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.

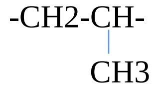
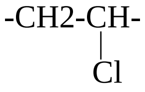
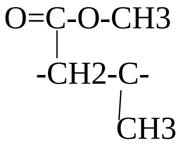
I.4. Polymer Nomenclature:

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
 $-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-$	Polypropylene (PP)	food packaging film
 $-CH_2-\underset{Cl}{\underset{\vert}{CH}}-$	Polyvinyl chloride (PVC)	Piping, margarine tubs
 $-CH_2-\underset{CH_3}{\underset{\vert}{\overset{O=C-O-CH_3}{\overset{\vert}{C}}}}-$	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.

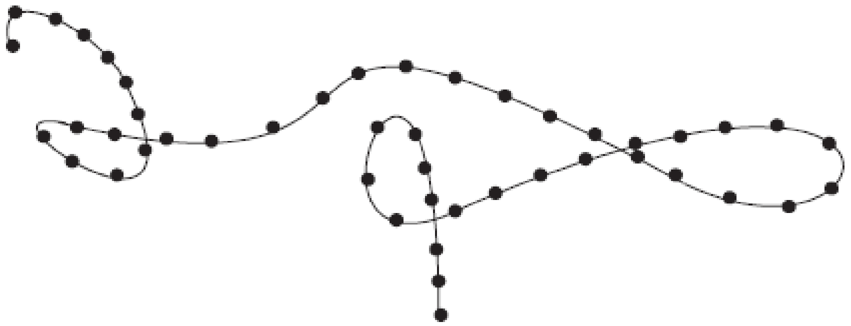


Figure I.1. Representation of the chain of a linear polymer.

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)**

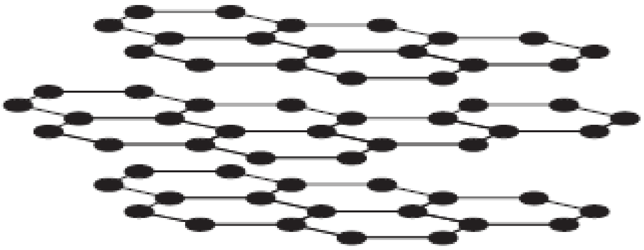


Figure I.2. Schematic representation of a two-dimensional polymer, here carbon graphite.

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**.

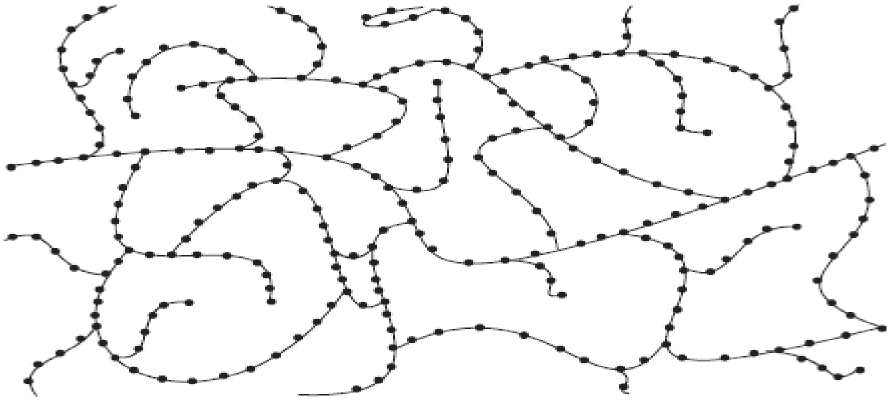


Figure I.3. Schematic representation of a three-dimensional polymer

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.

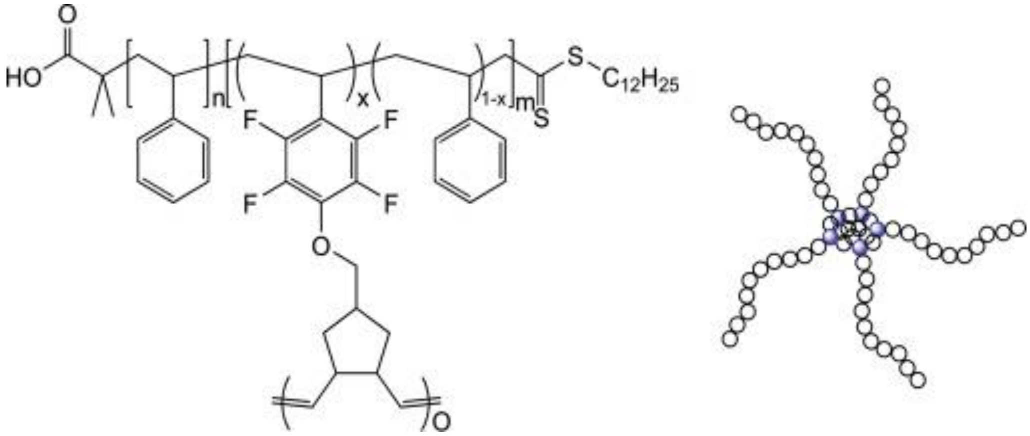


Figure I.4 Star polymer

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.

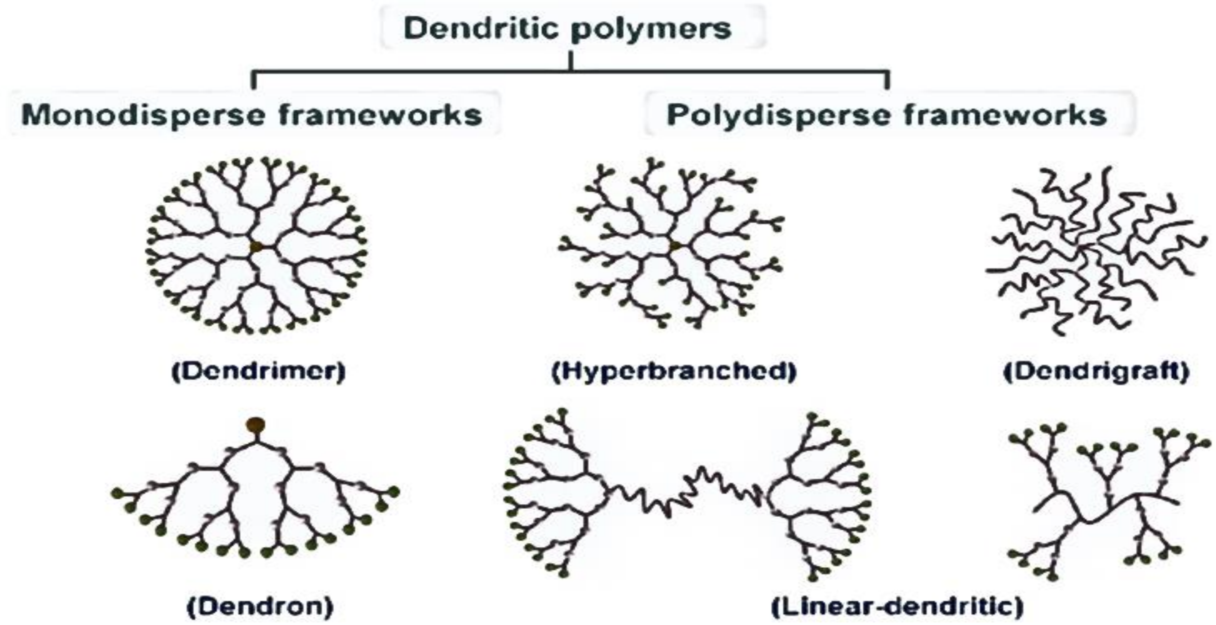


Figure I.5 Schematic classification of the dendritic polymers including two major categories and their subgroups.

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.

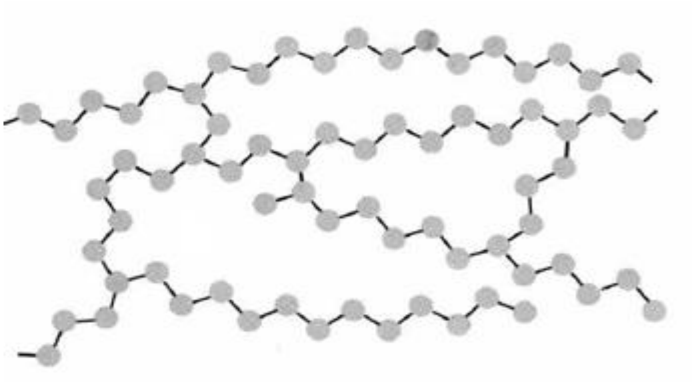


Figure I.6 Crosslinked polymers

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.

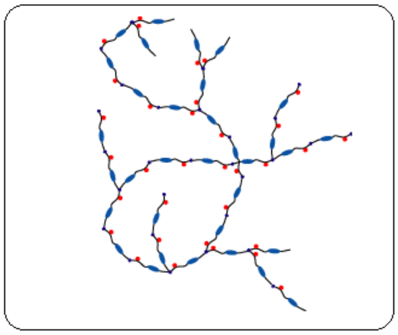


Figure I.7 Schematic representation of a thermoplastic polymer.

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.

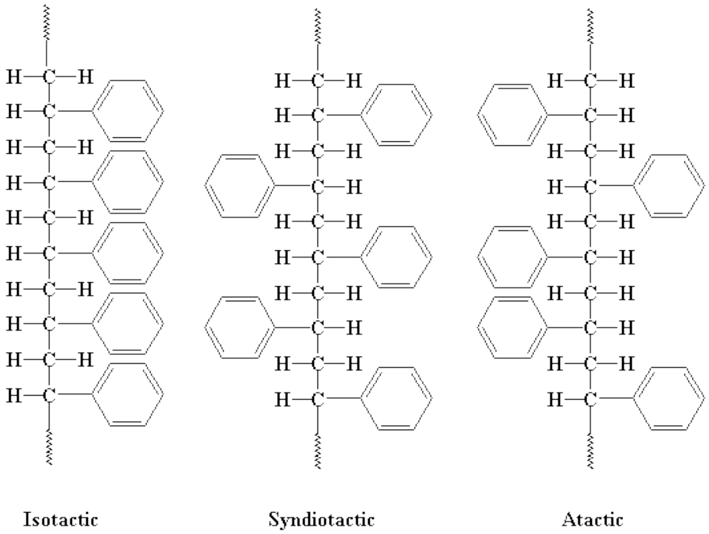


Figure I.10 The stereochemistry of polymers

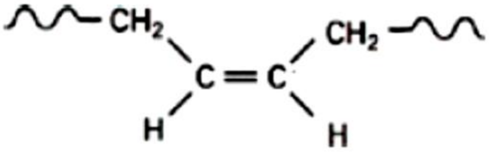
b) Cis-trans isomerism:

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.

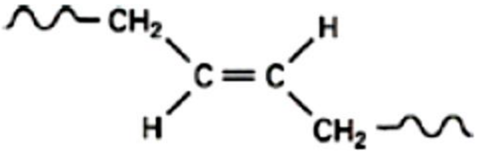
Polybutadiene polymerized in a 1,4 fashion.

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.

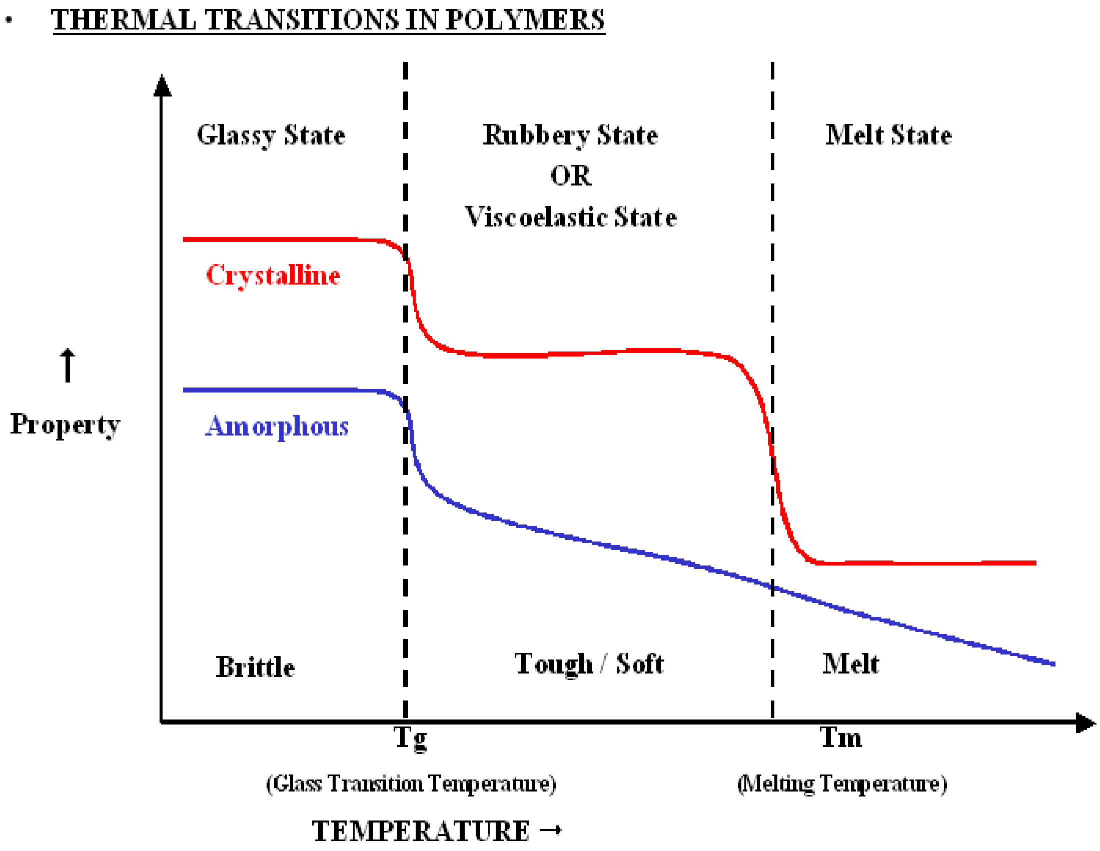


Figure I.12 Thermal transition in polymers

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.