

Title of Research: Analysis of Polymer Standards by Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance and Pyrolysis Gas Chromatography/Mass Spectroscopy and the Creation of Searchable Libraries.

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Abstract

Fibers, paints, adhesives, and tapes, often encountered as evidence in forensic cases, contain both organic and inorganic constituents, which can be analyzed using various instrumental methods. Fourier Transform Infrared Spectroscopy (FTIR) is one such method for identifying or characterizing both the organic and inorganic components of a sample. Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS) provides analytical information on the organic component of samples, especially in samples where the organic component in the IR spectrum is masked by the presence of the inorganic constituent(s). Also, Py-GC/MS is helpful in detecting and indentifying the minor organic component(s) in a multi-polymer mix. A FTIR library and a Py-GC/MS library were compiled to assist with the identification of forensic case samples.

Introduction

The physical evidence submitted to forensic laboratories often includes fibers, paints, adhesives, and tapes^{1,2,3}. Various instrumental analysis techniques such as FTIR and Py-GC/MS are used to characterize and identify the constituents in these products. In addition, polymers, the organic component, can be categorized based on their chemical type or synthesis method by FTIR and Py-GC/MS. Products made in different batches and by different manufacturers, as well as polymer branching or defects, can be differentiated using these analytical methods⁴.

Infrared (IR) spectroscopy is an established, non-destructive technique used to identify materials, and can provide qualitative analysis of samples based on the absorption or transmittance of the infrared radiation that is passed through the sample⁵. IR spectroscopy gives information about the molecular structure of a sample and can classify them into the generic and sub-generic classes^{6,7,8}. Also, FTIR has the ability to identify or characterize both the

organic and inorganic components of a sample⁹. The idea behind this analysis method is that no two molecules that are structurally different will produce the same infrared spectrum, which is useful in positively identifying samples. Different samples have different compositions, resulting in the various infrared absorption band intensities at different wavenumbers, which allows for the comparison and characterization of samples. This analysis method is accurate and reproducible, allowing for the positive identification of samples, and can be used for quality control or quality assurance applications⁵. FTIR is often used in forensics to analyze fibers, adhesives, tapes, paints, and powders¹⁰. The development of FTIR with an attenuated total reflectance (ATR) attachment has made sample preparation easier and allowed very small samples to be analyzed¹¹. ATR is also a quick and easy method as compared to transmission, a traditional method of collection, since the thickness of the sample is not a concern^{12,13}.

Py-GC/MS is another useful technique used for analysis of polymer based samples used in various fields within forensics and industry^{14,15}. Py-GC/MS can identify and distinguish between samples that may be hard to differentiate with other analytical techniques¹⁶. Pyrolysis allows for the analysis of samples that are insoluble in organic solvents or not readily volatile, as well as organic molecules (e.g. polymers) too large for analysis by gas chromatography¹⁰. Unlike FTIR, the Py-GC/MS technique is destructive^{4,17}. Pyrolysis involves the breaking down of compounds by exposing them to high heat for a very short period of time. This allows for the analysis of the compound structure or composition of the sample based on the resulting fragments and allows for the study of the thermal degradation mechanism of the sample. The pyrogram that results from this analysis can provide useful qualitative and quantitative information, as well as indications of the mechanism and kinetics behind the thermal

decomposition and fragmentation of compounds¹⁶. Careful control of the temperature is very important in pyrolysis, since the temperature and temperature programming can affect the results. Quickly increasing the probe temperature to the upper limits will usually result in smaller fragments whereas slowly increasing the probe temperature to a more moderate temperature will produce larger fragments¹.

Pyrolyzers are often coupled with gas chromatography (GC) and/or mass spectrometry (MS) for further analysis of the pyrolysis products. Integration with GC and MS allows for the separation, identification, and quantification of the pyrolysis products¹⁴. While Py-GC/MS has been used in environmental, taxonomy, and organic geopolymer studies, it is also useful in the field of forensics when analyzing fibers, paints, tapes, and adhesives^{16,18}. Analysis using pyrolysis techniques can provide a greater discrimination power compared to infrared spectroscopy, but it takes a considerable amount of time to conduct and cannot identify inorganic constituents. Thus, Py-GC/MS should be used as a complementary technique rather than used as a substitute of infrared spectroscopy¹⁹. Py-GC/MS is a valuable method in identifying the organic binder in samples that contain a lot of inorganic components, and it is helpful in detecting and indentifying the minor organic component in a multi-polymer mix. While the entire pyrogram is not searchable and retention times vary depending on chromatographic conditions, individual peaks in a pyrogram can be searched using the library software (eg. National Institute of Standards and Technology). However, this method may not identify the polymer(s) present in the sample and is time consuming. The instrument's mass spectrometer data analysis software can create a combined mass spectrum by averaging the scans in the pyrogram to produce a single mass spectrum representative of the polymer sample. The combined mass spectrum can

be added to an existing library or used to create a new library so a search and identification of an unknown sample can be performed.

Materials and Methods

A total of 100 polymer samples from the Scientific Polymer Products (SP²) Polymer Sample Kit Catalog No. 205 (lot number 600801012) were sampled and analyzed on the PerkinElmer Spectrum One FTIR Spectrometer with Specac single reflection diamond ATR and Spectrum software version 5.0.1. The samples were run from 4000cm⁻¹ to 450cm⁻¹ with 8 scans at a scan speed of 0.20cm/s and a resolution of 4.00cm⁻¹. Large sample pieces were cut using a razor blade to produce a fresh surface for analysis. Each sample was placed on the ATR diamond so that it was entirely covered and the sample was analyzed. The resulting spectra were normalized to 1.0 and major peaks were labeled. A notebook of the printed spectra was put together and a digital library of the polymer collection was also created using the software provided with the FTIR instrument. A copy of the printed spectra and the digital library were shared with other Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF) laboratories.

The SP² polymer samples were further analyzed with a CDS Analytical, Inc. Pyroprobe 5000 series, model 5150, with the PerkinElmer AutoSystem XL Gas Chromatograph and PerkinElmer Turbo Mass Gold Mass Spectrometer.

Individually, each polymer was sampled and a piece equal in volume to an equant 300um particle was inserted into the center of the pyrolysis quartz tube that contained quartz wool. The fine polymer powders had to be pressed to form a single intact particle then trimmed to obtain the correct particle size. The pyrolysis tube was then inserted into the pyroprobe for the polymer sample to be pyrolyzed and further analyzed by gas chromatography with attached

mass spectrometer. The pyrolyzer was set with an interface temperature of 300°C and an interface run time of 1 minute. The transfer line was set at 300°C. The sample was pyrolyzed at 750°C for 15 seconds with a ramp rate of 0°C. The gas chromatograph had an inlet temperature of 300°C, column flow of 1.5mL/min, and a split ratio of 50:1. The carrier gas was helium and the column used was a J+W DB-5MS (250um diameter and 30 meters long). The oven temperature program started at 40°C and was held for 2 minutes, then ramped at 12°C/min until 280°C and held for 4 minutes, for a total run time of 26 minutes. The mass spectrometer in the electron ionization mode was set to detect a mass range of 33 – 350 and scans were collected from 0.5 minutes to 26 minutes every 0.2 seconds, resulting in approximately 5055 MS scans in a 26 minute pyrogram run. The 5055 scans produced from each pyrogram were used to generate a combined mass spectrum of each polymer sample, which was then added to PYRO2008, the CDS Analytical Pyrolysis Library (Oxford, PA), and also used to create a new software searchable mass spectral library.

At the beginning of each week, a sample of Kraton® 1107, a styrene/isoprene copolymer, was analyzed to ensure the Py-GC/MS was working properly and the retention times were constant. Between each polymer sample, a blank was analyzed to ensure no residue was left on the column. If the blank was not clean, the column was cleaned by heating the GC column up to 290°C for a period of time and then blank was re-run.

Results

The analysis of the polymer standards using the FTIR and Py-GC/MS allowed for the development of an IR library and a Py-GC/MS pyrolysis combined spectra library, which can be helpful with the identification and differentiation of samples whose composition is initially

unknown. While some samples are easy to differentiate using the FTIR, others are harder to differentiate using the FTIR. For samples that were difficult to differentiate on the FTIR, the Py-GC/MS may provide an additional method of analysis for the characterization and identification of some these samples. In the examples of comparing the ethylene/vinyl acetate copolymers and comparing the 98% and 99.7% hydrolyzed poly(vinyl alcohol), both the FTIR and Py-GC/MS were not able to differentiate between the samples. But in the case of nylon samples, such as nylon 11 and nylon 12, Py-GC/MS provided an additional method of differentiation. There were a few samples where the FTIR was able to differentiate between samples while the Py-GC/MS provided no discrimination, as seen in the comparison between the low density polyethylene and the oxidized polyethylene. There were also samples that were easily differentiated on both the FTIR and the Py-GC/MS, as in the case of cellulose and polystyrene.

Similar IR spectra, similar pyrograms.

Ethylene/Vinyl Acetate Copolymers. The ethylene/vinyl acetate copolymers with different percentages of vinyl acetate produced similar IR spectra and pyrograms. As shown in Figure 1, the IR spectra of ethylene/vinyl acetate copolymer with 14% vinyl acetate and 40% vinyl acetate are quite similar. A couple of the bands (1121 cm^{-1} and 934 cm^{-1}) have a greater intensity in the copolymer containing 40% vinyl acetate than in the copolymer containing 14% vinyl acetate. The wavenumbers for both IR spectra can be found in Table 1. The pyrograms for both samples are also quite similar, as seen in Figure 2. Both contain multiple peaks about 1.0 – 1.5 minutes apart. The retention times of some of the peaks that eluted off both samples are shown in Table 2. For the sample containing 40% vinyl acetate, the peaks are less prominent towards the end of the run, but the peaks occurring during the rest of the run occur at the

same time. The combined mass spectra of these two samples show a few differences, as shown in Figure 3. In the ethylene/vinyl acetate copolymer with 40% vinyl acetate, the relative abundance of the mass-to-charge ratio (m/z) of 43, 55, and 67 are very close to each other and slightly larger than the m/z of 81 and 91 abundance. Compared to the ethylene/vinyl acetate copolymer with 14% vinyl acetate, the m/z of 55 is a bit larger than the other ones, while the m/z of 41, 69, 83, and 97 have similar abundance to each other. Even though the two samples contain similar m/z peaks, as seen in Table 3, the relative abundance of each peak differs, and this is what allows for the differentiation between samples when using combined mass spectra for analysis.

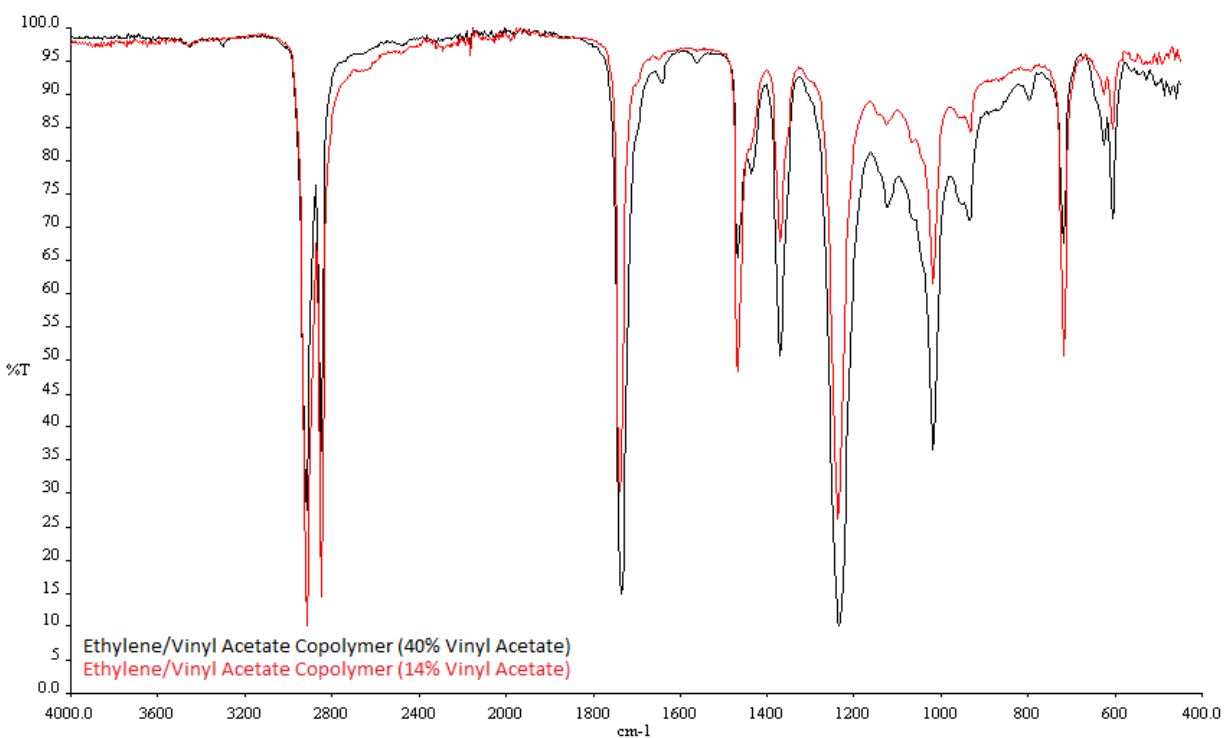


Figure 1. The IR spectra of ethylene/vinyl acetate copolymer with 14% vinyl acetate and ethylene/vinyl acetate copolymer with 40% vinyl acetate.

Table 1. The wavenumbers of major bands found in the IR spectra of ethylene/vinyl acetate copolymer with 14% vinyl acetate and ethylene/vinyl acetate copolymer with 40% vinyl acetate.

Ethylene/Vinyl Acetate Copolymer 14% Vinyl Acetate	Ethylene/Vinyl Acetate Copolymer 40% Vinyl Acetate
2913 cm ⁻¹	2913 cm ⁻¹
2845 cm ⁻¹	2845 cm ⁻¹
1737 cm ⁻¹	1734 cm ⁻¹
1465 cm ⁻¹	1465 cm ⁻¹
1370 cm ⁻¹	1370 cm ⁻¹
1236 cm ⁻¹	1233 cm ⁻¹
1121 cm ⁻¹	1121 cm ⁻¹
1018 cm ⁻¹	1018 cm ⁻¹
934 cm ⁻¹	934 cm ⁻¹
718 cm ⁻¹	718 cm ⁻¹
606 cm ⁻¹	606 cm ⁻¹

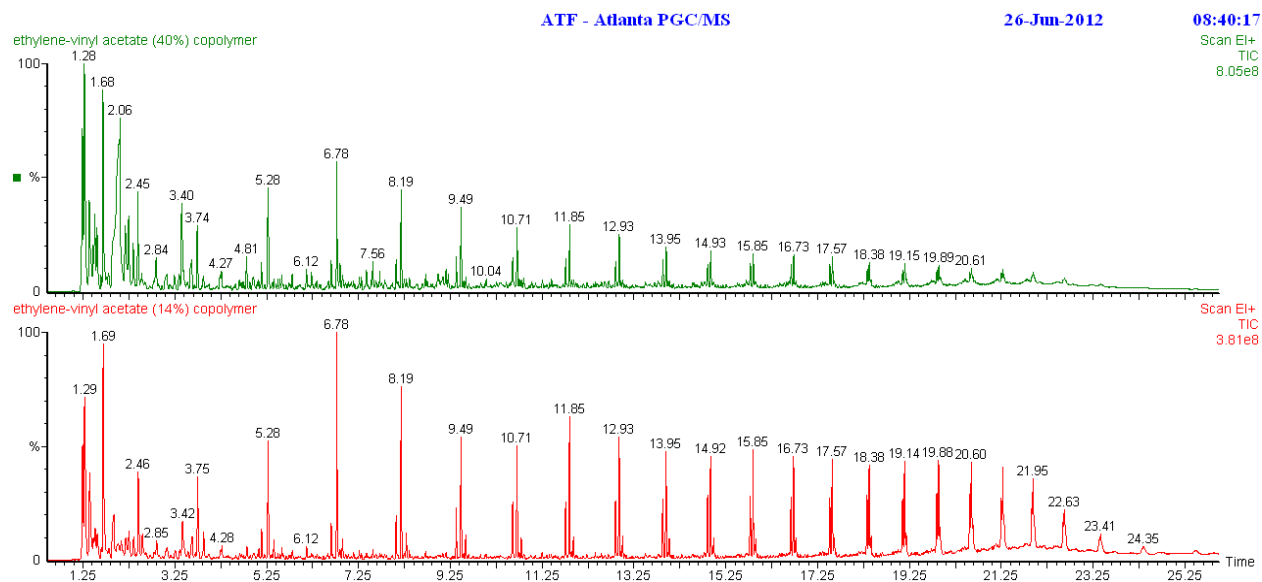


Figure 2. The pyrograms of ethylene/vinyl acetate copolymer with 14% vinyl acetate and ethylene/vinyl acetate copolymer with 40% vinyl acetate.

Table 2. The retention times of some peaks found in the pyrograms of ethylene/vinyl acetate copolymer with 14% vinyl acetate and ethylene/vinyl acetate copolymer with 40% vinyl acetate.

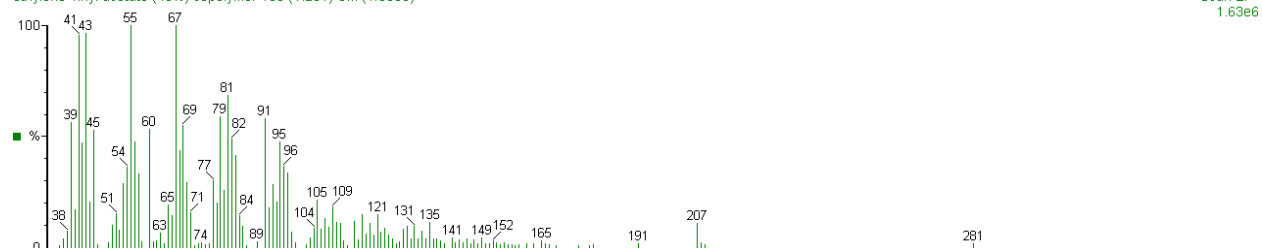
Ethylene/Vinyl Acetate Copolymer 14% Vinyl Acetate	Ethylene/Vinyl Acetate Copolymer 40% Vinyl Acetate
1.29 min.	12.8 min.
1.69 min.	1.68 min.
2.06 min.	2.06 min.
2.46 min.	2.45 min.
3.42 min.	3.40 min.
3.75 min.	3.74 min.
5.28 min.	5.28 min.
6.78 min.	6.78 min.
8.19 min.	8.19 min.
9.49 min.	9.49 min.
10.71 min.	10.71 min.
11.85 min.	11.85 min.
12.93 min.	12.93 min.
13.95 min.	13.95 min.
14.92 min.	14.93 min.
15.85 min.	15.85 min.
16.73 min.	16.73 min.
17.57 min.	17.57 min.
18.38 min.	18.38 min.
19.14 min.	19.15 min.
19.88 min.	19.89 min.
20.60 min.	20.61 min.
21.29 min.	21.29 min.
21.95 min.	21.95 min.
22.63 min.	22.63 min.
23.41 min.	-
24.35 min.	-

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ethylene-vinyl acetate (40%) copolymer 155 (1.281) Cm (1.5055)

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1.63e6



ethylene-vinyl acetate (14%) copolymer 1246 (6.783) Cm (1.5055)

Scan EI+
8.97e5

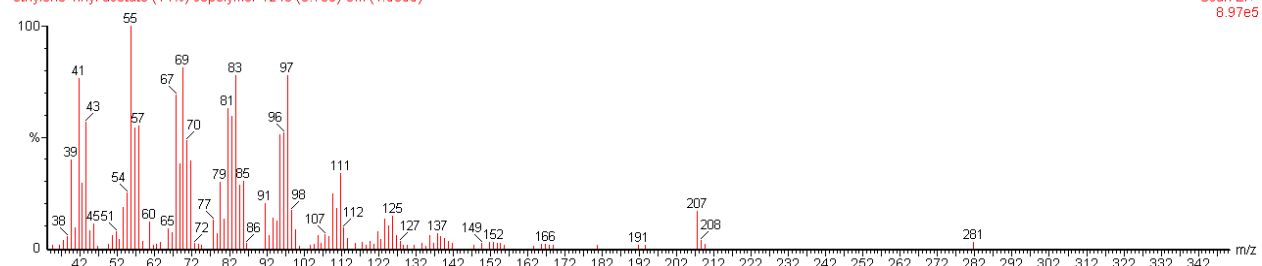


Figure 3. The combined mass spectra of ethylene/vinyl acetate copolymer with 14% vinyl acetate and ethylene/vinyl acetate copolymer with 40% vinyl acetate.

Table 3. The major m/z ratios found in the mass spectra of ethylene/vinyl acetate copolymer with 14% vinyl acetate and ethylene/vinyl acetate copolymer with 40% vinyl acetate.

Ethylene/Vinyl Acetate Copolymer 14% Vinyl Acetate	Ethylene/Vinyl Acetate Copolymer 40% Vinyl Acetate
41	41
55	55
69	67
83	81
97	91
111	109

Poly(vinyl alcohol), hydrolyzed. The 98% and 99.7% hydrolyzed poly(vinyl alcohol) standards show another example of polymers that produce both similar IR spectra and similar pyrograms, as seen in Figures 4 and 5. There is a band at 1709 cm^{-1} for the 98% hydrolyzed poly(vinyl alcohol) IR spectrum, which is absent in the 99.7% hydrolyzed poly(vinyl alcohol) IR spectrum. In the pyrogram of these two polymers, the 99.7% hydrolyzed poly(vinyl alcohol) contains three peaks towards the end of the run, after 20.00 minutes, which are not present in the 98%

hydrolyzed poly(vinyl alcohol). These are slight differences in the IR spectra and the pyrograms of the two polymers. The wavenumbers of the bands present in the IR spectra for the two polymers and the retention times of some of the peaks in the pyrograms of the two polymers can be found in Table 4 and Table 5, respectively. The mass spectra of the 98% and 99.7% hydrolyzed poly(vinyl alcohol) do not show much differences. As shown in Figure 6, both contain a large 44 m/z peak with the rest of the peaks being quite small, and the relative abundance of the peaks present are very similar between the two polymers. The major m/z peaks can be found in Table 6.

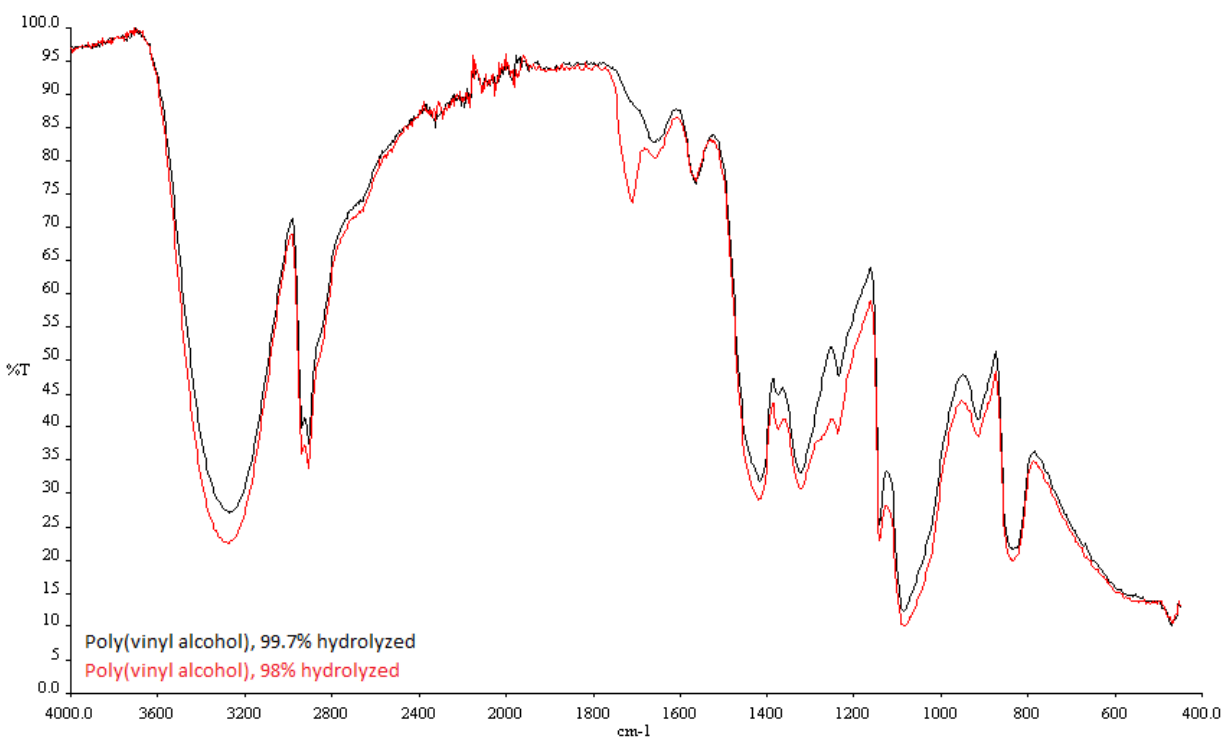


Figure 4. The IR spectra of 99.7% hydrolyzed poly(vinyl alcohol) and 98% hydrolyzed poly(vinyl alcohol).

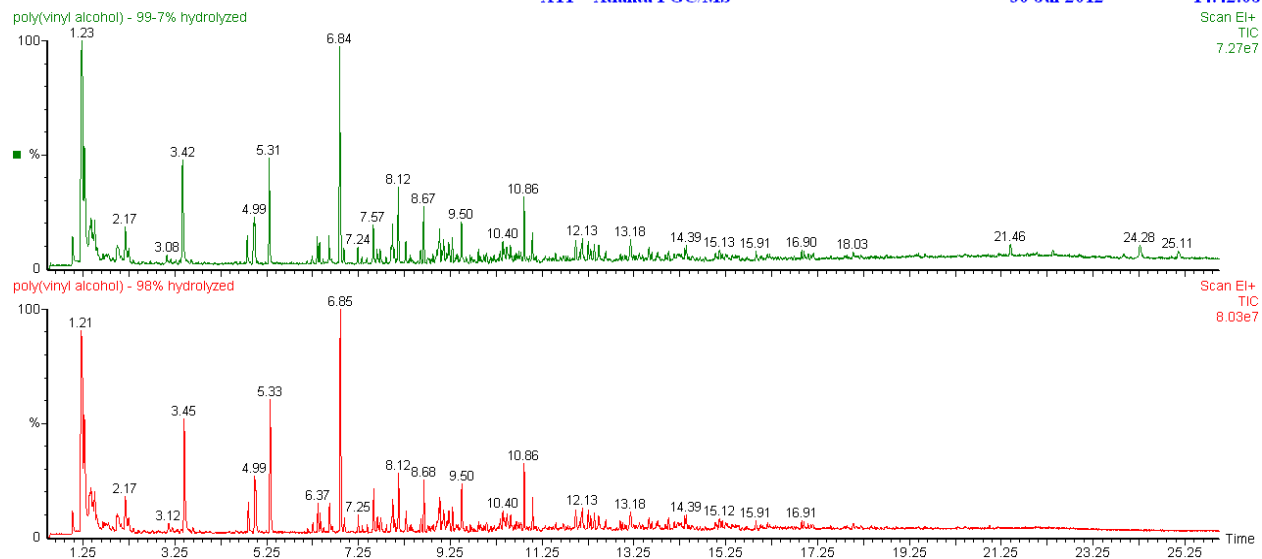


Figure 5. The pyrograms of 99.7% hydrolyzed poly(vinyl alcohol) and 98% hydrolyzed poly(vinyl alcohol).

Table 4. The wavenumbers of major bands found in the IR spectra of 99.7% hydrolyzed poly(vinyl alcohol) and 98% hydrolyzed poly(vinyl alcohol).

Poly(vinyl alcohol) 98% hydrolyzed	Poly(vinyl alcohol) 99.7% hydrolyzed
3279 cm ⁻¹	3272 cm ⁻¹
2935 cm ⁻¹	2935 cm ⁻¹
2908 cm ⁻¹	2906 cm ⁻¹
1709 cm ⁻¹	-
1653 cm ⁻¹	1658 cm ⁻¹
1560 cm ⁻¹	1563 cm ⁻¹
1419 cm ⁻¹	1417 cm ⁻¹
1323 cm ⁻¹	1324 cm ⁻¹
1236 cm ⁻¹	1236 cm ⁻¹
1141 cm ⁻¹	1141 cm ⁻¹
1086 cm ⁻¹	1087 cm ⁻¹
914 cm ⁻¹	914 cm ⁻¹
836 cm ⁻¹	837 cm ⁻¹

Table 5. The retention times of some peaks found in the pyrograms of 99.7% hydrolyzed poly(vinyl alcohol) and 98% hydrolyzed poly(vinyl alcohol).

Poly(vinyl alcohol) 98% hydrolyzed	Poly(vinyl alcohol) 99.7% hydrolyzed
2.17 min.	2.17 min.
3.45 min.	3.42 min.
5.33 min.	5.31 min.
6.85 min.	6.84 min.
7.59 min.	7.57 min.
8.12 min.	8.12 min.
8.68 min.	8.67 min.
9.50 min.	9.50 min.
10.86 min.	10.86 min.
12.13 min.	12.13 min.
13.18 min.	13.18 min.
14.39 min.	14.39 min.
15.91 min.	15.91 min.
16.91 min.	16.90 min.
18.03 min.	18.03 min.
-	21.46 min.
-	24.28 min.
-	25.11 min.

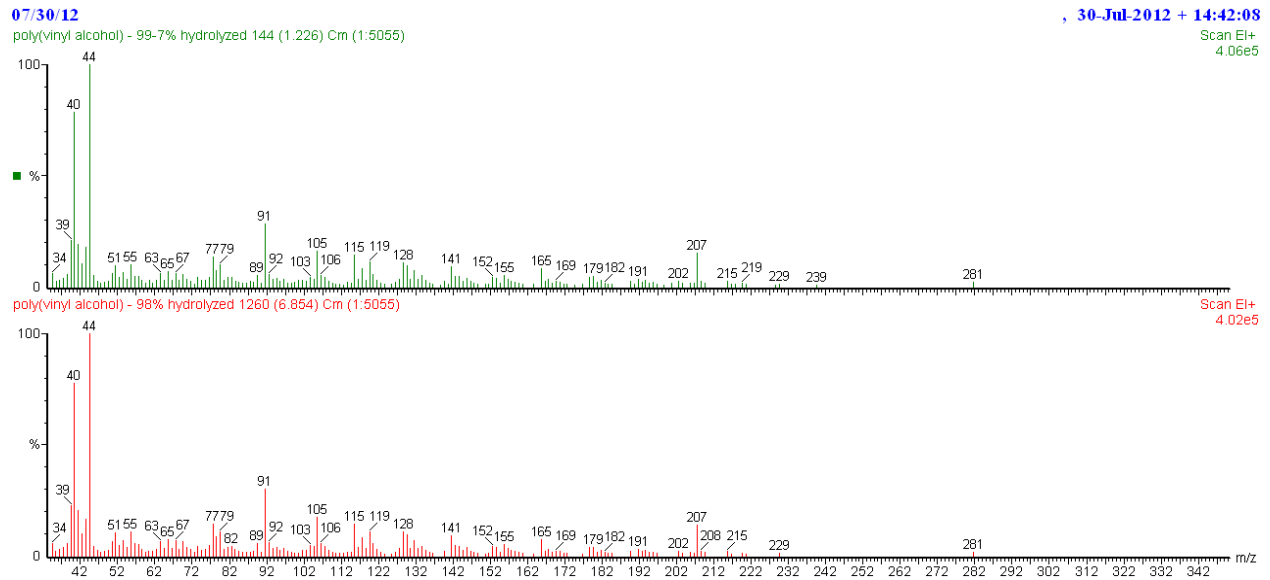


Figure 6. The combined mass spectra of 99.7% hydrolyzed poly(vinyl alcohol) and 98% hydrolyzed poly(vinyl alcohol).

Table 6. Some of the m/z ratios found in the mass spectra of 99.7% hydrolyzed poly(vinyl alcohol) and 98% hydrolyzed poly(vinyl alcohol).

Poly(vinyl alcohol) 98% hydrolyzed	Poly(vinyl alcohol) 99.7% hydrolyzed
44	44
77	77
91	91
105	105
115	115
128	128
141	141

Similar IR spectra, different pyrogram.

Nylons. Nylons are an example of polymers that produce similar IR spectra but different pyrograms when analyzed on the FTIR and the Py-GC/MS. This can be seen in the two nylon samples, nylon 11 and nylon 12. The IR spectra of nylon 11 and nylon 12 are quite similar, with minor differences in bands present in the two samples, as seen in Figure 7. The intensities of the bands above 1400 cm^{-1} are relatively the same, but the band intensities below 1400 cm^{-1} vary slightly. Some bands are more prominent than others. The wavenumbers of the bands present in nylon 11 and in nylon 12 can be found in Table 7. A comparison of the two nylon standards pyrograms can be found in Figure 8, and the retention times of peaks in the pyrograms can be found in Table 8. Up until 11.00 minutes, the peaks present appear at the same times and are all relatively the same height. The peak at 11.81 minutes for nylon 11 is quite a bit larger than the peak at 11.74 minutes in nylon 12. In nylon 11, there are two peaks occurring after 12.00 minutes, both of which are less than 10% of the height of the largest peak. As for nylon 12, there are about 10 peaks occurring after 12.00 minutes, with one very large peak at 12.86 minutes, two peaks that are about 20% the height of the largest peak and the

rest being less than 10% of the height of the largest peak. Though the IR spectra of nylon 11 and nylon 12 are very similar, the pyrograms show differences that indicate the two samples are different. The combined mass spectra for nylon 11 and nylon 12 show a few differences in the relative abundance of each m/z peak, as seen in Figure 9. For nylon 11, the 41 and 55 m/z peak have similar abundance and are quite a bit larger than the other peaks, but for nylon 12, the m/z peak at 55 is slightly smaller than the m/z of 41. Also, nylon 11 has a higher abundance at m/z peaks of 122 and 136 compared to the nylon 12 polymer. The major m/z peaks found in the two nylon standards are listed in Table 9.

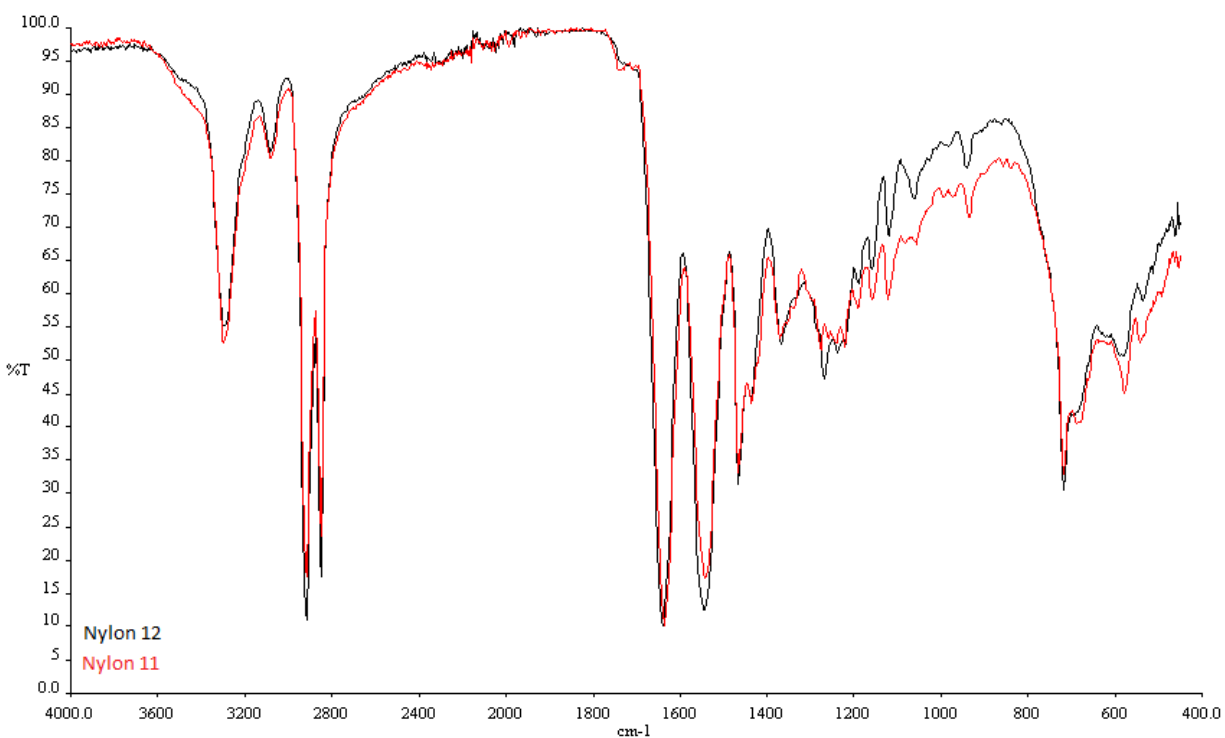


Figure 7. The IR spectra of nylon 11 and nylon 12.

Table 7. The wavenumbers of major bands found in the IR spectra of nylon 11 and nylon 12.

Nylon 11	Nylon 12
3294 cm ⁻¹	3294 cm ⁻¹
3081 cm ⁻¹	3075 cm ⁻¹
2913 cm ⁻¹	2913 cm ⁻¹
2845 cm ⁻¹	2845 cm ⁻¹
1636 cm ⁻¹	1639 cm ⁻¹
1541 cm ⁻¹	1541 cm ⁻¹
1465 cm ⁻¹	1465 cm ⁻¹
1370 cm ⁻¹	1367 cm ⁻¹
1275 cm ⁻¹	1267 cm ⁻¹
1188 cm ⁻¹	1188 cm ⁻¹
1158 cm ⁻¹	1158 cm ⁻¹
1121 cm ⁻¹	1118 cm ⁻¹
-	1062 cm ⁻¹
934 cm ⁻¹	939 cm ⁻¹
718 cm ⁻¹	718 cm ⁻¹
682 cm ⁻¹	-
579 cm ⁻¹	579 cm ⁻¹

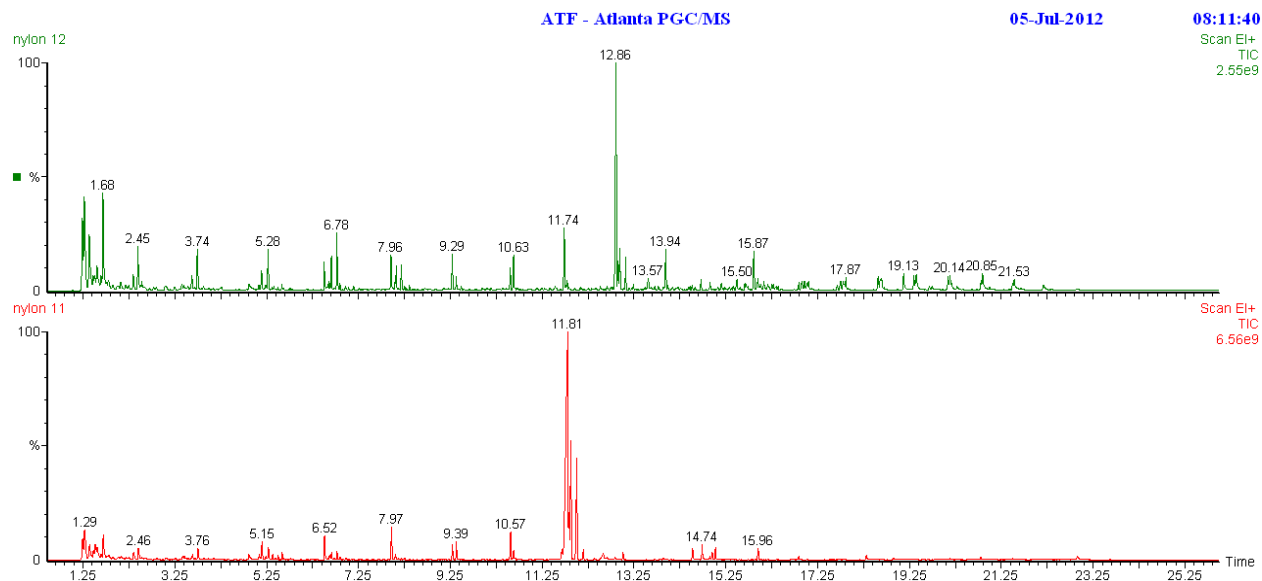


Figure 8. The pyrograms of nylon 11 and nylon 12.

Table 8. The retention times of some peaks found in the pyrograms of nylon 11 and nylon 12.

Nylon 11	Nylon 12
1.29 min.	1.28 min.
1.69 min.	1.68 min.
2.46 min.	2.06 min.
3.76 min.	3.74 min.
7.97 min.	7.96 min.
9.39 min.	9.29 min.
10.57 min.	10.63 min.
11.81 min.	11.74 min.
-	13.94 min.
14.74 min.	-
15.96 min.	15.87 min.
-	17.87 min.
-	19.13 min.
-	20.14 min.
-	20.85 min.
-	21.53 min.

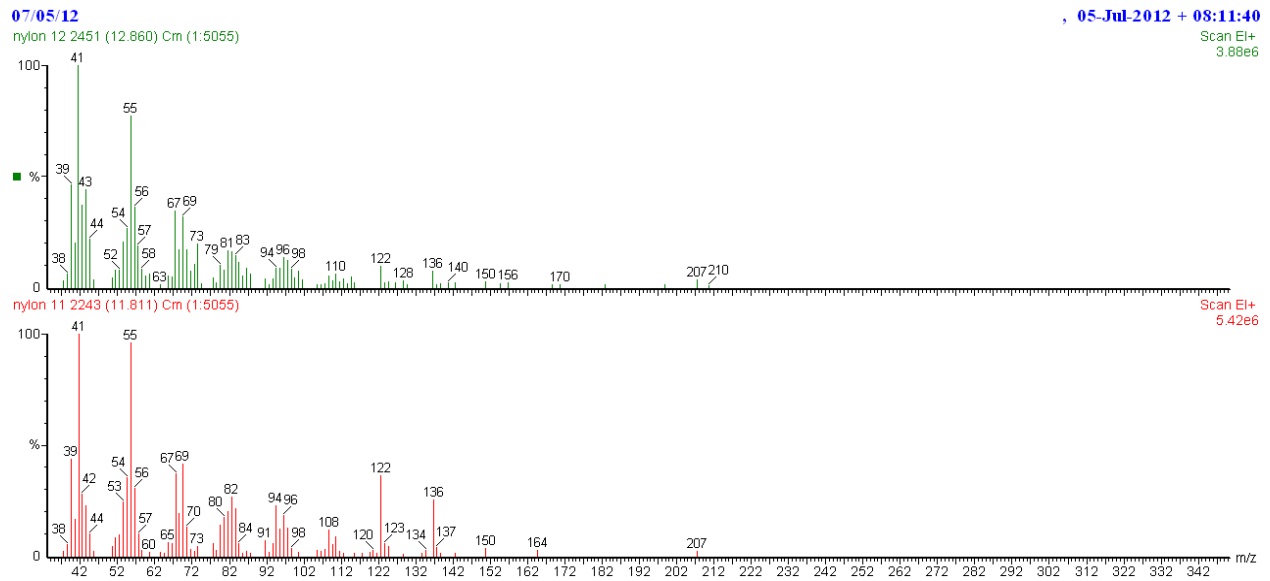


Figure 9. The combined mass spectra of nylon 11 and nylon 12.

Table 9. The major m/z ratios found in the mass spectra of nylon 11 and nylon 12.

Nylon 11	Nylon 12
41	41
55	55
69	67
82	81
94	96
-	122
-	136

Different IR spectra, similar pyrograms

Polyethylene. In some cases, the IR spectra may be more useful than the pyrograms. This can be seen in the low density polyethylene and oxidized polyethylene. The IR spectra of the two polymers are different in the region between 1000 cm^{-1} and 2000 cm^{-1} , as seen in Figure 10. Both polymers contain bands above 2000 cm^{-1} and below 1000 cm^{-1} at the same intensities, but the oxidized polyethylene has two bands that are not present in the low density polyethylene. The wavenumbers of these bands can be found in Table 10. The pyrograms of the two polymers are quite similar, with multiple peaks occurring about 1.0-1.5 minutes apart, as shown in Figure 11. For both polymers, the largest peak occurs at 1.69 minutes, followed by the peak at 6.80 minutes. The exact times of elution for each peak can be found in Table 11. The combined mass spectra for these two polyethylenes appear to be very similar, as shown in Figure 12. For both polymers, the m/z peak at 41 and 55 are the most abundant, followed by the m/z peak at 69, then 83, and then 97. The oxidized polyethylene does contain a very small m/z peak at 153, which is not present in the low density polyethylene. The major m/z ratios for low density polyethylene and oxidized polyethylene can be found in Table 12.

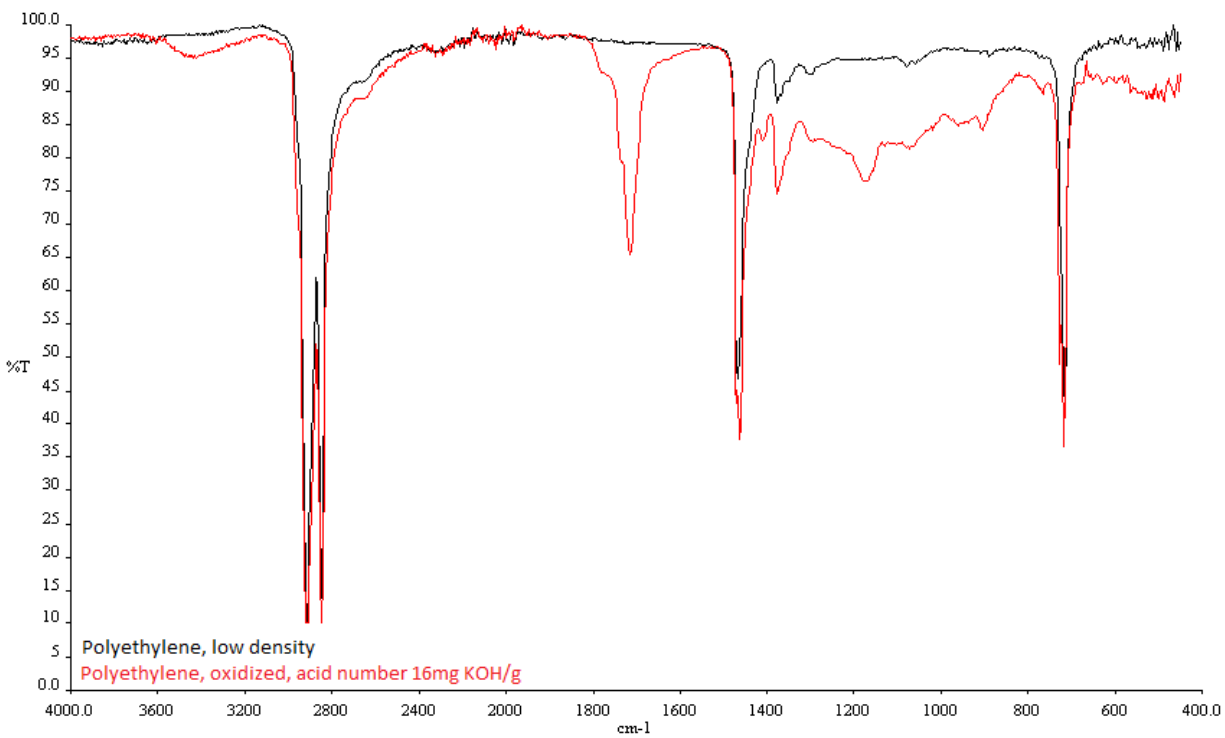


Figure 10. The IR spectra of low density polyethylene and oxidized polyethylene.

Table 10. The wavenumbers of major bands found in the IR spectra of low density polyethylene and oxidized polyethylene.

Polyethylene Low density	Polyethylene Oxidized
2913 cm ⁻¹	2913 cm ⁻¹
2845 cm ⁻¹	2845 cm ⁻¹
-	1714 cm ⁻¹
1465 cm ⁻¹	1462 cm ⁻¹
1376 cm ⁻¹	1376 cm ⁻¹
-	1172 cm ⁻¹
716 cm ⁻¹	718 cm ⁻¹

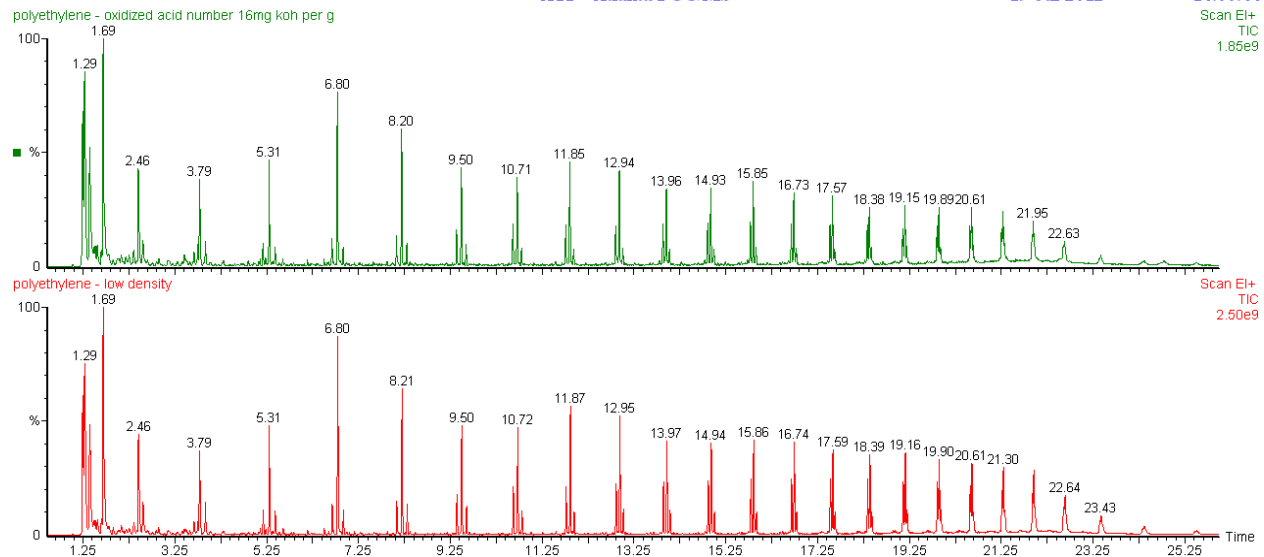


Figure 11. The pyrograms of low density polyethylene and oxidized polyethylene.

Table 11. The retention times of some peaks found in the pyrograms of low density polyethylene and oxidized polyethylene.

Polyethylene Low density	Polyethylene Oxidized
1.69 min.	1.69 min.
2.46 min.	2.46 min.
3.79 min.	3.79 min.
5.31 min.	5.31 min.
6.80 min.	6.80 min.
8.21 min.	8.20 min.
9.50 min.	9.50 min.
10.72 min.	10.71 min.
11.87 min.	11.85 min.
12.95 min.	12.94 min.
13.97 min.	13.96 min.
14.94 min.	14.93 min.
15.86 min.	15.85 min.
16.74 min.	16.73 min.
17.59 min.	17.57 min.
18.39 min.	18.38 min.
19.16 min.	19.15 min.
19.90 min.	19.89 min.
20.61 min.	20.61 min.
21.30 min.	21.29 min.
21.96 min.	21.95 min.
22.64 min.	22.63 min.
23.43 min.	23.42 min.
24.37min.	24.36 min.
-	24.80 min.
25.50 min.	25.50 min.

polyethylene - oxidized acid number 16mg koh per g 236 (1.690) Cm (1.5055)

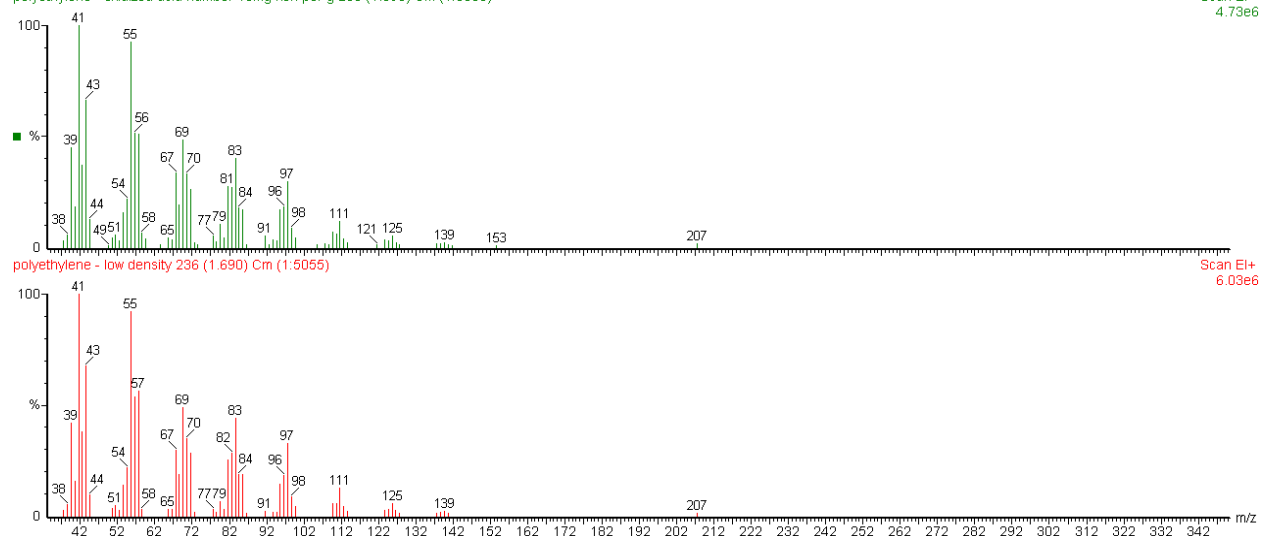
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4.73e6

Figure 12. The combined mass spectra of low density polyethylene and oxidized polyethylene.

Table 12. The major m/z ratios found in the mass spectra of low density polyethylene and oxidized polyethylene.

Polyethylene Low density	Polyethylene Oxidized
41	41
55	55
69	69
83	83
97	97
-	153

Different IR spectra, different pyrograms

Cellulose and Polystyrene. Some of the polymers have similar IR spectra and/or similar pyrograms, and these are usually samples that are similar in composition. As for polymers that are different in composition, their IR spectra and pyrograms will be different, which makes them easily distinguishable. A comparison of cellulose to polystyrene shows how both the IR spectra and pyrogram can be useful in differentiating between samples. As seen in Figure 13, the IR spectra of cellulose and polystyrene are very different from each other. Cellulose tends

to have peaks that are broad while polystyrene bands are sharp. The wavenumber of the bands for the two polymers can be found in Table 13. The pyrograms for the two samples are also different from each other, as seen in Figure 14. Polystyrene contains a very large peak at 5.35 minutes, which is absent in cellulose. Four peaks occurring at 6.66 minutes, 13.32 minutes, 15.27 minutes, and 16.80 minutes are not present in cellulose. Cellulose contains peaks at 6.57 minutes, 9.98 minutes, and 14.36 minutes that are not present in the polystyrene pyrogram. Also, in the cellulose pyrogram, the peak at 13.45 minutes is quite broad, and this is not seen in the polystyrene pyrogram. The peaks present in each sample are listed in Table 14. The combined mass spectra of these two samples are also quite different, as seen in Figure 15. Cellulose contains a major peak at the m/z of 60, while the major peak for polystyrene occurs at the m/z of 104. Cellulose also has m/z peaks at 44 and 73, both of which are at least 50% the abundance of the major peak. As for polystyrene, the m/z peaks that are at least 50% of the major peak occur at a m/z of 51, 78, and 91. The major m/z peaks for these two polymers can be found in Table 15.

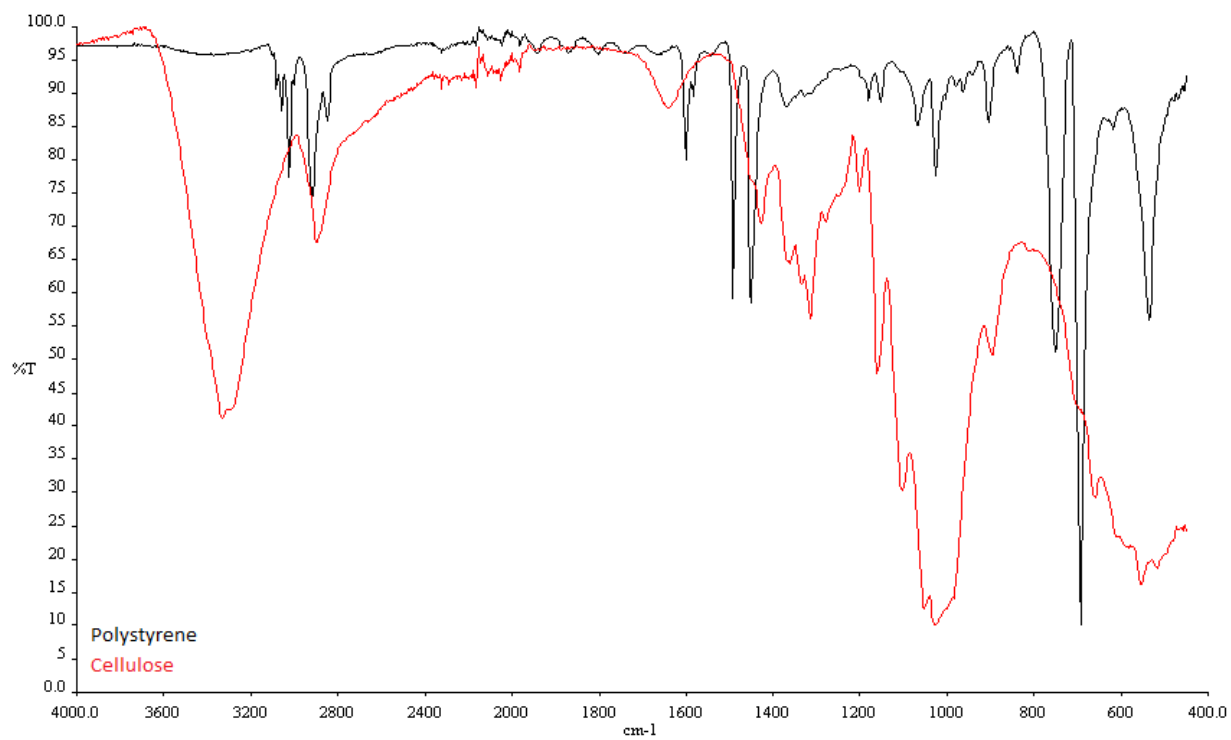


Figure 13. The IR spectra of cellulose and polystyrene.

Table 13. The wavenumbers of major bands found in the IR spectra of cellulose and polystyrene

Cellulose	Polystyrene
3327 cm^{-1}	3025 cm^{-1}
2896 cm^{-1}	2918 cm^{-1}
1426 cm^{-1}	1601 cm^{-1}
1314 cm^{-1}	1492 cm^{-1}
1160 cm^{-1}	1451 cm^{-1}
1102 cm^{-1}	1027 cm^{-1}
1026 cm^{-1}	905 cm^{-1}
895 cm^{-1}	753 cm^{-1}
660 cm^{-1}	694 cm^{-1}
556 cm^{-1}	537 cm^{-1}

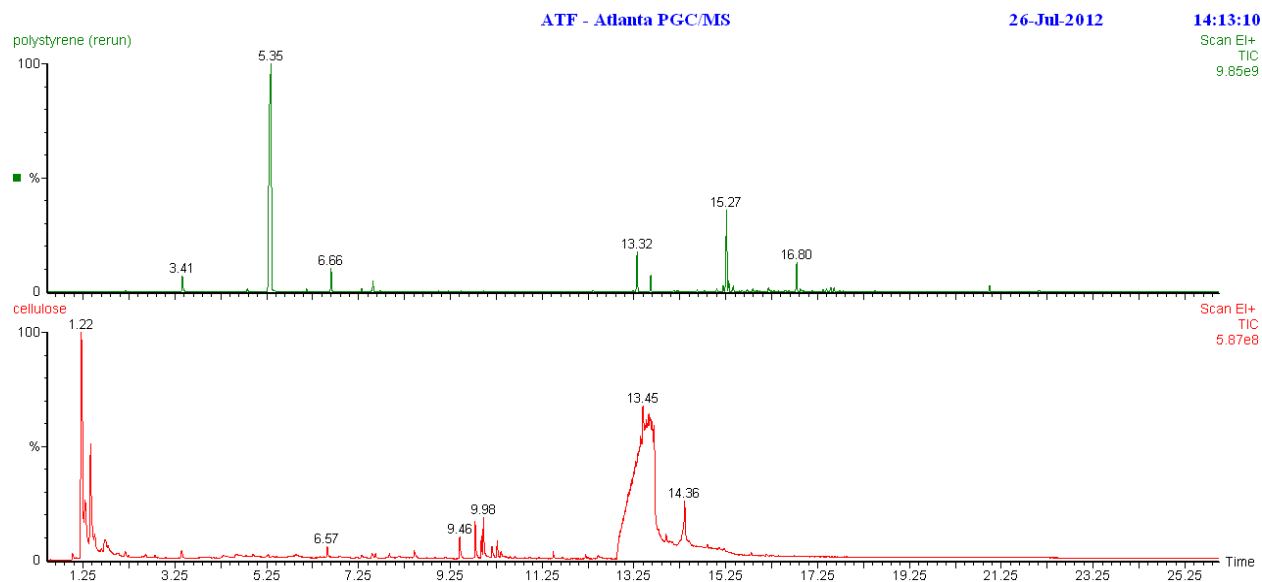


Figure 14. The pyrograms of cellulose and polystyrene.

Table 14. The retention times of the peaks found in the pyrograms of cellulose and polystyrene.

Cellulose	Polystyrene
1.22 min.	3.41 min.
6.57 min.	5.35 min.
9.98 min.	6.66 min.
13.45 min.	13.32 min.
14.36 min.	15.27 min.
	16.80 min.

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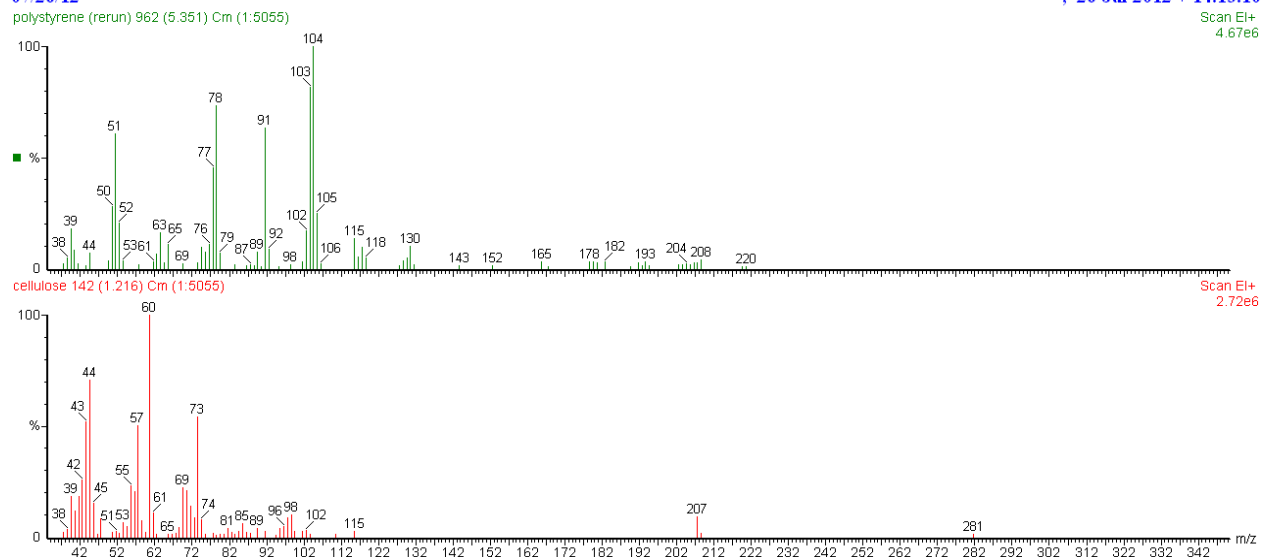


Figure 15. The combined mass spectra of cellulose and polystyrene.

Table 15. The major m/z ratios found in the mass spectra of cellulose and polystyrene.

Cellulose	Polystyrene
44	51
60	78
73	91
	104

Identifying certain compounds in a pyrogram. Certain compounds can be identified within a pyrogram, which is useful when the sample being analyzed is a mixture. This can be seen in samples containing styrene. Comparisons of the IR spectra, pyrograms, and combined mass spectra were conducted on three samples containing styrene: polystyrene, styrene/butadiene copolymer, and styrene/isoprene copolymer. The IR spectra of all three polymers are provided in Figure 16. All three polymers contain a bands at about 2900 cm^{-1} , but their intensities vary due to the different amounts of hydrocarbons present in each polymer, with the styrene/isoprene copolymer having a greater intensity than the other two polymers. The

styrene/isoprene copolymer also shows bands at 1450 cm^{-1} , 1375 cm^{-1} , 892 cm^{-1} , and 837 cm^{-1} at greater intensities than the other two polymers. As for the styrene/butadiene copolymer, it has more intense bands at 964 cm^{-1} and 910 cm^{-1} , which are less intense than the styrene/isoprene copolymer and polystyrene standards. When these same samples were run on the Py-GC/MS, the pyrograms produced were quite different, as seen in Figure 17. All three pyrograms contain a prominent peak at 5.30 minutes, the peak for styrene. This was confirmed through a search of the mass spectrum of that peak in the various samples containing styrene. The polymers can be differentiated due to the other peaks present in each of the pyrograms. Polystyrene contains three peaks after 13.00 minutes, which are not present in the other two polymers. The styrene/isoprene copolymer is the only sample that has a peak at 1.42 minutes and 7.35 minutes whereas styrene/butadiene copolymer is the only sample that has a peak at 1.28 minutes and 4.43 minutes. The combined mass spectra for all three polymers contain m/z peaks that identify the styrene in the sample. As seen in Figure 18, all three polymers have m/z peaks of 104, 91, 78, and 51, which are characteristic of styrene. The other m/z peaks in the mass spectra are due to the other compounds present in the polymer.

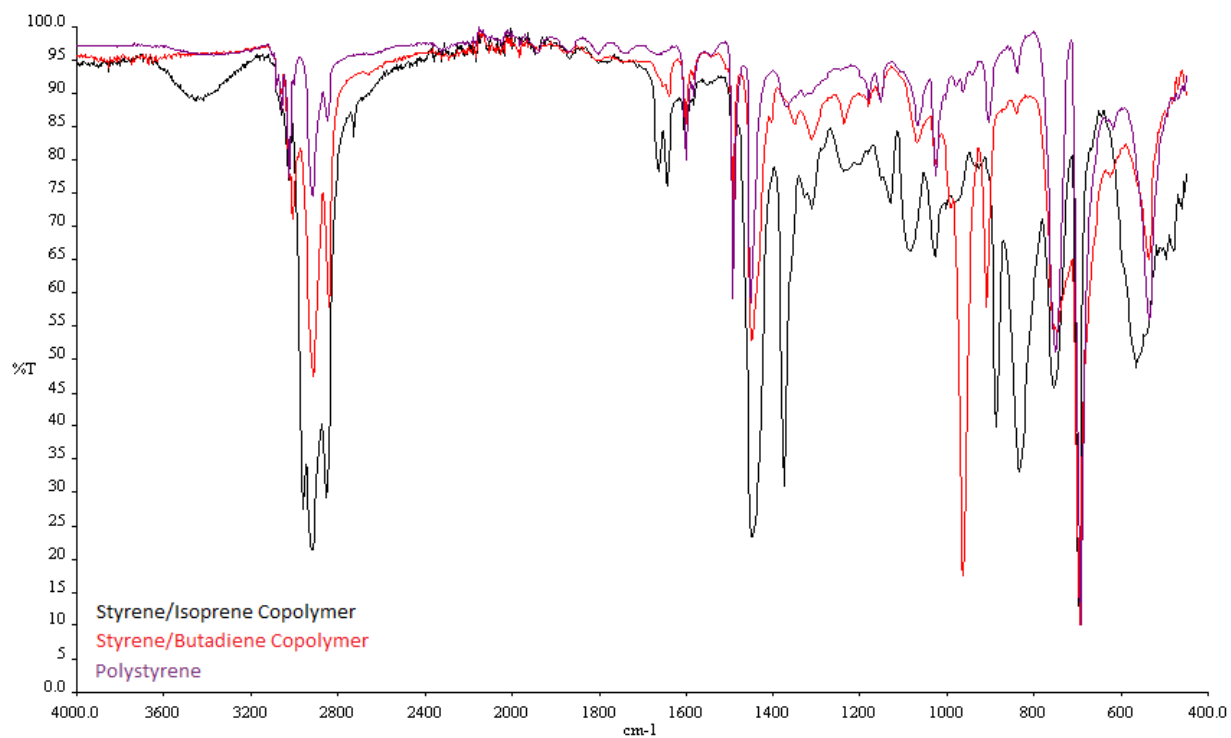


Figure 16. The IR spectra of polystyrene, styrene/butadiene copolymer, and styrene/isoprene copolymer.

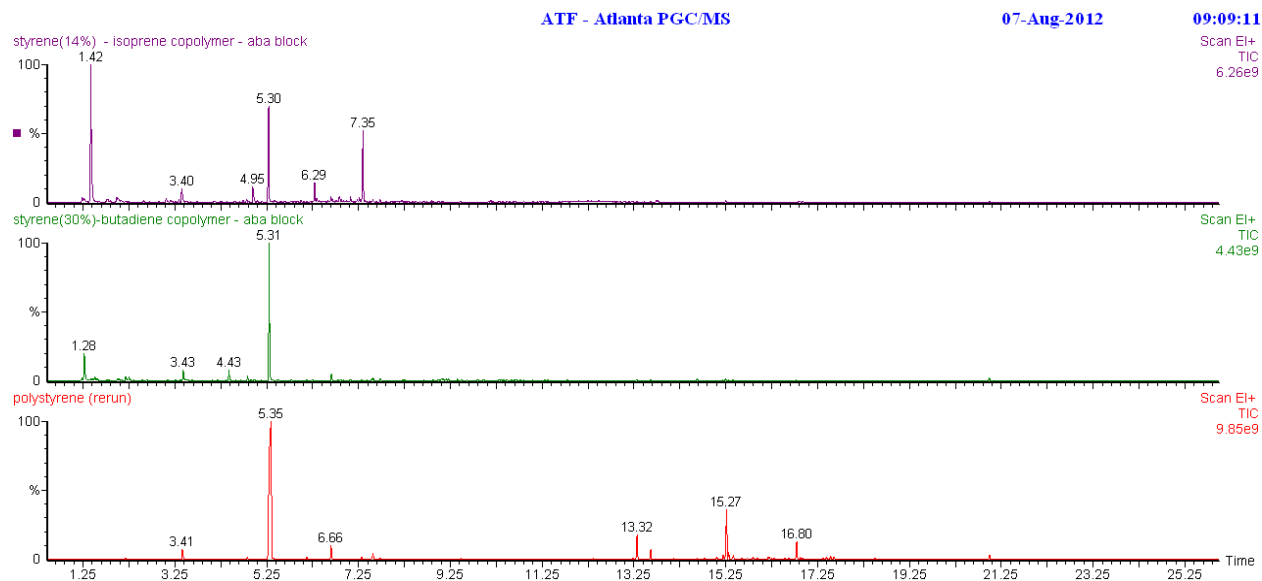


Figure 17. The pyrograms of polystyrene, styrene/butadiene copolymer, and styrene/isoprene copolymer.

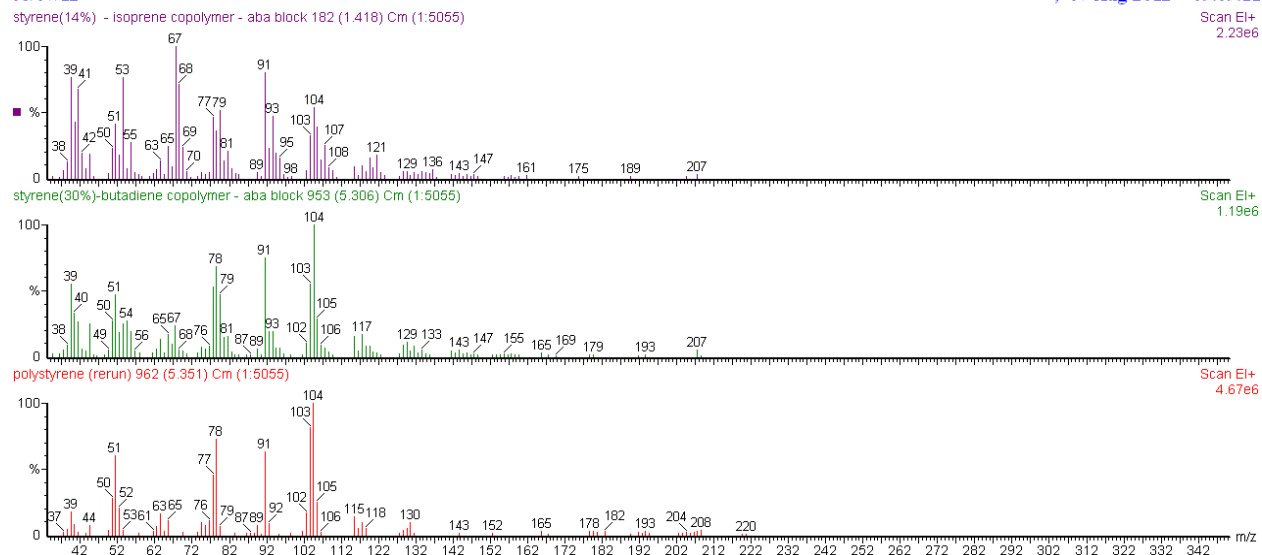


Figure 18. The combined mass spectra of polystyrene, styrene/butadiene copolymer, and styrene/isoprene copolymer.

Tire Rubber Test Sample. A tire tread rubber sample was run on the FTIR and the Py-GC/MS to test the discriminating power of the two instruments when a sample of unknown composition is analyzed. The tire tread rubber was difficult to identify using FTIR due to the carbon black pigment. When the tire tread rubber IR spectra was searched against the SP² polymer library, the top three matches were hydroxypropyl methyl cellulose (10% hydroxypropyl, 30% methoxyl), methyl cellulose, and hydroxypropyl cellulose. The IR spectrum of the tire tread rubber and the IR spectrum of hydroxypropyl methyl cellulose are quite different, as shown in Figure 19. However, when the tire tread rubber was run on the Py-GC/MS, it was easily identifiable as a styrene/butadiene copolymer using the pyrograms and combined mass spectra produced. The pyrogram and the combined mass spectrum of the tire tread rubber along with the pyrograms and combined mass spectra of three polymers containing styrene: polystyrene, styrene/butadiene copolymer, and styrene/isoprene copolymer, are found in Figures 20 and 21.

Both the tire tread rubber and the styrene/butadiene copolymer contain peaks at 1.28 minutes, which is absent in the styrene/isoprene copolymer and polystyrene pyrograms. Also, both samples contain peaks at about 3.40 minutes and 4.40 minutes. The polystyrene pyrogram contains peaks after 13.00 minutes, while the other three pyrograms do not, eliminating the polystyrene as a match to the tire tread rubber. The styrene/isoprene copolymer has a peak at 7.35 minutes, which is not present in the other three pyrograms, eliminating that as a match to tire tread rubber. The other peaks present in the tire tread rubber not present in the styrene/butadiene copolymer pyrogram are most likely due to the additives present in the tire tread rubber. As for the pyrogram comparison, the m/z peak at 67 shows greater abundance in the styrene/isoprene copolymer combined mass spectrum than in the tire tread rubber combined mass spectrum. Also, the tire tread rubber and the styrene/butadiene combined mass spectra contains a m/z peak at 39 with an abundance greater than 50%, while the same m/z peak in the polystyrene combined mass spectrum is less than 50% abundance. It was concluded that the tire tread rubber most closely matches the styrene/butadiene copolymer. A software search against a previously developed Py-GC/MS library was also performed on the tire tread rubber, and the closest match was a polystyrene/butadiene copolymer. As shown in Figure 22, the combined mass spectra of the two samples are quite similar, with the largest m/z peak at 91, and a few large peaks at m/z of 39, 77-79, and 104. As shown in Figure 23, the top matches were all polymers containing styrene and butadiene, indicating that those polymers are present in the tire tread rubber.

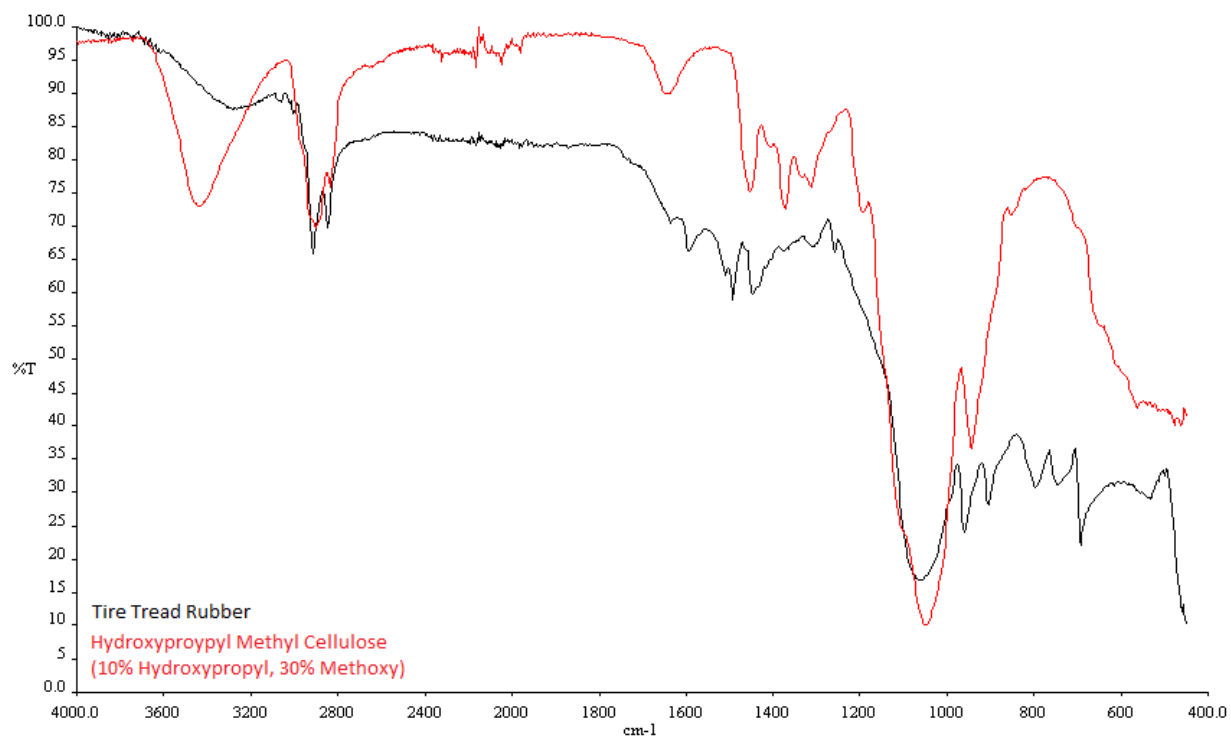


Figure 19. The IR spectra of tire tread rubber and hydroxypropyl methyl cellulose.

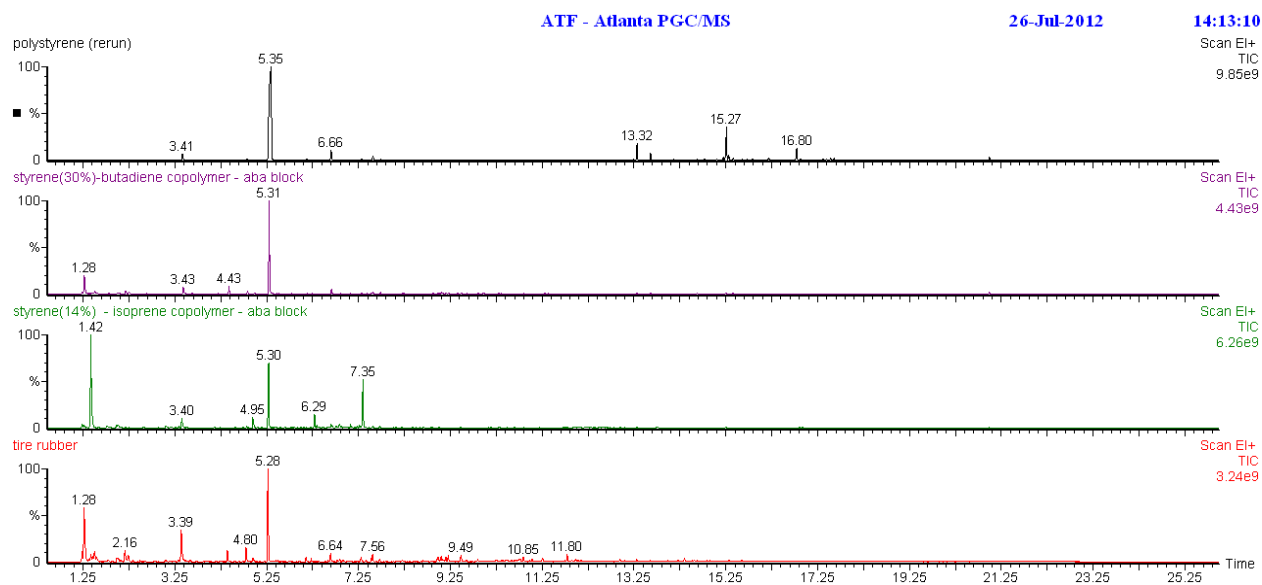


Figure 20. The pyrogram of tire tread rubber, polystyrene, styrene/butadiene copolymer, and styrene/isoprene copolymer.

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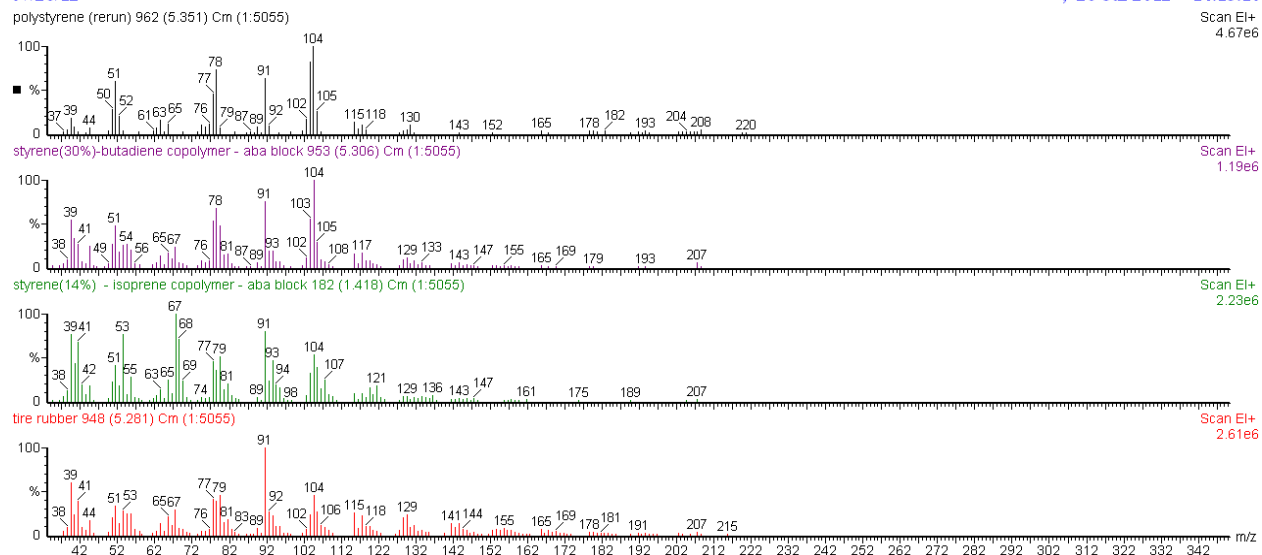


Figure 21. The combined mass spectra of the tire tread rubber, polystyrene, styrene/butadiene copolymer, and styrene/isoprene copolymer.

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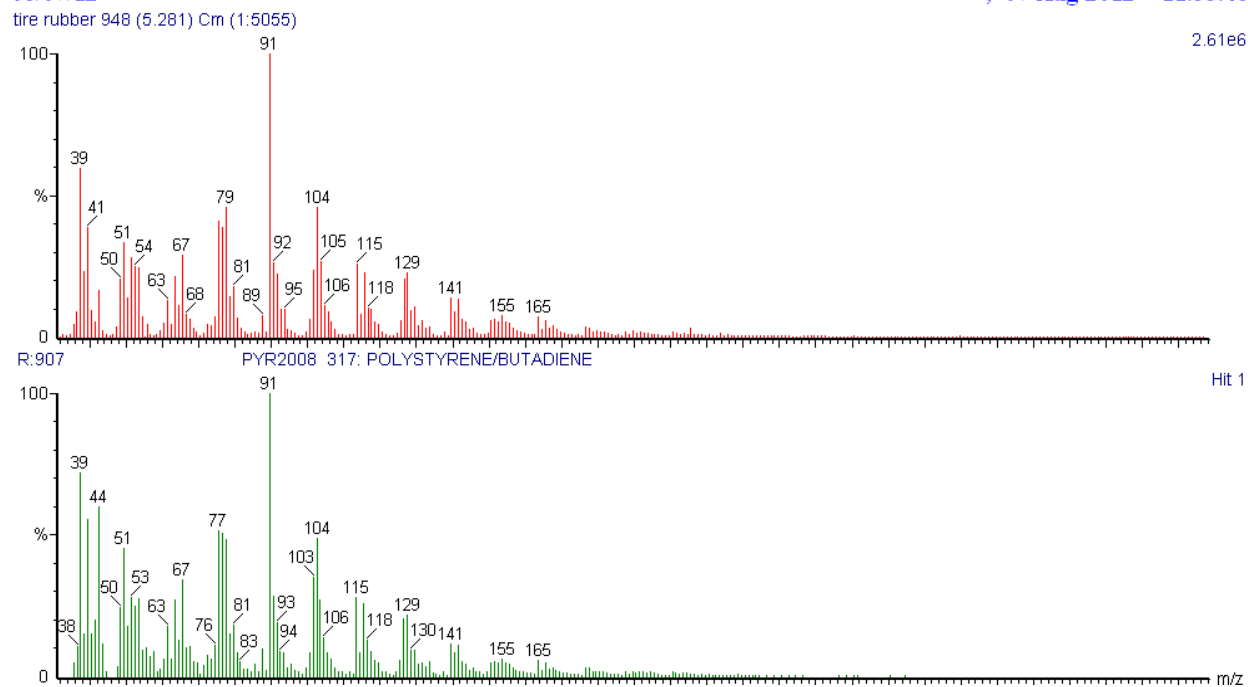


Figure 22. The combined mass spectrum match of the tire tread rubber when a library search was performed.

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Hit	REV	for	Compound Name	M.W.	Formula	CAS
1	907	883	POLYSTYRENE/BUTADIENE	0		0-00-0
2	892	799	POLYSTYRENE(28%)/BUTADIENE (72%)	0		0-00-0
3	887	846	Acrylonitrile/Butadiene/Styrene resin	0		0-00-0
4	885	761	POLY METHYL METHACRYLATE/BUTADIENE/STYRENE	0		0-00-0
5	876	820	STYRENE/BUTADIENE/METHYL METHACRYLATE	0		0-00-0
6	843	654	POLYSTYRENE/BUTADIENE (SBS)	0		0-00-0
7	837	774	Styrene(30%)-butadiene copolymer - ABA Block	0		0-00-0
8	827	727	PVC/STYRENE/MMA	999		0-00-0
9	821	705	STYRENE/BUTADIENE ADHESIVE	0		0-00-0
10	798	540	PHOTOCOPIY TONER (COLOR)	0		0-00-0
11	793	730	STYRENE/BUTADIENE/METHYL METHACRYLATE	0		0-00-0
12	766	516	PVC/STYRENE/MMA	0		0-00-0
13	764	475	STYRENE BUTYL ACRYLATE	999		0-00-0
14	751	485	POLYSTYRENE ACRYLONITRILE	0		0-00-0
15	742	555	TONER, PHOTOCOPIY	999		0-00-0
16	741	605	PACKAGING, CLEAR, WITH PHTHALATE	999		0-00-0
17	741	523	POLYVINYL CHLORIDE	0		0-00-0
18	740	674	POLYSTYRENE/ISOPRENE/BUTADIENE	0		0-00-0
19	736	421	POLYSTYRENE	0		0-00-0
20	728	455	HIGH IMPACT POLYSTYRENE	0		0-00-0

Figure 23. The list of matches to the tire tread rubber when a library search was performed on the combined mass spectra.

Development of FTIR Library. An IR library was created using the IR spectra of the 100 SP² polymer standards. The polymer sample list of the SP² polymer sample kit #205 can be found in Appendix I. A few samples from the SP² Polymer Kit #205 were run and searched against the library created to ensure that the library searches worked correctly and samples could be correctly identified. Once it was confirmed that the IR library correctly identified the polymers, the IR library was shared with other ATF laboratories, and they have reported that it has been very useful for them. The cover page to the FTIR library instructions and spectra can be found in Appendix II.

Development of Py-GC/MS Library. A software searchable pyrolysis combined spectra library was also compiled. The pyrograms of the polymers were searched against a previously developed Py-GC/MS library, and it was found that the library could correctly identify various polymer samples. A tire tread rubber sample was searched against the CDS Py-GC/MS library and was identified as a styrene/butadiene copolymer. The combined mass spectrum of the tire

rubber was added to a previously developed Py-GC/MS library and a search of the tire tread rubber combined mass spectra was performed. The top match was the tire tread rubber combined mass spectra, which shows that the Py-GC/MS library can correctly identify pyrolyzed samples. After creating a combined mass spectra of each polymer that were run on the Py-GC/MS, the combined mass spectra were added to an existing CDS Analytical Pyrolysis Library, PYRO2008, and a new pyrolysis library was developed.

Discussion

For reasons unknown, some polymer samples contained talc and kaolinite, inorganic constituents that are not characteristic of the polymer itself, which contribute bands in the spectra and may cause incorrect identification of the organic polymer by FTIR. In the 25% chlorinated polyethylene, 42% chlorinated polyethylene, and chlorosulfonated polyethylene samples, talc, was identified with bands at 3676 cm^{-1} , 1016 cm^{-1} , and 668 cm^{-1} . In the 36% chlorinated polyethylene sample, kaolinite was identified with the bands at 3692 cm^{-1} , 3619 cm^{-1} , 1090 cm^{-1} , 1029 cm^{-1} , 1006 cm^{-1} , 913 cm^{-1} , 536 cm^{-1} , and 467 cm^{-1} . This was determined by comparing the samples to the talc and the kaolinite IR spectra that were run previously. The IR spectra for these samples, with the bands identifying the inorganic constituents can be found in the figures in Appendix III.

The IR spectra were all normalized to 1.0 in order to produce IR spectra that were comparable to each other based on the intensity of the bands. The intensity of the bands reflects the relative amount of a certain molecule present in the sample, which can be useful in identifying and differentiating between samples. The IR spectra were displayed in percent transmittance mode, which allows for some of the smaller bands to be more prominent compared to the

absorbance view. The small bands are useful in the identification and comparison of samples, and when displayed in absorbance, some of these peaks may be overlooked.

Analysis of samples using Py-GC/MS provides information on the organic components. It removes any inorganic component in the polymer samples that may have masked the organic compounds in the FTIR analysis, and may help detect a minor organic component in a copolymer mix. Even though some samples produce similar IR spectra and pyrograms, other samples can be easily differentiated using either the IR spectra or pyrogram or both. However, pyrograms produced can vary based on the chromatographic conditions (eg. column, program parameters, etc), resulting in pyrograms containing peaks at different retention times. This creates difficulties when comparing the patterns of peaks in the pyrograms and prevents pyrograms from being searched against a library. While the mass spectrum of the individual peaks can be searched against a library, this can be a difficult and time consuming process, especially when a pyrogram contains multiple peaks.

A combined mass spectrum eliminates the problems mentioned above since the combined mass spectrum is independent of the chromatographic conditions of the instrument. The mass spectrometer's data analysis software produces a single combined mass spectrum of the sample by taking the average of the mass spectra of all the individual scans of the pyrogram. The combined mass spectrum can be added to an existing library or used to create a new library. A search of the combined mass spectrum, which is characteristic to that polymer, can be conducted just like the search of the mass spectrum of individual peaks, which is characteristic of individual molecules. A library

search of a SP² polymer against the CDS Analytical Pyrolysis Library created years ago with different chromatographic conditions showed that the combined mass spectrum can be used to correctly identify samples, even though the chromatographic conditions were different. This can be seen when comparing Figures 20 and 21 to the pyrograms and mass spectra of polystyrene and styrene/butadiene copolymer, found in Appendix IV.

The Py-GC/MS program used in this analysis had a total run time of 26.00 minutes. A blank, which used the same program, was run in between samples. Including the time it takes to cool the oven down before starting the next run, it took 1.5 hours to run one polymer standard. A number of samples, especially the polyethylene samples, did not completely elute off the column during the run, either because the temperature wasn't high enough or the run wasn't long enough. In order to remove the compounds in these samples, the column was heated by bringing the oven temperature up to 290°C for a period of time, which prolonged analysis time. Due to the long time required to run each sample and the limited time available to run all 100 polymer standards, the Py-GC/MS analysis of all the samples was not completed. Towards the end, only samples that are more commonly found in forensic case samples were selected to be analyzed. Some standards in the polymer kit contained the same components but in different percentages, and for these samples, only part of the group was run, as differences between the samples are likely to be very small. Polymers were selected this way in order to run as many different samples as possible in the limited time available.

Certain samples analyzed on the Py-GC/MS contained a large peak usually at the beginning of the run. At times this peak is so large that it suppresses the peaks that can be used to

characterize the sample, but the pyrogram can be expanded to show the suppressed peaks that characterize the polymer sample.

Conclusions and Future Needs (Add Budget for Grant Proposal)

A searchable FTIR library of the 100 SP² polymer standards was successfully created and was shared with the other ATF laboratories. A few of the samples contained inorganic constituents, talc and kaolinite, which were a component of the standard, which may cause some confusion or misidentification. Pyrograms and combined mass spectra of 77 (out of 100) SP² polymer standards were created and are being added to the existing CDS library, as well as a new library with the data generated in this study. Py-GC/MS analysis provides additional information and should be used as a complementary analysis method to FTIR, since organic constituents in samples may be masked by the inorganic constituents in the IR spectra. The combined mass spectra of polymer standards proved to be a very useful tool, in addition to the IR spectra and pyrograms, for the characterization and identification of polymer samples. Software searchable libraries created with the IR spectra and the combined mass spectra can be very useful tools in assisting forensic scientists with the identification of forensic case samples, but should not, in any way, replace the visual comparisons of the spectra. As additional polymer standards and commonly encountered forensic case samples are added to the FTIR and the Py-GC/MS libraries, the capability of the identification of unknown samples will be greatly enhanced. Also, duplicate or triplicate runs of selected polymers should be conducted to ensure that the resulting spectra and pyrograms are reproducible of the standards analyzed minimizing incorrect identifications.

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Sp²TECHNICAL
BULLETIN

SCIENTIFIC POLYMER PRODUCTS, INC.

POLYMER SAMPLE KIT.
CATALOG NO. 205
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Convenient for reference samples, analytical studies and small scale evaluations. The following items are contained in this kit. For your convenience samples listed below are in alphabetical order and may be readily identified in the kit by the cap number. Detailed information on these materials can be found in the SP² catalog.

Cap No.	Cat No.	Polymer	Cap No.	Cat No.	Polymer
1	051	Acrylonitrile/butadiene/styrene resin	53	185	Polyethylene, chlorinated, 36% chlorine
2	032	Alginic acid, sodium salt	54	186	Polyethylene, chlorinated, 42% chlorine
3	209	Butyl methacrylate/isobutyl methacrylate copolymer	55	107	Polyethylene, chlorosulfonated
4	660	Cellulose	56	041	Polyethylene, high density
5	083	Cellulose acetate	57	042	Polyethylene, low density
6	077	Cellulose acetate butyrate	58	405	Polyethylene, oxidized, Acid number 16 mg KOH/g
7	321	Cellulose propionate	59	136A	Poly(ethylene oxide)
8	031	Cellulose triacetate	60	138	Poly(ethylene terephthalate)
9	142	Ethyl cellulose	61	414	Poly(2-hydroxyethyl methacrylate)
10	534	Ethylene/acrylic acid copolymer, 15% acrylic acid	62	112	Poly(isobutyl methacrylate)
11	454	Ethylene/ethyl acrylate copolymer, 18% ethyl acrylate	63	106	Polyisoprene, chlorinated
12	939	Ethylene/methacrylic acid copolymer, 12% methacrylic acid	64	037A	Poly(methyl methacrylate)
13	358	Ethylene/propylene copolymer, 60% ethylene	65	382	Poly(4-methyl-1-pentene)
14	243	Ethylene/vinyl acetate copolymer, 14% vinyl acetate	66	391	Poly(p-phenylene ether-sulphone)
15	244	Ethylene/vinyl acetate copolymer, 18% vinyl acetate	67	090	Poly(phenylene sulfide)
16	245	Ethylene/vinyl acetate copolymer, 25% vinyl acetate	68	130	Polypropylene, isotactic
17	316	Ethylene/vinyl acetate copolymer, 28% vinyl acetate	69	039A	Polystyrene
18	246	Ethylene/vinyl acetate copolymer, 33% vinyl acetate	70	046	Polysulfone
19	326	Ethylene/vinyl acetate copolymer, 40% vinyl acetate	71	203	Poly(tetrafluoroethylene)
20	959	Ethylene/vinyl alcohol copolymer, 38% ethylene	72	166	Poly(2,4,6-tribromostyrene)
21	143	Hydroxyethyl cellulose	73	024	Poly(vinyl acetate)
22	401	Hydroxypropyl cellulose	74	002	Poly(vinyl alcohol), 99.7% hydrolyzed
23	423	Hydroxypropyl methyl cellulose, 10% hydroxypropyl, 30% methoxyl	75	352	Poly(vinyl alcohol), 98% hydrolyzed
24	144	Methyl cellulose	76	043	Poly(vinyl butyral)
25	374	Methyl vinyl ether/maleic acid copolymer, 50/50 copolymer	77	038	Poly(vinyl chloride)
26	317	Methyl vinyl ether/maleic anhydride, 50/50 copolymer	78	353	Poly(vinyl chloride), carboxylated, 1.8% carboxyl
27	034	Nylon 6 [Poly(caprolactam)]	79	012	Poly(vinyl formal)
28	331	Nylon 6(3)T [Poly(trimethylhexamethylene terephthalamide)]	80	102	Poly(vinylidene fluoride)
29	033	Nylon 6/6 [Poly(hexamethylene adipamide)]	81	132	Polyvinylpyrrolidone
30	156	Nylon 6/9 [Poly(hexamethylene azelamide)]	82	103	Poly(vinyl stearate)
31	313	Nylon 6/12 [Poly(hexamethylene dodecanediamide)]	83	494	Styrene/acrylonitrile copolymer, 25% acrylonitrile
32	006	Nylon 11 [Poly(undecanoamide)]	84	495	Styrene/acrylonitrile copolymer, 32% acrylonitrile
33	044	Nylon 12 [Poly(lauryllactam)]	85	393	Styrene/allyl alcohol copolymer, 5.4-6.0% hydroxyl
34	045A	Phenoxy resin	86	057	Styrene/butadiene copolymer, ABA block, 30% styrene
35	009	Polyacetal	87	595	Styrene/butyl methacrylate copolymer
36	001	Polyacrylamide	88	452	Styrene/ethylene-butylene copolymer, ABA block, 29% styrene
37	376	Polyacrylamide, carboxyl modified, low carboxyl content	89	178	Styrene/isoprene copolymer, ABA block, 14% styrene
38	377	Polyacrylamide, carboxyl modified, high carboxyl content	90	049	Styrene/maleic anhydride copolymer, 50/50 copolymer
39	026	Poly(acrylic acid)	91	068	Vinyl chloride/vinyl acetate copolymer, 10% vinyl acetate
40	385	Polyamide resin	92	063	Vinyl chloride/vinyl acetate copolymer, 12% vinyl acetate
41	688	1,2-Polybutadiene	93	070	Vinyl chloride/vinyl acetate copolymer, 17% vinyl acetate
42	128	Poly(1-butene), isotactic	94	422	Vinyl chloride/vinyl acetate/maleic acid terpolymer
43	961	Poly(butylene terephthalate)	95	911	Vinyl chloride/vinyl acetate/hydroxypropyl acrylate, 80% vinyl chloride, 5% vinyl acetate
44	111	Poly(n-butyl methacrylate)	96	064	Vinyl chloride/vinyl acetate/vinyl alcohol, 91% vinyl chloride, 3% vinyl acetate
45	952	Polycaprolactone	97	395	Vinylidene chloride/acrylonitrile copolymer, 20% acrylonitrile
46	035	Polycarbonate	98	058	Vinylidene chloride/vinyl chloride copolymer, 5% vinylidene chloride
47	196	Polychloroprene	99	369	n-Vinylpyrrolidone/vinyl acetate copolymer, 60/40 copolymer
48	010	Poly(diallyl phthalate)	100	021	Zein, purified
49	126	Poly(2,6-dimethyl-p-phenylene oxide)			
50	324	Poly(4,4'-dipropoxy-2,2'-diphenyl propane fumarate)			
51	113	Poly(ethyl methacrylate)			
52	184	Polyethylene, chlorinated, 25% chlorine			

FTIR-ATR Library of SP² Polymers – Kit #205

Attached is a hard copy of the infrared spectra of the 100 polymer samples obtained from the Scientific Polymer Products, Inc. (SP²) Polymer Sample Kit, Catalog No. 205. The spectra were collected using a PerkinElmer FTIR employing a Golden Gate Single Reflection ATR accessory. The polymer sample was placed on the diamond face and pressed down with the bridge anvil to obtain imminent contact. Eight scans were collected at a 4.00cm⁻¹ resolution and each spectrum was normalized to an absorbance of 1.0. The CD that is included contains both the PerkinElmer IR library and the Nicolet IR library. The CD also contains the raw spectra from which the library was created. This library can be loaded onto your FTIR and can be electronically searched against unknown samples. The Py-GCMS library of these samples will be provided at a later date.

Samples were collected by Shaina Chang, Summer Intern from Marshall University, under the direction of Forensic Chemist Thomas Hopen.

Note: Sample names in library may not exactly match the sample name in the catalog list due to insufficient space when adding the sample into the library. Consult the attached list from SP² for a complete description of the material.

Any questions, please contact:

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Appendix III

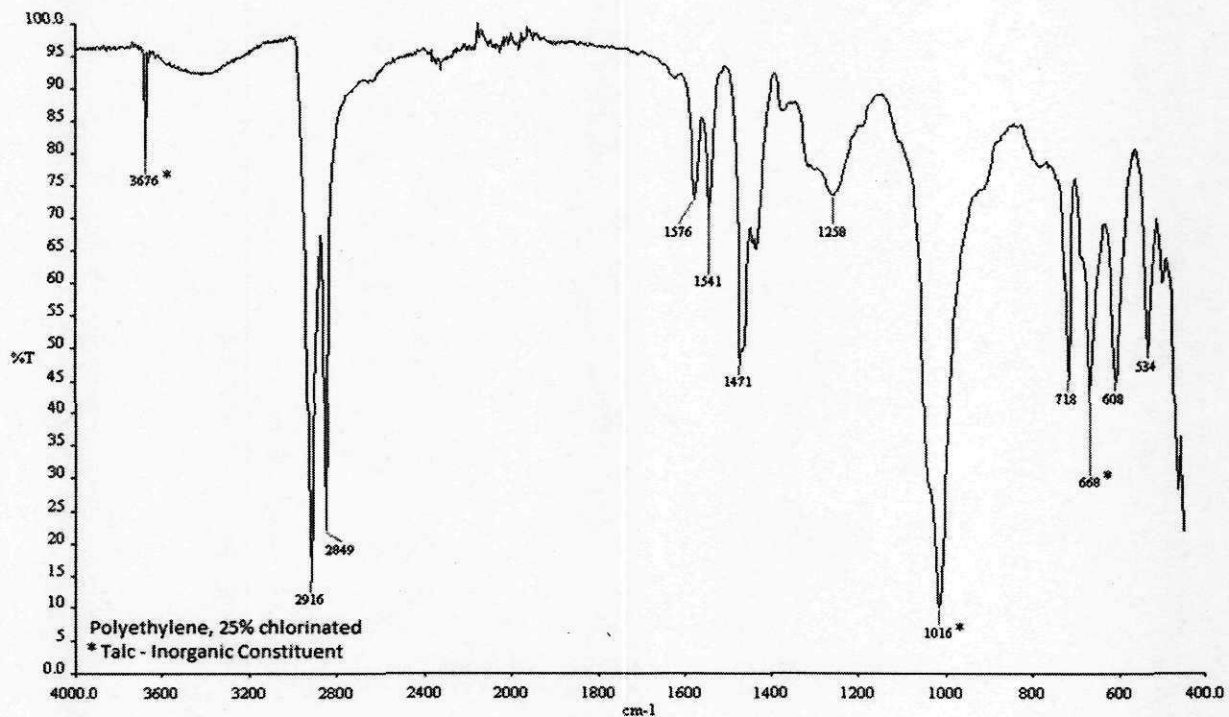


Figure 1. The IR spectrum of 25% chlorinated polyethylene with the inorganic constituent Talc.

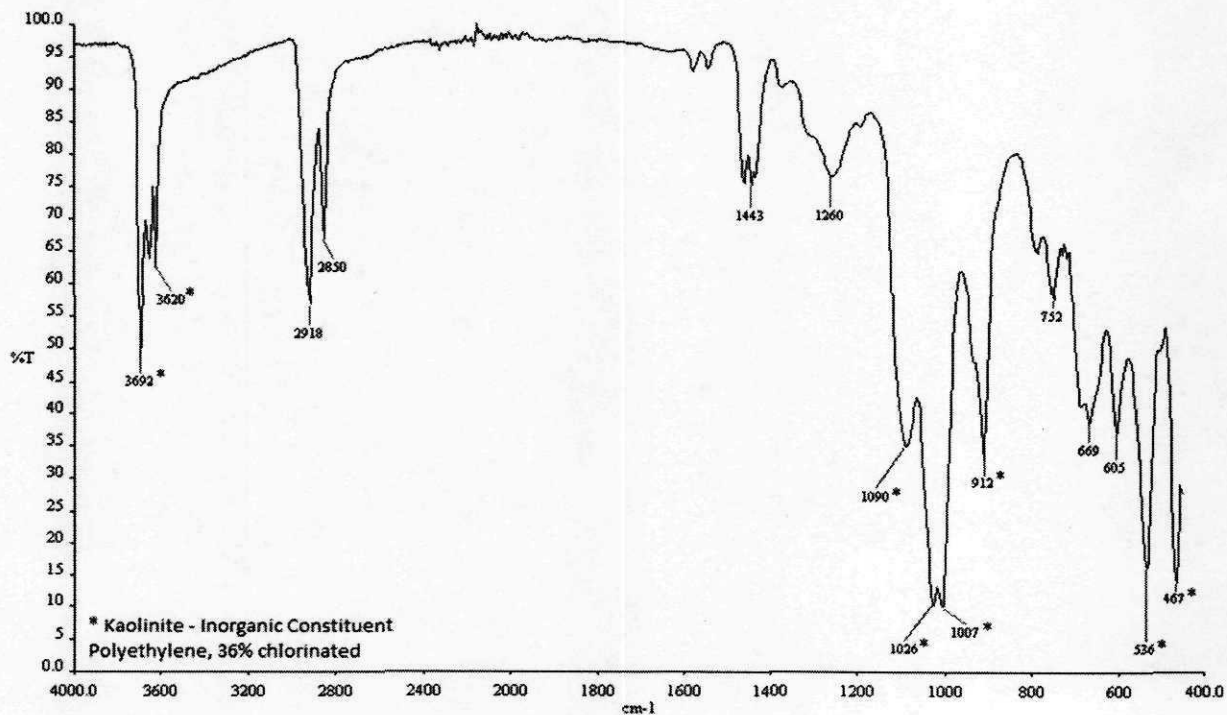


Figure 2. The IR spectrum of 36% chlorinated polyethylene with the inorganic constituent Kaolinite.

Appendix III continued

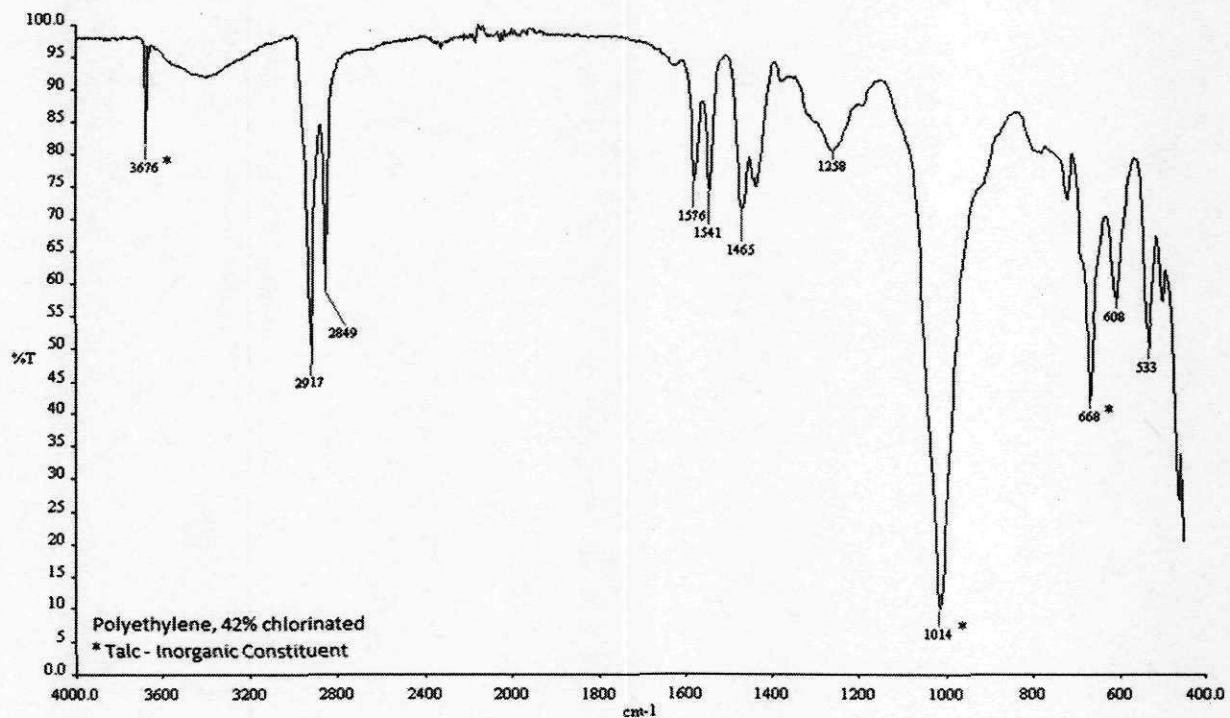


Figure 3. The IR spectrum of 42% chlorinated polyethylene with the inorganic constituent Talc.

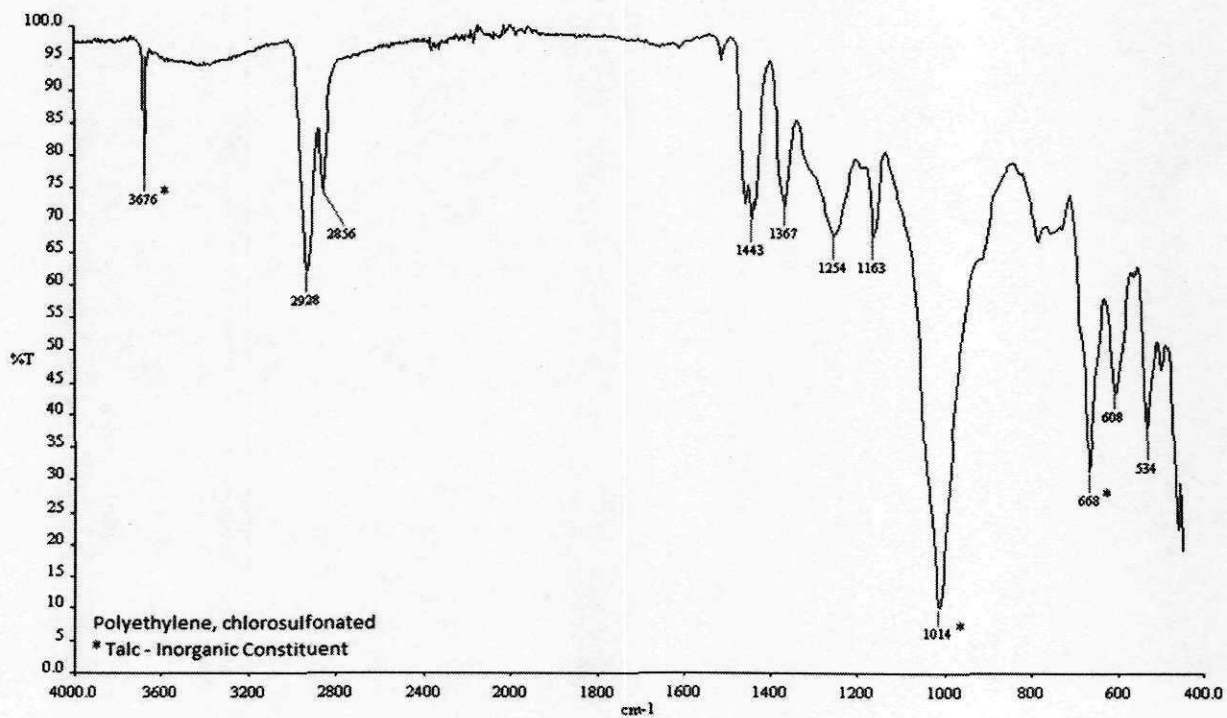
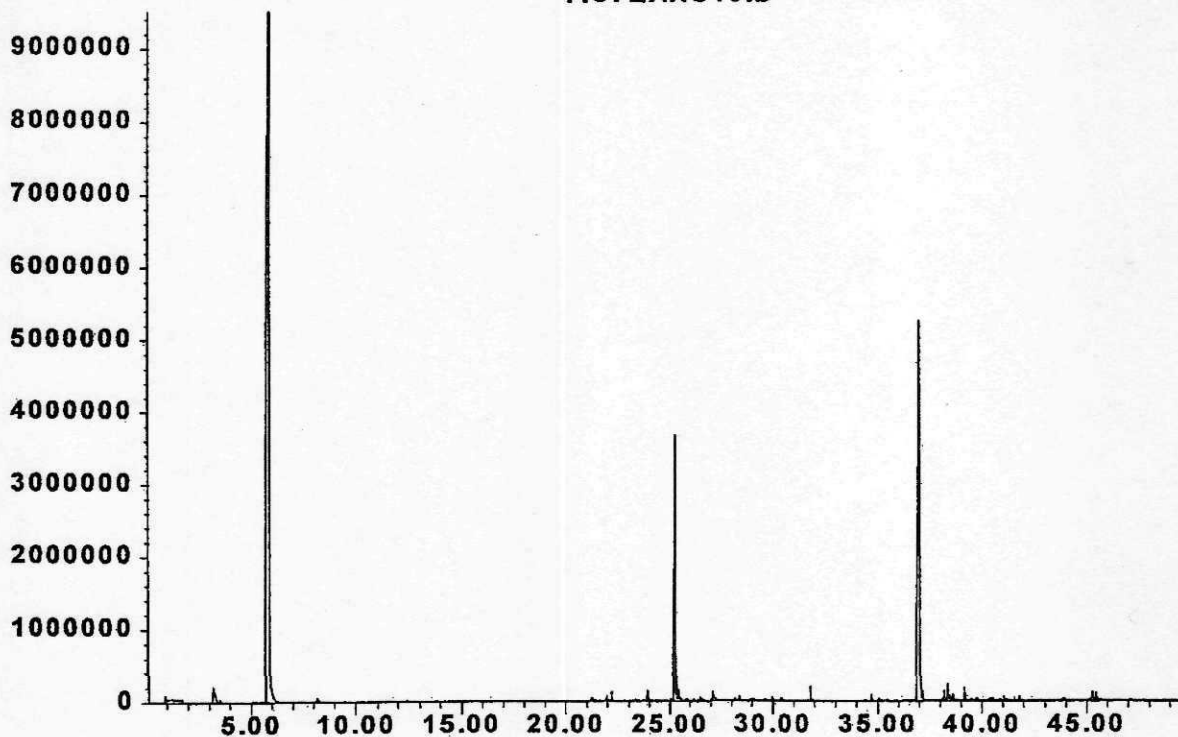


Figure 4. The IR spectrum of chlorosulfonated polyethylene with the inorganic constituent Talc.

Poly Styrene

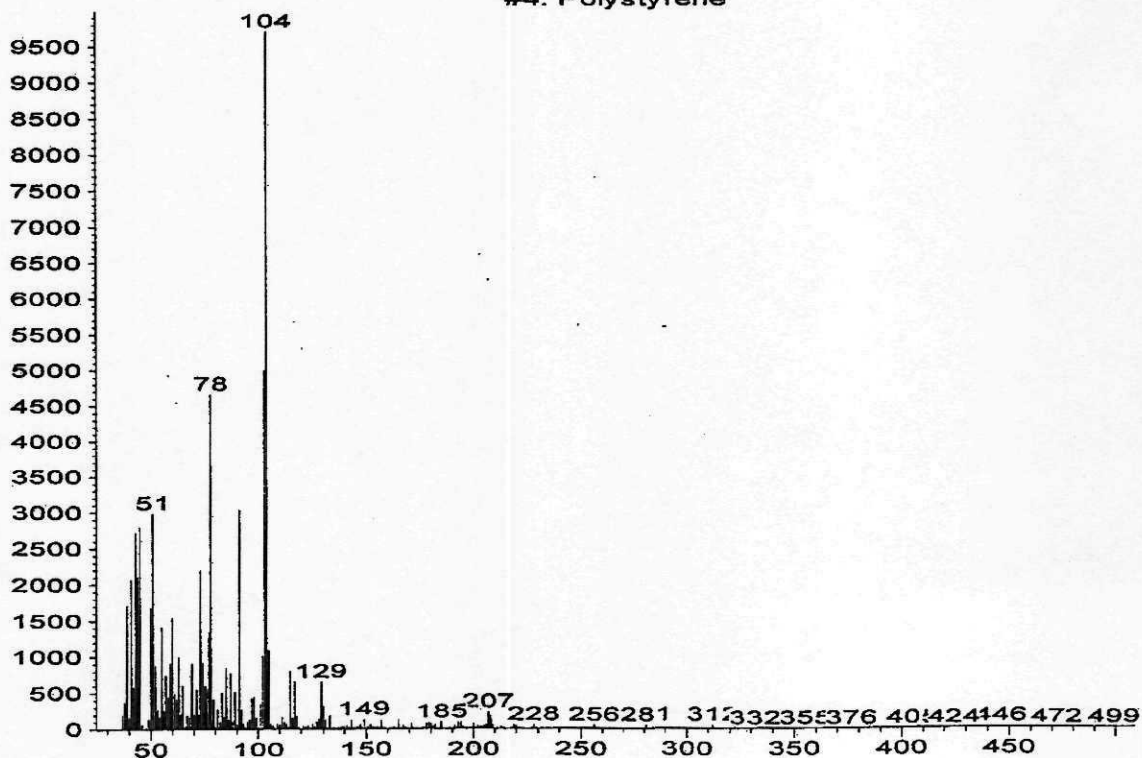
Abundance

TIC: ZARC19.D



Time-->
Abundance

#4: Polystyrene

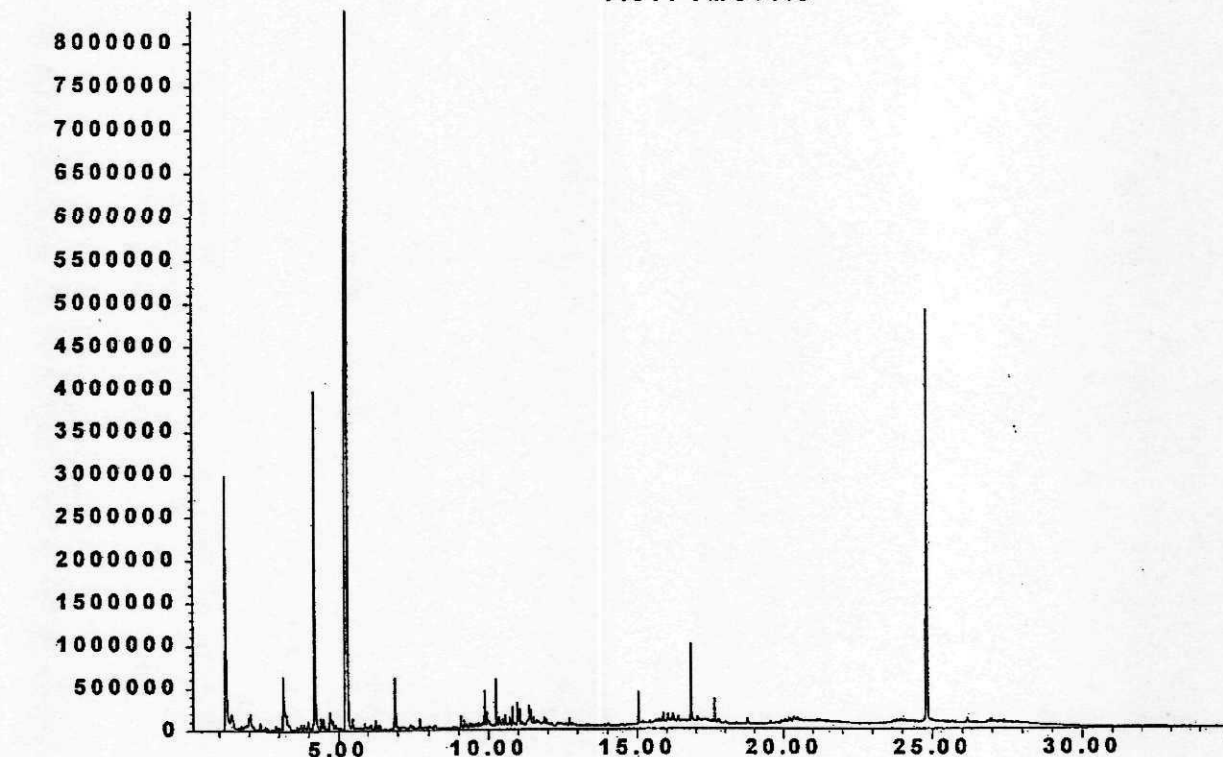


m/z-->

Poly Styrene (28%) Butadiene (72%)

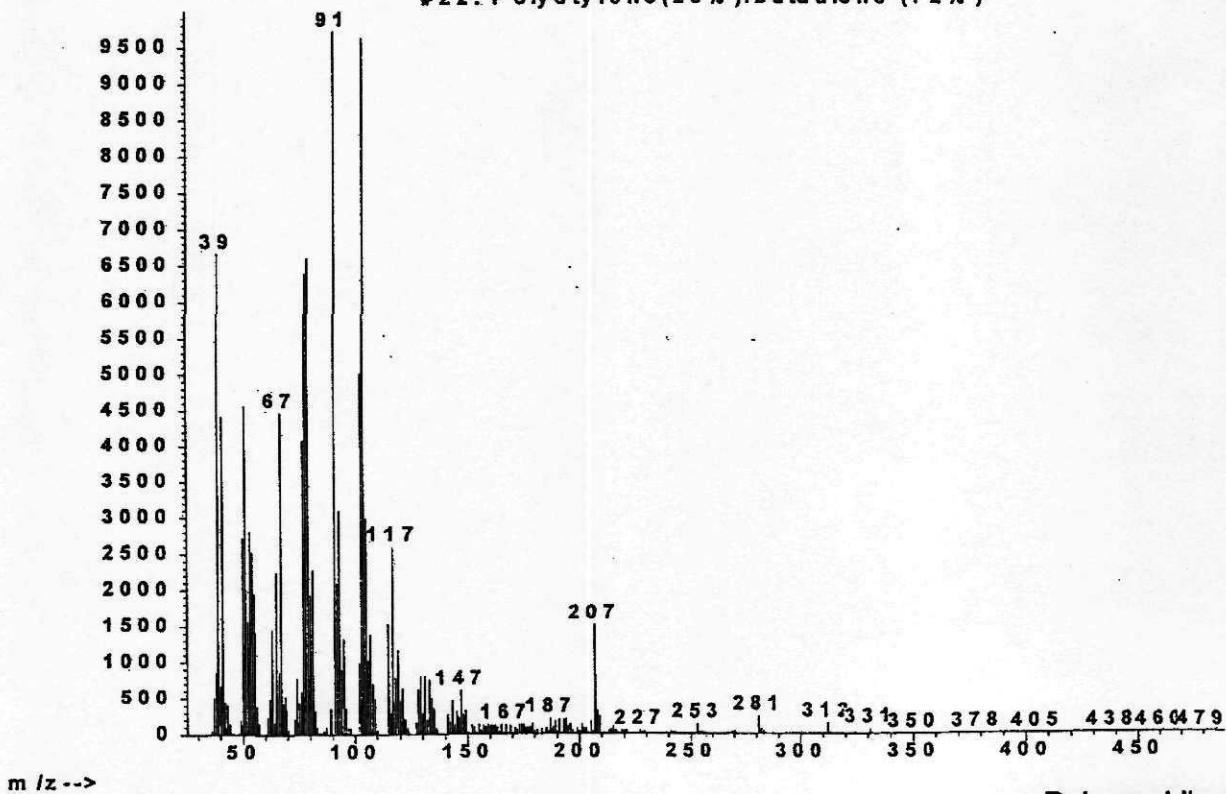
Abundance

TIC: PYMS09.D



Time-->
Abundance

#22: Polystyrene (28%) /butadiene (72%)



m/z-->

Polymer Library -41