CHARACTERIZATION OF POLYMER BY FTIR SPECTROSCOPIC TECHNIQUE

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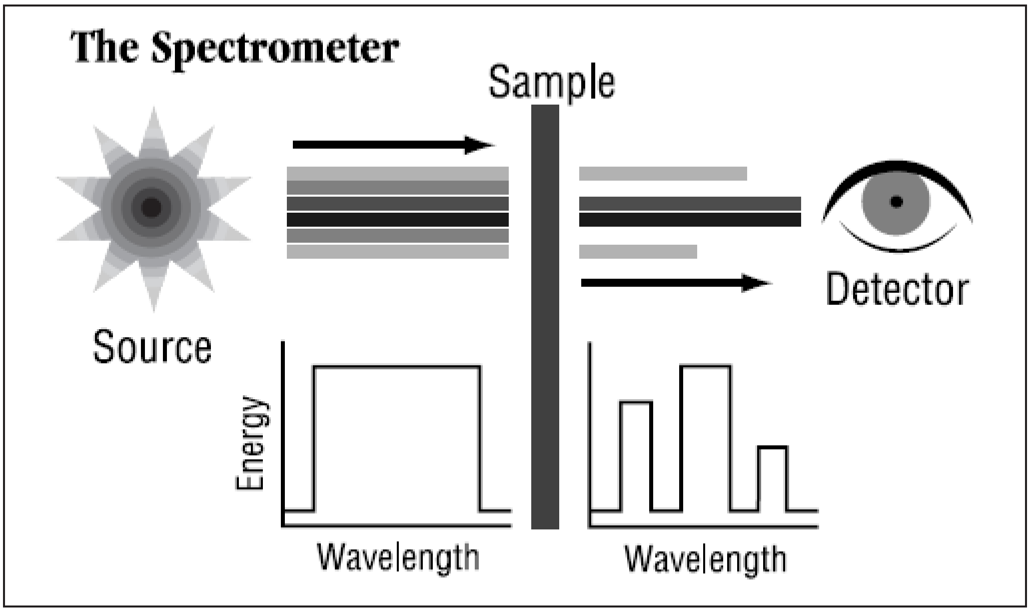
INTRODUCTION –

What is FT-IR? FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. So, what information can FT-IR provide? • It can identify unknown materials • It can determine the quality or consistency of a sample • It can determine the amount of components in a mixture this booklet is an introduction to the concepts behind FT-IR spectroscopy. It covers both the basic theory of FT-IR and how it works as well as discussing some the practical aspects of FT-IR use. We hope that it gives you a good understanding of the importance and usefulness of this powerful technique.



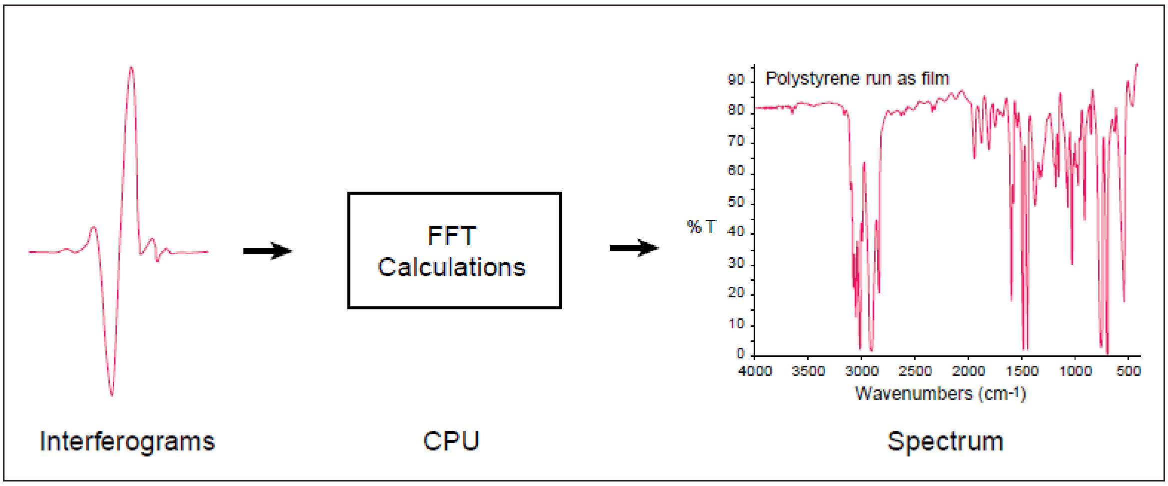
Why Infrared Spectroscopy? Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

Older Technology The original infrared instruments were of the dispersive type. These instruments separated the individual frequencies of energy emitted from the infrared source. This was accomplished by the use of a prism or grating. An infrared prism works exactly the same as a visible prism which separates visible light into its colours (frequencies). A grating is a more modern dispersive element which better separates the frequencies of infrared energy. The detector measures the amount of energy at each frequency which has passed through the sample. This results in a spectrum which is a plot of intensity vs. frequency.

Fourier transform infrared spectroscopy is preferred over dispersive or filter methods of infrared spectral analysis for several reasons:

- It is a non-destructive technique
- It provides a precise measurement method which requires no external calibration
- It can increase speed, collecting a scan every second
- It can increase sensitivity – one second scans can be co-added together to ratio out random noise
- It has greater optical throughput
- It is mechanically simple with only one moving part

Why FT-IR? Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimetres) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured; all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal cannot be interpreted directly. A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.



The Sample Analysis Process

The normal instrumental process is as follows:

1. The Source: Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

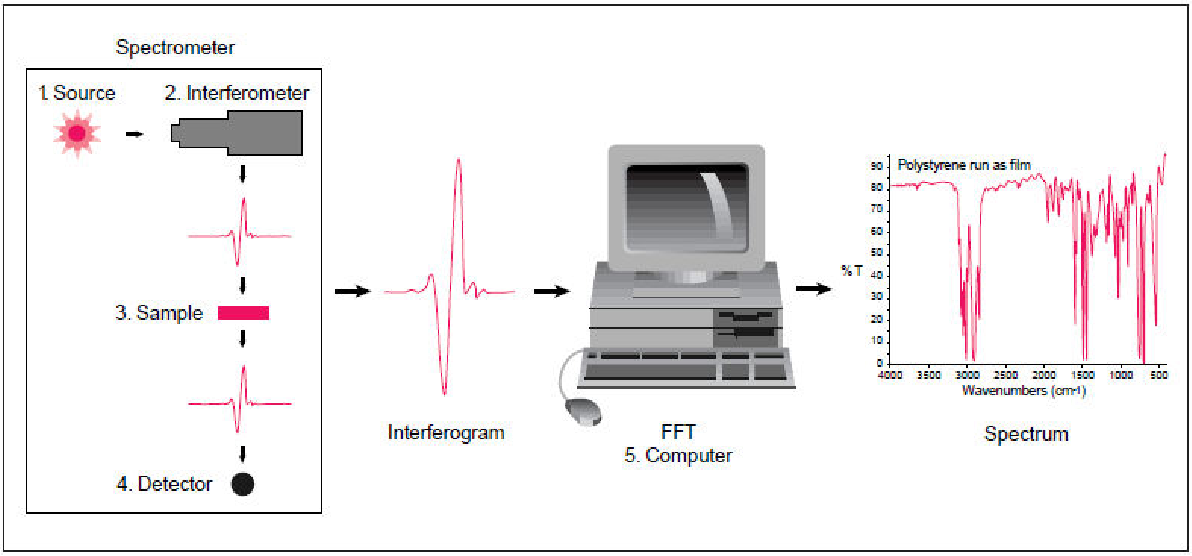
2. The Interferometer: The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

3. The Sample: The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

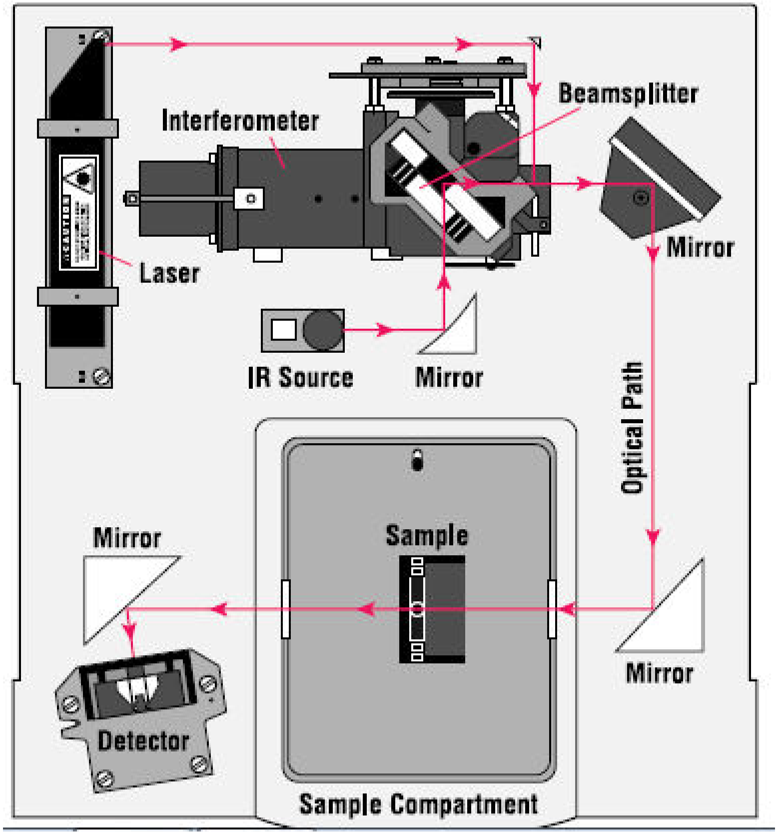
4. The Detector: The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

5. The Computer: The measured signal is digitized and sent to the computer where the Fourier transformation takes place.

The final infrared spectrum is then presented to the user for interpretation and any further manipulation. Because there needs to be a relative scale for the absorption intensity, a **background** spectrum must also be measured. This is normally a measurement with no sample in the beam. This can be compared to the measurement with the sample in the beam to determine the “percent transmittance”. This technique results in a spectrum which has all of the instrumental characteristics removed. Thus, all spectral features which are present are strictly due to the sample. A single background measurement can be used for many sample measurements because this spectrum is characteristic of the instrument itself.



A Simple Spectrometer Layout



Advantages of FT-IR

Some of the major advantages of FT-IR over the dispersive technique include:

- **Speed:** Because all of the frequencies are measured simultaneously, most measurements by FT-IR are made in a matter of seconds rather than several minutes. This is sometimes referred to as the **Felgett Advantage**.
- **Sensitivity:** Sensitivity is dramatically improved with FT-IR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher (referred to as the **Jacquinot Advantage**) which results in much lower noise levels, and the fast scans enable the coaddition of several scans in order to reduce the random measurement noise to any desired level (referred to as **signal averaging**).

- **Mechanical Simplicity:** The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.
- **Internally Calibrated:** These instruments employ a HeNe laser as an internal wavelength calibration standard (referred to as the **Connes Advantage**). These instruments are self-calibrating and never need to be calibrated by the user.

These advantages, along with several others, make measurements made by FT-IR extremely accurate and reproducible. Thus, it a very reliable technique for positive identification of virtually any sample. The sensitivity benefits enable identification of even the smallest of contaminants. This makes FT-IR an invaluable tool for quality control or quality assurance applications whether it is batch-to-batch comparisons to quality standards or analysis of an unknown contaminant. In addition, the sensitivity and accuracy of FT-IR detectors, along with a wide variety of software algorithms, have dramatically increased the practical use of infrared for quantitative analysis. Quantitative methods can be easily developed and calibrated and can be incorporated into simple procedures for routine analysis.

Thus, the Fourier Transform Infrared (FT-IR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by older technology. It has made the use of infrared analysis virtually limitless.

Method Of Preparation-

Homo polymerization of aniline

In a typical poly aniline experiment, doubly distilled aniline (10 ml, 0.1097 mol) dissolved in hydrochloric acid (HCl) solution (1 M, 100 ml) was placed in a flask equipped with a dropping funnel and cooled to 0 °C. If monomers were not completely soluble in this medium, an additional HCl solution (1 M, 50 ml) was added.

The oxidizing agent was prepared by dissolving (1.25 g, 0.0548 mol) ammonium persulfate in HCl solution (1 M, 100 ml). The oxidant solution was added drop wise to aniline solution with vigorous stirring at 0 °C. A green precipitate formed after 5–10 min. The reaction mixture was stirred for 4 h at 0 °C and for 20 h at room temperature. The reaction mixture was poured into 200 ml water to complete the precipitation and the polymer was collected on a glass frit, washed with distilled water and HCl solution (1 M) to remove un-reacted monomer. Collected green precipitates of emeraldine hydrochloride were washed with distilled water till these washings were colorless. The filtered and washed precipitates were then treated with aqueous solution of ammonium hydroxide (pH ≈ 9) under stirring for 6–8 h for effective un-doping to obtain emeraldine base. This reaction mixture was filtered, washed with distilled water till washings were neutral to a pH indicator paper. The blue emeraldine base powder obtained was then filtered and washed with a water and methanol mixture and finally dried under vacuum for 48 h.

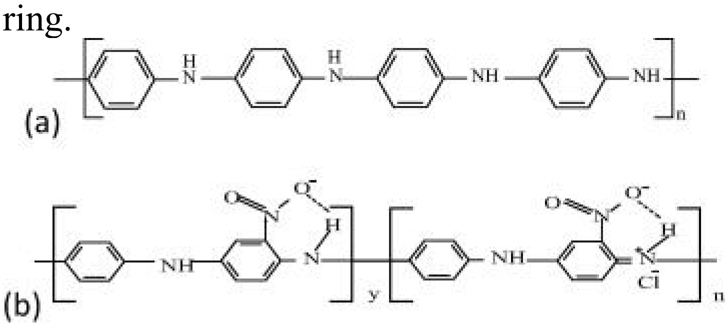
Copolymerization of aniline with o-nitro aniline (1:1, 1:4)

0.05 mol of each one of doubly distilled aniline and o-nitro aniline were dissolved in HCl solution (1 M, 150 ml) to prepare copolymer 1:1, and then placed in a flask was cooled to 0 °C. Based on the method of homo polymerization of aniline (2.2.1), (0.025 mol of aniline was mixed with 0.1 mol of o-nitro aniline to prepare copolymer 1:4).

RESULTS AND CHARACTERIZATION OF PANI -

The copolymers were synthesized using two different molar ratios of 1:1 and 1:4 of aniline: o-nitro aniline in the co monomers feed. The yield of the co polymers decreases with increasing o-nitro aniline content in the co-monomer feed. This could be due to the highly electron withdrawing nature of the nitro group which reduces the electron density on the ring and also the steric interferences hindering polymerization. Strong intermolecular interaction between nitro groups and the polaronic nitrogen atoms or hydrogen bonding can give rise to a favourable six member chelate ring, forming localized structure resulting in a lower conductivity. Scheme 1

The formation of hydrogen bonds between the oxygen of the $–NO_2$ group and the –NH hydrogen localizes the electron density on the ring leading to further decrease in the rate of polymerization, . It is of interest to note that o-nitro aniline does not homo polymerize under conditions employed for the polymerization of aniline and its derivatives. This could be due to the high electron withdrawing capacity of the nitro group in nitro aniline reducing the electron density of the ring.



Scheme 1. Structure of the (a) polyaniline and (b) copolymers (1:1 and 1:4).

Fourier transform infrared (FTIR)

FTIR spectra of both PANI and doped copolymer are shown in Fig. 1. The spectra of all the copolymers show the main bands in the region of 1590, 1508 and 1308 cm^{-1} corresponding to the ring-stretching vibrations of the quinoid and benzenoid rings of aniline and nitro aniline, respectively. Furthermore, the quinoid peak appears split, while the benzenoid band is not split in the spectra.

The quinoid band is sensitive to the structure, and hence, two bands at 1595 and 1560 cm−1 arising from quinoid stretching of aniline and nitro aniline ring segments are observed. A band near 1385 cm−1 is assigned to the CN+ stretching adjacent to the quinoid structure while a medium intensity band at 1310 cm^{-1} is associated with C–N stretching vibration in the alternate units of quinoid–benzenoid–quinoid rings as shown in Fig. 1. The peaks at 1304 and 1210 cm^{-1} correspond to N–H bending and the symmetric component of the C–C (or C–N) stretching modes. Most of the bands of the copolymers are asymmetric and symmetric stretching modes of the nitro group of o-nitro aniline which occur at 1510 and 1346 cm^{-1}, respectively.

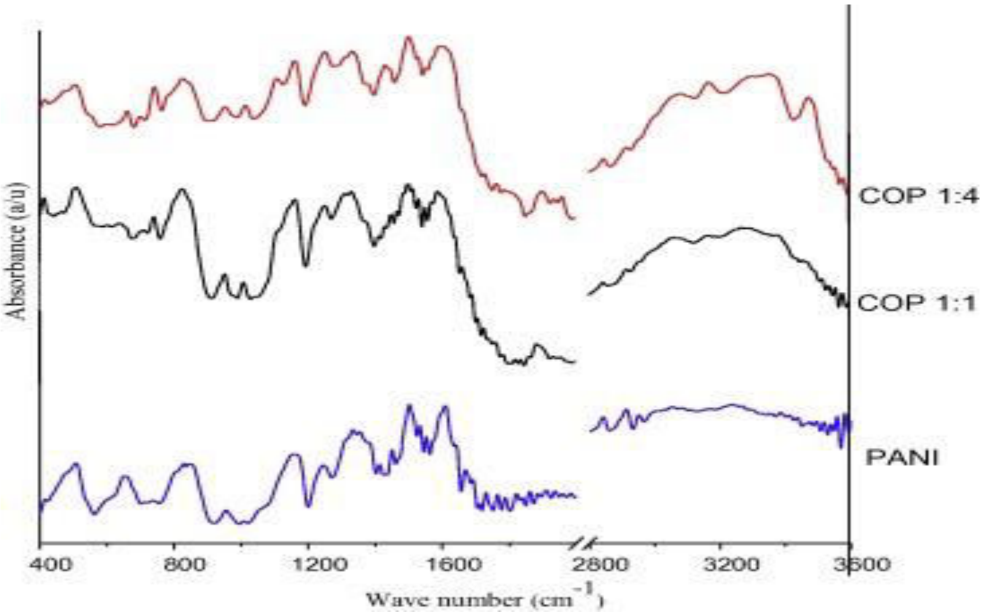


Figure 1. FTIR spectra of PANI, copolymer 1:1 and copolymer 1:4.

The band around 1170 cm^{-1} is attributed to B–(NH^+) Q structure which is formed during the protonation process. A band at 1110 cm^{-1} is assigned to the C–H in plane bending. This confirms the presence of o-nitro aniline segments in the copolymer and also suggests an increase in the conjugation of the nitro group with the ring. The significant lowering of the frequencies can be related to the hydrogen bonds formed between the oxygen of the nitro group and the hydrogen of the amine group.

The bands at 1145 and 831 cm^{-1} can be attributed to the in-plane and out-of-plane C–H bending modes, respectively. The strong band at 1145 cm^{-1} in the base is much intense and broader in the salt spectrum. In addition to the above peaks, the spectrum of the polyaniline exhibits peaks at 3320 cm^{-1} that could be attributed to NH_2 stretching mode and a band located at 1653 cm^{-1} related to the NH_2 bending vibration, while the peak at 684 cm^{-1} is attributed to NH_2 wagging. In addition, the peak at 1580 cm^{-1} confirms the presence of a protonated imine function, and the band characteristic of conducting protonated form is observed at 1242 cm^{-1}.

CONCLUSION

Depending on the acidity of the reaction medium used in the oxidation of aniline, the specific spectral features in the products have been identified. The o-nitro aniline was copolymerized with aniline by chemical oxidative polymerization with ammonium persulfate as the oxidizing agent in acidic medium using different feed ratios of the comonomers. Although o-nitro aniline does not homo polymerize, these copolymers exhibited higher conductivities and good solubility in solvent DMSO than the homo-polyaniline and this may be attributed to greater electron delocalization and the presence of hydrogen bonding and inter chain linking due to the nitro group of o-nitro aniline. FTIR indicate the presence of the quinoid ring in polyaniline structure.

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