**Polymer Characterization: Fourier Transform Infrared Spectroscopy (FTIR)**

*Instructor Support Document*

*How to Use This Document*

This document accompanies a set of slides produced by the ACS MACRO committee. It is meant to provide deeper explanation of the concepts and content found on these slides, supporting their use in the classroom. For each slide, we suggest how to walk students through the slide to promote learning, then we include background information that will assist you, the instructor, in teaching the material. This document is not intended for dissemination to students, but rather to bring you, the instructor, “up to speed” on this polymer content. You can choose what background information is relevant to your students and course, it is not necessary to include all background information in all teaching contexts.

*The Slides*

These slides are meant to serve as a way to incorporate polymer content into sophomore- or junior-level lecture and lab courses such as organic chemistry or instrumental analysis. The slides assume that students have already been exposed to the theory of FTIR, and thus only provide a brief refresher on the technique. Next, the slides cover the advantages and disadvantages of FTIR and its different sampling methods when it comes to analyzing polymer samples. The slides finish with several examples of polymer FTIR applications.

*MACRO Content Connections*

Depending upon your and your students’ familiarity with polymers, you may wish to include some or all of the “Polymers: Essential Background and Defintions” slides also found on the MACRO website. These slides also have an accompanying instructor document for your convenience. This document contains a great deal of fundamental information about polymers and an extensive jargon vocabulary list.

For organic chemistry, especially, these slides pair well with the module “Polymers: Synthesis by Acyl Substitution Reactions”. FTIR is a go-to method to characterize the functional group transformations that occur when making polymers by these mechanisms.

*Slide-by-Slide Guide*

Slide 2: FTIR Overview

Student walkthrough: Covalent bonds absorb infrared frequencies that match their bond vibration resonant frequencies. The exact value of this frequency is affected by the sizes of the atoms involved (heavier atoms have lower bond resonance frequencies) and the strength or stiffness of the bond (stronger bonds have higher resonances frequencies). By looking at the frequency placement and the intensity of the bands, we can identify the presence of absence of specific types of covalent bonds.

Additional background: Covalent bonds are usually modeled as Hooke-type springs, using the following equation:

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|  | where = the vibrational frequency (cm-1)  c = velocity of light (2.998x1010 cm·s-1)  *f* = force constant of bond (dyne·cm-1)  *Mx* and *My* = masses of atoms *x* and *y* (g) |

The table lists some of the most useful functional groups for analyzing the structure of condensation-type polymers (polyesters, polyamides, etc.).

Slide 3: Method Characteristics

Student walkthrough: The speed and ease of sampling in FTIR are attractive features of this technique. It is also useful because there is no need to dissolve the sample in a solvent, a feature useful for polymer analysis because of their limited solubility. Note the disadvantages as well and explain why they may provide misleading data.

Additional background: The large size of polymers means that they incur high entropy costs in dissolution. Many polymers, especially those prepared by condensation mechanisms like polyesters or polyamides, are particularly insoluble. Thus, FTIR may be the most convenient or only feasible way to interrogate their molecular structure. The advantages offered by FTIR analysis are readily understood.

Among the disadvantages, the more prominent is the difficulty of obtaining quantitative information in addition to the qualitative. In short, we can readily discern the presence and absence of certain functional groups, but determining the amount of a particular group present is challenging. There are established methods to create standard intensity curves to pull out this information, but like any relative technique the information produced will only be as good as the standard curve and should always be interpreted with care.

The second disadvantage is less commonly observed in small molecule sampling. Due to their large size, polymer samples are readily kinetically frozen in non-equilibrium conformations. This could occur if a molten polymer sample is cooled very quickly, or if a polymer is stretched during synthesis or processing. These changes can affect the shape and intensity of FTIR bands in ways that could lead to improper interpretations of the spectrum. Therefore, it is always important to note the processing history of a polymer sample being analyzed by FTIR. Processing can make the sample seem artificially disordered or highly ordered.

Slide 4: Choosing a Sampling Method

Student walkthrough: Help students compare and contrast the different sampling methods. Include any other sampling methods your institution may possess, or omit ones that are not relevant to your course. Encourage students to think about amounts of sample required for each method, sample processing concerns, etc.

Additional background: There are many different sampling methods for FTIR analysis, but these are the most common. Grinding a polymer/KBr powder and pressing a pellet allows for easy targeting of the proper spectrum intensity, but some polymers are mechanically strong and difficult to grind effectively. Pellet sampling also allows you to sample both surface and bulk composition of a polymer sample, but the sampling is destructive and may not be suitable for precious samples.

Similar to a pellet, the infrared beam can be passed through a thin film of the polymer. Preparing thin films of polymer can be non-destructive and allow for adjusting film thickness to control spectrum intensity, but larger amounts of material and sample preparation time are needed. Further, not all polymers are sufficiently robust to create free-standing films, so a support film may be needed and accounted for. Surface and bulk composition are analyzed, but the method used to process the films may affect the morphology of the polymer. For example stretching may induce a greater degree of order and crystallinity, or solvent-casting could result in trapped residual solvent within the film.

Attenuated Total Reflectance (ATR) sampling boasts great ease and convenience. The infrared beam is passed through a crystal, where it bounces off the interface between the crystal and a sample film, powder, or liquid placed on top of the crystal. Very small amounts of sample are required and may, with care, be recovered after analysis. This sampling method only analyzes the layer of sample closest to the crystal surface, generally 1-4 microns depending upon the refractive index of the sample material. It is not uncommon for polymers to display differences in properties in composition between the surface and the bulk, therefore it may be necessary to supplement ATR-FTIR with another characterization method. On the other hand, ATR-FTIR can also be used to distinguish surface characteristics from those deeper in the sample.

Slide 5: Structure Identification

Student walkthrough: Similarly to FTIR of small molecules, we can use the presence and absence of bands in the spectrum to obtain information about the molecular structure of a polymer.

Additional background: FTIR can be used in the place of Nuclear Magnetic Resonance spectroscopy to confirm polymer structure, particularly in the cases of polymers with limited solubility.

In the analysis of polymers prepared by condensation mechanisms, it is useful to compare the spectra of the monomer(s) to that of the resulting polymer. The presence or absence of monomer bands in the polymer spectrum can be a very rough estimate of relative chain length. If bands from the monomer spectra are prevalent in the polymer spectrum (for example, free NH and carboxylic acid bands in a polyamide sample), this is indicative of very low conversion of monomer to polymer. This could indicate a sample that has mostly converted to oligomers, rather than high molecular weight polymer. Very small or indistinguishable monomer bands are indicative of longer chains with higher molecular weights.

In the case of chain-growth polymers, usually the polymerizable functional group is an alkene. If this is the only alkene in the monomer, then the loss of alkene C-H and C=C bands can be an indicator of low or no monomer contamination in the final polymer product.

FTIR can also be used to verify post-modification of polymers. Frequently, functional groups desired in polymers may present compatibility issues with polymerization mechanisms. Such function can either be modified with a protecting group during polymerization, or it can be installed after polymerization through another reaction. Comparing the protected polymer to the deprotected or the as-polymerized to the post-modified polymer can verify that the desired transformation took place.

Slide 6: Crystallinity

Student walkthrough: Bond stiffness is directly related to band placement, so if all bonds of a given type are the same strength, they produce narrow FTIR band. We can get a sense of the relative amount of crystallinity in a polymer by examining the sharpness of its bands.

Additional background: Polymers are semicrystalline materials. This means they may display two types of solid-phase properties: ordered crystalline domains and disordered amorphous domains. The relative proportion of the crystalline and amorphous domains is dependent upon the identity of the polymer and how it was processed. Though Differential Scanning Calorimetry or X-Ray Diffraction methods provide more quantitative information on the semicrystalline behavior of a sample, FTIR can provide a qualitative way to obtain some of this data based upon the shape of the bands in the spectrum.

Sharp, narrow FTIR bands indicate that all bonds of that type in the sample share the same bond stiffness. This is more likely to occur when the bonds are all experiencing similar inter- and intra-molecular forces, which is why sharp bands are associated with highly crystalline polymers. The consistent ordering of the crystal lattice provides a homogeneous chemical environment. In more amorphous polymers, this is not the case. Intermolecular interactions may occur at different inter-chain distances, varying their strength and thus varying the stiffness of the bonds involved. This causes the FTIR bands to become broader.

Understanding the relative crystallinity of a polymer is important because of its strong effect on polymer properties. More crystalline content is associated with higher stiffness and brittleness and a resistance to aging and creep. It is strongly affected by processing conditions, such as faster or slower cooling or being drawn during cooling.

Slide 7: Bond Strength

Student walkthrough: Factors like intermolecular interactions and electronic conjugation can affect the strengths of covalent bonds. These differences can be spotted by their effect on the placement of specific FTIR bands. Factors that make bonds stronger will shift the band placement to slightly higher wavenumbers, while factors that make bonds weaker will shift the band placement to slightly lower wavenumbers.

Additional background: The fact that polymers are long chains of repeating units means that seemingly subtle differences to the repeat unit structure are amplified along the entire backbone and can lead to important shifts in thermal and mechanical properties. FTIR offers a way to spot which bonds and functional groups are changing, and in what ways, such that it can yield potential design principles when attempting to prepare a polymer structure with a desired set of properties.

Bonds that are affected by hydrogen bonding or dipole-dipole interactions can influence crystallinity and inter-chain attractions that can lead to greater stiffness or mechanical robustness. Electronic conjugation across the structure leads to longer persistence lengths along the backbone and higher glass transition temperatures.

*Additional Resources*

Silverstein, R. M.; Webster, F. X.; Kiemle, D. J. *Spectrometric Identification of Organic Compounds, 7th edition*; John Wiley and Sons, Inc.; Hoboken, New Jersey, 2005