.

In general, the degradation mechanisms experienced by polymers are free-radical processes initiated by bond dissociation at the pyrolysis temperature. The specific pathway followed by a particular polymer is related to the relative strength of the polymer bonds, and the structure of the polymer chain. These mechanisms are generally grouped into three large categories – random scission, unzipping and side-group elimination.

This Field Application Report shows an example of each of these three general degradation processes. The analytical system consisted of a PerkinElmer Clarus 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. The specific polymers used are Polyethylene, Poly methylmethacrylate and Poly vinylchloride.

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Experimental

Table 1. Instrument Parameters

Clarus 500 GC		Clarus 500 MS	
Injector Temp	300° C	Mass Range	30 - 550 u
Oven Program	40° for 2 min	Scan Time	0.39 second
Rate	6° C/min	InterScan Delay	0.01 second
	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	0 seconds
Carrier Gas	He (split ratio 50:1)	Source Temperature –	280 ° C
		Multiplier Voltage	350 V
Model 2500 Pyrolyzer		Trap Emission	100 mA
Oven	300° C	Threshold	xx
Transfer Line	300° C		
Pyrolysis Temperature	750°C		
Pyrolysis Time	15 seconds		
Heating rate ° C/ms	10		

* PerkinElmer part number (N9316077)

Samples of approximatel y 100 µg were analyzed using the conditions listed in Table 1. Sample preparation consisted of simply placing the sample into a quartz tube, which was introduced into the Pyroprobe automatically. No solvent is used, so there is no need for a solvent delay. In fact, some of the compounds found in the earliest eluting peaks may be important diagnostic products for the identification of a particular polymer. The GC column, carrier gas parameters, split ratio and so on are used in the same way as for samples introduced by any other means.
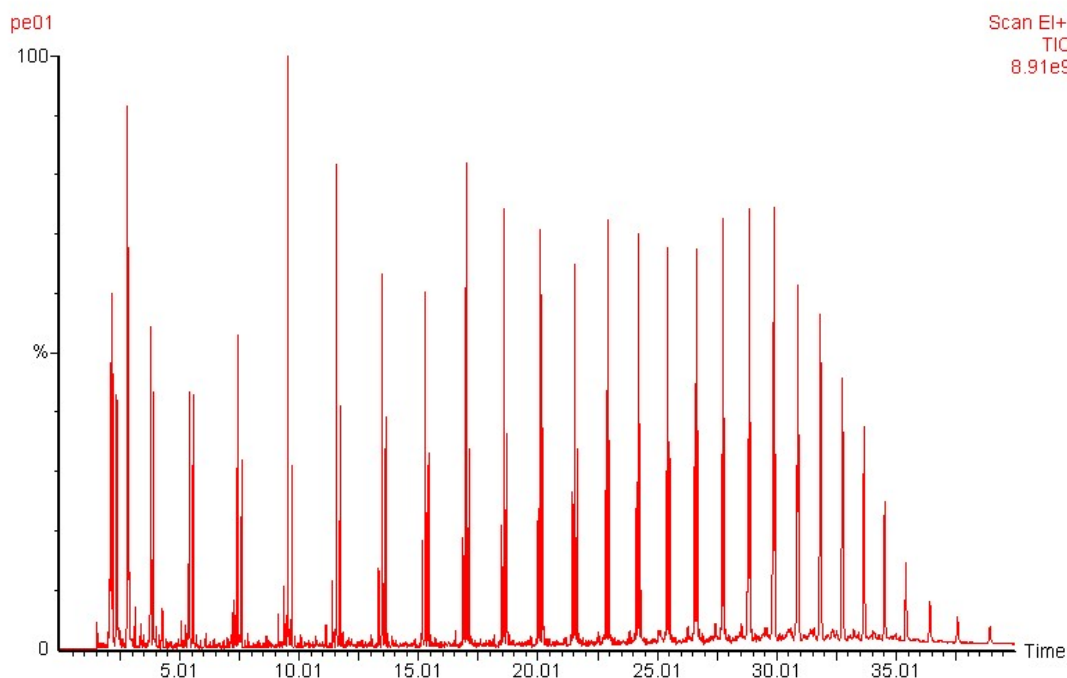
Results

Figure 1. Total Ion Chromatogram resulting from pyrolyzing Polyethylene at 750°C for 15 seconds.

Random Scission – Polyethylene

The total ion chromatogram for the pyrolysis of polyethylene (the pyrogram) is shown in Figure 1. Polyethylene is very high molecular weight hydrocarbon, and the fragments produced via pyrolysis are just pieces of the original molecule small enough to go through the GC. This produces a pattern of peaks for successively longer oligomers, which is common for polyolefins. For polyethylene, the pattern consists of triplets of peaks, as shown in the expanded chromatogram in Figure 2. These are all normal hydrocarbons, and as seen in Figure 3, may be identified as the alkane, alkene and diene of increasing chain lengths. Other polyolefins, such as polypropylene, polybutylene and so on, behave in the same manner, producing characteristic patterns of oligomers specific for that polymer.

Unzipping – Poly methyl methacrylate

Some synthetic polymers, including the methacrylates, simply unzip at pyrolysis temperatures, generating mostly monomer. This is the case for poly methyl methacrylate, shown in Figure 3. Instead of a series of increasingly longer oligomers, the chromatogram shows a large peak for monomer, and little else. This behavior is seen in copolymers involving methyl methacrylate monomer as well as in the pure homopolymer, and acrylic copolymers in general produce monomer peaks for each of the monomers used in the formulation.

Side-group Elimination – Poly vinyl chloride

In the polymers discussed above, the weakest bonds are those holding the chain together, so pyrolysis produces either fragmentation to smaller oligomeric units, or unzipping all the way to monomer. For some polymers, however, the groups attached to the side of the chain are held by bonds which are weaker than the bonds connecting the chain. In such cases, the side groups are stripped off from the chain before it is broken into smaller pieces, so no monomer or higher oligomers are

seen. This is the case for some vinyl polymers, including poly vinyl chloride, poly vinylidine chloride and poly vinyl acetate. In PVC, the carbon-chlorine bond is the weakest, so a chlorine free radical is generated at relatively low temperatures. This chlorine takes a hydrogen from the polymer, making HCl gas and leaving behind a highly unsaturated chain. The chain then degrades to produce aromatics, so the pyrolysis products from PVC include HCl, benzene, toluene and other aromatics, even naphthalene.
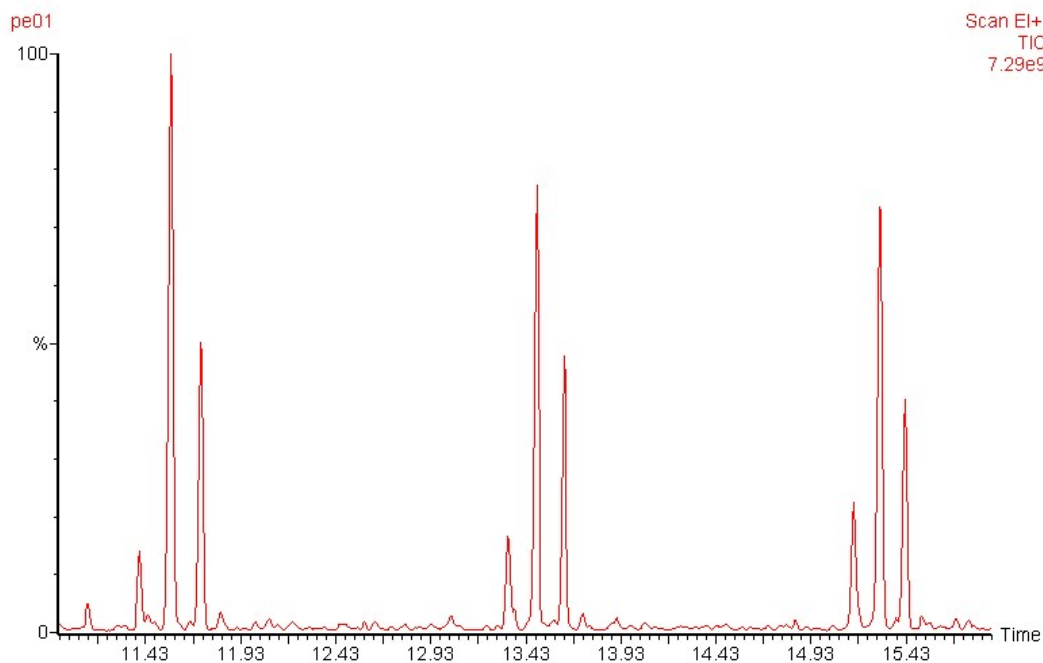
Figure 2. Expanded portion of the pyrogram shown in Figure 1.
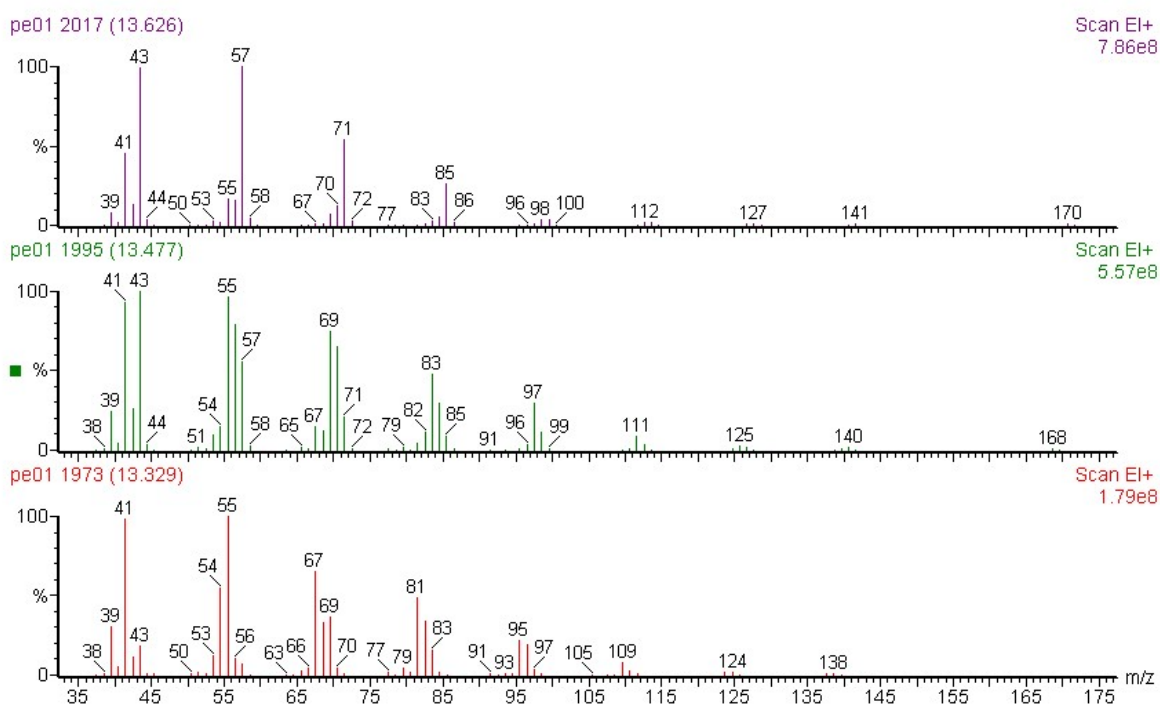
Figure 3. Mass spectrum from peaks at 13.3 to 13.6 minutes, identified using the Wiley 7 database as dodecadiene, dodecene and dodecane.

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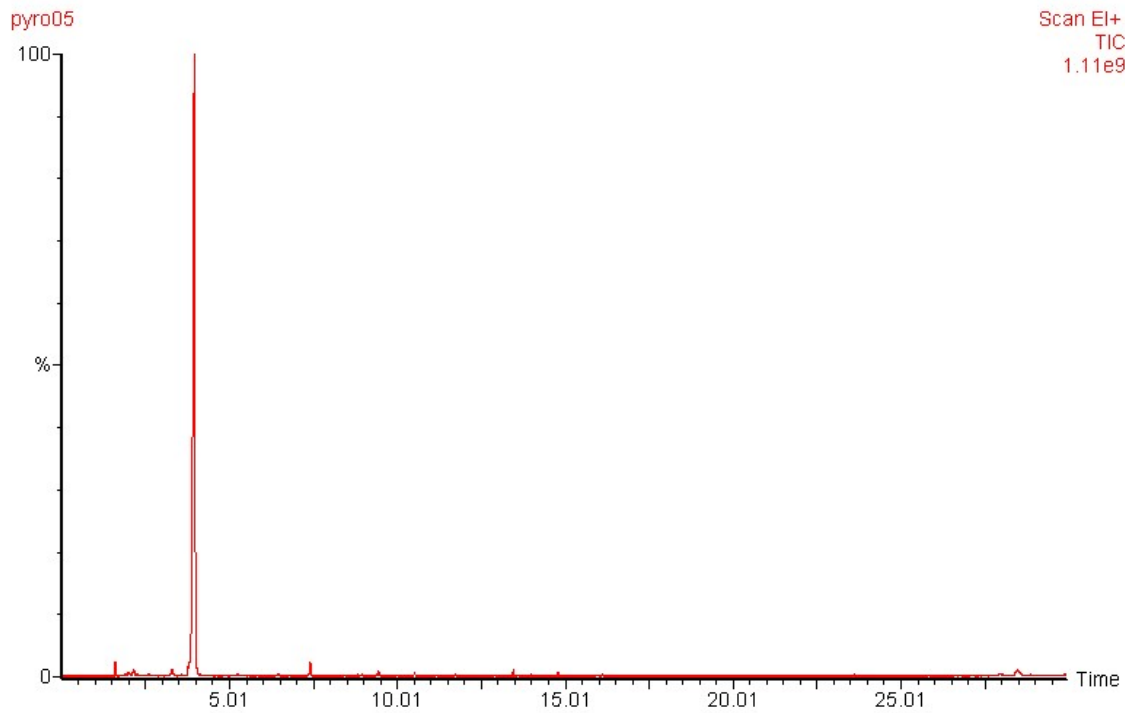
Figure 4. Pyrogram pf poly methyl methacrylate.
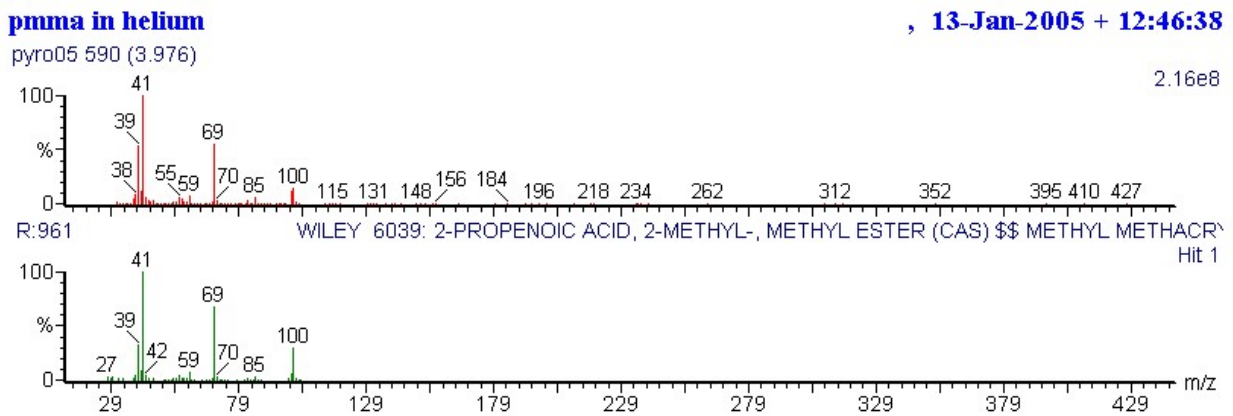
Figure 5. Spectrum of the peak at 4 minutes, identified as the monomer, methyl methacrylate.
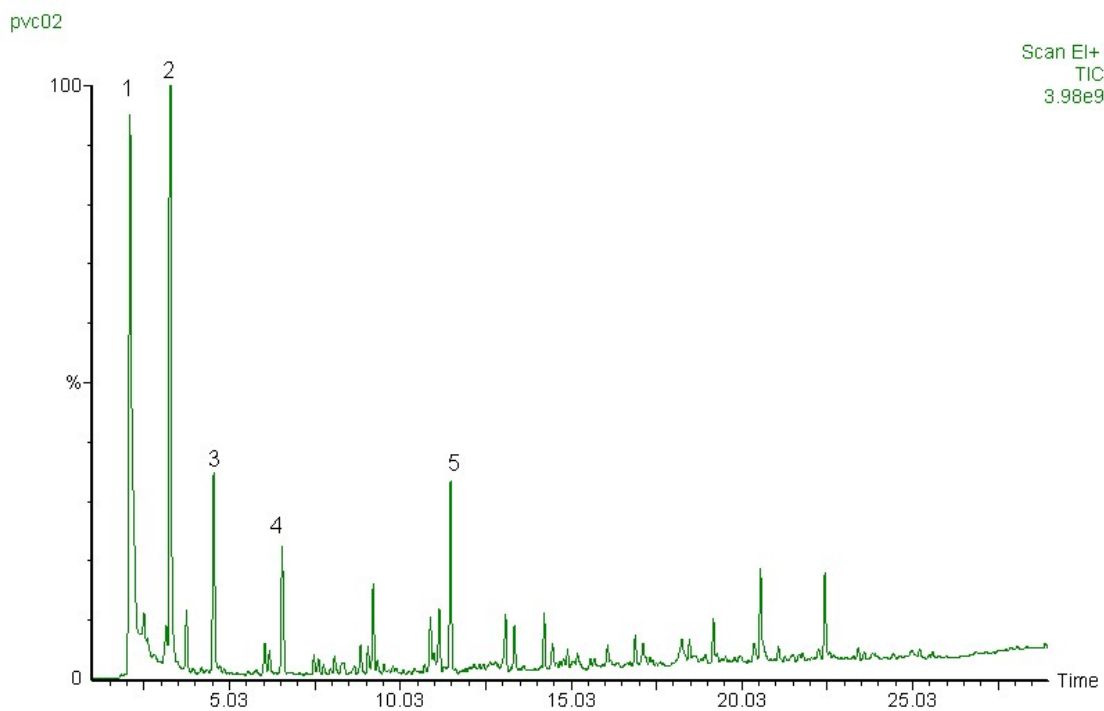
Figure 6. Pyrogram of poly vinyl chloride. Peak identification: 1)HCl, 2)Benzene, 3)Toluene, 4) Xylene 5) Naphthalene

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 PE 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 of just over 2%. The data provided may be used in product identification and deformulation, quality control assays of monomer content, forensic analysis, including the identification of paint fragments from crime scenes and polymer microstructure analysis.

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.

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