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CDS Solutions

APPLICATIONS INFORMATION USING ADVANCED GC SAMPLE HANDLING TECHNOLOGY

Thermal Degradation of Polymers in Air

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 just a few of the properties of 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

Figure 1

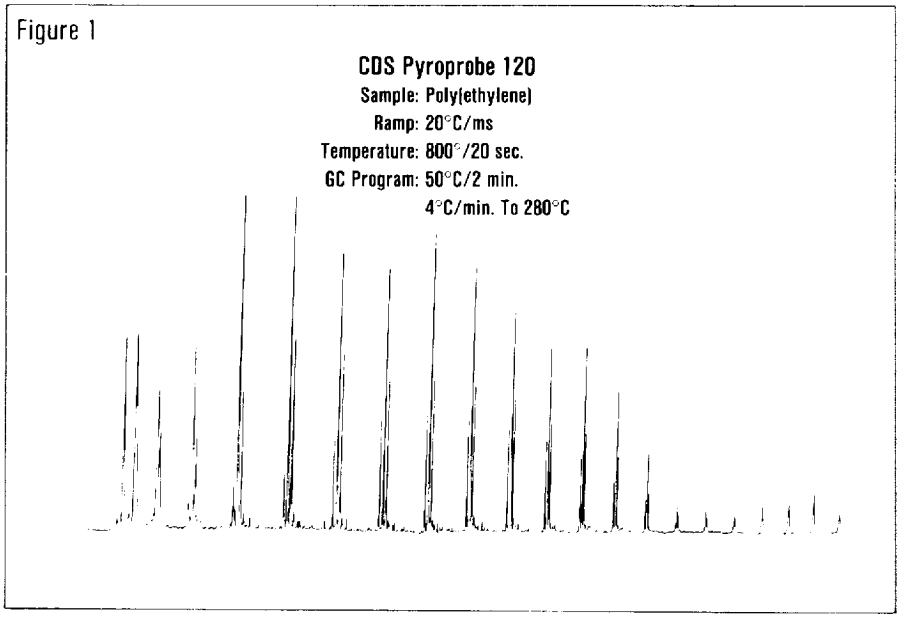
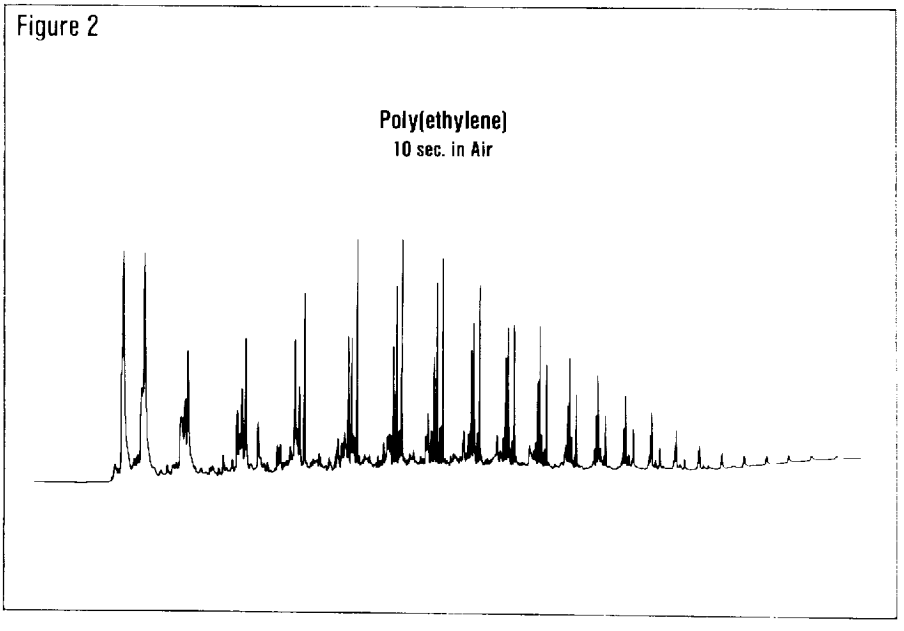


Figure 2



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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 Chemical Data Systems Pyroprobe 123, which combines a pyrolysis instrument with a sample concentrator. The carrier 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.

Equipment

PYROLYSIS
Pyroprobe 123, consisting of a Pyroprobe 122 and 320 Sample Concentrator
Pyrolysis temperature: 800° C for 10 seconds
Initial trap: Tenax at 35° C
Trap desorption: 280° C for 5 minutes

GAS CHROMATOGRAPH
Varian 3700 equipped with an FID
Column: 50m x 0.25mm SE-54 fused silica capillary
Program: 50° C for 2 min., then 8° C/min to 290° C
Split ratio: 60:1
Carrier: Helium

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

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).

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

ABOUT CDS

Chemical Data Systems (CDS), a subsidiary of Autoclave Engineers Inc., is a worldwide leader in the manufacture of instruments and equipment for research applications. With over 15 years of service to the research community, CDS is dedicated to the development of instrumentation for use in the preparation, separation and analysis of complex organics. We are also dedicated to providing researchers with the technical and applications information they need to perform their work efficiently. The purpose of CDSolutions is to supply the researcher with a constant stream of applications solutions for advanced GC sample handling. The article you just read is one of many available at no charge to our customers. For a complete list of topics, please write to our Technical Information Dept. in Oxford, Pennsylvania.

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