



Polymers

Chemistry (SRM Institute of Science and Technology)



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Module 4 – POLYMERS

POLYMERS

Polymers are high molecular weight organic compounds in which a large number of simple units repeat themselves in a regular fashion. The simple units are called as monomers. For any compound to be recognized as a true monomer, it should possess at least two functionalities (Not two functional groups necessarily---- as in some compounds, one functional group gives rise to only one functionality while in some compounds, one functional group gives rise to two functionalities), e.g.,

CH_3OH has one functional group and one functionality (Not a true monomer)

$\text{CH}_2=\text{CH}_2$ has one functional group and two functionalities (A true monomer)

$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ has two functional groups and two functionalities (A true monomer)

Therefore, it is clear that what is actually required for polymerization, is presence of at least two functionalities and not two functional groups, in the monomer.

Classification of Polymers

Polymers have been classified on different basis as follows:

(A). Classification on the basis of Origin/Source

On this basis, polymers have been broadly classified into **two types**:

1. Natural Polymers

They occur naturally and are found in plants and animals.

Examples: Proteins, Nucleic acids, Starch, Cellulose and Natural rubber.

2. Synthetic Polymers

These are man-made polymers. Plastic is the most common and widely used synthetic polymer.

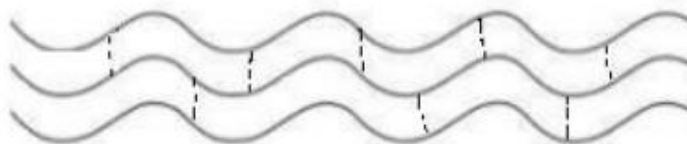
e.g., Nylons, Polythene, PVC, Synthetic rubbers, etc.

(B). Classification on the basis of Structure

On this basis, polymers have been broadly classified into **three types**:

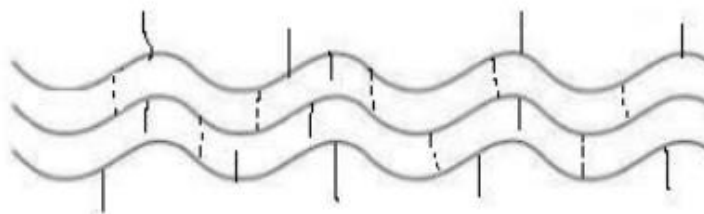
1. Linear Polymers

Polymers comprising of long and straight chains are called as linear or straight chain polymers. e.g., High density polyethene (HDPE)



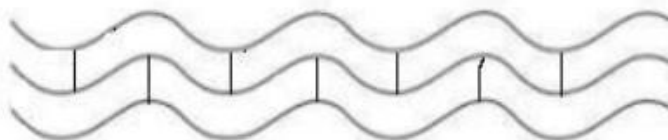
2. Branched-chain Polymers

Polymers comprising of linear chains with branches are called as branched chain polymers. e.g., Low-density polyethene (LDPE).



3. Cross-linked Polymers

Polymers in which various individual chains are connected together by covalent bonds (cross links) are called as cross linked polymers. These polymers are formed from bi-functional and tri-functional monomers and the additional functionality produces the cross links. e.g., Bakelite and Melamine.



(C). Classification on the basis of nature of Monomers

On this basis, polymers have been broadly classified into **two types**:

1. Homo-polymers

Polymers which are comprising of only one type of monomers are called as homo-polymers.

e.g., Polyethene, PVC, Nylon-6, etc. This can be represented as:

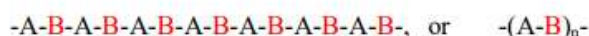


2. Co-polymers

Polymers which are comprising of more than one (generally two) types of monomers are called as homo-polymers. e.g., Nylon-6'6, Terylene, SBR, etc.

Co-polymers have further been classified into four types on the basis of relative arrangement of the monomer units with respect to each other. These are:

- i). **Alternate Co-polymers:** Polymers comprising of alternating A and B units. The order is regularly followed throughout the chain. This can be represented as:

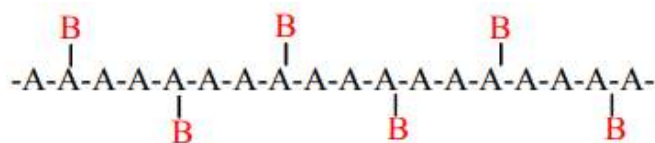


- ii). **Block Co-polymers:** Polymers comprising of regular alternating blocks of A and B units. The order is regularly followed throughout the chain. This can be represented as:



- iii). **Graft Co-polymers:** Polymers in which the main chain is comprising of one type of monomers and the other monomer forms the branches. Therefore, for being a graft co-polymer, the polymer must be branched.

This can be represented as:



- iv). **Random Co-polymers:** Polymers in which no regular order of arrangement is followed by the monomer units. This can be represented as:



The most common type of co-polymers are alternate co-polymers.

(D). Classification on the basis of Inter-molecular Forces

On this basis, polymers have been broadly classified into **four types**:

1. Elastomers

Polymers in which intermolecular (inter-chain) forces are very weak (van der Waals forces) are called as elastomers. These are rubber-like solids weak interaction forces are present.
e.g., Rubber.

2. Fibres

Polymers in which intermolecular (inter-chain) forces are very strong (Hydrogen bond or dipole-dipole interaction) are called as Fibres. These are strong, tough, with high tensile strength. e.g., Nylons, Terrylenes, etc.

3. Thermo-plastics

Polymers in which intermolecular (inter-chain) forces are intermediate are called as thermo-plastics. These polymers on heating become soft and on cooling again become hard and retain their original shape. In this case, the intermolecular forces, on heating, get weakened and the polymer becomes soft and vice-versa. It is purely a physical change and physical changes are generally reversible. Therefore, these polymers are recyclable, i.e., they can be moulded and re-moulded again and again. e.g., Polyethylene, Polyvinyl chloride, Polystyrene, etc.

4. Thermo-settings

Polymers in which there is extensive cross linking, are called as thermo-settings. These polymers on heating become soft and on cooling again become hard but do not retain their original shape. In this case, the cross links get broken and rearranged on heating. It is purely a chemical change and chemical changes are generally irreversible. Therefore, these polymers are not recyclable, i.e., once moulded, they cannot be moulded again. These polymers greatly improve the material's mechanical properties. e.g., Bakelite, Epoxy resins, etc.

(E). Classification Based on Synthesis

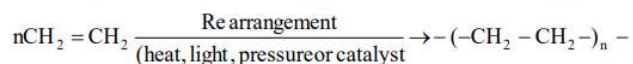
On this basis, polymers have been broadly classified into **two types**:

1. Addition Polymers

This type of polymerization reaction yields a product with an exact multiple of the original monomeric molecule without loss of any by-product. This type of reaction is initiated by the application of heat, light, pressure, or catalyst for breaking down the double bonds of monomers.

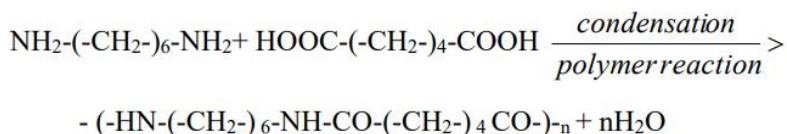
The main feature of addition polymerization is: (i) only olefin compounds undergo addition reactions. (ii) linear polymers are produced. (iii) the polymer produced has same elemental composition as that of monomer. (iv) the molecular weight of a polymer is an integral multiple of that of the monomer.

Example: Polymerization of ethylene monomer gives polyethylene



2. Condensation Polymers: It is the reaction which occurring between monomers containing polar groups. Condensation reaction proceed to produce the polymer by elimination of small molecules likes H_2O , HCl etc. The main features of condensation reaction are (i) monomers having two or more functional groups are undergo reaction (ii) chain growth is slow (iii) mostly catalyzed by acids or alkali (iv) elemental composition of polymer is generally different from that of the monomers.

Example: Formation of nylon 6, 6. It is obtained by the condensation reaction between hexamethylene diamine and adipic acid,

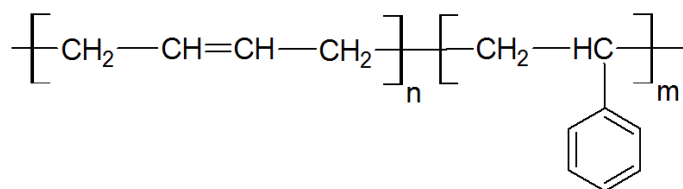


This type of reaction is an intermolecular combination, and it takes place through the different functional groups having affinity for each other.

When monomers contain poly functional groups, it may give rise to a cross-linked structure polymer. Some important functional groups are hydroxyl, carboxyl, amino, isocyanate, ester etc. which gives rise to strong covalent bond between the chains.

3. Co-polymerization: It is a reaction in which two or more different monomeric species undergo addition reaction to form a co- polymer with high molecular weight compounds. This process is known as co-polymerization. The polymer obtained in this process in known as co-polymer.

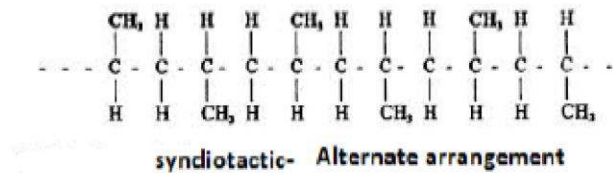
Example: Formation of SBR from Butadiene rubber and styrene plastic.



3.2. TACTICITY

The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly with respect to main chain. The spatial arrangements of molecule in a polymer is known as *Tacticity*, it affect the physical properties of polymer. The polymer can also be classified in to three types based on their tacticity. They are,

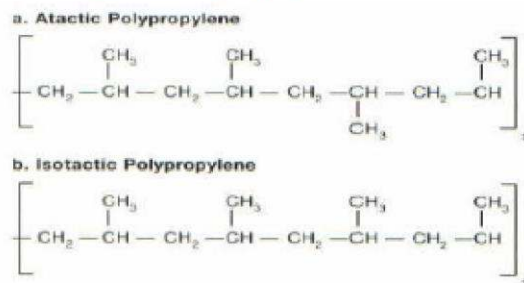
a. Syndiotactic: Arrangement of side groups or atoms is in alternating fashion



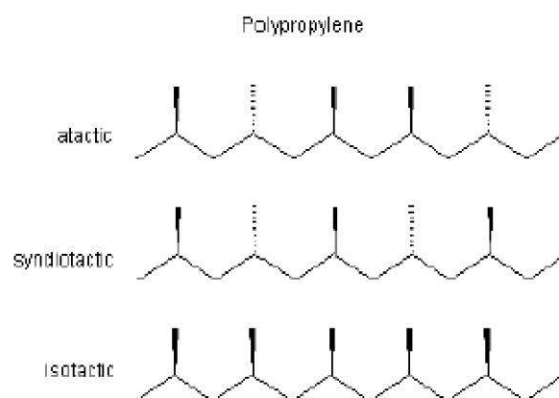
b. Isotactic Polymer: In this polymer, functional groups are all on the same side of chain

c. Atactic: Atactic polymer is obtained when the functional groups or atoms are arranged randomly around the main chain of polymer.

Example: The structural arrangements of polypropylene are shown



polypropylene polymers exist in all the different form of tacticity is schematically shown below:



3.3. FUNCTIONALITY

The number of bonding sites or reactive sites present in a monomer is called as 'functionality'.

Examples: reactive functional groups: $-NH_2$, $-X$, $-C=O$, $-COOH$ etc.

Monomers which are not having reactive functional groups such as ethylene, propylene and styrene but possess olefinic bonds such as $=$ bond \equiv bond can be used for the formation of

polymer by breaking of that bond. Their functionality is 2 and 3 respectively. The minimum functionality to form a polymer is 2.

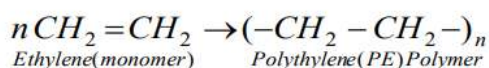
Depending upon the functionality of monomeric units, it is possible to get different type of structure. For example:

- i. In case of bifunctional monomers, two reactive groups or two monomer can attach side by side to each other forming linear and straight chain polymer.
- ii. In case the monomers which are polyfunctional in nature, on polymerization, which produce cross-linked structure polymer. The chains are linked by primary covalent bonds. Hence this polymer is strong and hard.

Degree of Polymerization (DP):

Degree of polymerization is defined as *the number of repeating units (n) present in a polymer*.

Example: Formation of polyethylene from ethylene monomer.



Where n = Degree of polymerization (DP)

Molecular weight

- The molecular weight of a synthetic polymer does not have a single value, since different chains will have different lengths and different numbers of side branches. There will therefore be a distribution of molecular weights, so it is common to calculate the average molecular weight of the polymer.
- However, there are several different ways to define the average molecular weight, the two most common being the number average molecular weight and the weight average molecular weight. Other averages exist, such as the viscosity average molecular weight.
- When studying a polymer, the most relevant average depends on the property being investigated: for example, some properties may be more affected by molecules with high molecular weight than those with low molecular weight, so the weight average is chosen since it highlights the presence of molecules with high molecular weight. The average molecular weight of a polymer sample can be determined using a variety of techniques, such as gel permeation chromatography, light-scattering measurements and viscosity measurements, and the type of average that is yielded depends on the technique.

Number average molecular weight, \bar{M}_N

The number average molecular weight is defined as the total weight of polymer divided by the total number of molecules.

$$\text{Total weight} = \sum_{i=1}^{\infty} N_i M_i$$

where N_i is the number of molecules with weight M_i

$$\text{Total number} = \sum_{i=1}^{\infty} N_i$$

The number average molecular weight is therefore given by:

$$\bar{M}_N = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}$$

This can also be written as:

$$\bar{M}_N = \sum_{i=1}^{\infty} x_i M_i$$

where x_i is the number fraction (or mole fraction) of polymer with molecular weight M_i .

Weight average molecular weight, \overline{M}_w

The weight average molecular weight depends not only on the number of molecules present, but also on the weight of each molecule. To calculate this, N_i is replaced with $N_i M_i$.

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$$

This can also be written as:

$$\overline{M}_w = \sum_{i=1}^{\infty} w_i M_i$$

where w_i is the weight fraction of polymer with molecular weight M_i .

Polydispersity Index

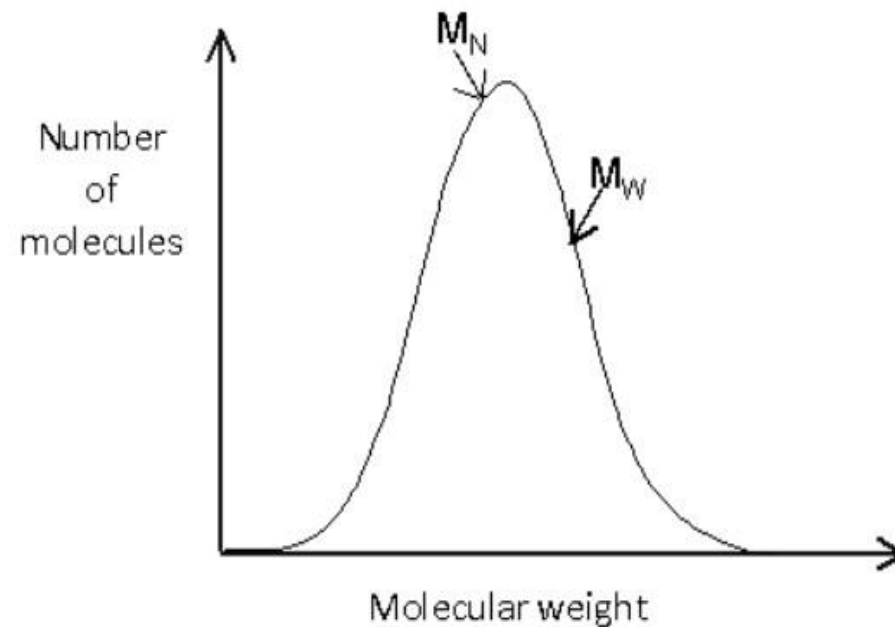
The polydispersity index is defined as the ratio of the weight average molecular weight to the number average molecular weight, and it gives a measure of the distribution of the molecular weight within a sample. It has a value greater than or equal to one: it is equal to one only if all the molecules have the same weight (i.e. if it is monodisperse), and the further away it is, the larger the spread of molecular weights.

$$\text{Polydispersity index} = \overline{M}_W / \overline{M}_N$$

Molecular weight distributions

The molecular weight distribution can be shown graphically by plotting the number of molecules against the molecular weight. It is worth noting that these plots are sometimes shown with molecular weight decreasing along the x-axis.

The distribution may be relatively simple, such as:



Number Average vs Weight Average Molecular Weight		
	More Information Online	WWW.DIFFERENCEBETWEEN.COM
	Number Average Molecular Weight	Weight Average Molecular Weight
DEFINITION	Number average molecular weight is the mole fraction of molecules in a polymer sample.	Weight average molecular weight is the weight fraction of molecules in a polymer sample.
EQUATION	$M_n = \sum N_i M_i / \sum N_i$	$M_w = \sum N_i M_i^2 / \sum N_i M_i$
VALUE	Always lesser than weight average molecular weight.	Always greater than the number average molecular weight.
DETERMINATION	By using gel permeation chromatography, viscometry and colligative methods such as vapour pressure osmometry.	By using static light scattering, small angle neutron scattering, X-ray scattering, and sedimentation velocity.

Effect of polymer structure on polymer:

- 1) Mechanical properties: (a) strength (b) plasticity (c) elasticity
- 2) Physical properties: (a) crystalline phase (b) amorphous phase
- 3) Chemical properties
- 4) Thermal properties
- 5) Electrical properties

4.6.1. Strength: Strength of polymers depends on magnitude and distribution of forces between the polymerization chain. In straight chain and branched-chain polymer, polymeric chains are held together by weak Vander wall's force of attraction. So the strength of these polymers is less. However, strength of the polymer increases by

(i) Chain length or molecular weight. Polymers of low molecular weight are quite soft and gummy but are brittle. Higher molecule weight polymer are tougher and posses greater resistance.

(ii) Presence of polar groups which increase the intermolecular forces and hence increase the strength. Example Nylon, Teflon, Poly ester.

(iii) Slipping power of one molecule over the other polymer molecule affects the resistance to slip and consequent deformation of a polymer.

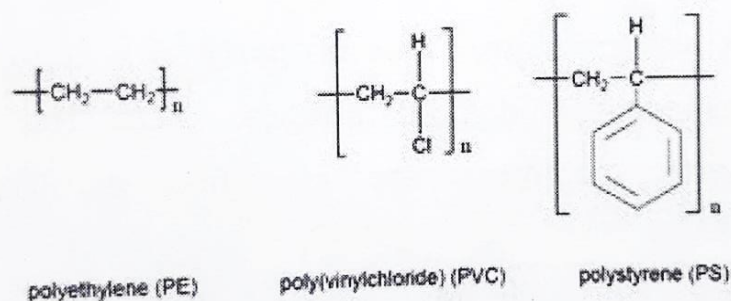
It can be explained by taking the structure of following polymer molecule.

Polyethylene: Structure is simple and uniform and not much restriction to movement of one molecule over another. Hence, strength of polyethylene is less.

Polyvinyl Chloride: It has large lumps of chlorine atom and restricts the movement of chains to some extent. Hence, the strength of the PVC is more than the polyethylene and also tougher and stronger.

Polystyrene

It has bulky benzyl group in side chain. The presence of bulky benzyl group restricts the movement of the chain. So the strength of the polystyrene is higher than polyethylene and PVC

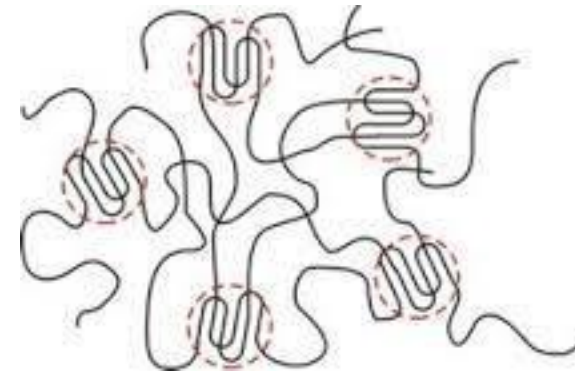


Bakelite

All the chains are interlinked by strong covalent forces extended in 3 dimensions result most strong and tough polymer with total restriction in the movements. So the strength of the polymer is higher than the polystyrene, polyethylene and PVC.

Physical phases:

- Based **on arrangement of polymer chains** w.r.t each other: two phases (amorphous and crystalline)
- Crystalline/amorphous components **influence** polymer **properties**
- **Amorphous phase:** characterized by completely disorderly or random, twisted, entangled arrangement of molecules
- **Crystalline phase :** consist of orderly regions which are embedded in an amorphous random matrix
- **Crystallites:** orderly regions in a polymeric substance
- **Factor** affecting the crystallinity: geometrical regularity
- **Stereoregular** polymers are crystalline • **Atactic** polymers are amorphous • **Factors supporting crystallinity:**
 - Strong hydrogen bonding between polymer chains
 - Longer molecules
 - Shorter repeating unit
 - e.g. HDPE (**H**igh **D**ensity **P**oly **E**thylene), linear polymer



- **Factors which do not support crystallinity:**
- Chain branching
- Long repeating unit
- Low degree of symmetry
- e.g. LDPE (Ligh **D**ensity **P**oly **E**thylene), branched polymer

Chemical resistance:

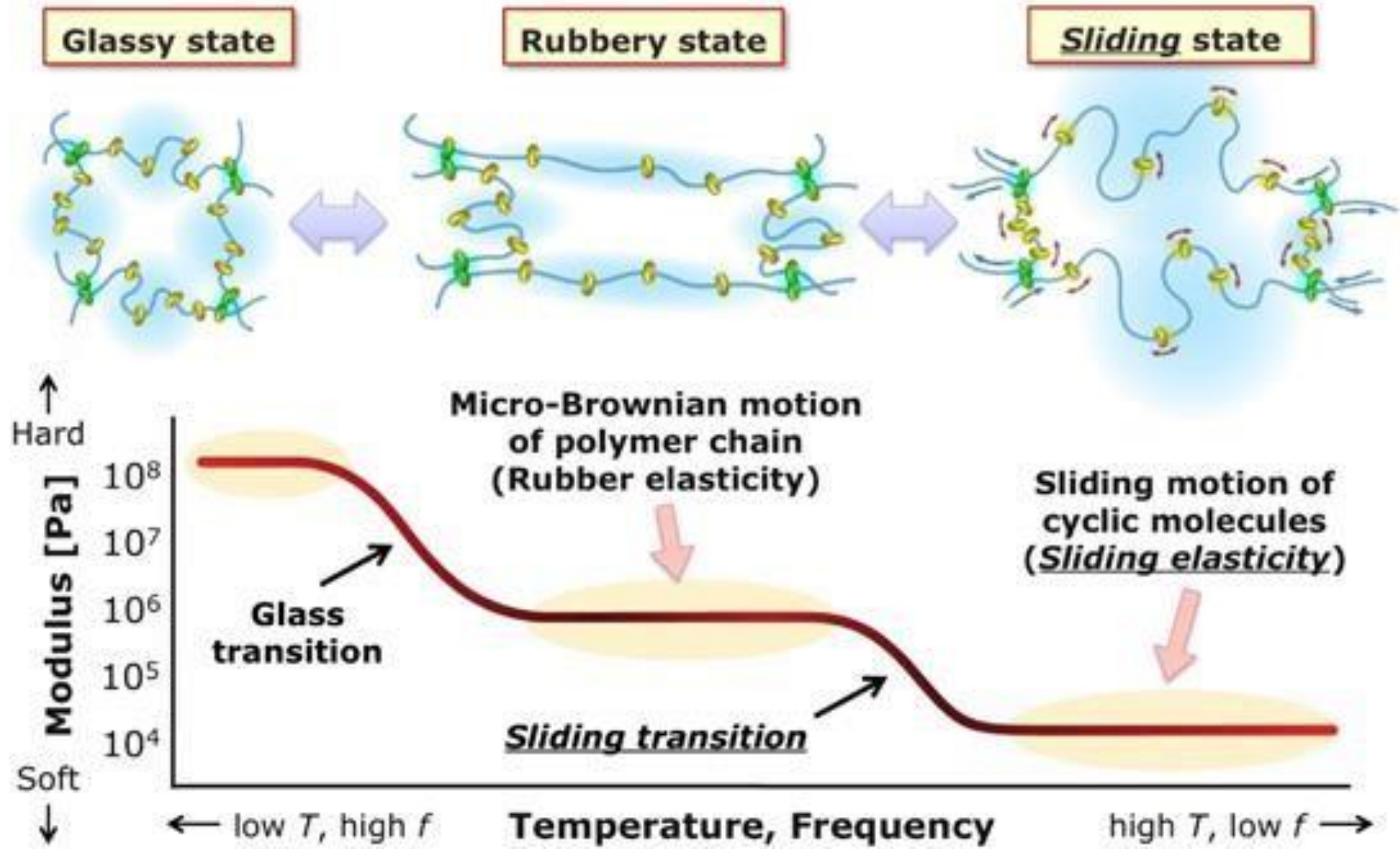
- Resistance of polymer to be attacked by other materials depends on the **chemical nature of monomer unit and their arrangement.**
- **Like dissolves like:**
- polar solvents (H_2O , alcohol, CHCl_3 etc.) dissolve polar polymers
- Non-polar solvents (benzene, toluene, petrol, hexane, CCl_4) dissolve non-polar polymers
- E.g. PVC dissolves in water
- and PS dissolves in toluene and not vice a versa

- Aliphatic solvent dissolve aliphatic polymers
- Aromatic solvents dissolve aromatic polymers
- **Factors** affecting solubility of a polymer **in particular** solvent:
 - Cross-linking
 - Molecular weight
 - crystallinity

Thermal properties:

- **Glass transition temperature (T_g)**: temperature above which polymer is soft, flexible, rubbery and below which it is hard, brittle, glassy.
- **Below T_g** : glassy state
- **Above T_g** : rubbery state
- **Factors affecting T_g** :
 - Molecular weight
 - Intermolecular forces

- Cross linking
- **T_g of some polymers:**
 - PE (branched) = -125 °C
 - PP = 0 °C
 - PVAc = 28 °C (polyvinyl acetate)
 - Nylon 66 = 50 °C
 - PVC = 81 °C
 - PS = 95 °C

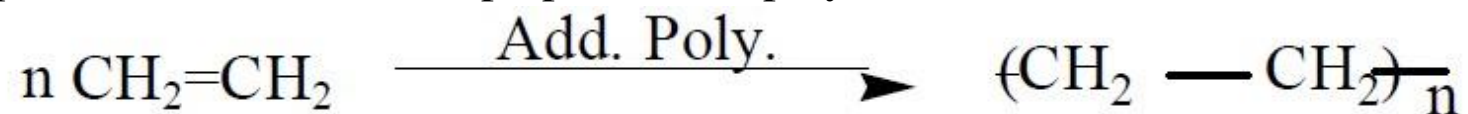


<u>Thermoplastic</u>	<u>Thermoset</u>
1. Formed by addition polymerization	1. Formed by condensation reaction
2. No crosslinking in structure	2. cross-linked 3D structure
3. Soften on reheating because of weak secondary forces	3. Softening on reheating not possible because of strong covalent bonds
4. Can be recycled from waste	4. Can not be recycled from waste

5. soft, weak and less brittle	5. hard, strong and more brittle
6. Dissolve in organic solvents	6. Not soluble in organic solvents
7. e.g. PE, PVC	7. e.g. bakelite, urea formaldehyde

Polyethene

Polyethene is a homo-polymer and its monomer unit is ethene (ethylene). It is the most common and with simplest structure among all plastics. The reaction for preparation of polyethene can be shown as:



Polyethene is broadly of two types: i). Low Density Polyethene (LDPE) ii). High Density Polyethene (HDPE)

i) Low Density Polyethene (LDPE):

- As the name itself indicates, it is a polymer of very low density.
- It is prepared via free radical mechanism at a temperature of **80 to 350 °C** under high pressure (**1000 to 3000 atm**) in presence of a oxygen or a peroxide (**Benzoyl peroxide**) as initiator, wherein extensive branch formation takes place and the density of the resultant polymer is very low in the range of **0.910–0.940 g/cm³**.

Properties:

- It is a waxy translucent material, exhibits high impact strength, low brittleness temperature, film transparency and outstanding electrical insulating properties.
- It is chemically inert and has good resistance to acids and alkalis. However, it swells in and is permeable to oils. It melts in temperature range of 107-120 °C. Its T_g(Glass Transition) value is -120°C. It is flexible over a wide temperature range.

Applications:

- It is used in making packaging materials for food, garments, etc.
- It is used in production of squeeze bottles, coatings, wrappings, etc.
- It is also used in cable and wire insulations.

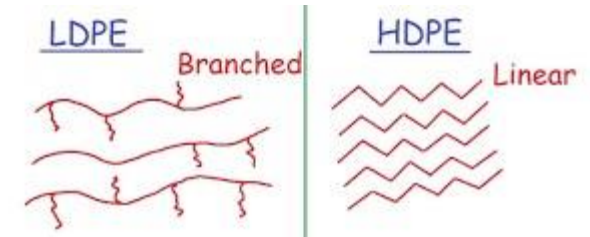
ii) High Density Polyethene (HDPE):

- It is a linear polymer with little or no branching.
- It is prepared via ionic mechanisms at a low temperature of **60 to 70 °C** and very low pressure (**6 to 7 atm**), wherein little or no branch formation takes place and the density of the resultant polymer is high in the range of **0.945–0.965 g/cm³**.

- However, HDPE is also prepared by **coordination polymerization** using Ziegler-Natta catalyst (Triethyl aluminium and Titanium tetrachloride).

Properties:

- It is opaque and has less impact strength, but, better barrier properties than LDPE.
- It has better chemical resistance than LDPE.
- It melts in temperature range of **130-138°C**. Its T_g (Glass Transition) value is **-20°C**.
- It exhibits better stiffness, toughness, good tensile strength and heat resistance.



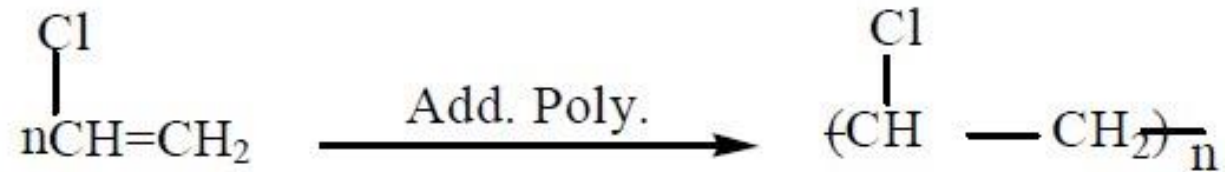
Applications:

- It is used in manufacture of dust bins, cans, buckets, fuel tanks, etc.
- It is used for making corrugated pipes.
- It is also used in cable and wire insulations.



Polyvinylchloride (PVC) (Addition Polymer)

Polyvinylchloride is a homo-polymer and its monomer unit is vinyl chloride (Chloroethene). It is a thermoplastic polymer. The reaction for preparation of Polyvinylchloride can be shown as:



Polyvinylchloride is of two types:

i). Un-plasticized PVC

ii). Plasticized PVC

Un-plasticized PVC is also known as Rigid PVC (PVC-R or PVC-U). It is strong, rigid, inherently flame retardant and with relatively good chemical resistance.

Plasticized PVC (PVC-P) is that PVC in which some chemical agents, called as plasticizers,

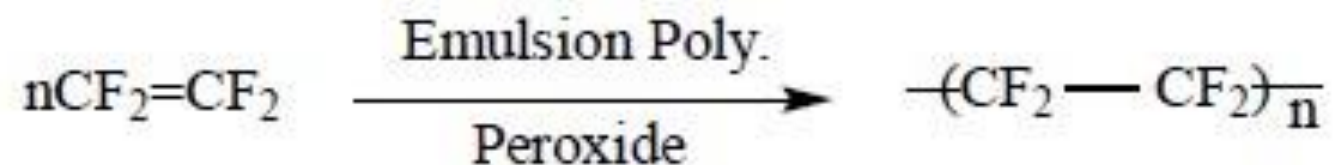
Properties:

- It is a colourless, odourless, non-flammable material.
- It is a chemically inert and is highly resistant to acids and alkalis. However, plasticized PVC is relatively less resistant to chemicals.
- It is resistant to atmospheric oxygen, i.e., resistant to oxidation.
- It possesses greater stiffness and rigidity compared to polyethene.
- Due to its versatile properties, such as lightweight, durability and easy processability, PVC is now replacing traditional building materials like wood, metal, concrete, etc.

Applications: PVC is used for making building and construction materials, pipes, flooring, vinyl siding. Plasticized PVC is used mainly in wire and cable insulations and in packaging materials. Flexible films and sheets are used as pool liners and roof coatings, carpet backing, rain coats, etc.

Polytetrafluoroethylene (PTFE) (Addition Polymer)

Polytetrafluoroethylene is commercially known as Teflon. It is a homo-polymer and its monomer unit is tetrafluoroethylene. It is a thermoplastic polymer. It is usually prepared emulsion polymerization of tetrafluoroethylene using peroxide or ammonium persulphate as initiators. The reaction for preparation of Teflon can be shown:



Properties:

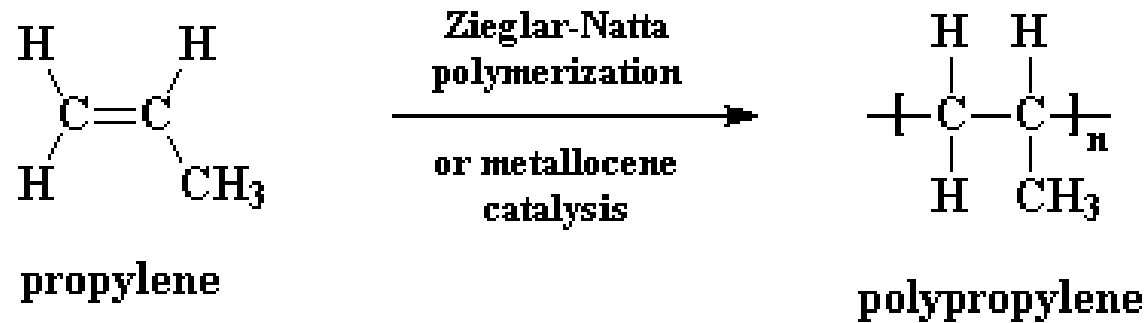
- It is a highly crystalline polymer (93-98% crystallinity).
- It has high chemical resistance.
- It is practically insoluble in all solvents and is not wetted by either water or oil.
- It has low coefficient of friction and remains slippery over a wide range of temperature (-40-300°C).
- It is resistant to temperature with high temperature stability.
- It has excellent electrical insulating properties.
- It is a **white solid compound** at room temperature. • Its density is about 2200 kg/m³ 2.2 g/cm³ • Its **melting point is 600 K**.
- It is a chemical resistance compound, the only chemicals that **can affect these compounds are alkali metals**.
- It shows **good resistance towards heat and low temperature**.

- It has a **low water absorption capacity**.
- It has an **anti-adhesion ability** due to which it is used as non-stick kitchen utensils.

Uses of Teflon

- It is used in making **waterproof fabric**.
- It is used in making **non-stick cookware**.
- It is used in making an **anti-friction device**.
- It is used for **coating medical appliances** (surgical devices).
- Due to its high resistance to corrosion, it is used for **coating the lining of laboratory appliances**.
- It is used on **weapons as an anticorrosive coat**.
- It is used as a **coating on pipes and tanks** for carrying and **storing corrosive chemicals**.

Polypropylene (Addition Polymer)



- Upon polymerization, PP can form three basic chain structures depending on the position of the methyl groups. They are:
 - **Atactic (aPP)** – This is soft and rubbery and has an Irregular or random methyl group (CH₃) arrangement. Hence, it is an amorphous solid lacking pattern. Its crystallization is difficult. It is used primarily in roofing modification and adhesives. An example is PVC or polyvinyl chloride.
 - **Isotactic (iPP)** - Methyl groups (CH₃) are on one side of the carbon chain. It is strong and hard, and resistant to stress, cracking, and chemical reactions. They have extremely high melting points. These have a semicrystalline structure and are polypropylene that has been industrially prepared. They are used in the production of synthetic fibers.
 - **Syndiotactic (sPP)** - Syndiotactic (sPP) - It has an arrangement of alternating methyl groups (CH₃). Syndiotactic polypropylene was only recently mass-produced. Though they are not as crystalline as isotactic, they have high melting points like them. It is softer than isotactic polymer, but it is also tough and clear. Because it is resistant to gamma radiation, it is used in medicine.

Physical Properties of Polypropylene

- The physical properties of PP are affected by its **molecular weight** and distribution, **crystallinity**, shape, and percentage of comonomer (if employed), and isotacticity.
- PP normally exists as a **white translucent solid**.
- It is elastic and tough.
- The density of polypropylene is between **0.895 and 0.92 g/cm³**. Lower density is utilized for molding.
- **Polypropylene and polyethylene** are alike in some aspects like solution behaviour and **electrical characteristics**, but polypropylene is **superior in terms of heat resistance and hardness**.

- It has a **large thermal expansion, high fatigue resistance, and insulation properties.**

Chemical Properties of Polypropylene

- High chemical resistance to most of the **acids and alkalies.**
- The majority of commercial polypropylene is isotactic, with a **crystallinity intermediate** between low and high-density polyethylene.
- Polypropylene is a **highly flammable material** that **retains mechanical and electrical properties at high temperatures, in humid conditions, and when immersed in water.**
- Environmental stress and cracking are not a problem for PP. • It is **susceptible to microbial attack** (bacteria, mold, etc.)
- It has a **high resistance to steam sterilization.**
- **Insoluble in most organic solvents** except in Xylene and some other nonpolar solvents
- **Resistance to** aldehydes, esters, aliphatic hydrocarbons, and ketones is excellent.
- Resistance to aromatic and halogenated hydrocarbons, as well as oxidizing agents, is limited.
- Chemical resistance is lesser than polyethylene

- Ultraviolet Exposure: When polypropylene is exposed to temperatures above 100 °C, its chain degrades. Normally, oxidation occurs at the tertiary carbon centers, causing the chain to split due to an oxygen reaction. Cracks and crazing are indicators of deterioration in exterior applications. UV-absorbing additives and anti-oxidants such as phosphites and hindered phenols can help to prevent polymer degradation.

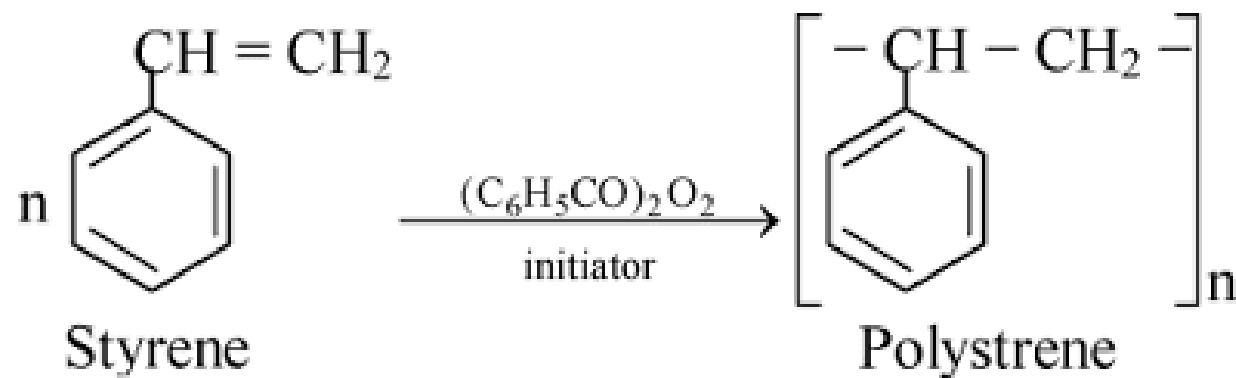
Uses of Polypropylene

- Polypropylene is extensively used in the production of plastic living hinges because of its **great fatigue resistance** (especially the **hinges on flip-top containers** and flip-top bottles).
- This polymer is also utilized to manufacture plastic piping systems. The material's strength and rigidity are major advantages for this application. Polypropylene piping also has the advantage of being resistant to chemical leaching and corrosion.
- Polypropylene may be used to make **plastic laboratory products as well as plastic medical items** since it has enough heat resistance to survive the high temperatures seen in autoclaves.
- Polypropylene is also utilized in the production of **home mats, rugs, and carpets**.
- Ropes are another prominent application of this polymer (especially because the ropes made from polypropylene are so light that they float in water). Furthermore, the strength of polypropylene ropes is approximately identical to that of polyester ropes.

- Polypropylene sheets are also used to make storage boxes, stationery folders, and other types of packaging.
- Loudspeaker drive units are also made from this thermoplastic polymer.
- Polypropylene-based fibers can be used to strengthen drywall joints.



Polystyrene (Addition Polymer): Preparation, Properties and Applications



- Polystyrene, also known as **Polyvinyl benzene**
- It is **hard, brilliantly transparent**, stiff resin which is produced by the free radical addition polymerization of styrene in the presence of **benzoyl peroxide**.
- Polystyrene is **non-biodegradable** and widely used in the food-service industry as rigid trays, containers, **disposable eating plates, bowls**, etc.

- It can be **reused and recycled**.
- It is **environmentally friendly**.

Properties of Polystyrene

- Polystyrene exists in an **amorphous** state because of the presence of bulky phenyl groups, packing of polystyrene chains is not efficient.
- Polystyrene is **non-polar** in nature.
- The polystyrene **melting point is 240** degrees Celsius.
- Polystyrene **density is 1.05 g/cm³**
- The polystyrene **boiling point is 430** degrees Celsius.
- Polystyrene has a **good optical property** like it is a transparent polymer allowing high transmission of all wavelengths. Moreover, its high refractive index gives it a particularly high brilliance.
- Due to the chain stiffening effect of the benzene ring, polystyrene is **hard but brittle**. It emits a characteristic metallic sound when dropped.

- Being a non-polar amorphous polymer, its softening temperature is low. It **cannot withstand the temperature of boiling water**.
- Polystyrene has a low tendency for moisture absorption. Moreover, it has **good electrical insulation characteristics**. Therefore, it is used in making polystyrene insulation products.
- Polystyrene has reasonable chemical resistance but mediocre oil resistance.

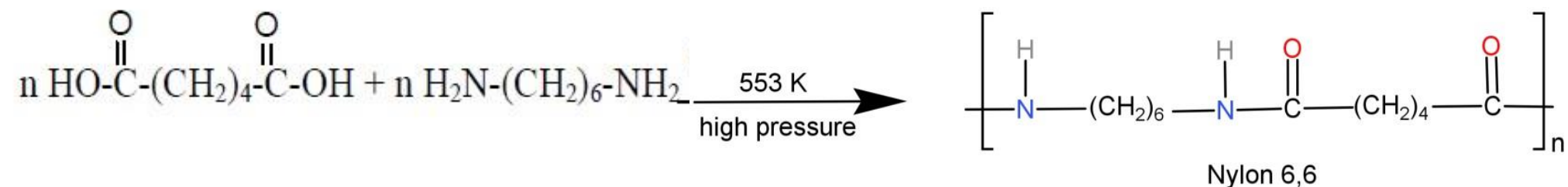
Use of Polystyrene

- It is used for making polystyrene products like polystyrene **sheets, polystyrene foam, brush handles, and combs**.
- It is used for making **talcum powder**.
- It is used for making polystyrene plastic like small jars, bottle caps, polystyrene cups, and storage containers.

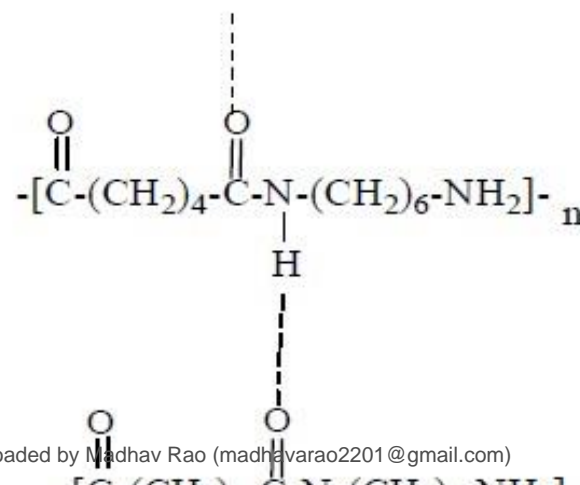
- It is used for making audio cassettes.
- **Food Packaging:** Polystyrene has been declared safe for use in food contact by the Food and Drug Administration for decades.

Nylon-6'6 (Condensation Polymer)

Nylon-6'6 is a co-polymer and its monomer units are adipic acid (Hexan-1,6-dioic acid) and heamethylene diamine (Hexan-1,6-diamine). Both these monomers can in turn be obtained from Buta-1,3-diene. The reaction for preparation of Nylon-6'6 can be shown as:



Innylon-6'6, various polymer chains are connected together by strong intermolecular forces, i.e., hydrogen bonding as;



Properties of Nylons:

- Nylon fibres are linear structures in which the molecular chains are arranged parallel to each other and held together by hydrogen bonding. The strong intermolecular forces make the structure of these fibres more crystalline and imparts them high strength, elasticity and high melting point.
- Nylons are chemically stable and resistant to abrasion.
- The yarn is smooth, long lasting and can be spun into fabric.
- The fabric is tough, lustrous, moisture resistant, easy to dye, retains colour and can be set by heat and steam.
- Nylon is Both **durable and lightweight**.
- Items made of nylon **dry rapidly** because the strands that make up this material are smooth and nonabsorbent.
- Nylon holds up well to filth and is not weakened by chemicals or perspiration.

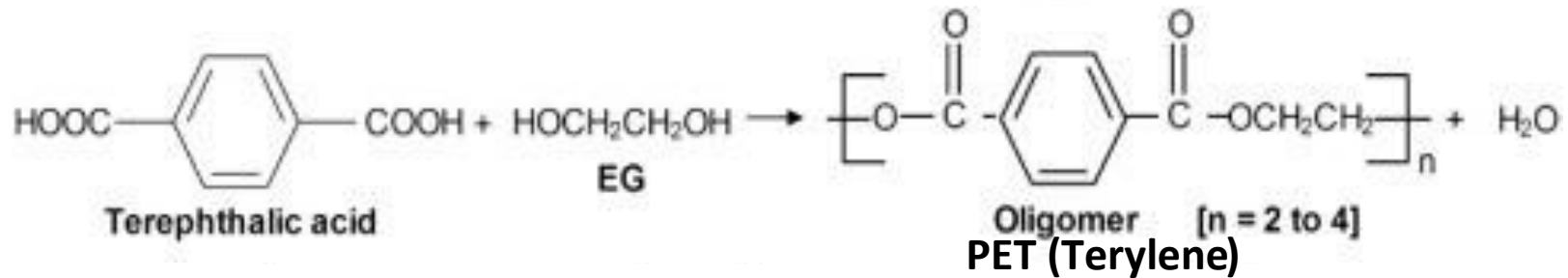
- Nylon **can melt at high temperatures**. This means that when ironing nylon-made things, you should use a low setting and iron the item from the wrong side.

Uses of Nylon 6,6

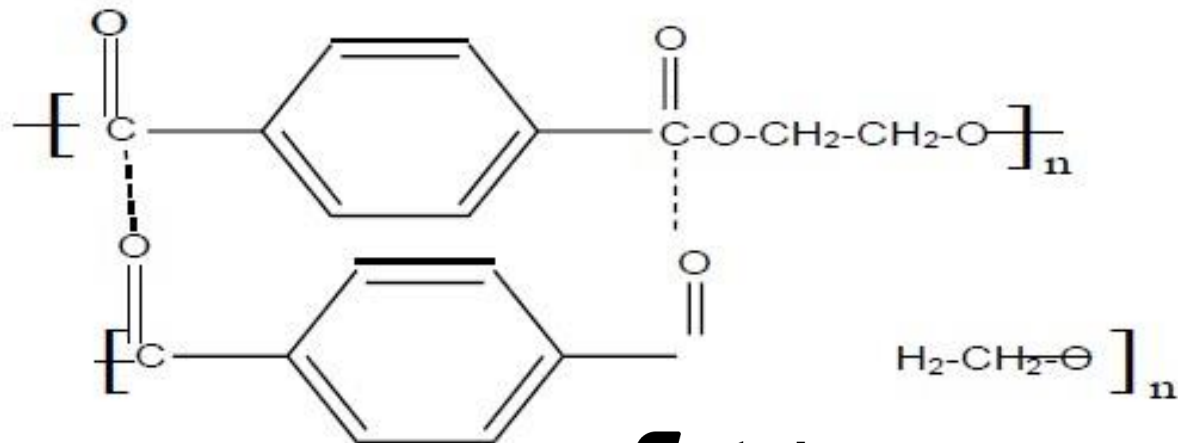
- Shirts, **swimwear**, lingerie, underwear, and sports gear.
- Used for making combs and tooth brush bristles.
- Conveyor and seat belts, airbags, parachutes, nets and ropes, thread, tarpaulins, and tents are a few examples of industrial usage.
- It is used to manufacture **fishnets**.
- It is used as plastic in the manufacturing of machine parts.
- For **jacketing electrical equipment**
- For making gears and bearings

Polyethylene Terephthalate (PET)

Polyethyleneterphthalate is a copolymer and its monomer units are terephthalic acid (Benzene-1,4-dicarboxylic acid) and ethylene glycol (Ethane-1,2-diol). It is commercially known as Terylene. The reaction for preparation of Terylene can be shown as:



In Terylene various polymer chains are connected together by strong intermolecular forces, i.e., dipole-dipole interactions, next stronger to hydrogen bonding, as;



Properties of Terylene:

- Terylene has high mechanical strength and dimension stability.
- It is a very strong fibre and will suffer very little loss in strength when wet.
- It is elastic in nature and possesses the property of high crease resistance.
- It is stable in the temperature range of $-40 - 100^{\circ}\text{C}$.
- It shows creep and abrasion resistance and good insulating properties.
- It shows low water absorption and at room temperature, it is resistant to water, dilute acids, salts, aliphatic and aromatic hydrocarbons and alcohols.

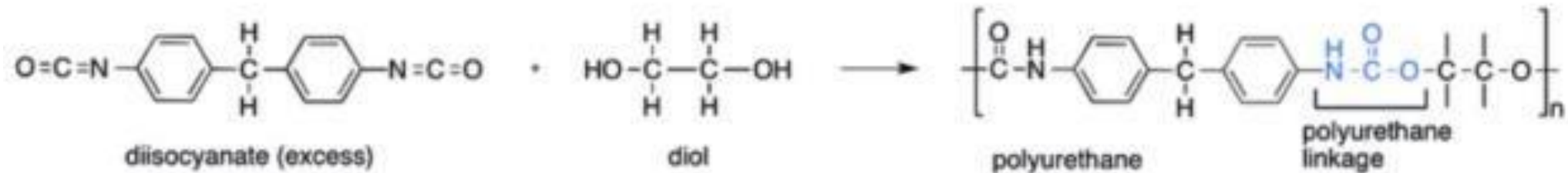
Polyethylene Terephthalate is used in various packaging applications, and the main ones are mentioned below:

- Due to the excellent water and moisture barrier material of Polyethylene Terephthalate, the **plastic bottles** are made from PET, and those are widely used for **carbonated soft drinks and mineral water**
- The high mechanical strength having in it makes Polyethylene Terephthalate films ideal for its use in tape applications.
- Non-oriented PET polymer sheet can be thermoformed to make packaging blisters and trays
- Together with other physical properties, its chemical inertness has made it particularly suitable for **food packaging** applications
- Other various packaging applications include microwavable containers, rigid cosmetic jars, transparent films, and many more.
- PET monofilament is primarily used for the production of mesh fabrics for screen printing, bracing wires for agricultural applications (greenhouses), filters for oil and sand filtration, woven/knitted ties, filter cloths, and other related industrial applications.
- PET/PETE has a wide range of applications in the textile industry. Polyester fabrics exhibit strong, flexible, and offer the additional **benefit of fewer wrinkles and shrinkage** over cotton. Polyester fabrics are reduced-wind, lightweight, drag-resistant, and more resistant to tears.
- Thanks to high structural and dimensional stability, good electrical insulating properties, polyethylene terephthalate are widely used in the electrical and electronics industry. It is an effective polymer to replace thermosets and die casts metals in applications such as solenoids, smart meters, **electrical encapsulation**, photovoltaic parts, solar junction boxes, and more. The outstanding flow characteristics of polymers enable design freedom and miniaturization to produce high-performance parts.

- PET polymer is being used successfully in several applications in the **automotive industry**. It is currently being employed in the applications, including wiper arm and gear housings, engine cover, headlamp retainer, and connector housings.

Polyurethane (PU or PUR)

- Polyurethanes can be prepared via the chemical reactions between **diisocyanates (that contain at least two isocyanate groups per molecule)** and **polyols** (that contain at least two hydroxyl groups per molecule).
- These reactions usually require the presence of a catalyst or some ultraviolet light in order to overcome the activation energy barrier.



- Polyols, by themselves, can also be considered polymers. For example, polyether polyols can be prepared by subjecting propylene oxide and ethylene oxide to copolymerization along with an appropriate polyol precursor. It can also be noted that the preparation of polyester polyols is quite similar to that of polyether polyols. However, for the production of polyurethanes, the chain length of the polyol and the functionality of the polyol must be controlled. These factors are known to contribute to the properties of the final polyurethane

products. For example, the polyols whose molecular weights lie in the hundreds yield rigid polyurethanes whereas the polyols whose molecular weights lie in the thousands yield relatively flexible polyurethanes. Thus, the chain length of the polyol used can be considered a factor that contributes to the flexibility of the polyurethane product.

Properties of polyurethanes:

- are highly dependent on the manner in which they are produced. For example, if the **polyol chain** (which is used as a raw material for the preparation of the polyurethane) is long and flexible, the final product will be soft and elastic.
- On the other hand, if the **extent of cross-linking** is very high, the final polyurethane product will be tough and rigid. The cross-linked structure of polyurethanes generally consists of three-dimensional networks which attribute very high molecular weights to the polymer. This structure also accounts for the thermosetting nature of the polymer, since polyurethane typically does not soften or melt when exposed to heat.

Advantages of Polyurethanes

- Polyurethanes have the **ability to be made into foams** (which is one of their most desirable properties). This is done by facilitating the production of a gas (usually carbon dioxide) during the urethane polymerization process.
- Another advantage of polyurethane is that high-density microcellular foams of the polymer can be produced without any blowing agents.

Applications of Polyurethane

- The primary application of polyurethane is in the **production of foams**. These foams are used in a variety of materials such as upholstery fabrics, domestic furniture, and refrigerator sheets.
- Polyurethane is also used in some garments.
- Polyurethane mouldings are also used in columns and door frames. In fact, it is not uncommon for such mouldings to be employed in window headers and balusters.
- The low-density foams of polyurethane which exhibit flexibility are widely used in mattresses and other forms of **bedding**. They are also used in **automobile seats** and upholstery.
- Flexible polyurethane is also used in the manufacture of partially elastic straps and bands.
- The low-density elastomers of polyurethane are widely used in the footwear industry.
- Another notable application of polyurethane is in the manufacture of bathroom and kitchen sponges. It is also used in seat **cushions and couches**.
- Flexible polyurethane foam is widely used as padding in a wide range of consumer and industrial items including bedding, underlay carpets, vehicle interiors, chairs, and packaging. This type of polyurethane foam can be produced in virtually any shape and firmness.

- It is known to be lightweight, comfortable, and durable. Rigid polyurethane foams are used in highly energy-efficient and flexible insulations. These foams are known to significantly reduce energy costs in residential and commercial properties.

Types of rubber

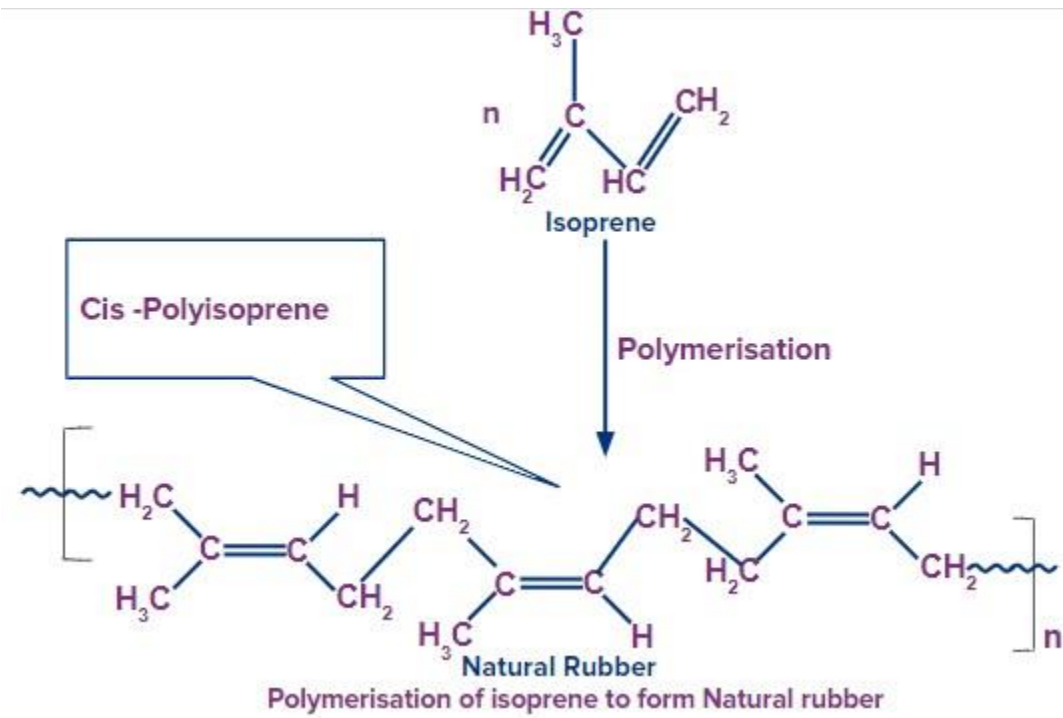
Rubber is an elastomer that can be obtained either naturally(natural rubber) or can be chemically produced in a laboratory(synthetic rubberlike- neoprene, butyl rubber etc). Broadly speaking, rubber can be classified into two categories namely:

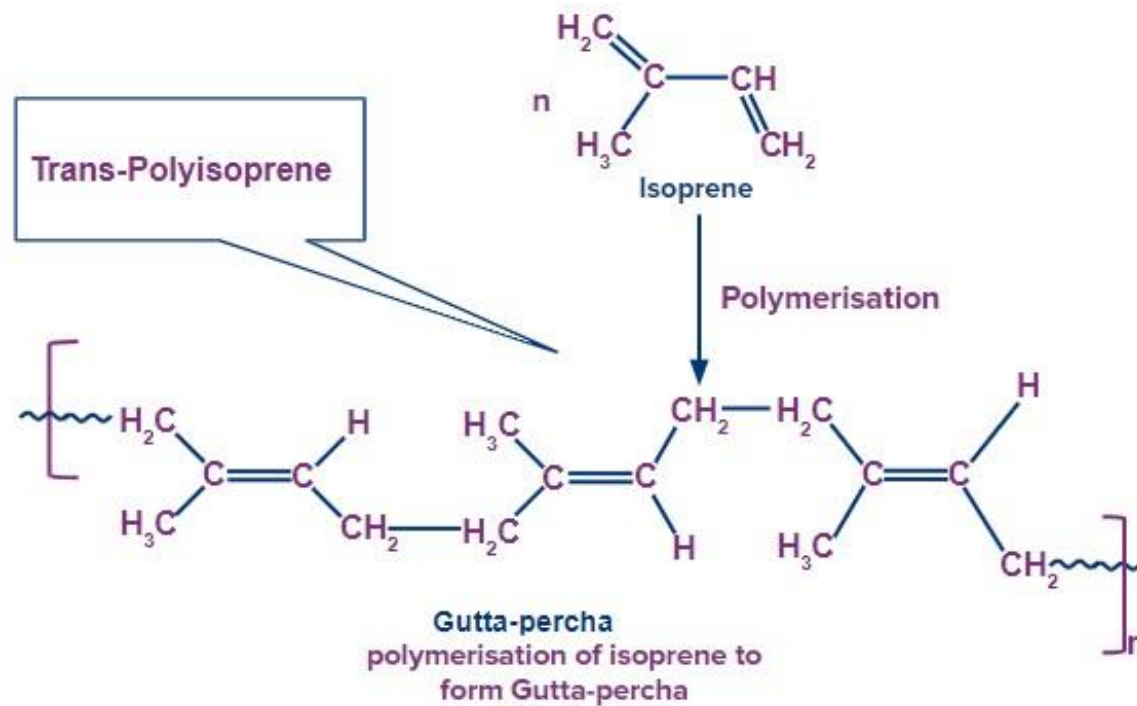
- 1.Natural rubber
- 2.Synthetic rubber

Natural rubber and its preparation

Natural rubber is manufactured from rubber latex, which is a colloidal dispersion of rubber in water. Natural rubber is a polymer of isoprene

(2 - *methyl* - 1, 3 - *butadiene*) with a chemical formula (C_5H_8) is joined together forming long polymer chain of *cis* - 1, 4 *polyisoprene* which is also known as natural rubber. India including the countries like Thailand, Indonesia, and Malaysia are one of the top natural rubber producing countries in the world.





Gutta-Percha is the trans isomer of isoprene. It is used to **fill tooth cavities** to prevent reinfection.

Properties of natural rubber:

- Soluble in non-polar solvents
- Non-resistant to attack by oxidising agents.
- High water absorption capacity.

Synthetic rubber and its preparation

Synthetic rubbers are artificial rubber produced chemically mainly from petroleum by-products and natural gas. Examples of synthetic rubber include **neoprene, Buna-N, Buna-S**, etc.,

Neoprene:

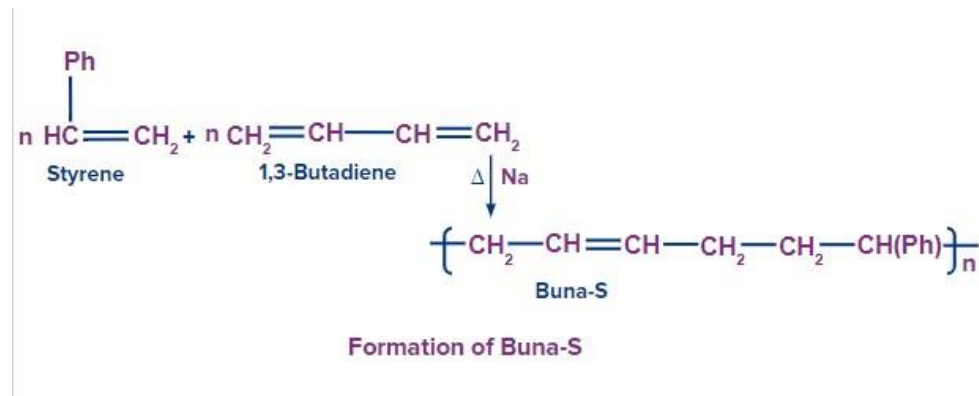
- It is obtained **by the free-radical polymerisation of chloroprene**
- Chloroprene exhibits properties like stability to aerial oxidation, and resistance to oil, gasoline and other solvents.
- It is used in the manufacturing of shoe heels, surgical instruments, diving suits, hoses, etc.



Formation of Neoprene

Buna-S:

- It is obtained by the copolymerisation of **1, 3 butadiene and styrene** in the presence of high temperature and sodium catalyst.
- It is used in manufacturing **tyres, waterproof shoes**, etc.,



Buna-N:

- It is obtained by the copolymerisation of **1, 3 butadiene and acrylonitrile** in the presence of high temperature and sodium catalyst.
- It is rigid and resistant to the swelling action of petrol and oils.
- It is used in making oil seals, tank linings, etc.

Properties of synthetic rubber:

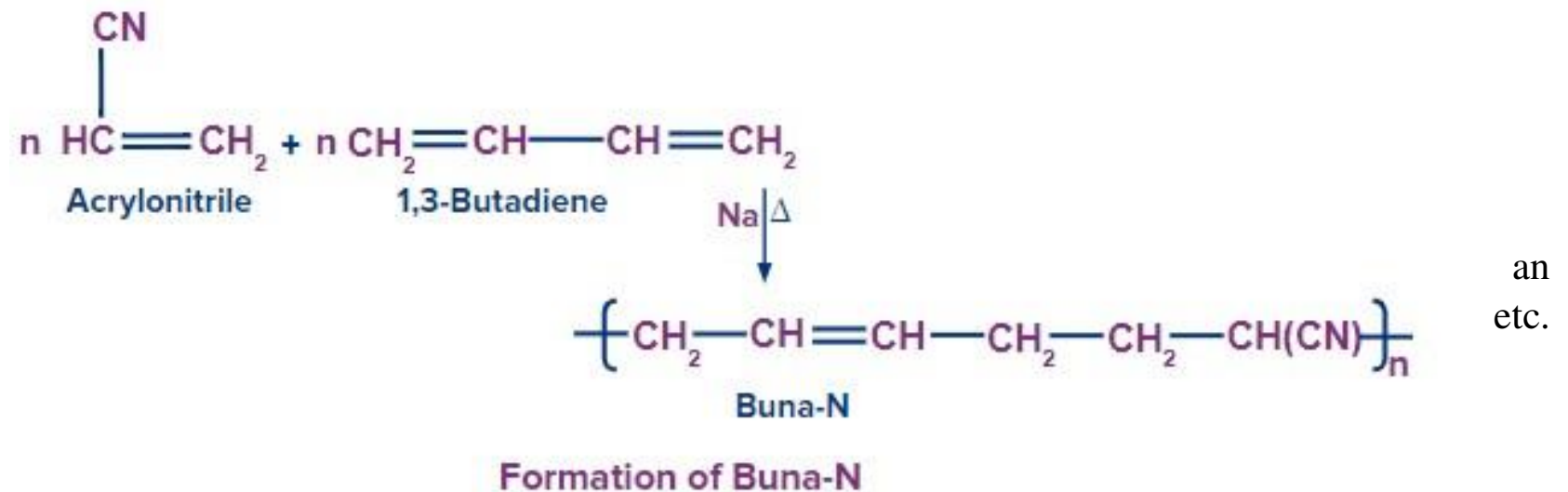
- Low-temperature heat resistance
 - Improvement in heat ageing
 - Excellent heat resistance.
- ### Uses of rubber

Rubber due to its properties like- waterproof, slip-resistance nature, act as insulator, high tensile strength, elasticity it can be used for different purposes which including:

- In the automobile industry for making **seats, airbags, padding in brakes** etc.
- In the clothing industry to produce **expandable clothes** like- cycling shorts, wetsuits etc.
- In the construction industry in the form of **tubes, elevator belts** etc.
- In the manufacturing of consumer goods like- **footwear, eraser** etc.

CONDUCTING POLYMERS

- Conducting polymers are organic polymers that conduct electricity. Until 1970, all organic polymers were used in electrical, electronic and other applications as insulators, taking advantage of their excellent insulation properties.
- Thus, organic polymers having electrical conductance of the order of conductors are now called as conducting polymers.
- Conducting polymers have been classified into two types:
 1. ExtrinsicalllyConducting Polymers
 2. Intrinsically Conducting Polymers



1. Extrinsically Conducting Polymers

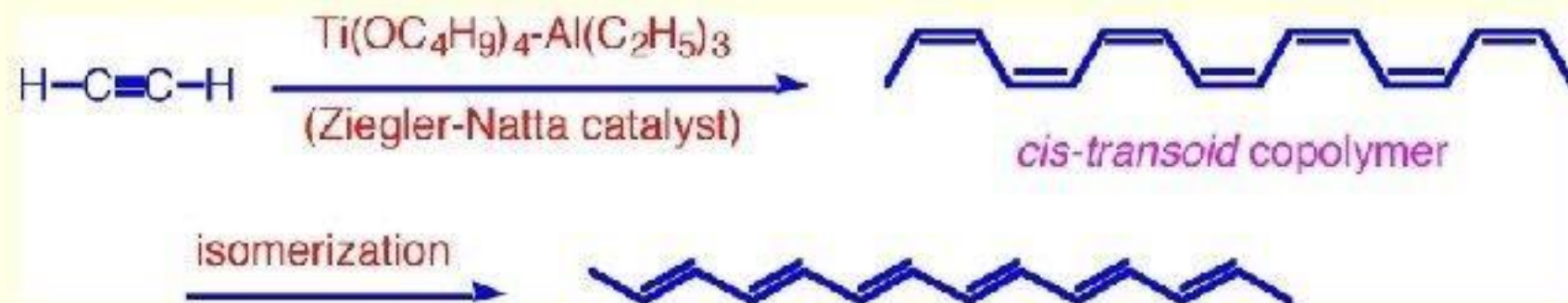
- They are prepared by mixing **conducting fillers like metal fibres , metal oxides or carbon black** with insulating polymers.
- These are also called as conductive element filled polymers.
- Here, insulating **polymer forms the continuous phase and added fillers form the conducting network**. A minimum concentration of conducting filler has to be added so that the polymer starts conducting.
- The **conductivity in this type of polymer is not due to the matrix polymer but due to conducting fillers** which are added.

2. Intrinsically Conducting Polymers

- In these type of polymers, **conductivity is due to the organic polymers themselves**.
- They conduct electricity **when doped with oxidizing or reducing agents or protonic acids**.
- The factor responsible for conductance in these polymers are **conjugated electrons**.
- Organic polymers with highly de-localized π -electrons having electrical conductance of the order of conductors are called as inherently or intrinsically conducting polymers or synthetic metals.

Synthesis of Polyacetylene

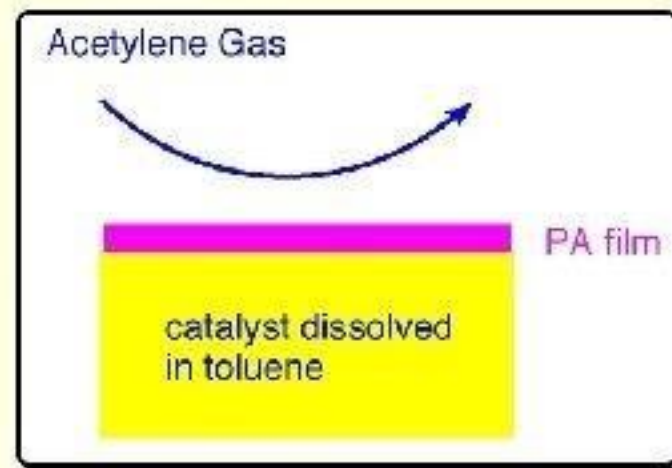
By Ziegler-Natta Catalyst



Effect of Temperature:

At $-78\text{ }^\circ\text{C}$ or below: all-*cis* PA

At $180\text{ }^\circ\text{C}$ or higher: all-*trans* PA

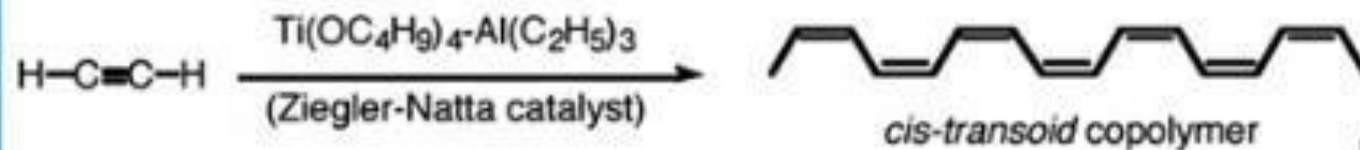


Polyacetylene (C_2H_2)_n:

Synthesis: The controlled synthesis of each isomer of the polymer, cis-polyacetylene or trans-polyacetylene, can be achieved by changing the temperature at which the reaction is conducted.

When acetylene gas is bubbled through heptane /toluene solvent containing Ziegler-Natta catalyst, Polyacetylene solid film is formed at the gas-liquid interface.

By Ziegler-Natta Catalyst



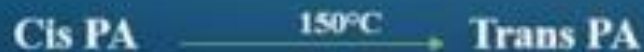
isomerization



Effect of Temperature:

At -78 °C or below: all-cis PA

At 180 °C or higher: all-trans PA



Trans-Polyacetylene:

Properties:

1. Insoluble and infusible and possess high porosity.
2. Sensitive to air, moisture and sunlight.
3. Light in weight and flexible.
4. It is a polymer with band gap of 1.5 eV
5. It is a semiconductor at room temperature with conductivity of $10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ for cis form and $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$.
6. It becomes an organic metal (metallic type of conductor) when doped with electron acceptors like I_2 , SbF_5 or AsF_5 with conductivity of $10^5 \text{ ohm}^{-1} \text{ cm}^{-1}$ (oxidation). It can also be doped with electron donors like Na, K, Cs, or Rb (reductive)

Trans-Polyacetylene:

Doping:

Conductivity can be increased by doping (adding impurity) the polymer.

Oxidative Doping using I_2 , SbF_5 or AsF_5 :

If electrons are taken away from the HOMO of the polymer then it is p-type of doping (oxidation). When polymer is doped with an oxidant (e-acceptor), it acquires positive charge and the acceptor gets negative charge

Reductive Doping using Na, K, Cs, or Rb:

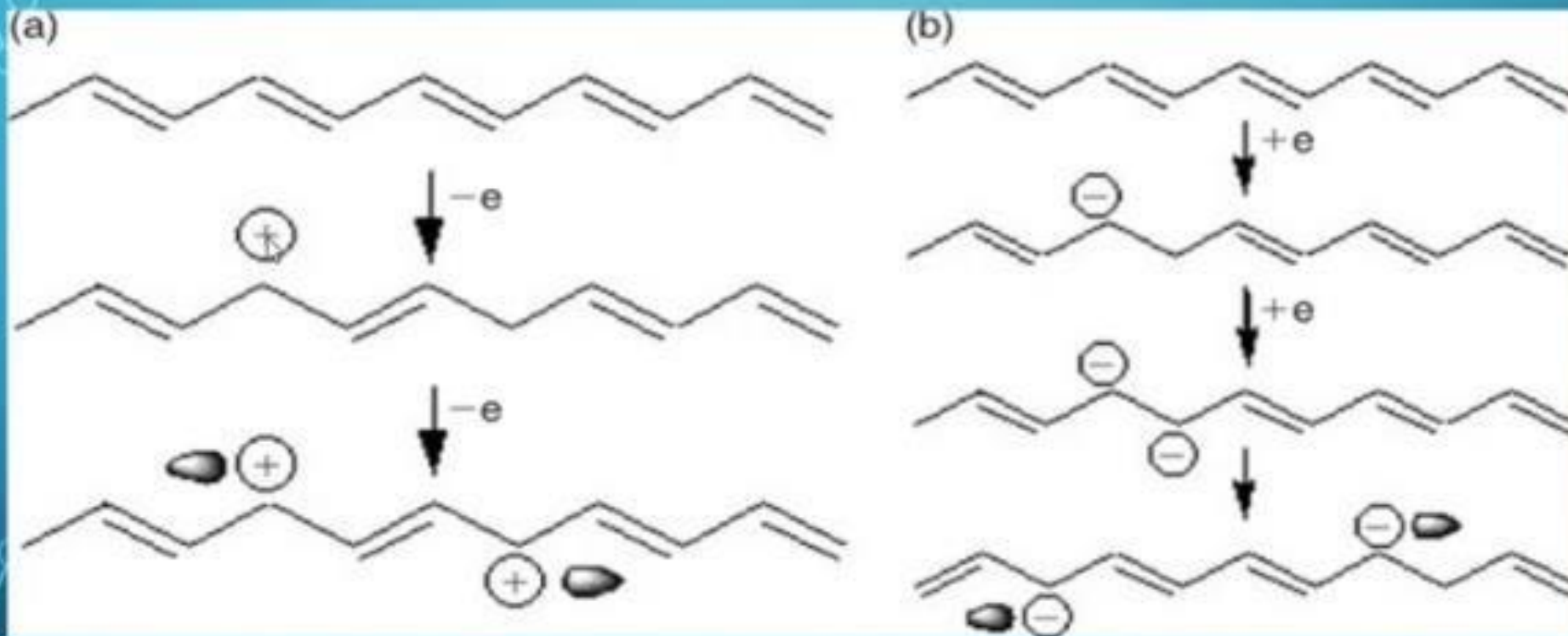
If electrons are added to the LUMO of the polymer then it is n-type of doping (reduction). When polymer is doped with a reductant (e-Donor), it acquires negative charge and the donor gets positive charge



Trans-Polyacetylene:

(a) Oxidative Doping

(b) Reductive Doping:



Trans-Polyacetylene:

Applications:

1. Used as light weight electrodes for rechargeable batteries.
2. Conducting films and powders.
3. Corrosion resistant paints/ antistatic coatings
4. Used in gas sensors, radiation and thermal sensors
5. Information storage devices and micro actuators.
6. Compact capacitors
7. Antistatic substances for photographic films
8. Electromagnetic shielding for computers, smart windows.
9. In solar cells, LEDs, and in mobile/television displays.





cis-polyacetylene

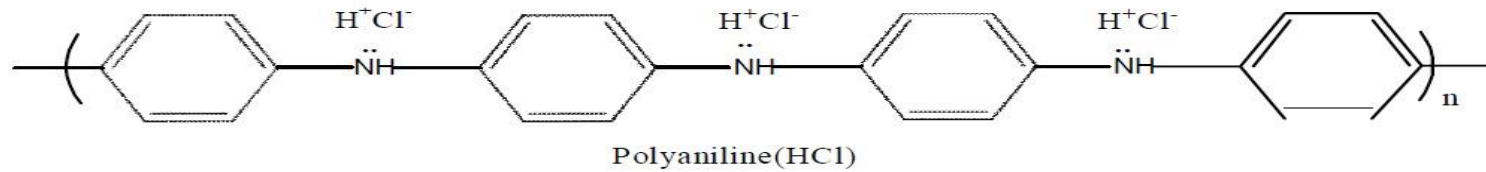


trans-polyacetylene

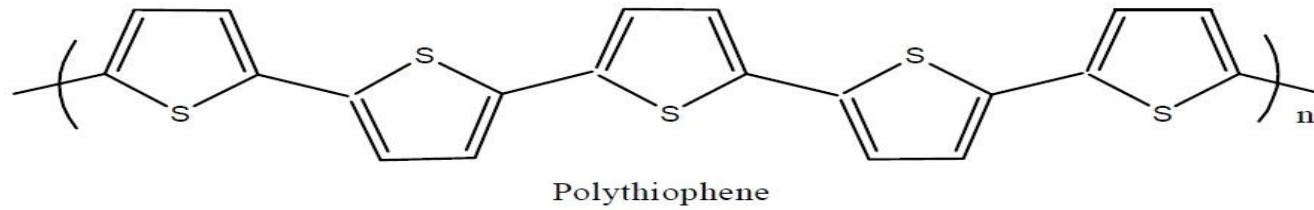
cis - branches on same side as double bond

trans - branches on opposite sides

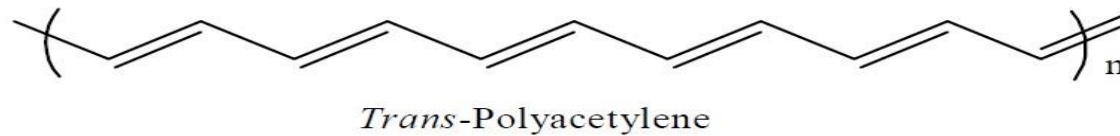
1. Polyaniline



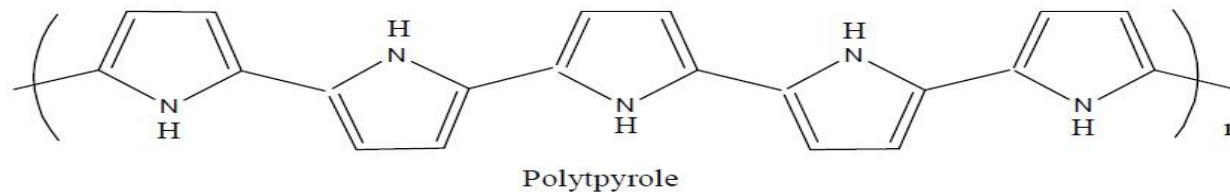
2. Polythiophene:

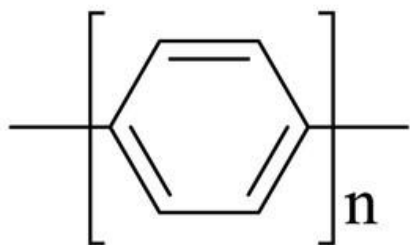


3. *Trans*-Polyacetylene

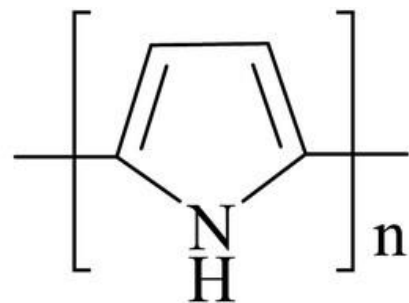


4. Polypyrrole:

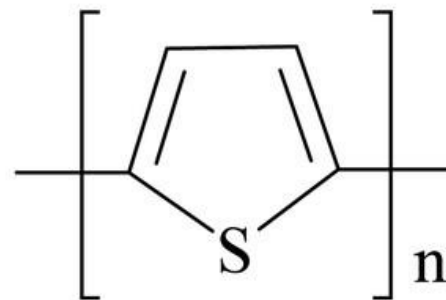




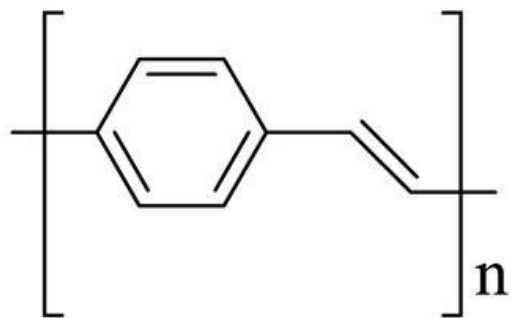
poly(p-phenylene)



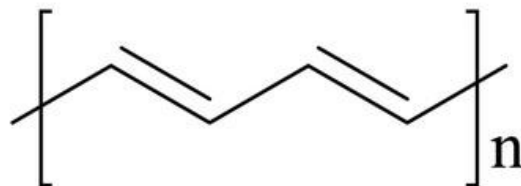
Polypyrrole



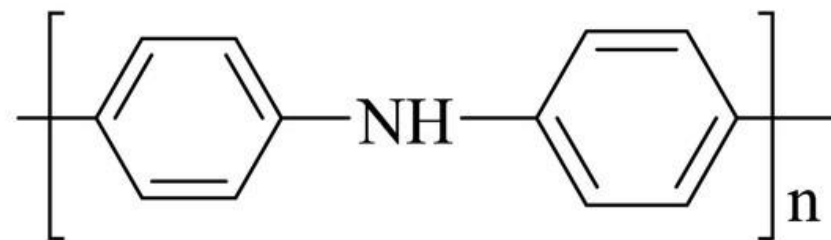
Polythiophene



poly(p-phenylene vinylene)



Polyacetylene



Polyaniline

Mechanism of Conduction

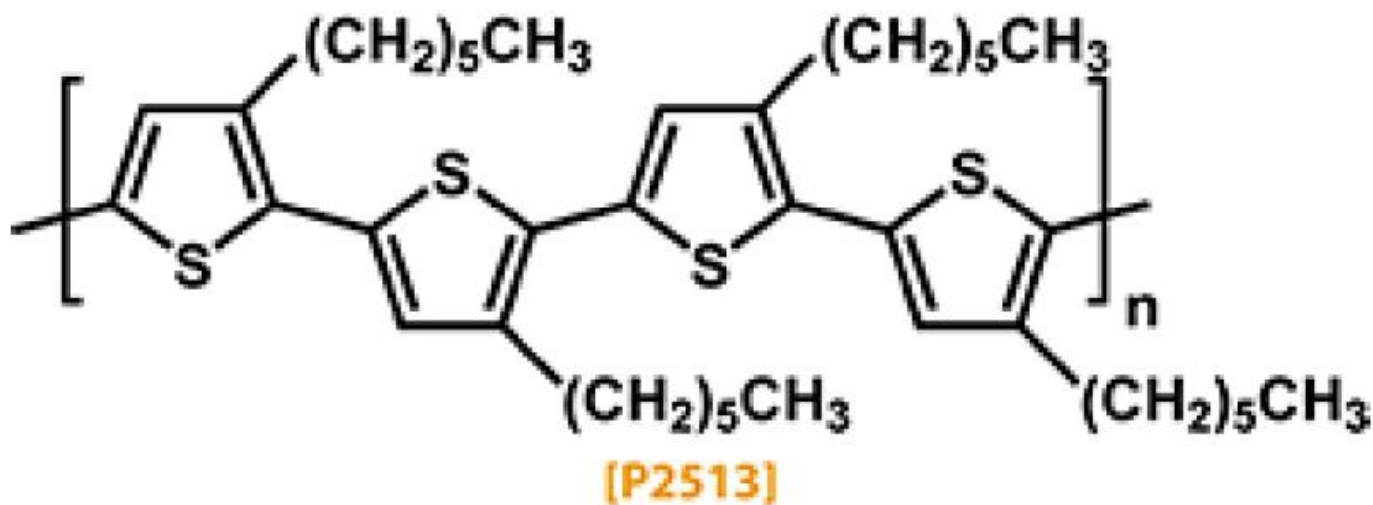
- These conjugated organic polymers in their pure state are insulators or semi-conductors. The π - electrons are normally localized and do not take part in conductivity.
- But, these electrons delocalize on doping and conduct electricity. The dopant may be oxidizing or reducing agent or protonic acid. Accordingly, they are called as *p*-doping, *n*-doping or H-doping polymers.
- In practice, most organic conductors are doped oxidatively to give p-type materials. The redox doping of organic conductors is similar to the doping of silicon semi-conductors with electron rich phosphorous or electron poor boron atoms to create n-type and p-type semi-conductors, respectively.

Applications of Conducting Polymers

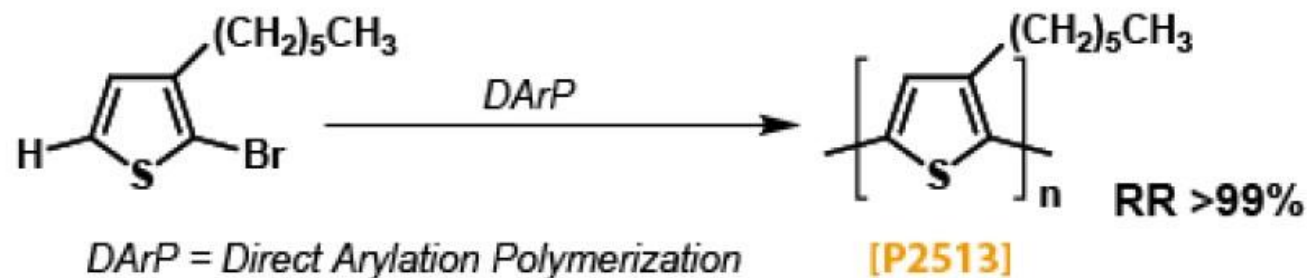
- In antistatic materials and as **electrode materials** in rechargeable batteries.
- In **light emitting diodes and display devices**.
- As **conductive track** on printed circuit boards (Polyaniline).
- As resistors for lithography (emeraldine base).
- In **information storage devices**.
- As humidity **sensors**, gas sensors, radiation sensors.
- In electro-chromic display windows.
- In **fuel cells** as electro-catalytic materials.
- As membrane for **gas separation**.

3.9 What is P3HT polymer?

- Regio regular poly(3-hexylthiophene-2,5-diyl), commonly known as P3HT, is a popular low band gap polymer donor with applications in organic photovoltaics, polymer solar cells, OLEDs and OFETs. Poly(3-hexylthiophene) (P3HT) is widely useful in organic electronics research fields, because it is one representative material of soluble organic semiconducting polymers. Normally performance of an electronics material is sensitive to the quality of the material.



3.9.1 Preparation and Applications



The data is extracted from Ref. 2)

Method	M_n (PDI)	RR /%	T_m (°C)	μ_{\max} (cm ² /V·s)
DAP	33,000 (1.8)	99.5	237	0.19
Rieke	25,000 (1.3)	95.5	224	0.02
GRIM	88,000 (1.5)	98.0	234	0.11

- P3HT: Hole transport material (HTM) Usable for a solution processable PSC device
Realizes high power conversion efficiency
- P3HT: p-Type semiconductor. Usable for a solution processable OFET device
- P3HT: Donor material. Usable for a solution processable OPV device. Fabricates a bulk heterojunction (BHJ) with a highly soluble donor and acceptor