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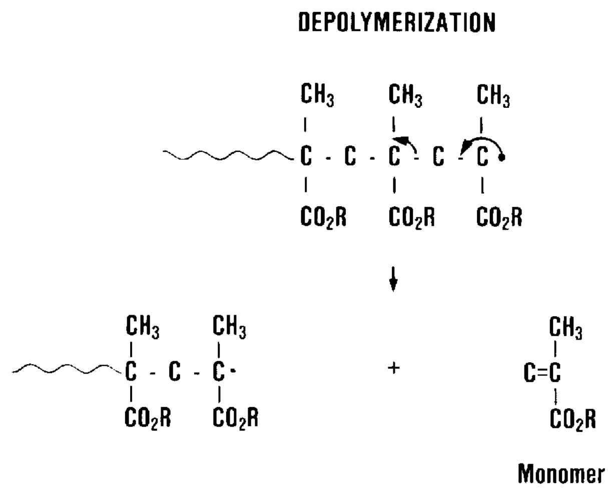
CDS Solutions

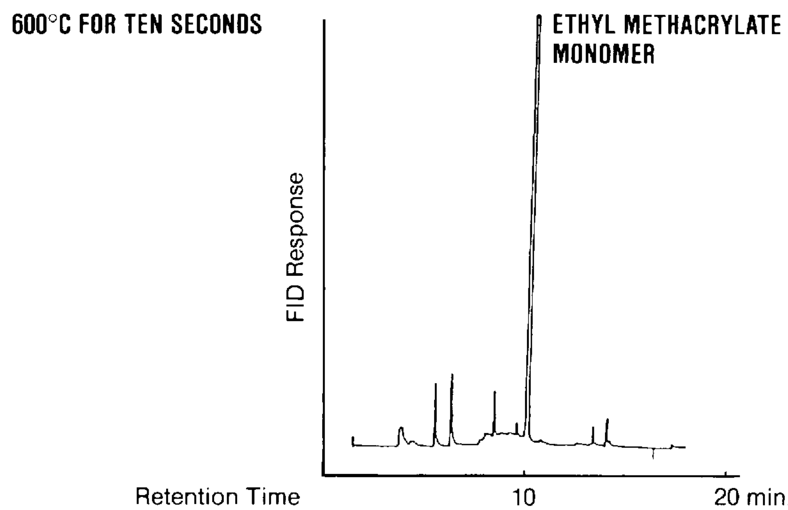
APPLICATIONS INFORMATION USING ADVANCED GC SAMPLE HANDLING TECHNOLOGY

DEGRADATION MECHANISMS - DEPOLYMERIZATION

When heated, polymers generally undergo thermal degradation in one of three basic mechanisms - depolymerization, side group elimination, or random scission. Depolymerization is a free radical mechanism in which the polymer essentially reverts to a monomer or monomers. Unlike random scission, which produces fragments of a variety of chain lengths, depolymerization generates a simple chromatogram consisting of large peaks for the monomers from which the polymer or copolymer was produced.



Several polymers degrade primarily by a free radical depolymerization, including polystyrene and polymethacrylates. When a free radical is produced in the backbone of polyethyl methacrylate, for example, the molecule undergoes scission to produce an unsaturated small molecule (ethyl methacrylate) and another terminal free radical. This radical will also cleave to form ethyl methacrylate and propagate the free radical. The net effect is often referred to as "unzipping" the polymer. The accompanying chromatogram shows the extent to which polyethyl methacrylate unzips when heated to 600°C for ten seconds. Copolymers of two or more methacrylate monomers will undergo the same degradation mechanism, producing a peak for each of the monomers used in the original polymerization.



EQUIPMENT

PYROLYSIS

CDS Model 120 Pyroprobe, coil probe with quartz tube
Temperature: 600°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: 1cm/min
Split ratio: 75:1
Carrier gas: Helium

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

Becker, W. and S. Paul. "Pyrolysis Gas Chromatography in the Analysis of Methyl Methacrylate (MMA) and Ethyl Acrylate (EA) Copolymers." *Journal of Coatings Technology,* Vol. 52, #661, (1980), pp. 47-55.

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.

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

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