Chapter III: Characterization of macromolecules and behavior in solution

III.1. Introduction:

The molecular weight of a polymer is of fundamental importance in the synthesis and application of the polymer. For example, the most important mechanical properties depend on and vary considerably with molecular weight. The interesting and useful mechanical properties associated with polymers are a consequence of their high molecular weight.

III.2. Average molecular weights of polymers:

The molecular weight of a polymer is quite different from that which applies to small molecules. Polymers differ from small molecules because they are polydisperse (or polymolecular), which means they are a mixture of macromolecular chains of different sizes. Even if a polymer is synthesized free of all impurities, it is still not a pure substance in the strict sense of the word. The reason for the polydispersity of polymers lies in the statistical variations present in the polymerization processes. When we talk about the molecular weight of a polymer, we are actually referring to its average molecular weight. The average molecular weight and the exact distribution of the different molecular weights in a polymer are necessary to characterize it properly. Control of molecular weight and molecular weight distribution is often used to achieve and improve certain desired physical properties in a polymer product.

Voici quelques définitions courantes de la masse moléculaire moyenne des polymères :

III.2.1. Average number molecular weight ($\overline{Mn}$):

It corresponds to the total mass of all oligomers in a sample divided by the total number of oligomers in the sample. This parameter gives an idea of the flexibility and adhesion of the polymer, properties that are related to the proportion of low molecular weight constituents. Methods for measuring Mn include those that measure colligative properties of solutions, NMR, UV-visible, CES, and MALDI-TOF.

$$\overline{Mn} = \frac{\Sigma MiNi}{\Sigma Ni}$$

where,

Ni is the average number of molecules

Mi is the average molecular mass.

III.2.2. Weight average molecular weight ($\overline{Mw}$):

It is based on the observation that a molecule of higher mass contains more of the total mass of the polymer sample than a molecule of lower mass. This parameter reflects the amount of high molecular weight constituents, which particularly affect the mechanical strength of the polymer. Mw is determined by CES, from light scattering measurements, MALDI-TOF, and other methods.

$$\overline{Mw} = \frac{\Sigma Ni\, Mi^2}{\Sigma NiMi}$$

III.2.3. Viscometric average molecular weight ($\overline{Mv}$):

It is determined from viscosity measurements of the solution for different concentrations of dissolved polymer. Unlike other average molecular weights, it is not an absolute value because it depends on the solvent used and the temperature.

$$\overline{Mv} = \ [\Sigma Wi\ Mi^a]\ ^{1/a}$$

where wi is the mass fraction of molecules with a molecular weight of Mi, and a is the exponent of the Mark-Houwink-Sakurada equation.

III.2.4. Z-average molar mass (Mz):

The **z-average molar mass** is the third moment or third power average molar mass, which is calculated by

$$\overline{Mz} = \frac{\Sigma Ni\, Mi^3}{\Sigma NiMi^2}$$

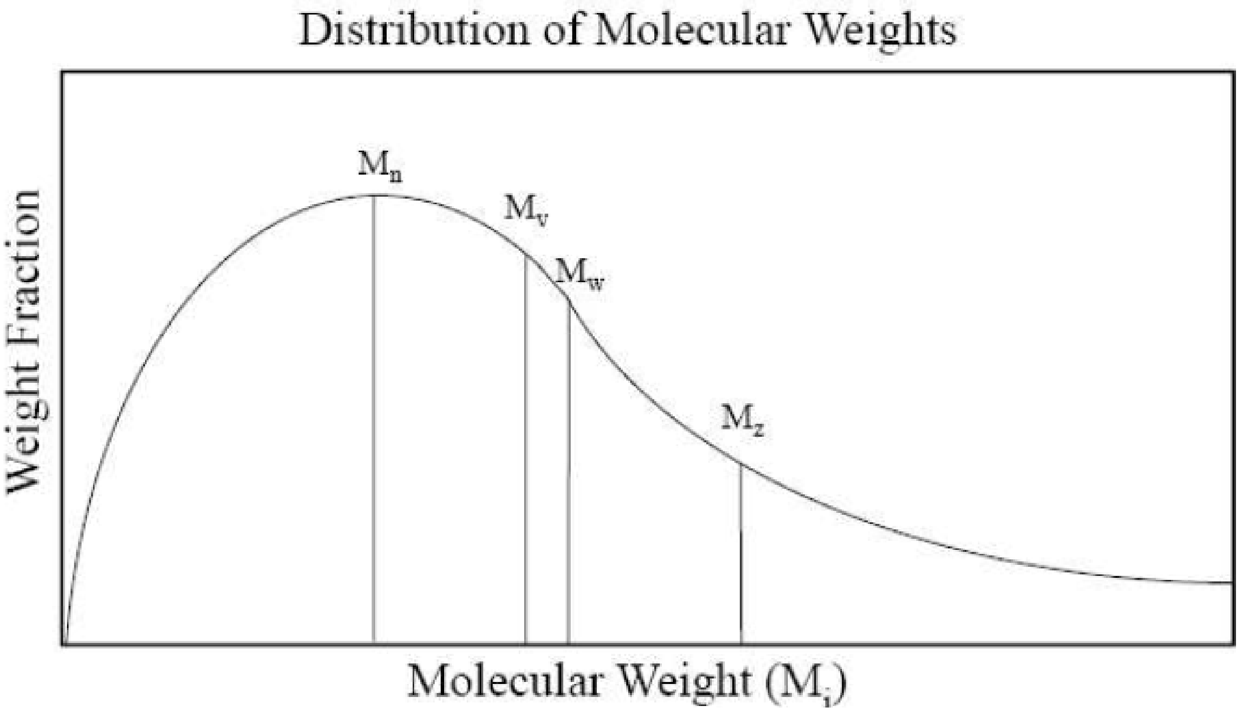
The z-average molar mass can be determined with ultracentrifugation. The melt elasticity of a polymer is dependent on $\overline{M}_z$.

III.2.5. Measurement:

These different definitions have true physical meaning because different techniques in physical polymer chemistry often measure just one of them. For instance, osmometry measures number average molar mass and small-angle laser light scattering measures mass average molar mass. $\overline{\mathrm{Mv}}$ is obtained from viscosimetry and $\overline{\mathrm{Mz}}$ by sedimentation in an analytical ultra-centrifuge. The quantity a in the expression for the viscosity average molar mass varies from 0.5 to 0.8 and depends on the interaction between solvent and polymer in a dilute solution. In a typical distribution curve, the average values are related to each other as follows:

$$\overline{\mathbf{Mn}} < \overline{\mathbf{Mv}} < \overline{\mathbf{Mw}} < \overline{\mathbf{Mz}}$$

The dispersity (also known as the polydispersity index) of a sample is defined as $\overline{\mathrm{Mw}}$ divided by $\overline{\mathrm{Mn}}$ and gives an indication just how narrow a distribution is.



III.2.6. Degree of polymerization:

The degree of polymerization is a measure of the size of a polymer molecule, which is the number of monomers that make it up. It is the average number of monomer repetitions in a polymer chain.

For example, if a molecule of polyethylene has a degree of polymerization of 1000, it means that it is composed on average of 1000 repeated units of ethylene monomers.

The degree of polymerization depends on several factors, such as the polymer synthesis method, reaction conditions, and the quality of the reactants used. It can be experimentally measured using techniques such as infrared spectroscopy or gas chromatography.
For a homopolymer, there is only one type of monomeric unit and the *number-average* degree of polymerization is given by :

$$\overline{DP} = \frac{\overline{Mn}}{M0}$$

$\overline{Mn}$ is the number-average molecular weight and M0 is the molecular weight of the monomer unit.

III.2.7. Polydispersity index (PDI):

Polydispersity index (PDI) is a measure of the distribution of particle sizes in a sample. It is commonly used in the fields of chemistry, material science, and biotechnology to characterize the size distribution of particles, such as polymers, nanoparticles, and biological molecules.

PDI is calculated as the ratio of the weight-average particle size to the number-average particle size. A PDI value of 1 indicates a monodisperse sample, meaning that all particles in the sample are the same size. A higher PDI value indicates a more polydisperse sample, meaning that the particles in the sample have a wider range of sizes.

$$\overline{DPI} = \frac{\overline{Mw}}{\overline{Mn}}$$

III.2.8. Techniques for determining average molar mass:

Various experimental techniques are available to determine the molecular weight of a polymer (as shown in the table below). Among these, size exclusion chromatography, MALDI mass spectrometry, and solution-based methods are included. For the latter, these include methods based on collative properties, light scattering, and viscosity. These different methods do not yield the same average molecular weight. In fact, different average molecular weights are obtained because the measured properties are used differently for polymers of different sizes. Some methods are used for larger polymers, while others are used for smaller polymers. The result is that the obtained average molecular weights are skewed towards larger or smaller molecules accordingly. Different methods (absolute and relative) for determining the molecular weight of a polymer sample are listed in the table below.

Table III.1: Techniques for determining average molar mass

Absolute methods		
Techniques	**Average molar mass**	**Molar mass limits**
Static light scattering	Mw	> 100 g/mol
X-rays and neutron scattering	Mw	> 500 g/mol
Ultracentrifugation (or sedimentation)	Mw, Mz	> 1000 g/mol
Ebullioscopy and cryoscopy	Mn	<20 000 g/mol
Membrane osmometry	Mn	> 5000 g/mol, <1 000 000 g/mol
Vapor pressure osmometry	Mn	<50 000 g/mol
Measurement of chain ends	Mn	<40 000 g/mol
MALDI-TOF mass spectrometry	Mn, Mw, Mz	<200 000 g/mol
Méthodes relatives		
Size exclusion chromatography	Mn, Mw, Mz	> 1000 g/mol
Viscometry	Mv	>1000 g/mol
Fractionation	Mn, Mw, Mz	> 1000 g/mol

III.3. Behavior in solution:

Understanding the behavior of polymers in solution is important for certain applications such as cosmetic gels and creams. It is possible to control the viscosity of the product obtained and to avoid possible demixing (phase separation).

III.3.1. Solvation:

Solvation of polymers is an important process that can affect the physical and chemical properties of polymers in solution. Polymers are macromolecules composed of many repeated units and have a large size, which makes them different from simple molecules.

In a solution, polymers can interact with solvent molecules in various ways, such as solvation of polar functional groups present on the polymer, solvation of electric charges, and hydrophobic regions.

When a polymer is introduced into a solution, solvent molecules organize around the polymer to form a "solvation envelope" called a solvation layer. This solvation layer can affect the conformation and flexibility of the polymer, as well as its solubility and viscosity.

In general, polar polymers tend to be more soluble in polar solvents and are therefore more easily solvated. On the other hand, non-polar polymers tend to be more soluble in non-polar solvents and therefore have less interaction with polar solvent molecules.

Solvation of polymers can also affect their chemical reactivity, permeability, and behavior in liquid phase. For example, solvation can modify the kinetics of chemical reactions involving the polymer in solution.

III.3.2. Flory-Huggins theory:

Flory-Huggins theory is a thermodynamic theory that describes the behavior of polymers in solution. It was developed by American chemists Paul Flory and Maurice Huggins in the 1940s.

Flory-Huggins theory considers the polymer-solvent solution as a mixture of two components and uses thermodynamic concepts to describe the properties of the solution. It assumes that polymers are linear chains of infinite size and that the polymer-polymer and polymer-solvent interactions are of an entropic nature.

Flory-Huggins theory uses the concept of Flory-Huggins parameter (chi), which describes the interaction between the polymers and the solvent. The chi parameter is calculated from the difference in Gibbs free energy between the polymer-solvent solution and the pure solvent or polymer solution.

$$\Delta Gm = \Delta Hm - T \Delta Sm$$

A change, denoted by Δ, is the value of a variable for a solution or mixture minus the values for the pure components considered separately. The objective is to find explicit formulas for ΔHm and ΔSm, the enthalpy and entropy increments associated with the mixing process.
The result obtained by Flory and Huggins is

$$\Delta\ Gm= RT[n1\ Ln\ \varnothing1 + n2\ Ln\ \varnothing2 + Ln\ \varnothing2\ \chi_{12}$$

The right-hand side is a function of the number of moles n1 and volume fraction $\varnothing1$ of solvent (component 1), the number of moles n2 and volume fraction $\varnothing2$ of polymer (component 2), with the introduction of a parameter χ to take account of the energy of interdispersing polymer and solvent molecules. R is the gas constant and T is the absolute temperature.

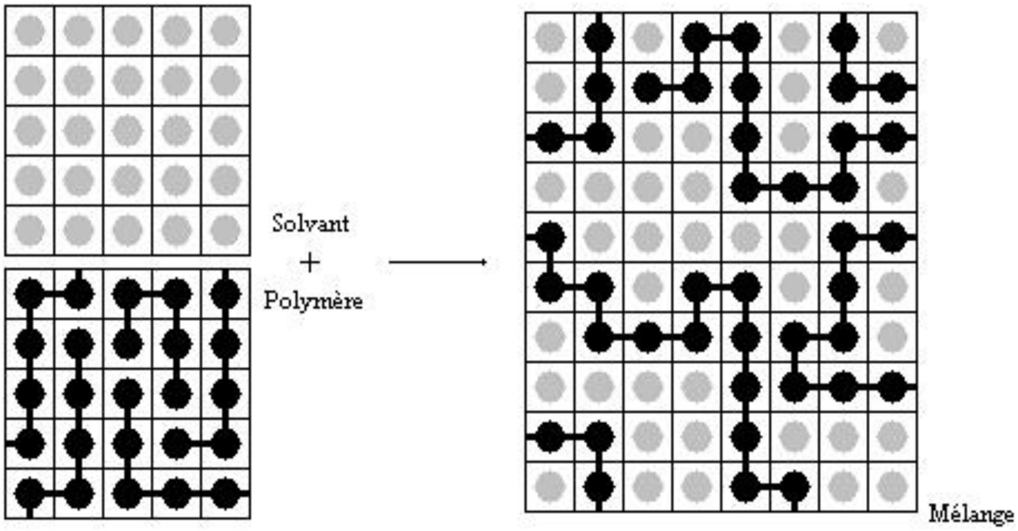


Figure III.1 Flory-Huggins theory

III.3.3. The hydrodynamic volume of a polymer:

The hydrodynamic volume of a polymer is a measure of its size and shape in solution. It is the volume of the polymer molecule that is accessible to solvent molecules, and it depends on a variety of factors, including the polymer's size, shape, and flexibility, as well as the properties of the solvent.

Hydrodynamic volume is typically determined using techniques such as gel permeation chromatography (GPC) or dynamic light scattering (DLS), which measure the diffusion of the polymer molecules in solution. By analyzing the diffusion behavior, it is possible to calculate the hydrodynamic radius or volume of the polymer.

Polymers with larger molecular weights and more compact shapes generally have larger hydrodynamic volumes, while more flexible or elongated polymers tend to have smaller hydrodynamic volumes. Solvent properties, such as viscosity and polarity, can also affect the hydrodynamic volume of a polymer.

The hydrodynamic volume is an important parameter for understanding the behavior of polymers in solution and their interactions with other molecules. It can also provide insight into the physical properties of polymer materials and their potential applications in fields such as biotechnology, materials science, and nanotechnology.

The hydrodynamic volume of a polymer can be influenced by different factors, such as temperature, polymer and solvent concentration, pH, and interactions with other molecules in solution. Therefore, the hydrodynamic volume is often used to study the solvation properties of polymers and their behavior in solution.

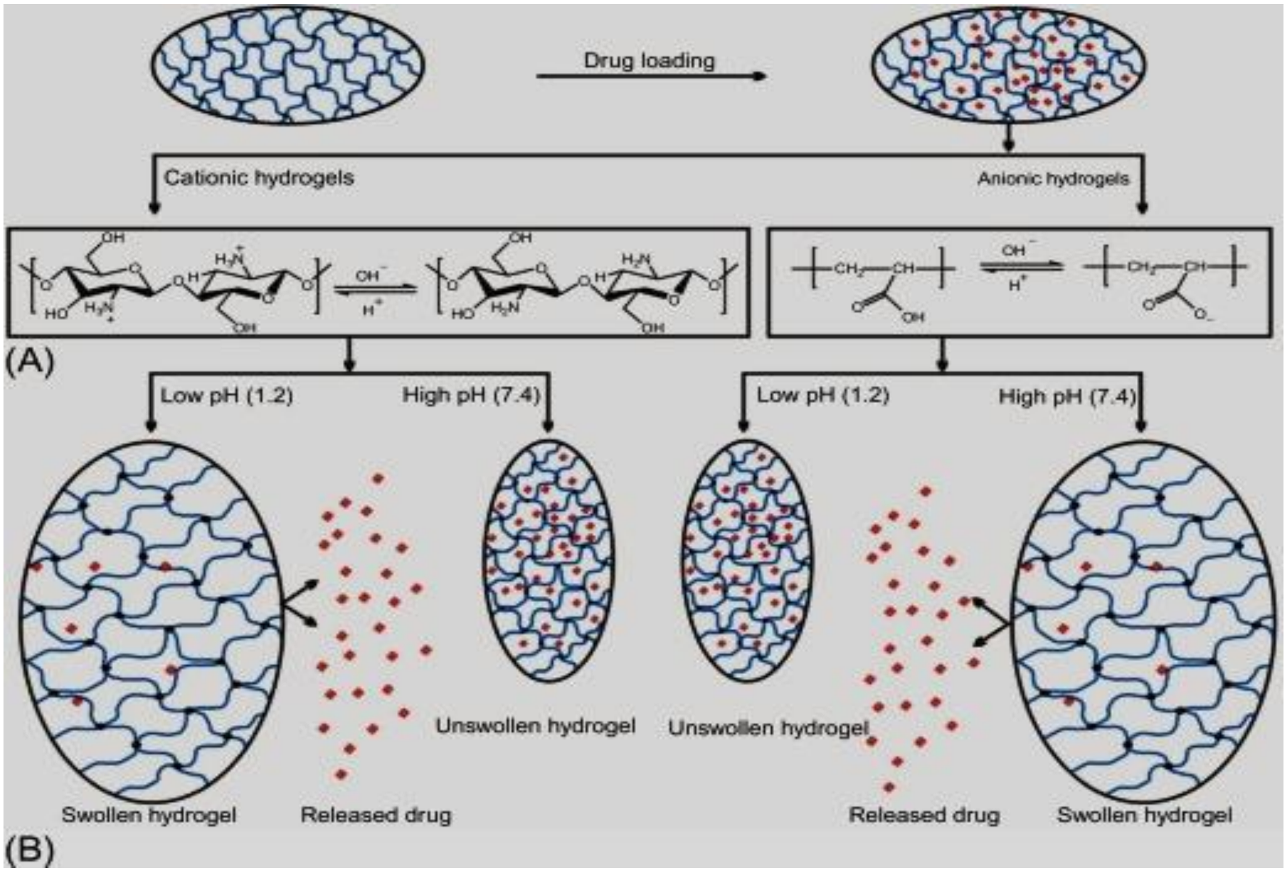


Figure III.2. hydrodynamic volume of a polymer

III.3.4. calculated of hydrodynamic volume:

The hydrodynamic volume of a polymer is a measure of its size in solution, taking into account the effects of its shape and interactions with solvent molecules. It can be calculated using various theoretical models or experimental techniques.

One common theoretical model is the random coil model, which assumes that the polymer is a flexible, randomly coiled chain in solution. The hydrodynamic volume (Vh) of a polymer can be calculated using the following equation:

$$\mathbf{Vh = (4/3)\ \pi\ Rg^3}$$

where Rg is the radius of gyration, a measure of the average distance between the polymer chain segments from the center of mass. Rg can be calculated using the following equation:

$$Rg = sqrt[(1/N)\sum i=1 \ N \ n^2]$$

The formula inside the square root, **$(1/N)\sum i=1 \ N \ n^2$**, represents the mean squared distance of the particles from the center of mass. Here, N is the total number of particles, and n^2 is the square of the distance of the ith particle from the center of mass.

The symbol **$\sum i=1 \ N$** indicates that we are summing up the squared distances of each of the N particles from the center of mass.

The factor of **(1/N)** in front of the sum indicates that we are taking the average of the squared distances.

Finally, taking the square root of this average gives us the root mean square radius, which is denoted by Rg.

III.4. The viscosity of a polymer:

The viscosity of a polymer is a measure of its resistance to flow. It depends on the size and molecular structure of the polymer, as well as its temperature and concentration. The larger and more branched a polymer is, the higher its viscosity will be.

Viscosity can be measured in various ways, including using a viscometer, which measures the force required to circulate a liquid through a known size tube. Viscosity can also be measured by observing the time it takes for a ball or needle to fall through a liquid, or by measuring the rate of flow of a liquid through a known-size orifice.

The viscosity of polymers can vary greatly depending on processing conditions such as temperature, pressure, and shear force. Polymers are often used in applications where their viscosity is important, such as in paints, adhesives, lubricants, drilling fluids, composite materials, plastics, and elastomers.

III.4.1. Measure the viscosity of a polymer:

The calculation of polymer viscosity depends on several factors such as the size and molecular structure of the polymer, temperature, and concentration. Here are some methods for calculating polymer viscosity:

III.4.1.1. Intrinsic viscosity calculation:

Intrinsic viscosity is a measure of the molecular size of the polymer and is calculated by measuring the passage time of the polymer through a capillary tube. This measurement is used to calculate the molecular mass of the polymer using the following formula:

$$[\eta] = (2.303RT/M) \log(t/t_0)$$

where $[\eta]$ is intrinsic viscosity, R is the gas constant, T is temperature in Kelvin, M is the molecular mass of the polymer, and t and t_0 are the passage times of the polymer and solvent, respectively.

III.4.1.2. Viscosity calculation from concentration:

The viscosity of a polymer can be calculated using the Huggins formula:

$$\eta = \eta 0 + K\ C$$

where η is the viscosity of the polymer, $\eta 0$ is the viscosity of the solvent, K is the Huggins constant, and C is the concentration of the polymer.

III.4.1.3. Viscosity calculation from temperature:

The viscosity of a polymer can also be calculated using the Arrhenius equation:

$$\eta = A \exp(Ea/RT)$$

where η is the viscosity of the polymer, A is a constant, Ea is the activation energy, R is the gas constant, and T is temperature in Kelvin.

It is important to note that these formulas are approximations and polymer viscosity can vary significantly depending on processing conditions. Experimental measurements are often necessary to determine the viscosity of a polymer under specific conditions.

III.5. Structural analysis of polymers:

Structural analysis of polymers is an important part of polymer characterization and can be carried out using different techniques. Here are some of the most common methods used for the structural analysis of polymers:

III.5.1. UV-Visible spectroscopy:

UV-Visible spectroscopy is a commonly used technique for polymer characterization. It allows the measurement of light absorption by polymers in the UV-Visible region of the electromagnetic spectrum.

UV-Visible spectroscopy is particularly useful for studying polymers that absorb light in the UV-Visible region, such as aromatic polymers, dyes, pigments, and chromophores. This technique allows for the measurement of the amount of light absorbed by polymers, which can provide information on their chemical structure and composition.

Using reference standards, it is possible to quantify the concentration of polymers in a solution. This technique can also be used to track changes in the chemical structure of polymers over time, such as measuring light absorption during polymerization or degradation of polymers.

UV-Visible spectroscopy can also be used to measure the refractive index of polymers, which is an important property for many applications, including optical materials.

III.5.2. Infrared Spectroscopy (IR):

Infrared Spectroscopy (IR) is a widely used analysis technique for the identification and characterization of polymers. It is based on the absorption of infrared light by the functional groups present in the polymer structure.

III.5.2.1. IR spectroscopy:

Identification of polymers: each polymer has a unique IR spectrum that allows for reliable identification.
Characterization of functional groups: the position and intensity of absorption bands in the IR spectrum can provide information about the functional groups present in the polymer structure.
Analysis of polymer structure: IR spectroscopy can be used to determine the structure of polymers by studying the vibration modes of atoms in the molecular structure.
Quantification of additives: IR spectroscopy can be used to quantify additives such as stabilizers, plasticizers, and colorants in polymers.

III.5.3. Nuclear Magnetic Resonance Spectroscopy (NMR):

Nuclear Magnetic Resonance Spectroscopy (NMR) is a very powerful analysis technique for studying polymers. It allows for the analysis of the molecular structure of polymers by determining the interactions between atomic nuclei in molecules.

NMR is based on the magnetic properties of atomic nuclei, which can be aligned in a magnetic field. By applying radiofrequency waves, the nuclei can be excited and transition from a low energy state to a higher energy state. When they return to their original state, the nuclei emit energy in the form of signals that are recorded and analyzed to provide information about the molecular structure.

III.5.3.1. NMR:

NMR can be used to determine the structure of polymers: NMR can be used to determine the structure of polymer chains, including the bonds between different monomers and substituents.
Study intermolecular interactions: NMR can be used to study interactions between polymer chains, interactions with solvents and additives, and interactions with other molecules.
Measure the size distribution of polymer chains: NMR can be used to measure the size distribution of polymer chains in a solution.
Study the dynamic properties of polymers: NMR can be used to study the dynamic properties of polymers, including molecular diffusion and spin relaxation.

III.5.4. X-Ray Diffraction (XRD):

X-ray diffraction (XRD) is an analysis technique used to study the crystalline structure of polymers. It is widely used in material characterization, including polymers, to determine their crystalline structure and chemical composition.

The basic principle of X-ray diffraction is that when X-rays are directed at a crystalline sample, they are diffracted by the regular crystal planes of the sample. The diffracted X-rays form characteristic angles that are detected and recorded as a diffraction pattern.

By using X-ray diffraction to study polymers, information can be obtained about the polymer's crystalline structure, molecular orientation, and morphology.

X-ray diffraction is particularly useful for studying semi-crystalline polymers, which have both crystalline and amorphous regions. It can also be used to study changes in crystalline structure caused by thermal or chemical treatments.

III.5.4.1. Interpret peaks:

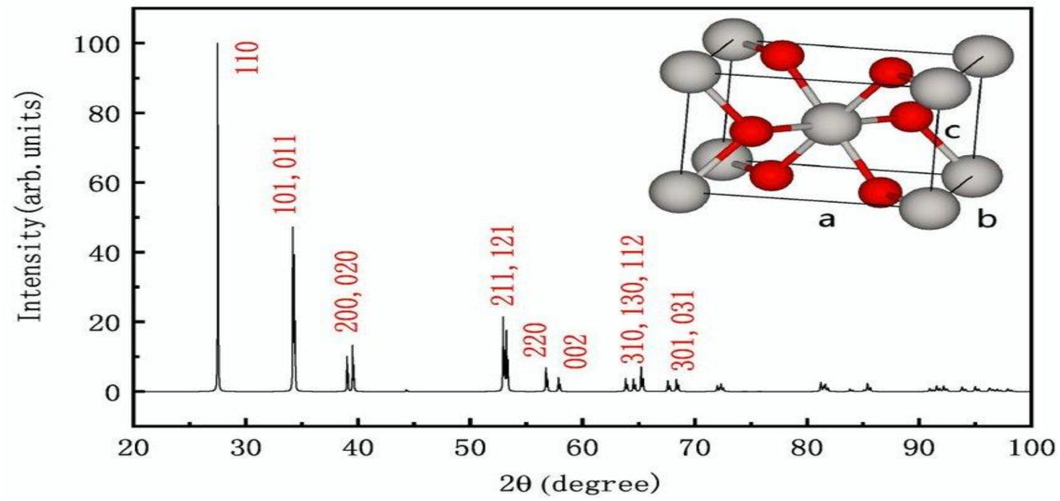


Figure III.3 XRD diagram

Identify Peaks: Peaks in an X-ray diffraction (XRD) diagram are represented by peaks of different heights. Each peak corresponds to a specific crystalline direction that diffracts X-rays. You can identify these peaks using X-ray diffraction data tables.

Analyze Peaks: The position of the peaks in the XRD diagram can provide information about the interplanar distance between the crystalline planes that diffract X-rays. The intensity of the peaks can be used to estimate the relative amount of different components in a material.

III.5.5. Raman Spectroscopy:

Raman spectroscopy is a commonly used analysis technique to characterize polymers. Polymers are macromolecular materials composed of repeating monomer units. The different configurations of monomers give unique physical and chemical properties to polymers.

Raman spectroscopy can be used to characterize the molecular structure of polymers, including chemical composition, molecular weight distribution, crystallinity, and intermolecular interactions.

Raman spectroscopy is a non-destructive technique that can be used to study polymers under different conditions, such as temperature and pressure, without disrupting their structure. It also allows for rapid and accurate analysis of polymer samples, which is important for industrial production.

When used for polymer analysis, Raman spectroscopy detects the molecular vibrations of chemical bonds in polymer chains. This technique is particularly useful for analyzing polymers in solid phase, such as films, fibers, and composite materials

Raman spectroscopy can also be used to determine the molecular weight distribution of polymers. By comparing Raman spectra of polymers with different molecular weights, it is possible to determine the molecular weight distribution of the polymer.

III.5.5.1. Interpretation of Raman Spectra:

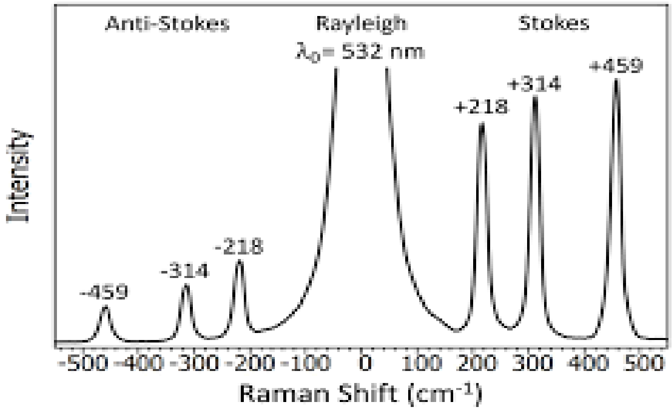


Figure III.4 Raman Spectrum of CCl_4 measured using a 532 nm laser

Interpreting a Raman spectrum involves analyzing the positions, intensities, and shapes of the Raman peaks. The positions of the peaks are related to the vibrational modes of the molecule and can provide information about the types of chemical bonds present in the sample. For example, stretching vibrations of C-H bonds typically appear around 2900 cm^{-1}, while stretching vibrations of C=C bonds typically appear around 1600 cm^{-1}.

The intensities of the Raman peaks can also provide important information about the sample. The intensity of a peak is related to the polarizability of the molecule, which in turn is related to the size, shape, and electronic structure of the molecule. Therefore, the intensities of the peaks can be used to identify different functional groups in a molecule and to monitor changes in the electronic structure of the molecule.

III.6. Scanning Electron Microscopy (SEM):

Scanning Electron Microscopy (SEM) is an imaging technique that allows observation of samples at a very small scale, up to resolutions on the order of nanometers. This technique is commonly used for characterizing polymers.

When used for polymer analysis, SEM provides high-resolution images of the surface of polymer samples. This technique can be used to study the topography of the surface of polymers, as well as to visualize surface defects such as cracks, pores, and bubbles.

SEM can also be used to determine the morphology of polymers, i.e. the shape, size, and arrangement of phases present in polymer samples. This information is important for understanding the physical and mechanical properties of polymers.

III.7. Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a high-resolution imaging technique that allows visualization of surface topography of samples at the nanoscale. This technique is very useful for polymer analysis, as it enables visualization of surface morphology, roughness, and particle size distribution in samples.

AFM uses an ultrafine probe to scan the sample surface and detect intermolecular forces that occur between the probe and the surface. By measuring these forces, AFM can generate a three-dimensional image of the sample surface at a scale of a few nanometers.

AFM can be used to study the morphology of polymers, such as particle size, shape, and distribution. It can also be used to study the roughness and porosity of polymer sample surfaces. Furthermore, AFM can be used to study the structure and texture of polymer sample surfaces, such as the presence of defects, cracks, and crystalline regions.

III.8. Differential Thermal Analysis (DTA):

Differential Thermal Analysis (DTA) is a thermal characterization technique that is widely used for polymer analysis. DTA measures the temperature variation of a sample as a function of time or temperature when it is heated or cooled at a constant rate. This technique allows for the measurement of polymer phase transitions such as glass transition, crystallization, melting, and thermal degradation.

Glass transition is an important phase transition that occurs in amorphous polymers when they are heated. This transition is characterized by an abrupt change in the physical properties of polymers such as stiffness, viscosity, and thermal expansion. DTA can be used to measure the temperature at which this transition occurs, which is important for understanding the mechanical properties of polymers.

Crystallization is another important process that occurs in polymers when they are heated. Crystallization is the process of forming crystalline structures in semi-crystalline polymers. DTA can be used to measure the temperature at which crystallization occurs and to study the kinetics of crystallization.

Melting is a process in which polymers melt and transition from the solid state to the liquid state. DTA can be used to measure the temperature at which melting occurs, as well as to determine the enthalpy of fusion of polymers.

Thermal degradation is a process that can occur when polymers are heated to high temperatures. DTA can be used to measure the temperature at which thermal degradation occurs, as well as to study the kinetics of degradation.

III.8.1. Interpretation of DTA:

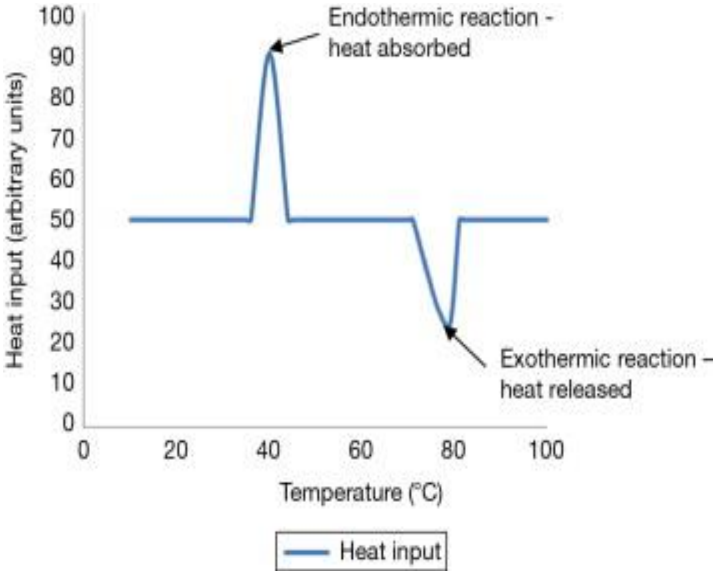


Figure III.5 Differential Thermal Analysis diagram

The interpretation of DTA results depends on the specific material being analyzed and the conditions under which the analysis is performed. Generally, DTA curves can be used to identify thermal events, such as melting, crystallization, phase transitions, and decomposition, that occur in the sample as it is heated or cooled.

In a DTA curve, the peaks or dips represent exothermic or endothermic thermal events, respectively. The magnitude of the peak or dip corresponds to the amount of heat released or absorbed during the thermal event, and the onset temperature of the event indicates the temperature at which the event starts.

III.9. Thermogravimetric Analysis (TGA):

Thermogravimetric Analysis (TGA) is a commonly used thermal characterization technique for polymers. It allows for the measurement of the mass of a sample as a function of temperature or time when it is heated in a controlled environment. This technique is often used to study the thermal stability of polymers their resistance to thermal degradation.

TGA can be used to measure the temperature at which polymers begin to degrade, which is called the initial degradation temperature (IDT). The IDT is an important property of polymers because it can impact their use under high-temperature conditions. TGA can also be used to measure the kinetics of thermal degradation of polymers, i.e., the rate at which they degrade at different temperatures.

By using different gas atmospheres, such as air, nitrogen, or argon, TGA can also be used to study the stability of polymers in specific environments. For example, TGA can be used to study the stability of polymers under oxidation or pyrolysis conditions.

III.9.1. Thermogravimetric Analysis interpretation:

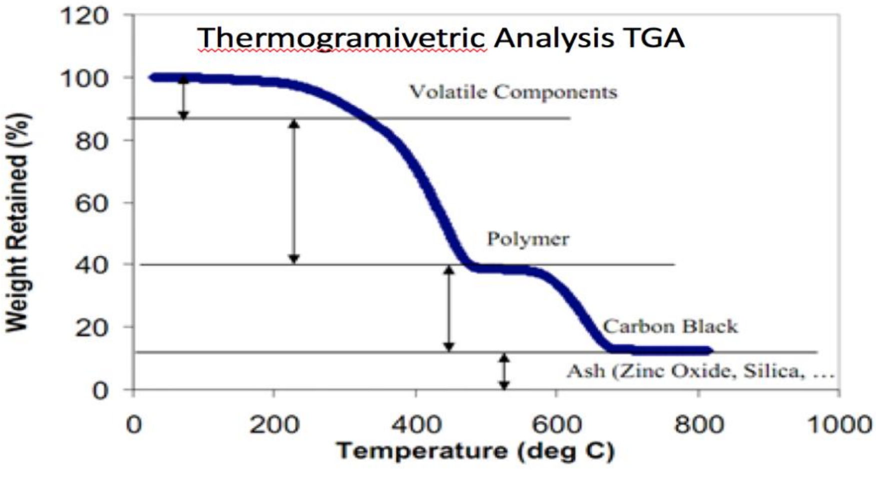


Figure III.6 Thermogravimetric Analysis (TGA)

Interpreting the data from a TGA experiment typically involves analyzing the following parameters:

1- Initial mass: This is the mass of the sample before heating or cooling. It provides a baseline for comparison with the mass at later stages of the experiment.

2- Mass loss: This is the difference between the initial mass and the mass at any given temperature. The rate and magnitude of mass loss can indicate the presence of volatile components, the onset of decomposition, and the thermal stability of the sample.

3- Temperature of onset of mass loss: This is the temperature at which the sample begins to lose mass. It is an important parameter for understanding the thermal stability and decomposition pathways of the sample.

4- Peak temperature: This is the temperature at which the maximum rate of mass loss occurs. It can indicate the presence of a particular decomposition pathway or chemical reaction.

5- Residue mass: This is the mass of the sample that remains after complete decomposition. It can provide information about the composition of the sample and the completeness of the decomposition process.

III.10. Differential Scanning Calorimetry (DSC) :

is a commonly used thermal characterization technique for polymers. It allows for the measurement of the heat absorbed or released by a polymer sample as a function of temperature or time when it is heated or cooled in a controlled environment.

DSC analysis can be used to determine the glass transition temperature (Tg) of a polymer. Tg is the temperature at which the polymer transitions from a rigid solid state to a softer, more malleable state, which has an impact on the mechanical properties and stability of the material. DSC can also be used to measure the melting and crystallization temperatures of polymers, which are important for the processing and transformation of polymer materials.

By using different heating and cooling methods, DSC can also be used to study the kinetic properties of polymers, such as rates of crystallization and melting. Additionally, DSC can be used to study chemical reactions such as polymerization, crosslinking, or degradation reactions of polymers.

III.10.1. Interpreting DSC results:

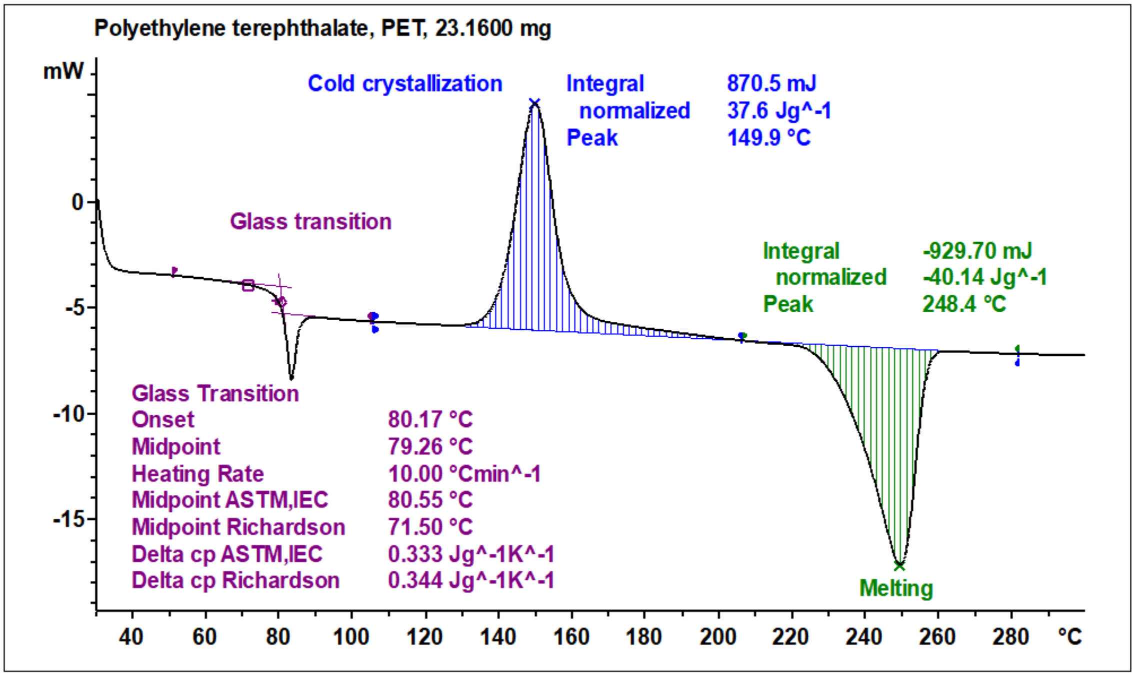


Figure III.7 DSC graph

Melting and Crystallization Transitions: DSC can detect melting and crystallization transitions in materials. A melting transition is indicated by a sharp endothermic peak on the DSC curve, while a crystallization transition is indicated by an exothermic peak. The onset and peak temperature of these transitions can provide information about the melting point, crystallinity, and purity of the sample.

Glass Transition: For amorphous materials, DSC can detect the glass transition temperature (Tg), which is the temperature at which the material transitions from a rigid glassy state to a more fluid or rubbery state. This transition is usually seen as a broad endothermic peak on the DSC curve.

Chemical Reactions: DSC can detect exothermic or endothermic reactions in samples as a function of temperature. These reactions can provide information about the thermal stability, decomposition, or curing behavior of the sample.

Heat Capacity: DSC can also be used to measure the heat capacity of a sample as a function of temperature. The heat capacity curve can provide information about the specific heat, thermal conductivity, and thermal diffusivity of the sample.

III.11. Particle Size Analysis (PSA):

Particle Size Analysis (PSA) is a commonly used technique for characterizing polymers in solution or suspension. It allows for the measurement of the size distribution of particles in a polymer sample by measuring the diffusion of light by the particles.

Using this technique, one can determine the average particle size as well as the distribution of particle size, which can provide important information about the morphology and stability of polymers. The PSA technique can be used to characterize a wide range of polymers, including synthetic and natural polymers, polymers in solution, and polymers in suspension.

The PSA technique can also be used to characterize the surface properties of polymers. By using polymers functionalized with specific chemical groups, it is possible to measure the interaction between polymer particles and their environment. This technique can also be used to study interactions between polymers and other components, such as proteins, lipids, and nanoparticles.

III.12. Size-exclusion chromatography (SEC):

This is the essential technique for characterizing polymers, including:
Distribution of molecular weights
Average molecular weights: $\overline{Mn}$, $\overline{Mw}$
Polydispersity index $\overline{Ip} = \overline{Mw}/\overline{Mn}$
SEC is a liquid-phase chromatography method used to separate macromolecules based on their hydrodynamic volume. It is commonly employed in polymer studies and is also known as gel permeation chromatography (GPC) depending on the nature of the two phases involved.

SEC is based on the difference in size of polymers in solution. Larger polymers have a lower penetration capacity into the chromatography gel than smaller polymers. By using a chromatography column filled with controlled-size gel, polymers are separated based on their size. The larger polymers are excluded from the chromatography gel and exit the column faster than smaller polymers.

Using known size standards, a calibration curve of SEC can be constructed, which can be used to determine the size of unknown polymers. SEC can also provide information on the size distribution of polymers in solution, as well as their average molecular weight, number-average molecular weight, and polydispersity.

SEC can be used to characterize polymers in solution, including synthetic polymers such as polyolefins, polyesters, polyamides, polyurethanes, as well as natural polymers such as DNA, proteins, and polysaccharides. This technique is also used to characterize copolymers and polymer blends.