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CDS Solutions

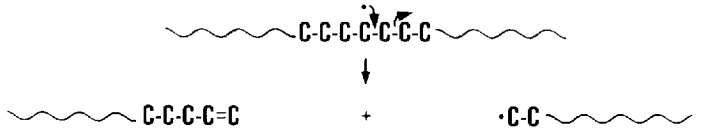
APPLICATIONS INFORMATION USING ADVANCED GC SAMPLE HANDLING TECHNOLOGY

# DEGRADATION MECHANISMS - RANDOM SCISSION

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 fragmented into smaller molecules of varying chain lengths. These fragments chromatograph to reveal a repeating series of oligomers 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

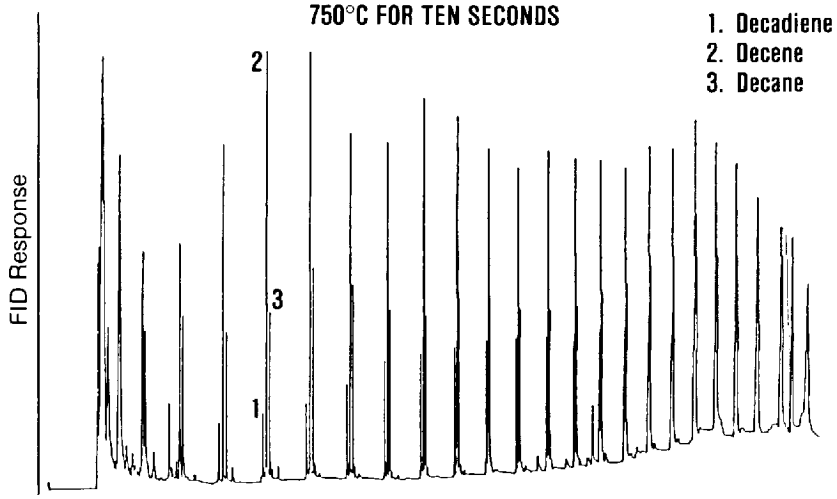
**RANDOM SCISSION**




**PRODUCING**

| | |
|---|---|
| $H_3C$ ~~~ $CH_3$ | Alkanes |
| $H_3C$ ~~~ $C=H_2$ | Alkenes |
| $H_2C=C$ ~~~ $C=CH_2$ | Dienes |

**PYROLYSIS OF POLYETHYLENE**
**750°C FOR TEN SECONDS**



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 $C_{10}$ fragments marked.

## EQUIPMENT

PYROLYSIS
- CDS Model 120 Pyroprobe, coil probe with quartz tube
- Temperature: 750° C for ten seconds
- Interface temperature: 280° C

GAS CHROMATOGRAPHY
- 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
- Chart speed: 1 cm/min
- 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. III, (1986), pp. 1065-1067.

Additional literature may be obtained from your Chemical Data Systems representative, or by writing to the CDS Applications Lab.

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