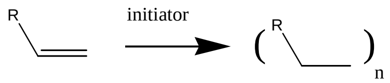
Lab 5
FTIR Determination of Polymers and Plasticizers

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.

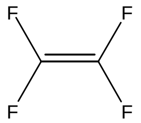
Overview of FTIR. The Fourier-transform infrared spectrometer gives an absorbance spectrum that can detect much higher absorbances than the UV-visible spectrometer. Here is a long-winded explanation of why, which might also help you understand the lecture portion of the class. The FTIR acquires an absorbance 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.



R = H	polyethylene
R = CH_3	polypropylene
R = C_6H_6	polystyrene
R = Cl	polyvinylchloride

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



Tetrafluoroethylene yields Teflon®.

Figure 5-1. Basic structure of polymers.

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. 5-1 shows several examples, all of which are 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 and into the food or beverage with which they are in contact for long periods of time. We will study one common example, Reynolds® Wrap. Reynolds® Wrap is polyvinyl chloride with di(2-ethylhexyl)adipate ($H_{17}C_8OOC(CH_2)_4COOC_8H_{17}$) added as a plasticizer to make it pliable. In this lab, you will extract the plasticizer out of Reynolds® Wrap, use FTIR to determine roughly how much 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.

The structure of the plasticizer, di(2-ethylhexyl)adipate, is shown in Fig. 5-2 at right. Its structure makes it soluble in fat. Since Reynolds® Wrap is often used to wrap cheese in grocery stores, and cheese is typically high in fat, people should be concerned about the plasticizer contaminating the outer portion of the cheese. As far as we know, it has not been proven that there is a specific health danger from di(2-ethylhexyl)adipate.

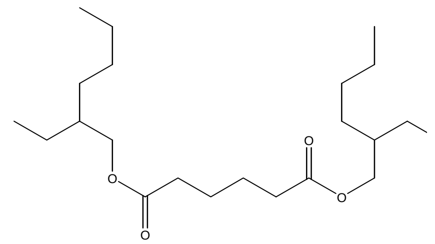


Figure 5-2. Structure of the plasticizer, di(2-ethylhexyl)adipate.

PRE-LAB ASSIGNMENT

1. Attached are the FTIR spectra of Reynolds® Wrap (Fig. 5-3) and the plasticizer di(2-ethylhexyl)adipate (Fig. 5-4). What is the frequency of the C–Cl stretch? Find the C–Cl stretching peak in the spectrum of Reynolds® Wrap and confirm that it is absent in the plasticizer spectrum. Identify the C=O stretch in the plasticizer spectrum. Decide if the Reynolds® Wrap has a detectable amount of plasticizer in it. Would the C=O stretching peak drop in intensity if the plasticizer were extracted out?
2. Both the plasticizer and the PVC have methylene stretches, H–C–H, and these have rather large molar absorptivities $\varepsilon_{H\text{-}C\text{-}H}$. State the wavenumber range in which you expect to see methylene stretches. Should these peaks disappear after extraction (i.e. removal) of the plasticizer?
3. 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 Reynolds® Wrap. Obtain its infrared spectrum. To see if it is possible to determine the amount of plasticizer gravimetrically, carefully weigh the film before and after your extraction. Your TA will show you how to dip the plastic wrap into methylene chloride to extract the plasticizer. Allow the remaining film to dry before weighing it and obtaining its post-extraction spectrum. Note any changes in its flexibility by gently handling the film. 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 a floppy disk, which you can later plot using Excel. *Note: be sure to save your methylene chloride solution in a tightly capped jar because we will use GC-MS in a future lab to identify the plasticizer by its mass spectrum. Save it in a syringe vial or screw-cap scintillation vial provided by the TA.*
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 of Reynolds® Wrap before and after extraction, and estimate roughly what percentage of plasticizer was removed by the methylene chloride. Show the infrared spectrum of the methylene chloride solution and state whether you can detect the plasticizer in the solution. Did removal of plasticizer have an effect on the pliability of the PVC?
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!*

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.

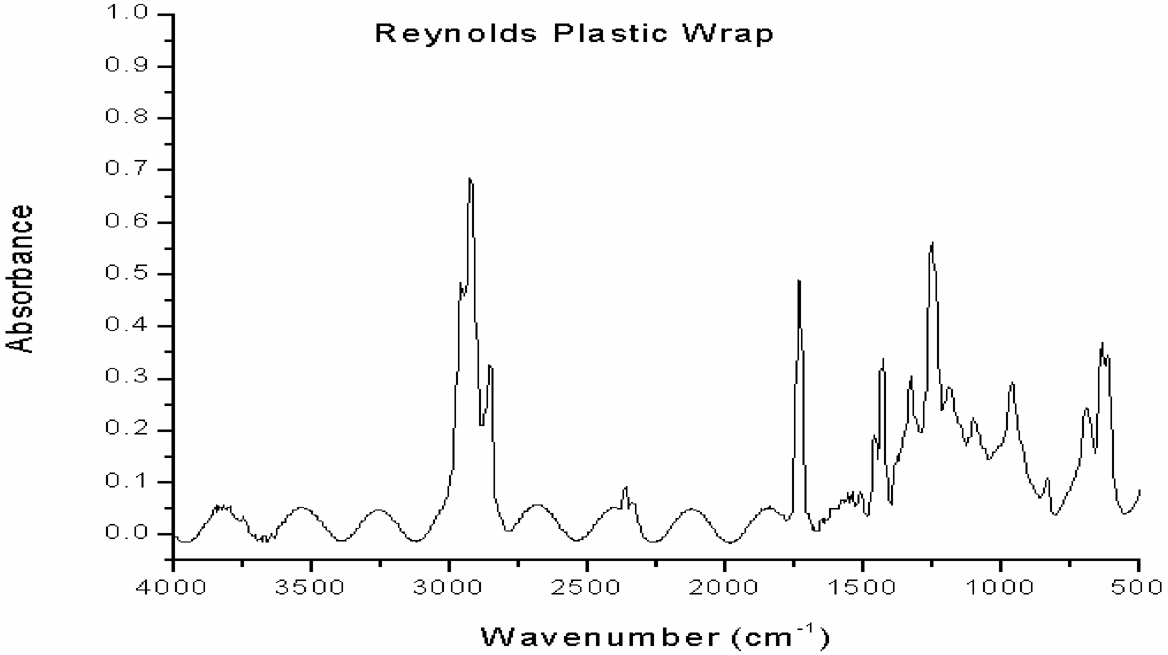


Figure 5-3. FTIR spectrum of Reynolds® Wrap. The sinusoidal baseline is due to the phenomenon of interference in the film, where the film acts like a light cavity. It can be used to calculate the film thickness.

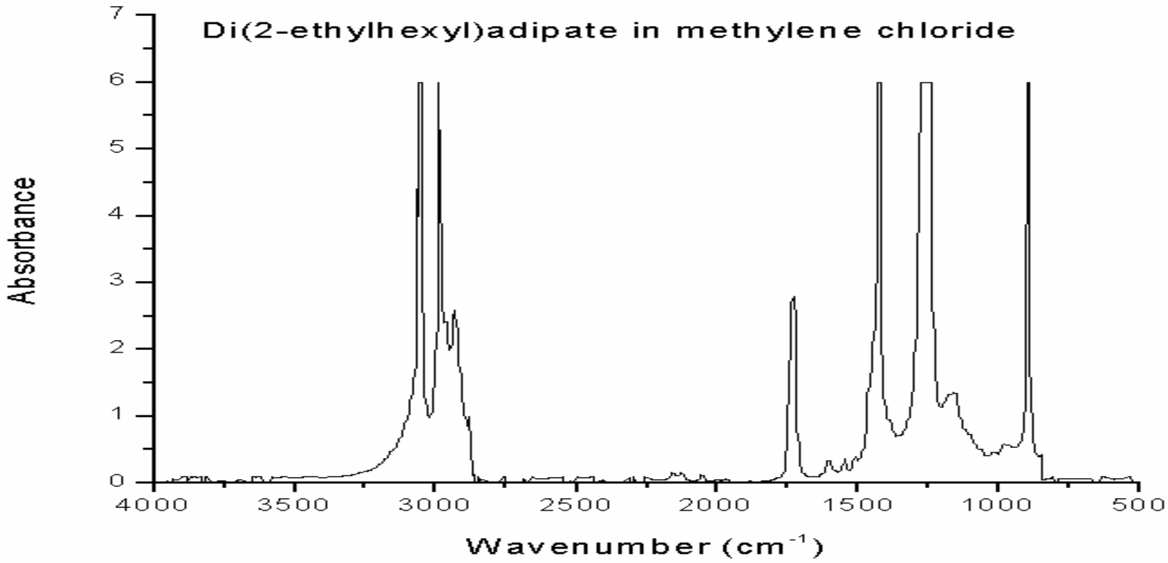


Figure 5-4. FTIR spectrum of di(2-ethylhexyl)adipate, the plasticizer found in Reynolds® Wrap. The interference pattern observed in Fig. 5-3 is now gone. Note that the absorbance scale saturates at A ~ 6 due to the high concentration of plasticizer.