



Thermal Degradation of Polymers in Air

Application Note

Pyrolysis in reactant gas

True pyrolysis is the thermal degradation of a substance in an inert atmosphere so that the resulting pyrolysates may be studied, and related to the original sample. Natural and synthetic polymers are routinely studied in this way, and the pyrolysates analyzed by GC, GCMS, MS, FTIR, or other analytical processes in an effort to understand the structure and nature of the original macromolecule. Monomer composition, branching, defect structures, and batch variations are polymers which have been studied using this technique.

It is sometimes of more interest to study what happens to a polymer when it is heated in a reactive atmosphere, such as air. The degradation mechanisms experienced in the presence of oxygen may be quite different from those in helium. These differences are especially important in combustion studies, toxicity studies, and in evaluating the atmospheric stability of a material. Most pyrolysis systems involve a pyrolyzer mounted in the carrier gas stream of the gas chromatograph, which makes oxidative studies impossible. In order to produce decomposition products in air or oxygen, and still analyze them in an inert carrier, an instrument is needed which permits gas stream switching and removal of the pyrolysis chamber from the analytical stream.

The two chromatograms shown here were produced using the Pyroprobe. The purge gas for the Pyroprobe is separate from the carrier for the gas chromatograph, so that two different gases may be used. The pyrolysates are collected onto a trap first, which retains the organic volatiles and vents the carrier. This trap is then flushed with GC carrier and heated to desorb the collected organics when the GC program is begun.

The first chromatogram shows the pyrolysates of polyethylene which was pyrolyzed in helium at 800° C. The peaks are all normal hydrocarbons and each triplet contains an alkadiene, an alkene and an alkane in that order. Each triplet has one more carbon in the chain than the triplet which eluted just prior to it. When the pyrolysis atmosphere contains oxygen, additional compounds are produced. The second chromatogram resulted from heating polyethylene in air. Each group of peaks still contains the three hydrocarbons seen before, but two additional peaks are also present just after the alkane, including the largest peak in the group. These peaks are the straight chain alcohol and aldehyde resulting from the oxidative degradation of the polymer. The relative abundance of the pyrolysis compounds and the oxidative compounds depends on the temperature and the rate of heating.

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

Instrument Conditions

Pyroprobe

Pyrolysis: 800°C 10 seconds

Trap: Tenax at 35°C

Trap Desorb: 280°C for 5 minutes

GC- FID

Column: 50m x 0.25mm SE-54

Program: 50°C for 2min

8°C/min to 290°C

Inlet: 300°C, 60:1 Split

J. Chien, and J. Kiang, "Oxidative Pyrolysis of Poly(propylene)," Makromol. Chem. 181 47-57, (1980).

T. Wampler and E. Levy, "Effects of Slow Heating Rates on Products of Polyethylene Pyrolysis," Analyst, Vol. 111 1065-1067 (1986).

T. Wampler and E. Levy, "Effect of Heating Rate on Oxidative Degradation of Polymeric Materials," J. Anal. Appl. Pyrol. 8, 153-161 (1985).

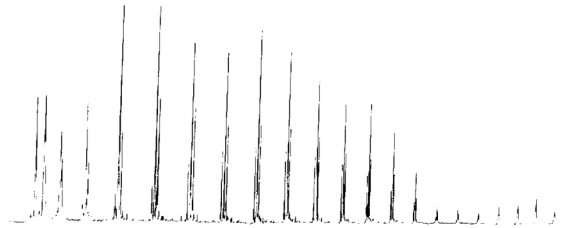


Figure 1: Polyethylene 800°C for 20 seconds

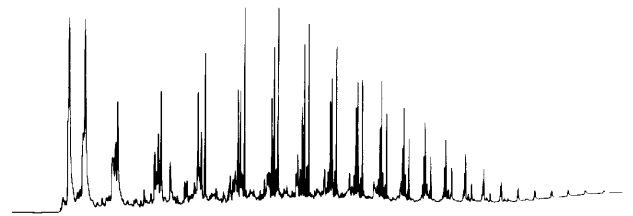


Figure 2: Polyethylene 10 seconds in air