

Polymer Degradation Mechanisms Encountered in Pyrolysis-GC/MS

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Introduction

The use of analytical pyrolysis¹ with gas chromatography/mass spectrometry (GC/MS) to study the structure of polymeric material must be based on an understanding of how these large molecules behave at 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.

Whether the sample represents evidence in a forensic lab, quality-control materials in the paint, adhesives, rubber or polymer industries or an unknown material for product comparison, the original polymeric structure is revealed in the compounds present in the chromatogram. The presence or absence of specific peaks in the pyrogram not only differentiates one sample from another, but may be crucial in identifying defects related to product performance. Understanding how these peaks

are produced from the polymer is important in weighing the significance of the data and essential in identifying unknown materials, whether it is contamination in industrial processes, competitors products or evidence from a crime scene.

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 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 by GC/MS. The specific polymers used are polyethylene, poly methyl methacrylate and poly vinyl chloride (PVC).

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Experimental

Samples of approximately 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

Random scission – polyethylene

The total ion chromatogram for the pyrolysis of polyethylene (the pyrogram) is shown in Figure 1. Polyethylene is a 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.² 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 shown by the spectra in Figure 3, they are 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 4. 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 the 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 chloride³, poly vinylidene 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 removes 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, as seen in Figure 6 (Page 4).

Table 1. Instrument Parameters.

Clarus 500 GC		Clarus 500 MS		Model 2500 Pyrolyzer	
Injector Temperature:	300 °C	Mass Range:	30-550 u	Oven:	300 °C
Oven Program:	40 °C for 2 min	Scan Time:	0.39 sec	Transfer Line:	300 °C
Rate:	8 °C/min	InterScan Delay:	0.01 sec	Pyrolysis Temperature:	750 °C
Final Temperature:	300 °C for 5.5 min	Transfer Line:	250 °C	Pyrolysis Time:	15 sec
Column:	Elite-5*	Source Temperature:	280 °C	Heating Rate:	10 °C/ms
Carrier Gas:	He (split 50:1)	Multiplier Voltage:	350 V		
		Trap Emission:	100 mA		

*PerkinElmer part number N9316077 (30 m, 0.25 mm ID, 1.0 µm film)

Conclusions

Interfacing a CDS Pyroprobe 2500 Pyrolysis Autosampler to a PerkinElmer Clarus 500 GC/MS is a simple way to extend the application of GC to the analysis of polymers. The high temperatures used in pyrolysis provide volatile fragments and characteristic compounds from the macromolecules, which may be identified by the GC/MS. Understanding the results obtained from unknown polymers is facilitated by a knowledge of how polymers behave at such high temperatures.

The behavior of most synthetic polymers during pyrolysis may be described as one of three general cases. Either the polymer breaks apart into smaller versions of the

macromolecule, producing oligomers, unzips all the way to monomer, or eliminates side groups and then fragments. Polyolefins like polyethylene and polypropylene are examples of polymers which produce a large array of oligomeric material, including monomers, dimers and trimers, but also fragments with ten or more monomeric units. Poly methacrylates, such as poly methyl methacrylate, unzip to produce a large peak for the monomer and very little else. Vinyl polymers like PVC and poly vinyl acetate first strip away the side group, making HCl or acetic acid, then produce aromatic compounds from the remaining backbone of the polymer. In all cases, these degradation products are reproducible and characteristic and may be used to identify polymers in an unknown formulation.

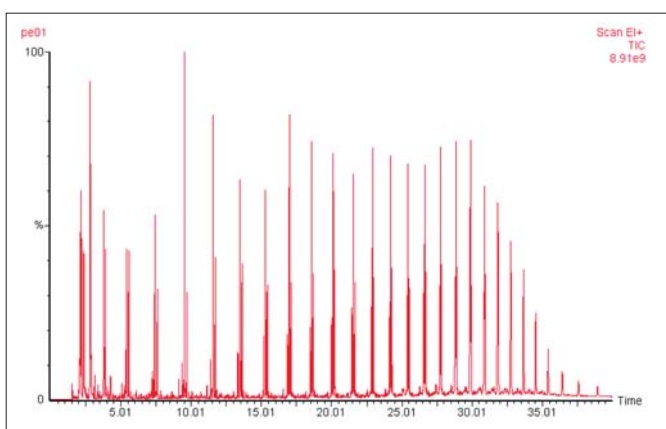


Figure 1. Total Ion Chromatogram resulting from pyrolyzing polyethylene at 750 °C for 15 seconds.

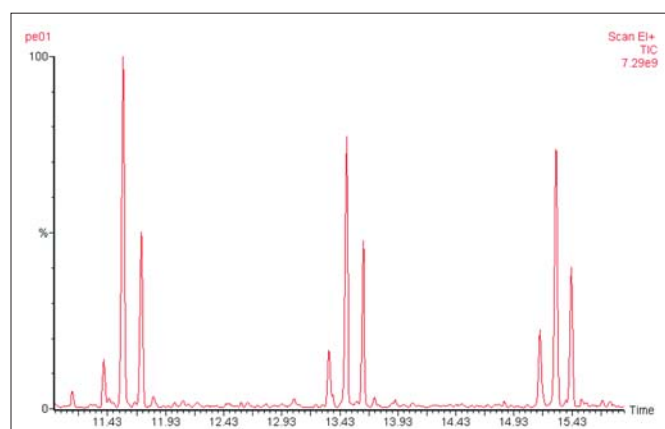


Figure 2. Expanded portion of the pyrogram shown in Figure 1.

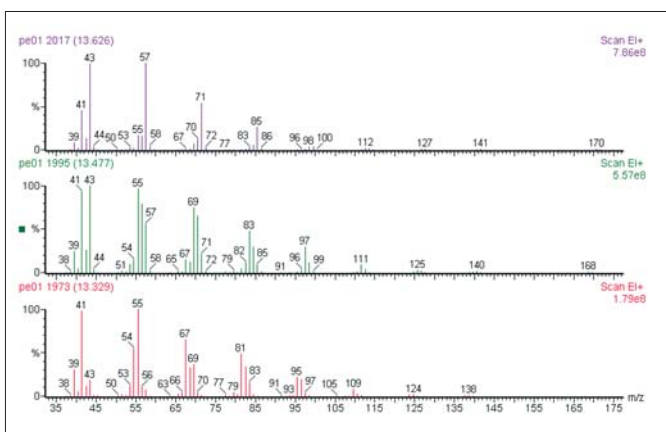


Figure 3. Mass spectra of peaks between 13.3 to 13.6 minutes (Figure 2). Identified using the Wiley 7 library as dodecadiene, dodecene and dodecane.

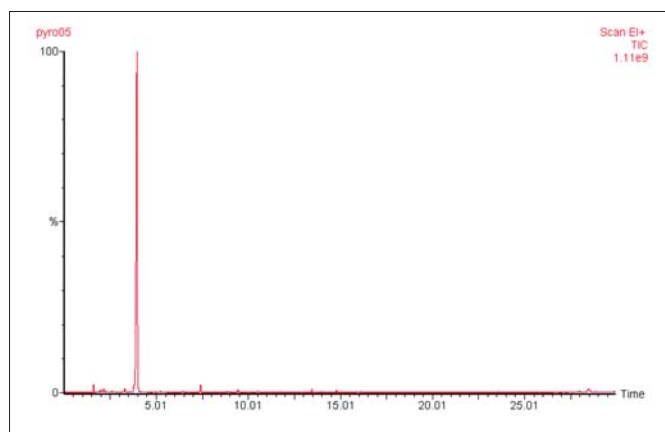


Figure 4. Pyrogram of poly methyl methacrylate.

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3. Zs. Czégény, E. Jakab, M. Blazsó, Thermal Decomposition of Polymer Mixtures Containing Poly (Vinyl Chloride) Macromol. Mater. Eng. 287 (2002) 277-284.

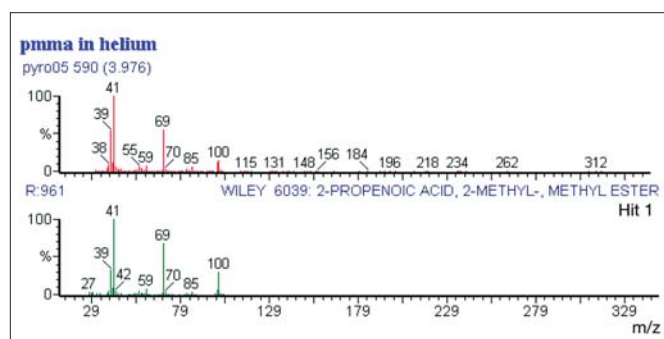


Figure 5. Spectrum of the peak at 4 minutes (from Figure 4), identified as the monomer, methyl methacrylate.

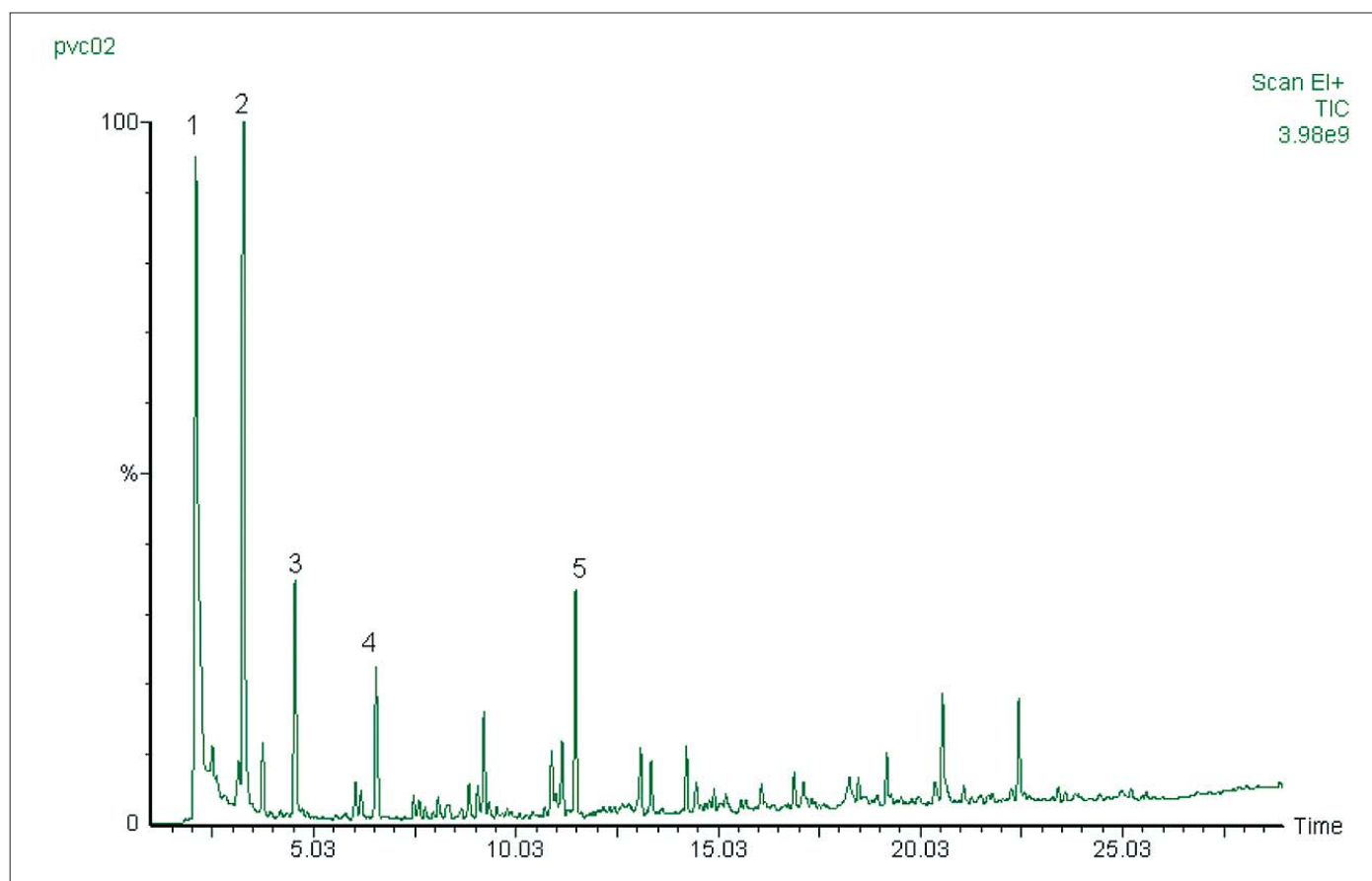


Figure 6. Pyrogram of poly vinyl chloride. Peak identification: 1 - HCl, 2 - Benzene, 3 - Toluene, 4 - Xylene, 5 - Naphthalene.

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