

Application Note

Pyrolysis- Theory

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Pyrolysis has been utilized as a sample introduction technique for gas chromatography for over four 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 polyisoprene 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.

Equipment:
PYROLYSIS

Pyrolysis: 700°C for 10 seconds
Interface: 275°C
Cryogenic collection: -100°C for 10 minutes
Revaporization: 275°C for 10 minutes

GAS CHROMATOGRAPHY

Varian 3700 equipped with flame ionization detector
Column: 50m x 0.25mm SE-54 Capillary
Initial temperature: 50°C for 2 minutes
Program rate: 7°C/minute to 290°C

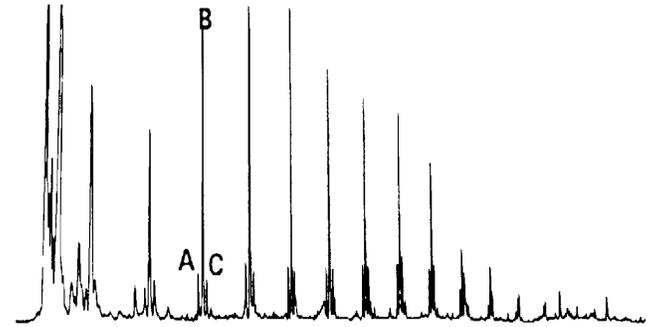


Figure 1

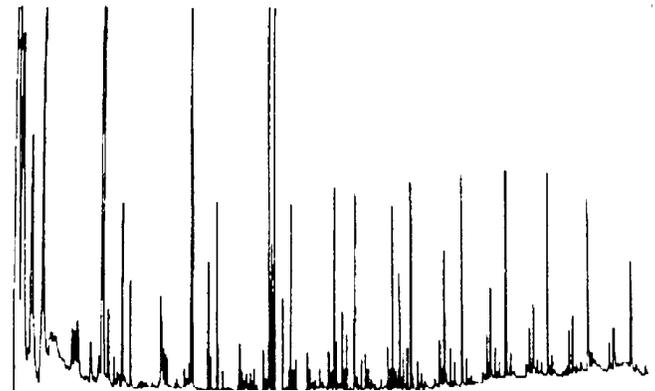


Figure 2

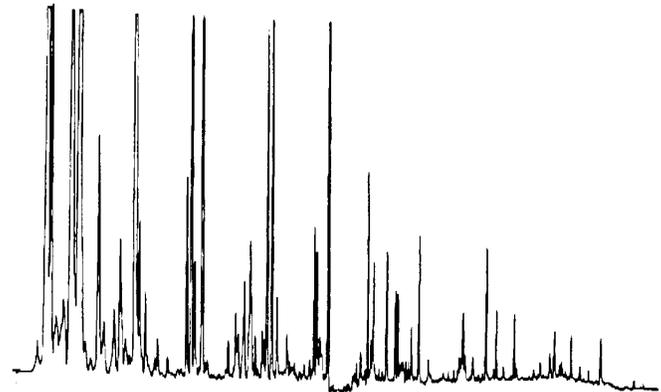


Figure 3

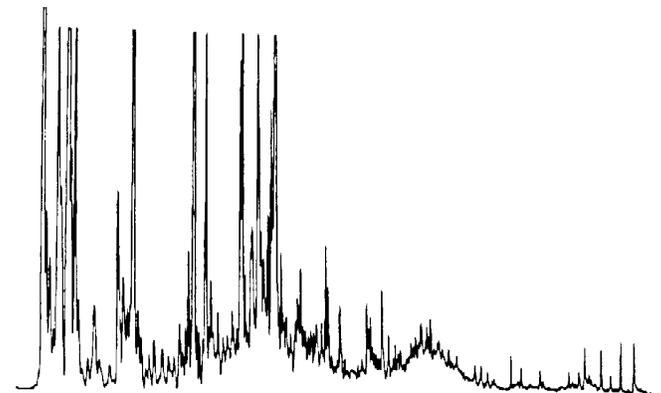


Figure 4

For more information on this and related applications, we recommend the following readings:

T. Wampler, and E. Levy, "Cryogenic Focusing of Pyrolysis Products for Direct (Splitless) Capillary Gas Chromatography," *JAAP*, 8, (1985), 65-72.

T. Wampler, and E. Levy, "Effects of Slow Heating Rates on Products of Polyethylene Pyrolysis," *Analyst*, 111, (1986), 1065-1067.

Y. Sugimura, T. Nagaya, S. Tsuge, and T. Murata, "Micro structural Characterization of Polypropylenes by High Resolution Pyrolysis-Hydrogenation Glass Capillary Chromatography," *Macromol.*, 1980, 13, 928.