

A Comparison of Polyolefins by Pyrolysis GC

Application Note

Pyrolysis Theory- Polyolefins

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Pyrolysis gas chromatography is a simple technique which has been utilized by scientists for almost three decades. The process of pyrolysis involves the liberation of organic material from a relatively nonvolatile matrix. Natural and synthetic polymers can be fragmented to form smaller, more volatile compounds which can be analyzed by capillary gas chromatography. Polymer samples can be pyrolyzed as solids in a quartz tube, or as polymer solutions dissolved in a solvent and deposited on a ribbon as a thin film.

Polyolefins are essentially very high molecular weight hydrocarbons. Upon pyrolysis, smaller hydrocarbons are produced which are characteristic of the polyolefin composition. Polyolefins undergo a process of random scission producing olefins, alkanes and diolefinic compounds. The presence of isoalkanes indicates branching in the polymer chain. The product distribution in pyrolysis is dependent on the pyrolysis temperature. Pyrolyzing polyolefins at higher temperatures will cause an increase in the abundance of pyrolysates at the earlier retention regions due to increased fragmentation.

Pyrolysis of polyethylene produces primarily straight chain alkanes and alkenes. The nature of the polyethylene chain produces oligomeric groups of pyrolysis fragments differing from each other by one carbon unit. This pattern is predictable and reproducible for polyethylene. Polypropylene (Figure 2), when pyrolyzed, produces fragments which are more highly substituted. The oligomeric groups in polypropylene pyrolysis vary by three carbon units. Structural defects may be determined in polyolefins by the degree of substituted alkanes produced by pyrolysis. Polyisobutylene and polytransisoprene (Figures 3 and 4), give more complex chromatograms due to the increased substitution of the polymer backbone. Polyisobutylene 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 polytransisoprene are isoprene monomer and dipentene. Pyrolysis can thus be used in a qualitative manner to identify polymers, but also in a quantitative sense in the analysis of copolymer blends.

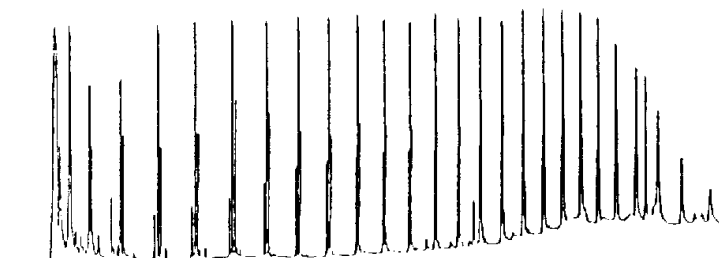


Figure 1. Polyethylene

Instrument Conditions
Pyroprobe

Pyrolysis: 750°C
Interface: 285°C

GC-FID

Column: 50 x 0.25mm SE-54
Injector: 300°C
Oven: 50°C for 3 minutes
then 8°C/min to 285°C

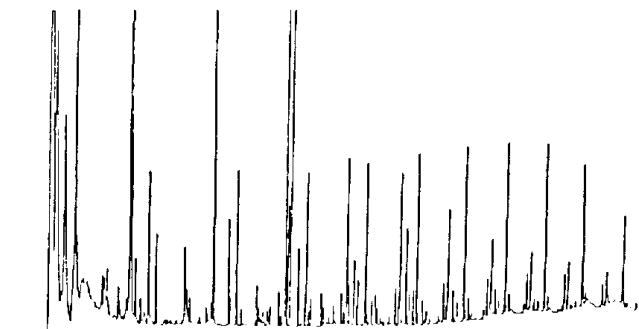


Figure 2. Polypropylene

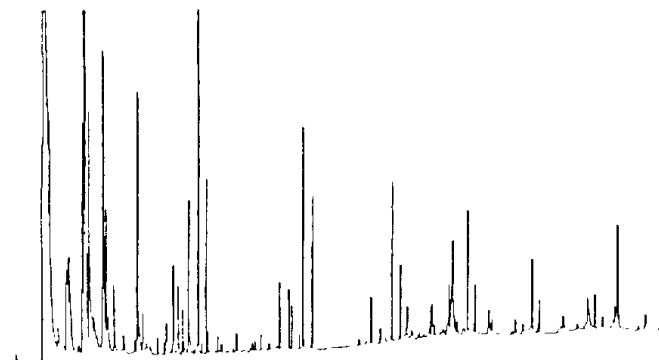


Figure 3. Polyisobutylene

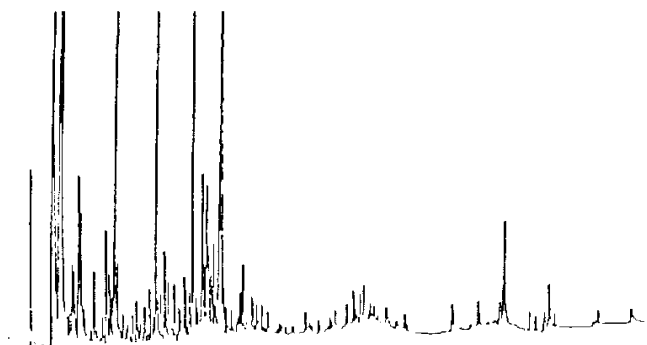


Figure 4. Poly(trans)isoprene

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

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

Nagaya, T. et al. "Microstructural Characterization of Polypropylenes by High Resolution Pyrolysis-Hydrogenation glass capillary gas chromatography." *Macromolecules*, Vol. 13, (1980).