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FTIR Determination of Polymers and Plasticizers

Introduction. Infrared spectroscopy has long been a valuable tool for identifying functional groups by virtue of their characteristic vibrational frequencies. IR was the technique of choice for structural identification before the invention of nuclear magnetic resonance (NMR) spectroscopy. NMR spectrometers have supplanted infrared spectrometers for routine structural determination of liquids and solids when there is a sufficient amount of sample. Infrared spectroscopy is still widely used when there is only a limited amount of sample, when a rapid analysis is needed, and in other cases when NMR is just not feasible. For example, infrared spectroscopy is used for identifying adsorbed compounds on glass and other surfaces, identifying chemical functionalities of fibers under a microscope, and in probing compositions of polymer films. This lab entails the last example.

Overview of FTIR. The Fourier-transform infrared spectrometer gives an absorbance spectrum that can detect much higher absorbances than the UV-visible spectrometer. Here is a long-winded explanation of why, which might also help you understand the lecture portion of the class. The FTIR acquires an absorbance spectrum without using a monochromator. Infrared spectrometers used to have monochromators, but the spectra were usually noisy because infrared detectors in are relatively insensitive. This is because thermal background noise is large in the infrared. The method of Fourier-transform was introduced to ease the disadvantage of the background noise.

The idea is that the instrument hits the detector with all wavelengths at once, so the signal will be well above the thermal background noise. This is what you might do if you wanted to weigh one sheet of paper using your bathroom scale. If you put a whole ream of paper on the scale at once, you would get a big signal, and you could then divide the total weight by the number of sheets to learn the weight of one sheet. This is called the *multiplex advantage*. The FTIR has a more complicated calculation to do, and it sorts out the spectrum by using an interferometer, where the interference of each wavelength is sensed to determine the intensity at each wavelength. The lamp power is now very bright compared to the detector noise because all wavelengths are striking the detector simultaneously. Consequently, much higher absorbances can be measured in FTIR than in UV-Vis. We saw for the UV-visible spectrometer that the peaks flattened out around 3.0 to 3.5 absorbance units. For the FTIR, the peaks flatten out around 6 absorbance units. In this lab, the polymer samples will sometimes result in these very large absorbances.
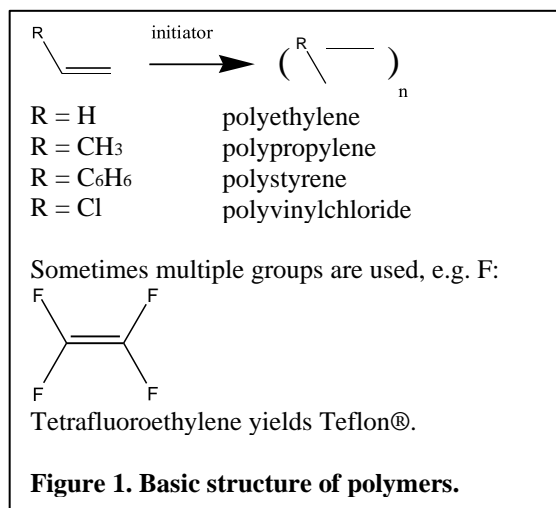
Many polymers are made by the polymerization reaction of a vinyl functionality, R = $-CH=CH_2$, shown in Fig. 5-1 at the left, to give very long polymer chains. The identity of R affects the chemical and mechanical properties of the polymer; there is a wide range of polymers. Fig. 1 shows several examples, all of which are

R = H   polyethylene
R = CH3   polypropylene
R = C6H6   polystyrene
R = Cl   polyvinylchloride

Sometimes multiple groups are used, e.g. F:

Tetrafluoroethylene yields Teflon®.

Figure 1. Basic structure of polymers.

commonly used in the food-packaging industry. Polyethylene is used for sandwich bags, polypropylene is used for soda bottles, polystyrene is used for coffee cups, and polyvinylchloride (PVC) is used for food wraps and piping. Teflon® (polytetrafluoroethylene) is a common material for making nonstick pans, as you know.

Polymers can readily be distinguished from one another using FTIR. You can imagine that it might be difficult to stuff a sandwich bag into an NMR tube; hence NMR is not usually the method of choice for studying polymer films. Infrared and Raman spectroscopy are always included in the polymer chemist's toolbox. The stretching frequency of the C-R bond is characteristic of the polymer. If R is more than one atom (i.e. if the polymer has a "side chain"), R might have its own characteristic spectrum.

Additives and Plasticizers. Low-molecular-weight additives are often used in polymers to affect the flammability and the pliability of polymers. People are concerned that these additives can leach out of the polymer especially in the beverage, food and medical industry. We will study one common example in the laboratory setting, Tygon® tubing. Tygon® tubing is polyvinyl chloride with a particular phthalate added as a plasticizer to make it pliable. In this lab, you will extract the plasticizer out of Tygon® tubing, use FTIR to determine the change of mass that has been removed, and feel the PVC to see if you can detect any qualitative change in its pliability. You will then use the FTIR to identify several different polymer samples. This means you will identify R in Fig. 5-1, and you will note how the mechanical properties of the polymer are affected by the identity of R.

PRE-LAB ASSIGNMENT

1. Compare and contrast between qualitative and quantitative data. Please explain and give examples of each within the confine of this experiment.

2. Attached are the NMR spectra (Fig. 2), FT-IR spectra (Fig. 3), and GC-MS spectra (Fig. 4) of the plasticizer phthalate (See below). The molecular formula for the molecule is $C_{24}H_{38}O_4$. With the given information, what is the name and structure of the plasticizer in the Tygon® tubing? In addition, label the peaks in the carbon and proton NMR spectra.

3. Both the plasticizer and the PVC have methylene stretches, H–C–H, and these have rather large molar absorptivities ε_{H-C-H}. State the wavenumber range in which you expect to see methylene stretches. Should these peaks disappear after extraction (i.e. removal) of the plasticizer?

4. You are going to measure the infrared spectra of polystyrene, polyethylene and Teflon®. Draw the structures and determine the characteristic frequencies for each of these three polymers.

EXPERIMENTAL

1. Your TA will provide you with some Tygon® tubing. Obtain its infrared spectrum. To see if it is possible to determine the amount of plasticizer gravimetrically, carefully weigh the tubing before and after your extraction. You will be using a reflux setup for the extraction. Place about 2 grams of your sample into the 50 mL round-bottom flask and place 30 mLs of methylene chloride so you can extract the plasticizer. Reflux the sample for about 1 hour inside the hood. After one hour, allow to the methylene chloride to come to room temperature. Collect the extract into a scintillation vial. Allow the remaining tubing to dry before weighing it and obtaining its post-reflux spectrum. Note any changes in its flexibility by gently handling the tubing. Your TA will also show you how to use salt plates or a liquid IR cell to obtain the infrared spectrum of the plasticizer dissolved in methylene chloride to see if you can detect the plasticizer by FTIR. Collect and save the text file of the spectra on USB drive, which you can later plot using Excel.
2. Using each of the three unknown samples, A, B, and C provided by your TA, obtain their FTIR spectrum. Identify which of the polymers is polyethylene, polystyrene or Teflon®.

WRITTEN REPORT

1. Compare the FTIR spectra for the tubing before and after reflux and for the methylene chloride extraction. Are you able to observe the removal of the plasticizer from the tubing? Can you detect the plasticizer in the methylene chloride extraction? Indicate the frequency regions you observed to answer these questions. Calculate the rough percentage of plasticizer removed by the methylene chloride. Did the removal of the plasticizer have any effect on the pliability of the tubing? Was the Tygon® sample completely dried before weighing it?
2. Show the spectra of the three polymer unknowns, state what vibrational frequencies you are using to identify the polymers and Label these frequencies in each spectrum. Identify which ample was polyethylene, polystyrene and Teflon®. What are the mechanical properties: which is most stretchy and which is the least? Are the films pliable without the plasticizer? *Note: reading about the materials science of polymers would provide some detail about the relation between the molecular-scale structure and the macroscopic properties. You should do this!*

Safety and Disposal

> *Warning:* ***Handle all solutions with gloves. Methylene chloride is considered a known* carcinogen. Phthalates are presently considered carcinogenic.**

Dispose of all solutions into the organic waste jug.

This laboratory was created by Professor Mary J. Wirth and graduate student Ms. Stuti Christie in March of 2003. It was revised by Professor Thomas P. Beebe, Jr., September 2003. We welcome your comments on how to improve the learning experience of this lab. The best time to communicate these comments is when you are working on the lab.
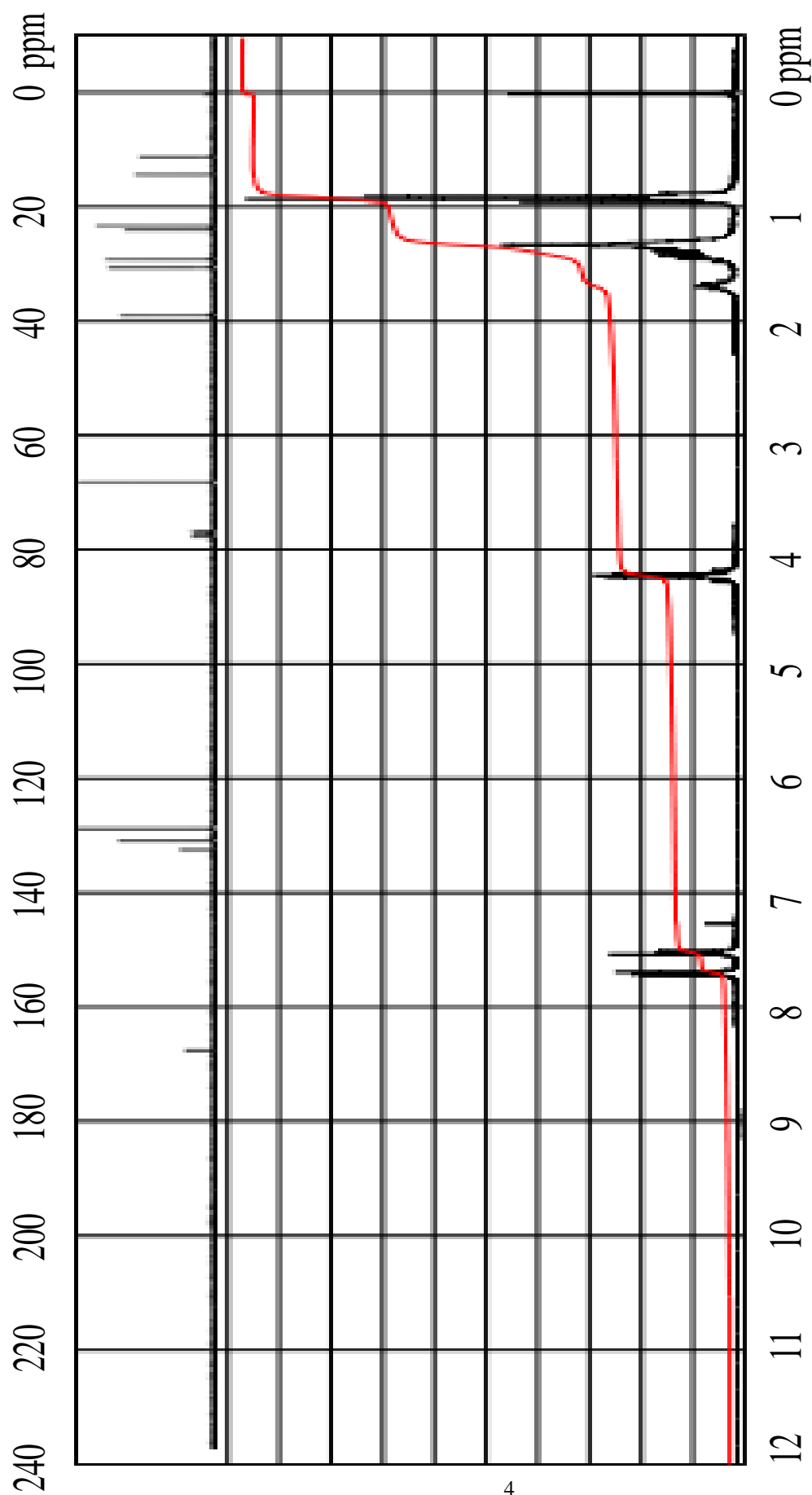
Figure 2. NMR spectra for the plasticizer. Top spectra is ^{13}C NMR and the bottom spectra is ^{1}H NMR. Data was taken using an QE310 NMR. The sample was dissolved in deuterated chloroform and TMS.
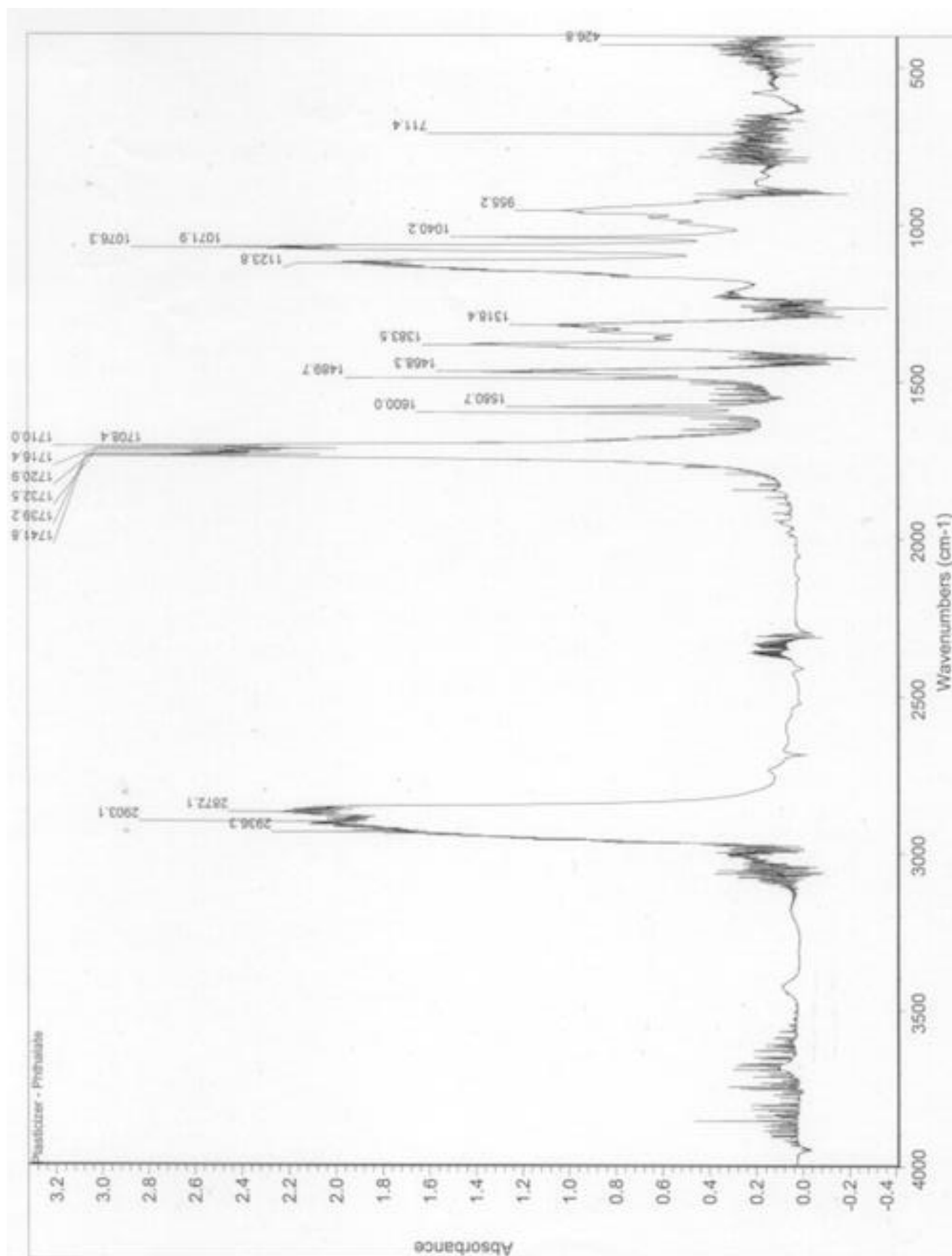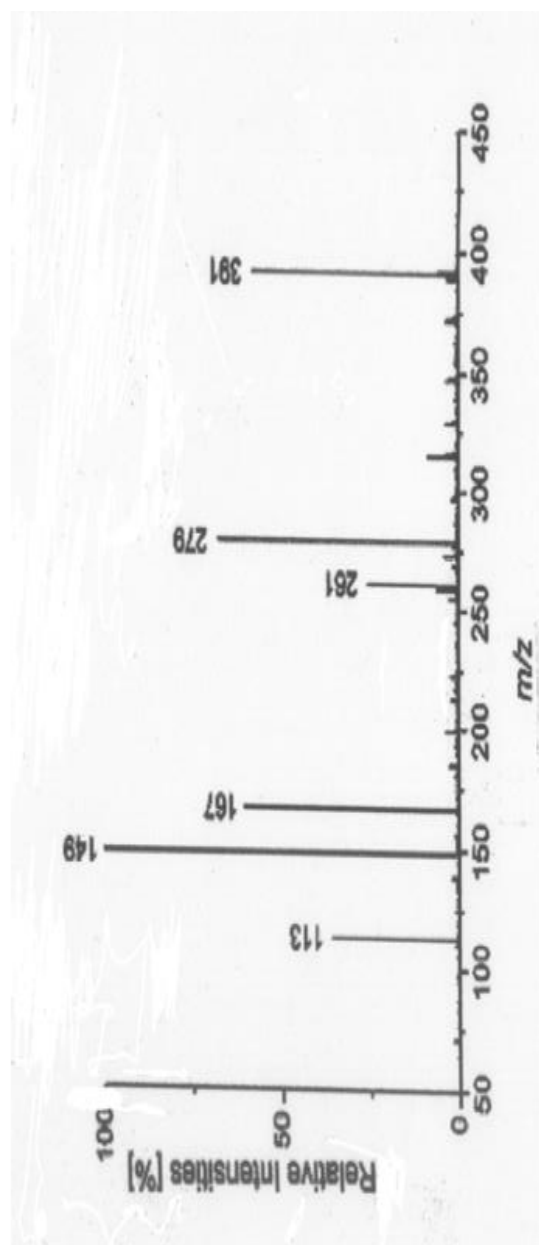
Figure 3 - FT-IR of plasticizer in methylene chloride

Figure 4 GC-MS Spectra.