CHEM 3281

Experiment Nine
Infrared Spectroscopic Characterization Of Polymer Films

Objective:

The objectives of this experiment are:
1. to gain experience in acquiring infrared spectra with a Fourier transform based spectrometer.
2. to elucidate the components of polymer film samples by comparison of the vibrational lines in the spectrum to the vibrational lines of characteristic functional groups.

Text Reference:


Other References:


Introduction:

Infrared spectroscopy is most often used for qualitative identification. An unknown material can be determined by comparing the infrared spectrum acquired on this sample to the spectra of known compounds. For a conclusive identification, all features of both spectra that are more intense than instrumental noise must match. Alternatively, IR spectral lines may be interpreted to provide clues to the structure of an unknown. Since the IR spectra of most organic compounds are reasonably complex, the first step in identifying a spectrum is to determine what functional groups (such as -C=O, -NH₂ etc.) are present in the molecule. A
correlation chart is used to compare the position of the strongest bands of the unknown compound with regions of the spectrum where each functional group shows its strongest absorption. Once the functional group has been identified, the area of search can be further limited by determining other physicochemical properties of the sample (such as the melting point, refractive index, glass transition temperature, etc.).

The infrared spectrum is rich in structural information. The spectral lines are produced by the absorption of incident radiation by the vibrational modes of functional groups in the molecule. The absorptions adhere to Beer's law. Thus, analysis of the infrared spectral band intensities as a function of solute concentration provides a straightforward means for determining the concentration mixture components.

Polymers are generally composed of simple repeating units that are cross-linked or covalently bonded to other units to form macromolecules. One common form of use for polymers is in sheets or films for packaging and other uses. Different properties of these polymer films can be engineered by the type of polymer used or by blending "plasticizers" into the formulation to create the flexibility, strength or surface characteristics needed in a particular film use. Plasticizers are generally butyl to decyl phthalates, citrates or other esters that are water insoluble and will adhere well to the film. Other characteristics can be engineered into the film by blending different types of polymers to obtain the desired characteristics. These blends are called copolymers.

Library work will be required to learn more about the particular polymers used in this experiment. The Aldrich Handbook of Spectra and the Hummel Library of Polymer Spectra (available as part of the software package on the instrument) contain many polymer entries that can be used for comparison purposes.

**Experimental:**

1. Ask the instructor to show you the procedure for initiating the FTIR and collecting a spectrum. FTIR spectroscopy is a single beam technique. The acquired spectral information must be stored in separate memory locations and manipulated (added, subtracted, ratioed, etc.) post-run. An IR spectrum of the gases in the sample compartment (air!) must be initially stored in the "BACKGROUND" memory location.

   - Open the COLLECT SETUP and look at the number of scans to be ensemble averaged, type of digital filtering to be used (apodization) and how background is to be subtracted off any sample scans. Decide if you want to run a background before each sample or use the same background over and over. Don’t change anything except background use to suit your team. Close COLLECT SETUP.
   - Open OPTICAL BENCH SETUP and look at the time interferogram being collected in real time, note detector spectral range. DO NOT CHANGE ANYTHING. Close OPTICAL BENCH SETUP.
   - Acquire a "BACKGROUND" by selecting 'Collect Background' under the Collect menu and add to Window 1. Plot the background spectrum by selecting 'Print' under the File menu and responding 'OK'. Make sure that the color option is set to 'All Color'. The computer will subsequently subtract the absorption lines from any data in "SAMPLE" or "REFERENCE" memory location before displaying it on the monitor. Note that the instrument may be set to display the spectral data in Absorbance. If this is the case, select '% T' under the Process
-Acquire a BACKGROUND spectrum with the door open to the sample compartment. Print it out to compare with the first background spectrum. Close sample door!

2. Run an FTIR of an empty salt cell. The modulations are interference patterns which occur due to beam reflection off the walls of the cell. All sample “cells” can show interference pattern in areas of non-absorption. Look for them as you run the polymer films. You can use this interference pattern to calculate film or “sample cell” thickness. You must obtain the wavelength interval for three polymers that have usable regions of interference and calculate their film thickness. See equation in discussion section.

2. Check the wavelength calibration by inserting the polystyrene calibrating film into the sample beam and record the spectrum from 4000-600 cm\(^{-1}\). A sharp, intense peak should be at 2924 cm\(^{-1}\). Expand the scale around the most intense peak by using the 'spectrum selection tool'  to draw a box around the area and then clicking inside the box and then selecting 'Full Scale' under the View menu. The limits will be displayed on the reduced spectra at the bottom of the window. To label the peaks select 'Find Peaks' under the Analyze menu. Alternatively, the %T and wavenumber of peaks can be obtained by using the 'annotation tool' \[T\]. Print this spectra using the same procedure as indicated above.

4. Obtain a spectrum for each of the films and label the peaks using the procedure detailed in part 2.

1. LDPE  low density polyethylene (0.918 g/cc)
2. HDPE  high density polyethylene (0.945 g/cc)
3. PP  polypropylene
4. PTP  polyethylene terephthalate (MYLAR)
5. PVC  plasticized polyvinylchloride
6. SARAN  vinylidene chloride/vinyl chloride copolymer (80/20)
7. 2% VA  ethylene/vinyl acetate copolymer
8. NYLON 6

In addition to the known samples, two unknown polymer films will be analyzed. Request these from the instructor. Bring a film sample of your own to the lab and record its spectrum.

Conduct a library search to determine the identity of each film. Under the Analyze menu, choose 'Search Setup'. Add the libraries you wish to use (Hummel polymer library) and press 'OK'. Then choose 'Search'. Obtain a printout of the search window and an overlaid spectra of the films and the best match obtained. Repeat this completely for each film.

Calculations:

1. Calculate the thickness of films #1-3 or whichever ones you chose (must have refractive index to calculate). The equation for an interference pattern is given by:
\[ 2t = \frac{m}{[n (v_1 - v_2)]} \]

where
- \( t \) = path length, film thickness, sample cell thickness
- \( m \) = # of peaks in the wavenumber interval
- \( n \) = the refractive index of the sample
- \( v \) = wavenumber

2. Tabulate the major peaks for each polymer. Assign the stretches if possible to known functional groups.

The report should consist of a brief description of FTIR, labeled diagram of your instrument, instrumental parameters used, raw data-labeled, calculated data-in tables, please), sample calculations for anything calculated, all plots and a short discussion of the results. In addition, the **discussion** section should contain answers to the following questions:

1. Draw the structures for each polymer and then illustrate how the major peaks correlate to this structure. If you have major peaks that do not correlate then explain why they are there.

2. Can the two forms of polyethylene be identified from their spectra? What are the major differences observed? What are the major differences between the spectra of vinyl chloride, vinyl acetate and vinylidene chloride? What are some of the characteristics that a plasticizer will introduce into a spectrum?

3. *Construct a flow chart that an inexperienced technician could use to clearly identify a film sample assuming that it was one of the eight films given for analysis.*

4. Why do some films give spectra whose lines appear to "bottom out"? What could you do to alleviate this?

5. Identify the major peaks in the background spectrum. What differences did you find between the first background spectrum and the one acquired with the door open? What causes the differences (if any) that you observed? Explain the function(s) of the gas scrubbers mounted on the back wall.