Pyrolysis of Synthetic Polymers Improved Sensitivity Using Cryogenic Focusing

Application Note
Pyrolysis and Cryofocusing

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Pyrolysis has been demonstrated to be a useful tool in the analysis of synthetic polymers, since it permits one to break down these large molecules and study the smaller fragments by gas chromatography. Considerable information may be obtained in this way concerning the basic structure of the polymer, as well as polymer defects, variations and degradation mechanisms. It is important for reproducible, quantitative results to use small samples, so that thermal gradients across the sample are minimized, but this may present a problem for some pyrolysis systems. Most pyrolysis is performed in a chamber located upstream from the injection port of the gas chromatograph, and the pyrolysates must be carried out of the pyrolysis chamber and into the GC. To compensate for the added volume and transfer effects, a high split ratio at the injector may be used, which moves the pyrolysates through the system and into the GC quickly, but then vents most of the analytes, requiring the use of a larger sample for analysis.

A Cryogenic Focuser provides a means of compensating for the system dead-volume while permitting analysis of very small samples. Inserted between the pyrolysis chamber and the gas chromatograph at the injection port, it permits on-column collection of the analytes prior to analysis. After pyrolysis, the volatiles are collected onto the capillary column using liquid nitrogen, and then revaporized at the beginning of the GC run.

Figure 1 is a chromatogram of the pyrolysates of polyisobutylene which have been focused at -100°C, then chromatographed without splitting. Even though the sample was only 2 micrograms, there is excellent sensitivity. Of equal importance is the resolution at the front end of the chromatogram. Because the pyrolysates were concentrated onto the column itself, the peak shape for even the earliest eluters is greatly improved, providing information that is lost using other techniques. Figure 2, by comparison, shows a much larger sample which was pyrolyzed using a split capillary GC system with a split ratio of 60:1. Not only is a larger sample required, but the resolution at the beginning of the chromato gram is inadequate for the identification of all the peaks seen in Figure 1. Clearly then, the addition of cryogenic focusing greatly enhances both sensitivity and resolution in the analysis of polymers by pyrolysis GC.

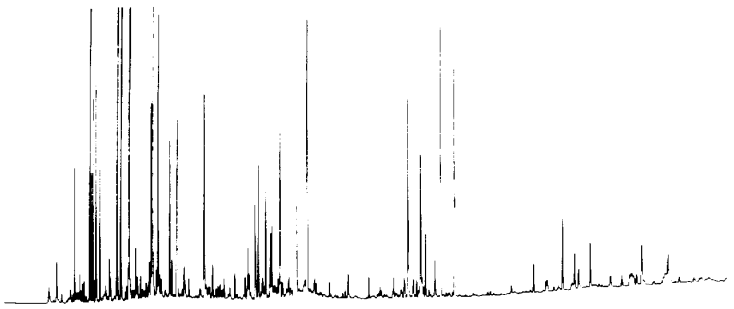

Figure 1. Pyrolysis of Poly(isobutylene) with On-column Cryofocusing

Instrument Conditions
Pyroprobe

Pyrolysis:	700°C for 10 seconds
Interface:	275°C
Cryo Collect	-100°C
Cryo Desorb:	280°C

GC-FID

Column:	50 x 0.25mm SE-54
Injector:	300°C
Carrier:	Helium
Oven:	50°C for 2 minutes then 7°C/min to 290°C

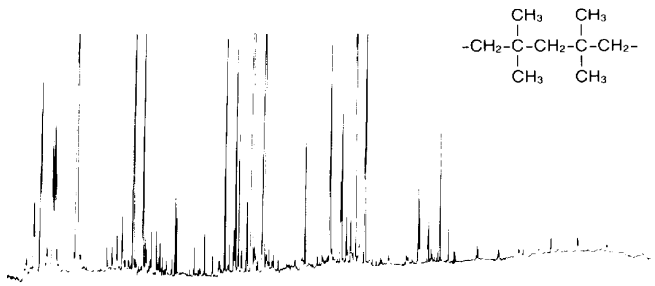

Figure 2. Pyrolysis of Poly(isobutylene)

FOR MORE INFORMATION
CONCERNING THIS APPLICATION, WE RECOMMEND THE
FOLLOWING READING

E. Levy, and T. Wampler, "Identification and Differentiation of Synthetic Polymers by Pyrolysis Gas Chromatography," J. Chem. Ed., 63, (1986), 64-68.

T. Wampler, and E. Levy, "Cryogenic Focusing of Pyrolysis Products for Direct (Splitless) Capillary Gas Chromatography," J.A.A.P., 8, (1985), 65-72.

T. Wampler, W. Bowe, J. Higgins, and E. Levy, "Systems Approach to Automatic Cryofocusing in Purge and Trap, Headspace, and Pyrolytic Analysis," American Lab., 1986, (August).