University of Jordan

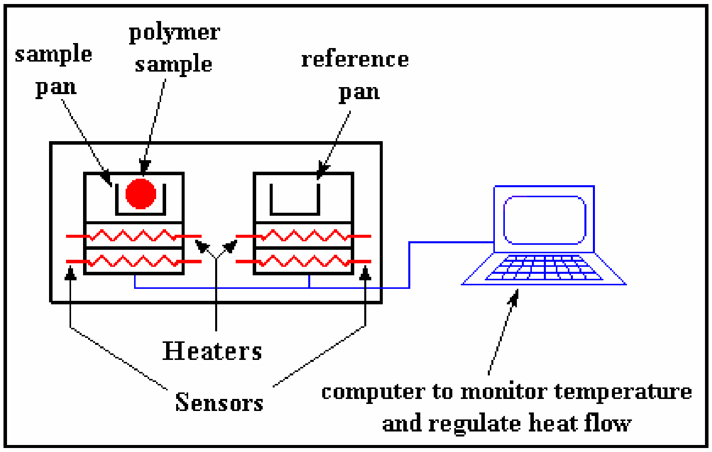
Department of Chemical Engineering
Polymers and Plastics Engineering (0905553)

Characterisation of Polymers

Thermal Analysis

Differential scanning calorimetry (DSC) has frequently been used for the measurement of thermal effects in polymers, as associated with melting, crystallisation and glass transition.

The power compensation DSC uses individual sample and reference micro-furnaces rather than a single large furnace. The micro-furnace lends itself to very fast heating and cooling rates, and rapid temperature equilibrium. The micro-furnaces, being made of Platinum-Iridium alloy, are very inert to chemical attack.



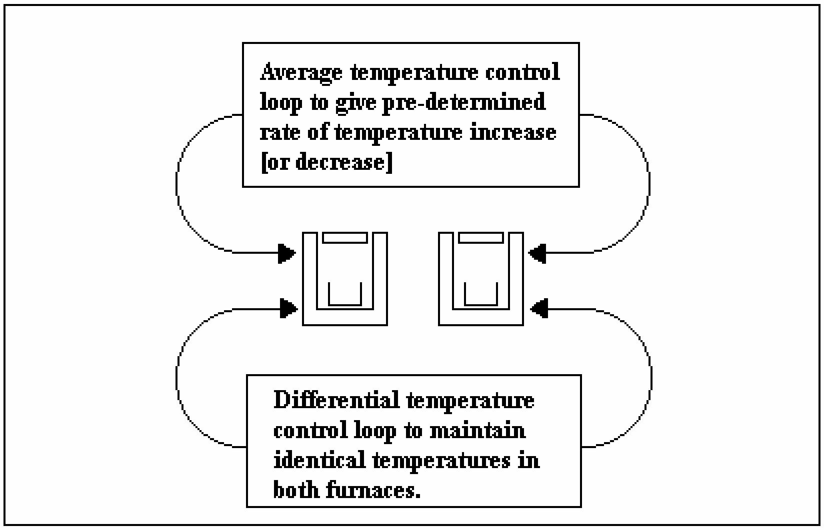
Temperature and energy measurements are made with platinum resistance thermometers. In the base of each furnace are two identical platinum resistance elements. One of these elements is used to provide power to the furnace. The other is used to detect the smallest change in the temperature of the furnace. These platinum windings are distributed over the area of the furnace base. This provides truly distributed heating and temperature monitoring.

Platinum resistance heaters and thermometers are used in the *DSC* to accomplish the temperature and energy measurements. The continuous and automatic adjustment of heater power (energy per unit time) necessary to keep the sample holder temperature identical to that of the reference holder provides a varying electrical signal equivalent to the varying thermal behaviour of the sample. This measurement is made directly in energy units (millwatts), providing true electrical energy measurement of peak areas.

Two separate control loops are used to precisely control the temperature of the sample and reference furnaces. These control loops are:

- **Average temperature control:**

This loop provides power to the sample and reference furnace in accordance with the programme temperature selected. For example, if the experiment is to heat the sample at *$10^oC/min$* from *50^oC* to *200^oC* then this control loop provides heat at the selected rate over that temperature range and ensures that the sample and the reference are always at the same temperature.



Schematic diagram for the control loops used to precisely control the temperature of the sample and reference furnaces.

- **Differential temperature control:**

This loop is the actual measuring circuit that derives the instrument output signal. In this loop, the system measures precisely any difference in the temperature that occurs between the sample and reference furnaces. If the material in the sample furnace gives out or takes up energy, the temperature of the sample furnace will change slightly from that of the platinum resistance thermometer in the base of the furnace. In response to this temperature difference, the differential control loop will adjust the power to bring the two furnaces back to the same temperature. Thus the system is always kept at a thermal null.

The amount of energy that must be provided or removed from the system to maintain the thermal null by the differential temperature control loop is directly proportional to the energy change of the system. Thus, direct measurement of energy and hence ΔH can be made.

DSC Calibration

All thermal analysers need to be calibrated to make sure that transition temperatures and energies recorded are in all respects accurate. DSC calibration needs to be performed both for temperature and energy ranges.

Very high purity indium and zinc are used to calibrate both the onset temperature and heat of fusion. Approximately *10mg* of each reference material is carefully cut using a scalpel, and crimped in an aluminium pan. A controlled heating rate of $10^{o}C/min$ is used to perform a heating scan passing through the melting temperature. From the melting endotherms, the onset temperature and heat of fusion are measured and compared with literature values shown in the Table. If the measured values are not correct, the instrument is adjusted until literature values are obtained

Onset temperatures and enthalpies of fusion for indium and zinc calibration standards.

Reference	***Onset Temperature (^{o}C)***	***Enthalpy of fusion (J/g)***
Indium	156.56	28.45
Zinc	419.50	119.27

Presentation of DSC Data

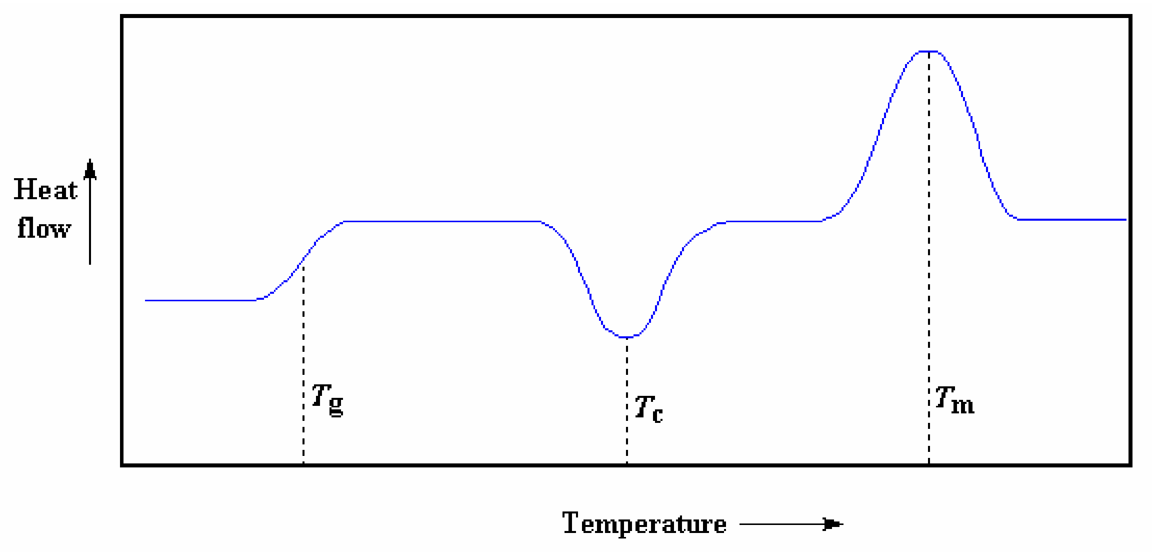
The following figure shows a typical glass, crystallisation and melting transition DSC curve, the following definitions are applied:

T_g is the glass transition temperature, the temperature at which a polymer changes from hard and brittle to soft and pliable. Polymers have a higher heat capacity above the glass transition temperature than they do below it. Because of this change in heat capacity that occurs at the glass transition, DSC can be used to measure a polymer's glass transition. Changes in heat capacity do not occur suddenly but take place over a temperature range. Usually the middle of the incline is taken to be the T_g.

When polymers crystallise they give off heat. The computer-controlled heater under the sample pan does not therefore have to put out much heat to keep the temperature of the sample pan rising. This drop in the heat flow can be seen as a big dip in the plot of heat flow versus temperature. The temperature at the lowest point of the dip is usually considered to be the polymer's crystallisation temperature, or T_c.

If one keeps heating the polymer past its T_c, eventually another thermal transition will be reached which is called the melting transition. When the polymer crystals melt, they must absorb heat in order to do so. The heater under the sample pan has to put extra heat into the polymer in order to both melt the crystals and keep the temperature rising at the same rate as that of the reference pan. This extra heat flow during melting shows up a peak on the DSC plot. Usually the temperature at the top of the peak is the polymer's melting temperature, T_m.

T_{onset} is the onset temperature, the temperature at which the curve first departs from the pre-programmed baseline on the low temperature side of the endotherm or the high temperature side of the exotherm.



Typical DSC curves showing the glass, crystallisation, and melting transitions.

Integration of the area of the crystallisation dip and division by the weight of the polymer sample will give the latent heat of crystallisation for the polymer. Integration of the area under the melting peak and division by the weight of the polymer sample will give the melting enthalpy (ΔH_m). Using the melting enthalpy obtained, percentage crystallinity can be calculated using the relationship:

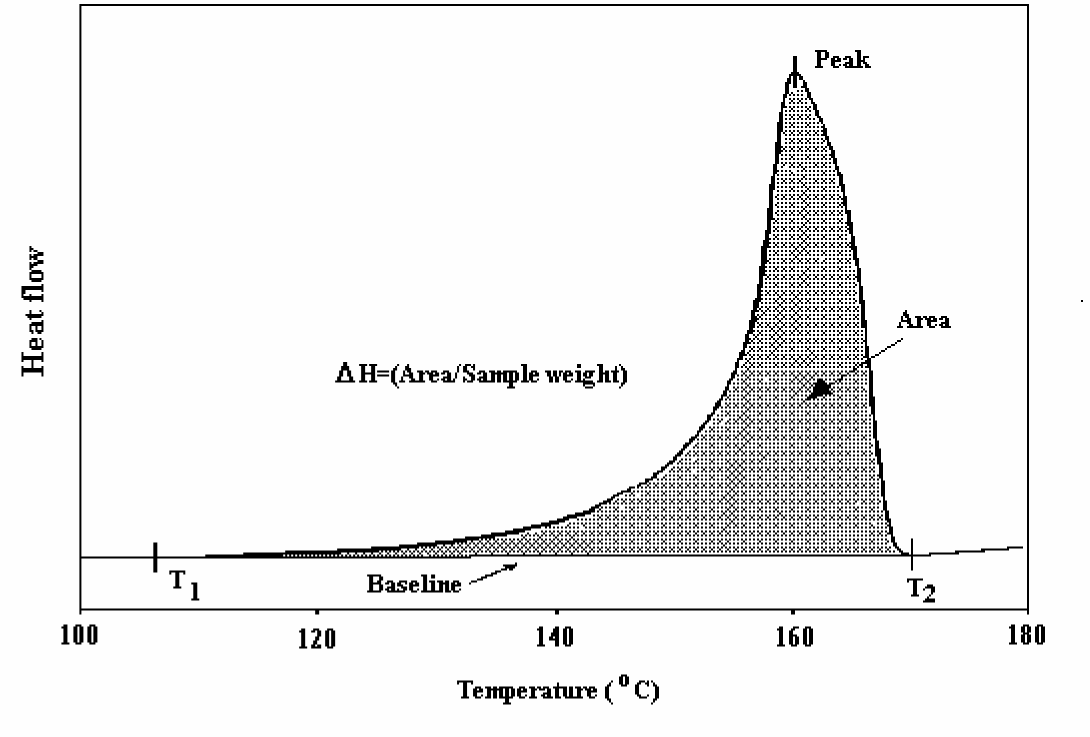
$$\%Crystallinity = \frac{\Delta H_m}{\Delta H_f^o} * 100$$

where ΔH_m is the enthalpy of fusion for the sample under study (*J/g*) and ΔH_f^o is the enthalpy of fusion for a *100%* crystallinity polymer sample (*J/g*).

Isothermal Crystallisation

Usually small fragments of sample are carefully cut using a scalpel and accurately known weight of approximately *5±0.1mg* is crimped in aluminium pans. Efficient enscapulation of the sample in the aluminium pan is essential as this ensured good thermal contact between the sample and furnace.

For an isothermal crystallisation run the sample is loaded at room temperature into the DSC, heated up rapidly ($40^oC/min$) to the required temperature passes through the melting point and maintaining it at this temperature for *3-5* minutes to remove thermal history. Melted samples are cooled down rapidly ($100^oC/mim$) to the required crystallisation temperature and allowed to crystallise. The required time to complete the crystallisation run depends on the crystallisation temperature, higher crystallisation temperatures requiring longer times. On completion of the crystallisation, the sample is cooled down to the room temperature. To measure the percentage crystallinity within the crystallised sample, a second controlled heating rate of $10^oC/min$ is used to heat up the sample from room temperature up to the required temperature passing through the melting point.

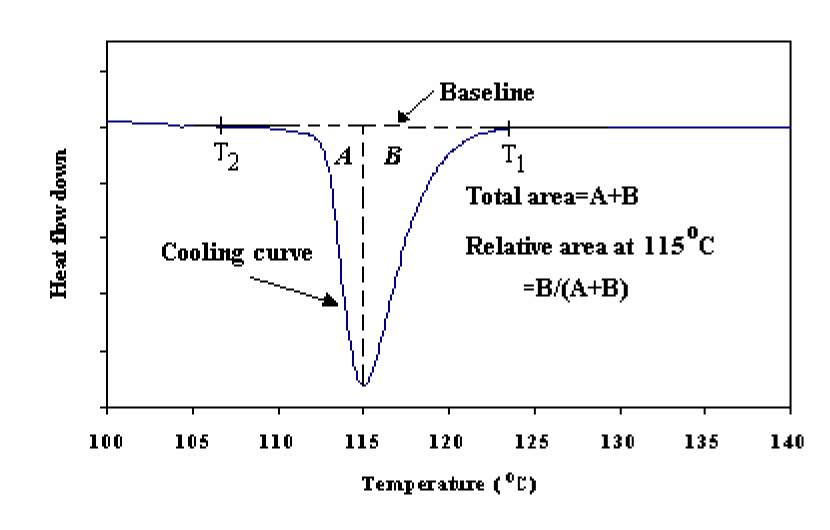


Typical DSC melting endotherm for isotactic polypropylene.

Non-isothermal Crystallisation

For non-isothermal crystallisation the sample is loaded at room temperature into the DSC, heated up rapidly (*40^{o}C/min*) to the required temperature passing through the melting point and maintained at this temperature for *3-5* minutes to remove thermal history. The melted sample is then cooled at constant rate down to room temperature.

For characterising the beginning of crystallisation, the time corresponding to the intersection between the extrapolation of the DSC curves after crystallisation (T_2) and the same curve before crystallisation (T_1) is selected. The relative crystallinity, which develops on cooling to temperature T, is defined as the fractional area confined between the rate time curve and the baseline on the measured DSC exotherm.



Calculation of relative crystallinity from cooling DSC curve.

Growth Rate Measurement

The growth rate of crystallisation was measured by using a polarising light microscope fitted with a hot stage. Real time crystallisation runs are recorded on videotapes and then analyzed. The hot stage must be calibrated for temperature using such example high purity benzoic acid (melting point 122.35^oC).

Thin sample of polymer ($< 10\mu m$) is sandwiched between two microscope slides and heated up to the required temperature for *5* minutes to remove thermal history. For isothermal growth rates, the molten samples are rapidly (cooling rate $40^oC/min$) cooled down to the proposed crystallisation temperatures. On completion of crystallisation, the sample is cooled down to room temperature. Non-isothermal growth rates are measured by cooling down the molten samples at constant rates to room temperature. A newly prepared sample is used for each observation.

Using the recorded real times crystallization, images are captured. Images are analysed by measuring the spherulite radius as a function of time.

Scanning Electron Microscopy

Scanning electron microscopy is used exclusively for examination of sample surfaces where the electron beams is rastered across the sample. The image is produced by collecting secondary electrons emitted from the excited surface by means of a scintillator and then reproducing the scintillator image in a display synchronized with the beam sweep.

A comprehensive understanding of the properties of materials has always required a thorough knowledge of their structure as well as their composition. Most materials, whether of natural or synthetic origin, have a complex structure when observed through the optical or electron microscope. Etching techniques have proved very valuable in giving information at all levels.

Permanganic etching is employed to selectively eliminate the amorphous phase of melt crystallised samples and reveal the strongly pronounced surface structure of the crystalline phase.

A thin film ($< 0.5mm$) is placed in a sealable test tube containing a *60:40* mixture of concentrated H_3PO_4 and H_2SO_4 (the purpose of which is to minimise the occurrence of artefacts) with approximately *0.5wt%* potassium permanganate ($KMnO_4$). The solution is agitated in an ultrasonic bath for one hour to mix before the polymer samples are floated in the dark green etching solution and agitated for *1 hr*. The solution must be contained in a fume cupboard at all times as a precaution against the spontaneous production of manganese heptoxide, an unstable and explosive by-product of the etching solution.

After the desired treatment the following five stage cleansing procedure is carried out:

The specimen is washed in a dilute solution of $7H_2O:H_2SO_4$. It is then cleaned in hydrogen peroxide to destroy the permanganate. After this it is washed in distilled water, then in acetone and finally dried in a vacuum oven at 40^oC for *1 hr*.

The etched samples are mounted on aluminium stubs with double-sided sticky pads. Each sample is sputtered with a very thin layer of gold this is to eliminate any undesirable charge effects during the SEM observations. Samples are examined using an election microscope.

X-ray Diffraction

X-ray diffraction is a definitive technique for measuring the degree of crystallinity in polymers. The method is based on the assumption that it is possible to separate the intensity contributions arising from crystalline and amorphous regions.

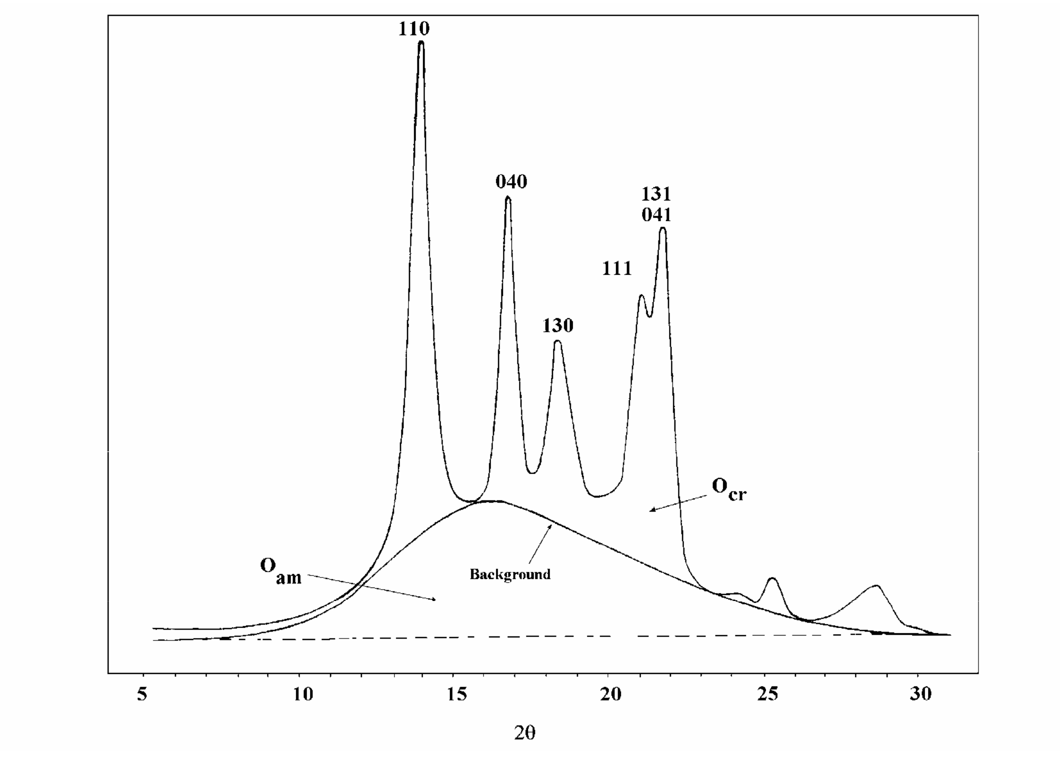
Samples of dimensions $10\times10mm$ were mounted perpendicularly to the X-ray beam on a quartz slide and held in place with a small amount of grease.

Degree of Crystallinity

The Hermans-Weidinger method is used to determine the degree of crystallinity from X-ray diffractograms. Crystalline intensity is taken as proportional to the integral area of all the crystalline peaks above the background line, and the area beneath the background is proportional to the amorphous intensity once the contributions of factors such as incoherent scattering, thermal scattering and air scattering are subtracted. This method is simplified when the crystallinity of different samples of the same material is studied, provided that samples are submitted to the same radiation. The crystalline fraction X is calculated using the following equation:

$$X = \frac{1}{1 + 1.297\, O_{am} / O_{cr}}$$

Where O_{cr} is the total surface of the main peaks above the background, O_{am} is the total surface between the background and the zero line, a quantity proportional to the amorphous faction.



Typical example of isotactic polypropylene X-ray curve showing the amorphous and crystalline areas.

Crystallite Size

The crystallite size is measured using the Debye-Scherrer equation in which the half-width of the diffraction peaks is considered as inversely proportional to the crystallite size. Although the Debye-Scherrer equation does not give the crystallite size very precisely it provides a fairly good approximation for small crystals and because of its simplicity it is often used. The crystals average length *t* (*Å*) is given by:

$$t_{hkl} = \frac{0.9\lambda'}{\left(B\cos\left(\theta_{hkl}\right)\right)}$$

Where t_{hkl} is crystallite dimension perpendicular to the lattice plane (*hkl*), λ' is the wavelength of the X-rays (*1.54178 Å*), *B* is the width at half-height of the diffraction maximum (Rad) and θ_{hkl} is the Bragg angle corresponding to the *hkl* plane (°).

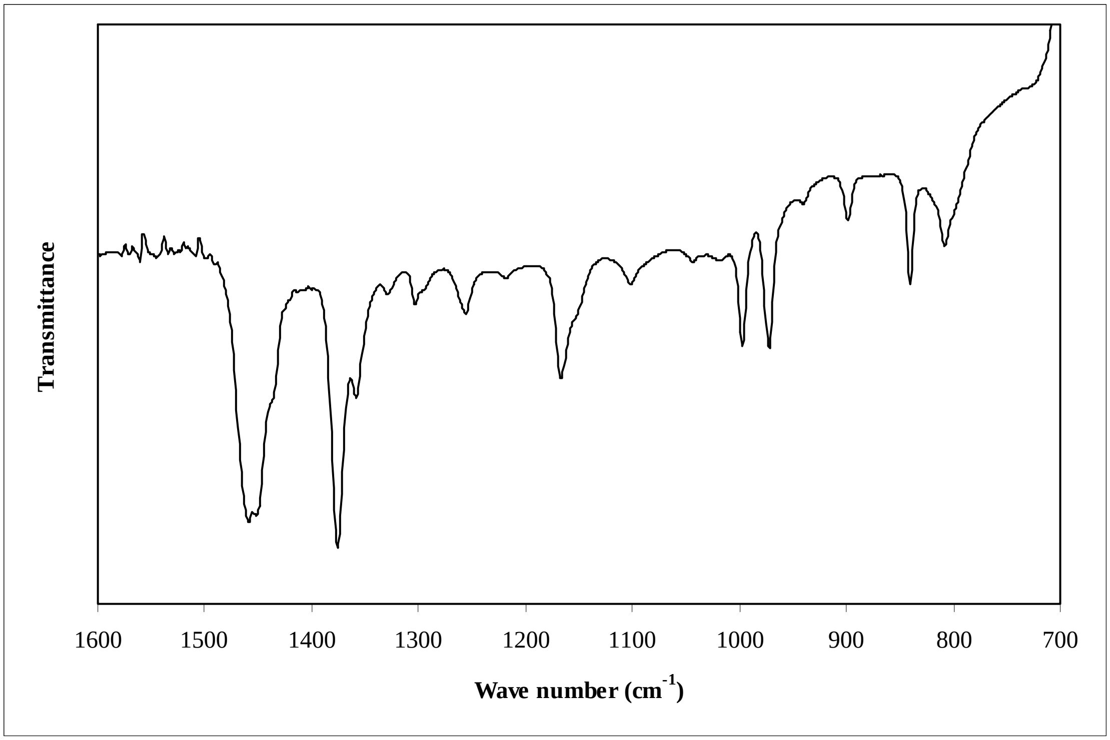
Fourier Transform Infrared Spectroscopy

Infrared (IR) spectroscopy is one of the most powerful techniques available to organic and analytical chemists. It serves both research applications and more routine studies carried out in application and process-control laboratories. Infrared analysis is applicable to both qualitative and quantitative analysis.

A Fourier transform is a complex mathematical computation which is performed by computer. Infrared, an invisible part of the electromagnetic spectrum between visible and radio waves, refers to the radiation used by the spectrometer to perform its measurement. A Fourier transform infrared (FTIR) spectrometer is an instrument that provides information about the molecules present in a given sample or matter as well as the quantities.

Fourier transform infrared spectrometers record the interaction of IR radiation with the experimental sample, measuring the frequencies at which the sample absorbs the radiation and the intensities of the absorption.

Determining these frequencies allows identification of the sample’s chemical makeup, since chemical functional groups are known to absorb light at specific frequencies. Intensity and frequency of sample absorption are depicted in a two-dimensional plot called a spectrum. Intensity is generally reported in terms of absorbance, the amount of light absorbed by a sample, or percent transmittance, the amount of light passing through it. Frequency is usually reported in terms of wavenumbers.



FTIR spectra for isotactic polypropylene sample

Density Measurement

Density measurements are made using a digital balance fitted with density measurement equipment (*Mettler Toledo PG 503-S*). The sample weight is recorded in air and in water and the density calculated using the relationship:

$$\rho = \frac{A'}{A' - B'} \rho_o + 0.0012$$

Where A' is the sample weight in air, B' the sample weight in water, ρ_o the water density at the test temperature, and *0.0012* is a correction factor for the air displaced by the sample.