CDSolutions

APPLICATIONS INFORMATION USING ADVANCED SAMPLE HANDLING TECHNOLOGY

Pyrolysis/GC of Polyolefins

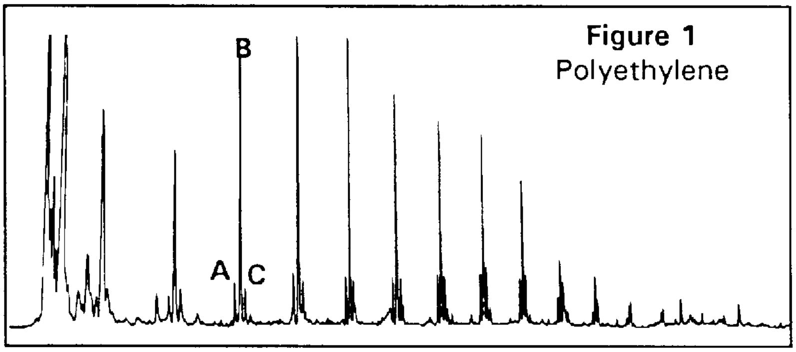

Figure 1
Polyethylene

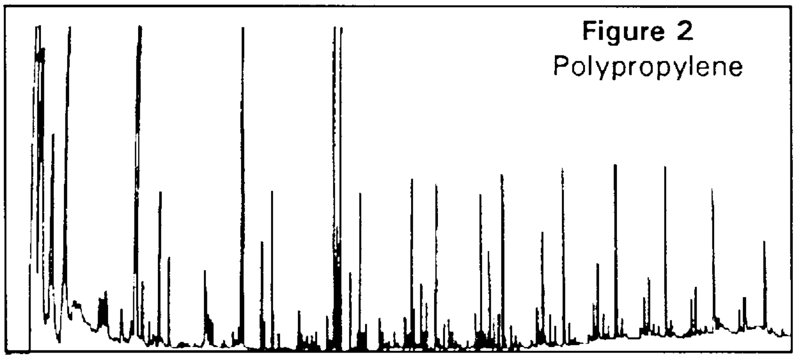

Figure 2
Polypropylene

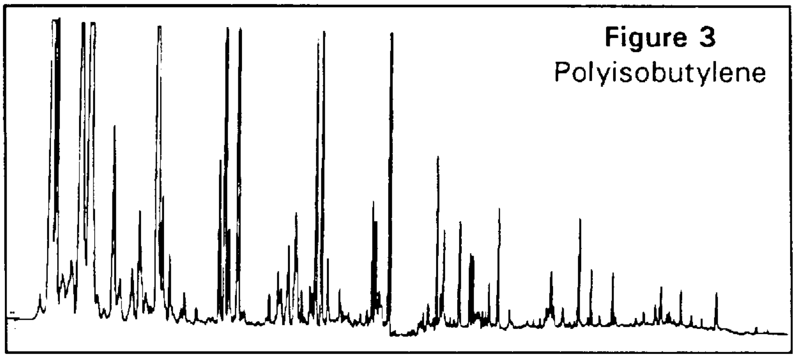

Figure 3
Polyisobutylene

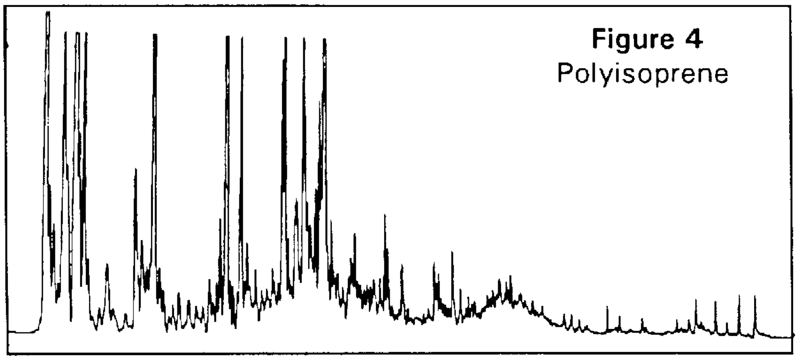

Figure 4
Polyisoprene

Pyrolysis has been utilized as a sample introduction technique for gas chromatography for over three decades. Pyrolysis is the breaking of chemical bonds using heat energy. When large, complex molecules are pyrolyzed, they degrade into volatile fragments that are amenable to analysis by gas chromatography. Thus the powerful analytical technique of GC can be performed on materials that were previously nonvolatile.

Polyolefins (or alkenes) are unsaturated aliphatic hydrocarbons which have been combined into high molecular weight polymers. Upon pyrolysis, smaller hydrocarbons are produced which are characteristic of the polyolefin composition of the polymer chain. Polyolefins undergo a process of random scission during pyrolysis, producing alkenes, alkanes, and diolefinic compounds. The presence of isoalkanes in the pyrolysate indicates branching in the original polymer chain. The product distribution in pyrolysis is dependent on the pyrolysis temperature, with higher temperatures producing smaller fragments that elute at earlier GC retention times.

Pyrolysis of polyethylene (Figure 1) produces primarily straight chain hydrocarbons. The nature of the polyethylene chain produces oligomeric groups of pyrolysis fragments differing from each other by one carbon unit, with each group consisting of a diene (A), alkene (B), and alkane (C). This pattern is predictable and reproducible. When polypropylene is pyrolyzed (Figure 2), fragments are produced which are more highly substituted than in straight chain polyolefins. The oligomeric groups produced by polypropylene pyrolysis vary by three carbon units. Polyisobutylene and polyisoprene give more complex chromatograms due to the increased substitution of the polymer backbone. Polyisobutylene (Figure 3) can be identified by alternate carbons in the polymer chain being disubstituted with methyl groups, causing a greatly different pattern than that of polyethylene and polypropylene. The primary pyrolysis products of polysisoprene are isoprene monomer and dipentene (Figure 4). Because much of the material reverts to monomer, the series of fragments with increasing carbon numbers does not appear as pronounced as it does in the other polyolefins.

In addition to providing ready identification of polymer pyrolysis fingerprint patterns, pyrolysis/GC provides structural details. It gives quantitative information in the analysis of copolymer blends. Structural defects may be determined in polyolefins by the degree of substituted alkanes produced by pyrolysis. Extraneous peaks are generally additives or contaminants in the polymer.

Instrumentation

A *CDS Analytical Model 2000 Pyroprobe* with a platinum coil interfaced to a Hewlett-Packard 5890 Gas Chromatograph were used for pyrolysis. The GC column was a 30 m by 0.53 mm SE54. The GC temperature program was: start 40 C, hold 6 minutes, then ramp at 6 C/min to 300 C. The carrier flow was 8 ml/min helium. The interface of the Pyroprobe was held at 280 C. The samples were placed in a quartz tube, inserted into the platinum coil of the pyroprobe, placed in the interface, and pyrolyzed at a temperature of 850 C for 10 seconds. The heating ramp rate was 20 C/Msec.

FOR MORE INFORMATION CONCERNING THIS APPLICATION, WE RECOMMEND THE FOLLOWING READING:

Degradation Mechanisms-Random Scission. CDS Solutions.

Levy, E.J. and T.P. Wampler. *Effects of Slow Heating Rates on Products of Polyethylene Pyrolysis.* Analyst, Vol III, (1986) 1065-1067.

K.V. Alekseeva. *Gas Chromatic Identification of Polymers Using Individual Pyrolysis Products.* J. anal. App. Pyrolysis, 2 (1980) 19-34.

J.W. Washall and T.P. Wampler. *Analytical Pyrolysis of Complex Muticomponent Samples.* J. Chromatogr. Sci., 27 (1989) 144-148.

Additional literature on this and related applications may be obtained by contacting your local CDS representative, or directly from CDS at the address below.

Produced by M.J. Matheson 993.

ABOUT CDS

CDS Analytical, Inc. is a leader in the design and manufacture of laboratory instruments for sample preparation and analysis. With 25 years experience in the field, CDS is dedicated to providing the best possible instruments for both research and routine analysis. Well known in the field of analytical pyrolysis, CDS manufactures the Pyroprobe 1000 and 2000 for the introduction and analysis of solid materials by GC, MS and FT-IR. CDS offers a complete line of purge and trap instruments for the analysis of volatile organic compounds in the environmental, food and pharmaceutical areas, as well as custom systems for complex, multicomponent materials investigation. Our customers, their requirements and applications are important to us. To help meet their needs, we offer a wide range of analytical information and the services of our applications laboratory. If you would like additional information, please contact us at the address below, or call us at 1 800 541 6593.

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