People’s Democratic Republic of Algeria
Ministry of higher Education and Scientific Research
Djilali Bounaama Khemis Miliana University
Faculty of Science and Technology
Departement of Material Sciences

Field: Chemistry
Specialty: Pharmaceutical Chemistry (2nd year Master's degree)

Accreditation course

Macromolecular chemistry

Prepared by:

Dr: HAMMOUDI Mounir

MCB

(2023)

Foreword

This course is intended for second year Master's degree students in pharmaceutical chemistry. It covers the essential content of the course program in Macromolecular Chemistry intended for this category of students and draws inspiration from reference works in the field, including some direct applications related to the course.

In this course, we will explore the structure, synthesis and behavior of macromolecules, which are giant molecules made up of many repeating units. Macromolecules are present in many materials and products, such as plastics, rubbers, fibers and composite materials.

In the first chapter, we will address a general introduction to macromolecular chemistry, examining the properties and characteristics of macromolecules as well as their classification based on their structure and composition.

The second chapter will focus on polymer synthesis methods, which are macromolecules formed by the repetition of monomer units. We will discuss the different types of polymerization and factors that influence the polymerization reaction.

In the third chapter, we will explore the characterization of macromolecules and their behavior in solution, examining the analysis techniques and measurement of polymer properties such as viscosity, molecular weight and conformation.

Finally, in the fourth chapter, we will address the structural, thermal and mechanical behavior of polymers, studying the properties that determine the strength and durability of polymeric materials.

CONTENTS

Chapter I : Fundamental Concepts of Polymers

Chapter II: Polymer synthesis methods

Chapter III: Characterization of macromolecules and behavior in solution

Chapter IV: Thermal and mechanical behavior of polymers

I.1. Introduction:

Before we go into details of the chemistry of polymers it is appropriate to briefly outline a few landmarks in the historical development of what we now know as polymers. Polymers have been with us from the beginning of time; they form the very basis (building blocks) of life. Animals, plants — all classes of living organisms — are composed of polymers. However, it was not until the middle of the 20th century that we began to understand the true nature of polymers. This understanding came with the development of plastics, which are true man-made materials that are the ultimate tribute to man’s creativity and ingenuity. As we shall see in subsequent discussions, the use of polymeric materials has permeated every facet of our lives. It is hard to visualize today’s world with all its luxury and comfort without man-made polymeric materials.

I.2. Historical:

Polymers have a long history dating back to antiquity, but their large-scale use began in the 20th century. In 1907, the Belgian chemist Leo Baekeland invented the first synthetic plastic, Bakelite, by polymerizing phenol and formaldehyde. This discovery paved the way for a massive use of polymers in industry, especially in the production of electrical materials, insulation, and plastic objects.

Over the decades, research on polymers has intensified, leading to the development of new polymers such as nylon, polystyrene, and PVC. These polymers have enabled significant advancements in many fields, such as the textile industry, packaging, and automobiles.

In recent decades, research on polymers has further intensified, leading to the development of high-performance polymers for specialized applications such as composite materials, adhesives, and coatings. Today, polymers are ubiquitous in our daily lives and their use continues to grow to meet the needs of our modern society.

I.3. Definition:

A polymer is a macromolecule, organic or inorganic, composed of the repeated linking of the same pattern, the monomer (from the Greek monos: single or alone, and meros: part), linked to each other by covalent bonds.

The concept of polymer is less than a century old, because for a long time chemists did not accept that a molecule could be very large. A polymer is indeed a macromolecule obtained by repeating a constituent unit, also called a repeating unit, consisting of a group of atoms linked by covalent bonds. The terms "constituent unit" and "repeating unit" are nowadays preferred over "monomer motif" or "monomer unit". A polymer can be schematized by the following covalent linking, called a macromolecular chain:

-A-A-A-A-A-A-A-A-A-A-A-A-

where -A- represents the constituent unit.

Our nA----------------- An

The letter n is called the "degree of polymerization" or "polymerization index," and for high values of n (n > 100), we speak of macromolecules. Most synthetic macromolecules have a similar appearance, as long, flexible threads.

Example: polyethylene

$H_2C=CH_2$	$H2C^{*}-{}^{*}CH2$	$-(H2C-CH2)_n-$
Ethylene monomer	repeat unit	polymer polyethylene

- **Macromolecule:** A large molecule composed of repeating units derived from monomers.
- **Monomer:** A simple starting molecule (from the Greek monos mono: single or alone, and meros: part).
- **Constituent motif:** A small periodic structure that repeats along the chain, composed of one or more basic units (monomers).
- **Polymerization:** The reaction that assembles monomers into macromolecules.

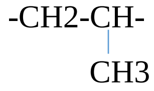
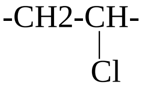
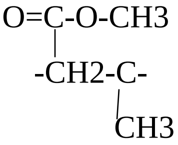
I.4. Polymer Nomenclature:

The nomenclature of polymers is based on the name of the monomer from which the polymer is derived. The name of the polymer is formed by adding the prefix "poly-" to the name of the monomer. For example, the polymer derived from the monomer ethylene is called polyethylene.

In some cases, the polymer name may also include a numerical prefix that indicates the degree of polymerization. For example, a polymer of ethylene with a degree of polymerization of 100 is called polyethylene-100.

For copolymers, the names are formed by adding the prefix "co-" and listing the names of the monomers in the order of their relative proportions. For example, a copolymer derived from ethylene and propylene is called poly(ethylene-co-propylene).

Table I.1 summarizing the main synthetic polymers:

Structural formula of the monomer unit	Common name and standardized abbreviation	Applications
$-CH_2-CH_2-$	Polyethylene (PE)	Car tanks, bottles
 $-CH_2-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-$	Polypropylene (PP)	food packaging film
 $-CH_2-\underset{\underset{\displaystyle Cl}{\vert}}{CH}-$	Polyvinyl chloride (PVC)	Piping, margarine tubs
 $-CH_2-\overset{\overset{\displaystyle O=C-O-CH_3}{\vert}}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}-$	Polymethyl methacrylate (PMMA)	Car taillights, lenses Cameras
$-CF_2-CF_2-$	Polytetra fluoroethylene (PTFE)	non-stick coatings

I.5. Classification of Polymers

There are several ways to classify polymers based on the properties used to characterize them. The most common classifications are listed below.

I.6. Classification of Polymers by Chemical Nature:

- Mineral Polymers:

Mineral polymers are composed of chains containing either a single simple substance such as diamond, graphite, phosphorus, and sulfur, or chains containing multiple heteroatoms such as silicates, polyphosphoric acids, and polyphosphonitrile chlorides.

- Organic Polymers:

  This is the richest class of polymers, comprising almost all of the polymers used in everyday applications. The main synthetic organic polymers are polyolefins, polyvinyls, polydienes, polyamides, polyesters, and polyacrylates.

- Mixed Polymers:

  Mixed polymers have interesting properties, including good thermal resistance (300-350°C). The heteroatom can be either in the main chain or in the side groups.

I.7. According to the chain structure :

Polymers can also be classified into three categories as a function of their structure (dimensionality):

a) Linear arrangement:

1. Linear and one-dimensional polymers:

Linear (or monodimensional) polymers, which consist of a (possibly) high (but finite) number of monomeric units; such systems are obtained by the polymerization of bivalent monomers, and a linear macromolecule can be schematically represented by a continuous line divided into intervals to indicate the monomer units **(Figure I.1);** an assembly of polymer chains consists of entities with variable length, a characteristic designated by the term disparity.

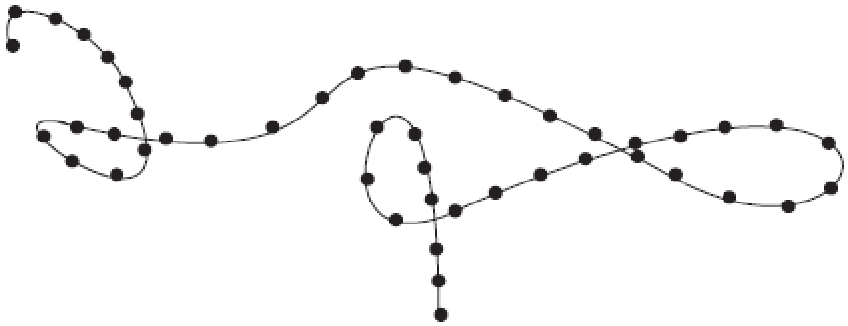


Figure I.1. Representation of the chain of a linear polymer.

2. Two-dimensional polymers:

Two-dimensional polymers are mainly found in Nature (graphite, keratin, etc.); two-dimensional synthetic polymers are objects that have not yet crossed the boundaries of laboratories. They appear in the form of two-dimensional layers with a thickness comparable to that of simple molecules **(Figure I.2)**

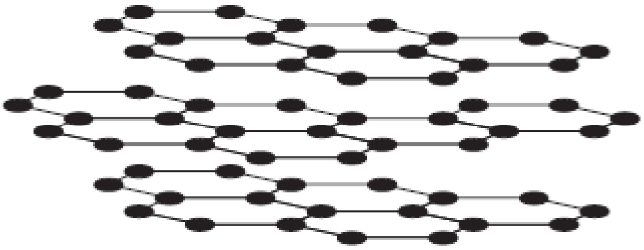


Figure I.2. Schematic representation of a two-dimensional polymer, here carbon graphite.

3. Three-dimensional polymers:

Three-dimensional polymers result either from the polymerization of monomers whose average valence is higher than two or from the cross-linking of linear polymers (formation of a three-dimensional network) through physical or chemical means. Their molecular dimension can be regarded as infinite for all covalently linked monomeric units of the sample are part of only one simple macromolecule. Chains grow at the same time in the three dimensions of space, and a volume element of such a system can be represented as shown in **Figure I.3**.

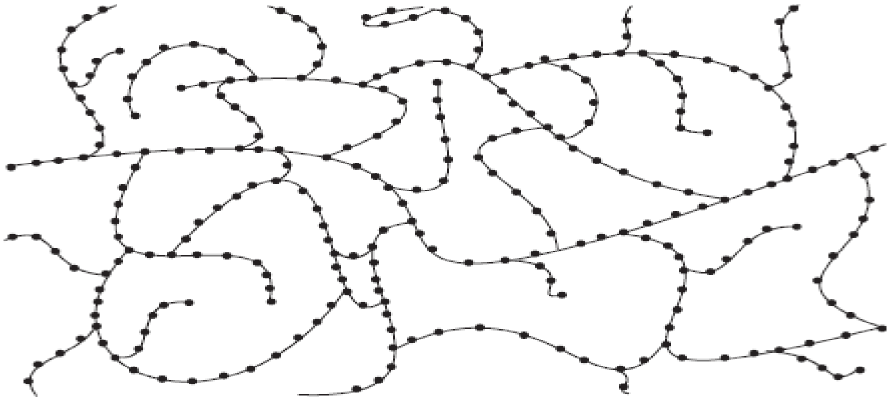


Figure I.3. Schematic representation of a three-dimensional polymer

b) Non-linear arrangement:

In this type of arrangement, we mainly encounter:

1.Star polymer:

A star polymer is a macromolecule formed by a central motif that is linked to multiple polymer chains. This star-shaped structure gives the polymer unique properties, such as greater thermal stability and improved solubility in certain solvents.

The central motif can be an atom, molecule, or functional group. The polymer chains can have the same length or different lengths, and they can be branched or linear. The star structure can also vary depending on the number of polymer chains that are linked to it.

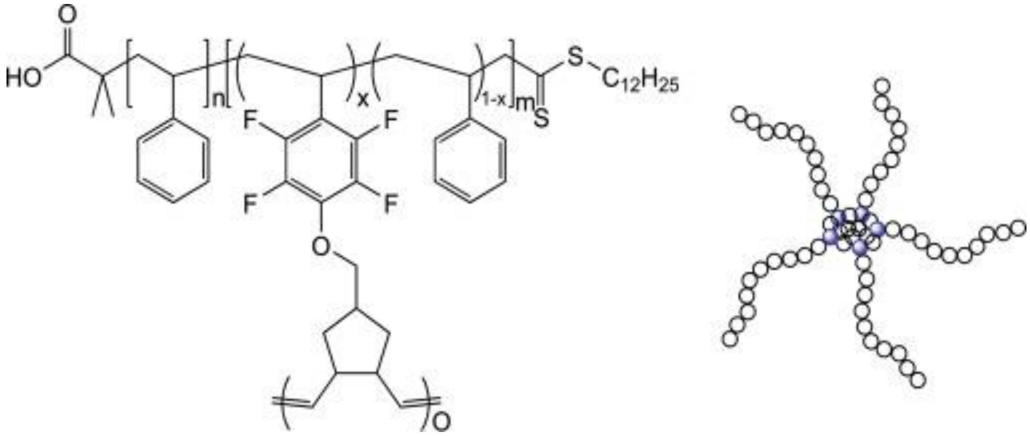


Figure I.4 Star polymer

2.Dendritic Polymers :

A dendrimer is a type of polymer that has a highly branched, tree-like structure. It is composed of repeated units called "monomers" that are linked together to form a core, branches, and end groups. The name "dendrimer" comes from the Greek word "dendron," which means tree.

Dendrimers have unique properties that make them useful in a wide range of applications. For example, their highly branched structure gives them a high surface area, which can be used for drug delivery, gene therapy, and other medical applications. They can also be used as catalysts, sensors, and in electronic devices.

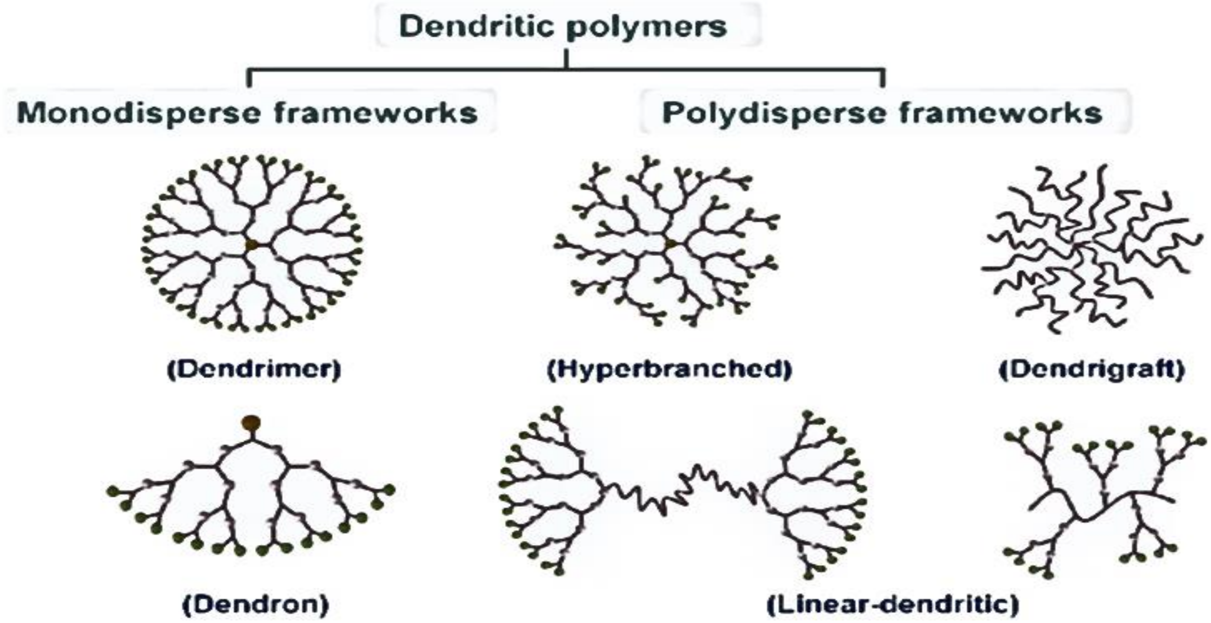
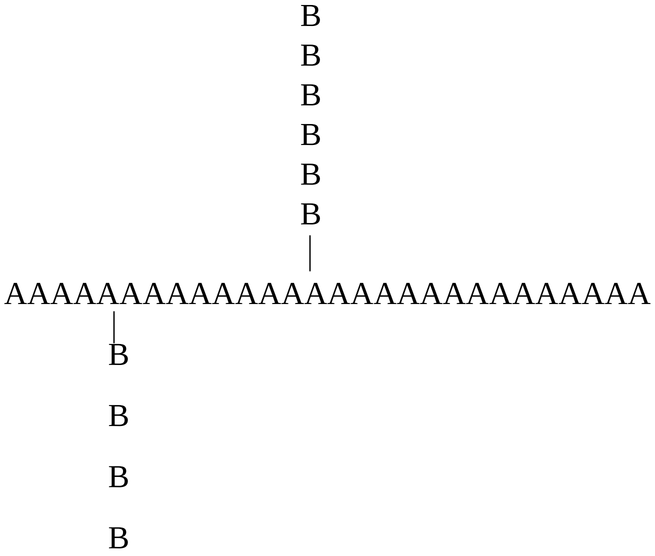


Figure I.5 Schematic classification of the dendritic polymers including two major categories and their subgroups.

3.Branched polymer:

is a polymer that has at least one branching point. During polymerization, homopolymeric or copolymeric chains can be grafted onto the main chain. The branched chain is called a graft when its composition is different from that of the main chain.



```
             B
             B
             B
             B
             B
             B
             |
AAAAAAAAAAAAAAAAAAAAAAAAAAAA
    |
    B

    B

    B

    B
```

4.Crosslinked polymers:

Crosslinked polymers are a type of polymer in which individual polymer chains are connected to each other by covalent bonds, forming a three-dimensional network. The crosslinks can be created either during the polymerization process or after the polymerization is complete.

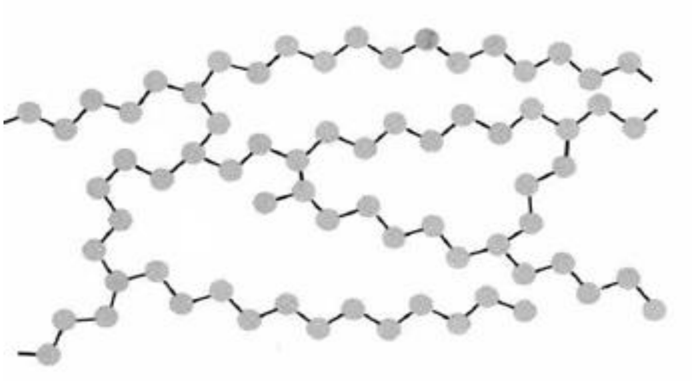


Figure I.6 Crosslinked polymers

I.8. According to the number of motifs:

According to this type of classification, we find:

I.8.1. Homopolymers:

Homopolymers are polymers made up of a single type of monomer unit that is repeated multiple times. The monomers in a homopolymer are identical and are linked together through covalent bonds, forming long chains or macromolecules.

-AAAAAAAAAAAAAAAAA-

Homopolymers can be naturally occurring, such as proteins, nucleic acids, and cellulose, or can be synthesized artificially, such as polystyrene, polyethylene, and polypropylene. The properties of a homopolymer depend on the nature of the monomer unit and the arrangement of the polymer chains.

I.8.2. Copolymers:

Copolymers are a type of polymer that is composed of two or more different monomers. These monomers are chemically linked together in a repeating pattern to form a long-chain molecule. Copolymers can be made up of any combination of monomers, which can result in a wide range of physical and chemical properties.

- **Random copolymer:**

The repeating units are arranged randomly on the chain molecule. It we represent the repeating units by A and B, then the random copolymer might have the structure shown below:

-AABBABABBAAABAABBA-

- **Alternating copolymer:**

There is an ordered (alternating) arrangement of the two repeating units along the polymer chain:

-ABABABABABAB-

- **Block copolymer**

The chain consists of relatively long sequences (blocks) of each repeating unit chemically bound together:

-AAAAA- BBBBBBBB –AAAAAAAAA- BBBB

I.9. According to their origin:

I.9.1. Natural polymers:

They are obtained from plant or animal sources and are in the form of fibers. Plant fibers include wood, paper, cotton, latex (extracted from the Hevea tree), etc. Animal fibers include leather, silk, and wool.

I.9.2. Artificial (or regenerated) polymers:

although the base constituent is of natural origin, they result from a chemical transformation of the functions carried by the monomer units, for example: cellulose derivatives whose basic molecule is cellulose.

I.9.3. Synthetic polymers:

The monomer molecules that allow them to be obtained do not exist in nature, however it can be noted that the structures produced by synthesis are often similar to those of natural polymers.

I.10. According to thermal behavior:

I.10.1. Thermoplastic:

thermoplastic is a linear or branched polymer that can be softened by heating and hardened by cooling within a specific temperature range. These polymers can be either amorphous or semi-crystalline thermoplastics, such as polyethylene (PE), polyvinyl chloride (PVC), or polystyrene (PS), and can be shaped using various techniques such as injection molding, blow molding, extrusion, or rotational molding.

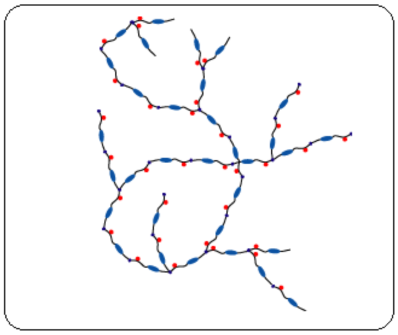


Figure I.7 Schematic representation of a thermoplastic polymer.

I.10.2. Thermodurcissable:

Thermodurcissable is a term used to describe a product (solid molding powder or liquid resin) that is irreversibly transformed by polymerization into a three-dimensional, infusible and insoluble network that is called a thermoset. In the industry, it is common to misuse the term "thermodurcissable" to refer to both the initial reactive system, which is soluble and fusible, and the final product, which is infusible.

Figure I.8 Thermodurcissable

I.10.3. Elastomers:

An elastomer is a linear or branched polymer transformed by vulcanization into a weakly cross-linked three-dimensional network that is infusible and insoluble.

Elastomers differ from thermosets in their rubber-like elasticity property, which means they can undergo very large reversible deformations under mechanical stress.

They can achieve very large elongations (up to 500%) while still capable of returning to their initial geometry by releasing the energy that was supplied to them during deformation.

Figure I.9 Elastomers

I.10.4. Thermoplastic elastomers:

A thermoplastic elastomer is a linear or branched polymer that exhibits both the rubber-like elasticity of an elastomer and the processing ease of a thermoplastic.

Thermoplastic elastomers are often block copolymers (or blends of homopolymers and/or copolymers) whose solid-state structure always results from the association of at least two distinct non-miscible phases:

A soft phase (glass transition temperature between 90°C and 40°C) associated with a rigid phase (glass transition temperature or melting temperature above 90°C).

Therefore, it is a multiphase material where the rigid phase is dispersed in the soft phase.

I.11. According to technological uses:

We can distinguish:

Synthetic fibers (nylon, polyester) or natural fibers (cotton, silk).

Plastics: this includes plastics in the broad sense, including thermosets and thermoplastics.

Elastomers: materials with elastic and/or rubbery properties.

Synthetic rubbers: polymers made from butadiene, isoprene, chloroprene.

Natural rubbers.

I.12. According to economic importance:

For polymers, like any industrial product, there is a correlation between volume and price. This allows for the distinction of three major categories of commercial polymers.

- High-volume polymers: whose sales and production volumes are high and whose price is low. Examples include polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC).
- High-performance polymers: whose sales volume is the lowest and prices are the highest.
- Technical polymers: whose volume and price are intermediate between the two preceding categories. Examples include polyamide.

-

I.13. According to use:

Adhesives and glues, paints, varnishes, sealants, plastics, rubber, textiles, foams, etc.

I.14. According to lifecycle:

disposable materials (lifespan less than one year), durable materials (lifespan between 1 and 20 years), and infrastructure materials (lifespan greater than 20 years).

I.15. Configuration isomerism

a) Tacticity:

The concept of tacticity only applies to asymmetric molecules; these are molecules with the same chemical formula but with a different arrangement of the monovalent radicals R along the molecule's backbone from one chain to another.

Let's consider the case of ethylene and PE to which a radical R has been grafted in place of a hydrogen atom. R can be a Cl atom, an F atom, or a CH_3 or C_6H_5 group.

The R group makes the monomer asymmetric; there are several ways to attach it to the backbone of the –[CH_2-CH_2]-n chain:

There are three stereoisomeric configurations:

- Atactic configuration: where the side groups appear randomly along the chain.
- Isotactic configuration: where the side groups are located on the same side of the chain.
- Syndiotactic configuration: where the groups appear in a regular alternating pattern along the chain.

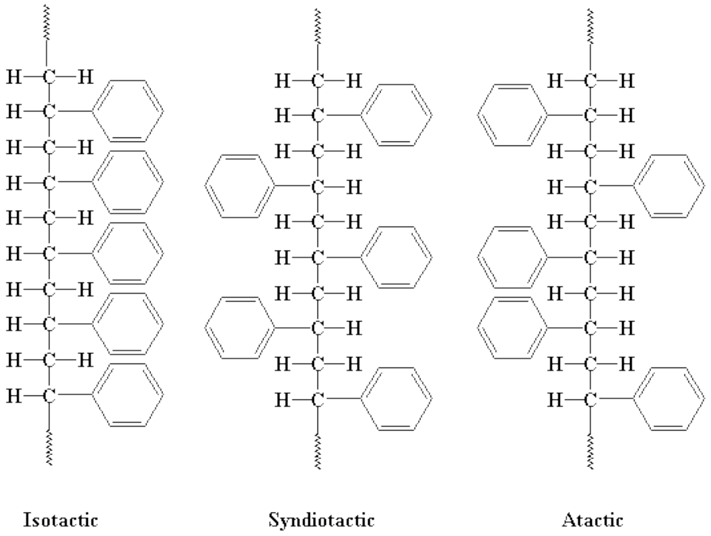


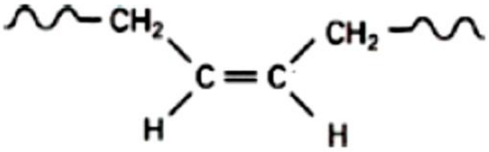
Figure I.10 The stereochemistry of polymers

b) Cis-trans isomerism:

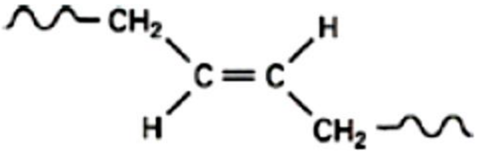
Some polymerizations, such as that of conjugated dienes (particularly 1,4-butadiene - CH2=CH-CH=CH2), can result in the maintenance of double bonds in the macromolecular backbone. Polybutadiene polymerized in a 1,4 fashion.

The rigidity of the ethylenic groups -CH=CH- fixes the relative orientation of their two macromolecular substituents, which can be:

- **in cis positions:**



- **in trans position:**



When there is a regular repetition of one or the other type of structure, there is configurational regularity, hence a stereoregular polymer. A change in configuration requires the breaking of two covalent bonds, and it can be assumed that the configurational structure of a macromolecule cannot change without the destruction of the macromolecular backbone.

I.16. Amorphous and crystalline polymer arrangement:

Polymers are large molecules made up of repeating units called monomers. They can have different arrangements of their molecules, which can either be amorphous or crystalline.

I.16.1. Amorphous polymers:

Amorphous polymers have a disordered molecular structure and lack a repeating pattern. The polymer chains are randomly oriented, making them more flexible and able to stretch without breaking. Examples of amorphous polymers include polycarbonate, polystyrene, and amorphous polyethylene terephthalate (APET).

I.16.2. Crystalline polymers:

Crystalline polymers have a regular and ordered molecular structure, with the polymer chains arranged in a repeating pattern. This arrangement makes the polymers more rigid and less flexible than amorphous polymers. Examples of crystalline polymers include high-density polyethylene (HDPE), polypropylene (PP), and polyethylene terephthalate (PET).

The degree of crystallinity in a polymer depends on its processing conditions, such as cooling rate and annealing temperature. When cooled rapidly, polymers tend to form amorphous structures, while slower cooling or annealing at higher temperatures can lead to crystalline structures. In some cases, polymers can have both amorphous and crystalline regions, which is referred to as semi-crystalline.

Figure I.11amorphous and crystalline polymer arrangement

The glass transition temperature "Tg" and the melting temperature "Tf" are the two fundamental temperatures required in the study of polymer materials.

The glass transition temperature is particularly important for amorphous polymers, especially amorphous thermoplastics, for which there is no significant cohesive force other than entanglement.

The characteristic temperatures of a single material can then be classified as follows:
Glass transition temperature < Crystallization temperature < Melting temperature < Thermal decomposition temperature.

Depending on the temperature to which it is subjected, a polymer material may exhibit different mechanical behaviors. This can occur for semi-crystalline thermoplastics in even a narrow temperature range.

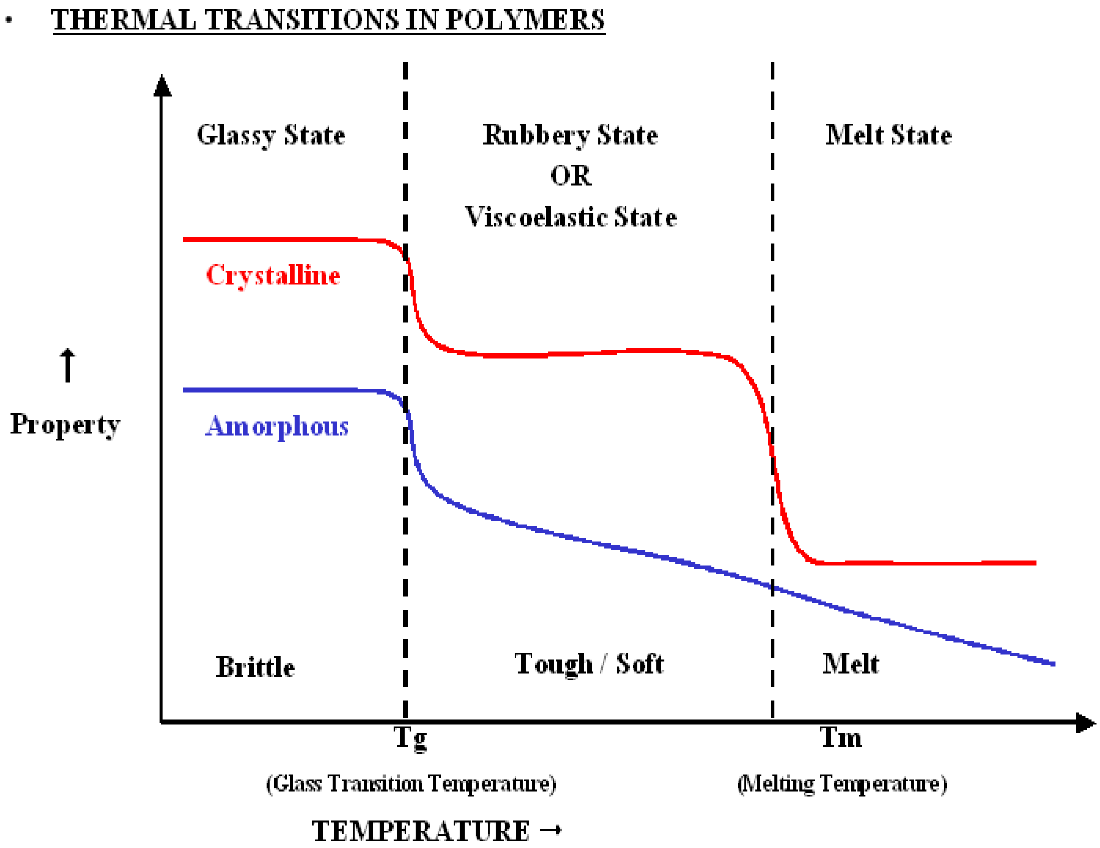


Figure I.12 Thermal transition in polymers

I.17. Applications of polymers:

Polymers are one of the main technical revolutions of the 20th century. They are used for an extraordinary number of applications at all levels of life. (See Table I.2)

Table I.2 Application of polymers

Fields	Exemples
The construction sector.	Doors, water pipes, and sanitation, painting of walls, floors and ceilings, and floor coverings.
Packaging industry	Bottles, yogurt pots, mailboxes, thermal insulation, and video film coating.
Medicine and healthcare.	Blood bags, gloves, contact lenses, eyeglass lenses, artificial organs, syringes, dental industry, prostheses, surgical tools
Household items.	Tupperware, garbage cans, buckets, dishes.
Electrical and electronic equipment and communications.	Isolation voltage, insulation, washing machines, computers and cameras, radio and television, telephone.
Automobile industry	Clear glass system, carpet, bodywork, optics, dashboard, interior trim, television facades, cable coating.
Textile industry	Clothing, natural and synthetic textile fibers, bags, faux leather, synthetic leather, non-woven materials.
Sports and leisure	Certain parts of buildings, airplanes and boats, DVDs, magnetic tapes, fishing lines and cords used, swimming pools, boat hulls.
Chemical industry	Piping, tanks, coatings.
Food industry	Food processing methods, packaging (bottles, yogurt cups, milk cartons, egg cartons) or industrial (detergent bottles, sachets and bags, crates).
household equipment	Furniture, crockery, accessories…; Used in industry to keep equipment from a violent collision.

II.1. Introduction:

The definition of polymerization is the process in which small molecules, called monomers, combine together to form long-chain polymers. Polymers are built from simple molecules of the same kind, and monomers are known as basic units of polymers. The name polymer was taken from the Greek word 'Polymeres'. What does polymerization mean? It is the process of formation of polymers, where polymers mean "having many parts".

Two types of polymerization reactions:

- **Step-growth polymerization:**

macromolecules formed by step-wise reactions between reactive chemical groups carried by monomer or polymer molecules. Each molecule can grow by reacting with any other molecule (mono-, di-, tri-, tetra-, etc-mer).

- **Chain-growth polymerization:**

a single initial active center (ion, radical, or organometallic complex) from an initiator allows the formation of a polymer chain. The chain can only grow by the reaction of a monomer with the reactive chemical group located at the end of the growing chain.

II.2. Step-growth polymerization:

Polymers formed by successive reactions between two chemical groups (X, Y,...) carried by molecules containing at least two chemical groups. The reactions occur by simple heating or in the presence of a catalyst, and stop when the active medium is cooled or when one of the initial reactants is completely consumed. Examples: polyesters, polyamides (nylon), polyurethanes, epoxy resins, phenoplasts. Two types of step-growth polymerization:

II.2.1. Polycondensation:

Condensation polymers are formed by a reaction between two different bifunctional or tri-functional monomer units. These monomeric units undergo a condensation reaction to form polymers and small molecules of simple compounds like HCl (Hydrogen chloride), H_2O (Water), alcohol, etc. are eliminated. Silicon, Bakelite, Nylon, etc. are some of the examples of condensation polymers.

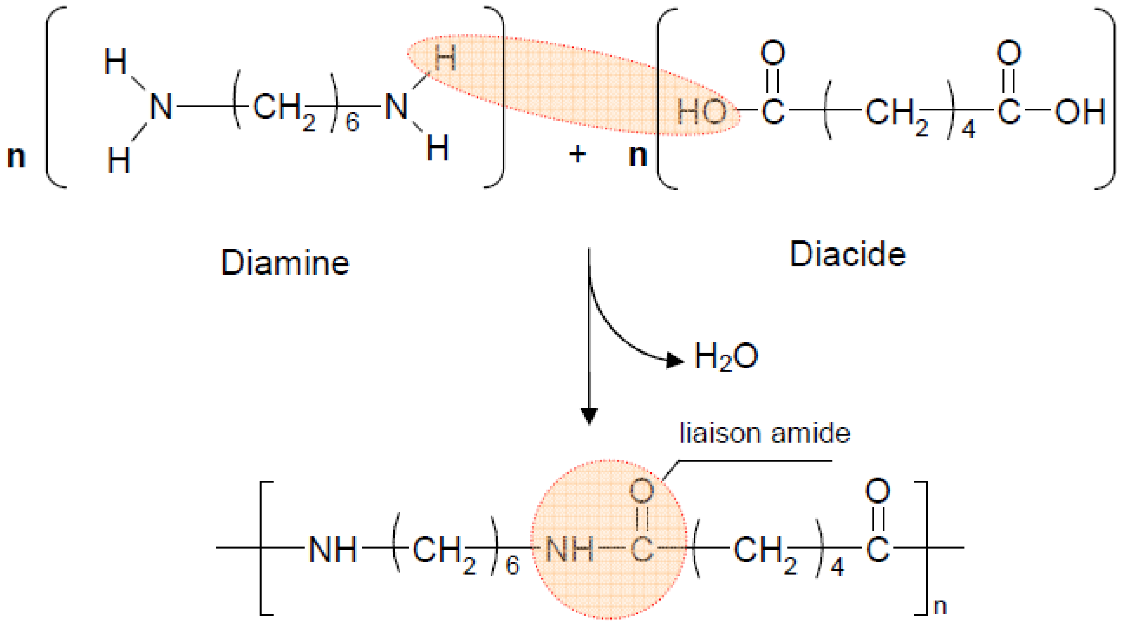
a) Synthesis of linear molecules by step-growth polymerization of bifunctional molecules (Thermoplastics).

1) 2 monomères possédant chacun un type de fonction chimique (X, Y)

X--- A--- X +	Y ---B--- Y ⟶	X--- A--- B--- Y	+ X--- Y
Monomère	monomer	bifunctional dimer	
Dimer	monomer	trimer	
dimer	dimer	tetramer	
n-mer	m- mer	(n+m)-mer	

Synthesis of nylon by polycondensation (elimination of a water molecule).

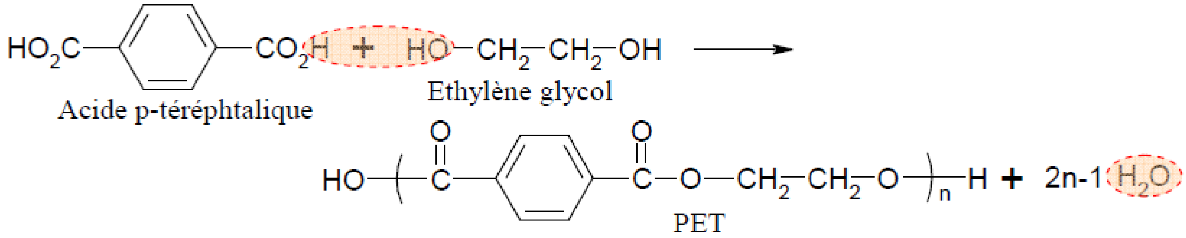
One of the monomers has 2 amine functions (-NH_2), the other monomer contains 2 carboxylic acid functions (-CO_2H).



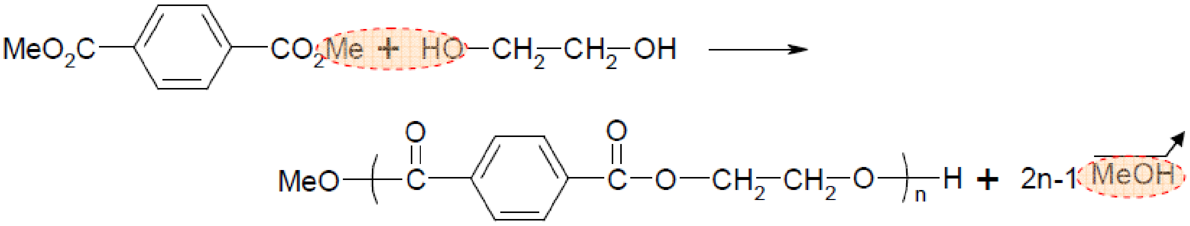
Polyamide 6,6 « *nylon* »

Other examples of polycondensation: polycondensation has great industrial importance, as mechanical properties are improved even though molecular weights are generally lower than with other polymerization techniques.

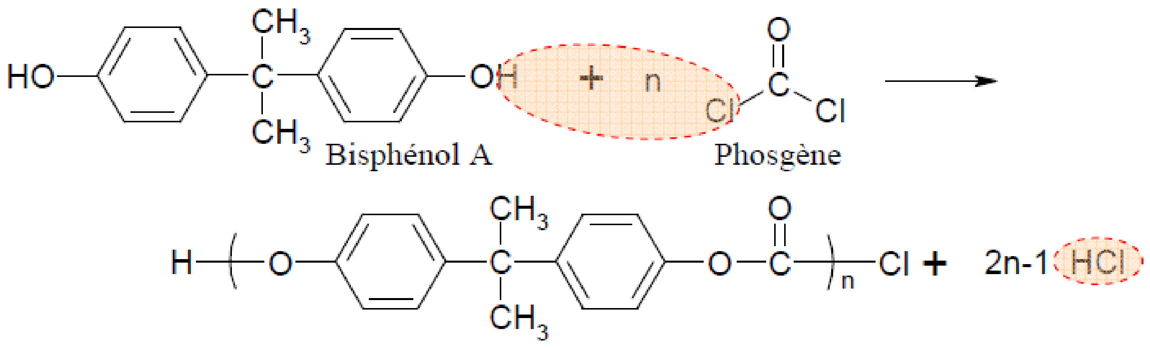
Polyester (Tergal)



The industrial process uses transesterification to easily remove MeOH and shift the equilibrium towards polymer formation.



If the alcohol has a functionality greater than 3, cross-linking (3D network) occurs. This is the case with alkyds (paints)



The degree of polymerization (DP) rarely exceeds 500 (ρ = 0.998), and the molecular weight ($\overline{Mn}$) is less than 5.10^{-4} g.mol-1 due to by-products formed during the reaction, such as oxidation, decarboxylation, and anhydride formation.

To increase the molar mass: increase the purity of the reactants, perfect equimolarity of reactants.

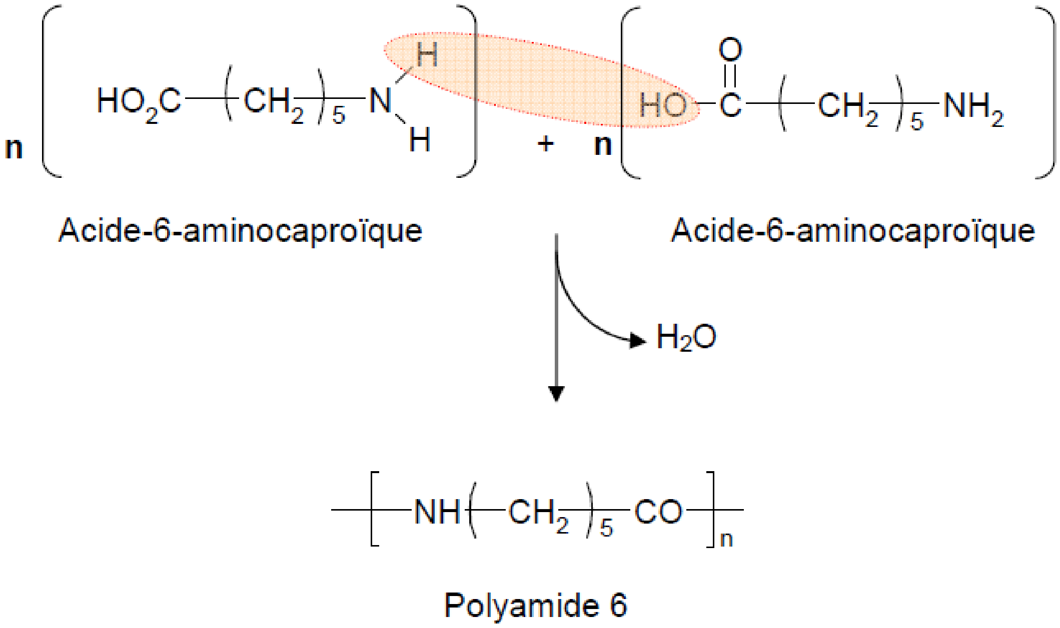
2) 1 single monomer with 2 types of chemical function (X, Y)

X--- A--- Y + X--- A---Y $\longrightarrow$ X--- A--- A--- Y + X Y

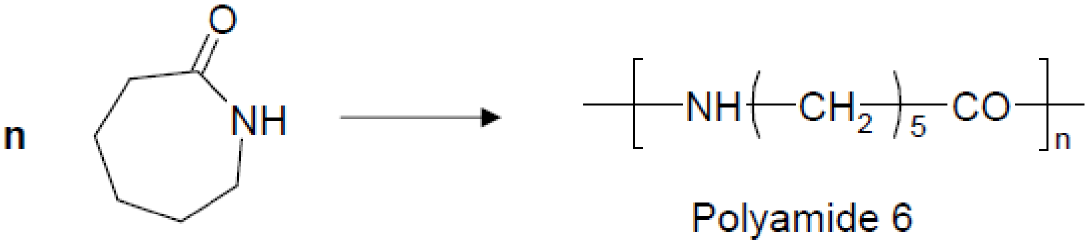
Monomère	monomer	bifunctional dimer
Dimer	monomer	trimer
dimer	dimer	tetramer
n-mer	m- mer	(n+m)-mer

Synthesis of nylon by polycondensation of 6-aminocaproic acid.

The monomer has an amine function ($-NH_2$) and a carboxylic acid function ($-CO_2H$)

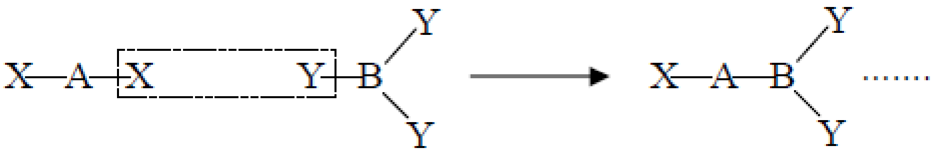


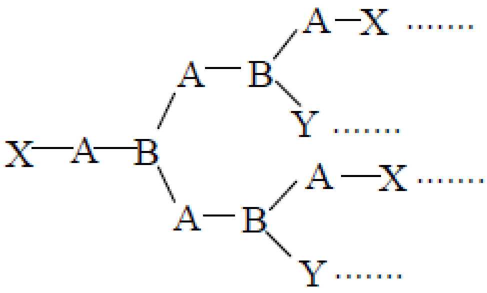
Synthesis of nylon by polyaddition of caprolactam.



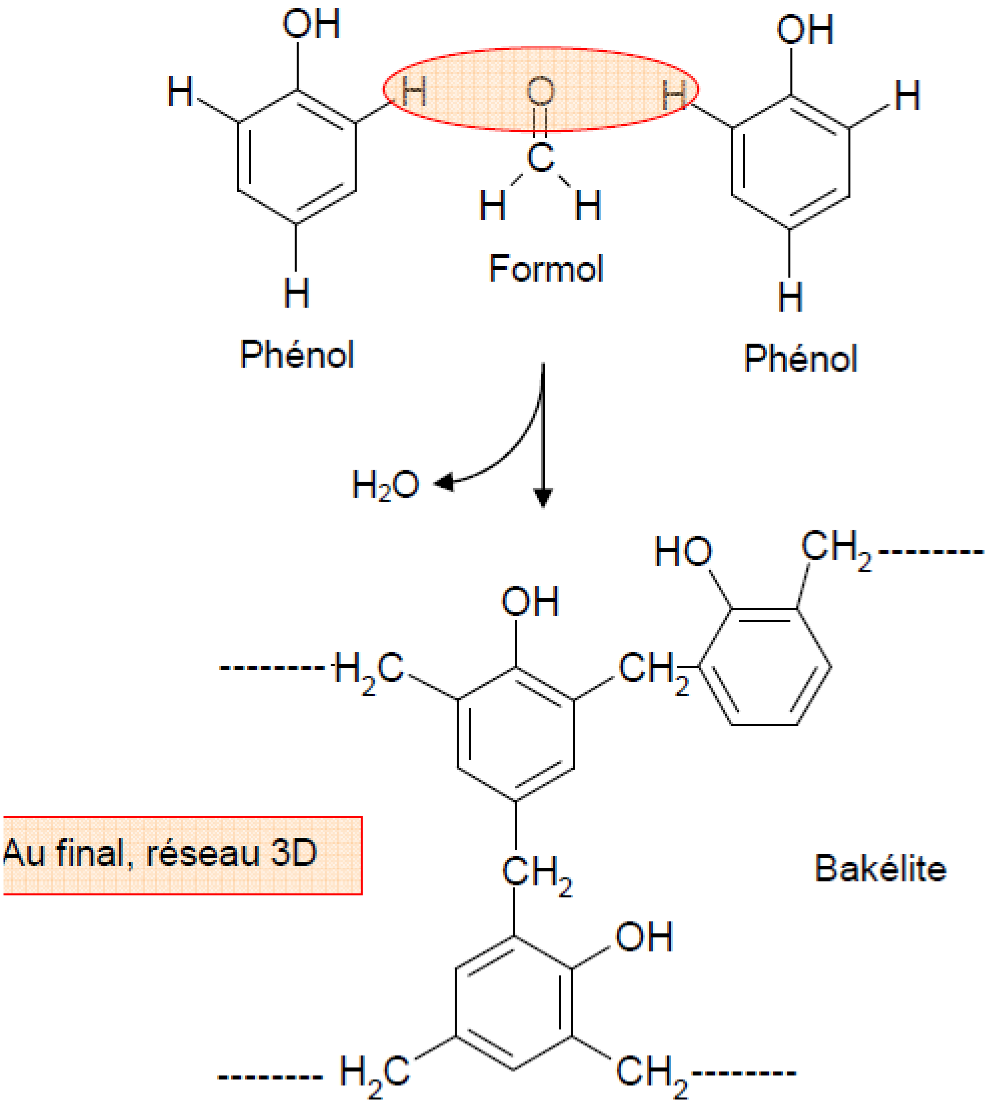
b) Synthesis of three-dimensional molecules by step-growth polymerization of molecules with more than two functions (Thermosetting).

In general, at least one bifunctional monomer and one trifunctional monomer are required. However, the system can be more complicated.





Synthesis of Bakelite: polycondensation from phenol and formaldehyde. Belongs to the family of phenol-formaldehyde resins (phenoplasts).



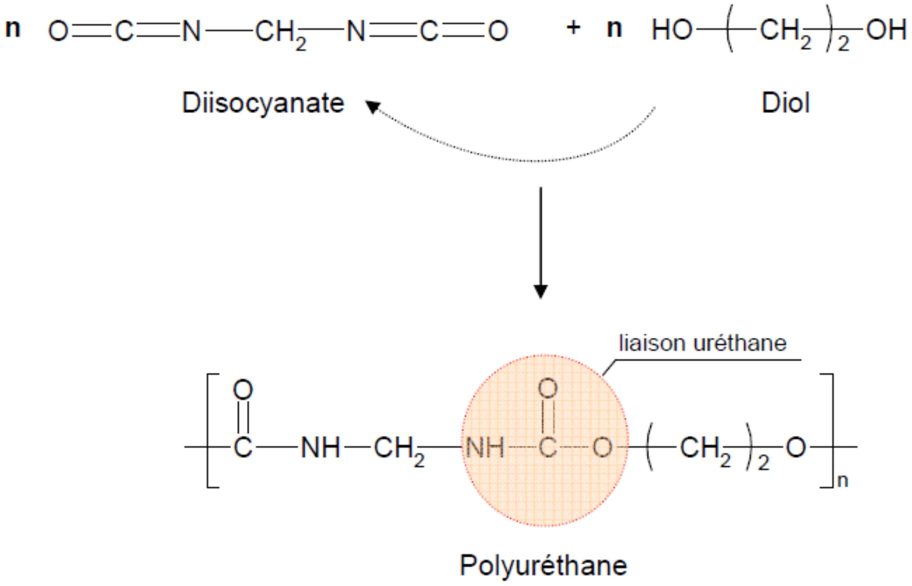
Au final, réseau 3D

II.2.2. Polyaddition:

In case of addition polymerisation, double or triple bond monomers are repeatedly added to form a polymer. In this type of reaction, no by-products are formed. For instance, propene (C_3H_6) helps in the formation of poly-propene ($(C_3H_6)n$) and polythene ($(C_2H_4)n$) is formed by the addition reaction of ethene (C_2H_4) molecules.

Example:

Synthesis of polyurethane by polyaddition.



Remarks on polyurethanes:

- Polyols are generally of the polyether or polyester type. They provide flexibility to the PU. Triols => three-dimensional network.
- Diisocyanates: Toluene diisocyanate (TDI) is the most commonly used. Methylene-bis-4-phenylisocyanate (MDI) is also widely used for rigid foams. They make up the rigid segments of PU. Triisocyanates => three-dimensional network.
- Amines react with isocyanates to form urea bonds
- $-R\text{-}N{=}C{=}O + R'\text{-}NH_2 \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}R'$, which allow for chain extension or cross-linking.

II.3. Chain Polymerization

II.3.1. Generalities

A chain reaction is a reaction during which a monomer molecule M is added to an active center carried by the growing chain.

If we call n M* a chain consisting of n building blocks and equipped with an active center, the polymerization can be schematized as:

$$M_n^* + M \text{-----------------} M^*_{n+1}$$

The point indicates the site of an unpaired electron located on the molecular chain with which a new bond can be formed to increase the size of the chain. The atom on the chain with this unpaired electron constitutes the active center.

Chain reactions occur in 3 steps:

- Initiation (or triggering)
- Propagation (or growth)
- Termination.

Depending on the nature of the active center that triggers the addition of the constituent (parent) units, chain polymerization is classified into one of the following groups:

- Radical polymerization
- Ionic polymerization.

II.3.2. Radical Polymerization:

II.3.2.1. Initiation

This step refers to the formation of an active center on a monomer molecule M. It occurs in 2 steps:

- Formation of a free radical R* from an initiator molecule I.

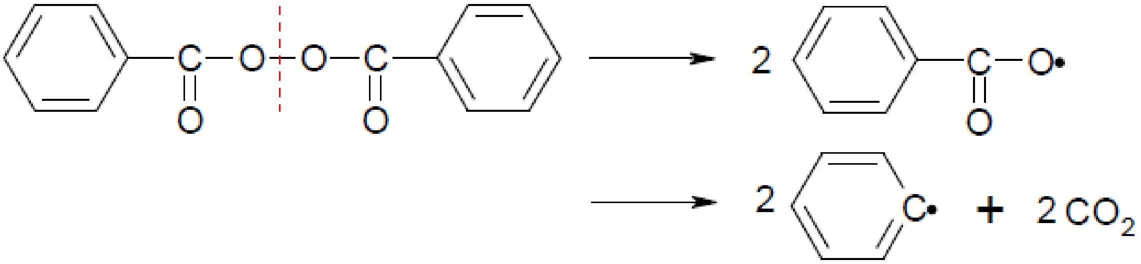
  I ---------n R* (with n = 1 ou 2)
- Addition of the free radical to a mole of monomer M, which then carries an active center.

  R* + M ------------ RM*

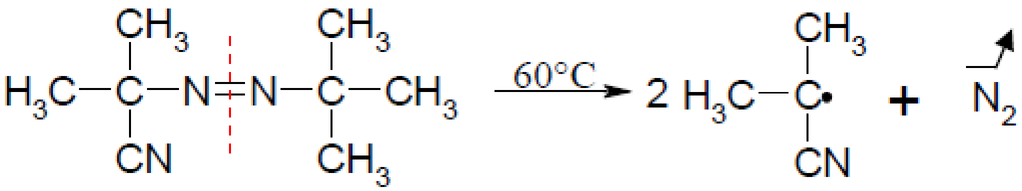
The most common initiators are referred to as "initiating agents".

- **Radicals**

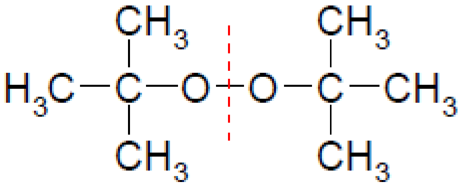
Benzoyl peroxide



AIBN



Peroxyde de tBu



- **Redox**

$H_2O_2 + Fe^{2+} \xrightarrow{\quad} HO^{*} + OH^{-} + Fe^{3+}$

- **Radiation γ, β, $h\nu$**

$RH \xrightarrow{\quad} R^{*} + H^{*}$

II.3.2.2. Propagation:

This is the step where a large number of successive additions of monomer molecules M occur on the formed active center. The time required to add a monomer is very brief, on the order of milliseconds. As a result, several thousand additions can occur in a matter of seconds.

$RM^* + M \longrightarrow RMM^*$

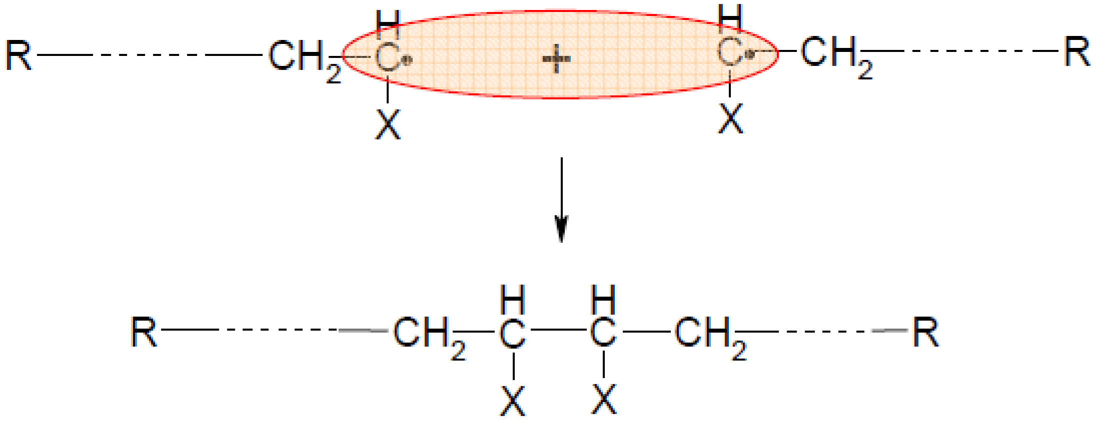
$RMM^* + M \longrightarrow RM\,M^*$

$R\,M\,M^* + M \longrightarrow R\,(M_{n+1})\,M^*$

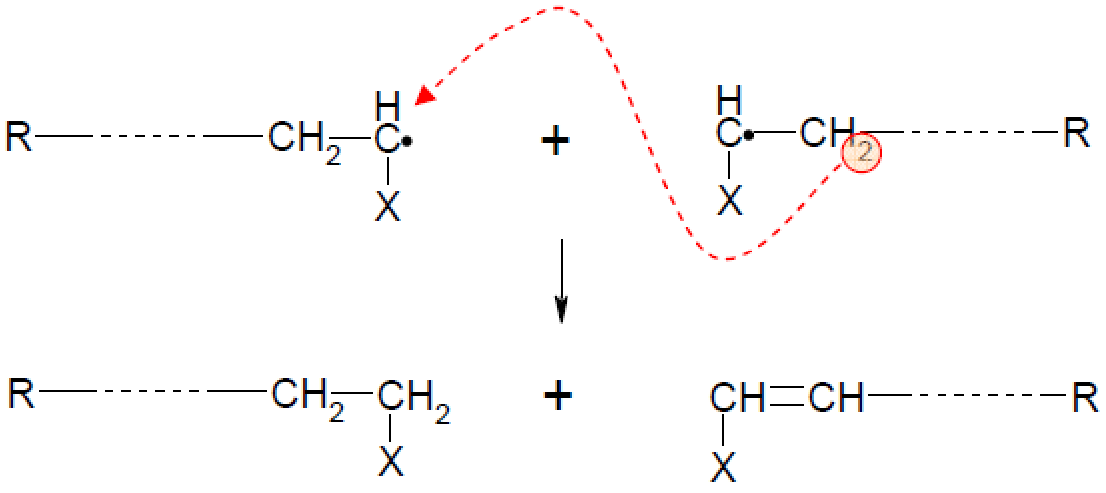
II.3.2.3. Termination:

At this stage, the growth of the polymer chain stops. The active center disappears. Termination reactions are bimolecular involving 2 growing molecules. The mechanism is:

- **Combination:**



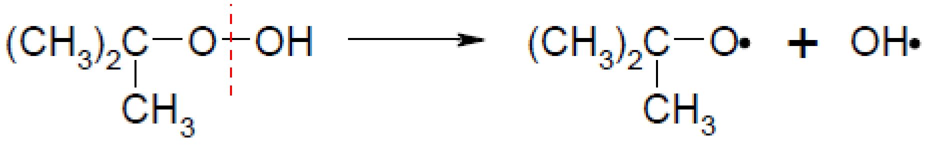
- **Disproportionation**: transfer of an H atom.



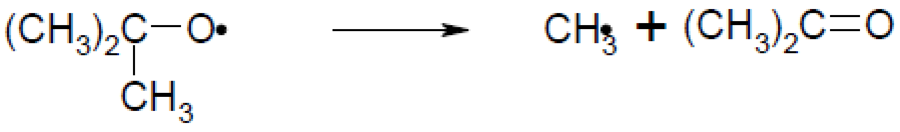
Example of radical polymerization: vinyl monomer, 2 different initiators.

1- initiation

-by breaking a covalent bond (O-O) of the initiator



$$(CH_3)_2\underset{\underset{CH_3}{|}}{C}-O-OH \longrightarrow (CH_3)_2\underset{\underset{CH_3}{|}}{C}-O^\bullet + OH^\bullet$$



$$(CH_3)_2\underset{\underset{CH_3}{|}}{C}-O^\bullet \longrightarrow CH_3^\bullet + (CH_3)_2C=O$$

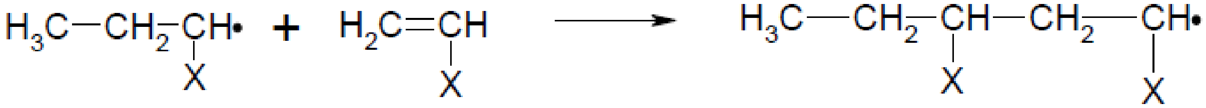
-by oxidation-reduction reaction

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH- + OH^\bullet$$

Then addition of the free radical to the vinyl monomer CH2=CHX and creation of an active center on the molecule.

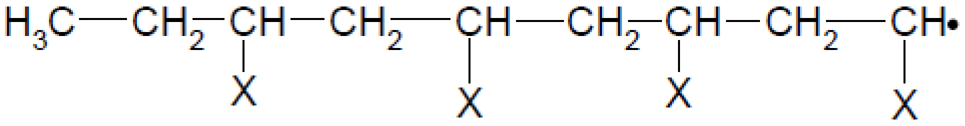
$$CH_3^{\bullet} + H_2C{=}\underset{X}{CH} \rightarrow \begin{cases} H_3C-CH_2-\underset{X}{CH}^{\bullet} \\ H_3C-\underset{X}{CH}-CH_2^{\bullet} \end{cases}$$

2- Propagation



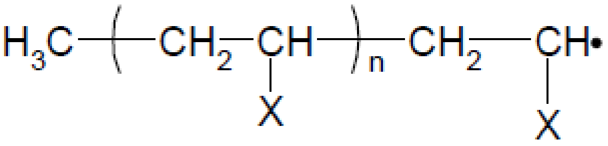
$$H_3C-CH_2-\underset{X}{CH}^{\bullet} + H_2C{=}\underset{X}{CH} \longrightarrow H_3C-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}^{\bullet}$$

Then addition of other monomers......



$$H_3C-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}^{\bullet}$$

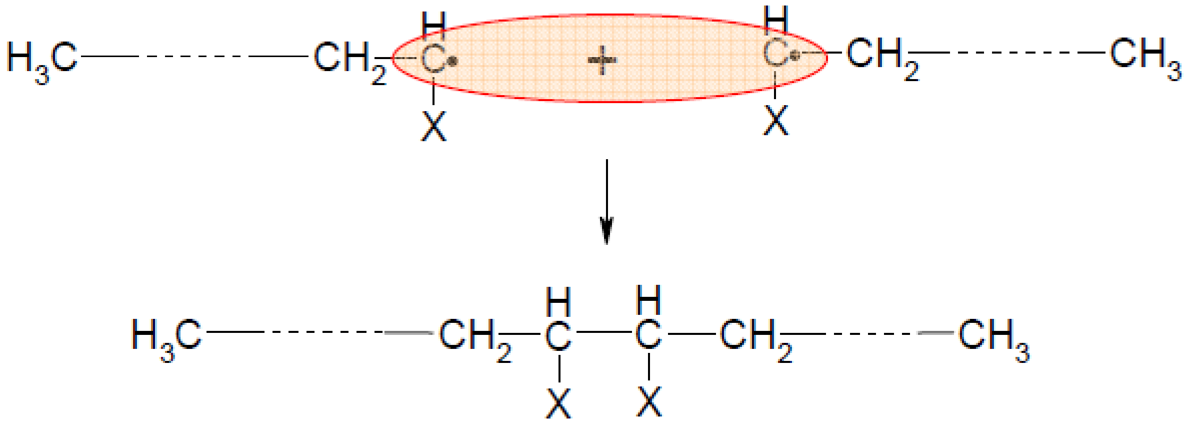
Our



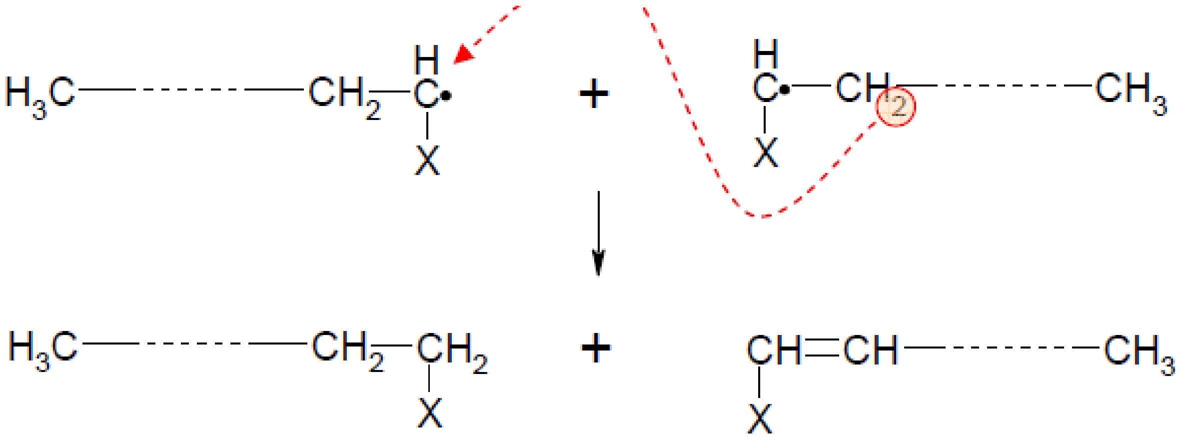
$$H_3C\left(-CH_2-\underset{X}{CH}-\right)_n CH_2-\underset{X}{CH}^{\bullet}$$

3- termination

- **by combination**



- by disproportionation



II.4. Radical Polymerization Kinetics:

a- Initiation

Benzoyl peroxide and AIBN decompose into two radicals R*

$$A - A \xrightarrow{k_d} 2A^{\bullet}$$

kd is the dissociation constant of [A].

$$Vd = 2\ Kd[A]\ .f$$

$$A^{\cdot} + M \xrightarrow{k_a} A\text{-}M^{\cdot}$$

ka is the polymerization initiation constant.

$$Va = Ka[M][A^*]$$

vd is the limiting velocity because it is the slowest. Overall, we have:

$$Va = 2f\ K_d\ [A]$$

b- propagation

A-M* + M -----------------A-M-M*

There is equi-reactivity of active centers regardless of the length of the chain carried by the monomer. (AM*---AMMM*---$A(M)_nM^*$)

$$M^{\cdot} + M \xrightarrow{k_p} M^{\cdot}$$

kp is the propagation constant of the polymer.

$$Vp=Kp[M][M^*]$$

Determining [M*] is difficult because any chain carrying M* can be written as M*.

c- Termination

M*-------------M

There will be deactivation of the radical monomer. In this case, we observe two scenarios:

The first scenario is a recombination reaction.

/\/\/\/\/\/\/\/\- $M^{\cdot}$ + $M^{\cdot}$-/\/\/\/\/\/\/\/\ □ /\/\/\/\/\/\/\/\-M-M-/\/\/\/\/\/\/\/\

In this case, we statistically have a doubling of the mass.

The second scenario is a disproportionation reaction.

/\/\/\/\/\/\/\/\-CH_2-$C^{\cdot}H$-X + X-$HC^{\cdot}$-/\/\/\/\/\/\/\/\ □ /\/\/\/\/\/\/\/\-CH=CH-X + \/\/\/\/\/\/\/\/\-CH_2-CH_2-X

In this case, we have two inactive species. This reaction does not have much influence on the masses.

$$M^{\cdot} + M^{\cdot} \xrightarrow{k_t} 2\,M$$

We then have the termination speed Vt

$$Vt = 2\ Kt\ [M^*]^2$$

The 2 does not have a real significance but is rather there by convention.

Note:

The quasi-steady state assumption (QSS) is the state where, at any given moment, there are as many active centers.

destroyed active centers as formed ones. So we have: $\frac{dM*}{dt}$ =0 and therefore:

$$Va=Vt \text{ et donc } f\ K_d[A] =Kt[M^*]^2\ .$$

From this, we can deduce [M*] because Kd is stable, f is known, [A] is chosen and Kt is measured.

So we have : [M*] : [M*]= $\sqrt{\frac{f\ Kd\ [A]}{Kt}}$

We then substitute this into Vp = Kp [M] [M*] and we obtain:

$$Vp = Kp\ [M]\ x\ \sqrt{\frac{f\ Kd\ [A]}{Kt}}$$

Thus, generally, we equate Vp, the propagation rate, to the polymerization rate.

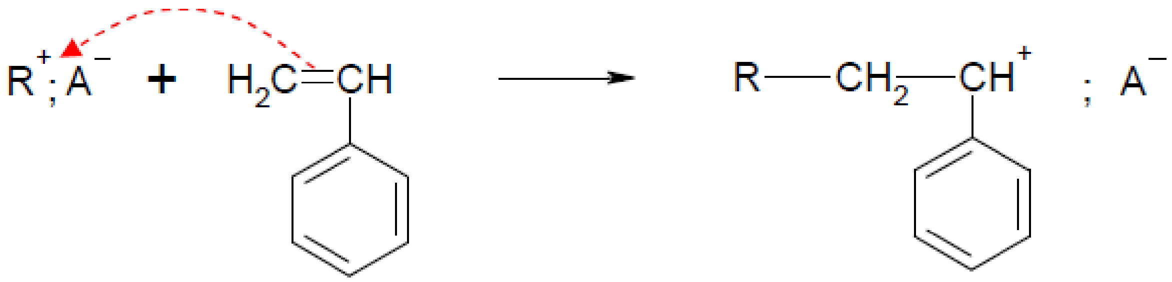
d- Ionic polymerization

The active center is formed by an ion instead of a free radical. There are two types of ion polymerization reactions:

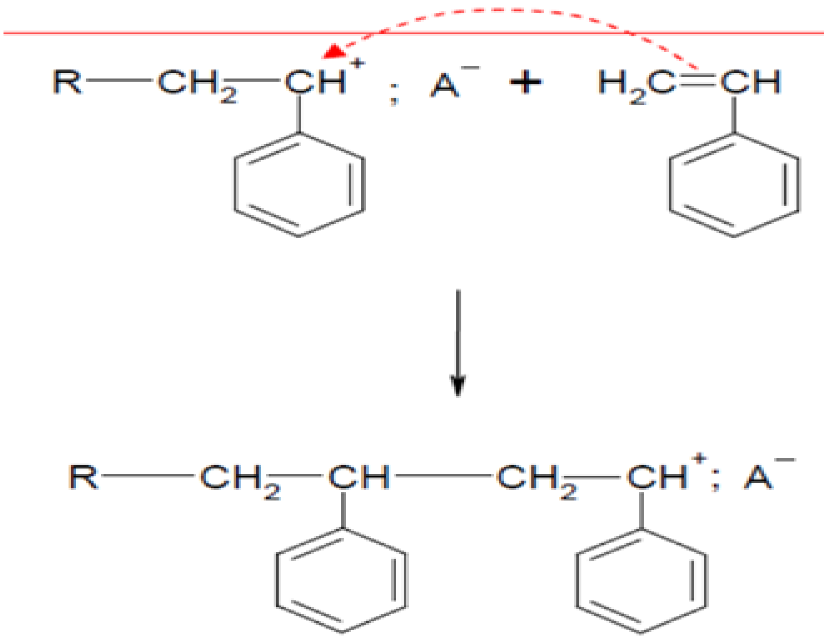
- Cationic polymerization: the carbon of the active center of the growing chain carries a positive charge
- Anionic polymerization: the carbon of the active center of the growing chain carries a negative charge

II.5. Cationic Polymerization: Example of polystyrene synthesis.

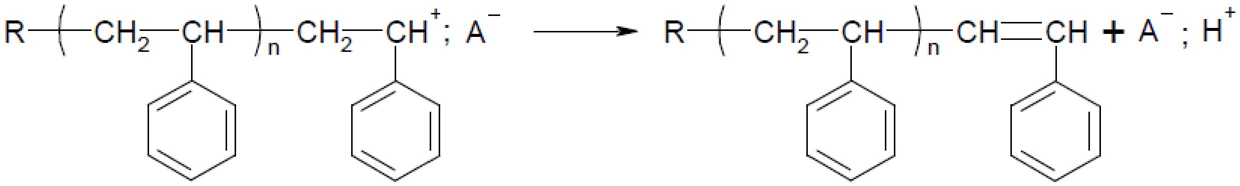
a. Initiation



b. Propagation



c. Termination



Note: by cooling or in certain cases (THF), termination and transfer reactions can be limited, and a living polymer can be obtained.

II.5.1. Kinetics:

For the purpose of establishing the kinetics of generalized cationic polymerization, let A represent the catalyst and RH the cocatalyst, M the monomer, and the catalyst–cocatalyst complex $H^+ AR^-$. Then the individual reaction steps can be represented as follows:

$$A + RH \xrightarrow{K} H^+ AR^-$$

$$H^+ AR^- + M \xrightarrow{Ki} HM^+ AR^-$$

$$HM^+n\ AR^- + M \xrightarrow{Kp} HM^+_{n+1}\ AR^-$$

$$HM^+n\ AR^- \xrightarrow{Kt} Mn + H^+ AR^-$$

$$HM^+n\ AR^- + M \xrightarrow{Ktr} Mn + HM^+ AR^-$$

The rate of initiation Ri is given by:

$$Ri = Ki\,[H^+ AR^-]\,[M] = ki\,K\,[A]\,[RH]\,[M]$$

The termination step is first order

$$Rt = Kt\,[M^+]$$

where $[M^+]$ is the concentration of all the chain carriers $[HM^+n\ AR^-]$. The retention of the terminating agent AR^- in the vicinity of the chain carrier is responsible for the primary difference between the kinetics of cationic polymerization and that of free-radical polymerization. Assuming that steady state holds, then Ri = Rt and

$$[M^+] = \frac{KKi}{Kt}\,[A]\,[RH]\,[M]$$

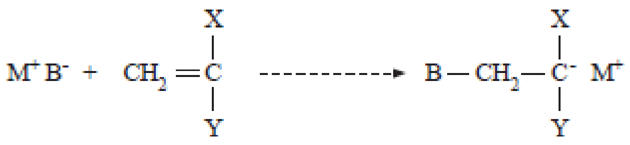
The overall rate of polymerization, Rp is given by

$$Rp = Kp\,[M+]\,[M] = K\,\frac{KiKp}{Kt}\,[A]\,[RH]\,[M]^2$$

II.6. Anionic polymerization:

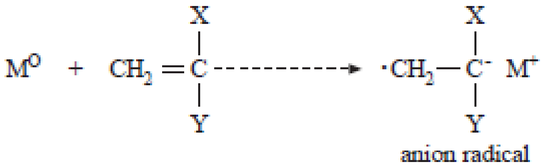
Monomers with electronegative substituents polymerize readily in the presence of active centers bearing whole or partial negative charges. For example, a high-molecular-weight polymer is formed when methacrylonitrile is added to a solution of sodium in liquid ammonia at –75°C. Typical electronwithdrawing substituents that permit the anionic polymerization of a monomer include –CN, –COOR, –C6H5, and –CH› CH2. The electronegative group pulls electrons from the double bond and consequently renders the monomer susceptible to attack by an electron donor. Catalysts for anionic polymerization include Grignard reagents, organosodium compounds, alkali metal amides, alkoxide, and hydroxides.

- Initiation may occur in two ways:
  a direct attack of a base on the monomer to form a carbanion.



$$M^+B^- + CH_2{=}C(X)(Y) \dashrightarrow B{-}CH_2{-}C^-(X)(Y)\ M^+$$

or by transfer of an electron from a donor molecule to the monomer to form an anion radical.

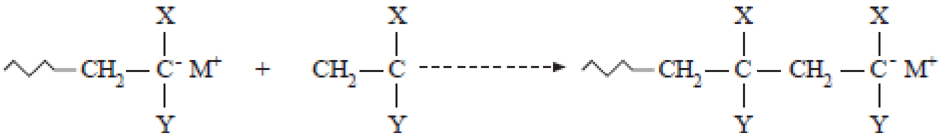


$$M^{O} + CH_2{=}\overset{X}{\underset{Y}{C}} \dashrightarrow \cdot CH_2-\overset{X}{\underset{Y}{C^-}}\ M^+$$

M^+B^- may be a metal amide, alkoxide, alkyl, aryl, and hydroxide depending on the nature of the monomer.

The effectiveness of the catalyst in the initiation process depends on its basicity and the acidity of the monomer.

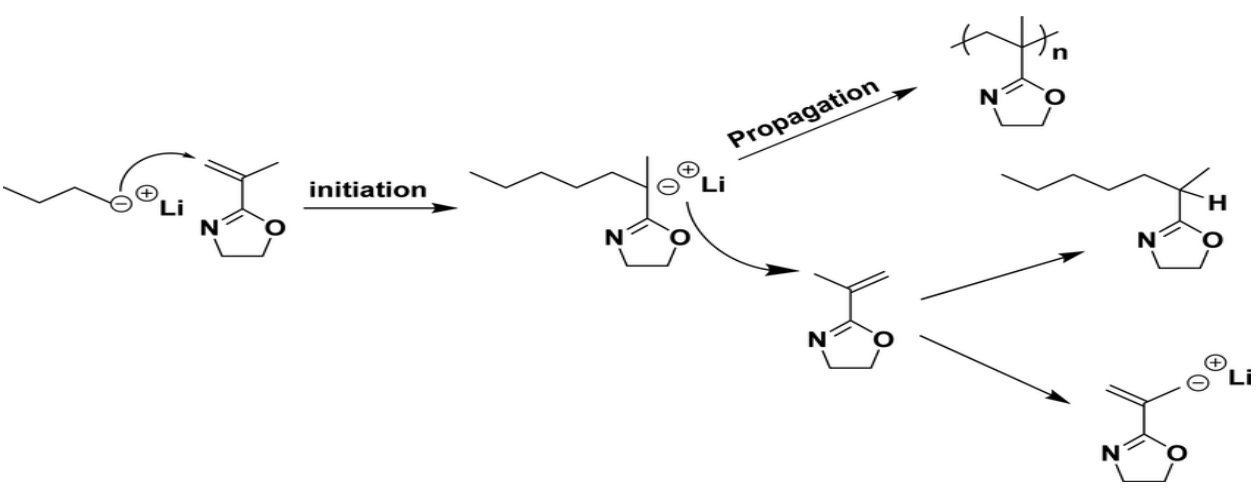
- Propagation in anionic polymerization proceeds according to the following reactions:



$$\sim\!\sim CH_2-\overset{X}{\underset{Y}{C^-}}\ M^+ + CH_2-\overset{X}{\underset{Y}{C}} \dashrightarrow \sim\!\sim CH_2-\overset{X}{\underset{Y}{C}}-CH_2-\overset{X}{\underset{Y}{C^-}}\ M^+$$

Here, M^+ represents a counterion that accompanies the growing chain. In most cases, M^+ is an alkali metal ion, whereas X and Y are either electron-withdrawing groups or unsaturated groups capable of resonance stabilization of the negative charge.

Example:



The termination reaction can be due to a compound capable of reacting with a carbanion (proton generator), present as an impurity or intentionally introduced. In the absence of such a compound, anionic polymerization can be living: no termination reaction occurs and the chains retain their active ends after complete consumption of the monomer.

II.6.1. Kinetics:

Available kinetic data for the polymerization of styrene by potassium amide in liquid ammonia support the following steps in the mechanism of anionic polymerization.

$KNH_2 \xrightarrow{K} K^+ + NH_2$

$NH^-_2 + M \xrightarrow{Ki} NH_2M^-$

$NH_2\ M^-n + M \xrightarrow{Kp} NH_2M$

$NH_2M^-n + NH_3 \xrightarrow{Ktr} NH_2MnH + NH^-_2$

Considering the relatively high dielectric constant of the liquid ammonia medium, the countering K^+ can be neglected. Assuming steady-state kinetics:

$$Ri = Ki\ [NH_2^-]\ [M]$$

$$Rt = tr\ [NH_2\ Mn^-]\ [NH_3]$$

II.7. Heterogeneous polymerization:

Heterogeneous polymerization is a polymerization method that involves the presence of a solid phase, usually a solid catalyst, in the reaction medium. Unlike homogeneous polymerization where the catalyst is dissolved in the liquid phase, heterogeneous polymerization allows for easier recovery of the catalyst and better control of the polymerization.

Heterogeneous polymerization can be performed by different methods, including suspension polymerization, emulsion polymerization, and bulk polymerization.

- **Suspension polymerization** is used for the production of polymers such as polystyrene, PVC, and polyacrylonitrile. In this method, the monomer is dispersed in an aqueous medium with a surfactant to form monomer particles. The catalyst is then added and the reaction is initiated, resulting in the formation of polymer chains inside the particles. The resulting polymer particles remain suspended in the reaction medium and are separated from it once the reaction is complete.

- **Emulsion polymerization** is used for the production of polymers such as polyvinyl acetate and latex. In this method, the monomer is emulsified in an aqueous medium with a surfactant to form monomer droplets. The catalyst is then added and the reaction is initiated, resulting in the formation of polymer chains inside the droplets. The resulting polymer droplets are kept in suspension in the reaction medium and are separated from it once the reaction is complete.

- **Bulk polymerization** is used for the production of polymers such as expanded polystyrene and cross-linked polyethylene. In this method, the monomer is directly mixed with the solid catalyst in a reactor. The polymerization reaction is initiated and the polymer chains are formed inside the bulk monomer. The final product is then extracted from the reactor and can be processed to obtain the desired final form.

Heterogeneous polymerization offers advantages such as better recovery of the catalyst and greater ability to control the polymerization, but it also has disadvantages such as greater difficulty in controlling the chain size distribution and a tendency to form polymer aggregates that can be difficult to disperse uniformly.

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 ($\overline{\text{Mw}}$):

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 ($\overline{\text{Mv}}$):

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.

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

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

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

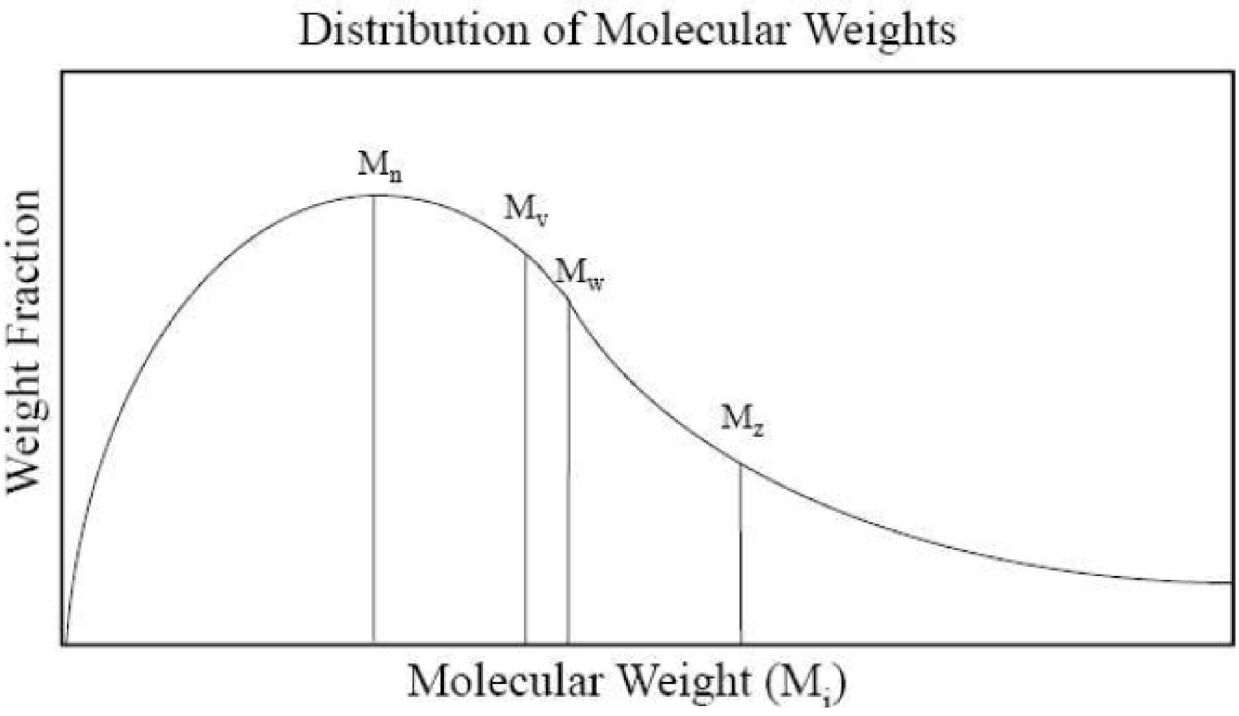
The z-average molar mass can be determined with ultracentrifugation. The melt elasticity of a polymer is dependent on $\overline{M}_z$.

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

$$\Delta Gm= RT[n1 \mathrm{Ln} \varnothing 1 + n2 \mathrm{Ln} \varnothing 2 + \mathrm{Ln} \varnothing 2 \chi_{12}$$

The right-hand side is a function of the number of moles n1 and volume fraction $\varnothing 1$ of solvent (component 1), the number of moles n2 and volume fraction $\varnothing 2$ 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.

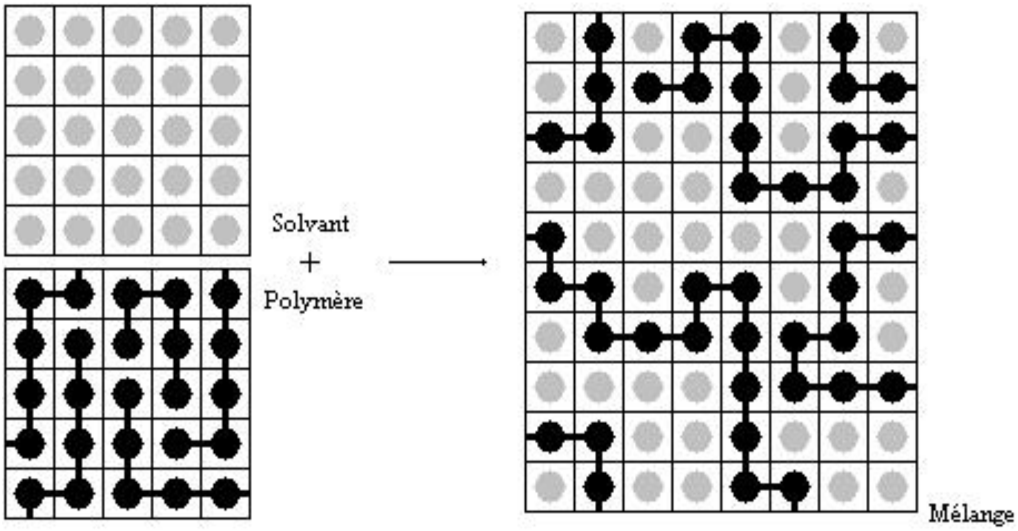


Figure III.1 Flory-Huggins theory

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.

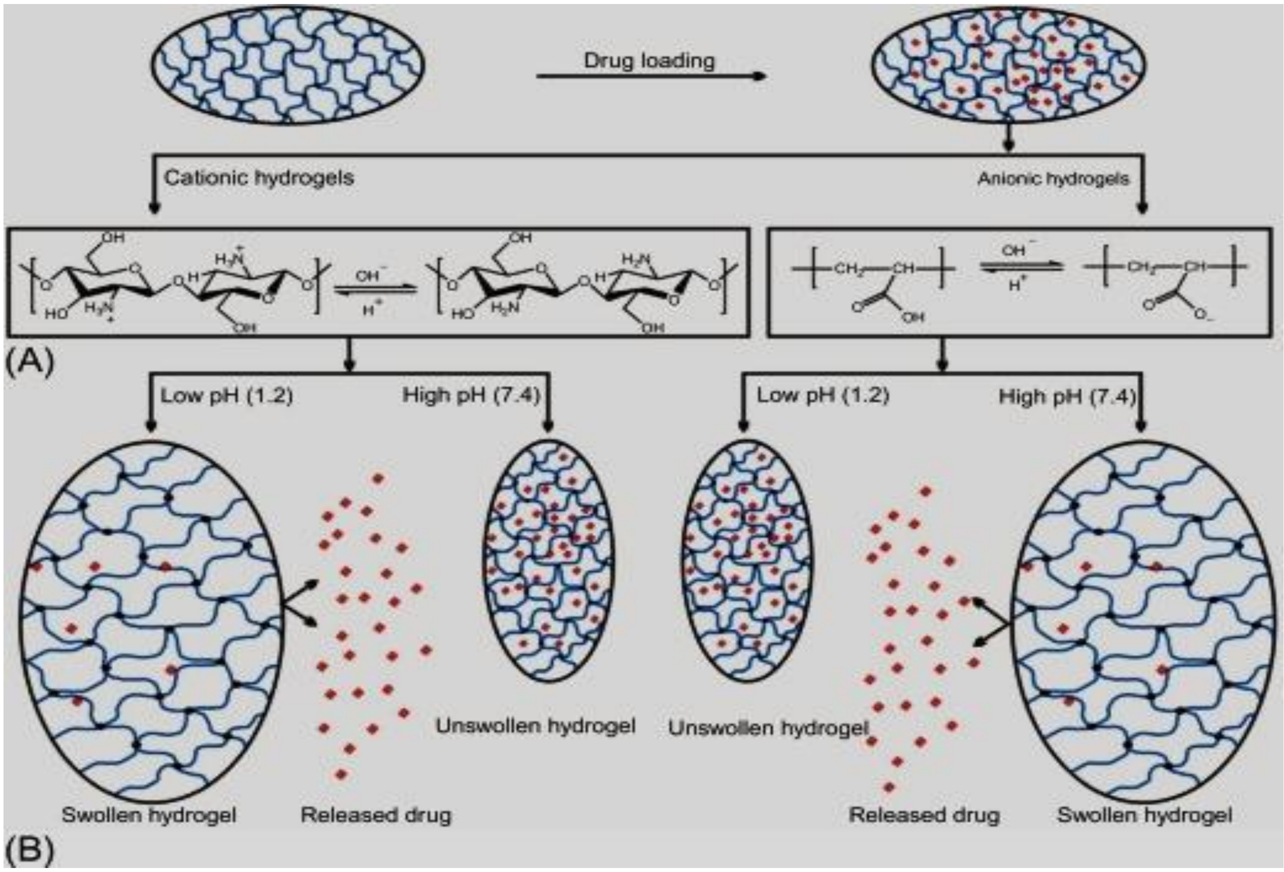


Figure III.2. hydrodynamic volume of a polymer

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:

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

The formula inside the square root, $\mathbf{(1/N)\sum i=1\ N\ n^2}$, 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 $\mathbf{\sum i=1\ N}$ 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:

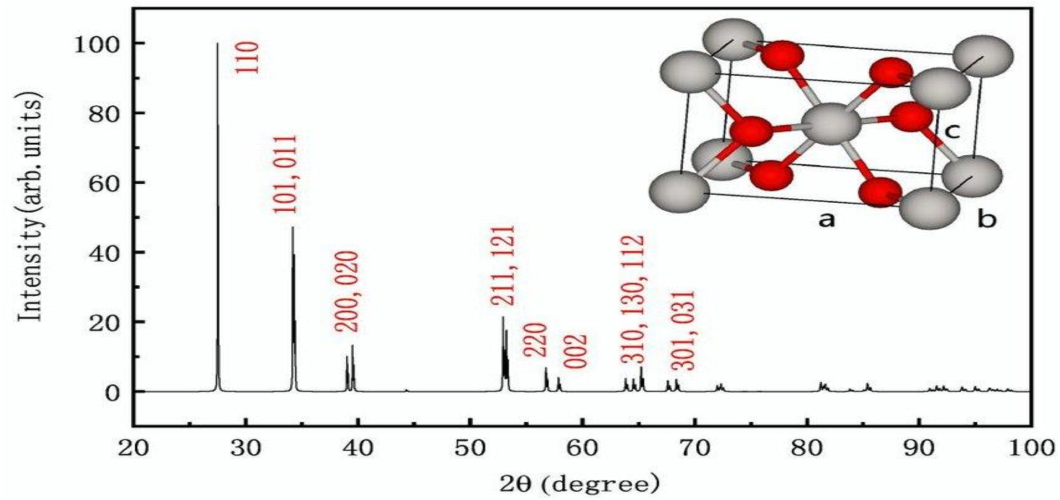


Figure III.3 XRD diagram

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:

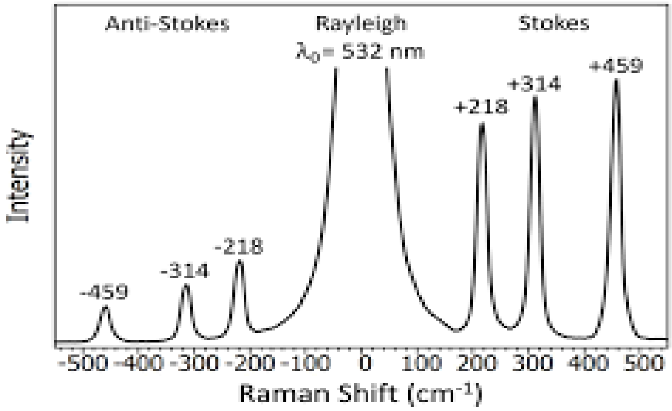


Figure III.4 Raman Spectrum of CCl4 measured using a 532 nm laser

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:

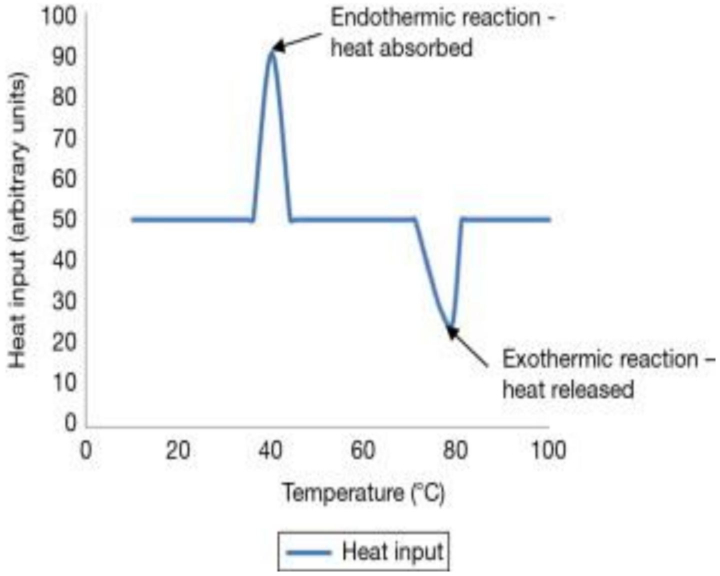


Figure III.5 Differential Thermal Analysis diagram

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:

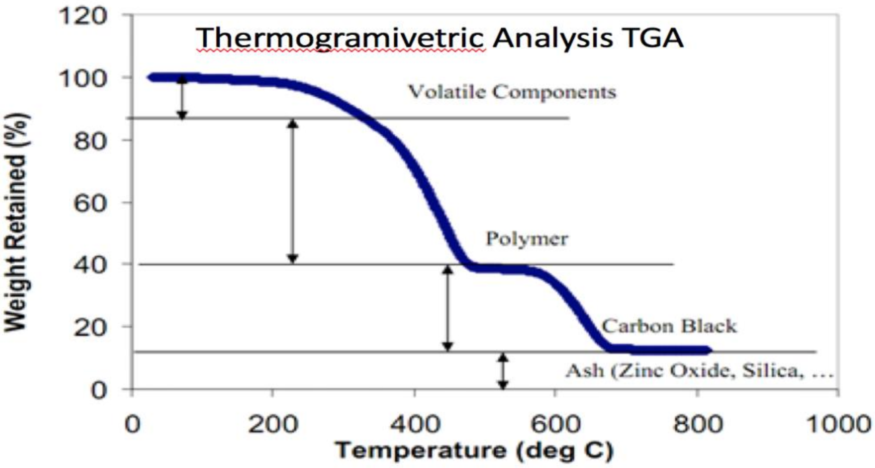


Figure III.6 Thermogravimetric Analysis (TGA)

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:

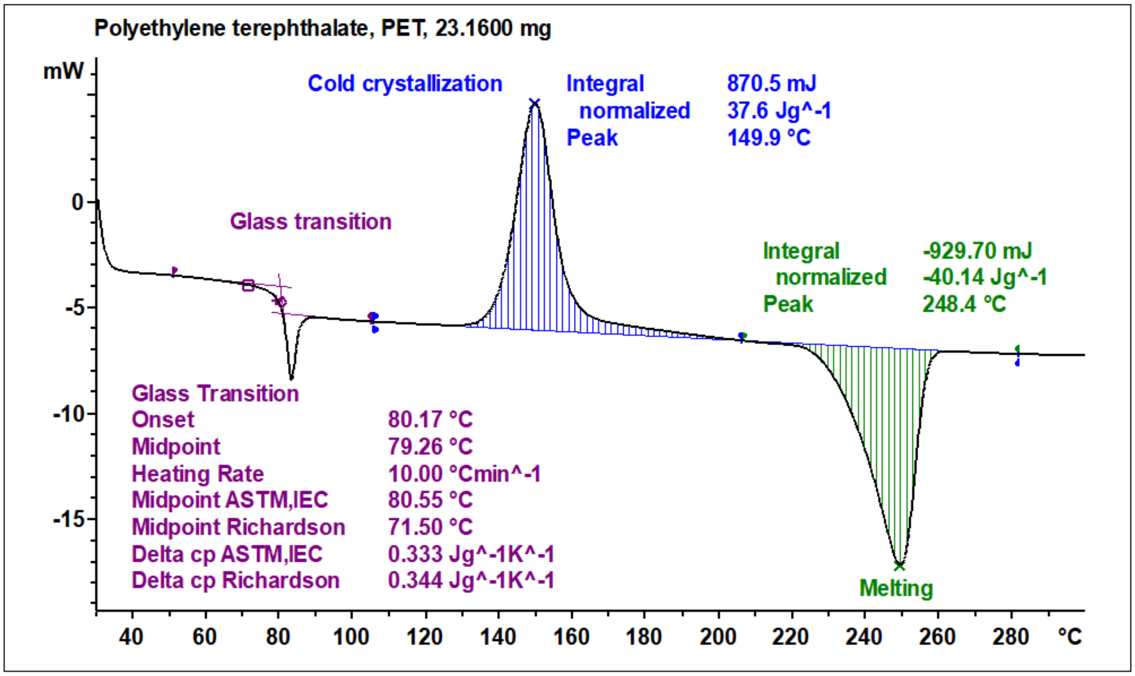


Figure III.7 DSC graph

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.

IV.1. Introduction ;

Les polymères sont des matériaux organiques constitués de macromolécules. Ils sont largement utilisés dans de nombreuses applications industrielles, notamment dans l'emballage, l'automobile, la construction, la médecine, etc. La structure moléculaire des polymères peut être amorphe, semi-cristalline ou cristalline. Le comportement thermique des polymères est principalement influencé par leur structure moléculaire. Dans ce cours, nous discuterons en détail des polymères amorphes, semi-cristallins et cristallins. Nous explorerons également les transitions de phase, la viscoélasticité et le comportement mécanique des polymères.

IV.2. Amorphous phase:

When the regular arrangement of macromolecular chains is not achieved, an amorphous structure is obtained. In other words, an amorphous phase is a phase where there is an absence of long-range order. It is often represented as a "plate of cooked spaghetti (Figure VI.1). The amorphous structure of polymers is directly related to the flexibility of the chains, which is defined by several factors: chain length, branching, and steric hindrance. It is particularly due to the possibility of rotation around the σ bonds, which are the main bonds in the skeleton of macromolecular chains.

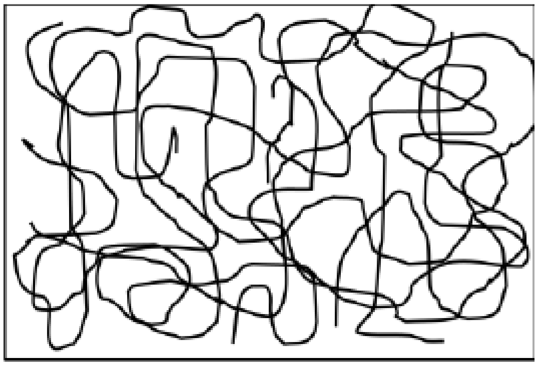


Figure IV.1: Diagram of an amorphous structure.

An amorphous polymer can be obtained by rapidly cooling the material from the molten (or liquid) state, due to branching, cross-linking, or large groups within the monomer preventing the periodic organization of the structure. At low temperatures, polymers are hard and brittle. However, at high temperatures, they are soft and viscous. An amorphous polymer is typically physically characterized by its glass transition temperature (Tg). The glass transition was first observed in elastomers (natural rubber), but quickly it was observed in all non-crosslinked polymers, consequently in thermoplastics. The glass transition is a phenomenon related to the possibility of movement of segments of macromolecular chains within the amorphous phase. Above this temperature, the amorphous polymer transitions from a glassy behavior to a rubbery behavior (Figure IV.2). In the rubbery state, the polymer is characterized by a low elastic modulus. It corresponds to a high capacity for reversible deformation related to greater mobility of the molecular chains. Below the Tg, in the glassy plateau, materials are much stiffer, not very ductile or even completely brittle.

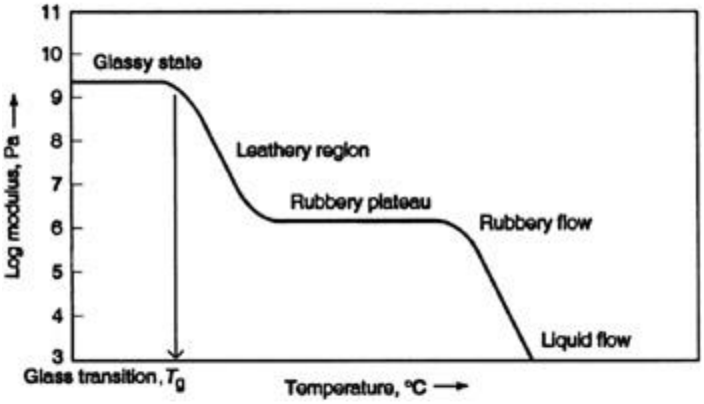


Figure IV.2 Variation of the elastic modulus of an amorphous polymer as a function of temperature.

The glass transition temperature of an amorphous polymer depends on several structural parameters: the rigidity of the main chain, the side groups, the effect of isomerism, the molecular weight, and cross-linking.

IV.2.1 Amorphous phase in the rubbery state:

For polymers with a glass transition temperature lower than room temperature, the amorphous phase exhibits a rubbery behavior at room temperature. This corresponds to non-linear elasticity, not obeying Hooke's law. This type of behavior corresponds to the long amorphous chains, each of which can take an infinite number of possible conformations. The amorphous phase in the rubbery state is characterized by the shear modulus beyond Tg , which is defined by the theory of rubber elasticity:

$$G_n^0 = \frac{\rho RT}{Me}$$

Where ρ is the density of the amorphous phase, R is the gas constant, and is the molar mass between entanglements.

IV.2.2 Amorphous phase in the glassy state:

For polymers with a glass transition temperature above room temperature, the amorphous phase exhibits a glassy behavior at room temperature, such as PET and PLA. At low stresses, the deformation varies linearly with stress. The behavior is therefore linearly elastic, and the behavior law obeys Hooke's law. Below the Tg, the movements of the main chains and the sliding of the segments are blocked. The elasticity module of the amorphous phase is significant.

IV.2.3 Techniques d'analyse des polymères amorphes :

There are several techniques for analyzing amorphous polymers, such as infrared spectroscopy (IR), X-ray diffraction (XRD), and differential scanning calorimetry (DSC).

X-ray diffraction (XRD) is used to determine the crystalline structure of semi-crystalline polymers. However, XRD can also be used to determine the amorphous structure of amorphous polymers. XRD can help understand the structure of amorphous polymers and differentiate between amorphous and semi-crystalline polymers.

Differential scanning calorimetry (DSC) is used to measure phase transitions in amorphous polymers. DSC measures the heat absorbed or released by the polymer when it undergoes a phase transition. DSC is used to determine the glass transition temperatures of amorphous polymers, which can help understand their properties.

IV.3. Phase cristalline

IV.3.1. Microstructure of the crystalline phase

The crystalline structure can be considered as the result of the periodic repetition in space of an elementary unit cell, which generates ordered regions. These ordered regions are composed of chains aligned parallel to each other. The organization of the ordered regions in a semi-crystalline polymer is observed differently depending on the different scales:

- The crystalline phase which consists of elementary unit cells whose lattice parameters are of the order of angstroms. An elementary unit cell is a set of chain segments that organize regularly.
- The crystalline lamellae, which are sets of folded chains with a thickness of the order of tens of nanometers.
- Spherulites are aggregates of lamellae in the form of spheres whose size is of the order of micrometers (from 10 to 100 microns).

IV.3.2 The crystalline network:

In the liquid state, polymer molecules are disordered in the form of coils. At the crystallization temperature, the molecular chains come closer to each other and align in parallel until they reach an equilibrium state where the molecular chains are arranged regularly. This arrangement forms an ordered zone that can be defined by a crystalline lattice. However, the order will be very different in the direction of the chains and in the plane perpendicular to them.

The most common polymer crystalline lattices are: monoclinic, triclinic, orthorhombic, quadratic, and rhombohedral (trigonal). Figure IV.3 shows the crystalline structure of polyethylene terephthalate (PET) given by Bunn et al. The parameters of the triclinic lattice are as follows: a = 0.457 nm, b = 0.595 nm, c = 1.075 nm.

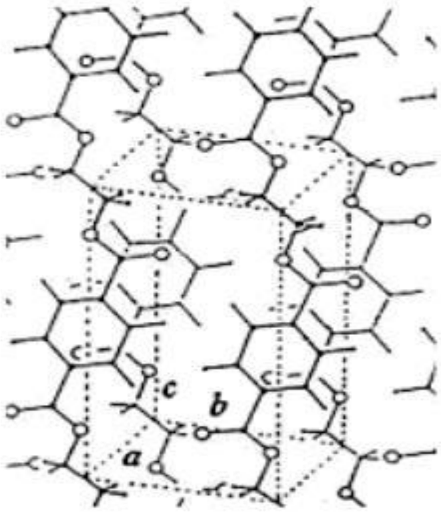


Figure IV.3: Triclinic unit cell of the crystalline phase of PET.

A polymer can exist in different crystalline structures such as poly(lactic acid) (PLA) : orthorhombic form α, β, and γ.

Due to the difference between intramolecular (van der Waals) and intermolecular (covalent) bonds, polymer crystals are highly anisotropic from a mechanical point of view. Cohesion in the axis c is greater than that in the axes a and b.

IV.3.3 The crystalline lamellae:

The structure of a semi-crystalline polymer is formed of the crystalline zone where the molecular chains are ordered and the amorphous zone where the chains are disordered. The crystallized zones are denser than the amorphous zones. The lamellae typically have a thickness of 10 to 20 nm , which is much smaller than the length of macromolecular chains, which are about 10 to 20 µm in length. figure IV.4

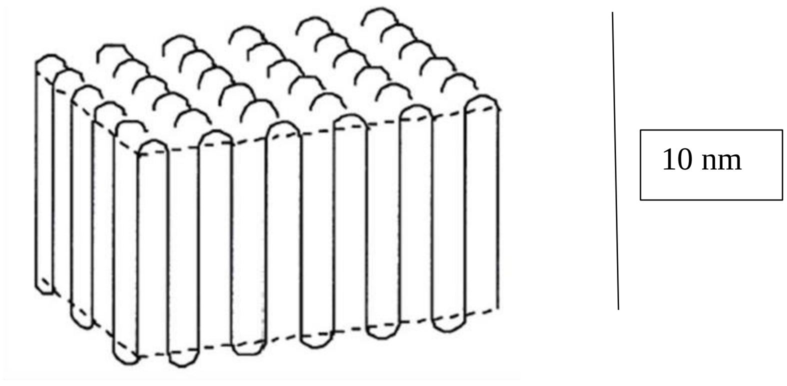


figure IV.4: Chain folding model in a single crystal

IV.3.4. Determination of crystallinity

IV.3.4.1. By densimetry

Densimetry is a method used to determine the crystallinity of a semi-crystalline polymer. This method is based on the difference in density between the crystalline phase (ρc) and the amorphous phase (ρa). It is often used when the values of ρc and ρa are sufficiently far apart to obtain sufficient precision. First, the density of a semi-crystalline polymer is measured by weighing a sample in air and then in a liquid. The liquid used in these measurements is distilled water. The density of the semi-crystalline polymer is calculated using the following formula:

$$\rho = (m_{air}\ \rho_{wather})/(m_{air} - m_{\ wather})$$

Where m_{air} is the mass of the sample in air.

m_{wather} is the mass of the sample in water.

ρ_{wather} is the density of water at the temperature of the test.

The degree of crystallinity (Xm) by mass is calculated using the formula below:

$$Xm = \rho_c(\rho - \rho_a) \ / \ \rho(\rho_c - \rho_a)$$

and in volume as:

$$X_v = (\rho - \rho_a) / \rho(\rho_c - \rho_a)$$

This technique is only used for PET as the densities of the crystalline and amorphous phases are sufficiently different, unlike PLA. The mass density of the crystalline and amorphous phases of PET are $\rho c = 1.445$ g/cm^3 and $\rho a = 1.335$ g/cm^3, respectively, which is a density difference of 0.11 g/cm^3. For PLA, the values are $\rho c = 1.29$ g/cm^3 for the mass density of the crystalline phase and $\rho a = 1.24$ g/cm^3 for the amorphous phase, which is a density difference of 0.05 g/cm^3.

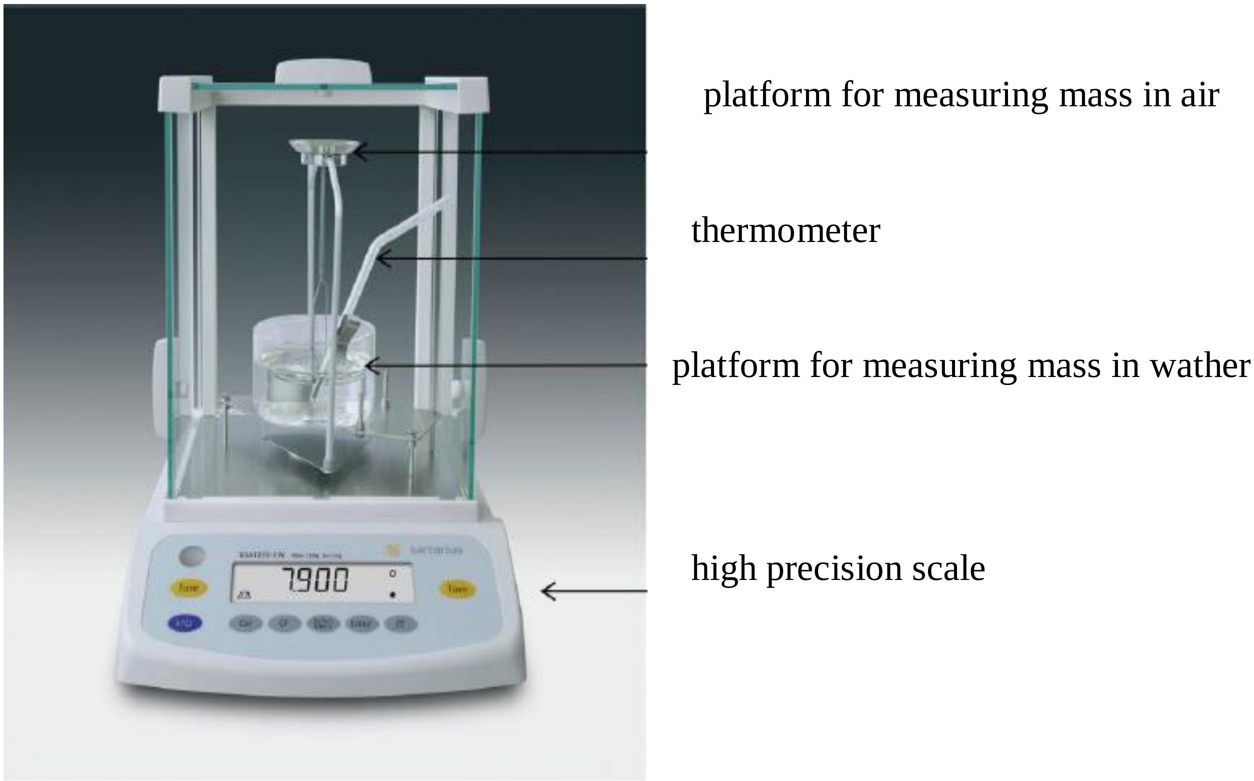


figure. IV.5 Sartorius YDK01 Density Device

IV.4. Semi-crystalline Polymers:

Semi-crystalline polymers have a molecular structure that includes both crystalline and amorphous regions. The crystalline regions have a regular and ordered structure, while the amorphous regions have a disordered structure. Semi-crystalline polymers are common and are used in many applications, including food packaging films, pipes, and wires.

IV.4.1. Crystalline Structure of Semi-Crystalline Polymers:

The crystalline structure of semi-crystalline polymers is formed by the regular stacking of polymer chains. The chains are arranged in a regular and ordered manner, creating a crystalline structure. The size and shape of the crystals depend on many factors such as temperature, pressure, and cooling rate. Crystals can be small and irregular or large and regular.

IV.4.2. Properties of Semi-Crystalline Polymers:

Semi-crystalline polymers have unique properties that distinguish them from amorphous polymers. The crystalline regions are more rigid and stronger than the amorphous regions. The mechanical properties of semi-crystalline polymers depend on the amount and size of crystals present in the material. Semi-crystalline polymers also have better heat resistance than amorphous polymers.

IV.4.3. Applications of Semi-Crystalline Polymers:

Semi-crystalline polymers are used in many applications due to their mechanical and thermal properties. They are commonly used in food packaging films, pipes, wires, toys, and sports equipment. Semi-crystalline polymers are also used in the automotive industry to manufacture interior and exterior parts.

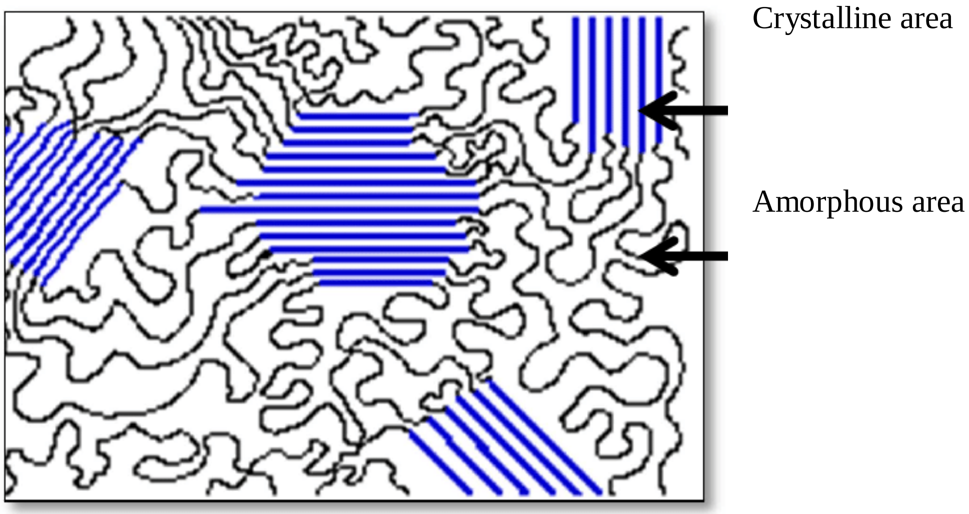


figure IV.6 Schematic of a semi-crystalline polymer

IV.5. Thermal behavior: (glass transition)

IV.5.1. Glassy state:

In the glassy state (at low temperatures or high speeds), the molecular movements accessible to the polymer cannot initiate cooperative movements along the chain skeleton. The accessible deformations are therefore weak and the modulus is high. Elastic deformation is controlled by the enthalpic term of its internal energy, as in metals. Despite being in a glassy state, the polymer is not frozen. There are always temporal and spatial fluctuations of conformation, controlled by temperature: they are more rapid and numerous as temperature increases. Therefore, it becomes "easier" to deform the material as its temperature increases. The modulus is thus thermodependent and decreasing. Similarly, the material remains viscoelastic. Under high stress, plastic deformation processes can be activated at medium temperature and speed, but are inoperative at low temperatures or high speeds. This results in the existence of a temperature (and/or speed) of ductile/fragile transition, lower than the glass transition temperature. Let us say that the apparent behavior of the polymer when it is in a glassy state is viscoelastic, viscoplastic, with more or less developed macroscopic ductility depending on temperature and speed.

IV.5.2 Transition zone:

The D transition zone, associated with glass relaxation, or the viscoelastic zone, marks the moment when global conformational changes, i.e. cooperative movements along the chain skeleton, become possible. The modulus therefore decreases rapidly and the behavior is highly evolving.

IV.5.3 Rubber zone:

In the rubber zone, the temperature is sufficient for the chain to spontaneously sweep all its possible conformations in a time much shorter than the representative time of the solicitation. However, the temperature is too low to allow the unraveling of the chains on a large scale. Macroscopically, the chains therefore appear flexible, but flow is prohibited. The material gradually becomes hyperelastic, in fact viscohyperelastic, if it is not cross-linked. Plastic processes give way to entropic elasticity at large deformations.

The existence of crystals partly compensates for the loss of modulus and cohesion of the amorphous polymer. Thus, the rubber plateau of a semicrystalline material is not only higher but also longer than that of an amorphous material. These two points explain why a semicrystalline material, such as PP or PE, can be used above its a transition, while an amorphous material, such as PS, will be limited to its glassy plateau. To use an amorphous material beyond its glass transition, it must be cross-linked, which are elastomers. In parallel, the crystal always has enthalpic elasticity and plasticity processes. A semicrystalline polymer thus remains viscoplastic, with structural hardening and/or damage, on its rubber plateau (Figure IV.7).

It is also important to note in Figure 3 that PC and PP have very similar macroscopic behaviors, although they are the sites of very different processes: amorphous and glassy for one, and semicrystalline and rubbery for the other.

IV.5.4 Fluid zone:

The fluid zone appears when chain disentanglements become probable. The chains appear statistically independent of each other. The solicitation can therefore easily move them relative to each other. The behavior becomes mostly viscous, but remains viscoelastic.

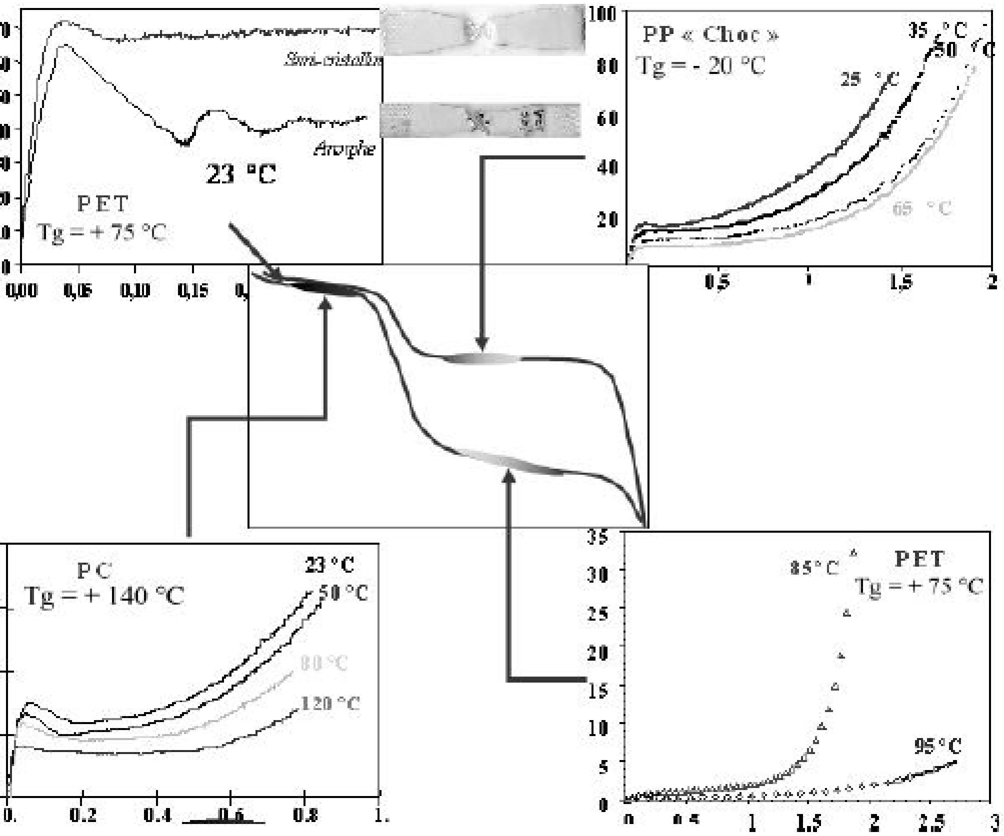


Figure IV.7 : Example of tensile behaviors of polymers at 0.001 s^{-1} as a function of temperature (given with respect to their respective Tg).

IV.6. Viscoelasticity:

Viscoelasticity is a phenomenon that characterizes the mechanical behavior of materials, especially polymers. It refers to the ability of a material to exhibit both viscous and elastic responses to an external force. In other words, viscoelasticity combines the characteristics of both a liquid and a solid material. Understanding viscoelasticity is crucial in the development of many everyday products that we use, such as rubber bands, tires, and plastics. In this paper, we will discuss the viscoelastic behavior of polymers, its importance, and its applications.

IV.6.1 Viscoelastic Behavior of Polymers:

Polymers are long chains of molecules that have a complex internal structure. They are made up of repeating units called monomers, which are joined together to form a chain. Polymers can be classified as either amorphous or semi-crystalline, depending on their structure. Amorphous polymers have a disordered structure, while semi-crystalline polymers have regions of ordered structure, called crystallites, within a disordered matrix.

When a stress is applied to a polymer, it deforms elastically up to a certain point, after which it deforms plastically. At low deformation rates and high temperatures, the polymer exhibits a viscoelastic behavior. This means that the polymer exhibits both viscous and elastic behavior, depending on the rate of deformation and the temperature. The viscous response is characterized by a time-dependent flow, while the elastic response is characterized by a time-independent deformation.

The viscoelastic behavior of polymers can be understood by considering the motion of the polymer chains. At low deformation rates, the polymer chains have enough time to move and align themselves along the direction of the applied stress. This alignment results in a viscous response, which causes the polymer to flow. At high deformation rates, the polymer chains do not have enough time to align themselves and instead deform elastically.

IV.6.2 Mechanical Models:

The linear viscoelastic response of polymeric solids can be described for many years by a number of mechanical models that can provide a useful picture of time dependent deformation processes. It is possible to analyze the deformation of viscoelastic materials with appropriate combinations of elastic springs, which obey Hook's law and viscous dashpots that obey Newton's law of viscosity; the dashpot is imagined as a piston moving in a cylinder of viscous fluid.

IV.6.3 Maxwell model:

the Maxwell model consists of spring and dashpot in series as shown in Fig. (IV.8).

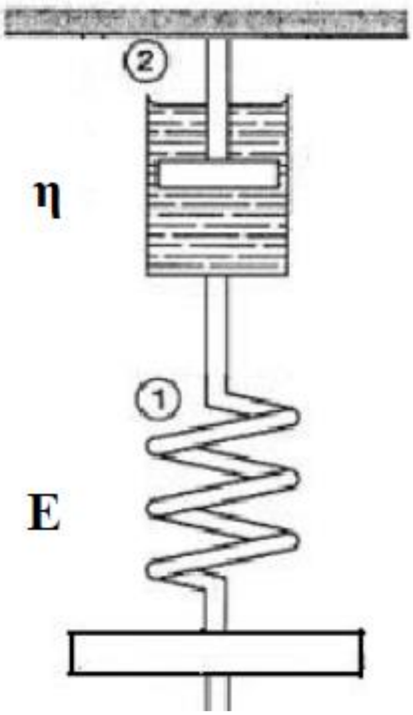
For creep, stress is constant ($\sigma = \sigma_o$),

strain will change with time;

so $d\sigma/dt = 0$. ($\sigma = \sigma 1 = \sigma 2$, $\varepsilon = \varepsilon 1 + \varepsilon 2$)

The final equation of Maxwell model is :

$$\varepsilon = \sigma_o t / \eta \qquad \text{(IV.1)}$$



Eq.IV.1 corresponds to the response of only viscous element, which is not very realistic form of behavior because in this equation strain increases linearly with time (viscous behavior). This is not generally true for viscoelastic materials where the creep behavior is more complex.

IV.7. Mechanical characterizations:

IV.7.1 Tensile test:

This is a basic test for homogeneous plastics. It allows determining the stress at break, the elongation at break, and the modulus of elasticity.

A specimen with a well-defined geometry (see figure IV.9) is clamped at both ends using jaws or grips. One of these fixed jaws is connected to a dynamometric system for measuring forces via a ball joint so that the axis of forces is aligned with that of the specimen. The other mobile jaw is connected to a driving system that operates at a constant speed or a constant load, but less commonly (see figure IV.10).

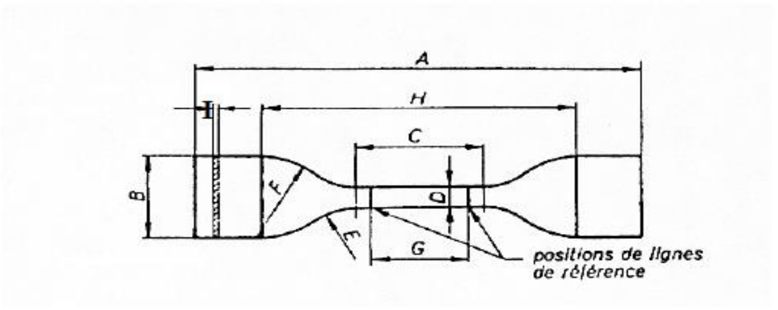


Figure IV.9: Altered specimen for tensile testing.

Dimensions:

A : Longueur totale minimale.	75.00 mm
B Width of the ends	12.5 ± 1.0 mm
C Length of the calibrated part	25.0 ± 2.0 mm
D Width of the calibrated part	4.00 ± 0.4 mm
E Small radius	8.00 ± 1.0 mm
F Large radius	12.5 ± 2.0 mm
G Distance between reference lines	20.0 ± 1.0 mm
H Initial distance between jaws	62.5 ± 5.0 mm
I Thickness.	2.00 mm

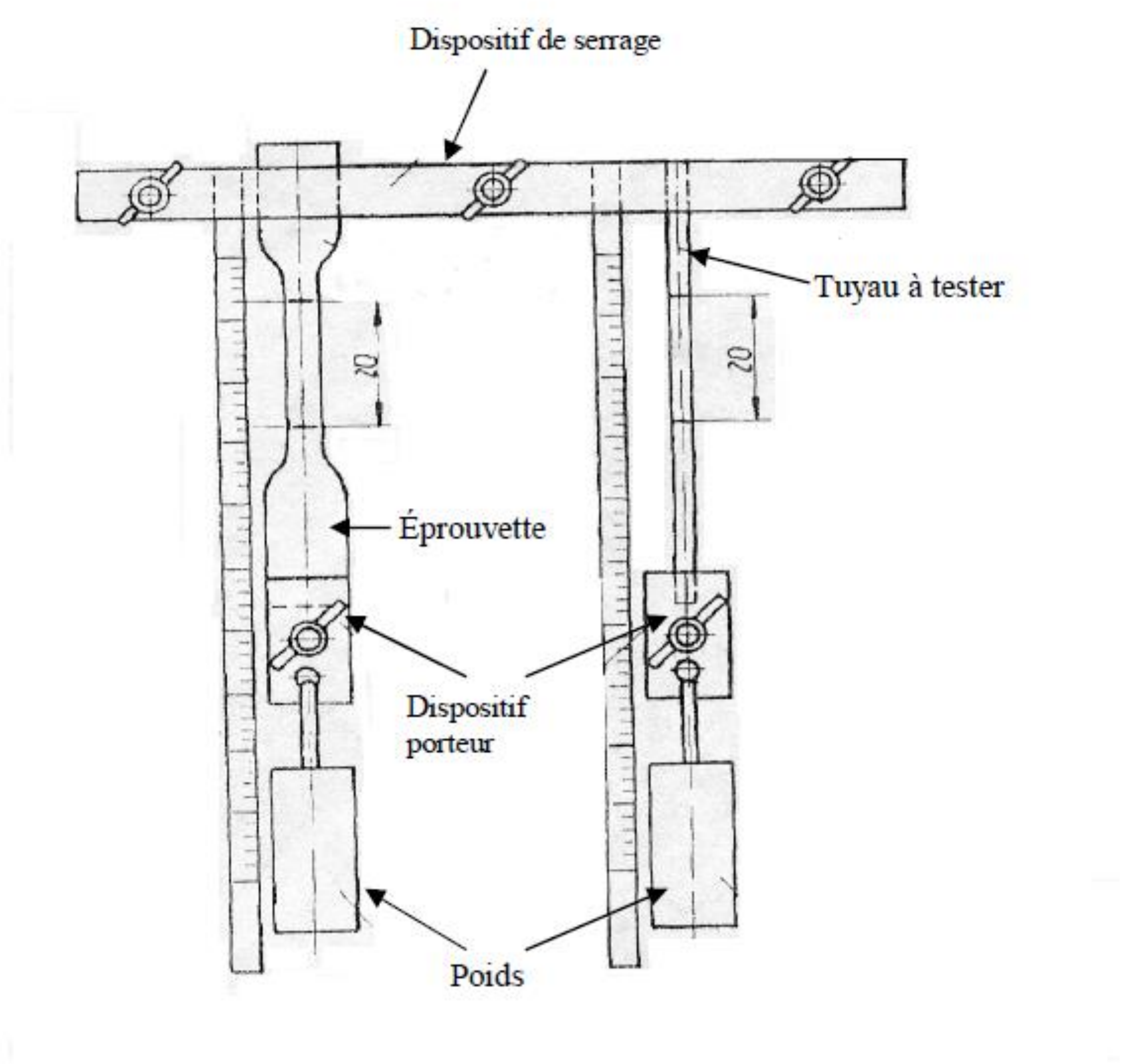


Figure IV.10 depicts a diagram of a tensile testing machine at break.

The stress at failure was calculated using the following equation:

$$R\ (\sigma) = F/\ S$$

F: The applied force (N)

S: section of the specimen (mm)

The elongation at break was calculated using the following equation:

$$\text{All \%} = [(l - l_0) / l_0] \times 100$$

All: elongation at break in %

l : final elongation measured in mm, l_0 : initial test elongation measured in mm.

IV.7.2 Hardness test:

The hardness of a material is its resistance to penetration by a given shaped and sized indenter (a steel ball or a diamond cone).

The Shore hardness penetration index, commonly referred to as Shore A or Shore D hardness, is the result of a measurement carried out according to a specific procedure using a Shore A or a Shore D durometer.

The specimen can have any shape (square, rectangular or disc) provided that the dimensions allow for at least five measurements at different locations at least 6 mm apart from each other and at least 12 mm away from the edges of the specimen. The surface of the specimen to be measured should be as flat as possible. It is preferable to use specimens with two parallel faces to have a flat and horizontal testing face.

The test is performed after checking the marked mass of 1 kg for the Shore A durometer or 5 kg for the Shore D durometer and ensuring proper positioning of the specimen on the mobile plate, as shown in Figure IV.11

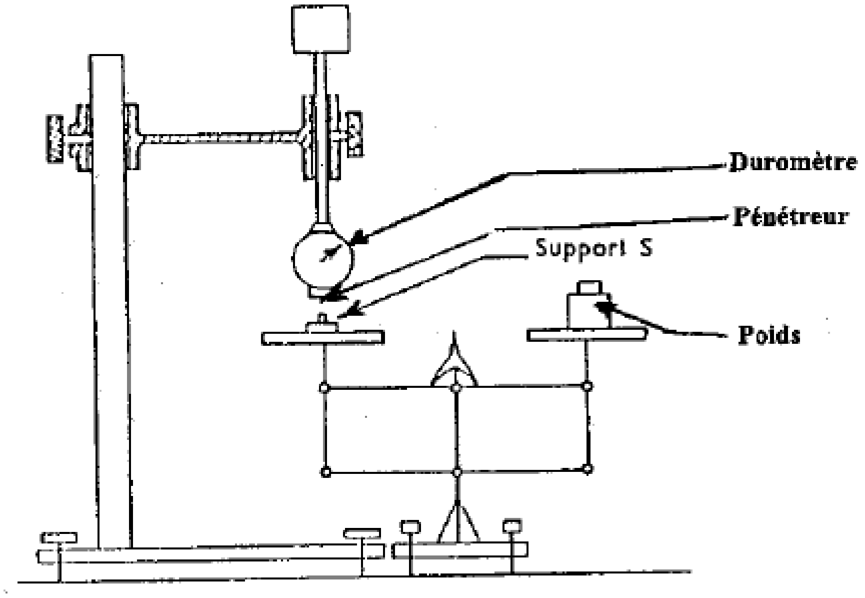


Figure IV.11 Schematic of a hardness tester

One quickly raises the platform to apply the presser foot on the specimen without impact, as soon as stable contact is established, the durometer is triggered, and the reading is taken after (15 ± 1) seconds.

Shore hardness is expressed as follows:

$$\text{Dur. Shore } X = M$$

X: represents the letter corresponding to the type of Shore durometer used: A or D.
M: represents the calculated average value.

IV.7.3 A loss of mass

All the tests mentioned above are instantaneous tests, that is to say, they make it possible to determine the characteristics of the material in the short term. It is certain that depending on the conditions of use, these characteristics will evolve over time. It is therefore necessary to consider long-term tests that take into account mechanical stresses.

The mass loss is based on weighing the sample before and after the heat treatment.

The mass loss was calculated using the following formula:

$$P = \Delta P / S$$

P: loss of mass in g/cm2

ΔP: difference in weight in g.

S: surface area of the specimen in mm2.

where this surface area is calculated using the following formula:

$$S = (180\ E + 1256)/100$$

E : thickness of the specimen in mm.

BIBLIOGRAPHY

[1] Abdulakh K.Mikitaev And Mukhamed Kh. Ligidov, “Polymers, Polymer Blends, Polymer Composites And Filled Poymers: Synthesis, Properties And Applications”. Nova Science Publishers, Inc. New York (2006).

[2] Christopher S. Brazel And Stephen L. Rosen, “Fundamental Principles Of Polymeric Materials”. Published by John Wiley & Sons, Inc., Hoboken, New Jersey (2012).

[3] Donald E. Hudgin , “ Polymers, Specialty Polymers, and Their Applications”. Taylor & Francis (2007).

[4] Thanh Loan NGUYEN ‘’Approche multi-échelles dans les matériaux polymères : de la caractérisation nanométrique aux effets d’échelles’’. Université de Technologie de Compiègne.

[5] Timothy P. Lodge and Paul C. Hiemenz, ‘’Polymer Chemistry’’. Taylor & Francis Group, LLC. (2020).

[6] Robert O. Ebewele, ‘’Polymer Science And Technology’’. Boca Raton New York (2000).

[7] Jean-Pierre Mercier, Ernest Maréchal, ‘’Chimie des polymères (TM volume 13) - Synthèses, réactions, dégradations’’. PPUR presses polytechniques. (1996).

[8] Yves Gnanou Michel Fontanille, ‘’Chemistry Of Polymers’’. A JOHN WILEY & SONS, INC., PUBLICATION. (2008).

[9] Charles E. Carraher, Jr.‘’ Polymer Chemistry’’. Marcel Dekker, INC. New York • Basel. (2003).

[10] Paul C. Hiemenz, Timothy R Lodge. ‘’Polymer chemistry’’. Taylor & Francis. (2007).

[11] L. M. Harwood, C. J. Moody. ‘’Polymer chemistry’’. Oxford University Press. (2004).

[12] K.J.SAUNDERS . ‘’ Organic Polymer Chemistry’’. Springer-Science+ Business Media, B.V. (1973).

[13] Bengt Kronberg, Krister Holmberg, Björn Lindman. ‘’Surface Chemistry of Surfactants and Polymers’’. John Wiley & Sons, Ltd. (2014).

[14] L.G. Wader,Jr. ‘’Organic Chemistry’’. Pearson Education, Inc. (2006).

[15] Yves Gnanou, Michel Fontanille. ‘’ Organic And Physical Chemistry Of Polymers’’. A John Wiley & Sons, Inc., Publication. (2008).

[16] W. Henderson. ‘’Main Group Chemistry’’. Royal Society of Chemistry. (1999).

[17] Manas Chanda. ‘’ Introduction to Polymer Science and Chemistry’’. Taylor & Francis. (2013).

[18] Vijay Kumar Thakur and Manju Kumari Thakur. ‘’ Handbook of Polymers for Pharmaceutical Technologies’’. Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts. Published simultaneously in Canada. (2015).

[19] John A. Tyrell. ‘’ Fundamentals of Industrial Chemistry (Pharmaceuticals, Polymers, And Business)’’. Published by John Wiley & Sons, Inc., Hoboken, New Jersey Published Simultaneously in Canada. (2014).

[20] Susheel Kalia l B. S. Kaith l Inderjeet Kaur. ‘’ Cellulose Fibers: Bio- and Nano-Polymer Composites’’. Springer is part of Springer Science+Business Media. (2011).