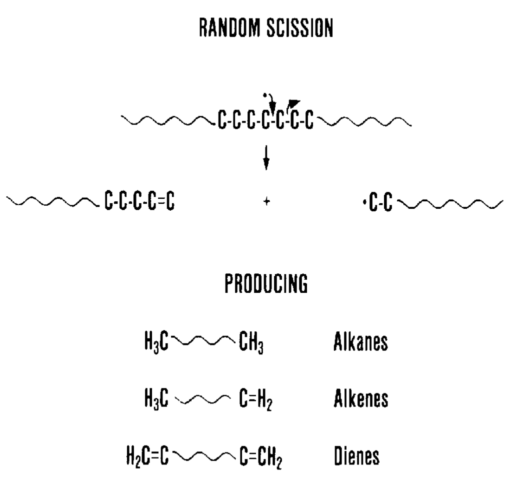
Degradation Mechanisms - Random Scission

Application Note

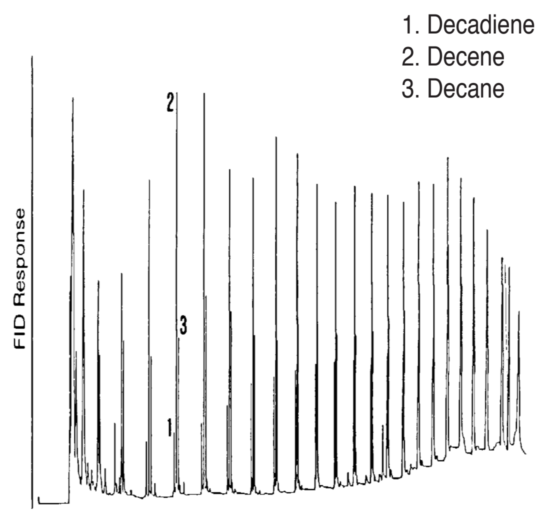
Theory

During pyrolysis, polymeric materials may degrade via a number of mechanisms which are generally grouped into three classes - random scission, depolymerization, and side group elimination. Random scission results from the production of free radicals along the backbone of the polymer which causes the macromolecule to be frag mented into smaller molecules of varying chain lengths. These fragments chromatograph to reveal a repeating series of olig omers frequently differing in chain length by the number of carbons in the original monomer.

The polyolefins generally degrade through a random scission mechanism, and polyethylene is a good example of this behavior. When a free radical is formed along the chain of polyethylene, chain scission occurs, producing a molecule with an unsaturated end and another with a terminal free radical. This free radical may take a hydrogen from a neighboring carbon, producing a saturated end and a new radical, or combine with another free radical to form an alkane. Multiple cleavages produce molecules small enough to be volatile, with double bonds at both ends, one end or neither. Since the scission was random, molecules are made with a wide variety of chain lengths. These appear in the pyrogram as a series of triplet peaks. Each triplet consists of an alkane, an alkene and a diene of a specific chain length. The hydrocarbons in each triplet have one more carbon than the molecules in the triplet which eluted just prior to it. The accompanying chromatogram resulted from the pyrolysis of polyethylene at 750°C showing oligomers containing up to 30 carbons, with the C10 fragments marked.



Degredation Mechanism, Random Scission



Pyrolysis of Polyethylene, 750°C for 10 seconds

CDS Pyrolyzer Conditions:

Pyroprobe Temperature:	750°C for 10 seconds
Interface Temperature:	280°C

GC Conditions:

Column:	25m x 0.25mm fused silica capillary SE-54
Detector:	Flame ionization
Initial temperature:	50° C for 2 minutes
Rate:	8°C/min
Final temperature:	300° C for 10 minutes
Split ratio:	75:1
Carrier gas:	Helium

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

Irwin, William J. Analytical Pyrolysis: A Comprehensive Guide. Marcel Dekker, publisher.

Levy, E. J. and S. A. Liebman. Pyrolysis and GC in Polymer Analysis. Marcel Dekker, publisher.

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