CDS ANALYTICAL PYROLYSIS LIBRARY

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INTRODUCTION

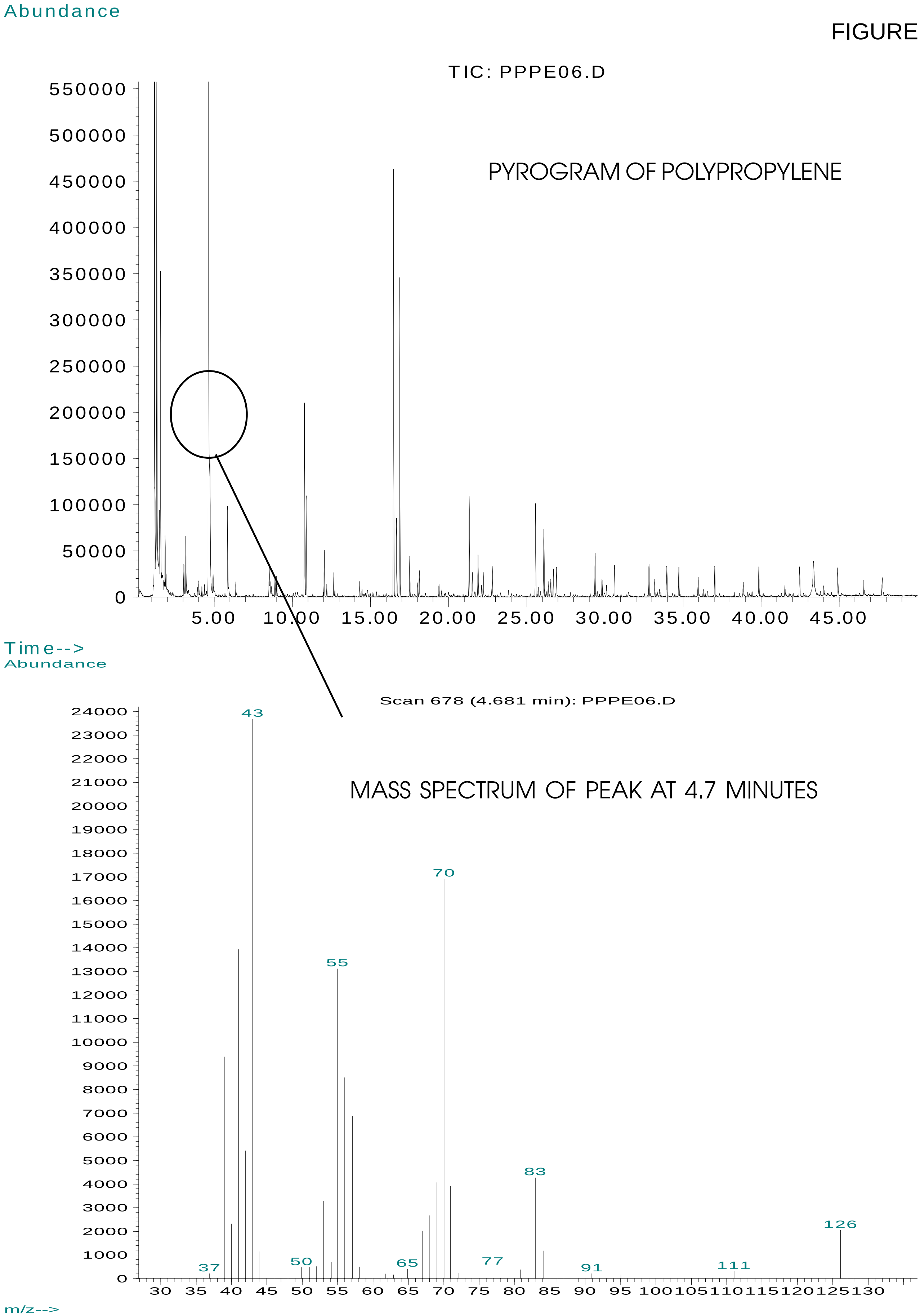
Analytical pyrolysis is the most direct way to use a gas chromatograph for the analysis and identification of polymers. Since polymer molecules in general are too large to be compatible with analysis by gas chromatography, pyrolysis is used to break these molecules into smaller pieces which are volatile enough to pass through the GC column. The mass spectrometer may then be used as in any analysis by GC-MS, to identify the individual peaks in the pyrogram, which are fragments and degradation products of the original macromolecule. Figure 1 shows a typical example of polymer analysis by Py-GC/MS, polypropylene at 750°C, with a spectrum of the peak at 5 minutes shown below it. Figure 2 shows the comparison of the mass spectrum from that peak to the library spectrum of 2, 4-dimethyl heptene, which is the trimer of propylene. Other polyolefins pyrolyze to produce pyrograms of fragment molecules, for example the normal hydrocarbons seen in a pyrogram of polyethylene, or a combination of normal and branched hydrocarbons seen in a copolymer of ethylene and propylene, shown in Figure 3.

The pattern of peaks created by the pyrolysis products of a polymer is frequently characteristic for that polymer in the same way that the pattern of mass fragments in a mass spectrum is characteristic of a specific molecule. It is therefore a logical extension of the process to try pattern recognition techniques to match unknown polymers to pyrograms of known materials and thereby identify the unknowns.

Unfortunately, the pattern of peaks in a chromatogram is more difficult to reproduce and recognize than the pattern in a mass spectrum, since the spacing along the x axis (time) is variable with column dimensions and pneumatic parameters. In addition, a reconstructed ion chromatogram consists of thousands of individual spectra, making it a very large data file, so storage of pyrograms for comparison rapidly uses disk space.

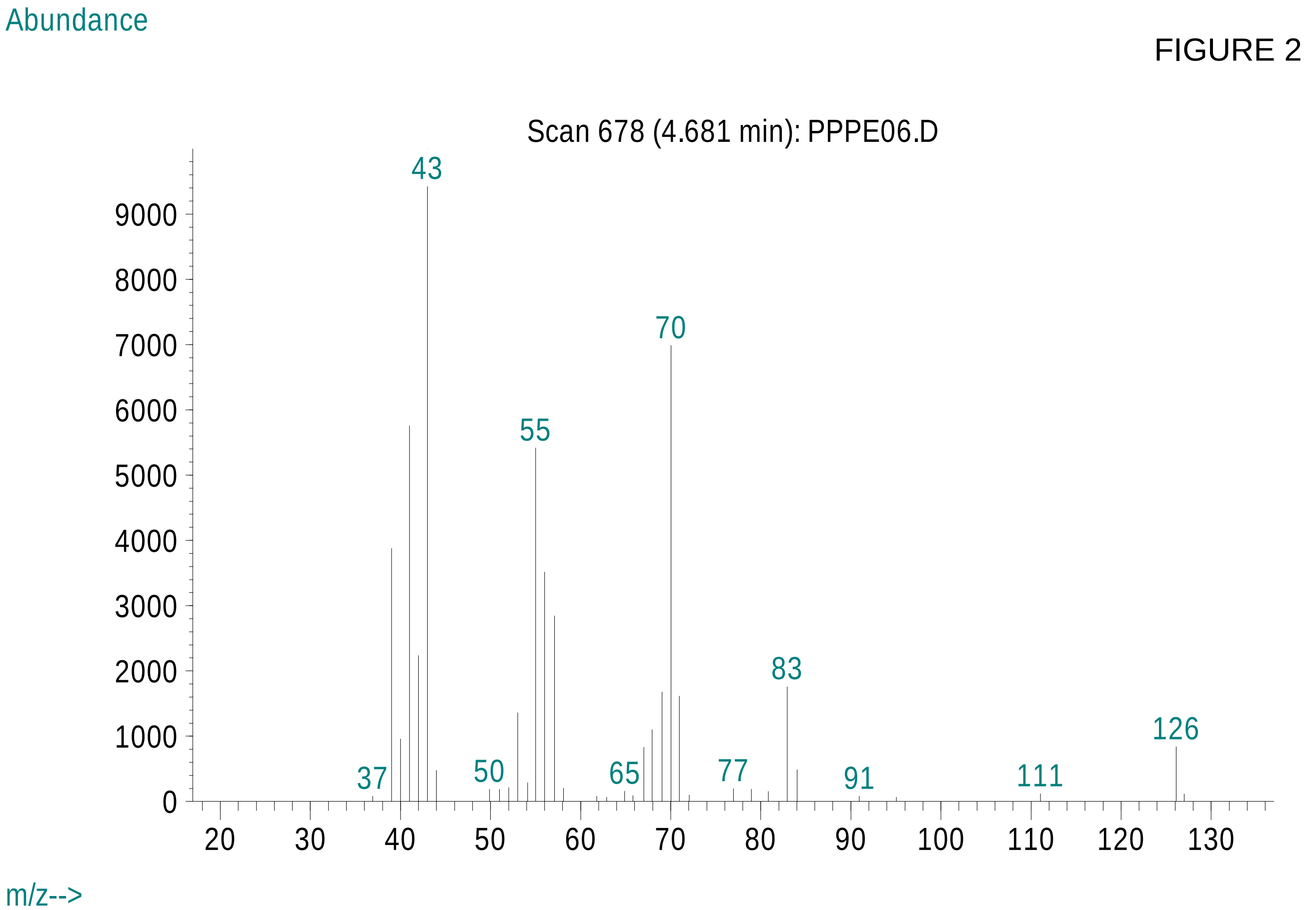
The data analysis software of the mass spectrometer permits averaging spectra under a peak, which produces a single spectrum representative of a section of the chromatogram. There is no limit on the amount of time which may be incorporated into this averaging, and, in fact, the entire chromatogram may be averaged and stored as a single spectrum, requiring only about 0.02% of the disk space needed to store the original chromatogram. This averaged spectrum for the pyrogram may be added to the mass spectrometer's library, or a new library of pyrolyzed polymer spectra created. The computer of the mass spectrometer can search and match these spectra to identify unknown polymers just as it does for the mass spectra of individual compounds. The averaged mass spectra for the pyrograms become a simulated pyrolysis-mass spectrum, independent of chromatographic conditions. The combination of the averaged mass spectra and the pyrogram tic provides a very powerful two-pronged technique for the analysis of polymeric systems, since it permits analysis of the individual peaks in the pyrogram using standard searching libraries while providing the chro-

FIGURE 1

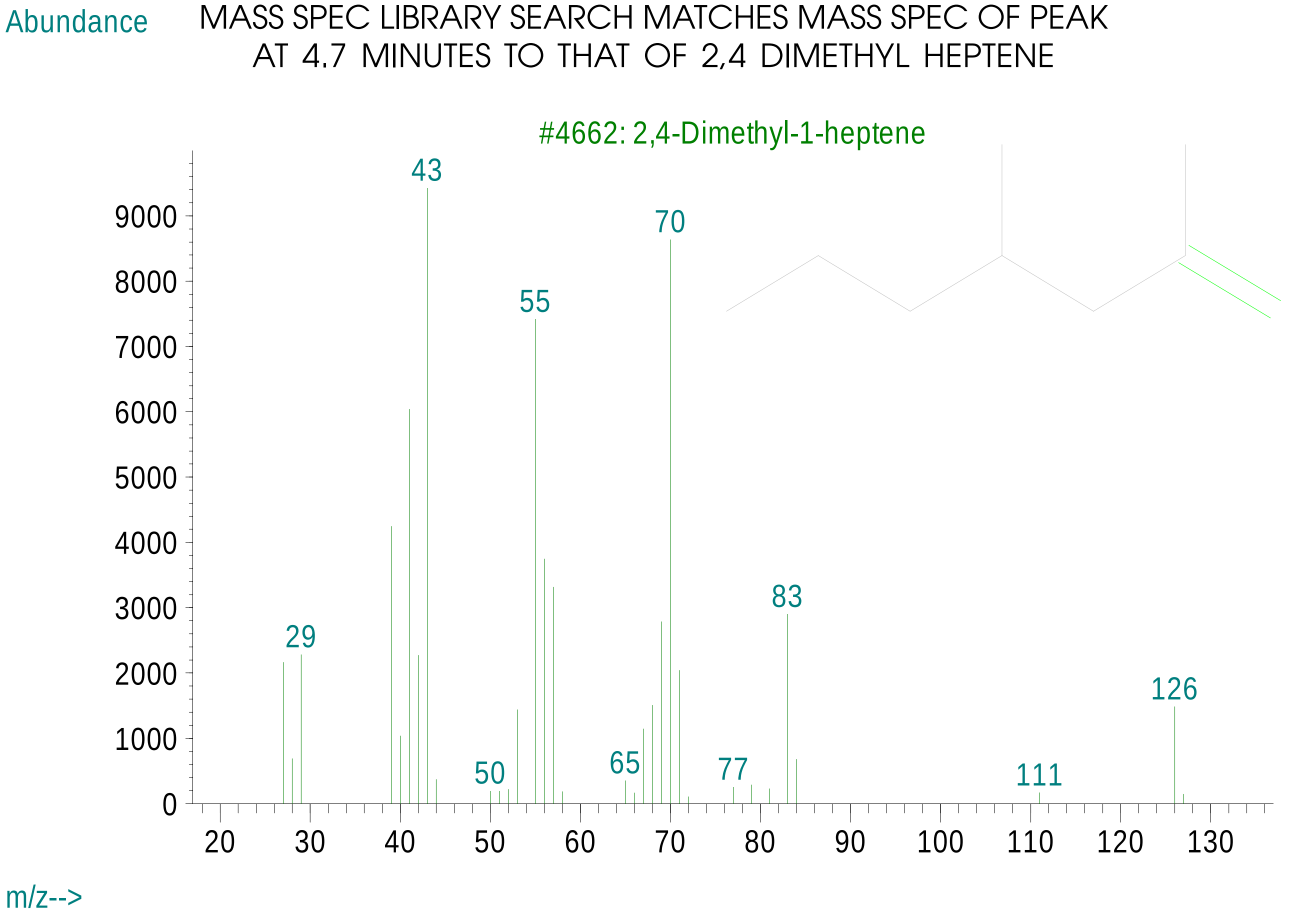


Abundance
TIC: PPPE06.D
PYROGRAM OF POLYPROPYLENE
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
5.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 45.00
Time-->
Abundance
Scan 678 (4.681 min): PPPE06.D
MASS SPECTRUM OF PEAK AT 4.7 MINUTES
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
43
70
55
83
126
37
50
65
77
91
111
30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130
m/z-->

FIGURE 2

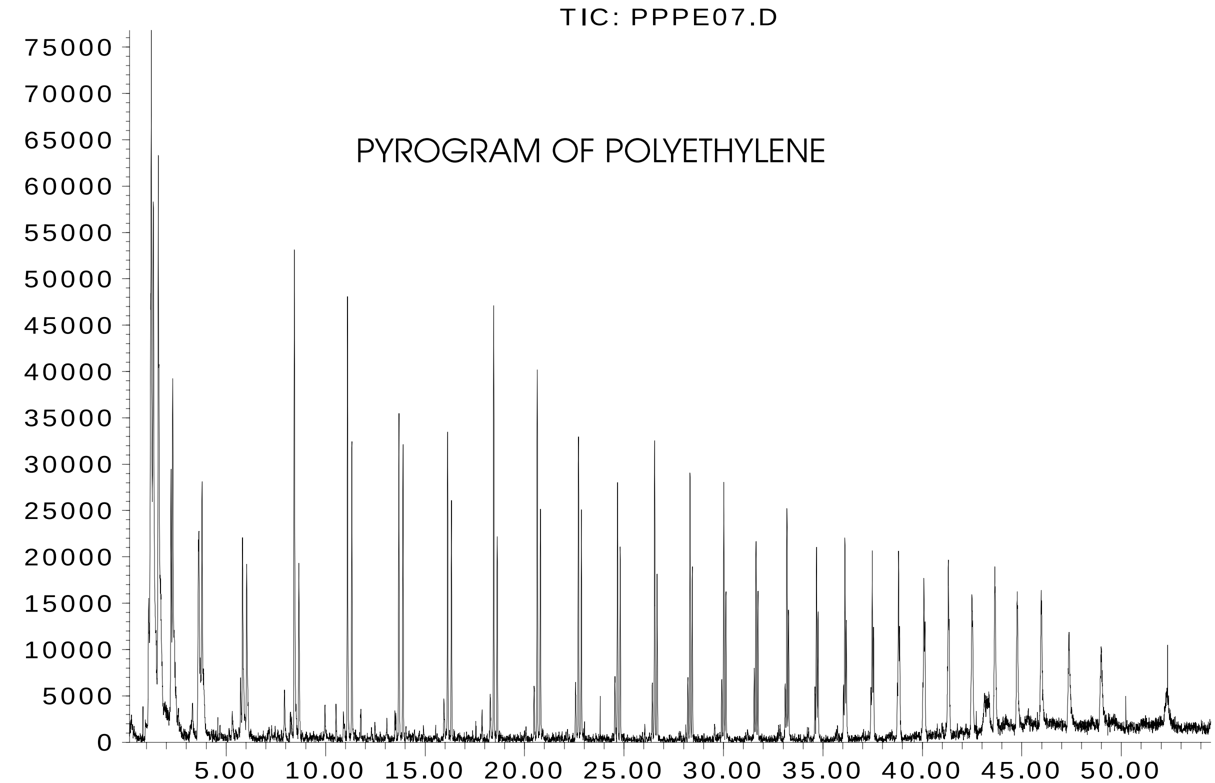


MASS SPEC LIBRARY SEARCH MATCHES MASS SPEC OF PEAK AT 4.7 MINUTES TO THAT OF 2,4 DIMETHYL HEPTENE

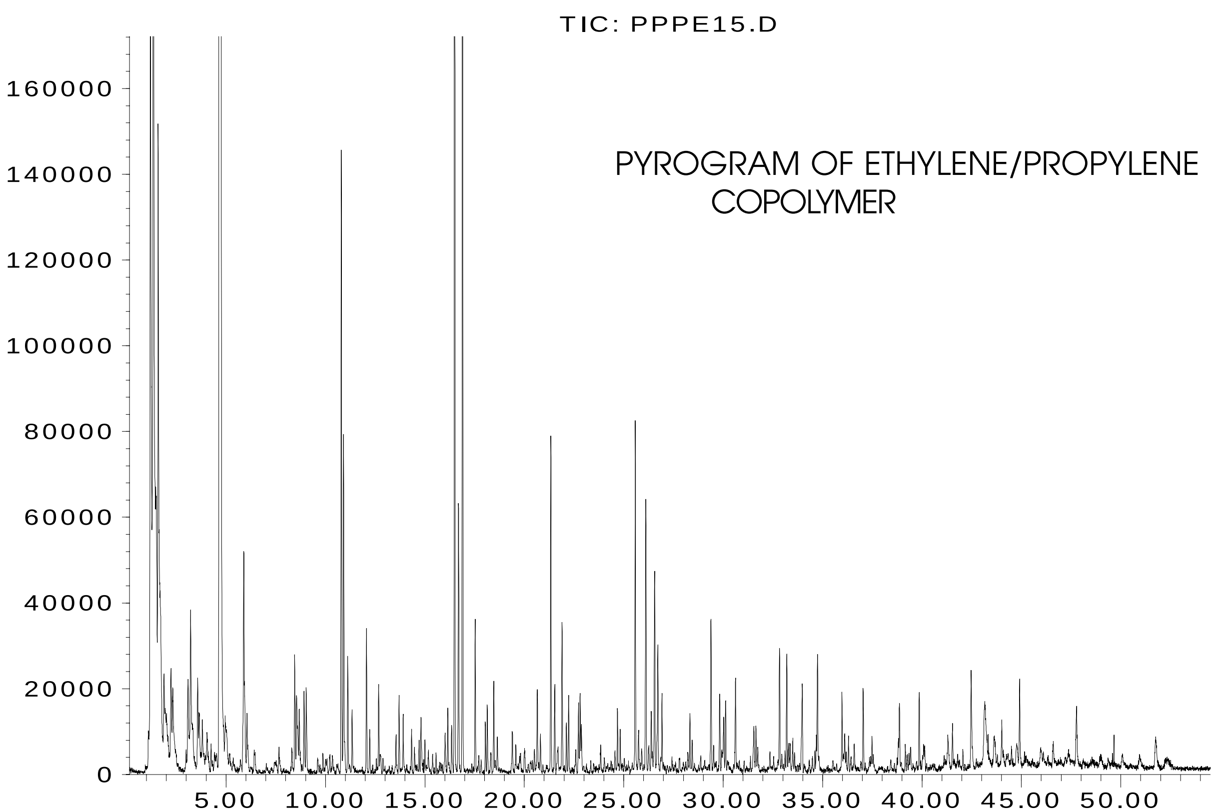


Abundance

FIGURE 3



Time-->
Abundance



Time-->

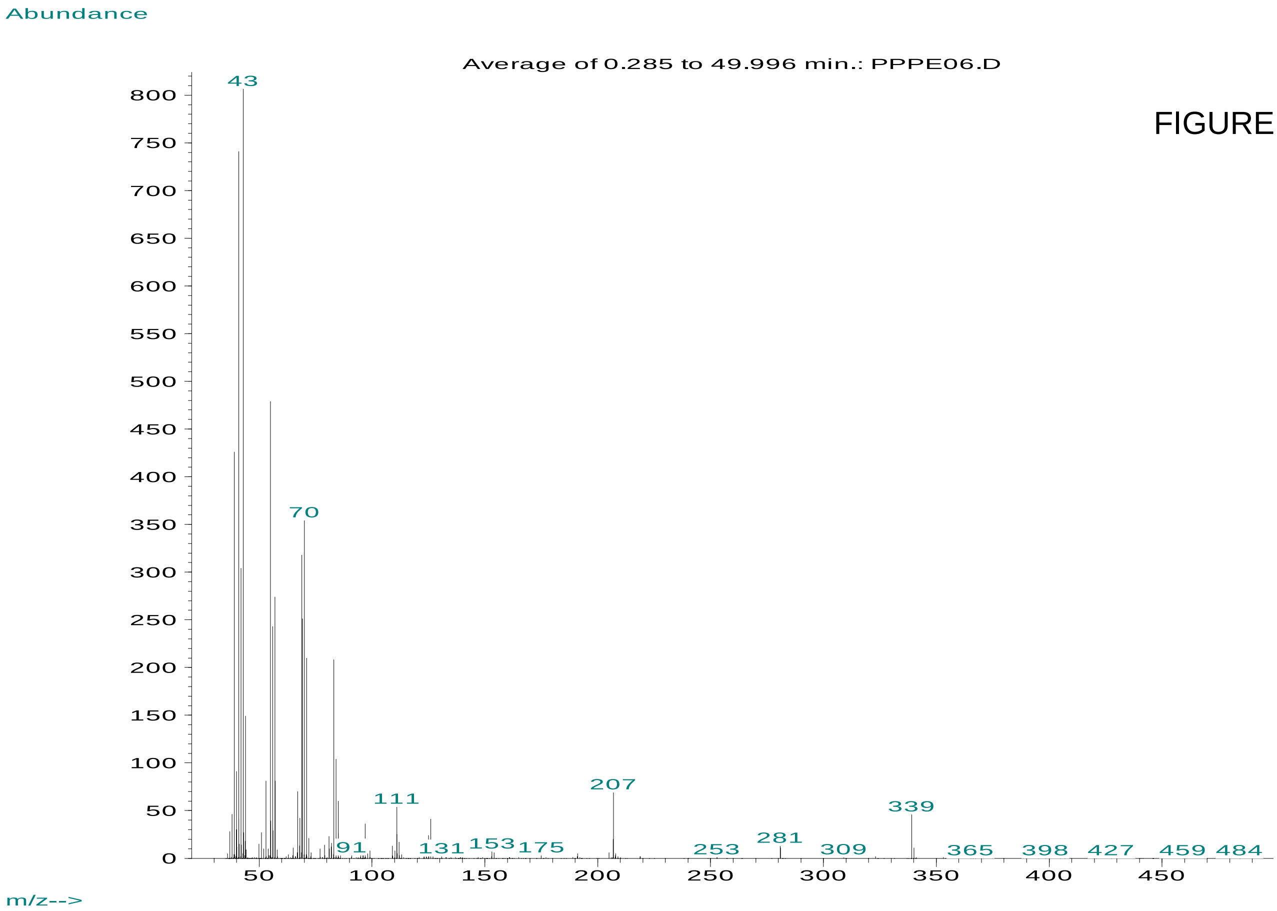


FIGURE 4

Instead of selecting one mass spectrum from the TIC, you can average the mass spectra from a peak, region, or the whole chromatogram. This is a single mass spectrum which averages all the data for the entire chromatogram obtained by pyrolyzing polypropylene. This single, average spectrum may be stored in a library and compared to other spectra, especially to spectra obtained for known materials.

matographic pattern characteristic of the polymer and also permits use of the existing computer searching techniques to be applied to the polymer as a whole.

Figure 4 shows an average spectrum for all the peaks in the pyrogram of polypropylene shown in Figure 1. If this spectrum is searched in a library of spectra produced for a variety of polymers, it is matched to the polypropylene spectrum. Another example is shown in Figure 5. At the top is the pyrogram of poly vinyl chloride, pyrolyzed at 750°. When pyrolyzed, PVC eliminates chlorine as HCl, then the carbon backbone cyclizes to generate aromatics. At the center of Figure 5 is the spectrum for the peak at 1.9 minutes, which identifies this peak as benzene. Other aromatics, including naphthalene, are present in the pyrogram, while the HCl is the first large peak to elute. The averaged mass spectrum for the whole pyrogram, shown at the bottom of Figure 5, includes significant peaks at 36, from the HCl, 78 from the benzene, as well as higher masses from larger aromatics.

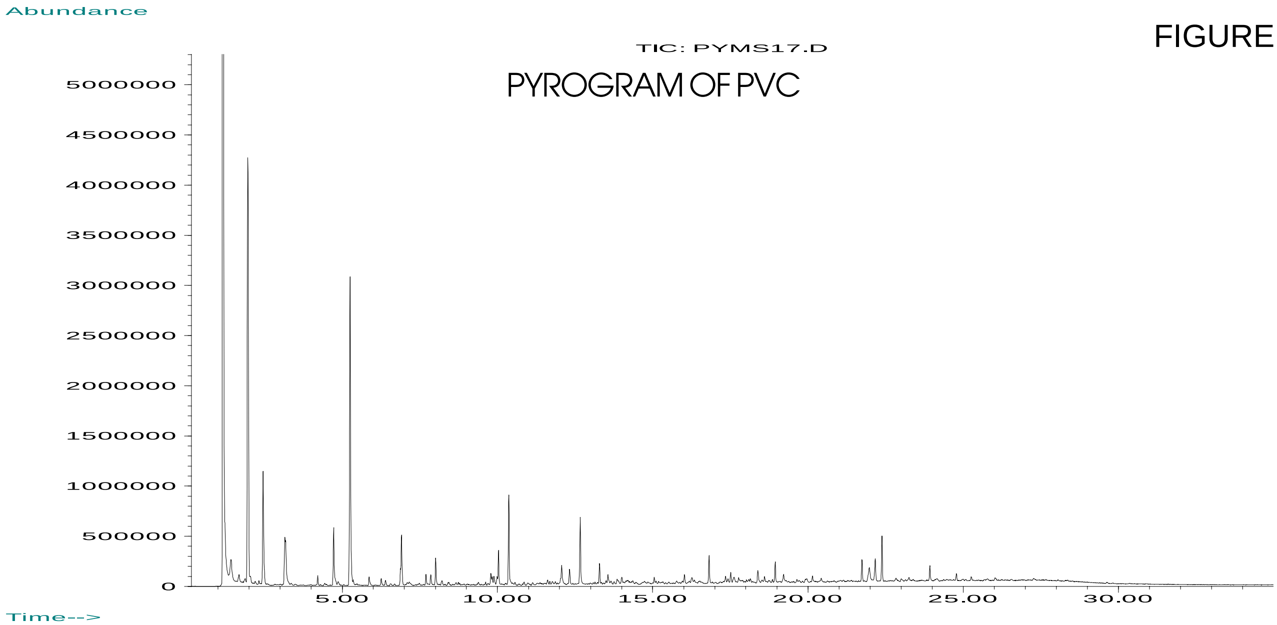
Just as the pyrograms of different polymers should be distinguishable, the averaged mass spectra from these pyrograms should be specific for each polymer. Figure 6 compares the averaged mass spectra for four different polymers - a polyolefin, an acrylic, a polyamide and a polyester - all clearly different. Within a group, different polymer formulations may be distinguished by pyrolysis-GC, and should still generate different averaged mass spectra. Averaged mass spectra for pyrograms of Nylon 6, 12, 6/6 and 6/12 are shown in Figure 7, revealing some similarities, as well as some significant differences.

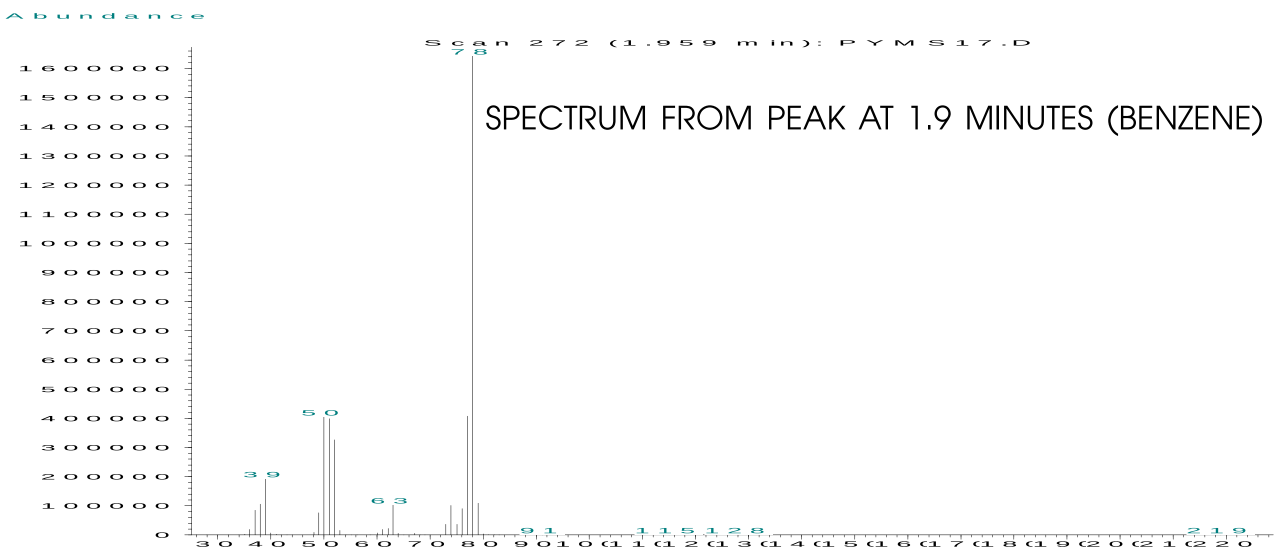
When applying this averaged spectrum concept to actual sample materials, the presence of non-polymeric materials, additives, contaminants and so on may introduce peaks in the pyrogram and in the mass spectrum prepared from it which could reduce the quality of matching with the library spectra. None-the-less, the results of the library search should at least give direction in the investigation of the unknown. In Figure 8, a pyrogram is presented which was obtained from colored carpet fibers. The pyrogram was averaged, then searched in the polymer library, and the best fit was for Nylon 6/6. This identification was subsequently confirmed by a comparison of the pyrogram of the carpet fibers to a pyrogram of Nylon 6/6 reference material.

Figure 9 shown a pyrogram for Tygon tubing, which includes peaks for HCl, benzene, naphthalene, and other aromatics, indicating PVC. In addition, there is a large peak at about 25 minutes not seen in PVC, which the mass spectrometer identifies as bis-2-ethylhexyl phthalate, a plasticizer. The averaged spectrum for the pyrogram up to 25 minutes (excluding the plasticizer) is recognized by the data system as PVC. If the total pyrogram is averaged, as shown in the center of Figure 9, it now contains a large peak at 149. This spectrum may be added to the library as PVC plus the plasticizer, and in future analyses, plasticized PVC can be identified for both the polymer and plasticizer used.

A final example is shown in Figure 10. This is a sample of clear plastic taken from a storage box made for computer disks. When pyrolyzed, it produced styrene monomer, dimer and

FIGURE 5


Abundance
TIC: PYMS17.D
PYROGRAM OF PVC
Time-->


Abundance
Scan 272 (1.959 min): PYMS17.D
SPECTRUM FROM PEAK AT 1.9 MINUTES (BENZENE)

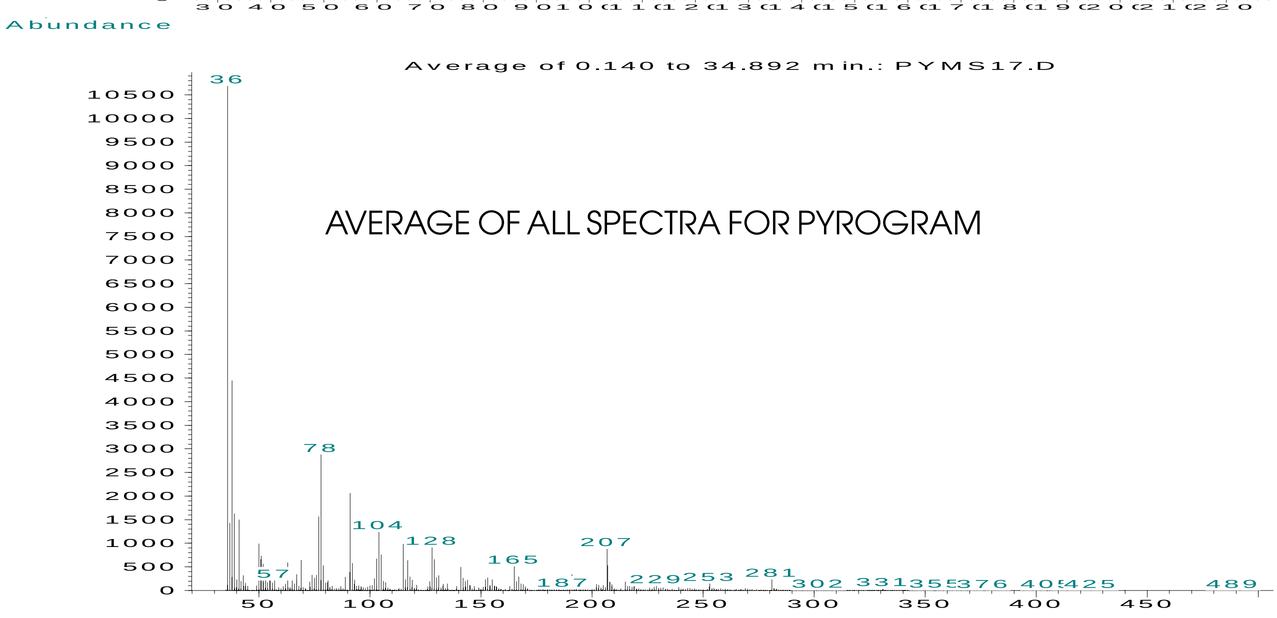
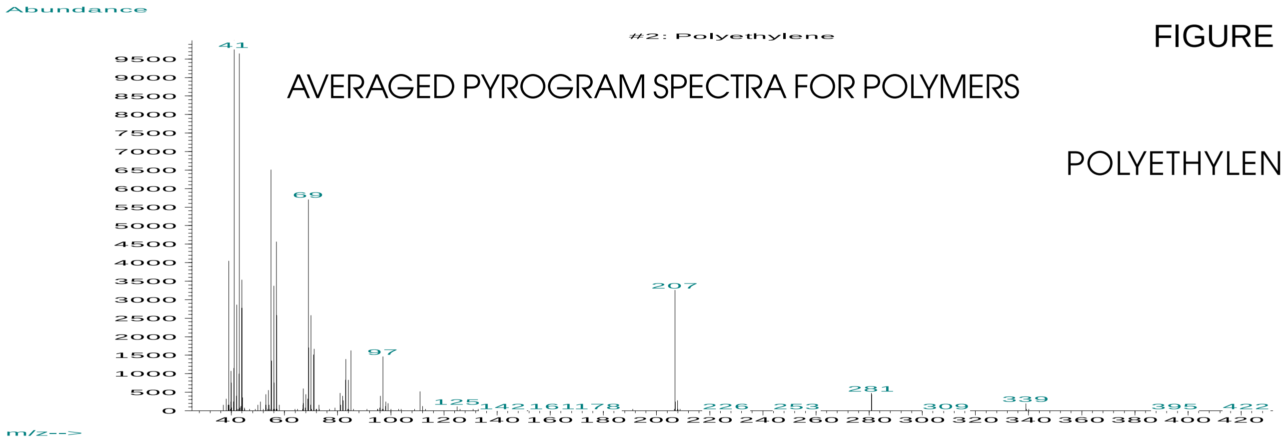

Abundance
Average of 0.140 to 34.892 min.: PYMS17.D
AVERAGE OF ALL SPECTRA FOR PYROGRAM
m/z-->

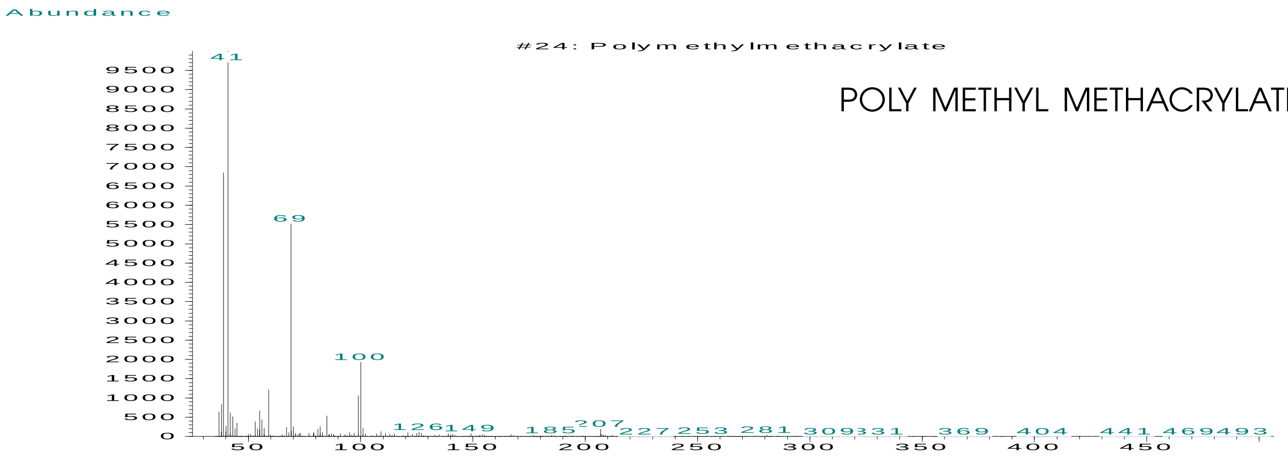
FIGURE 6

AVERAGED PYROGRAM SPECTRA FOR POLYMERS

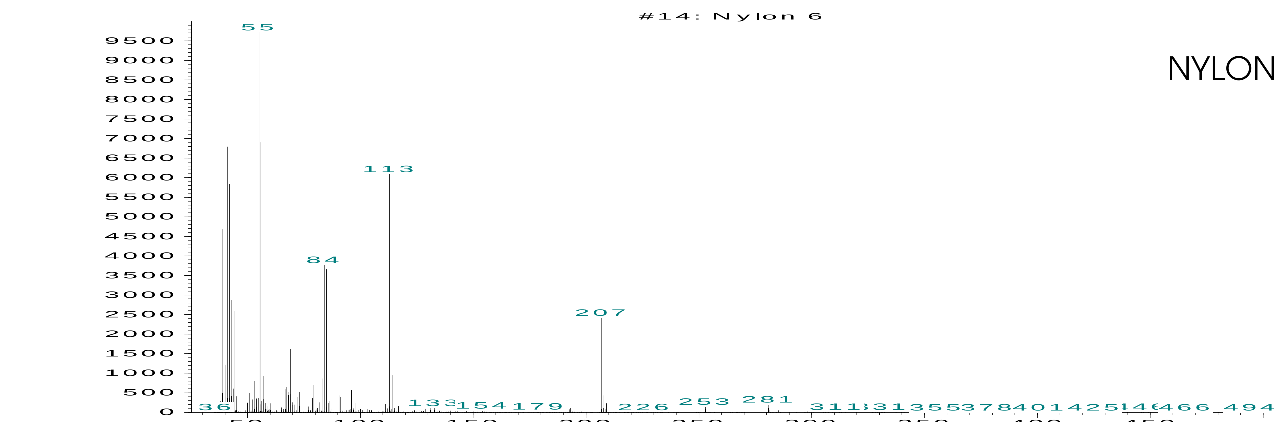
POLYETHYLENE



POLY METHYL METHACRYLATE



NYLON 6



POLY ETHYLENE TEREPHTHALATE

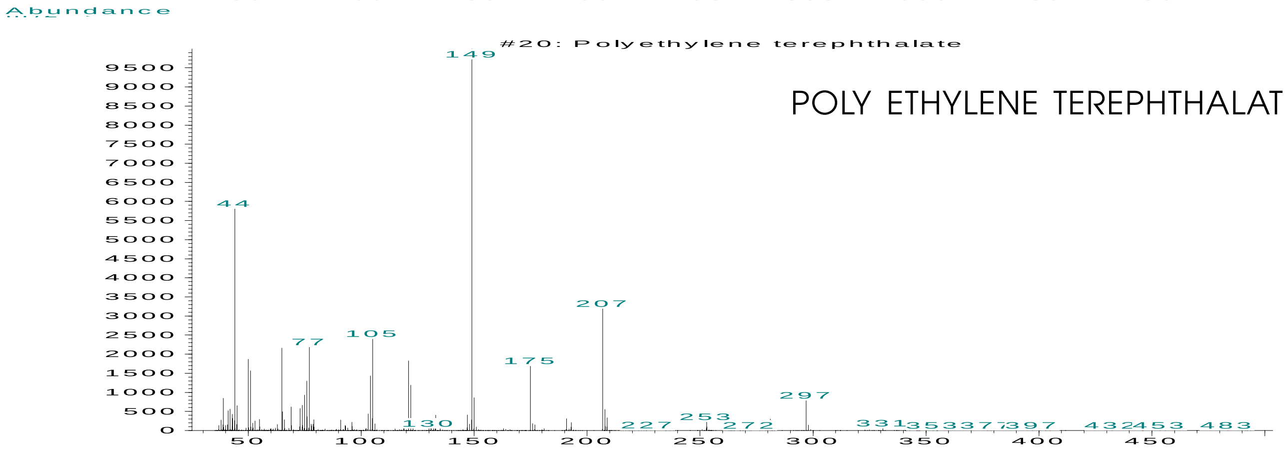


FIGURE 7

AVERAGED PYROGRAM SPECTRA

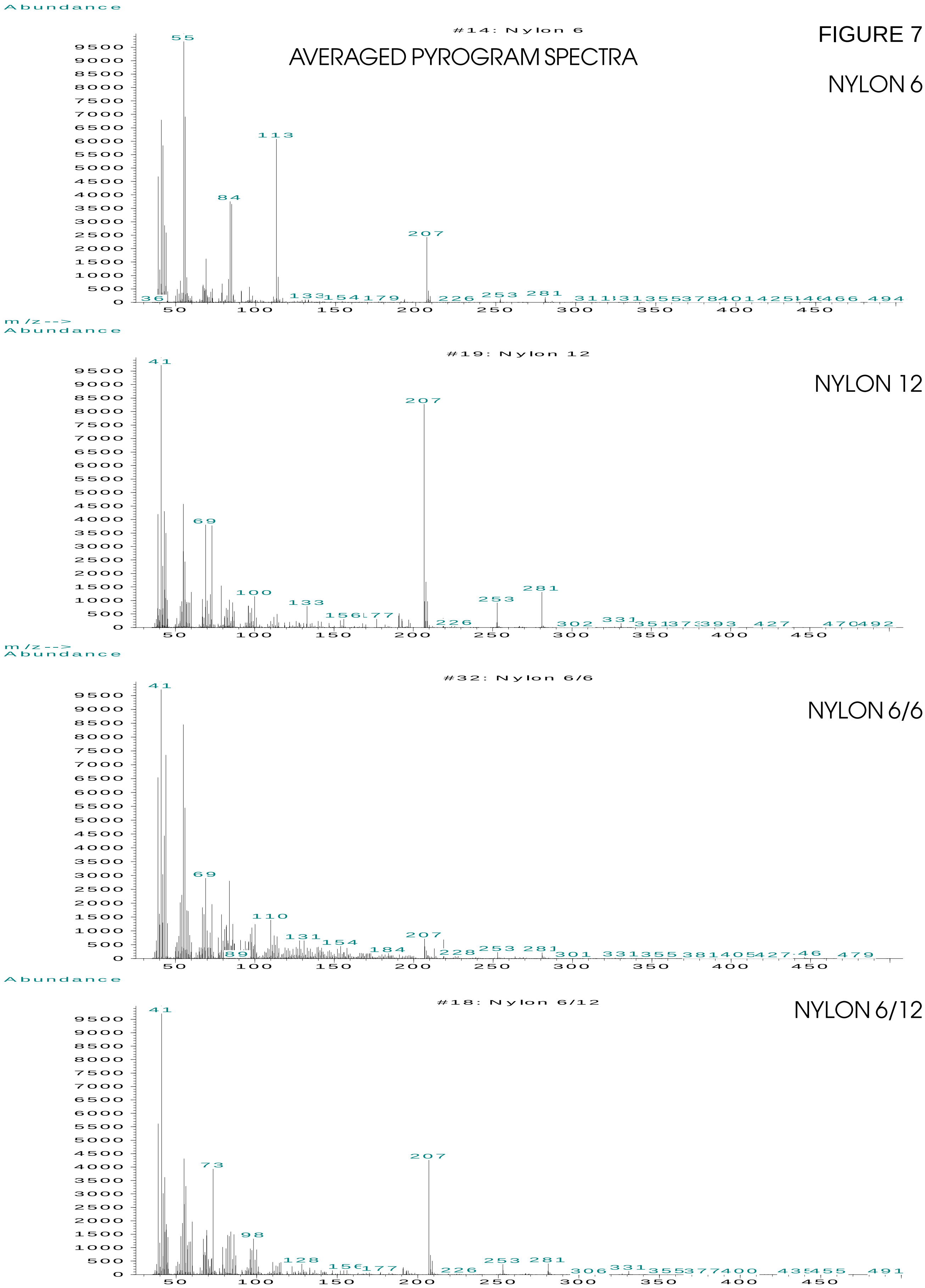
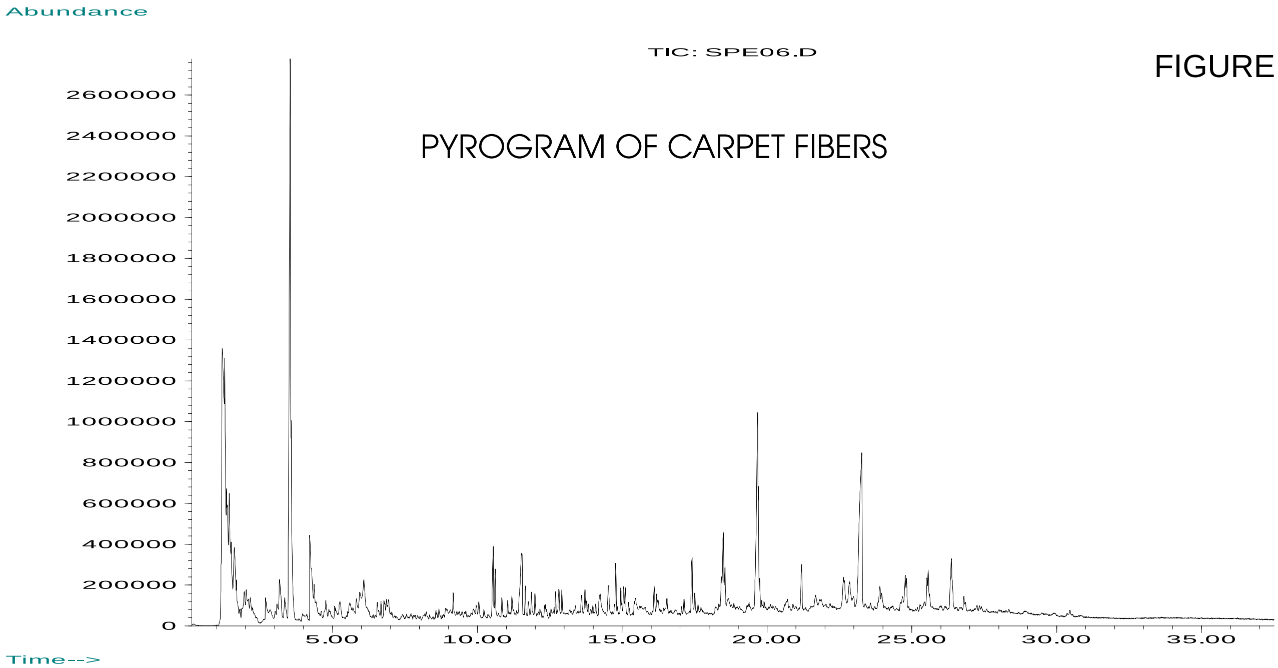
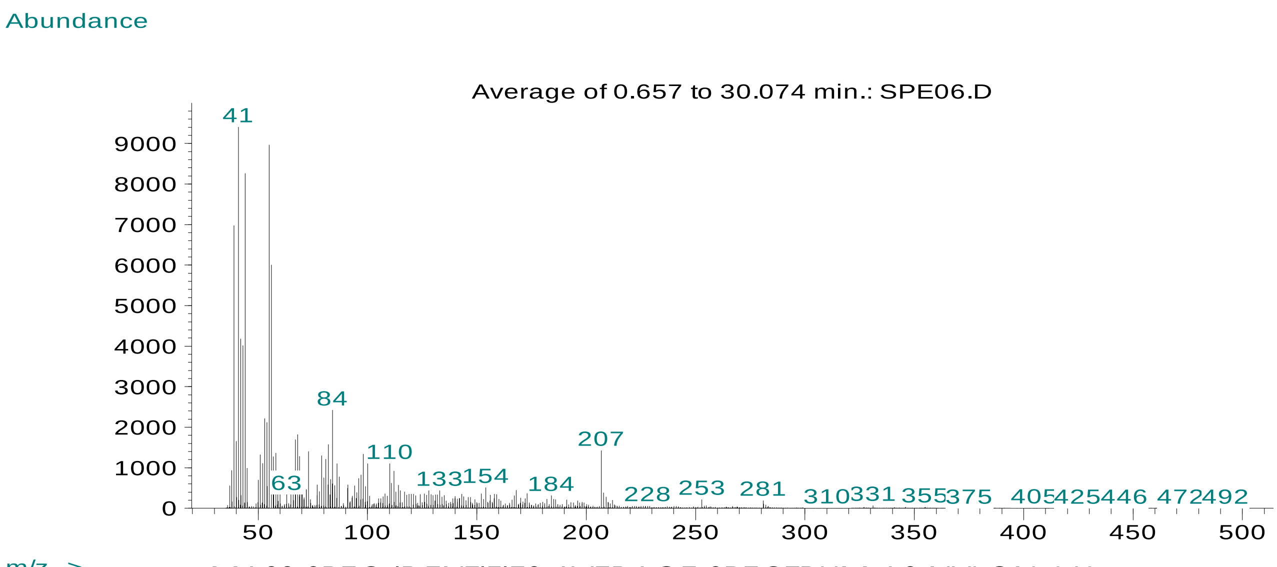


FIGURE 8





MASS SPEC IDENTIFIES AVERAGE SPECTRUM AS NYLON 6/6

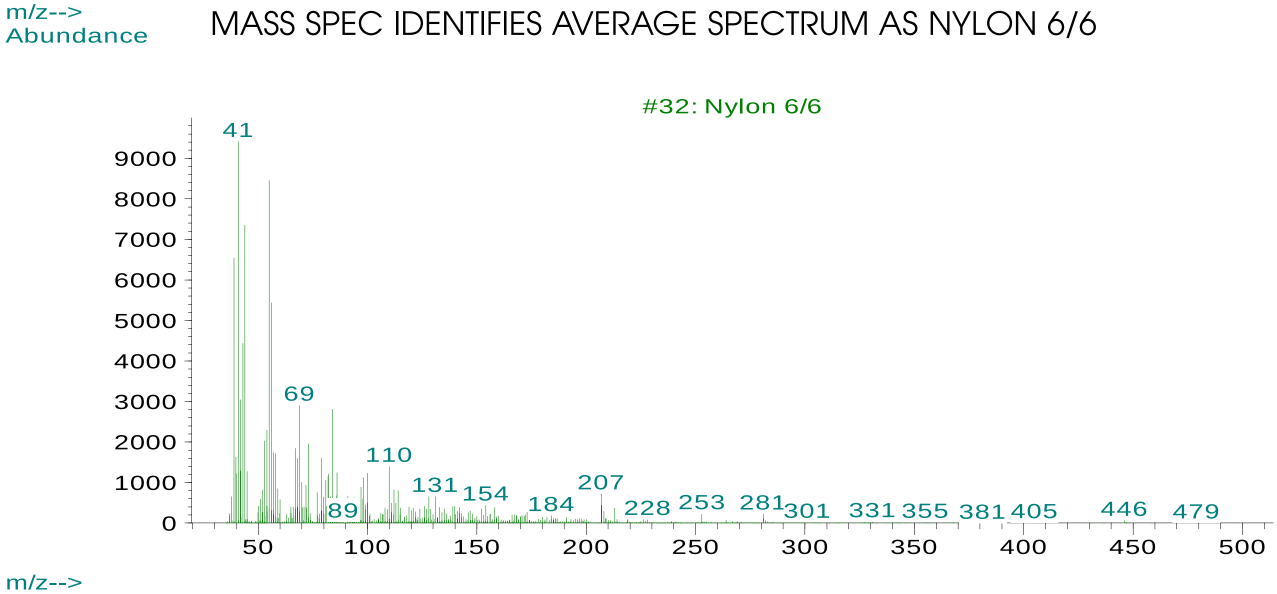
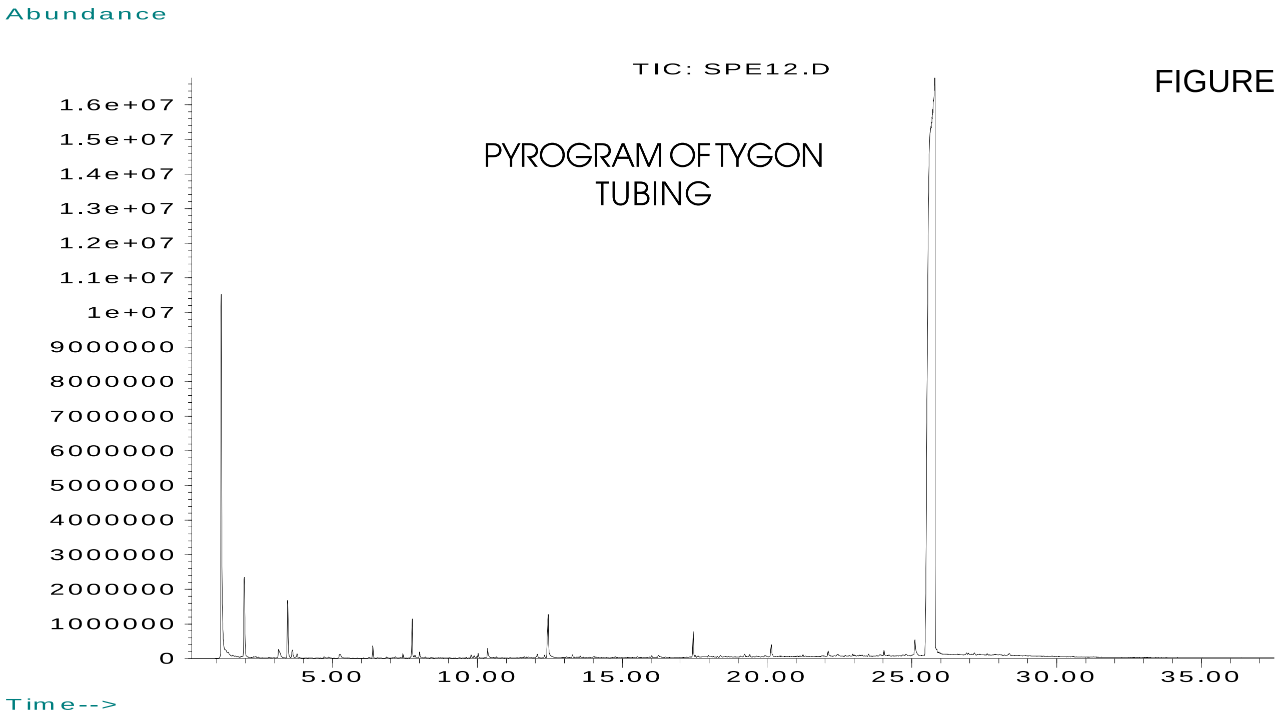
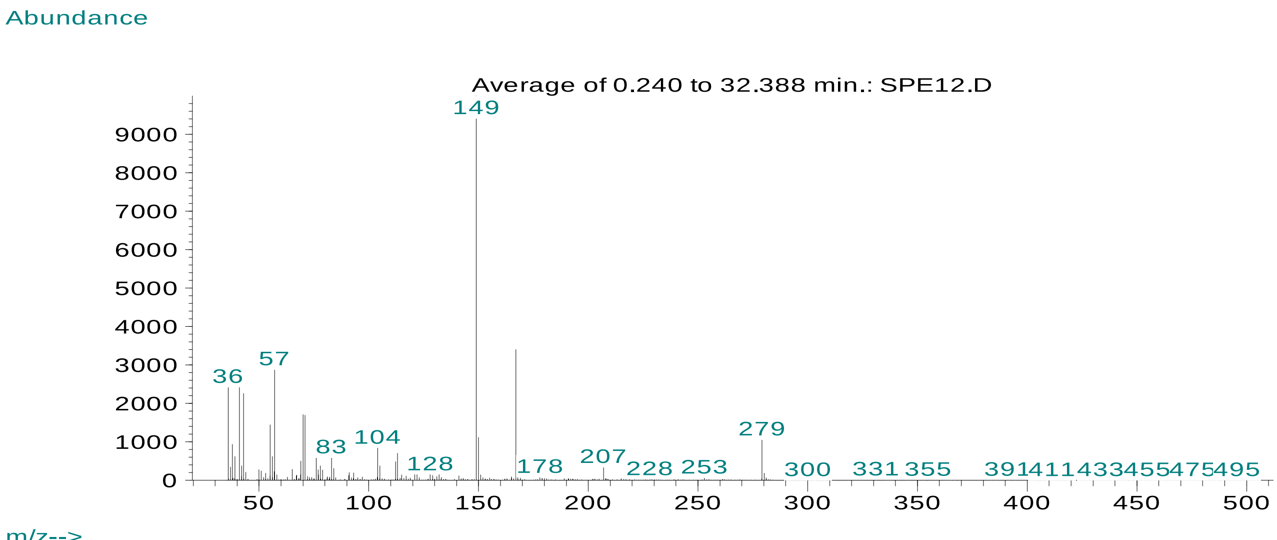


FIGURE 9





MASS SPEC IDENTIFIES AVERAGE SPECTRUM AS PVC WITH PLASTICISER

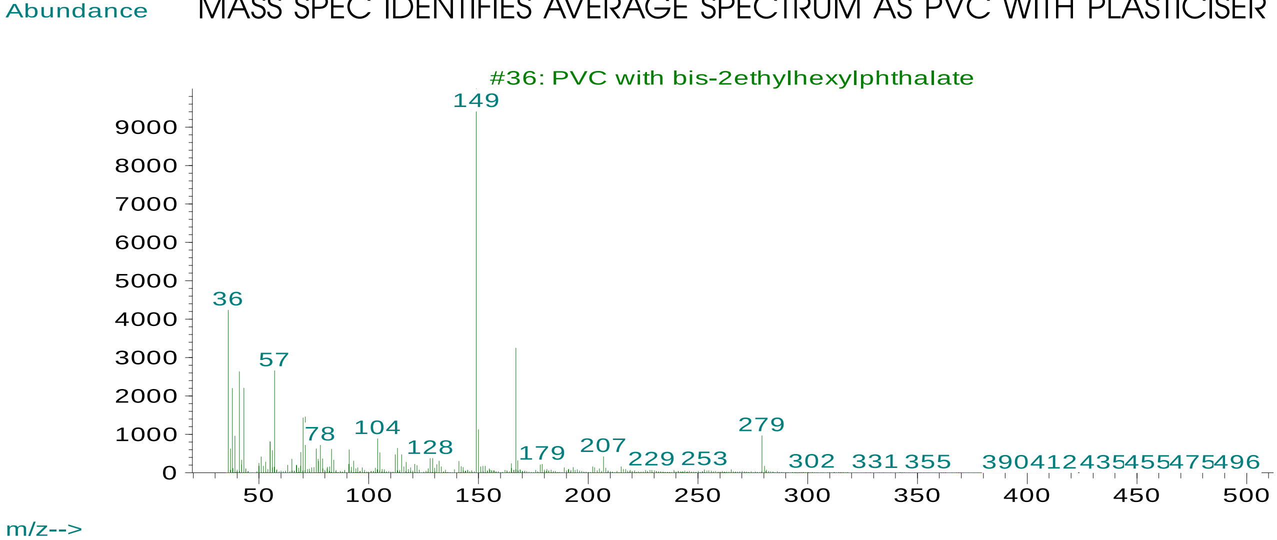
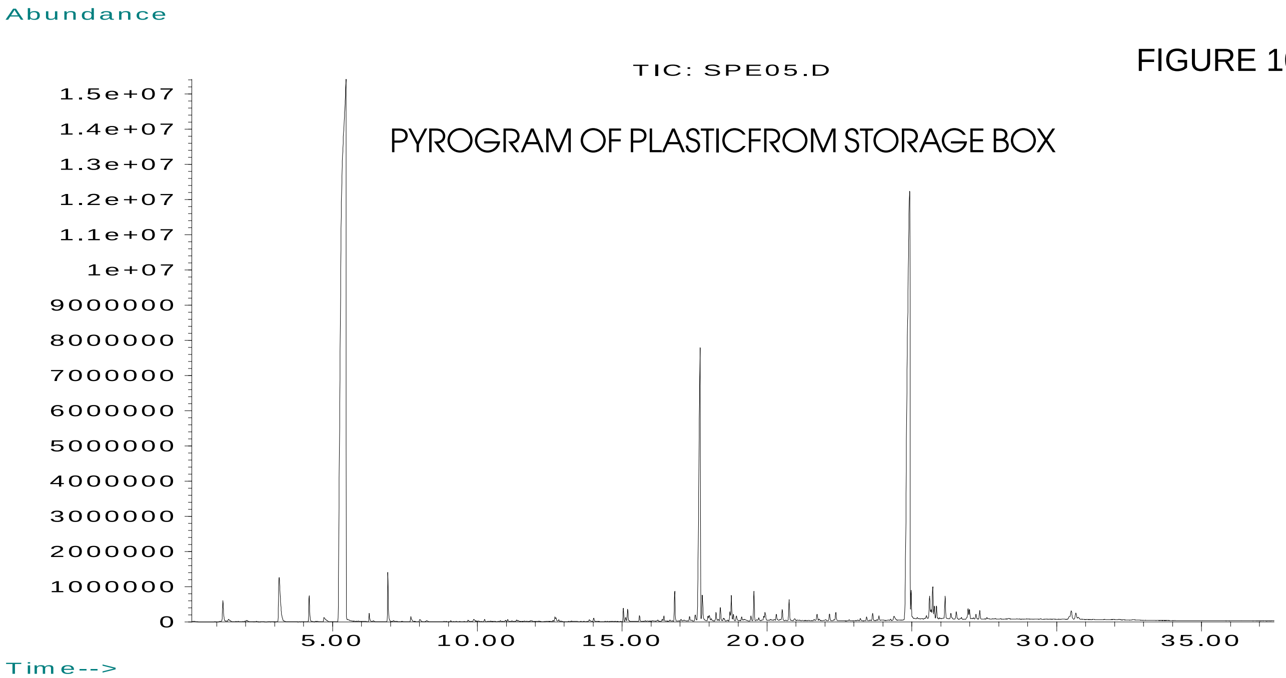
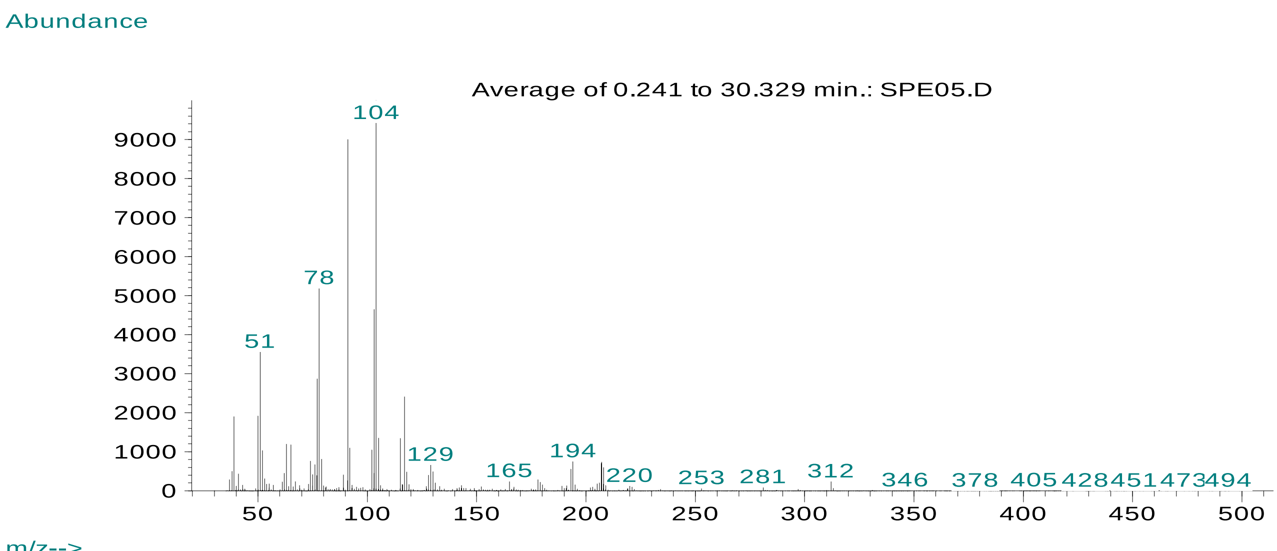


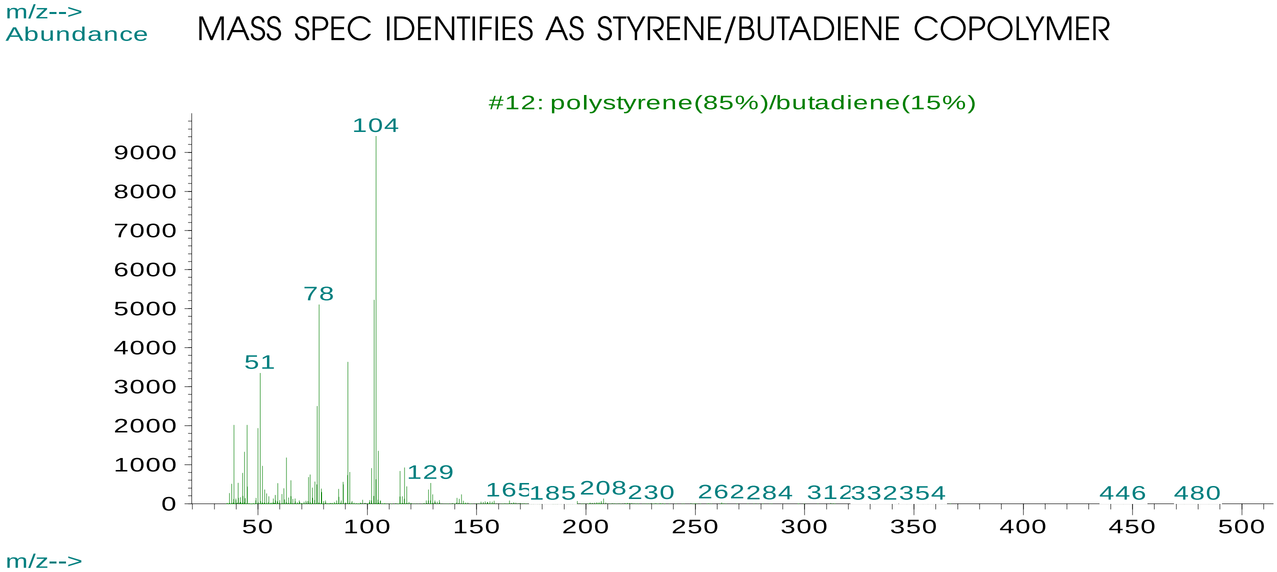
FIGURE 10

PYROGRAM OF PLASTICFROM STORAGE BOX





MASS SPEC IDENTIFIES AS STYRENE/BUTADIENE COPOLYMER



trimer, indicating polystyrene, which is a logical choice for this kind of material. When the pyrogram was averaged and searched, however, the best fit was for a copolymer of styrene and butadiene, not for pure polystyrene. Closer investigation of the smaller peaks in the pyrogram did reveal the presence of butadiene oligomers, information which may have been missed by just a visual inspection of the pyrogram.

This manual contains a list of samples such as polymers and copolymers which have been pyrolyzed, typically at 750°C. The pyrogram, using a HP-5 capillary column, and the averaged spectrum for the whole pyrogram are displayed together for each sample. The averaged pyrolysis mass spectra for the samples have been compiled as a library called “Pyrolysis” (Pyr2003.l) and may be searched for matching to pyrolysis spectra produced the same way for unknowns. As additional information, the pyrograms themselves may be compared for similarity of pattern to the pyrogram of the unknown material.

INSTALLATION

The pyrolysis identification library is used just as any other library in the mass spectrometer for searching matches. The only difference is that the spectra in the pyrolysis library are not spectra of pure materials, but composites of all the peaks in pyrogram. The pyrol.l library is installed from the disk onto the data station hard drive, as for any other library of spectra. Installing it into the Chemstation Database location permits easy selection of the pyrolysis library for searching the whole pyrogram, and easy return to the standard library (for example, NBS75K.l) for identifying individual peaks in the pyrogram.

To install the library, insert the floppy disk or CD into the appropriate drive of the computer. In the Windows Explorer program, click on that drive to display the files on the disk. Select the **pyr2003.l** file and copy it to the Database section of the Chemstation [C] hard drive, either by the copy function or just dragging it to the right location with the mouse.

The Database section of the hard drive should show both the standard library and the pyrolysis library now (along with some others possibly, such as Demo.l).

USING PYR2003.L

The standard library of spectra (such as the NBS75K.l) should be used as usual for identifying the pyrolysis materials which elute as individual peaks in the pyrogram. When the run is complete, the entire pyrogram should be averaged, just as the spectra for a single peak could be averaged, but for the whole pyrogram. It will probably take the computer a minute to do this, but when it is done, it will display the averaged spectrum.

To search the pyrolysis library for a match to this spectrum, click on SELECT LIBRARY in the SPECTRUM menu, and change from C:\DATABASE\NBS75K.L (or whatever the current library is) to C:\DATABASE\PYR2003.L.

The computer will now search the averaged pyrogram spectrum against the library of averaged polymer pyrogram spectra, and present the best match in the same way that it does for an individual peak.

For the maximum information, it is advised that the individual peaks in the pyrogram be searched using a standard library in addition to searching the averaged pyrogram spectra. This not only gives confirming information that the proper pyrolysis products are present in the pyrogram, but will help identify materials which may be present in the pyrogram but which are not actually pyrolysis products, such as residual solvents, plasticizers and contaminants.

LIBRARY OF PYROGRAMS