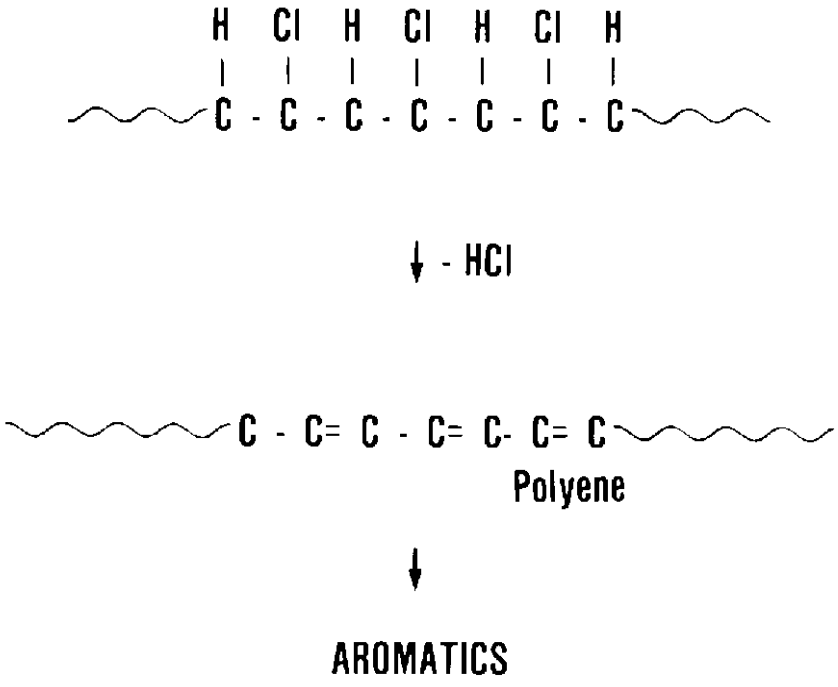
Degredation Mechanisms
Side Group Elimination

Application Note

Pyrolysis Theory

When heated to the point of bond dissociation, polymers generally degrade in one of three major pathways - random scission, side group elimination or depolymerization. Side group elimination is usually a two stage process in which the polymer chain is first stripped of atoms or molecules attached to the backbone of the polymer, leaving an unsaturated chain. This polyene then undergoes further reactions, including scission, aromatization and char formation.

A good example of a material which pyrolyzes in this way is polyvinylchloride. PVC first undergoes a loss of HCl to form a conjugated polyene backbone. This unsaturated chain is further degraded, mostly to form aromatics, as well as some smaller, unsaturated hydrocarbon fragments. As is shown in the accompanying figure, the principle pyrolysis products produced from PVC (in addition to HCl) are benzene, toluene and napthalene. Small amounts of chlorinated aromatics may also be produced, which indicate that some chlorines are still attached to the polymer chain during aromatization. This results from defects in the PVC which placed two chlorine atoms either on the same carbon or on neighboring carbons, so that one remained after HCl was eliminated from the original polymer.



Degredation Mechanism, Side Group Elimination

CDS Pyrolyzer Conditions:

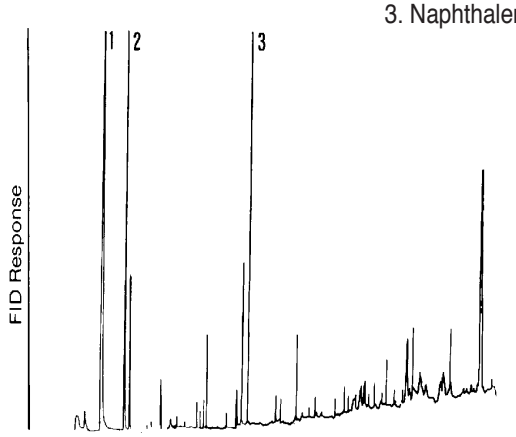
Pyroprobe
Temperature: 600°C for 10 seconds

Interface
Temperature: 280°C

GC Conditions:

Column: 25m x 0.25mm fused silica cap illary 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

1. Benzene
2. Toluene
3. Naphthalene



Pyrolysis of Polyvinyl Chloride, 600°C for 10 seconds

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

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

Kroenke, W. J. and R. P. Lattimer. "The Formation of Volatile Pyrolyzates from Poly(vinyl chloride) ." Journal of Applied Polymer Science, Vol. 25, (1980), pp. 101-110.

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