



**Polymers:** Introduction, classification of polymers, synthesis and conducting mechanism of polyaniline and its commercial applications.

**Polymer** is a giant or macromolecule formed by the repeated union of several simple molecules (monomers).

**Ex.** Polyethylene (-CH<sub>2</sub>- CH<sub>2</sub>)<sub>n</sub>, Polystyrene (-CH<sub>2</sub>- CHC<sub>6</sub>H<sub>5</sub>-)<sub>n</sub>, Teflon etc.

The repeated units in the polymer chain are linked through strong covalent bonds. The average molecular mass of a polymer is normally in the range of  $10^3$ - $10^7$ .

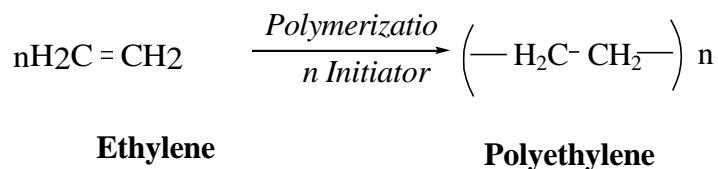
## Monomers:

A monomer is simple molecule having two or more bonding sites through which each can link to other monomers to form a polymer chain. Monomers are often called as “Building blocks” of a polymer chain.

**Ex:** Ethylene, Styrene, Vinyl chloride etc.

## Polymerization:

The process by which the monomer molecules are linked together to form a macro or giant molecules are called polymerization. All polymerization reactions need suitable initiators.



# **CLASSIFICATION OF POLYMERS**

The polymers are classified based on their sources, thermal behaviour, mechanism and existing forms/properties are as follows.

## 1. Based on the source

<b>a. Natural polymer</b>	<b>b. Synthetic polymer</b>
The polymer which are obtained from natural sources such as plants and animals. Ex. Cotton, Wool, Cellulose, Natural rubber, leather etc.	The polymers which are synthesized from simple molecules. Man-made polymers Ex. PVC, Polyethylene, Polystyrene, Nylon etc





## 2. Based on thermal behaviour

a. Thermoplastic polymer	b. Thermosetting polymer
The polymers are soft on heating and hard on cooling.	The polymers undergo chemical changes and cross linking on heating and become permanently hard, rigid and infusible.
The process carried out many times Without affecting their chemical properties	Once set, cannot be reshaped Chemical properties changes
<b>Ex.</b> Polyethylene, PVC, Teflon etc.	<b>Ex.</b> Phenol-formaldehyde resin, Urea-formaldehyde resin, epoxy resins etc.

## 3. Polymerization mechanism

a. Addition polymerization	b. Condensation polymerization
Self-addition of several monomers to each other without elimination of by-products.	The polymers which are formed by condensation reaction through functional groups of monomers with continuous elimination of by-products.
<b>Ex.</b> PVC, Polyethylene, Polystyrene, etc.	<b>Ex.</b> Polyesters, Nylon, P-F resin, U-F resin etc.

## 4. Based on their properties/structure

a. Elastomers	b. Fibres	c. Plastics	d. Resins
The polymers which undergo a very large elongation when pulled, but return to the original length on release of force	Fibres are long, thin and thread like polymer chain which do not undergo starching or deformation	Molded into desired products by the application of heat and pressure	Low molecular mass polymers
Polymer chains of elastomers are long, coiled and entangled.	Long chains held up together by H-bonding	<b>Ex.</b> Plexiglass, PVC, Teflon etc.	Exists in the form of Liquid or solid
No intermolecular forces except weak van der walls forces.	Fibre-forming materials may be synthetic or natural ones.		Used as adhesives or molding powder.
<b>Ex.</b> Natural rubber, Buna S, silicon rubber etc.	<b>Ex.</b> Wood, Cotton, Jute, Nylon 6, Terylene etc.		<b>Ex.</b> P-F resin, U-F resin, Epoxy resins etc.

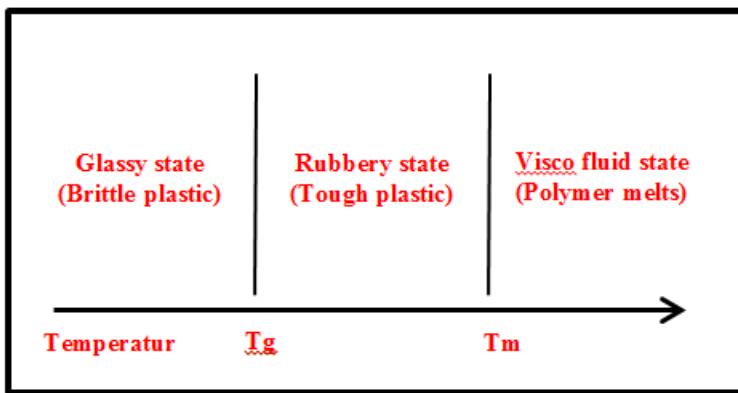


## GLASS TRANSITION TEMPERATURE

When an amorphous polymer is heated, the temperature at which the polymer structure turns "viscous liquid or rubbery" is called the Glass Transition Temperature,  $T_g$ . It is also defined as a temperature at which amorphous polymer takes on characteristic glassy-state properties like brittleness, stiffness and rigidity (upon cooling). This temperature (measured in  $^{\circ}\text{C}$  or  $^{\circ}\text{F}$ ) depends on the chemical structure of the polymer and can therefore be used to identify polymers.

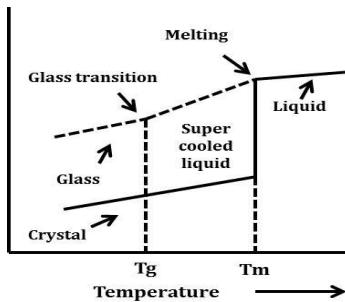
- Amorphous polymers only exhibit a  $T_g$ .
- Crystalline polymers exhibit a  $T_m$  (melt temperature) and typically a  $T_g$  since there is usually an amorphous portion as well ("semi"-crystalline).

The value of  $T_g$  depends on the mobility of the polymer chain, and for most synthetic polymers lies between 170 K to 500 K.



### Effect of temperature on polymer:

The hard and brittle state is the glassy state and soft-flexible state is the viscoelastic state. If viscoelastic state of polymer is heated further, the polymer becomes a viscous liquid and can flow. This state is known as viscofluid state.





- Below Tg the molecules in polymer do not move apart and do not have movements within the molecular chains. Therefore, a stress transfer property is lost and polymer below Tg is brittle.
- Above Tg the polymers in the viscoelastic state have flexibility or stress transfer properties.
- Above Tm, the kinetic energy of the polymer molecules is high enough to cause movement with the chain segments as well to move from one position to another. Therefore, this state has flow character like liquids.

Applications include Identifying the Tg of polymers is often used for quality control and research and development. Also, it is an important tool used to modify physical properties of polymer molecules.

### **STRUCTURE AND PROPERTY RELATIONSHIP IN POLYMERS**

Polymer structure can affect the chemical, mechanical, electrical, and optical properties

#### **Effect of Structure on properties of polymer:**

<b>Effect on chemical properties:</b>	1. Effect on Solubility  2. Chemical reactivity  3. Ageing and weathering  4. Diffusion	1a. Polarity  1b. Molecular weight  1c Degree of Crosslinking
<b>Effect on mechanical properties:</b>	1. Toughness  2. Strength  3. Elasticity	
<b>Effect on electrical properties:</b>	1. Electrical conductivity	
<b>Effect on optical properties:</b>	1. Amorphous & crystalline	

#### **EFFECT ON CHEMICAL PROPERTIES:**

##### **1. Effect on solubility or swelling behaviour:**

**1a. Polarity:** Polymers having polar groups (OH-, COOH- etc.) will dissolve easily in polar



solvents like water, alcohol, aldehydes and ketones etc. Polymers having non polar groups (alkyl, aryl, etc.) will be more soluble in non-polar solvents like benzene, toluene etc.

1b. Molecular weight: Solubility of a polymer in a particular solvent decrease with increase in molecular weight of polymer.

**1c. Degree of cross linking:** More the degree of cross linking in the polymer, lesser will be the solubility.

1) **Chemical reactivity** of a polymer changes by changing the nature of functional group in the polymers. Example: - a) Nylon and polyester can undergo hydrolysis because they have amide and esteric linkage. b) Teflon is chemically inert because it has only C-C and C-F bonds. c) Rubber have C=C, which can easily be attacked by oxygen and ozone.

2) **Ageing and weathering (light and heat):** Different polymers shows different resistance power against weathering. Example: - a) Teflon has more resistance power towards heat than PVC. b) Teflon and cellulose degraded under high energy radiations.

3) **Diffusion:** Amorphous polymers are non-uniform in arrangement of monomers, while crystalline polymers have regular arrangement. So amorphous polymers have more free space, hence more diffusion is possible in Amorphous polymers.

## **EFFECT ON MECHANICAL PROPERTIES**

1) **Effect on strength and toughness:** Strength of polymer depend upon magnitude of intermolecular force of attraction between monomers. More the magnitude of intermolecular force of attraction more will be the strength of the polymer. Intermolecular force of attraction is of the order of Cross linked  $\geq$  Branched  $\geq$  linear. Order of strength is also same.

**Reason-**The movement of molecules over each other decreasing due to increase in the no of bulky groups (side groups), so the strength of polymer also increases. Intermolecular force are more in polymers having polar groups than in polymers with non-polar groups. Crystalline polymers have high strength than amorphous.

2) **Effect on stress (load bearing capacity):** The extent of stress is determined by stress/strain ratio. Where stress=Applied force strain =Extent of stretch



- 3) **Effect on elasticity:** Amorphous polymers are more elastic than crystalline.

### **EFFECT ON ELECTRICAL PROPERTIES**

Plastic substances act as electrical insulators. Insulation property of polar polymers destroy in humidity because water has high dielectric constant, which raise the overall dielectric constant of polymer-water mixture. So resistivity decreases and electrical conductivity increases. In case of nonpolar polymer vice-a-versa is true.

### **EFFECT ON OPTICAL PROPERTIES**

Amorphous polymers are generally transparent because they have non-uniform arrangement of monomers.

Crystalline polymers may or may not be transparent because they have uniform arrangement of monomers.

### **Conducting Polymers:**

Organic Polymer that has delocalized pi electrons in their back bone and conduct electricity are called conducting polymers.

In polymer, electrons are localized and do not take part in conduction and also there a wide energy gap between valence band and conduction band. This makes polymer exhibit poor conductivity. But doping can delocalize the electrons responsible for conduction. The insulating polymer with conjugated backbone consisting of alternative double and single carbon-carbon bonds, can be converted into a conductor by doping it with either an electron acceptor such as  $I_2$ ,  $FeCl_3$  (oxidative dopant) or an electron donor such as sodium naphthalide (reductive dopant) or a protonating agent like HCl.

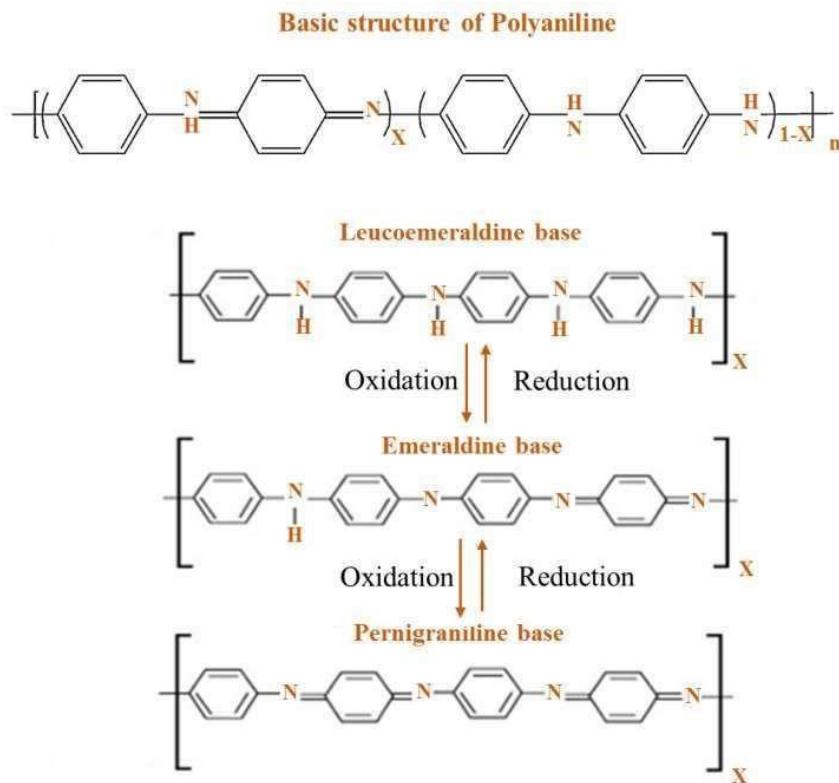
- i) Oxidative dopant takes away electrons from the  $\pi$ -backbone of polymer and creates holes in the chain, resulting in the increase of conductivity of polymer. Ex- Polyacetylene
- ii) Reductive dopant donates electrons to  $\pi$ -backbone of the polymer. These electrons are free to move along c-chain, resulting in the increase of conductivity of polymer. Ex- Polyacetylene.
- iii) Protonating agent creates positive and negative charges in the polymer chain, resulting in the increase of conductivity. Ex- Polyaniline.

## STRUCTURE & APPLICATION OF CONDUCTING POLYANILINE:

Polyaniline (PANI) is a famous conductive polymer, and it has received tremendous consideration from researchers in the field of nanotechnology for the improvement of sensors, optoelectronic devices, and photonic devices. PANI is doped easily by different acids and dopants because of its easy synthesis and remarkable environmental stability.

### Synthesis:

Monomer used in the preparation of PANI is Aniline. PANI can be prepared by electrochemical polymerization or by chemical oxidative polymerization



### Properties:

- The Synthesis of polyaniline nano-structure is facile.
- Variation in oxidative states with variation in their conducting properties.
- The emeraldine base polyaniline function as a semiconductor when doped with a protic acid.
- Leucoemeraldine are poor conductor of electricity.



**Applications:**

- Printed circuit board manufacturing
- PANI may be used as an electrode material
- Organic field transistor
- Polymer light diode
- Energy storage