

ENGINEERING

CHEMISTRY

UNIT-III

CHEMISTRY OF POLYMERS AND NOVEL CARBON COMPOUNDS

CONTENTS:

a) **Polymers:** definition, classification of polymers on the basis of thermal behaviour, properties of polymers: degree of polymerization, crystallinity, T_g & T_m and factors affecting T_g . Polymerization and its types. Advanced polymeric materials: Structure, properties and applications of liquid crystal polymer – Kevlar, conducting polymers - Polyacetylene, electroluminescent polymer – PPV and biodegradable polymers – PHBV.

b) **Nanomaterials:** definition, types of nanomaterials and properties of nanomaterials. Quantum dots: Types, properties and applications of QDs. Structure properties and applications of Graphene and Carbon Nano Tubes (CNTs).

INTRODUCTION:

POLYMER-DEFINITION:

Polymers are the substances consisting of giant or macromolecules made by linking a large number of smaller molecules (monomers).

Polymer is a molecule formed by joining of thousands of smaller molecular units together by chemical bonds.

A chemical process that leads to the formation of polymer is known as polymerization.

Monomer and Polymer:

1) Under the proper conditions of temperature, pressure and catalyst, the micro (Smaller) molecules are combining together to form a macro (big) molecule. This process is called Polymerization. Micro molecules are called 'Monomer'. Macro molecule is 'Polymer'.

2) Requirements of a monomer: a) multiple bonds or b) reactive functional groups.

3) The number of monomers present in a polymer is 'Degree of polymerization'(n).
Degree of Polymerization = $\frac{\text{Mol. Wt of polymer}}{\text{Mol. Wt of monomer}}$

If n = low, Mol.Wt = 500 – 5000 Dalton units, it is Oligo polymer.

If n = High, Mol.Wt = 10,000 – 2,00,000 Dalton units, it is High polymer.

Classification of Polymers Based on Thermal Behaviour:

Polymers are categorized into Thermoplastics and Thermosetting Polymers based on their response to heat.

1. Thermoplastics:

Thermoplastics are polymers that soften when heated and harden upon cooling. This process is reversible and can be repeated multiple times without significant changes in the material's properties.

Key Characteristics:

- **Reversible Softening and Hardening:** The polymer chains do not form covalent cross-links, allowing them to move freely when heated.
- **Linear or Branched Structure:** Chains are arranged in a linear or slightly branched manner, which allows for flexibility.
- **Recyclability:** Can be reshaped and reused multiple times, making them environmentally favourable.

- Lower Thermal Stability: They lose mechanical strength at high temperatures.

Properties:

- Malleable when heated.
- Less brittle compared to thermosetting polymers.
- Soluble in organic solvents.
- Poor resistance to high temperatures and chemicals.

Examples:

- Polyethylene (PE): Used in plastic bags, bottles, and containers.
- Polypropylene (PP): Found in food containers, textiles, and automotive parts.
- Polystyrene (PS): Used in disposable cutlery, packaging foam, and CD cases.
- Polyvinyl Chloride (PVC): Commonly used in pipes, flooring, and medical equipment.
- Polymethyl Methacrylate (PMMA): Known as acrylic, used in lenses and light covers.

Applications:

- Packaging materials (e.g., plastic wraps).
- Electrical insulation.
- Consumer goods (e.g., toys, bottles).
- Automotive parts.

2. Thermosetting Polymers:

Thermosetting polymers, or thermosets, undergo a chemical reaction during their initial processing, forming a rigid, three-dimensional network. Once set, they cannot be softened or reshaped by heating.

Key Characteristics:

- Irreversible Hardening: Once cured, the material becomes infusible and insoluble.
- Cross-Linked Structure: The presence of covalent cross-links between polymer chains creates a rigid and stable network.
- High Thermal Stability: Resistant to deformation and degradation at high temperatures.
- Non-Recyclable: Cannot be melted or reprocessed.

Properties:

- Excellent resistance to heat and chemicals.

- Hard and brittle.
- Excellent electrical and thermal insulation properties.
- Durable and resistant to wear.

Examples:

- Bakelite: Used in electrical switches, handles, and utensils.
- Epoxy Resin: Found in adhesives, coatings, and composites.
- Melamine: Used in kitchenware, laminate flooring, and decorative panels.
- Urea-Formaldehyde: Used in adhesives, molding compounds, and wood products.
- Polyurethane: Common in foams, insulation, and coatings.

Applications:

- Electrical insulators (e.g., switchboards, circuit breakers).
- Adhesives and coatings.
- Kitchenware and utensils (e.g., plates, laminates).
- Automotive and aerospace components.

Comparison Between Thermoplastics and Thermosetting Polymers:

Property	Thermoplastics	Thermosetting
Structure	Linear or branched	Cross-linked network
Thermal Behaviour	Softens when heated, hardens when cooled	Irreversibly hardens upon curing
Recyclability	Recyclable	Non-recyclable
Durability	Less durable, lower thermal resistance	Highly durable, excellent thermal resistance
Brittleness	Less brittle	Brittle
Examples	PE, PVC, PP, PS	Bakelite, epoxy resin, melamine
Applications	Packaging, consumer goods, insulation	Electrical insulators, adhesives, cookware

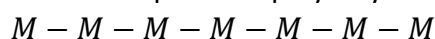
Nomenclature of Polymers:

Polymer nomenclature is generally based upon the type of monomer residues comprising the polymer.

Homopolymers:

Polymers that contain only a single type of repeat unit are known as homopolymers.

Examples: Polystyrene is composed only of styrene monomer residues, and is therefore classified as a homopolymer. Other examples are: polyethylene, polypropylene.



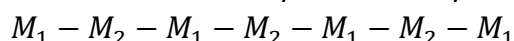
where, M is a monomer unit

Structural Example: Monomer: Ethylene; Polymer: Polyethylene

Heteropolymers or Copolymers:

Polymers containing a mixture of repeating units are known as copolymers or heteropolymers.

Example: Ethylene-vinyl acetate polymer contains more than one type of repeating unit and is thus a copolymer. The two monomers are ethylene and vinyl acetate.

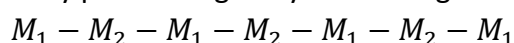


where, M_1 and M_2 are the different monomer units.

Structural Example: Monomers: Ethylene and Acrylic acid; Polymer: Ethylene acrylic acid copolymer.

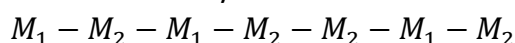
Based on the arrangement of the monomers along the backbone of a copolymer, the following types of copolymers are obtained:

1. Alternating copolymers: They possess regularly alternating monomer units.



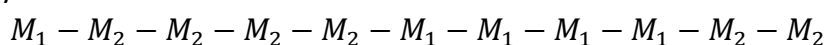
M_1 = vinyl chloride and M_2 = vinyl acetate

2. Statistical copolymers: They are polymers having the monomer units arranged according to a known statistical rule. A statistical copolymer in which the probability of finding a particular type of monomer residue at a particular point in the chain is independent of the types of surrounding monomer residue may be referred to as a truly random copolymer.



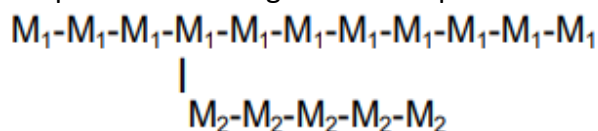
M_1 = Styrene and M_2 = Butadiene

3. Block copolymers: These polymers have two or more homopolymer subunits linked by covalent bonds. Polymers with two or three blocks of two distinct chemical species (e.g., M_1 and M_2) are called diblock copolymers and triblock copolymers, respectively. Polymers with three blocks, each of a different chemical species (e.g., M_1 , M_2 , and M_3) are termed triblock terpolymers.



M_1 = acrylic acid and M_2 = methyl methacrylate

4. Graft or grafted copolymers: These polymers contain side chains that have a different composition or configuration compared to the main chain.

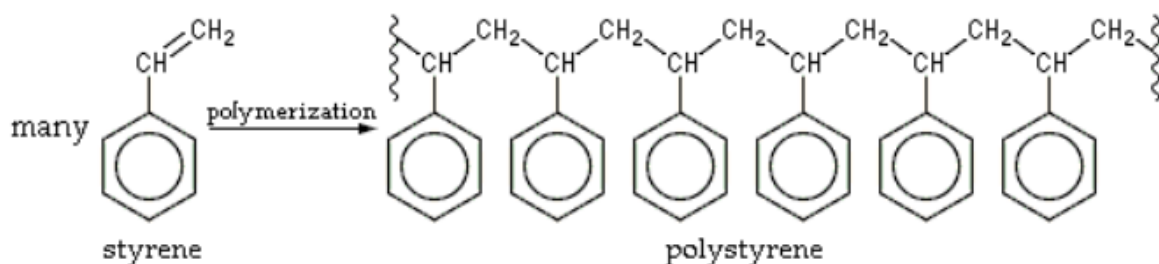


M_1 = vinyl chloride and M_2 = styrene

Homochain polymer: It is a polymer in which the main chain is made up of same atomic species.

Example: Polyethylene, Polystyrene

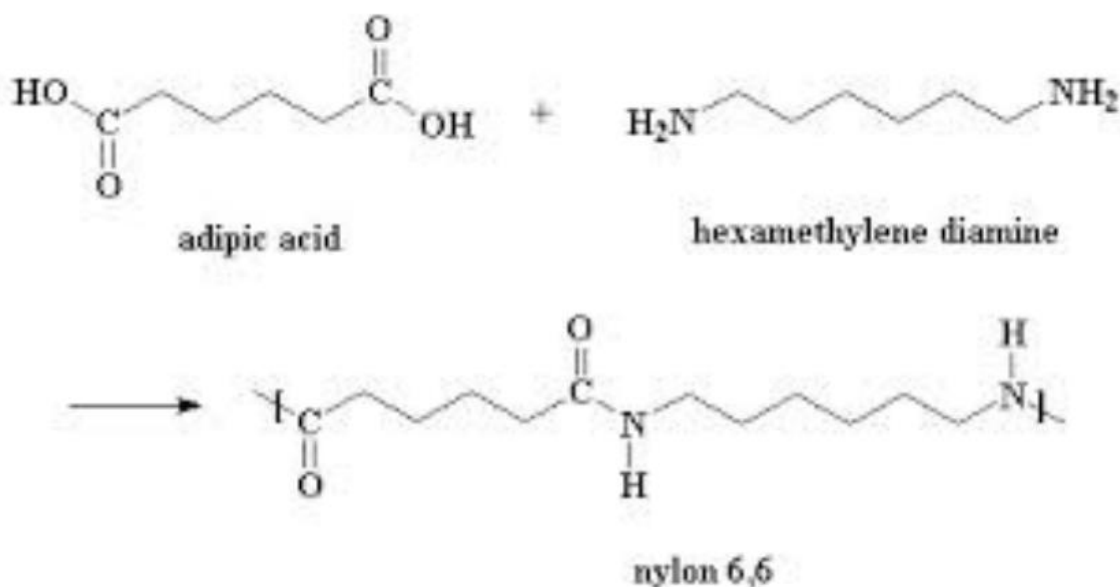
Structural Example: Monomer: Styrene; Polymer: Polystyrene



Heterochain polymer: A polymer in which the main chain has more than one atomic species is called a heterochain polymer.

Example : Nylon 6,6

Structural Example: Monomer: adipic acid and hexamethylene diamine; Polymer: Nylon 6,6



Functionality:

It is the number of covalent bonds that a monomer molecule or monomeric unit in a macromolecule or oligomer molecule can form with other reactants. In other words, functionality (F) denotes the number of bonding sites or active centres or reacting functional groups in a monomer. It can also be defined as number of reactive sites present in a monomer is called 'Functionality'.

Examples: -

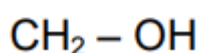
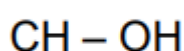
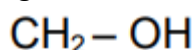
$\text{CH}_2 = \text{CH}_2$, the double bond is acting as two reactive site, So, Ethylene functionality is 2.

1. There are no monofunctional monomers.
2. If $F = 2$, a linear chain macromolecule or a macrocycle can be formed.
3. If $F > 2$, a branch point can be formed leading to a branched macromolecule, a network or a micro network.
4. Ethene and ethylene glycol are examples of bifunctional monomers, glycerol is an example of a trifunctional monomer, and divinylbenzene and pentaerythritol are examples of tetrafunctional monomers.

1. Significance of Bifunctional Monomers: A bifunctional monomer forms a linear or straight chain polymer in which the monomer units are linked by strong covalent bonds and the

chains are held by weak Van der Waal's force of attraction. Hence the movement of polymer chains is restricted, whereby; soft and flexible polymers with less strength, low heat resistance is formed. Bifunctional monomers can also form branched chain polymers in which there is high resistance to movement of the polymer chains.

2. Significance of Trifunctional Monomers: A trifunctional monomer forms a cross-linked, three-dimensional polymer network in which the monomers are held by strong covalent bonds which completely prevents the movement of the polymer chains. Such polymers have high strength, hardness, toughness, high heat resistance and are commonly insoluble in all organic solvents.



In glycerol three $-\text{OH}$ groups present. So, functionality = 3.

SIGNIFICANCE OF FUNCTIONALITY:

1. Substances having only one bonding or reactive site are called —monofunctional monomers.

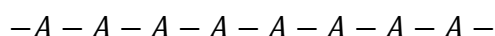
e.g. $\text{CH}_3 - \text{COOH}$

They cannot undergo polymerization.

2. If $F = 2$, they form linear chain structure.

e.g. Ethylene.

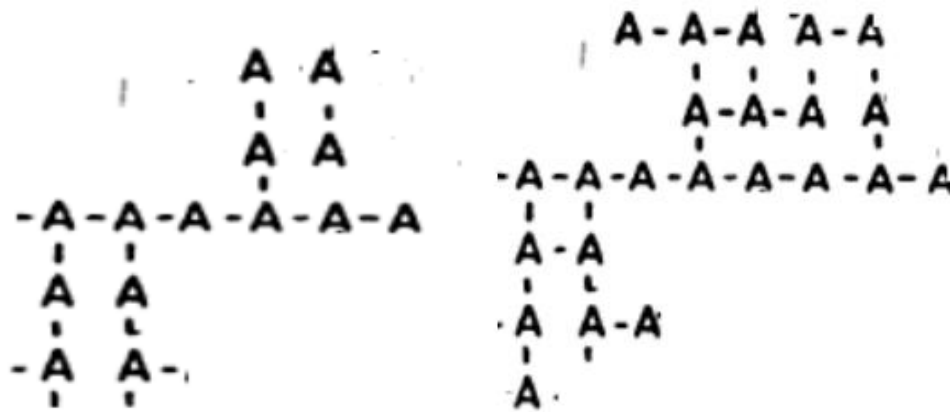
Because of the weak Vander Waal's attraction, there is no restriction for the movement of one polymer chain over another chain. They have less strength, low heat resistance, softness and flexibility.



3. If $F=3$, they form branched structure.

e.g. Glycerol

Because of the strong covalent bond, the movement polymer chain is restricted. They have high strength, high heat resistance, hardness.



4. If $F \geq 4$, then they form complexed 3D structure.

Properties of Polymers:

A. Degree of Polymerisation:

The number of repeat units (or) monomeric units available in the polymer is known as degree of polymerization. It is a key parameter that determines the molecular size of the polymer and directly influences its physical and mechanical properties.

$$DP = \frac{\text{Molecular weight of the repeating unit (monomer)}}{\text{Molecular weight of the polymer}}$$

B. Crystallinity:

Crystallinity is the extent to which polymer chains are packed into a well-ordered, lattice-like structure. It is expressed as a percentage and quantified using techniques like X-ray diffraction or differential scanning calorimetry (DSC).

Crystalline vs. Amorphous Regions:

- **Crystalline Regions:**
 1. Highly ordered and tightly packed chains.
 2. Contribute to the material's strength, stiffness, and thermal stability.
- **Amorphous Regions:**
 1. Disordered and randomly arranged chains.
 2. Contribute to flexibility, impact resistance, and optical transparency.

Factors Affecting Crystallinity:

1. **Polymer Structure:**
 - a. **Linear polymers** (e.g., polyethylene) are more likely to form crystalline regions.
 - b. **Branched polymers** (e.g., low-density polyethylene) tend to be less crystalline.
2. **Nature of Monomers:**
 - a. Regular and symmetrical monomers favour crystallinity.
 - b. Irregular monomers hinder packing, reducing crystallinity.

3. Processing Conditions:

- a. Slow cooling during solidification increases crystallinity.
- b. Rapid cooling can freeze the polymer in an amorphous state.

4. Additives:

- a. Nucleating agents can promote crystalline growth.

Properties of Crystalline Polymers:

- 1. **Density:** Crystalline regions have higher density compared to amorphous regions.
- 2. **Melting Point:** Polymers with higher crystallinity have well-defined melting points.
- 3. **Mechanical Strength:** High crystallinity contributes to increased tensile strength and rigidity.
- 4. **Optical Clarity:** Crystalline polymers are often opaque, while amorphous ones are transparent.

Advantages of Crystallinity:

- a. Higher mechanical strength and stiffness.
- b. Greater thermal stability and resistance to solvents.
- c. Improved wear resistance.

Disadvantages of Crystallinity:

- a. Reduced flexibility and toughness.
- b. Lower optical transparency.
- c. Harder to process due to higher melting or softening temperatures.

Crystallinity in Applications:

- a. High Crystallinity: Suitable for applications requiring strength, rigidity, and chemical resistance (e.g., pipes, Fibers, containers).
- b. Low Crystallinity: Used for applications demanding flexibility, transparency, and elasticity (e.g., packaging films, lenses).

Examples of Crystalline and Amorphous Polymers:

Polymer	Crystalline/Amorphous	Remarks
Polyethylene (PE)	Crystalline	Linear structure enhances crystallinity.
Polypropylene (PP)	Semi-crystalline	High strength and melting point.
Nylon	Crystalline	Used in textiles due to toughness and strength.
Polystyrene (PS)	Amorphous	Transparent and brittle.
Polycarbonate (PC)	Amorphous	High impact resistance and transparency.

C. Glass Transition Temperature:

The **Glass Transition Temperature (T_g)** is a critical thermal property of amorphous and semi-crystalline polymers. It marks the temperature at which a polymer transitions from a hard, glassy state to a soft, rubbery state. This change occurs due to increased molecular mobility of polymer chains.

Definition:

The Glass Transition Temperature (T_g) is the temperature at which the amorphous regions of a polymer change from a rigid and brittle state (below T_g) to a flexible and rubbery state (above T_g).

Characteristics of T_g :

1. Below T_g :
 - a. Polymer chains are frozen and unable to move freely.
 - b. The material is hard, brittle, and glass-like.
2. Above T_g :
 - a. Chains gain sufficient thermal energy to overcome intermolecular forces.
 - b. The material becomes soft, flexible, and rubbery.

Significance of T_g :

1. Mechanical Properties:
 - a. Below T_g : High rigidity and stiffness.
 - b. Above T_g : Increased elasticity and deformability.
2. Application Temperature Range:
 - a. Materials must be used in temperatures appropriate to their T_g .
 - b. For example, rubbery polymers are preferred for elasticity above T_g , while glassy polymers are used for strength below T_g .
3. Design and Performance:
 - a. T_g determines the suitability of a polymer for various applications, especially in high- or low-temperature environments.

Factors Affecting T_g :

1. Polymer Structure:
 - a. Rigid chains with bulky side groups increase T_g .
 - b. Flexible chains or those with low intermolecular interactions lower T_g .
2. Intermolecular Forces:
 - a. Strong forces (e.g., hydrogen bonds, dipole interactions) raise T_g .
 - b. Weak forces (e.g., van der Waals forces) lower T_g .
3. Molecular Weight:
 - a. Higher molecular weight increases T_g due to reduced chain mobility.
4. Plasticizers:
 - a. Plasticizers lower T_g by increasing chain mobility.

Examples of Polymers and Their T_g :

Polymer	Glass Transition Temperature (T_g)	State at Room Temperature
Polyethylene (PE)	-125°C	Rubbery
Polypropylene (PP)	-20°C	Rubbery
Polystyrene (PS)	100°C	Glassy
Polyvinyl Chloride (PVC)	80°C	Glassy
Polycarbonate (PC)	150°C	Glassy
Polymethyl Methacrylate (PMMA)	105°C	Glassy
Nylon	40-80°C	Glassy/Rubbery

Applications of T_g :

1. Below T_g :
 - a. Used in structural applications (e.g., pipes, car parts).
 - b. Provides strength, rigidity, and dimensional stability.
2. Above T_g :
 - a. Used in elastic applications (e.g., rubber seals, gaskets).
 - b. Provides flexibility and impact resistance

D. Melt Transition Temperature:

The Melt Transition Temperature (T_m) is the temperature at which the crystalline regions of a polymer melt, resulting in the transformation from a solid to a liquid-like state.

Characteristics of T_m :

1. Below T_m :
 - a. Polymer exists as a rigid solid, with crystalline regions maintaining their ordered structure.
 - b. The material has high mechanical strength and rigidity.
2. Above T_m :
 - a. Crystalline regions lose their ordered structure and flow begins.
 - b. The material behaves like a viscous liquid.

Significance of T_m :

Thermal Stability:

T_m is an indicator of the polymer's ability to withstand high temperatures.

1. Processing Temperature:
 - a. T_m determines the temperature required for processing techniques like molding and extrusion.

2. Mechanical Properties:

- Below T_m : The polymer is strong and rigid due to crystalline regions.
- Above T_m : The polymer softens, allowing shaping and forming.

Factors Affecting T_m :

1. Polymer Structure:

- Symmetrical and regular chains promote higher T_m due to easier packing into a crystalline structure.
- Irregular or branched chains reduce T_m by hindering crystallinity.

2. Degree of Crystallinity:

- Polymers with higher crystallinity have a higher T_m .

3. Intermolecular Forces:

- Stronger forces (e.g., hydrogen bonding) result in a higher T_m .

4. Molecular Weight:

- Higher molecular weights slightly increase T_m due to stronger intermolecular interactions.

Examples of Polymers and Their T_m :

Polymer	Melt Transition Temperature (T_m)
Polyethylene (PE)	~120-135°C
Polypropylene (PP)	~160°C
Nylon-6	~220°C
Polytetrafluoroethylene (PTFE, Teflon)	~327°C
Polyethylene Terephthalate (PET)	~250°C

Applications of T_m :

- Below T_m : Polymers retain their solid shape, used in structural applications (e.g., pipes, containers).
- At or above T_m : Used for processing and moulding the polymer into desired shapes.

T_m vs. T_g :

Property	Glass Transition Temperature (T_g)	Melt Transition Temperature (T_m)
Occurs In	Amorphous regions of a polymer	Crystalline regions of a polymer
State Change	Glassy to rubbery	Solid to liquid

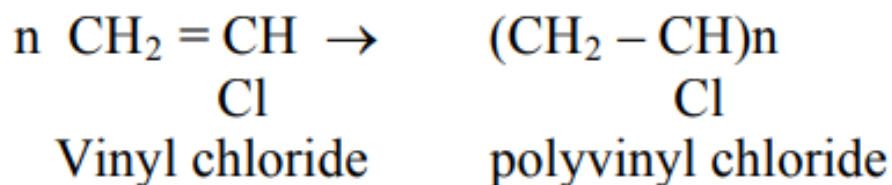
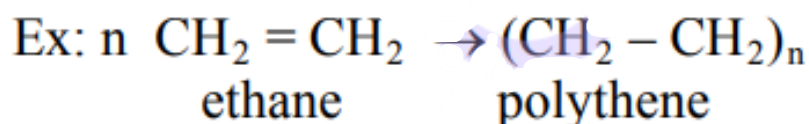
Property	Glass Transition Temperature (T _g)	Melt Transition Temperature (T _m)
Temperature Range	Lower	Higher
Example Impact	Affects flexibility and brittleness	Affects thermal stability and melting

POLYMERISATION:

Polymerization is a chemical process in which small molecules called monomers combine to form large, chain-like molecules called polymers. This process involves the formation of covalent bonds between monomers and is fundamental in producing materials like plastics, rubbers, and fibres.

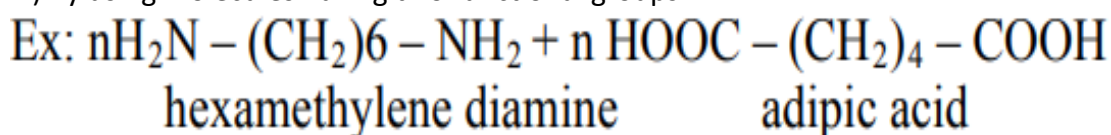
The different ways of doing polymerization are –

i) By opening a double bond:



ii) By opening a ring

iii) By using molecules having two functional groups:



Mechanisms of Polymerization:

1. Free-Radical Polymerization:

- Involves free radicals to initiate and propagate the chain reaction.
- Used in the synthesis of polyethylene, polystyrene, and PVC.

2. Cationic Polymerization:

- Initiated by a cationic species.
- Common in the production of polyisobutylene.

3. Anionic Polymerization:

- Initiated by an anionic species.
- Used in the production of synthetic rubbers like polybutadiene.

4. Coordination Polymerization:

- Involves transition metal catalysts (e.g., Ziegler-Natta catalysts).
- Produces polymers with controlled structures, such as isotactic polypropylene.

Classification of Polymers Based on Polymerization:

Type	Example Polymers	Mechanism
Addition Polymers	Polyethylene, Polypropylene, PVC	Free-radical, cationic, anionic
Condensation Polymers	Nylon, Polyester, Bakelite	Step-growth mechanism

Applications of Polymerization:

- Plastics: Polyethylene, polypropylene, and PVC for packaging, pipes, and household items.
- Fibers: Nylon and polyester for textiles.
- Rubbers: Polyisoprene and polybutadiene for tires and seals.
- Adhesives and Coatings: Epoxy resins and polyurethanes.
- Engineering Polymers: Polycarbonate and PTFE for high-strength and thermal stability applications.

Importance of Polymerization:

- Enables the creation of materials with diverse properties (flexibility, strength, resistance to chemicals).
- Provides the foundation for modern industries like plastics, textiles, and biomedical devices.
- Advances in polymerization techniques (e.g., controlled/living polymerization) allow for precise control over polymer structure and properties.

Types of Polymerizations:

Polymerization is broadly classified into Addition Polymerization and Condensation Polymerization based on the reaction mechanism.

1. Addition Polymerization:

Monomers having multiple bonds (double or triple bond) undergo addition polymerization. Monomers combine to give polymer through addition reaction without elimination of any smaller molecules.

It is also known as chain-growth polymerization.

Key Features:

- No By-Products:** The entire monomer unit is incorporated into the polymer chain.
- Initiation Required:** The reaction is started by an initiator that generates active species such as free radicals, cations, or anions.
- High Reaction Rates:** Addition polymerization occurs rapidly compared to condensation polymerization.

4. Thermoplastic Polymers: Most polymers formed by addition polymerization are thermoplastics (e.g., polyethylene, polystyrene).

Mechanism of Addition Polymerization/ Chain-Growth Polymerization:

The process typically involves three main stages: Initiation, Propagation, and Termination. Depending on the nature of the active species, addition polymerization can occur through free-radical, cationic, or anionic mechanisms.

Polymer synthesized by addition polymerization has the same empirical formula as that of monomer.

No molecule is evolved during polymerisation and the polymer is an exact multiple of the original monomeric molecule.

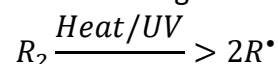
1. Free-Radical Polymerization:

- Monomer: Contains a double bond (e.g., ethylene, styrene, vinyl chloride).
- Initiator: A compound that decomposes to form free radicals, such as benzoyl peroxide or azobisisobutyronitrile (AIBN).

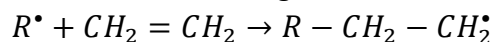
Steps:

1. Initiation:

The initiator decomposes under heat or UV light to form free radicals.

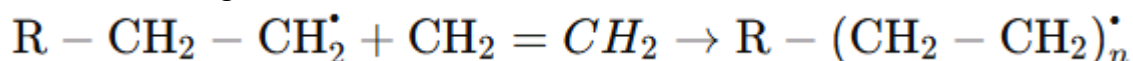


The radical reacts with the monomer, forming an active center.



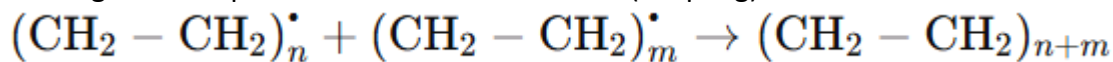
2. Propagation:

The active chain grows as the radical reacts with more monomers.



3. Termination:

Chain growth stops when two radicals combine (coupling) or transfer reactions occur.



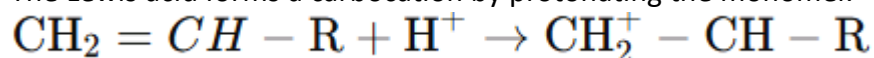
2. Cationic Polymerization:

- Monomer: Typically contains electron-donating groups (e.g., isobutylene, vinyl ethers).
- Initiator: A Lewis acid (e.g., BF_3) in the presence of a proton donor.

Steps:

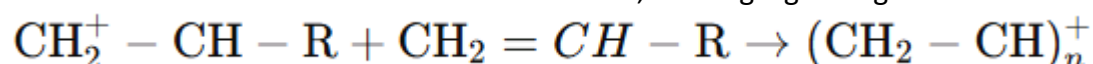
1. Initiation:

The Lewis acid forms a carbocation by protonating the monomer.



2. **Propagation:**

The carbocation adds successive monomer units, forming a growing chain.



3. **Termination:**

Termination occurs when the growing chain reacts with a base or loses a proton.

3. Anionic Polymerization:

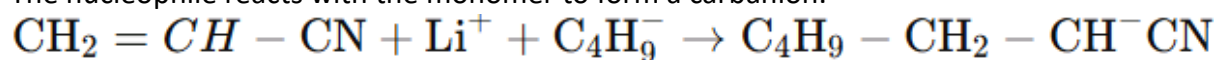
a. Monomer: Contains electron-withdrawing groups (e.g., acrylonitrile, styrene, methyl methacrylate).

b. Initiator: A strong nucleophile (e.g., butyllithium).

Steps:

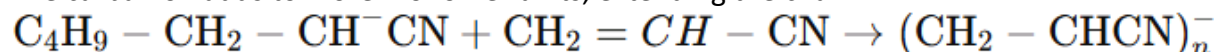
1. **Initiation:**

The nucleophile reacts with the monomer to form a carbanion.



2. **Propagation:**

The carbanion adds to more monomer units, extending the chain.



3. **Termination:**

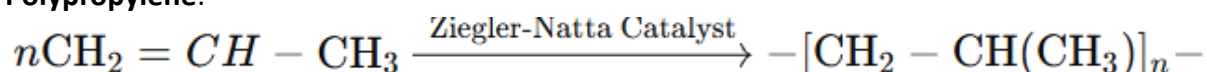
Termination is rare; living polymerization occurs until a quenching agent is added.

Reactions of Addition Polymerization:

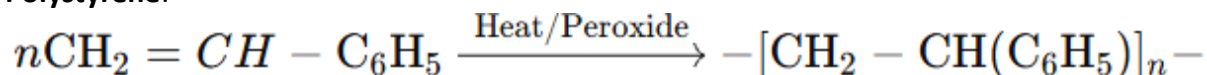
1. **Polyethylene:**



2. **Polypropylene:**



3. **Polystyrene:**



Applications of Addition Polymerization:

1. **Polyethylene (PE):**

- a. Packaging materials (bags, bottles).
- b. Insulation for wires and cables.

2. **Polypropylene (PP):**

Automotive parts, furniture, food containers.

3. **Polystyrene (PS):**
Disposable cups, insulation foam.
4. **Polyvinyl Chloride (PVC):**
Pipes, flooring, window frames.
5. **Acrylic Polymers:**
Paints, adhesives, and transparent sheets.
6. **Synthetic Rubber (Polybutadiene, SBR):**
Tires, footwear, seals.

Advantages:

- a. High reaction rates.
- b. Ability to produce high molecular weight polymers.
- c. No by-product formation simplifies processing.

Limitations:

- a. Limited to unsaturated monomers.
- b. Requires specific initiators and catalysts.
- c. Some polymers degrade at high temperatures.

Addition polymerization is essential for producing versatile and widely used polymers that form the backbone of modern materials science and industry.

2. Condensation Polymerization:

Condensation Polymerization, also known as step-growth polymerization, is a chemical process in which monomers with two or more functional groups react to form covalent bonds, producing polymers along with the elimination of small by-products like water, ammonia, or hydrogen chloride. This type of polymerization is characteristic of polyesters, polyamides, and phenolic resins.

Key Features:

1. **By-Product Formation:** Small molecules like water, HCl, or methanol are eliminated during the reaction.
2. **Stepwise Reaction:** Monomers combine step-by-step, and polymer chains grow gradually.
3. **Requires Functional Groups:** Monomers must have reactive functional groups (e.g., $-OH$, $-COOH$, $-NH_2$).
4. **Can Involve Different Monomers:** Often involves two different monomers, although a single monomer with two functional groups can also polymerize.

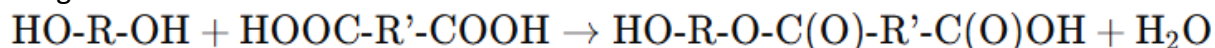
Mechanism of Condensation Polymerization:

The process generally involves three stages: Initiation, Propagation, and Termination.

1. Initiation:

- a. Monomers with reactive functional groups interact to form a dimer.

e.g.



2. Propagation:

- a. The dimer reacts with more monomers or oligomers to grow the polymer chain.

e.g.



3. Termination:

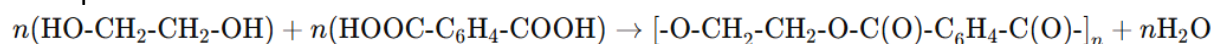
The reaction ends when the supply of monomers is exhausted, or when no further functional groups remain to react.

Types of Condensation Polymers:

1. Polyesters:

Formed by the reaction of diols (e.g., ethylene glycol) with dicarboxylic acids (e.g., terephthalic acid).

Example:

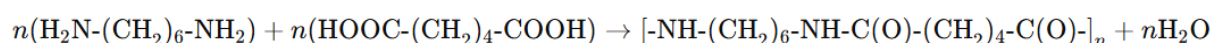


Polymer: Polyethylene terephthalate (PET), used in textiles and bottles.

2. Polyamides:

Formed by the reaction of diamines (e.g., hexamethylene diamine) with dicarboxylic acids (e.g., adipic acid).

Example:

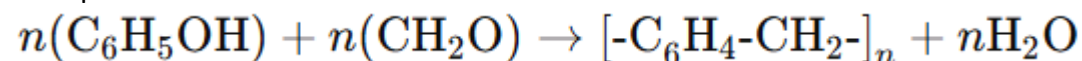


Polymer: Nylon-6,6, used in textiles and engineering plastics.

3. Phenol-Formaldehyde Resins:

Formed by the reaction of phenol with formaldehyde under acidic or basic conditions.

Example:

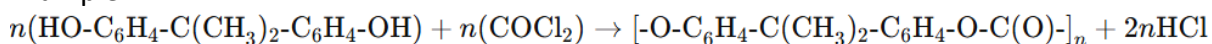


Polymer: Bakelite, used in electrical insulators and moulded products.

4. Polycarbonates:

Formed by the reaction of bisphenol A with phosgene.

Example:



Polymer: Polycarbonate, used in bulletproof glass and optical discs.

Properties of Condensation Polymers:

1. **Strength:** Usually stronger than addition polymers due to intermolecular forces like hydrogen bonding (e.g., in polyamides).

2. **Thermal Resistance:** Good thermal stability, making them suitable for high-temperature applications.
3. **Recyclability:** Often more difficult to recycle compared to addition polymers.

Applications:

1. **Polyesters:** PET: Used in clothing fibers, beverage bottles, and food packaging.
2. **Polyamides:** Nylon: Used in textiles, gears, and ropes.
3. **Phenolic Resins:** Bakelite: Used in electrical insulators and cookware handles.
4. **Polycarbonates:** Used in eyewear lenses, CDs, and safety equipment.
5. **Urea-Formaldehyde and Melamine-Formaldehyde Resins:** Used in adhesives, laminates, and moulded articles.

Advantages:

1. Produces a wide range of high-performance polymers.
2. Allows precise control over polymer properties by varying monomers and conditions.
3. Suitable for high-strength and high-temperature applications.

Limitations:

1. Slower reaction rates compared to addition polymerization.
2. Requires removal of by-products, which may complicate the process.
3. Recycling is more challenging.

Condensation polymerization is essential in creating durable, high-performance materials for diverse industrial and consumer applications.

Comparison: Addition vs. Condensation Polymerization:

Property	Addition Polymerization	Condensation Polymerization
By-Products	None	Small molecules (e.g., H ₂ O, HCl)
Growth Mechanism	Chain-growth	Step-growth
Functional Groups	Requires unsaturated bonds	Requires functional groups (-OH, -COOH, etc.)
Reaction Rate	Faster	Slower
Examples	Polyethylene, polystyrene	Nylon, polyester

3. Copolymerization:

Copolymerization is the process of polymerizing two or more different types of monomers to form a polymer chain. The resulting polymer, called a copolymer, exhibits properties that are often a blend of the individual monomers' characteristics or may have unique properties not found in homopolymers (polymers made from a single monomer type).

Importance of Copolymerization:

1. **Enhanced Properties:** Combines properties of different monomers, such as flexibility, strength, or chemical resistance.
2. **Customization:** Allows fine-tuning of mechanical, thermal, and chemical properties.
3. **Versatility:** Creates polymers for specific applications where homopolymers may not suffice.

Types of Copolymers:

1. **Random Copolymers:**

Monomers are randomly arranged along the polymer chain.

Example:



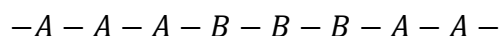
Properties: Often intermediate between the two monomers.

Example Copolymer: Styrene-butadiene rubber (SBR) used in tires.

2. **Block Copolymers:**

Monomers are grouped in blocks along the chain.

Example:



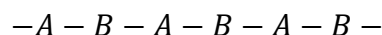
Properties: Can exhibit phase separation, leading to unique mechanical properties.

Example Copolymer: Poly(styrene-butadiene-styrene) (SBS), used in adhesives and footwear.

3. **Alternating Copolymers:**

Monomers alternate in a regular sequence.

Example:



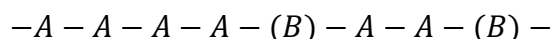
Properties: Uniform composition along the chain, providing consistent properties.

Example Copolymer: Maleic anhydride-styrene copolymer, used in coatings.

4. **Graft Copolymers:**

One type of monomer forms the backbone, and branches (grafts) of another monomer are attached.

Example:



Properties: Combines the properties of both backbone and graft monomers.

Example Copolymer: Polypropylene grafted with polyethylene, used in impact-resistant plastics.

Mechanism of Copolymerization:

Copolymerization can proceed through the same mechanisms as homo-polymerization: free-radical, ionic, or coordination polymerization. However, the reactivity of the monomers determines the copolymer's composition and structure.

1. Reactivity Ratios:

The relative reactivity of monomers influences the arrangement in the copolymer.

a. Reactants: Monomer A and monomer B.

Reactivity ratios r_A and r_B describe the preference of each monomer for reacting with itself or the other.

b. Outcome: If r_A and r_B are both close to 1: Alternating copolymer.

If $r_A \gg r_B$ More of monomer A will form the polymer backbone.

If $r_A, r_B \gg 1$: Block copolymer.

2. **Kinetic Considerations:** The rate of polymerization depends on the monomers' reactivity and the initiator.

Examples of Copolymers and Applications:

Copolymer	Monomers	Applications
Styrene-Butadiene Rubber (SBR)	Styrene, Butadiene	Tires, footwear, adhesives
Nitrile Rubber (NBR)	Acrylonitrile, Butadiene	Oil-resistant seals, gaskets
Acrylic-Styrene Copolymer	Acrylic acid, Styrene	Paints, coatings
Ethylene-Vinyl Acetate (EVA)	Ethylene, Vinyl acetate	Foam, shoe soles, films
ABS (Acrylonitrile-Butadiene-Styrene)	Acrylonitrile, Butadiene, Styrene	Automotive parts, electronics housings

Advantages of Copolymerization:

1. **Property Enhancement:** Combines the best properties of different monomers (e.g., toughness, flexibility).

2. **Cost Efficiency:** Reduces the cost by blending expensive monomers with cheaper ones.
3. **Thermal Stability:** Improved heat resistance in certain copolymers.
4. **Impact Resistance:** Graft and block copolymers are highly durable and impact-resistant.

Limitations:

1. **Complexity in Synthesis:** Requires precise control over monomer reactivity and ratios.
2. **Phase Separation:** In block copolymers, differences in monomer solubility can lead to phase separation.
3. **Recycling Challenges:** Copolymers are often harder to recycle than homopolymers.

Applications:

1. **Rubber Industry:** SBR and NBR are widely used in automotive tires and seals.
2. **Packaging:** EVA copolymers are used in flexible packaging and heat-sealing films.
3. **Electronics:** ABS copolymers are used for durable casings and housings.
4. **Textiles:** Acrylic copolymers are used for fabrics with improved dyeing properties.
5. **Adhesives and Coatings:** Styrene-acrylic copolymers are popular in paints, adhesives, and surface coatings.

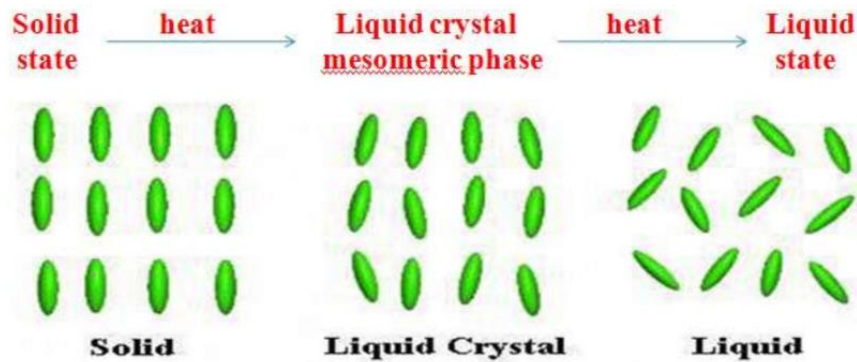
Copolymerization offers the flexibility to design polymers with tailored properties, making it a powerful tool in material science. By adjusting the type and ratio of monomers, copolymers can meet diverse industrial demands, from high-performance materials to everyday consumer products.

ADVANCED POLYMERIC MATERIALS:

1. Liquid Crystal Polymer (LCP):

Liquid Crystal Polymers (LCPs) are a class of aromatic polymers that exhibit liquid crystalline properties, meaning they combine characteristics of both liquids and crystalline solids. LCPs have unique structural and physical properties, making them suitable for advanced technological applications.

LCPs are those polymers which have tendency to align their chains parallel over a long distance before crystallization from their melt or solution, under suitable conditions of temperature, pressure and concentration.



This means that in LCP, polymer chains are present in the organized manner even when the polymer is physically not crystallized.

This intermediate phase is called an mesophase & individual polymer chains are called as mesogens.

E.g. Kevlar(Aramid)

Structure of Liquid Crystal Polymers:

1. Chemical Composition:

LCPs are primarily composed of rigid rod-like molecular structures with aromatic rings, ester groups, or amide linkages.

These molecular structures allow for ordered alignment in the liquid state.

2. Phases:

Mesophase: The intermediate state between solid and liquid where molecules are aligned in an ordered structure.

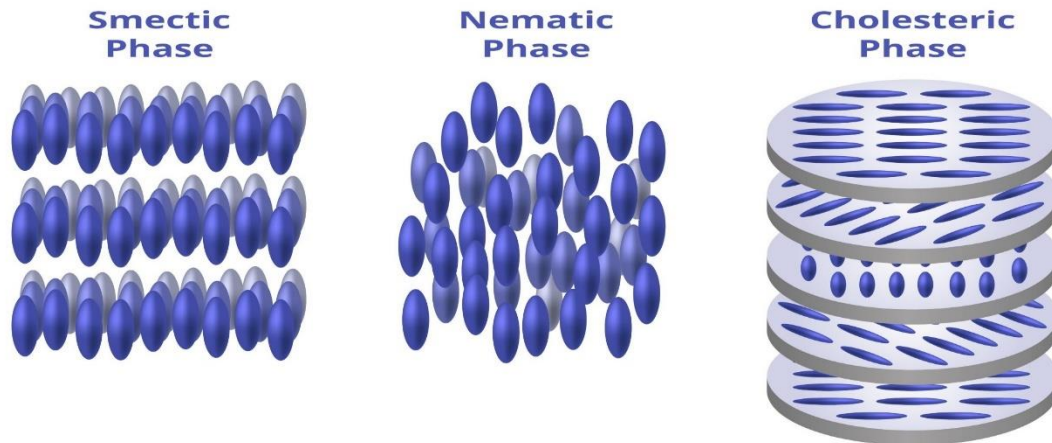
Common phases include:

- **Nematic Phase:** Molecules are aligned in parallel but do not form layers.
- **Smectic Phase:** Molecules are aligned in layers with some positional order.
- **Cholesteric Phase:** Molecules are arranged in layers with a helical twist.

3. Molecular Arrangement:

The rigid backbone of LCPs creates anisotropic properties, meaning the material behaves differently in different directions.

Liquid Crystals



Properties of Liquid Crystal Polymers:

1. Mechanical Properties:

- High tensile strength and stiffness.
- Excellent impact resistance.

2. Thermal Properties:

- High melting points ($>300^{\circ}\text{C}$).
- Exceptional thermal stability, withstanding temperatures above 200°C without significant degradation.

3. Chemical Resistance:

- Resistant to acids, bases, and organic solvents.
- Low moisture absorption, enhancing dimensional stability.

4. Electrical Properties:

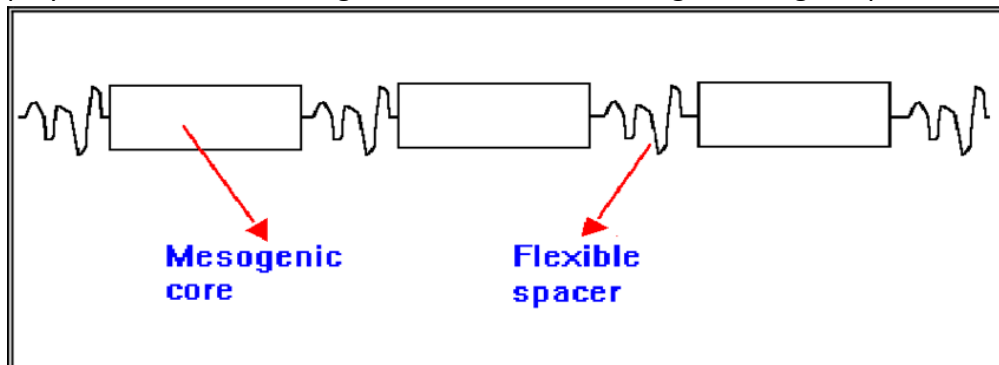
- Good dielectric properties.
- Low thermal expansion makes them ideal for electronic applications.

5. Processing Properties:

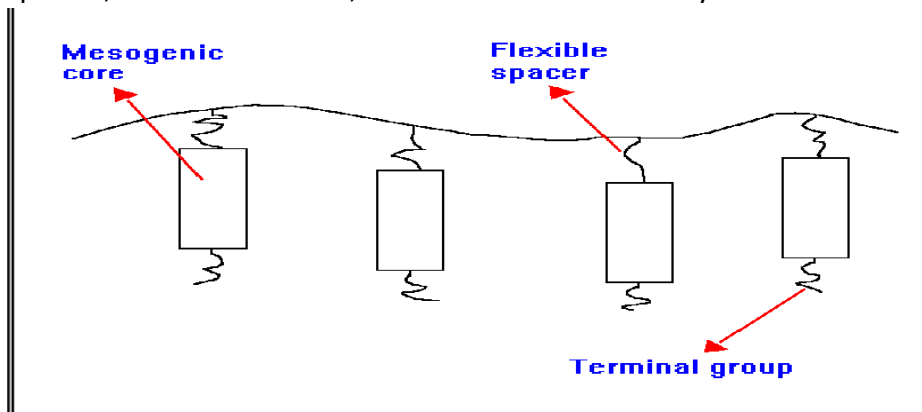
- High melt flow, allowing easy molding of complex and thin-walled components.
- Fast cooling and solidification during manufacturing.

Ways of Construction of LCP:

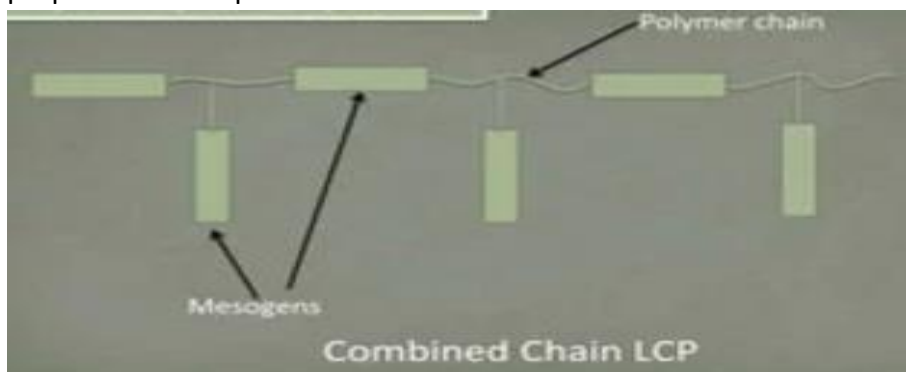
1. Main chain LCPs (MCLCPs): is a type of polymer with rigid, rod-like mesogens in its polymer backbones. This gives main chain LCPs a high melting temperature.



2. Side-chain LCPs (SCLCPs): are a type of LCP with mesogens attached to the polymer backbone as side pendants. The mesogens are usually linked to the backbones by flexible spacers, but in some cases, the side chains are directly linked to the backbones.



3. A combined main-chain/side-chain LCPs (MCSCSLCP) is a type of soft matter that combines the chemical characteristics of both main-chain and side-chain LCPs. The interactions between the main-chain and side-chain mesogens in the same molecule create unique properties and supramolecular structures.



Types of LCPs based on formation:

1. Lyotropic LCPs: Those LCPs which have tendency to form parallel aligned chains over a long distance before crystallization from their solution, during wet processing are Lyotropic LCPs.

2. Thermotropic LCPs: Those LCPs which have tendency to form parallel aligned chains over a long distance before crystallization from their melt, during melt processing are Thermotropic LCPs.

Structure conditions for LCPs:

1. Organic polymer molecules should have highly polarised chain structure.
2. The polymer molecules should have aromatic rings in chain so that their structure is like strip.
3. The polymer molecule should be like disc.

Applications of LCPs:

1. Electronics:

- Used in connectors, switches, and circuit boards due to excellent dielectric and thermal properties.
- Ideal for components requiring precise dimensions, such as smartphone parts and microelectronics.

2. Aerospace and Automotive:

- Lightweight components for aircraft and vehicles.
- Used in engine parts, fuel system components, and other high-temperature environments.

3. Medical Devices:

- Surgical instruments and implants due to biocompatibility and sterilizability.
- Used in diagnostic devices and precision instruments.

4. Packaging:

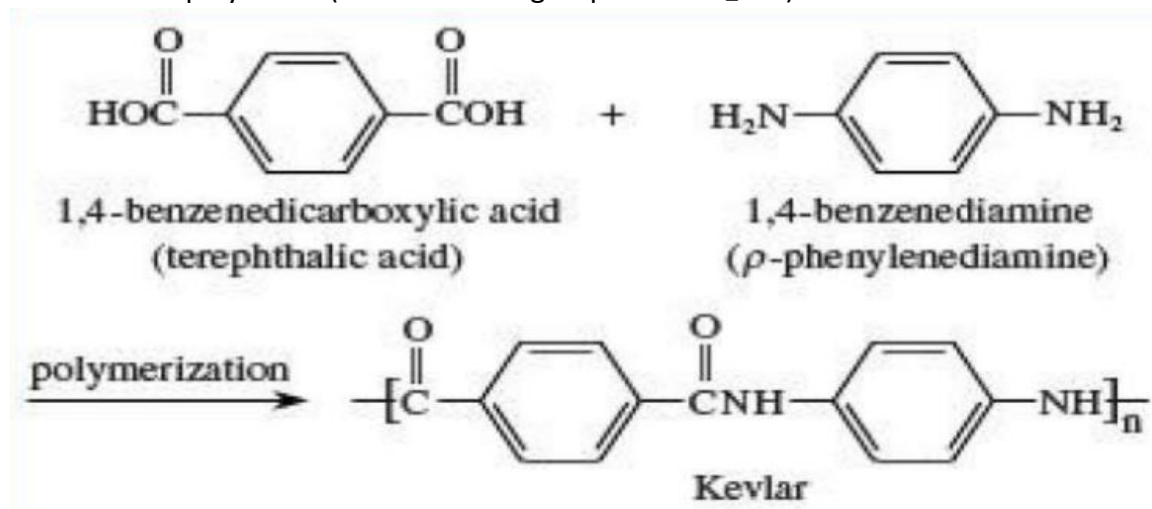
- High-barrier films for food and pharmaceutical packaging, offering protection against moisture and gases.

5. Optical and Communication Systems:

- Fiber optics and waveguides.
- Used in LCD (liquid crystal display) technology and light-modulating devices.

Kevlar:

It is aromatic polyamide (contain amide group i.e. $-CO-NH$)



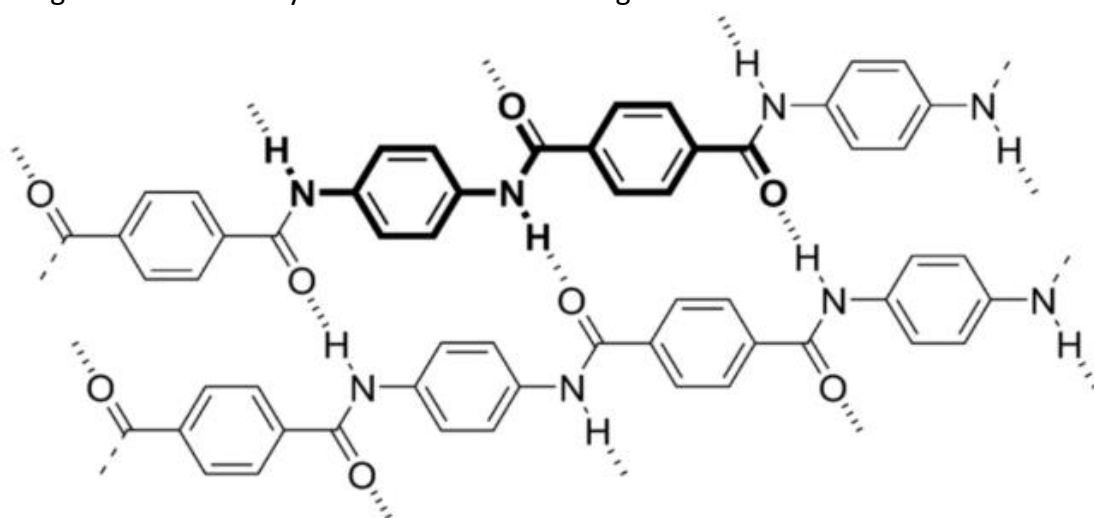
Structure: another name is Aramide (Ar – aromatic, amide).

It is poly para phenylene terephthalamide.

Properties of Kevlar:

1. 5 times stronger than steel, 10 times stronger than Al on equal weight basis.
2. High stability, so it can be used for continuous high temperature operation.
3. It is very strong.
4. Although its M.P. is very high, it can be easily moulded and drawn into filaments.
5. High tensile strength.
6. Because of fibrous nature, these plastics behave as "Self-reinforced Plastics" with excellent mechanical properties.
7. Because of strip like orientation, the LCP has property of multiple internal reflections of light (optical fibre).

The good thermal stability and exceptional strength is due to Intermolecular Hydrogen Bonding between Carbonyl of one chain with Nitrogen of another.



Due to their stiff elongated shape, polymers are ordered in the solution to form nematic phase.

Applications:

1. Kevlar in combination with C-fibres and embedded in epoxy resin to form hybrid composite. Used in aircraft body and wing structure.
2. Kevlar can also be used in light weight boat hulls, high performance race cars.
3. Used for fire retardant fabric due 4th and 5th property.
4. Cables for drilling platforms, parachute lines, fishing lines, pulley ropes.
5. Protective coating and body armour.

2. Conducting Polymers:

Conducting polymers are a class of polymers that exhibit electrical conductivity, which is achieved through the presence of conjugated π -electron systems along their backbone, allowing electrons to move freely.

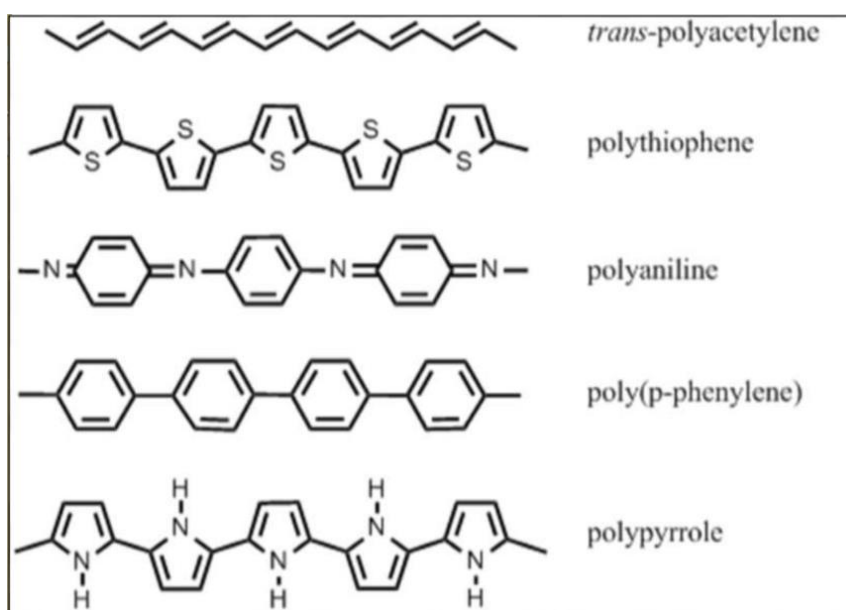
Conducting polymers are of 2 types:

Intrinsic Conducting Polymers (ICP) and Extrinsic Conducting Polymer (ECP).

Structural Requirements:

An organic polymer shows good conductivity if:

1. The polymer chain contains conjugation (alternate σ and π bonds) so that there are more electrons for conductivity.
2. Such polymer is highly crystalline and there is high planarity in structure.
3. Presence of aromatic rings in the chain with continuous resonance enhances conductivity.
4. Polymer should have linear chains.



A. Intrinsically conducting Polymer (ICP) or Conjugated π electrons conducting polymer:

These polymers are linear & have high planarity in structure & possess conjugation (alternate double bond & single bond) in the polymer chain.

When electric field is applied, conjugated π electrons of the polymer get excited & can be transported through the polymer.

Increase in conjugation increase the conductivity to a largest extent.

e.g. i) Trans-polyacetylene ii) Polyaniline

iii) Poly(para)phenylene

Heteroaromatic conducting polymers:

They are used in polymer light emitting diodes (PLED), photodiodes and in solar cells.

E.g. i) Polypyrrole ii) Polythiophene

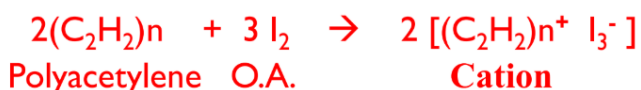
B. Doped Conducting Polymer:

ICP are poor conductors but their conductivity can be improved by creating positive or negative charges on the polymeric chain. This is called Doping.

i) P-Doping or Oxidative Doping:

Doping of suitable oxidizing agent (Lewis's acid like I_2 , Br_2 , $FeCl_2$, PF_6) to conjugated polymer chains.

The oxidizing agents extract a pair of π electrons from chain & make it a positively charged cation.

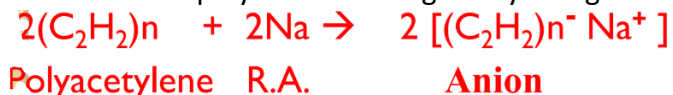


Delocalization of positive charge (hole) takes place over the whole polymer chain & it becomes conducting.

ii) N-Doping or Reductive Doping:

A suitable reducing agent (Lewis's base like Na, Li, K, Metals, naphthyl amines) are added to conjugated polymer chain which donate a pair of electrons to polymer chain.

This makes the polymer chain negatively charged anion & it becomes conducting.



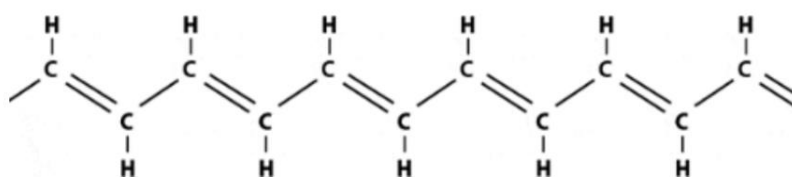
This is called reductive doping because polymer chain has accepted electrons from the metal atom.

C. Extrinsically Conducting Polymer:

Conducting materials like metallic fibres, metal oxides mixed with polymer while moulding. Blending conducting polymer with conventional polymer physically or chemically.

Polyacetylene:

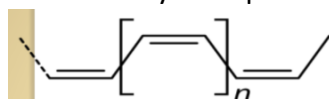
Accidentally discovered in lab of Prof. H. Shirakawa.



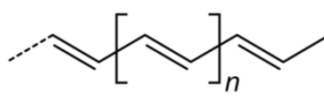
Shirakawa later on collaboration with Heeger and MacDiarmid found that Oxidation of PA increase conductivity of it.

Conductivity of Pure PA: 4.4×10^5 S/cm

Conductivity of doped PA: 400 S/cm



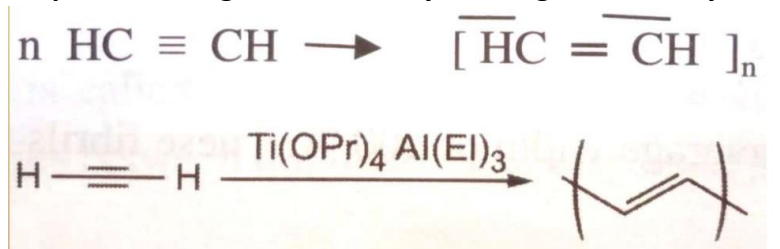
Cis-Polyacetylene



Trans-Polyacetylene

Preparation: Zeigler-Natta catalyst with gaseous acetylene.

Preparation: Zeigler-Natta catalyst with gaseous acetylene:



Properties:

1. Cis form is flexible & coppery, trans form is silvery and brittle.
2. PA has bulk density 0.4 g/cm^3
3. Insoluble in solvents, making it difficult to process the material.
4. High thermal stability
5. When PA is exposed to air oxidation takes place.

Applications of Doped PA:

1. Doped conducting polymers are used in rechargeable light weight batteries.
2. In optical display devices.
3. In electronics: For photodiodes, light emitting wall papers, light emitting diodes (LED) & data storage.
4. In telecommunication system.
5. As antistatic material: To avoid static electricity in plastic carpets in offices, theatres, explosive industry, computer industry.
6. In Molecular wires & Molecular switches.
7. In Solar Cells.
8. As Optical filter to absorb radiation from computer screen.

Limitations:

1. Few large-scale applications due to high cost
2. Problems in processing due to insolubility, infusibility, brittleness.
3. Long term instability.

Electroluminescent polymer:

Electroluminescence (EL) is an optical phenomenon and electrical phenomenon in which a material emits light in response to the passage of an electric current or to a strong electric field.

This occurs through recombination of electrons from one electrode in transistors by holes to other electrode and subsequent decay of excited electron –hole state.

The property in which a material produces bright light of different colours when stimulated electronically is known as electroluminescence.

The material which shows electroluminescence is called as electroluminescent material. Electroluminescent polymers emit light in response to the passage of electric current or presence of strong electric current.

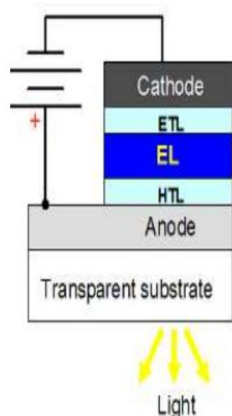
First reported in poly (phenylene vinylene) i.e. PPV used as semiconductor layer between metallic electrodes.

Construction and Working:

The organic electroluminescent device consists of a transparent anode, hole transport layer, emitter layer of an organic polymeric material and a cathode.

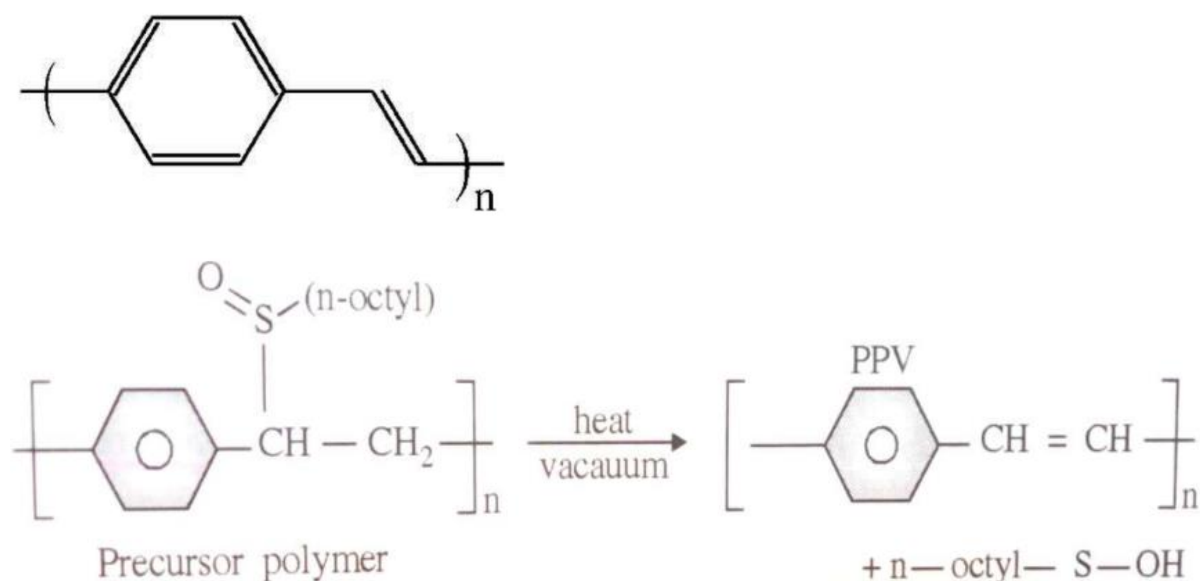
The anode injects a hole towards hole transport layer then an electron is injected by cathode layer into emitter layer.

Then the hole and electron recombine in the emitter layer to excite the emitter layer which results in emission of light, during the return of excited matter to ground layer.

**Polyphenylene Vinylene or Poly (p-phenylene vinylene) or PPV:****Preparation:**

PPV is prepared from precursor polymer poly (-n- octyl sulphonyl paraphenylene ethylene) by heating in vacuum.

Also prepared by CVD of dichloro p- xylene at 500-700 °C.



Properties:

1. Self-emitting device of high brightness.
2. High efficiency.
3. Direct current low voltage operation.
4. No heat and long life.
5. High speed response.
6. PPV is a diamagnetic material.
7. Low intrinsic electrical conductivity (10-13 S/cm)
8. Conductivity increases upon doping with I_2 , $FeCl_3$ or metals.
9. Alkoxy substituted PPV shows ease of oxidation
10. Water insoluble
11. Gives bright yellow-green fluorescence on application of electric field.
12. Ease of processing, high tensile strength and elastic nature renders PPV to be used under harsh conditions.

Applications:

1. In the form of thin films for information display.
2. Automotive instrument panel backlighting.
3. Backlight for LCD's.
4. Electroluminescent night lamps.
5. Long life, full colour displays.
6. Flat panel displays.
7. Photovoltaic cells.
8. PPV also used as electron donating material in organic solar cells.