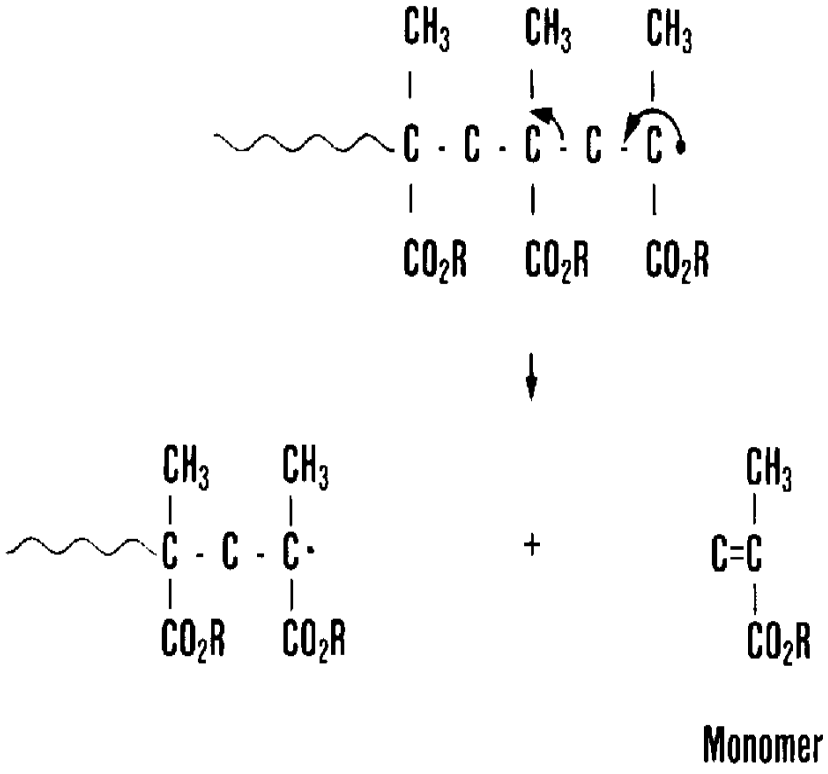
Degredation Mechanisms
Depolymerization

Application Note

Pyrolysis Theory

When heated, polymers generally undergo thermal degradation in one of three basic mechanisms - depolymerization, side group elimination, or ran dom 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.



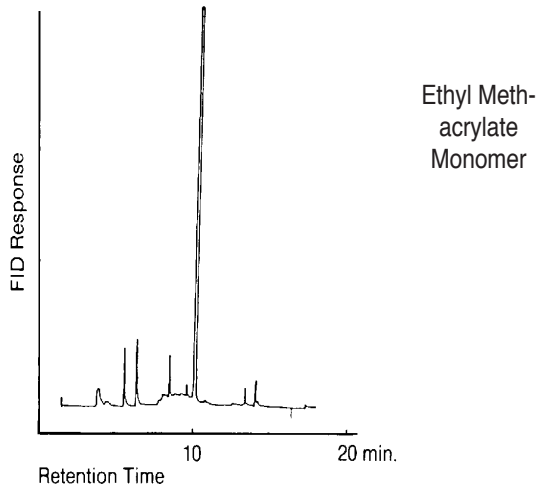
Degredation Mechanism, Depolymerization

CDS Pyroprobe Conditions:

Pyroprobe Temperature:	600°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



Pyrolysis of Polyethyl Methacrylate, 600°C for 10 seconds

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) Co-polymers.” Journal of Coat ings 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.