Chapter N° 4:
Polymers

1. Introduction

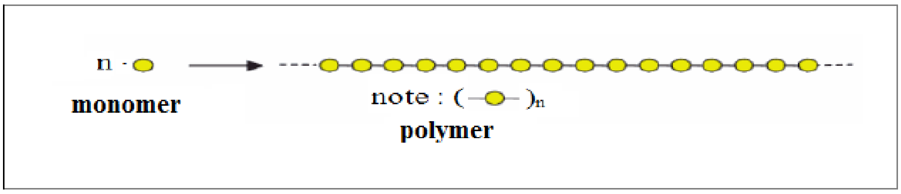
Polymers are large molecules composed of repeating structural units, known as monomers, which are chemically bonded together. These macromolecules can consist of thousands or even millions of atoms, giving them unique and versatile properties.

Definition of Polymers

A polymer is a large macromolecule made up of repeating structural units called monomers, which are covalently bonded together in a chain-like or network structure. These repeating units may be identical (homopolymer) or different (copolymer).

The term polymer (from the Greek **polus** which means "**many, several**" and **mêros** which means "**unit, part**").

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



2. Brief History of Polymers

Ancient Times (Natural Polymers):

Natural polymers like rubber, silk, and cellulose have been used for centuries.

Example: The ancient Mesoamericans used natural rubber for making balls and tools.

19th Century (Early Synthetic Polymers):

1839: Charles Goodyear developed vulcanized rubber, a stronger and more durable form of natural rubber.

1862: Alexander Parkes introduced "Parkesine," the first man-made plastic, derived from cellulose.

1907: Leo Baekeland created Bakelite, the first fully synthetic polymer, marking the beginning of the modern plastics industry.

Early 20th Century (Development of Synthetic Polymers):

1920: Hermann Staudinger proposed the macromolecular theory, confirming that polymers consist of long-chain molecules.

1930-1940: Key discoveries included Nylon (Wallace Carothers), Polystyrene, Polyethylene, and Polytetrafluoroethylene (Teflon).

Post-War Era (Plastic Revolution):

Rapid expansion of polymer applications, including in packaging, textiles, and construction.

Development of high-performance plastics like Polycarbonate and Acrylic.

Modern Era (Advanced Polymers):

Development of specialty polymers for electronics, aerospace, and medicine (e.g., biocompatible polymers for prosthetics).

Focus on biodegradable polymers and sustainable materials to address environmental concerns.

Polymers have revolutionized industries and everyday life, evolving from natural origins to a cornerstone of modern science and technology.

3. Nomenclature of Polymers

The nomenclature of polymers provides a systematic way to name polymeric substances based on their structure, type of monomers, and method of polymerization. It ensures consistency and clarity in identifying polymers in scientific and industrial contexts.

3.1. Based on Source

3.1.1. **Natural Polymers**: Named after their biological source or function.

Example: Cellulose, Silk, Starch.

3.1.2. **Synthetic Polymers**: Named based on their monomer or polymerization process.

Example: Polyethylene, derived from ethene monomers.

3.2. Based on Structure

3.2.1. **Linear Polymers**: Name reflects the monomer repeated in the chain.

Example: Polypropylene (repeating unit: propene).

3.2.2. **Branched Polymers**: Named by specifying the type and position of branching.

Example: Low-Density Polyethylene (branched version of polyethylene).

3.2.3. **Crosslinked Polymers**: Described using terms like "network" or "crosslinked" if highly interconnected.

Example: Crosslinked Polyacrylamide.

3.3. IUPAC Nomenclature

IUPAC provides a systematic approach to naming polymers:

Prefix “**poly**” followed by the name of the monomer in parentheses.

For monomers derived from complex chemical groups, the group name is enclosed in brackets.

Examples:

Homopolymers:

- Polyethylene (poly(ethene)).
- Polystyrene (poly(phenylethene)).

Copolymers:

If the polymer contains two or more monomers, all monomers are listed in order.

Example: Poly(styrene-co-butadiene) (styrene and butadiene units).

4. Different Types of Polymerization and Co-Polymerization

4.1.Types of Polymerization

4.1.1. Addition Polymerization (Chain-Growth Polymerization):

- Monomers add to a growing polymer chain one at a time.
- Typically involves unsaturated monomers like alkenes and alkynes.

Examples: Polyethylene, Polypropylene.

Mechanisms:

- **Free Radical Polymerization**: Initiated by free radicals.
- **Cationic Polymerization**: Uses cationic initiators.
- **Anionic Polymerization**: Uses anionic initiators.

Coordination Polymerization: Catalyzed by coordination complexes (e.g., Ziegler–Natta catalysts).

4.1.2. Condensation Polymerization (Step-Growth Polymerization):

- Monomers join by eliminating small molecules (e.g., water, methanol).
- Typically involves bifunctional or polyfunctional monomers.

Examples: Polyesters, Polyamides, Polycarbonates.

4.1.3. Ring-Opening Polymerization:

- Involves the opening of cyclic monomers to form polymers.

Examples: Nylon-6 from caprolactam, Polycaprolactone.

4.2.Types of Co-Polymerization

Co-polymerization involves two or more different types of monomers. Common types include:

4.2.1. Random Co-Polymerization:

Monomers are randomly distributed along the polymer chain.

Example: Styrene-butadiene rubber (SBR).

4.2.2. Alternating Co-Polymerization:

Monomers alternate in a regular pattern.

Example: Maleic anhydride and styrene co-polymer.

4.2.3. Block Co-Polymerization:

Large blocks of one type of monomer alternate with blocks of another.

Example: Polystyrene-block-polybutadiene.

4.2.4. Graft Co-Polymerization:

One type of monomer forms the main chain, and another forms side chains grafted onto it. **Example**: Graft polymers of natural rubber.

Each type of polymerization and co-polymerization is tailored to achieve specific properties in the final material.

5. Physical properties of polymers

First of all, let us recall that there is a great variety of plastics, just as there are a large number of metal alloys. One of the general physical characteristics of polymers is:

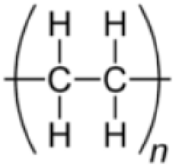
Density: the density of plastics is low. The lightness of polymers is undoubtedly one of the qualities that have most significantly contributed to their widespread use.

In terms of the ratio of tensile strength to density, some polymers are, in fact, superior to metallic materials.

The low density of plastics is due to the low atomic weight of the main atoms in their chains, primarily hydrogen and carbon.

6. Study of polymers

6.1. Polyethylene



Polyethylene (abbreviated **PE**) or polythene (IUPAC name **polyethene** or **poly(methylene)**) is the most common **plastic**. Its primary use is within packaging (plastic bag, plastic films, geomembranes, containers including bottles, etc.). Many kinds of polyethylene are known, but they almost always have the chemical formula **$(C_2H_4)_nH_2$**. Thus, **PE** is usually a mixture of similar organic compound that differ in terms of the value of **n.**

6.1.1. Properties

6.1.1.1. Physical properties

Polyethylene is a **thermoplastic polymer** consisting of long hydrocarbon chains. Depending on the crystallinity and molecular weight, a melting point and glass transition may or may not be observable. The temperature at which these occur varies strongly with the type of polyethylene. For common commercial grades of medium- and high-density polyethylene the melting point is typically in the range **120 to 130 °C**. The melting point for average, commercial, low-density polyethylene is typically **105 to 115 °C**.

6.1.1.2. Chemical properties

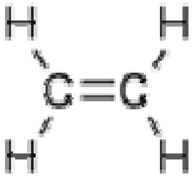
Most **LDPE, MDPE** and **HDPE** grades have excellent chemical resistance, meaning that it is not attacked by strong acids or strong bases. It is also resistant to gentle oxidants and reducing agents. Polyethylene **burns** slowly with a blue flame having a yellow tip and gives off an odour of paraffin. The material continues burning on removal of the flame source and produces a drip. Crystalline samples do not dissolve at room temperature. Polyethylene (other than cross-linked polyethylene) usually can be dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene, or in chlorinated solvents such as trichloroethane or trichlorobenzene.

6.1.2. History

Polyethylene was first synthesized by the German chemist Hans von Pechmann who prepared it by accident in 1898 while heating diazomethane. When his colleagues Eugen Bamberger and Friedrich Tschirner characterized the white, waxy, substance that he had created they recognized that it contained long -CH2- chains and termed it polymethylene.

6.1.3. Process

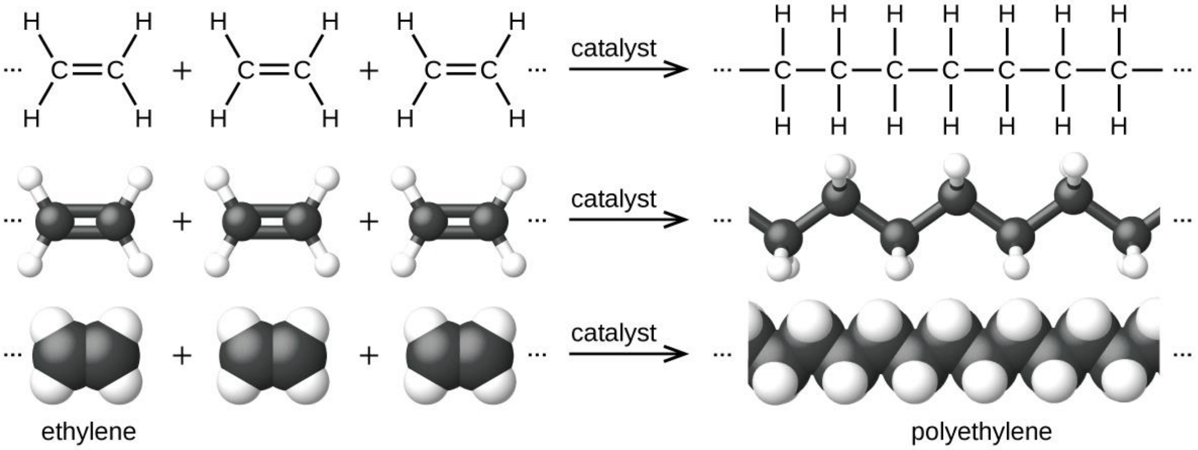
Monomer The ingredient or monomer is ethylene (IUPAC name ethene). It has the formula C_2H_4, consisting of a pair of CH_2 groups connected by a double bond, thus:



6.1.4. Polymerization

Polymerization of ethylene to polyethylene is described by the following chemical equation:

$n\ CH_2{=}CH_2\ (\text{gas}) \rightarrow [-CH_2-CH_2-]_n\ (\text{solid}) \qquad \Delta H/n = -25.71 \pm 0.59\ \text{kcal/mol}\ (-107.6 \pm 2.5\ \text{kJ/mol})$



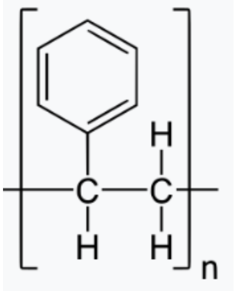
6.1.5. Biodegrading plastics

One of the main problems of polyethelyne is that without special treatment it is not biodegradable, and thus accumulates. In Japan getting rid of plastics in an environmentally friendly way was the major problem discussed until the Fukushima disaster in 2011. It was listed as a $90 billion market for solutions. Since 2008 Japan has rapidly increased the recycling of plastics, but still has a large rate of plastic wrapping which goes to waste.

6.1.6. Bio-based polyethylene

Braskem and Toyota Tsusho Corporation started joint marketing activities to produce polyethylene from **sugarcane**, and will produce high-density and low-density polyethylene from bioethanol derived from sugarcane.

6.2. Polystyrene



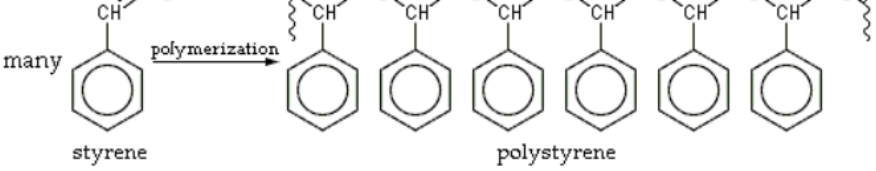
Polystyrene (PS) is a synthetic polymer made from monomers of the aromatic hydrocarbon styrene. Polystyrene can be solid or foamed. General-purpose polystyrene is clear, hard, and brittle. Polystyrene is a polymer obtained from monomer styrene, which is a hydrocarbon obtained from petroleum. Polystyrene is used in solid form and it is naturally transparent material, however it can be coloured by adding colourants. Being thermoplastic polymer, polystyrene is in solid form at room temperature but flows if heated above 100oC (its glass transition temperature). It gets solidified again when it is cooled

6.2.1. History

Polystyrene was discovered in 1839 by Eduard Simon, an apothecary from Berlin.

6.2.2. Synthesis

Polystyrene is an addition polymer that results when styrene monomers polymerize (interconnect). In the polymerization, the carbon-carbon π bond of the vinyl group is broken and a new carbon-carbon σ bond is formed, attaching to the carbon of another styrene monomer to the chain. Since only one kind of monomer is used in its preparation, it is a homopolymer. The newly formed σ bond is stronger than the π bond that was broken, thus it is difficult to depolymerize polystyrene.



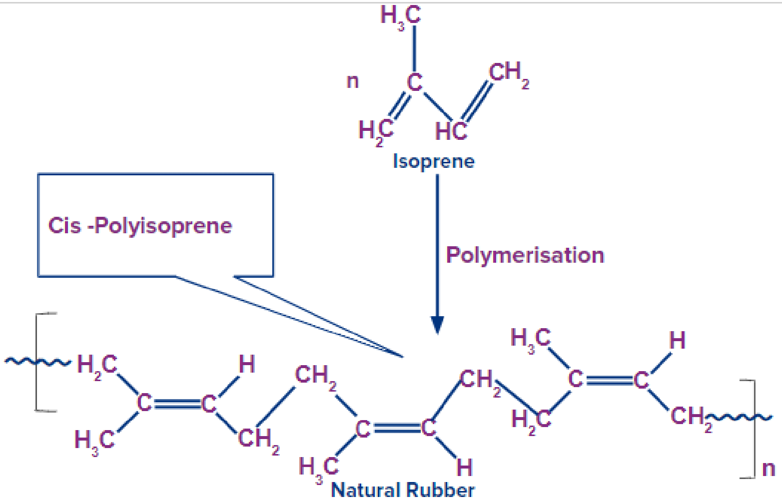
6.3. rubber

A synthetic rubber is an artificial elastomer. They are polymers synthesized from petroleum byproducts.

6.3.1. Natural Rubber

Natural rubber is an **addition polymer** that is obtained as a milky white fluid known as latex from a tropical rubber tree. Natural rubber is from the monomer **isoprene (2-methyl-1,3-butadiene)**, which is a conjugated **diene** hydrocarbon. In natural rubber, most of the double fonds formed in the polymer chain have the **Z** configuration, resulting in natural rubber's elastomer qualities.

Charles Goodyear accidentally discovered that by mixing sulfur and rubber, the properties of the rubber improved in being tougher, resistant to heat and cold, and increased in elasticity. This process was later called vulcanization after the Roman god of fire. Vulcanization causes shorter chains to cross link through the sulfur to longer chains. The development of vulcanized rubber for automobile tires greatly aided this industry.



Polymerisation of isoprene to form Natural rubber

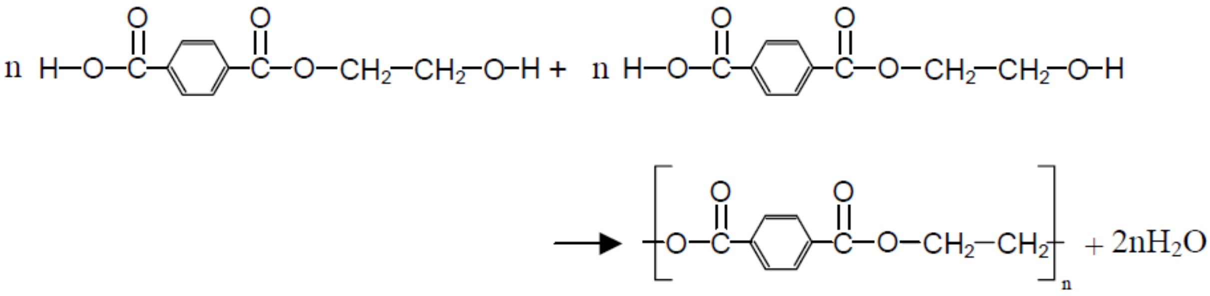
6.3.2. Synthetic Rubber

Important conjugated **dienes** used in synthetic rubbers include **isoprene (2-methyl-1,3-butadiene), 1,3-butadiene,** and **chloroprene (2-chloro-1,3-butadiene)**. Polymerized 1,3-butadiene is mostly referred to simply as polybutadiene. Polymerized chloroprene was developed by DuPont and given the trade name Neoprene. In a number of cases, monomers which are not dienes are also used for certain types of synthetic rubber, often copolymerized with dienes. Some of the most commercially important addition polymers are the copolymers. These are polymers made by polymerizing a mixture of two or more monomers. An example is styrene-butadiene rubber (SBR) - which is a copolymer of 1,3-butadiene and styrene which is mixed in a 3 to 1 ratio, respectively.

6.4. POLYESTER : EXEMPLE DU TERGAL

polymérisation

$$n\,A + n\,B \longrightarrow P + 2n\,H_2O$$



Tergal