

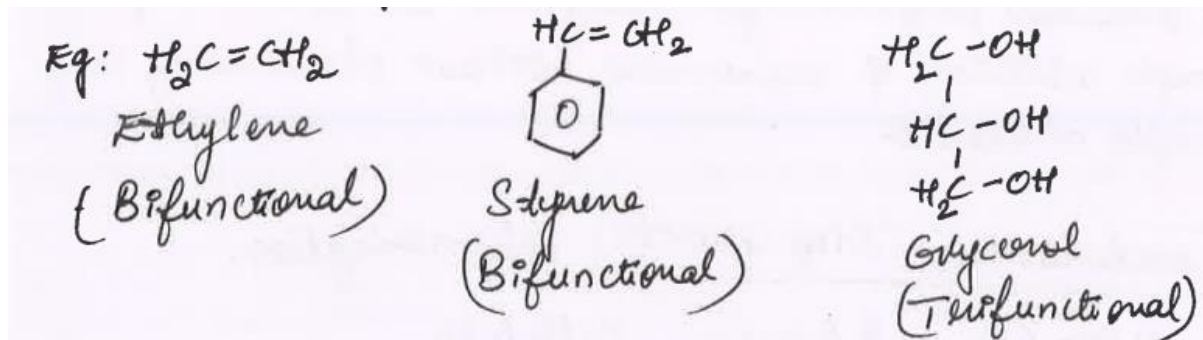
POLYMERS

- ❖ The term 'Polymer' is derived from ancient Greek;
Polus: meaning 'many'
Meras: meaning 'parts'
- ❖ The term 'polymer' was coined by Jöns Jacob Berzelius in 1833
- ❖ Polymers exhibit unique properties, such as;
 - Stiffness, strength, density
 - Heat resistance
 - Light weight nature
 - Corrosion resistance
 - Abrasion resistance
 - Electrical resistance
 - High strength - -to-weight ratio, etc.

Because of the above listed properties, polymers are used extensively in clothing, home furnishing, food packing, transportation, information technology, medical devices, coatings, adhesives, structural & engineering materials, etc.

❖ Terminologies:

- i) **Polymer:** It is a high molecular compound (or macromolecule) made by the combination of large number of repeating units called monomers.
- ii) **Monomer:** It is a simple molecule which combine together to form polymers
Monomers are called as 'building blocks' of polymer chain
Example: Ethylene, Vinyl chloride, adipic acid, etc.
- iii) **Polymerization:** It is a chemical process by which monomers are converted into polymers
- iv) **Degree of polymerization (n):** It is the total number of monomers present in a straight chain of polymer
High polymers: Polymers in which 'n' is very large (>10)
Oligomers: Polymers in which 'n' is less than 10
- v) **Functionality:** It is the number of binding sites or functional groups present in a monomer



***All simple molecules are not monomers. Justify.**

Ans: Simple molecules which have binding sites or functional groups only can act as monomers. Because, these binding sites are required for the combination of repeating units during polymerization process to form polymers.

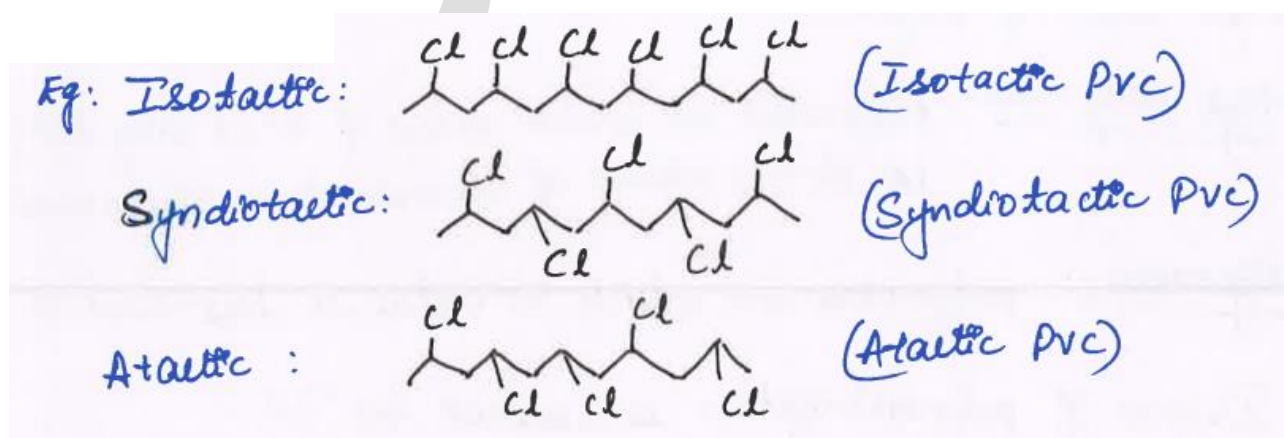
Therefore, only those simple molecules containing at least 2 binding sites (bifunctional) can act as monomers.

Example: Ethylene, Styrene, etc.

vi) Tacticity of polymers (Stereoregularity)

It refers to the arrangement of functional groups along polymer chain.

- Isotactic polymers** - The polymers in which all the side groups/functional groups are arranged on the same side of the main chain
- Syndiotactic polymers** - The polymers in which arrangement of functional groups is in alternating fashion around the main chain
- Atactic polymers** - The polymers in which arrangement of functional groups is random around the main chain



Molecular weight of polymers

Molecular weight of the polymer is directly related to the physical properties of polymers such as glass transition temperature (T_g), strength of polymer, etc.

***Actual molecular mass of a polymer cannot be calculated. Justify.**

(or Average molecular weight is calculated for a polymer. Justify)

In case of polymers, average molecular weight is calculated instead of actual molecular weight. Because,

- During the formation of polymers, different polymers have different degree of polymerization, i.e. different number of monomers and different polymer chain length
- Therefore, mass of each chain will be different.

Two ways of calculating average molecular weight of polymers;

- I. Number average molecular mass (\overline{M}_n)
- II. Mass average (weight average) molecular mass (\overline{M}_w)

Number average molecular mass (\overline{M}_n)

Definition: It is the mass obtained when total mass of all the molecules of a polymer sample is divided by the total number of molecules.

Suppose, in a particular sample,

N_1 molecules have molecular mass M_1 each

N_2 molecules have molecular mass M_2 each

N_3 molecules have molecular mass M_3 each, so on...

Then,

Total mass of all the N_1 molecules = N_1M_1

Total mass of all the N_2 molecules = N_2M_2

Total mass of all the N_3 molecules = N_3M_3 , so on....

Therefore,

$$\begin{aligned}\text{Total mass of all the molecules} &= N_1M_1 + N_2M_2 + N_3M_3 + \dots \\ &= \sum N_iM_i\end{aligned}$$

$$\begin{aligned}\text{Total number of all the molecules} &= N_1 + N_2 + N_3 + \dots \\ &= \sum N_i\end{aligned}$$

Hence, the number average molecular mass is given by,

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \dots}{N_1 + N_2 + N_3 + \dots}$$

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

\bar{M}_n is usually determined by **Osmotic pressure** method.

Mass average molecular mass (\bar{M}_w)

Definition: It is the mass obtained when sum of the products of mass of molecules and their respective molecular masses is divided by total mass of all the molecules.

Suppose, in a particular sample,
 N_1 molecules have molecular mass M_1 each
 N_2 molecules have molecular mass M_2 each
 N_3 molecules have molecular mass M_3 each, so on...

Then,
 Total mass of all the N_1 molecules = N_1M_1
 Total mass of all the N_2 molecules = N_2M_2
 Total mass of all the N_3 molecules = N_3M_3 , so on....

The products of total mass of different groups of molecules with their respective molecular masses will be,

$(N_1M_1 \times M_1)$, $(N_2M_2 \times M_2)$, $(N_3M_3 \times M_3)$

i.e. $N_1M_1^2$, $N_2M_2^2$, $N_3M_3^2$, etc.

Sum of the products = $N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \dots$
 = $\sum N_i M_i^2$

Total mass of all molecules = $N_1M_1 + N_2M_2 + N_3M_3 + \dots$
 = $\sum N_i M_i$

Hence, mass average molecular mass is given by,

$$\bar{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \dots}{N_1M_1 + N_2M_2 + N_3M_3 + \dots}$$

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

\overline{M}_w is generally obtained by,

- **Ultra-centrifugation**
- **Sedimentation**

Numericals on average molecular weight:

1. In a sample of a polymer, 100 molecules have molecular mass 10^3 g/mol, 250 molecules have molecular mass 10^4 g/mol, 300 molecules have molecular mass 10^5 g/mol. Calculate the number average and weight average molecular mass of the polymer. Calculate PDI and comment on it.

Solution:

$$\begin{aligned} N_1 &= 100, & M_1 &= 10^3 \text{ g/mol} \\ N_2 &= 250, & M_2 &= 10^4 \text{ g/mol} \\ N_3 &= 300, & M_3 &= 10^5 \text{ g/mol} \end{aligned}$$

$$\overline{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots}{N_1 + N_2 + N_3 + \dots}$$

$$\overline{M}_n = \frac{100 \times 10^3 + 250 \times 10^4 + 300 \times 10^5}{100 + 250 + 300} = 50,153 \text{ g/mol}$$

$$\overline{M}_w = \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2 + \dots}{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots}$$

$$= \frac{100 \times (10^3)^2 + 250 \times (10^4)^2 + 300 \times (10^5)^2}{100 \times 10^3 + 250 \times 10^4 + 300 \times 10^5}$$

$$= \frac{100 \times 10^6 + 250 \times 10^8 + 300 \times 10^{10}}{100 \times 10^3 + 250 \times 10^4 + 300 \times 10^5}$$

$$= \frac{(100 \times 1 + 250 \times 10^2 + 300 \times 10^4) 10^6}{(100 \times 1 + 250 \times 10 + 300 \times 10^2) 10^3}$$

$$\overline{M}_w = \frac{(3025100)10^6}{(32600)10^3} = 92,794.5 \text{ g/mol}$$

$$\text{PDI} = \frac{\overline{M}_w}{\overline{M}_n}$$

$$\text{PDI} = \frac{92,794.5}{50,153} = 1.85$$

Here, the sample has $\text{PDI} > 1$

Therefore, it is a **polydisperse polymer** having wide range of molecular masses

2. In a sample of a polymer, 20% of molecules have molecular mass 15000 g/mol, 35% of molecules have molecular mass 25000, and remaining molecules have molecular mass 20000 g/mol. Calculate the number average and weight average molecular mass of the polymer. Calculate PDI and comment on it.

$$\overline{M}_n = 20,750 \text{ g/mol}$$

$$\overline{M}_w = 21,385.5 \text{ g/mol}$$

$$\text{PDI} = 1.03$$

Polymer is monodispersed in nature because $\text{PDI} = 1$

Glass transition temperature (T_g)

Definition: The temperature at which a polymer is transformed from stiff, hard and glassy state to soft, flexible and rubbery state is called glass transition temperature.

- ❖ T_g is characteristic property of a polymer; every polymer has its own T_g value.
- In solid state, polymer chains occupy definite positions and hence there is no movement in the molecule.
- The polymer will be stiff, hard and glassy
- Polymers are amorphous solids; therefore, they don't have sharp melting point. They melt over a range of temperature

- On increasing temperatures beyond certain value, the chain segments within polymer start moving. This kind of motion where only chain segments move but not entire chain is called segmental motion.
- On further raise in temperature, the whole chain starts moving. It is called molecular motion.

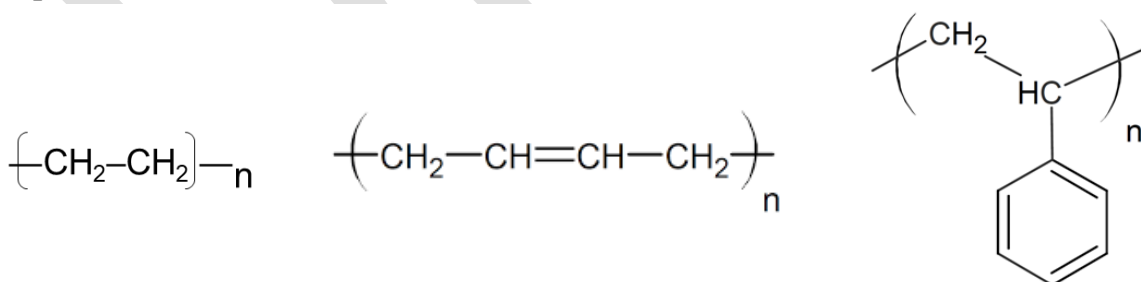
Factors affecting glass transition temperature (T_g)

- Flexibility of the chain
- Branching and cross linking
- Intermolecular forces
- Stereoregularity
- Molecular weight
- Addition of plasticizer

i) Flexibility of the chain

- Flexibility of the polymer chain and T_g are always inversely related
- Higher flexibility of a polymeric chain leads to higher segmental mobility and hence lower will be the T_g
- A polymer chain becomes flexible if there is free rotation along the chain
- Therefore, linear polymers having $-C-C-$, $-C-N-$, $-C-O-$ bonds (single bonds) have high degree of rotation and hence more flexible
- Rigid groups such as cyclic/aromatic ring or bulk groups, double bonds reduce flexibility of the chain by restricting the rotation and hence T_g is increased.

Examples:



(Question: Explain the effect of flexibility on T_g of polymer. Or Polystyrene has higher T_g value than polythene. Give reason.)

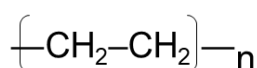
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ii) Branching and cross linking

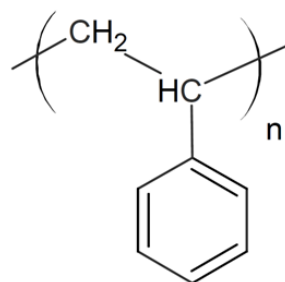
- Branching and cross linking increase the T_g value of polymers

- However, a small number of branches in the polymeric chains provides free volume for free rotation of chains and hence causes lower T_g value.
- Higher branching reduces free rotation, hence T_g will be high
- When the chains are cross linked through covalent bonds, there is almost no mobility of segments and chains. Therefore, T_g value increases considerably when there are cross links.

Examples:



Polyethylene: -110 °C



Polystyrene: +100 °C

iii) Intermolecular forces

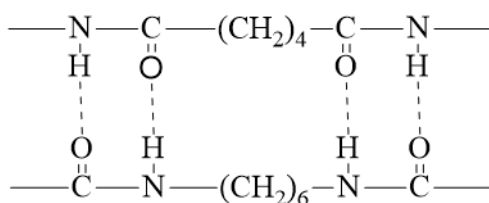
- The presence of intermolecular forces between molecules of polymer results in higher T_g value.
- Intermolecular forces arise due to polar groups, dipolar interactions, hydrogen bonding, etc. which exert strong force of attraction between neighbouring chains
- Therefore, chains are held together tightly, restricting segmental motion of the chains.
- Hence, T_g value increases.

Examples:

T_g of polypropylene (intermolecular forces): -18 °C

T_g of Nylon 6,6 (hydrogen bonding): 57 °C

T_g of Polyvinyl chloride (PVC, dipolar interactions between -C-Cl bonds: 80 °C



Nylon 6,6

iv) Stereoregularity of the polymer

- Polymers having stereoregularity in their structure will have higher T_g values

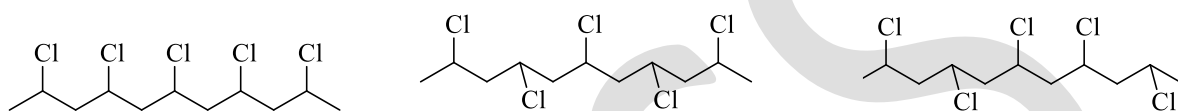
- Stereoregularity represents symmetry in polymer structure.
- When the structure is symmetric, chains are closely and strongly held together leading to increase in crystallinity
- Hence T_g value increases.
- Isotactic polymers are more symmetric than syndiotactic and atactic polymers. Therefore, they exhibit high T_g value

T_g value is in following order;

Isotactic polymers > Syndiotactic polymers > Atactic polymers

Example:

T_g of isotactic PVC > T_g of syndiotactic PVC > T_g of atactic PVC



v) Molecular weight

- Higher the molecular weight of polymer, higher is its T_g
- T_g increases with increase in molecular mass up to 20,000; beyond which it will have negligible effect on T_g
- When molecular weight is high, the long polymer chains coil and entangle with one another
- This restricts free mobility of the chains and results in higher T_g value
- Under low molecular weight, a greater number of small chains will have number of loose bonds; this results in fundamental/segmental motion, resulting in lower T_g

vi) Addition of plasticizer

- Addition of plasticizers decreases T_g value of a polymer
- Plasticizer molecules readily penetrate in between polymer chains and weaken the intermolecular forces of attraction
- Thus, segmental motion is achieved easily and T_g value decreases.

Example: Diisooctyl phthalate

PVC is extremely stiff; addition of diisooctyl phthalate (plasticizer) to PVC reduces its T_g value from 80 °C to below room temperature.

Other plasticizers are triceryl phosphate, dimethyl phthalate, triphenyl phosphate and camphor

Significance of T_g

- T_g value is the measure of flexibility of polymer. It is a kind of response exhibited by the polymer to mechanical stress. T_g will, therefore decide whether a polymer will behave like rubber or plastic at the operating temperature.
- At T_g, many polymers show an abrupt change in their physical properties. Thus, values of heat capacity, refractive index, coefficient of thermal expansion, etc. at T_g determine the usefulness of polymer over a temperature range.
- Knowledge of T_g helps in choosing right processing temperature for subjecting polymers into processes like moulding, calendaring and extrusion.
- Right processing temperature is the temperature range in which the polymer can be converted into useful finished products through different processing techniques.

Plasticizers: These are the substances used to decrease T_g. Plasticizer molecules can readily penetrate in between polymer chains to dilute the intermolecular forces of attraction.

Structure – Property relationship

The structure of polymer imparts different physical and mechanical properties to the polymeric material. These properties then decide their usefulness in various applications.

- I. Crystallinity
- II. Tensile strength
- III. Chemical resistance

I. Crystallinity

- Polymers are generally amorphous in nature.
- In polymers with certain degree of crystallinity, there is a short ranged orderly arrangement (crystallites) embedded in an amorphous matrix
- Linear polymers with more symmetry are highly crystalline
- Crystallinity decreases in branched polymers
- Homopolymers are more crystalline than copolymers
- Presence of polar groups in the molecule increases crystallinity, whereas bulky side groups decrease crystallinity
- This is because, polar groups facilitate intermolecular forces which hold the polymer chains together
- Polymers with high stereoregularity/symmetry, like isotactic polymers, exhibit high tensile strength
- Polymers with high molecular mass have high strength

- Higher crystallinity leads to sharp melting point, lower solubility, lower permeability to gases and liquids, higher chemical resistance, higher density and rigidity, etc.

Example:

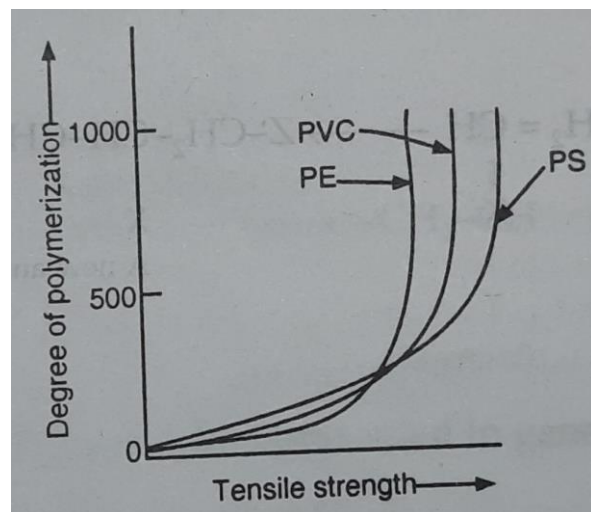
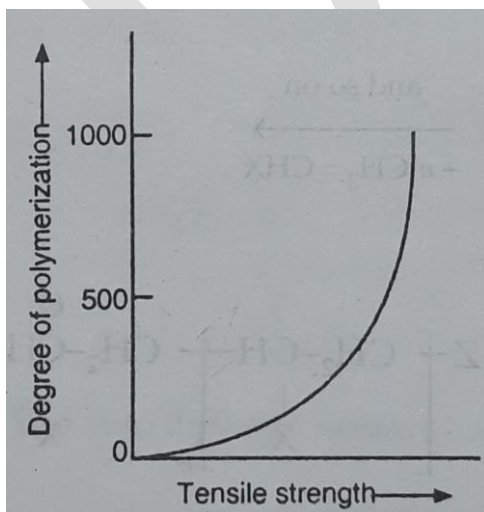
- Polythene is a linear polymer. It is more crystalline than polystyrene, which contains bulky side group
- Nylon is more crystalline due to intermolecular hydrogen bonding

II. Tensile strength

- Tensile strength is the maximum stress that the material can withstand.
- Tensile strength of a polymer depends on molecular weight
- It increases with increase in molecular weight, up to certain point and then it becomes constant
- Because, Van Der Waals force holding the chains increase the strength of polymer with increase in chain length or molecular weight
- At higher molecular weight, melt viscosity of polymer increases sharply
- The presence of polar groups such as $-OH$, $-C=O$, etc. increase the intermolecular force of attraction. This increases the strength of polymer

Example: Nylon

- If the chains are linked through covalent bonds, the mobility of chains is totally restricted. Such polymers will have high strength
- Example: Bakelite
- A polymer should have low melting viscosity, high tensile strength and impact strength to be more useful commercially



III. Chemical resistance

- Chemical resistance of polymer is its resistance to swell, soften and lose strength by a solvent or a chemical
 - Polymers having polar groups –OH, –COOH, etc. are soluble in polar solvents like water, alcohol, etc.
 - Polymers with non-polar groups are soluble in non-polar solvents
 - Chemical resistance of polymers increases with increase in crystallinity
 - This is due to denser packing of chains, which makes solvent penetration into the polymer structure difficult
 - Chemical resistance in polymers increases with high degree of cross linking
 - Higher molecular weight also contributed to higher chemical resistance
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Classification of polymers based on strength/magnitude of intermolecular forces:

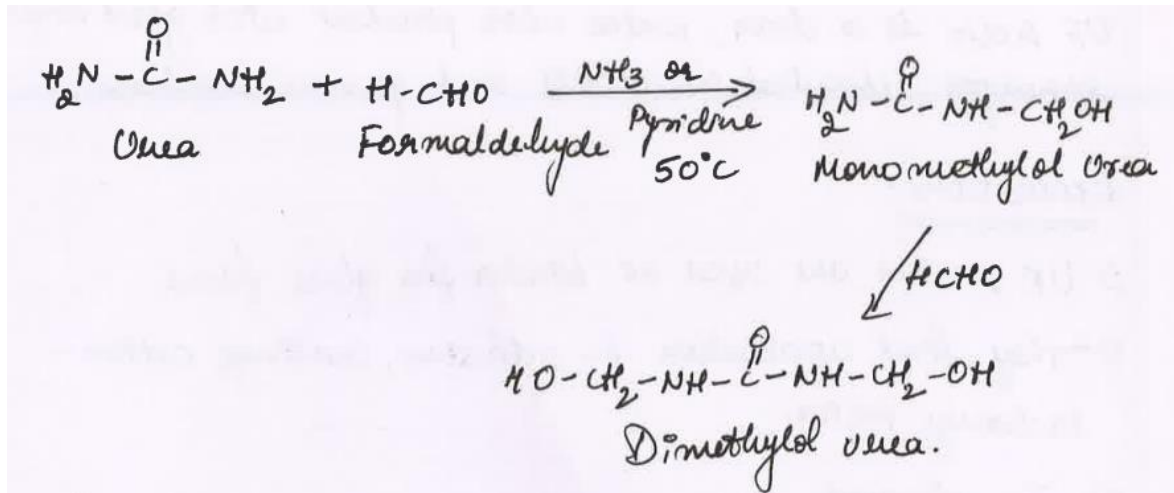
- I. Resins
- II. Elastomers
- III. Plastics
- IV. Fibers

I. Resins

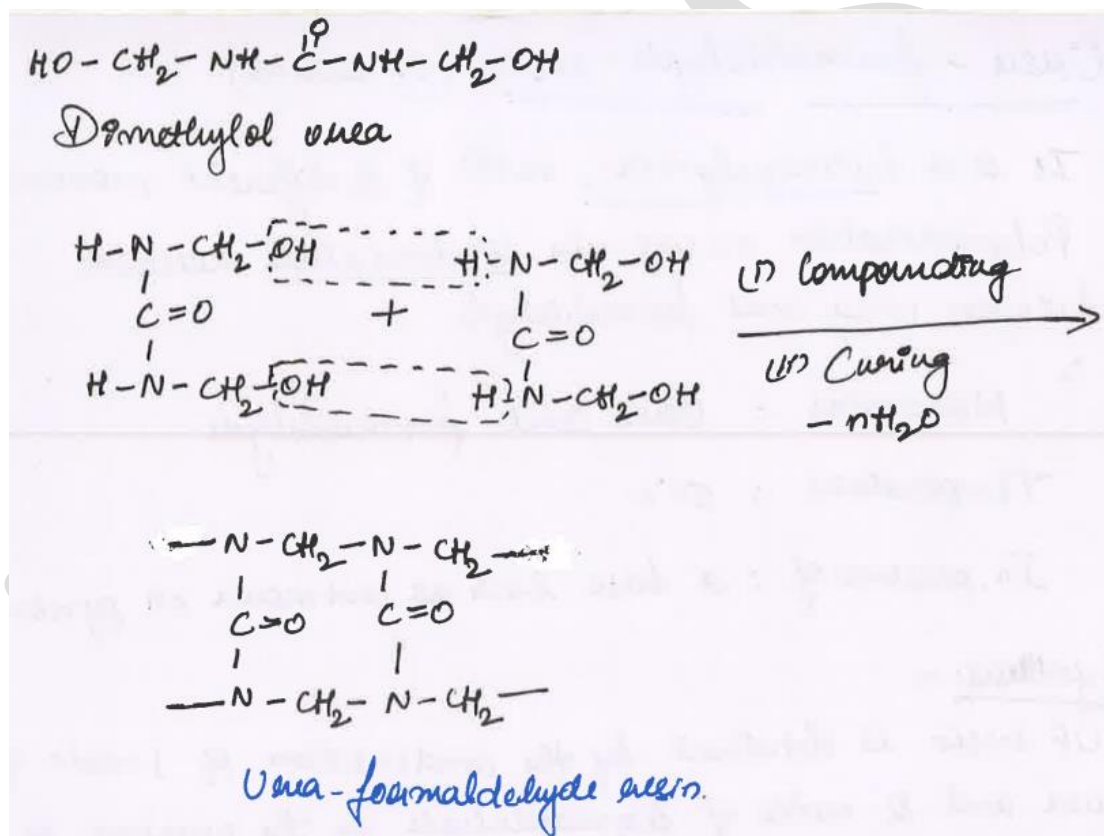
- Resins are low molecular weight, linear, soluble and fusible polymers
- They are also called as prepolymers
- They are available in powder or liquid form
- They undergo further polymerization and cross-linking during moulding, forming hard and rigid networks
- They are used as adhesives, coatings, etc
- Examples: Epoxy resins, amino resins, etc.

***Synthesis, properties and applications of UF resin**

- It is a heteropolymer
- It is made of two different monomers, Urea and Formaldehyde
- The polymerization occurs at a temperature of 50 °C, in presence of a base such as Ammonia or Pyridine
- Urea-Formaldehyde resin is obtained by the condensation of 1 mole of Urea and 2 moles of Formaldehyde, in a stainless-steel reactor;



- Dimethylol urea is compounded by adding filler, plasticizers, pigments, etc.
- It is cured by applying heat and pressure to obtain long, cross linked polymer



Properties:

- UF resin is a clear, water white polymer product
- It exhibits good tensile strength, chemical resistivity and greater hardness

Applications:

- UF resins are used as binder for glass fibres
- They are used in adhesives, and coatings
- They are used as cation-exchange resins in water purification
- Provide good insulation

Compounding: A process of mixing of additives to resin/polymer

Curing: Toughening or hardening of a polymer by heat/pressure/chemical additives

II. *lastomers*

Definition: Elastomers are the polymers of high molecular weight, which can be easily elongated (deformed) by applying force and return to original shape when applied force is removed.

- This property is called Elasticity
- Elasticity is due to uncoiling and recoiling of polymeric chain on applying force.

Vulcanization: It is a process of heating the natural rubber with Sulphur and other reagents at 120 – 150 °C for 1 – 4 hours, to improve its strength/utility value.

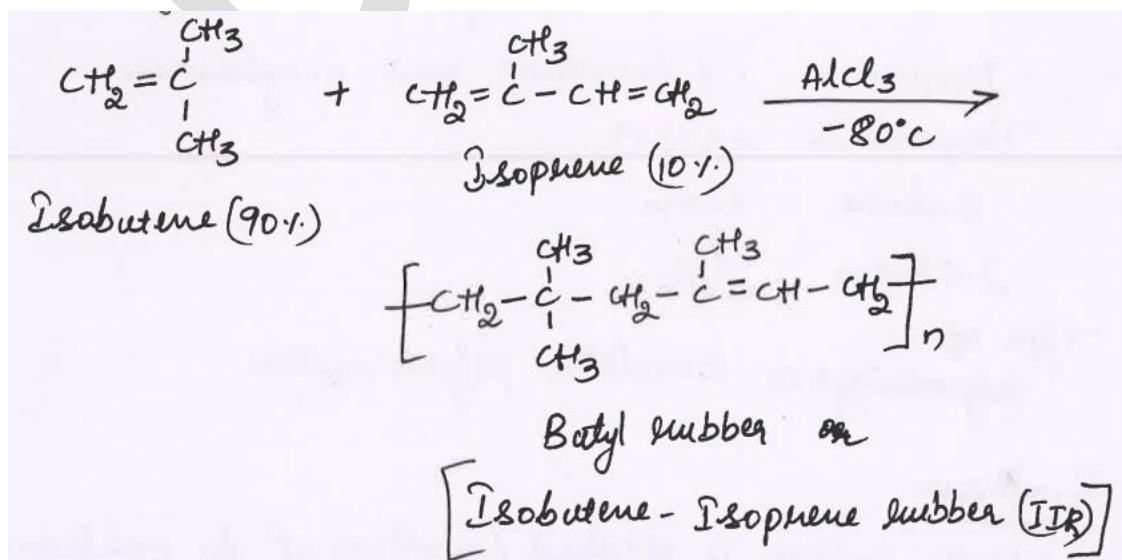
- The degree of vulcanization depends on the amount of Sulphur added
- Tyre industry uses 3 – 5% Sulphur
- Ebonite – hard and rigid rubber produced when amount of Sulphur is ~30%

*Synthesis, properties and applications of Butyl rubber (IIR)

- It is a synthetic rubber; copolymer

Monomer : Isobutylene and Isoprene
Solvent : Methyl chloride
Catalyst : Aluminium Chloride (AlCl₃)
Temperature: –80 °C
Polymerization type: Copolymerization

Process: Butyl rubber or Isobutylene-Isoprene rubber is obtained by copolymerization of Isobutene (90%) and small amount of isoprene (10%) using methyl chloride as solvent, in the presence of AlCl₃ catalyst. The process temperature is –80 °C.



Properties:

- IIR has good chemical resistance
- Low gas permeability
- Less sensitive towards oxidative aging, better ozone resistance
- It has good solvent resistance

Applications:

- Butyl rubber is used in the manufacture of inner tubes of tyres like in cycles and automobile tubes
- It is used in the manufacture of insulating materials for high voltage transmission lines and cables

*Synthesis, properties and applications of Nitrile rubber (NBR)

- It is a synthetic rubber; copolymer
- Also known as NBR – Nitrile Butadiene rubber or Buna-N rubber or Acrylonitrile rubber

Monomer : 1,3 butadiene and acrylonitrile

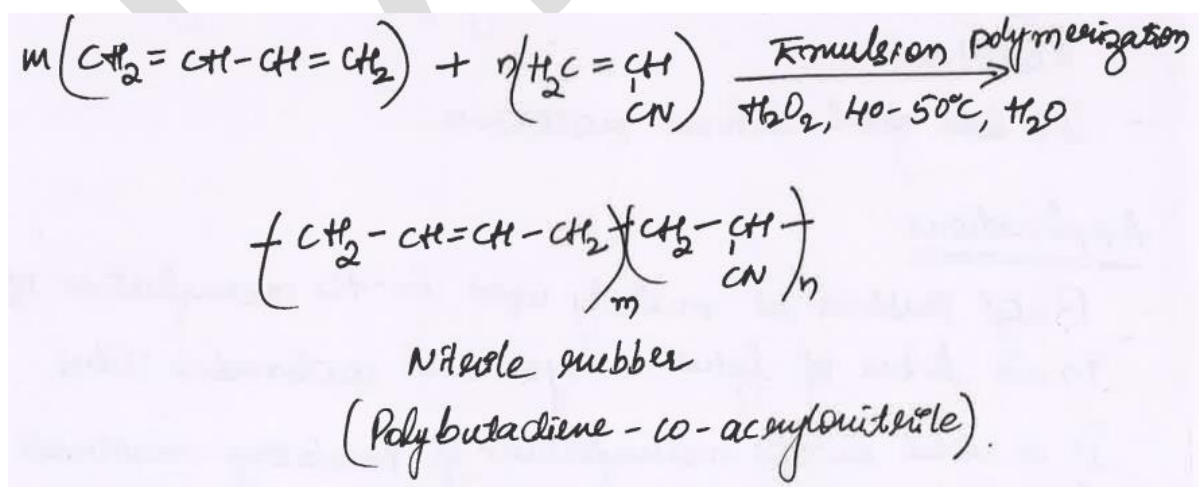
Solvent : Water

Initiator : Hydrogen peroxide (H_2O_2)

Temperature: 40 - 50 °C

Polymerization type: Emulsion

- Nitrile rubber is obtained by polymerization between butadiene and acrylonitrile in a steel reactor, at 40 – 50 °C, using water as solvent
- H_2O_2 is used as a free radical initiator



Properties:

- Nitrile rubber possesses excellent resistance to sunlight, heat, oil, acids and salts

- It is less resistant to alkali than natural rubber because of presence of cyano- (nitrile, $-\text{CN}$) group
- It can withstand a wide range of temperature from -40°C to 100°C .

Applications:

- Nitrile rubber is used in nuclear, medical and aeronautical industrial applications, since it can withstand low and high temperatures
- It is used in nuclear industry to make protective gloves
- It is also used to produce moulded goods, footwear, adhesives, sealants, sponges, expanded, expanded foams, floor mats, etc.

III. Plastics

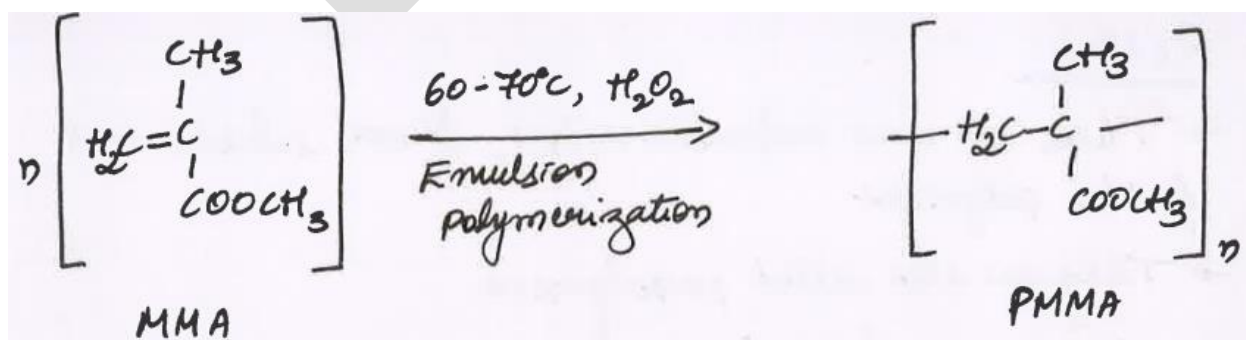
- Plastics are high polymers in which intermolecular forces of attraction are intermediate of fibres and elastomers
- They can be mould into any shape by applying heat and pressure
- Examples: PVC, PMMA, Polystyrene, etc.

*Synthesis, properties and applications of PMMA

- PMMA: Polymethylmethacrylate; it is an addition polymer and homopolymer
- It is also called as Plexiglass

Monomer : Methyl methacrylate
 Initiator : Hydrogen peroxide (H_2O_2)
 Temperature: $60 - 70^\circ\text{C}$
 Polymerization type: Emulsion

- PMMA is obtained by heating methyl methacrylate at a temperature of $60 - 70^\circ\text{C}$, in presence of H_2O_2 initiator



Properties:

- PMMA is an amorphous and transparent plastic; it is more transparent than glass

- ii) It has good optical clarity but poor scratch resistance
- iii) It has resistance towards water, alkali, inorganic solvents; but dissolve in organic solvents
- iv) It has good resistance to acids and environmental deterioration

Applications:

- It is used in the manufacturing of automotive lenses, aircraft windows, signal boards, etc.
 - Used in paints and adhesives
 - In protective coatings and plastic jewellery
 - Used for making artificial teeth and contact lenses, laser disks, DVDs, etc.
-

Polymer composites

- Polymer composites are defined as materials composed of at least two dissimilar materials acting in harmony
- They have properties significantly different from the polymers used in composite preparation
- The constituents of a composite do not dissolve or merge completely into each other but act together, while retaining their individual identities
- Composites are composed of two phases; **i) Matrix phase ii) Dispersed phase**

Superior properties or Advantages of polymer composites:

- i) They possess superior properties like higher yield strength, fracture strength and tensile strength
- ii) They possess higher specific strength and lower specific gravity
- iii) Exhibit lower electrical conductivity and thermal expansion
- iv) High corrosion resistance and heat resistance
- v) Maintain good strength even at high temperature

Matrix Phase:

- It is a primary phase, continuous phase and it surrounds or holds dispersed phase
- It is, usually, more ductile and less hard
- It binds the fibres together and acts as medium so that it can transmit and distribute any externally applied stress
- It protects individual fibre from surface damage

- It acts as barrier and prevents the propagation of brittle cracks
- Examples: Polyester, Polyurethane

Dispersed Phase:

It is dispersed throughout the matrix

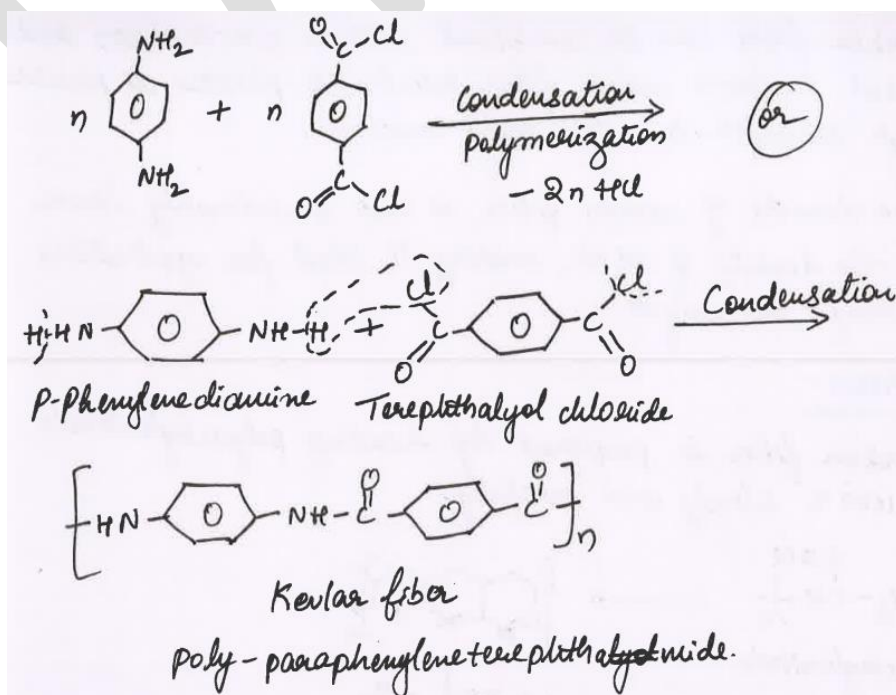
Fiber-reinforced composite:

- It is a common type of polymer composite
- It is a composite where fibres are embedded between two matrix layers
- Here, matrix is a continuous phase and fibre is a dispersed phase
- The commonly used fibres are thin glass sheets, carbon fibres and Kevlar fibres
- Fiber reinforced composites exhibit high strength, stiffness, high abrasion and impact resistance, high corrosion resistance
- They possess low weight and low density

*Synthesis and applications of Kevlar fiber

- It is an aromatic polyamide
- Kevlar is the Dupont company's brand name for synthetic fiber poly-phenylene terephthamide
- It is the first organic fiber with sufficient tensile strength and structural rigidity to be used in advanced composites

Synthesis:



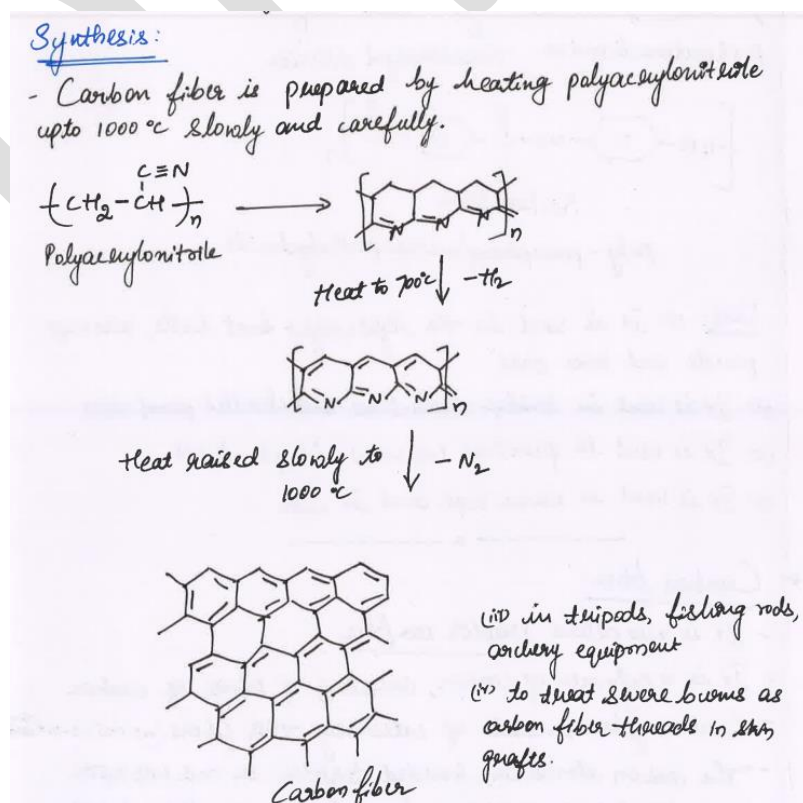
- Kevlar fiber is synthesized using the monomers 1,4-phenylenediamine and terephthaloyl chloride (1,4-benzene dicarbonyl chloride) in the solution of N-methyl pyrrolidone (NMP) and calcium chloride
- It is a condensation reaction which takes place with the liberation of HCl as byproduct

Uses:

- Kevlar fiber is used in the boat hulls, aircraft panels and race cars
- It is used in bridge structures
- Used in bullet proof vests
- Used in puncture resistant bicycle tyres
- Use in woven rope and in cables

*Synthesis and applications of carbon fiber

- It is also called Graphite fiber
- It is a polymer of carbon, consisting of carbon rings
- It consists of extremely thin fibers (0.005 – 0.10 mm)
- Carbon fiber can be combined with a plastic resin and moulded to form carbon fiber reinforced plastics to provide a high strength-to-weight ratio material
- The density of carbon fiber is lower than the density of steel, making it ideal for applications requiring low weight



Applications:

- Carbon fibers are used in making parts of aeroplanes, space shuttle, modern motor bikes
 - Used in tennis rackets, guitar strings, golf clubs
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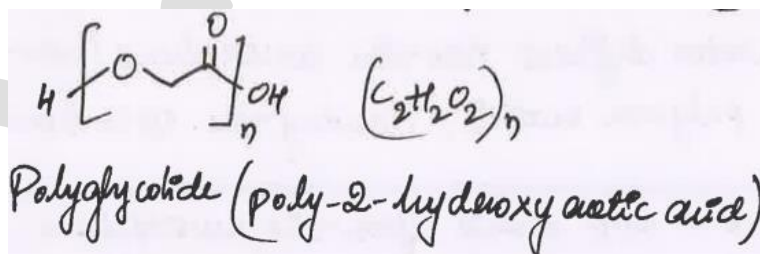
Biodegradable Polymers:

Definition: 'The polymers that can be decomposed (decay) by microorganisms are called biodegradable polymers'

- These polymers are degraded by microorganisms with a suitable period so that these polymers and their degraded products do not cause any serious effect on environment
- Examples: Polyglycolic acid (PGA), Polyhydroxy butyrate (PHB), etc.

*Synthesis, degradation and applications of polyglycolic acid (PGA) or polyglycolide

- It is a biodegradable, thermoplastic polymer
- It is a linear, aliphatic polyester formed from glycolic acid (glycolide) monomer



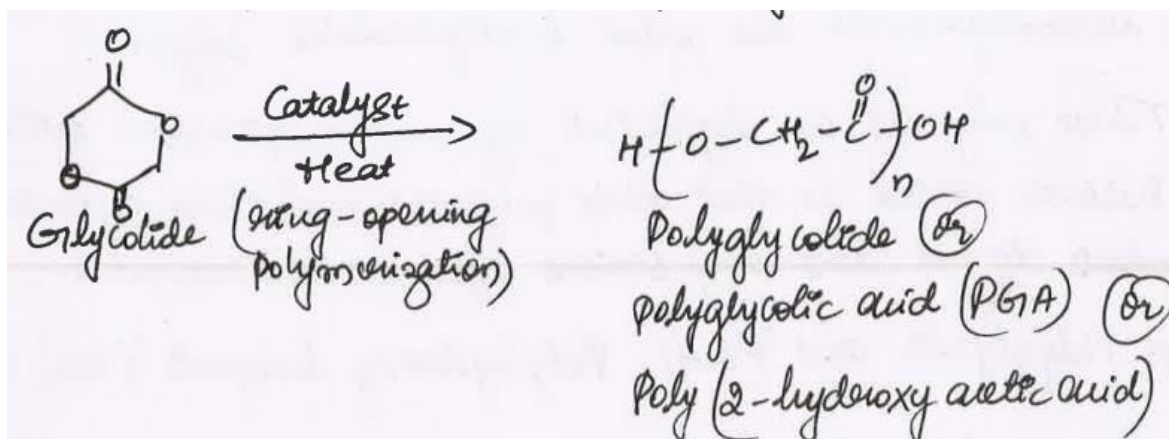
Synthesis:

- PGA is obtained by 'ring opening polymerization' of glycolide

Monomer	:	Glycolide
Catalysts	:	Antimony trioxide (Sb_2O_3), Antimony trihalide, Zinc compound (like zinc lactate), tin alkoxide
Initiator	:	Stannous octate [$\text{Sn}(\text{oct})_2$]
Mechanism	:	Ring open polymerization
Temperature	:	195 – 230 °C

- A catalytic amount of initiator is added to glycolide under nitrogen atmosphere at 195 °C
- The reaction is allowed to proceed for 2 hours and then temperature is raised to 230 °C for 30 min.

- After solidification, the resulting polymer is collected.



Degradation mechanism:

- PGA degrades into the formation of its monomer, glycolic acid
- Degradation of PGA takes place in 2 steps;
 - i) Water diffuses into the amorphous regions of polymer matrix, cleaving the ester bonds
 - ii) The crystalline sites of the polymer become susceptible to hydrolytic attack, after the amorphous region; Upon collapse of the crystalline regions, the polymer chain dissolves

Therefore, the **driving force in the degradation of PGA is hydrolysis of ester linkages.**

Uses:

- It is a synthetic, completely absorbable, non-toxic product
- Used in several biomedical applications such as drug delivery, dentistry, tissue engineering, etc.
- Desired polymer by physicians due to its excellent degradation behaviour

Conducting polymers

- Also called 'Synthetic metals'

Definition – Conducting polymers are the organic polymers with highly delocalized π -electrons system which is having electron conductivity in the order of a conductor.

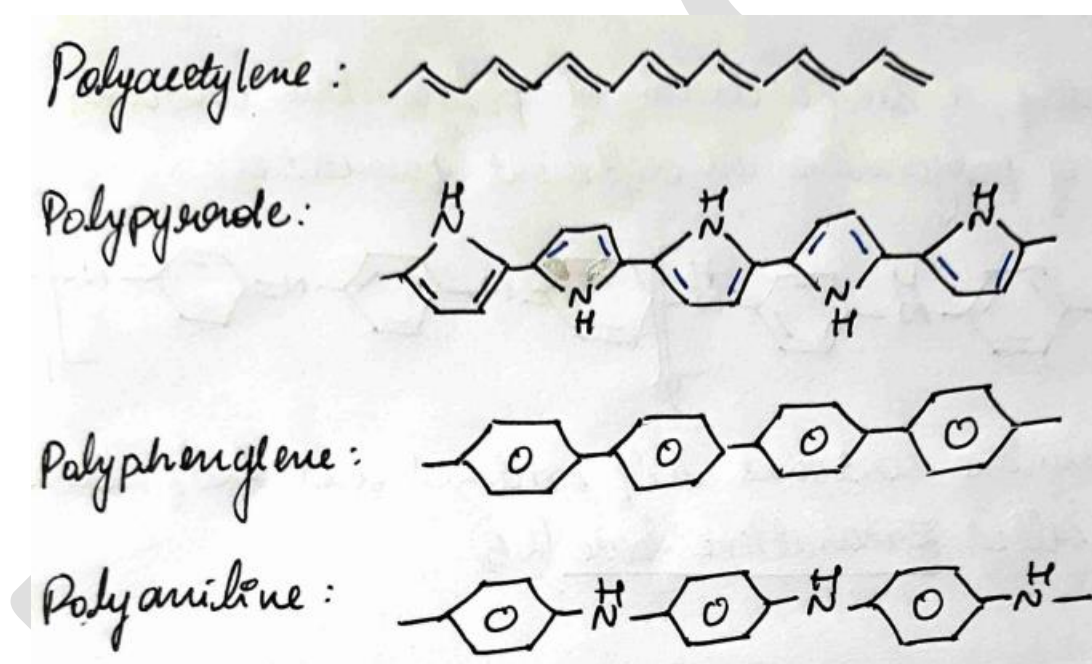
Note:

- Polymers are usually electrical insulators.
- But an organic polymer can be converted into a conducting polymer if it has;

- Linear structure
- Extensive conjugation in polymeric backbone (π -back bone)
- On suitable doping, the conductivity can be increased considerably
- Example: Conductivity of polyacetylene is 4.4×10^{-5} S/cm; whereas, doped polyacetylene is 400 S/cm.

In 1977, for the first time, conducting polymer was accidentally discovered by Shirakawa. He added a catalyst 1000 times more than the required amount, during polymerization of polyacetate, resulting in conducting polyacetate.

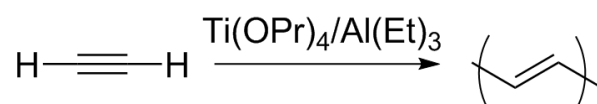
Examples for conducting polymers:



Synthesis and conduction mechanism in Polyacetylene:

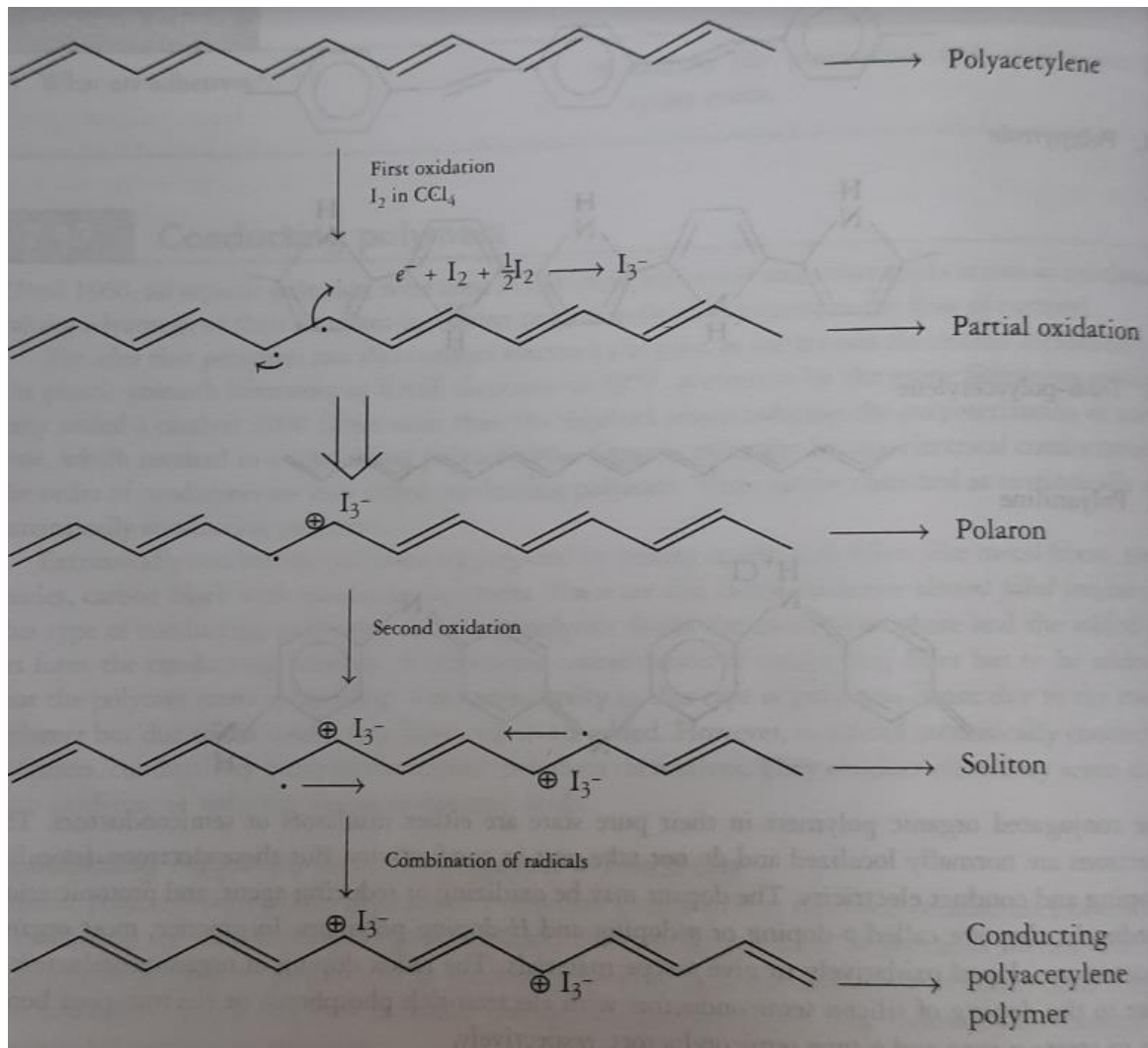
Synthesis: Polyacetylene is obtained by reacting acetylene with a Ziegler Natta catalyst, $\text{Ti}(\text{OiPr})_4/\text{Al}(\text{C}_2\text{H}_5)_3$ [Titanium(IV) isopropoxide/triethyl aluminium].

$[\text{Ti}(\text{OiPr})_4 : \text{Ti}\{\text{OCH}(\text{CH}_3)_2\}_4]$



Conduction mechanism:

- Polyacetylene can be conductive by **oxidative doping** or p-doping



- In this process, pi-back bone of polymer is partially oxidized using a suitable oxidizing agent.
- This creates positively charged sites on polymer back bone, which are current carriers for conduction
- The oxidizing agents used are iodine vapour, iodine in CCl_4 , etc.
- The removal of an electron from polymer back bone leads to the formation of delocalized radical ion called Polaron
- A second oxidation of a chain containing polaron, followed by radical recombination yields two charge carriers on each chain
- The positive charge sites on the polymer chains are compensated by anions I_3^- formed by the oxidizing agent during doping
- The delocalized positive charges on the polymer chain are mobile.
- Thus, these charges are current carriers for conduction.
- These charges move from chain to chain as well as along the chain for bulk conduction.

- On doping polyacetylene with iodine in CCl_4 , the conductivity increases from 10^{-5} S/cm to $10^3 - 10^5 \text{ S/cm}$.

Applications:

- i) Doped polyacetylene offers high electrical conductivity; therefore, it can be used in electric wiring
 - ii) It can be used as electrode material in light weight rechargeable batteries
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Dr. S.