

UNIT-4

POLYMERS:

The polymer chemistry is a part of material science which involves creation of new materials to replace metals, glass, ceramics, wood, cardboard and paper.

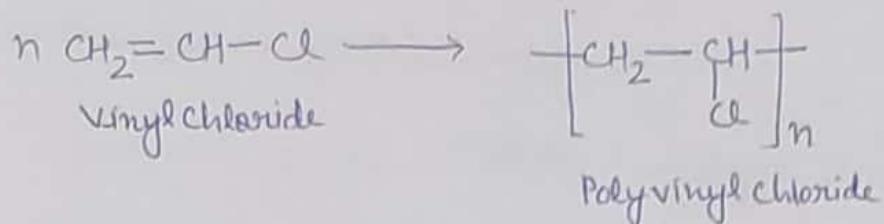
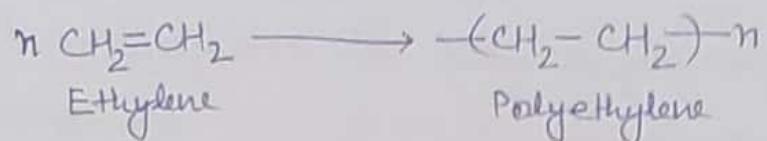
The polymers are complex, giant, high molecular weight macromolecules formed by the combination of a large number of one or more type of a small molecules of low molecular weight.

The word polymer implies 'many part' (Greek: poly means 'many' and mer-means 'part'). All the substances referred to as polymers, are big molecules with molar masses ranging from several thousands to several millions.

The chemical reactions that joins the monomers together is called polymerisation. The total number of monomer units combined together to form a polymer is known as degree of polymerisation.

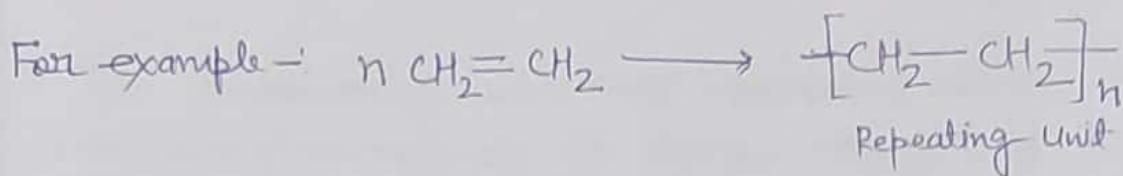
Monomer: A monomer is a molecule that combines with other molecules of the same or different type to form a polymer.

For example:



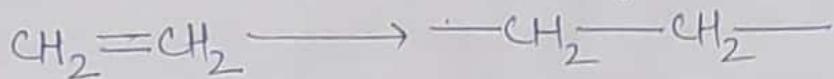
Repeating Unit

A unit, which on repetition gives the whole chain of the polymer is known as the repeat unit of the polymer. The repeat unit is enclosed by brackets or parentheses.



Functionality

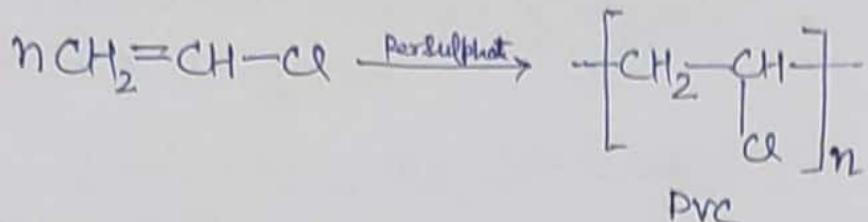
The number of binding sites in a monomer is referred to as its functionality e.g. in an alkene, the double bond can be considered as bifunctional because when the double bond is broken, two single bonds become available for combination.



Nomenclature:

1. Homopolymer: The polymer formed one kind of monomers is called homopolymer.

Example: Polyvinyl chloride (PVC)



2. Copolymer / Mixed Polymer:

When polymer formed from more than one kind of monomers is called co-polymer or mixed polymer.

Ex: Nylon-66, polyethylene-vinyl acetate (PEVA)

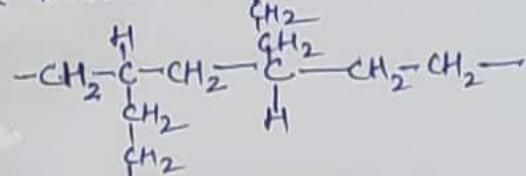
3. The monomeric units may combine with each other into a macromolecule to forms polymers of linear, branched or cross linked.

(i) Linear Polymer: Each monomeric unit is linked with two monomeric units on either side, forming a continuous chain.

e.g. polyethylene $\rightarrow -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}-$

(ii) Branched Polymer: In some cases, while the polymer chain is growing in a linear manner, some side growth also takes place from the main chain. Most of the monomeric units are linked with two others on either side and some monomeric units also linked with a third monomeric units.

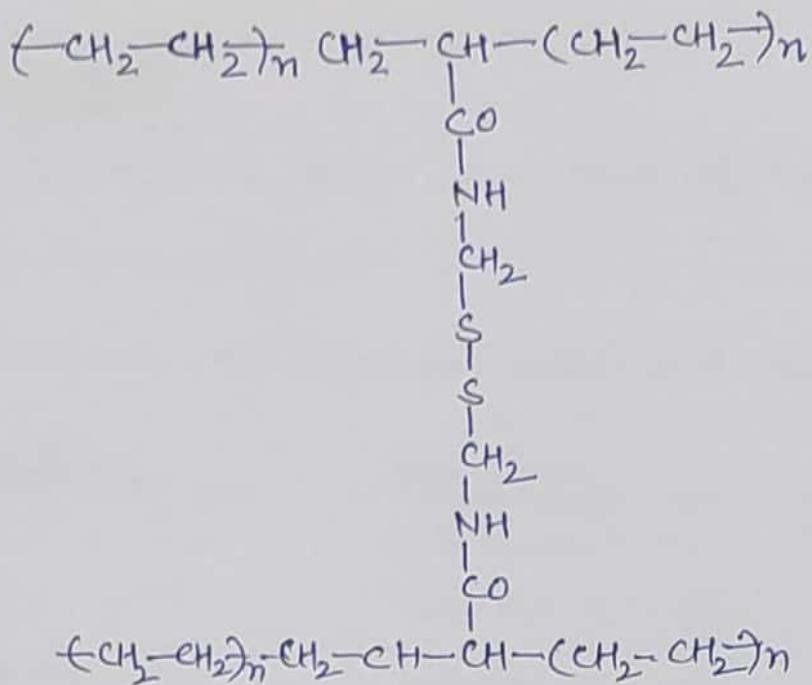
e.g. Branched Polyethylene:



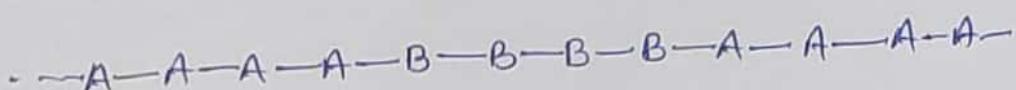
(iii) Cross linked Polymers:

Cross-linked polymers have many interesting properties which make them very attractive materials. By cross-linking, the structure of a polymer solution can be fixed. The resulting polymer networks show elastic properties.

e.g.: Cross linked polymer of ethylene and monomer containing -SH group.

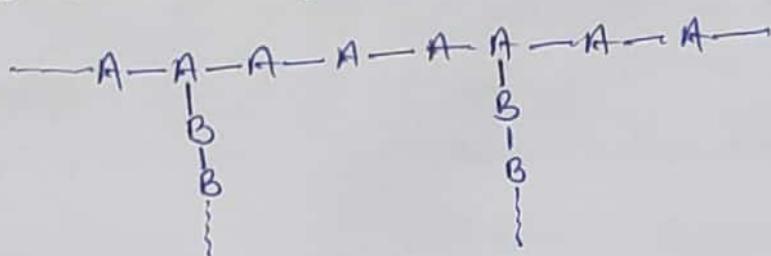


(iv) Block copolymers: Linear copolymers in which the units of each type form fairly long continuous sequences (blocks) are called block copolymers.



(v) Graft copolymers:

Branched copolymers with one kind of monomers in their main chain and another kind of monomers in their side chains are called 'Graft copolymer'.



CLASSIFICATION OF POLYMERS

Polymers are divided into two broad categories depending upon the nature of the repeating units. These are:

- (1) Homopolymers
- (2) Copolymers

Homopolymers:

The polymer formed from one kind of monomers is called homopolymers.

Some examples of homopolymers and their monomers-

<u>Homopolymer</u>	<u>Monomer</u>
Starch	Glucose
Cellulose	Glucose
Polyethylene	Ethylene
Teflon	Tetrafluoroethylene
Polyvinyl acetate	Vinyl acetate
Nylon-6	Caprolactum

Copolymer

The polymer formed from more than one kind of monomers is called co-polymer or mixed polymer.

<u>Copolymer</u>	<u>Monomer</u>
Nylon-66	Hexamethylene dianiline & adipic Acid
Buna-S, SBR	Styrene & Butadiene

Terylene

Terephthalic acid & dimethyl glycol
vinyl chloride & vinylidene chloride

Classification on the basis of source

Natural polymers

Biopolymers

Synthetic polymers (Man made polymers)

Semisynthetic polymers

Natural Polymers:

The polymers, which are isolated from natural materials mostly plants and animals sources, are called natural polymers.

Ex: Starch, cellulose, proteins, nucleic acid, natural rubber etc.

Biopolymers: Natural polymers which take part in metabolic process are known as biopolymers.

Ex: Starch, Proteins, RNA, DNA etc.

Synthetic Polymers (Man made polymers)

The polymers which are prepared in the laboratory ~~are~~ from their monomers are known as synthetic polymers.

Ex: Polyethylene, polystyrene, teflon, nylon, bakelite, orlon, polyester etc.

Semisynthetic Polymers

Polymers which are prepared from natural polymers are known as semi-synthetic polymers.

Ex: cellulose acetate, cellulose nitrate and rayon.

Classification based on structure:

Linear polymers

Branched chain polymers

Crossedlinked or three-dimensional polymers

Linear polymers:

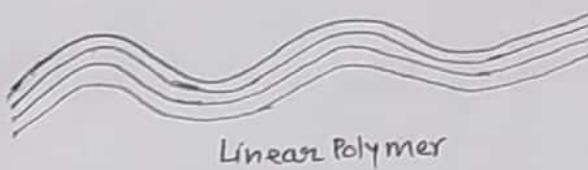
~~These polymers are~~ In linear polymer, monomeric units are linked together to form long straight chains.

The polymeric chains are stacked over one another to give a well packed structure due to this, structure is closely packed in nature. Such polymers have high densities, high tensile strength and M.P.

Linear polymers can be converted into fibres due to these properties.

for Example:

- Polyethylene
- Nylon
- Polyester.



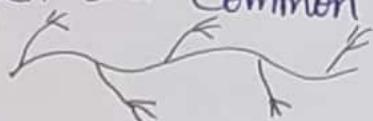
Linear Polymer

Branched Chain polymers:

Monomeric units are linked to ~~not~~ constitute long chains, which are also called main-chain. There are side chains of different lengths which - constitute branches.

Branched chain polymers are irregularly packed and thus, they have low density, lower tensile strength and lower melting points as compared to linear polymers.

Amylopectin and glycogen are common example of such type



Cross-linked or Network Polymers:

In this type of polymers, the monomeric units are linked together to constitute a three dimensional network. The links involved are called cross links. Cross linked polymers are hard, rigid, and brittle because of their network structure.

Example: Bakelite, formaldehyde resin, melamine etc.



Classification based on Tacticity:

This classification is based on the orientation of monomeric units in a polymer. The orientation (configuration) of monomeric units in a polymer can take an orderly or disorderly fashion with respect to chain chain. The difference in configuration (tacticity) do affect their physical properties.

The head to tail polymerisation of vinyl monomers of the structure $\text{CH}_2=\text{CHR}$ produce a polymer in which alternate carbon atom is a chiral carbon. The polymer has many chiral carbons. Due to these chiral carbons three predominant stereochemistry is possible. On the basis of these stereochemistry the polymers are classified into-

Isotactic polymers ($\text{iso}=\text{same}$)

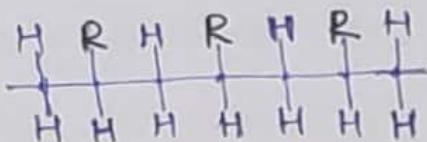
Syndiotactic (meaning alternate order) Polymer

Atactic polymer (no order)

Isotactic polymers:

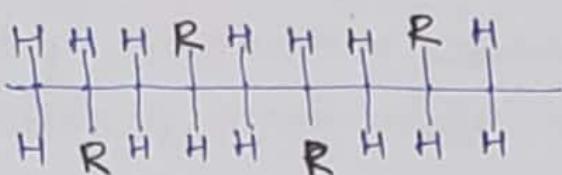
If the side groups (i.e. gp. R) are on the same side of the polymer backbone, the polymer is called isotactic polymer (iso , meaning - "same" and tactic means "order").

The configuration of the chiral centers are either all (R) or all (S).



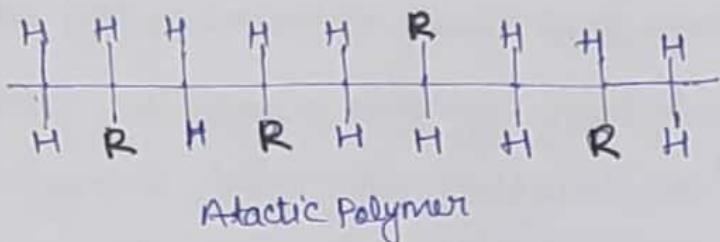
Syndiotactic:

If the side groups are alternate from one side to the other on the polymer backbone, the polymer is called syndiotactic. The configuration of the chiral centres would alternate (R), (S), (R), (S) and so on.



Atactic Polymer (no order)

If the side groups occur randomly on either side of the polymer backbone, the polymer is called atactic.



CLASSIFICATION BASED ON SYNTHESIS :

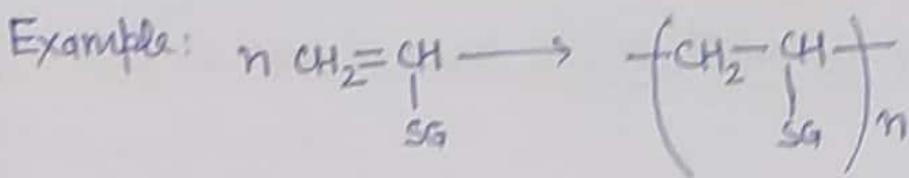
Addition polymers

Condensation polymers

Addition Polymers:

Addition polymers are formed by successive addition of monomers without elimination of any molecule.

These additions are chain reactions (radical chain reaction or ionic chain reaction) and hence this mode of polymerisation is known as chain polymerisation and polymers are called chain-growth polymers.



Where, -SG = Substituent Group i.e. -H polyethene

-CH₃ polypropylene

-Cl polyvinyl chloride

-C₆H₅ polystyrene

Condensation polymers or

Step growth polymers:

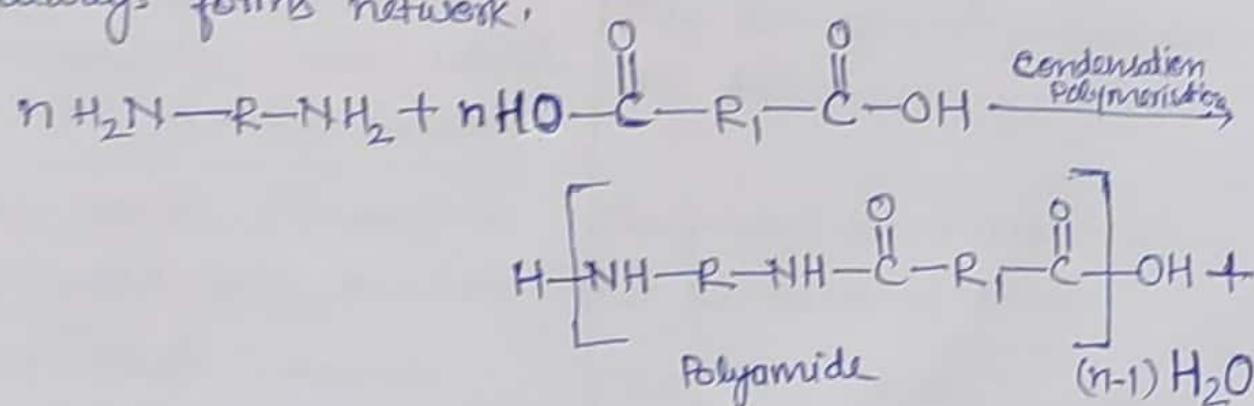
It is formed by the reaction between two monomers with elimination of small molecules such as water or alcohol, are known as condensation polymer.

The process is known as condensation polymerisation.

Since, condensation polymerisation formed by several successive condensation reactions, so the process is also called step polymerisation and step growth polymer.

Bifunctional monomer always gives linear condensation polymer. When a trifunctional monomer is mixed in a small amount with the excess amount of a bifunctional monomer, a branched chain condensation polymer is formed.

Trifunctional and polyfunctional monomer always forms network.



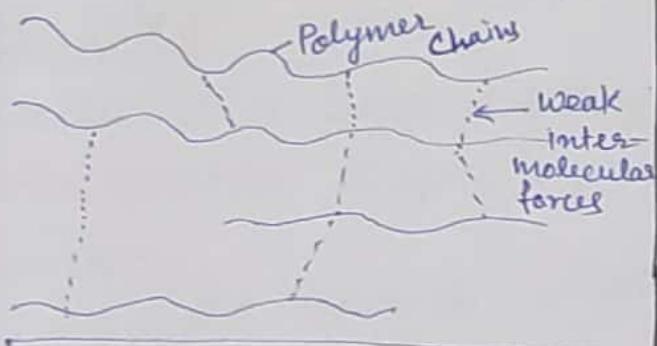
Classification based on Action of Heat

Thermoplastic

Thermoset polymer

Thermoplastic

- 1 They are formed either by addition or by condensation polymerisation.
- 2 They have either linear or branched structures.
- 3 Adjacent polymer chains are held together by either van der waals forces or dipole-dipole forces or H-bonds
- 4 They soften on heating and stiffen on cooling.
- 5 Low molecular weight thermoplastics are soluble in their suitable solvents.
- 6 They can be remoulded, re-shaped and reused.
- 7 They ^{are} tough materials.

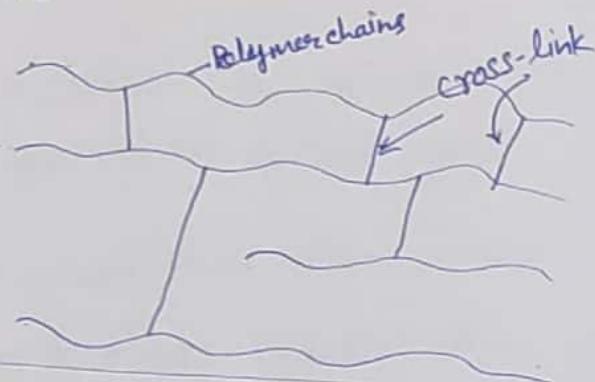


Thermosets polymer

They are formed by condensation polymerisation reaction.

They have three dimensional cross-linked network structure

Adjacent polymer chains are held together by strong covalent bond called cross-links.



They do not soften on heating.

They are generally insoluble in any solvent.

They can't be remoulded and can not be reused.

They are brittle materials.

Bakelite, Epoxy resin, duroplast, Polyester, Polyurethane

Examples: Toys, buckets, Polyethylene
Nylon, teflon, Polystyrene, PVC etc.

Classification based on the Use of the Polymer

Plastics
Fibres
Rubber (elastomers)
Adhesives
Coatings

The utility of these polymers depends upon their mechanical properties i.e. tensile strength, elasticity modulus (stiffness). These mechanical properties depend upon the nature and strength of secondary forces operating in polymer. Intermolecular secondary forces present polymeric chains are -

- (i) Van der Waals force
- (ii) Dipole-dipole interactions &
- (iii) H-Bonds.

Magnitude of secondary forces depends upon the size of the molecule and the number of functional group along polymeric chains.

Plastics:

Plastic is a synthetic polymer, which can be converted into complex shapes by the application of heat and pressure.

All synthetic polymer other than fibres and rubbers are usually known as plastics. Plastics are classified into two categories:

(a) Thermoplastic: A thermoplastic polymer will soften when heated above glass transition temperature (T_g). On heating it will soften again and can be reshaped if required before hardening when temperature drops. This cycle can be carried out repeatedly.

Example: Polyethylene, Polypropylene, polyvinyl chloride, Polystyrene etc.

Thermosetting Plastics

The thermosetting materials become permanently hard when they are heated above the critical temperature and will not soften again on reheating - due to cross linked in this state.

Examples: Phenol-formaldehyde resin, urea-formaldehyde resin, epoxy resin, and melamine formaldehyde resins.

Name	Uses
Phenolic resins	Radio and TV cabinets, electrical filaments, utensils, sports goods, buckets, handles etc.
Amino resins	Light weight tables, counter and table surfaces
Polyester resins	Paints, surface coatings where oxidation during drying forms a cross linked film which provides a tough resistant finish.
Epoxy resins	Adhesives, surface coatings and gives flexible enamel-like finishes.

Fibres: Fibres are characterised by having high tensile strength and modulus, good elongation (stretchability), good thermal stability and spinnability (the ability to be converted to filaments).

Fibres are linear polymers in which the individual chains of a polymer are held together by very strong secondary forces, i.e. hydrogen bonds. Dipole-Dipole interactions are also present between the chains.

Due to strong intermolecular forces of attraction and highly ordered geometry.

There are two types of fibers.

- ① Natural fibres: cotton and wool
- ② Synthetic fibres:
 - (i) Cellulosic fibres - e.g. Acetate, rayon
 - (ii) Noncellulosic fibres: e.g. Polyester, nylon, Olefin, Acrylic

Rubber (elastomers):

Those polymers which on pulling elongate to many times (over ten times) its length without breaking and return to their original shape on release of the stress are known as elastomers.

It is a randomly oriented amorphous polymer. It must have some cross-linking between the polymeric chain so that chains do not slip over one another. In elastomers polymeric chains are held together by the weakest intermolecular forces, i.e. van der waals forces. Elastomers becomes soft on heating and can be moulded into any shape.

Ex. Polyurethane (PU), Styrene Rubber (Buna-S or SBR), Nitrile rubber (Buna-N or NBR)

Coating and Adhesives:

The coating materials used in the form of interior latex and wall paints using styrene - butadiene copolymer and exterior latex wall paints containing polyvinyl acetate and polyacrylate esters.

Adhesive are mainly used in wood industry. Examples → phenol-formaldehyde and urea-formaldehyde polymers and cyanoacrylates.

PREPARATION OF SYNTHETIC POLYMERS

The processes involved in the synthesis of polymers can be divided into the following two categories—

- ⊕ Addition or chain-growth polymerisation
- ⊖ Condensation or step-growth polymerisation.

(A) ADDITION, OR CHAIN-GROWTH, POLYMERISATION.

In addition polymers the repeating units have the same molecular formula as the monomer and the molecular weight of the polymer is the multiple of the molecular weight of the monomers.

The chain-growth polymerisation, is a chain reaction involving three steps namely chain initiation, propagation and termination.

The chain growth polymerisation may follow the following four different routes—

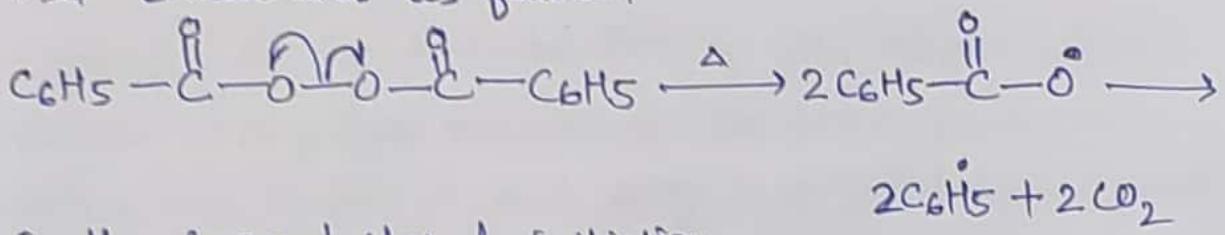
- (i) Free radical polymerisation
 - (ii) Cationic polymerisation
 - (iii) Anionic polymerisation
 - (iv) coordination polymerisation

(i) FREE RADICAL POLYMERISATION:

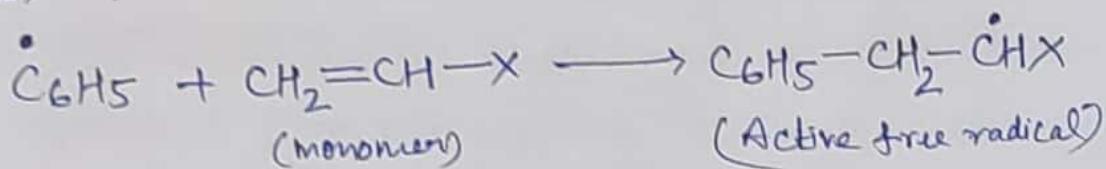
INITIATION STEP: It involves the formation of free radicals in the initiation step.

The free radicals are formed as a result of homolytic dissociation of the initiator in the presence of heat, light or catalyst. Commonly used free radical initiators are azo-compounds ($-N=N-$), disulphides ($-S-S-$), peroxides ($-O-O-$), hydroperoxides, peracids and peresters.

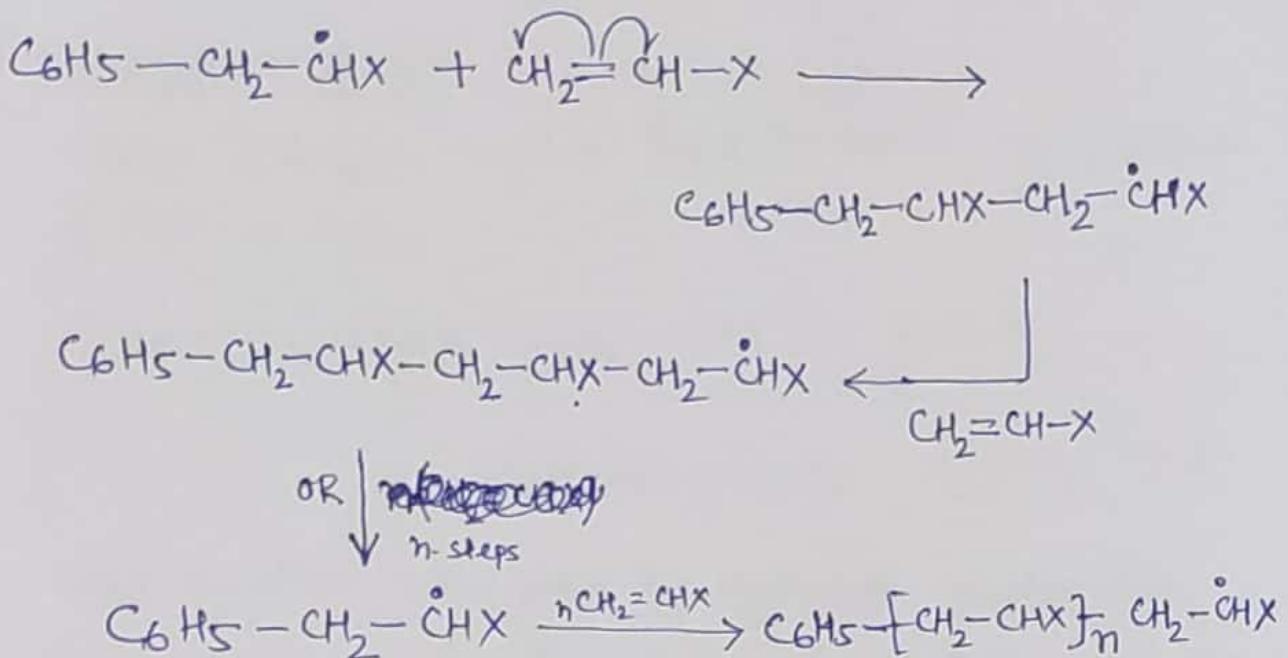
Example of free radical initiator is benzoyl peroxide that dissociates as follows:



In the second step of initiation,
a monomer molecule (M) is attached to the initiator radical.
Considering vinyl as the monomer, can be represent
as —



PROPAGATION: In this step, the initiated monomer species adds additional monomer units as follows:

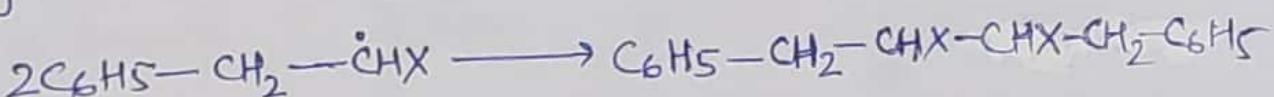


* The addition is always head to tail addition because propagation takes place by formation of more stable free radical.

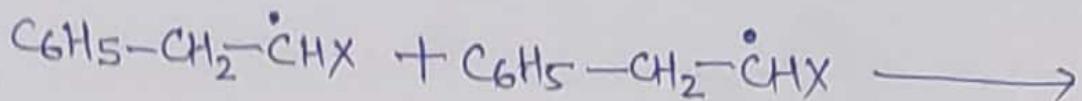
TERMINATION:

- By combination or coupling
- By Disproportionation
- By Chain Transfer

Coupling: As the decomposition of the ~~chain~~ initiator produces many free radicals at the same time, many chains are initiated and ~~propagated~~ propagated simultaneously. The two growing chains can come close, collide and get deactivated.

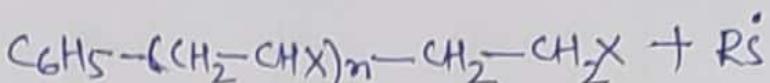
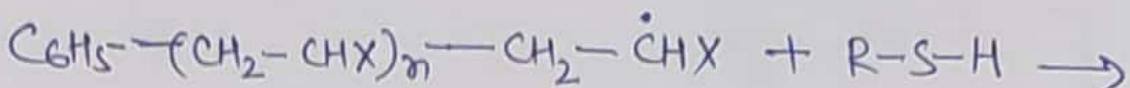


Disproportionation: In this kind of chain termination, the Hydrogen(H) from one growing chain is abstracted by the other growing chain and results in the formation of two polymer molecules, one saturated and other unsaturated.



Chain transfer:

Chain transfer reaction takes place in the presence of RSH or CHCl_3 .



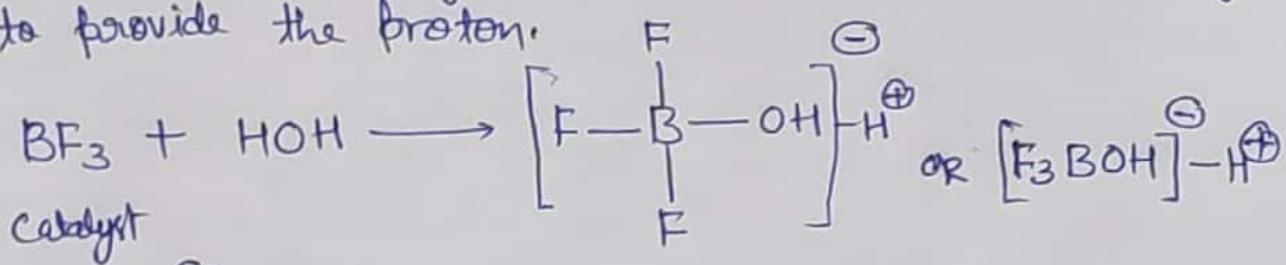
This reaction takes place by Hydrogen abstraction from either solvent or some impurities in the system.

(ii) CATIONIC Polymerisation:

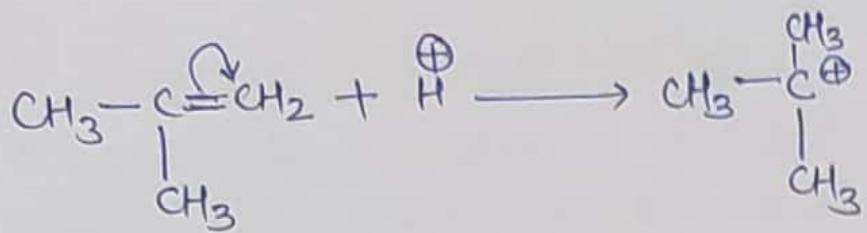
Cationic polymerisation is initiated by Lewis acid or ~~or~~ by proton acid.

cationic polymerisation is given by those monomers which forms stable carbocation in the ~~initial~~ initiation ~~step~~ step.

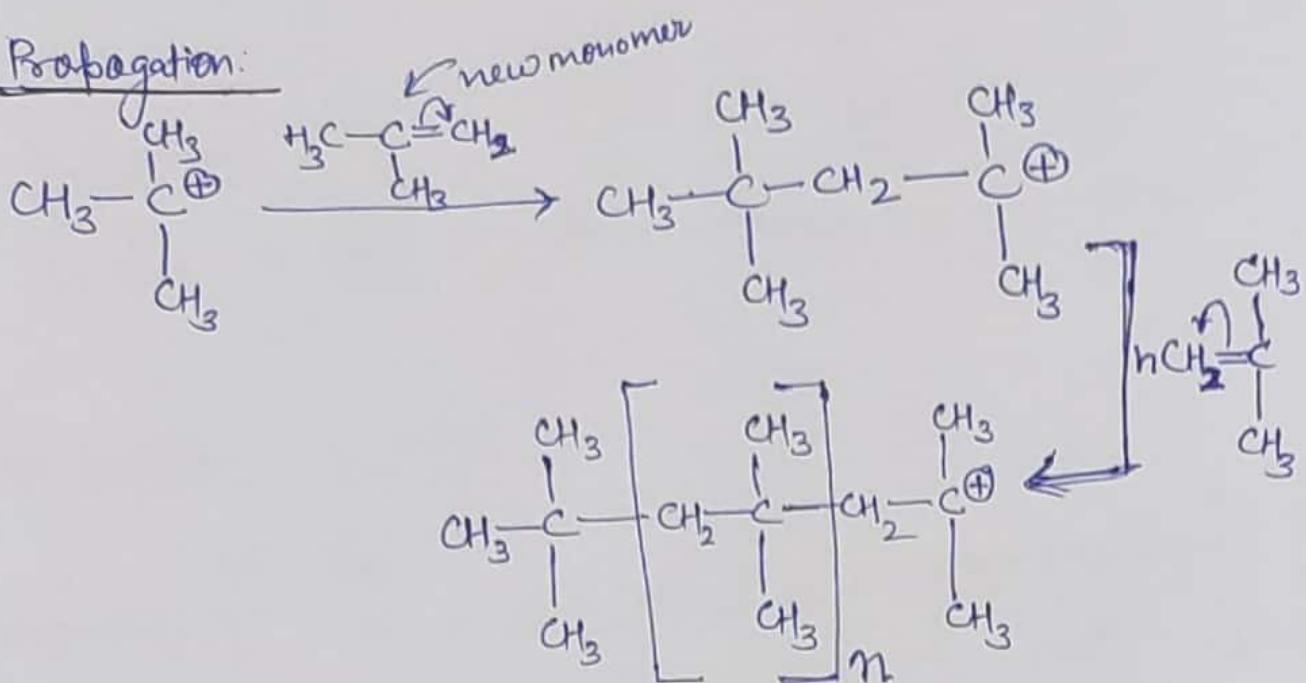
Initiation: Strong Lewis acids like BF_3 and AlCl_3 are used as catalysts. water exists as a co-catalyst to provide the proton.



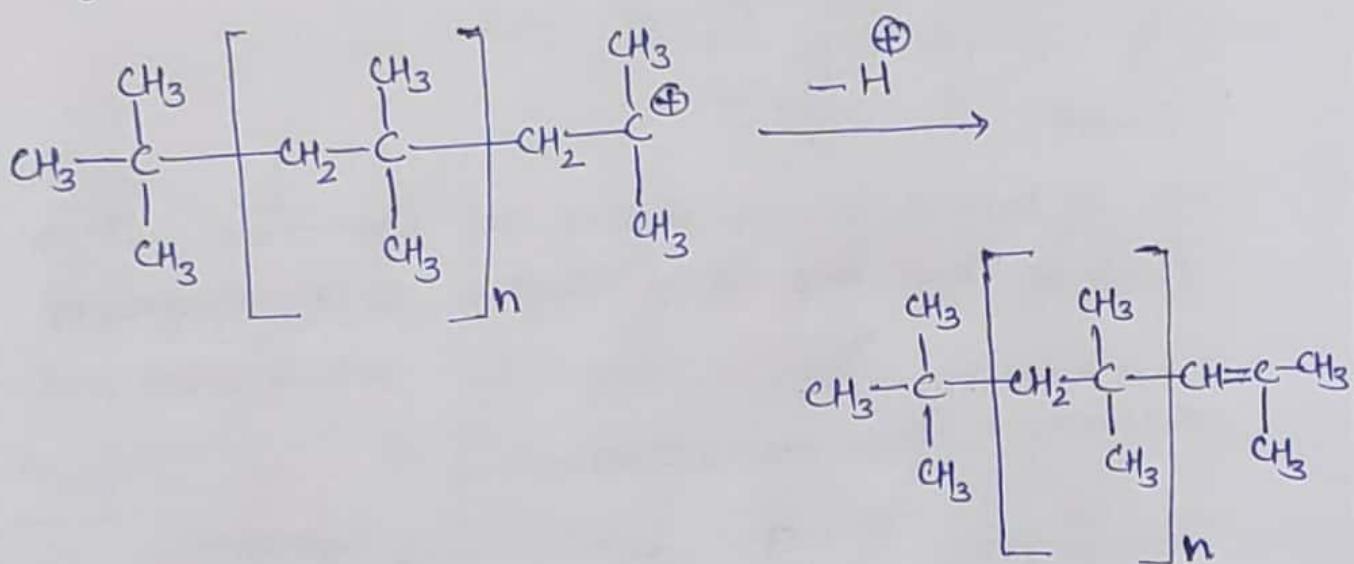
Where, H^{\oplus} is the cationic initiator, it attacks the π -electron cloud of monomer and a carbocation is formed.



Propagation:



Termination: Donation of proton to counterion by the growing chain resulting in the formation of a double bond at the end of the polymeric chain.

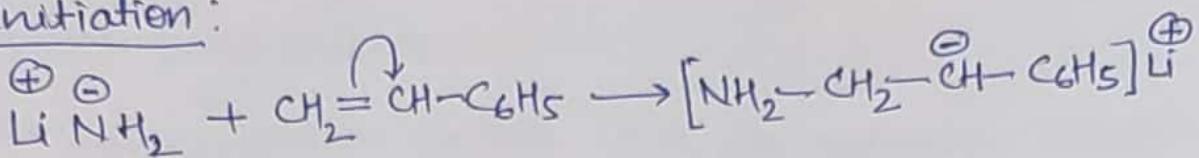


(iii) Anionic Polymerisation:

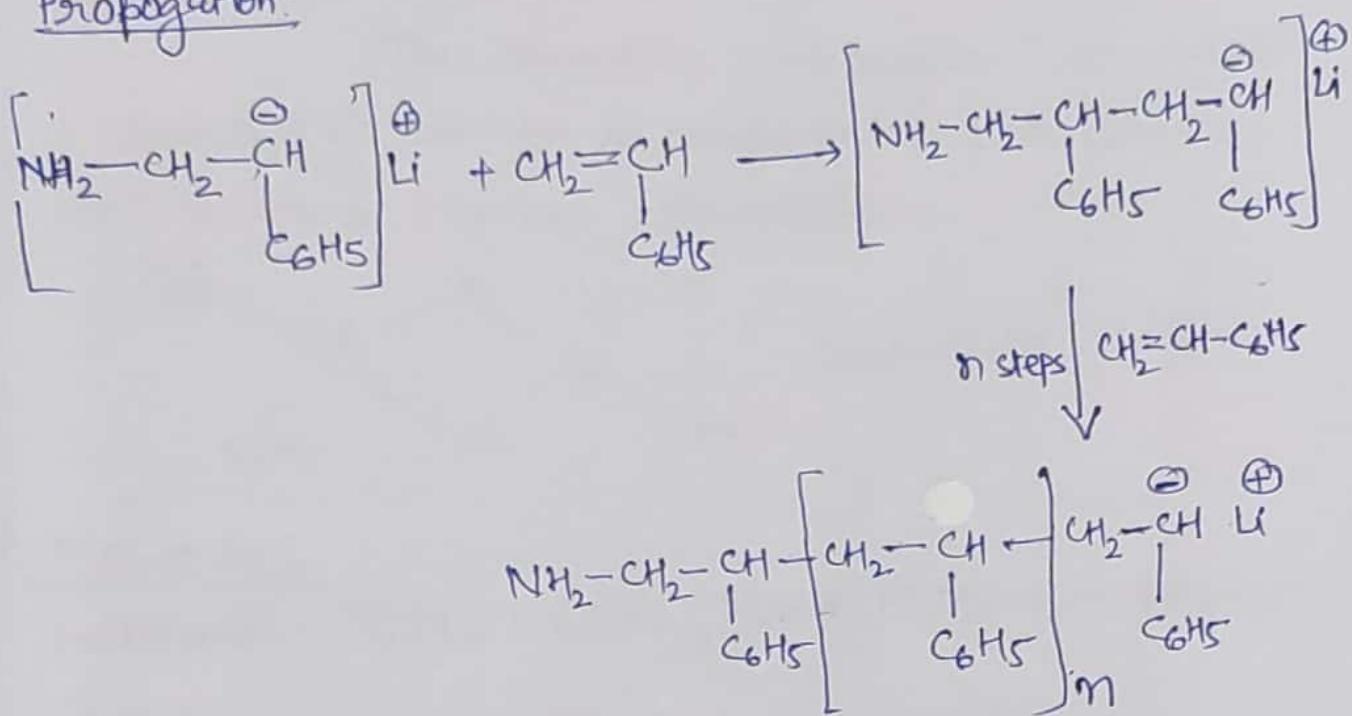
Anionic polymerisation is initiated by strong bases such as alkyl lithium and lithium or sodium amide.

Mechanism:

Initiation:

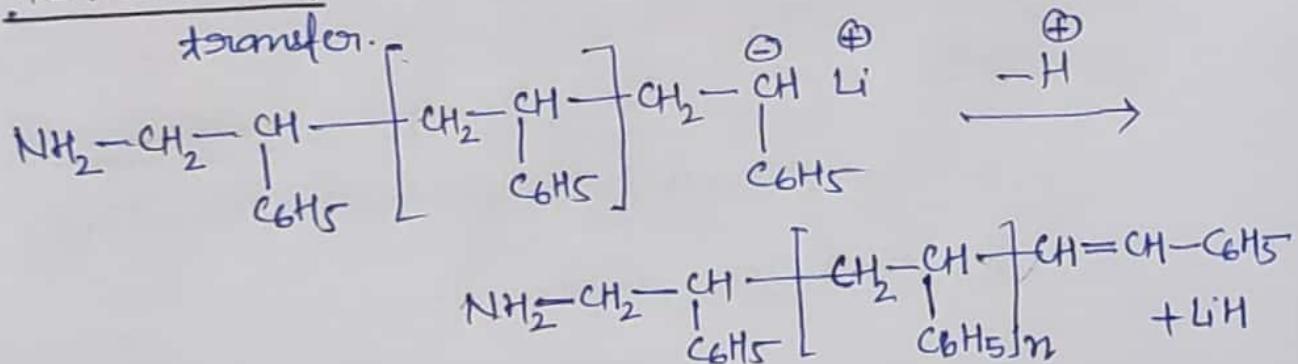


Propagation:



* this macromolecular anionic species formed in the propagation step is quite stable and kept as such for many years.

Termination: Termination occurs with hydride ion transfer.



(iv) COORDINATION POLYMERISATION :

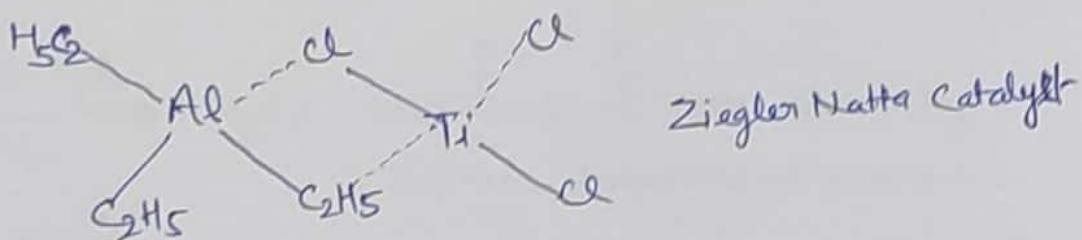
OR
Ziegler-Natta Polymerisation.

Addition polymerisation which takes place in the presence of Ziegler Natta catalyst is known as coordination polymerisation.

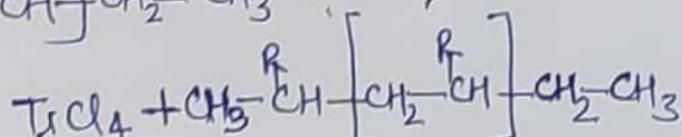
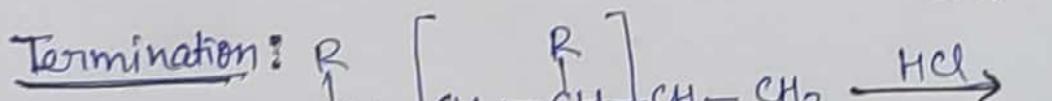
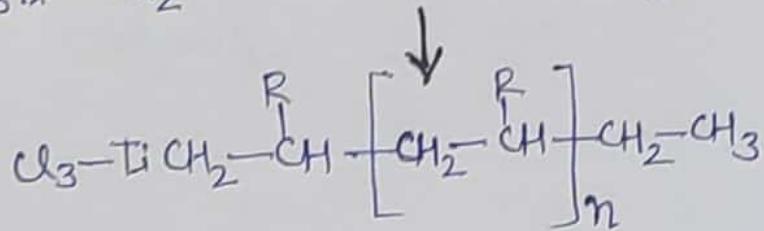
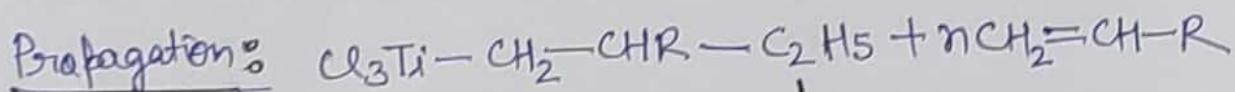
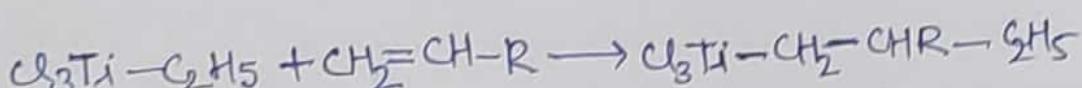
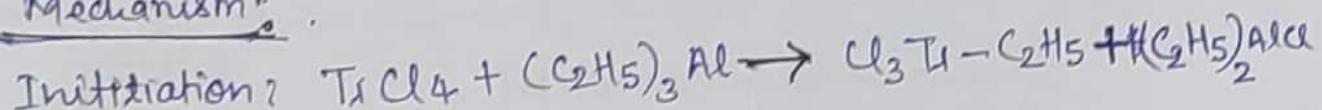
This polymerisation occurs in a stereospecific manner.

The polymer so produced is either isotactic or syndiotactic.

The commonly used Ziegler-Natta catalyst is triethylaluminium in combination with titanium trichloride or titanium tetrachloride.



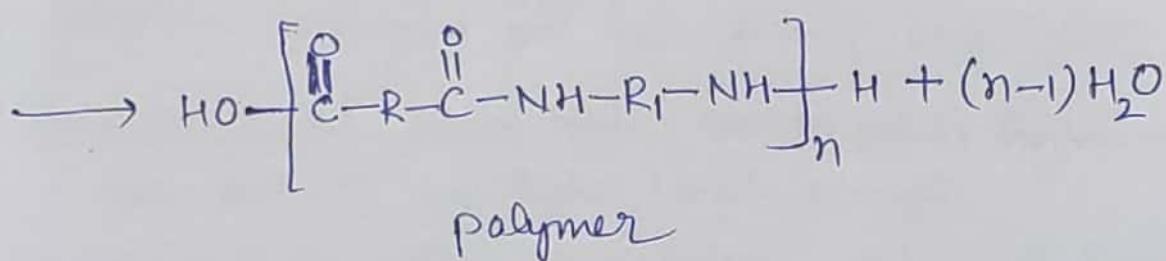
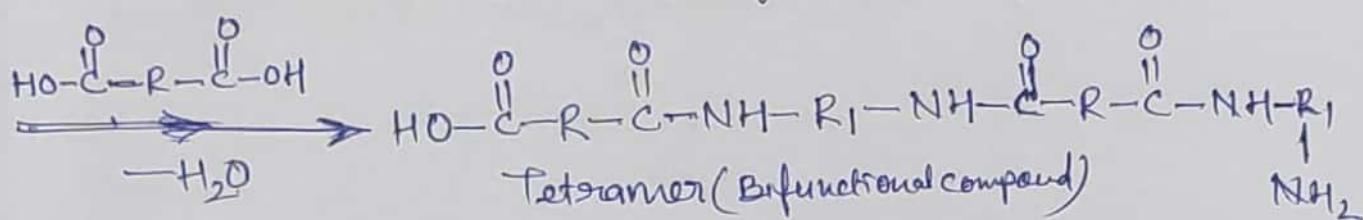
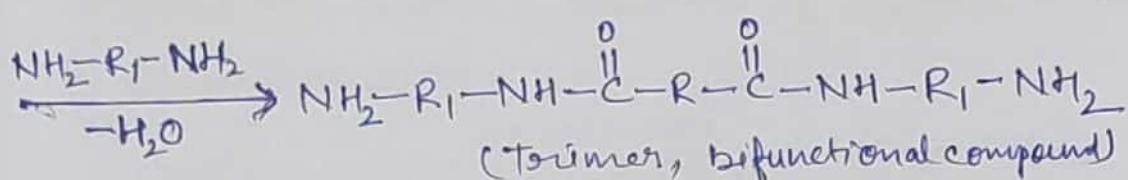
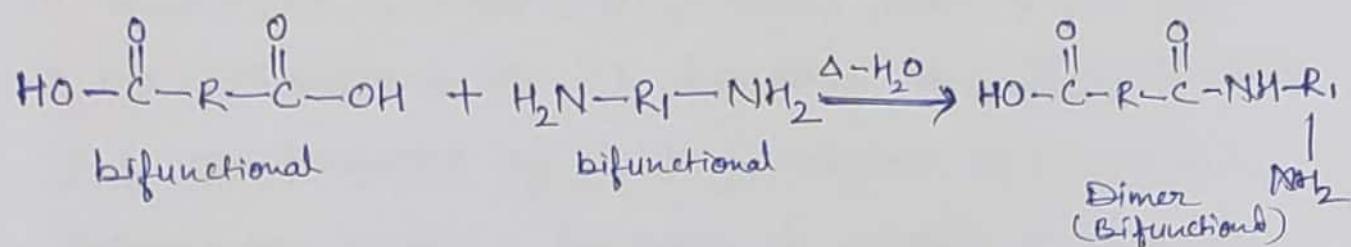
Mechanism:



(B) CONDENSATION POLYMERISATION.

In this type of polymerisation, a large number of monomer molecules combine together with the elimination of simple molecules like water, alcohol, ammonia, carbon dioxide etc. to form a polymer.

Condensation polymerisation generally occurs between bifunctional monomers and polyfunctional monomers.



SYNTHESIS, PROPERTIES AND USE OF — ADDITION POLYMERS

1. POLYETHYLENE

There are two variety of polyethylene

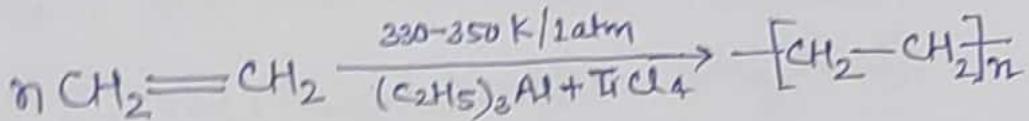
(i) High Density Polyethylene (HDPE)

(ii) Low density Polyethylene (LDPE)

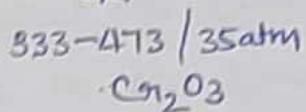
(i) High density Polyethylene (HDPE)

In this process, ethylene in a hydrocarbon solvent is heated to 330–350 K temperature under a pressure of one atmosphere in the presence of $(C_2H_5)_3Al + TiCl_4$.

It is also prepared by heating ethylene at 333–473 K temperature under a pressure of 35 atm in presence of Chromium oxide.



OR



These molecules are pack close together hence the polyethylene so formed are high density polyethylene.

Properties: (i) It shows higher melting point, higher density (0.941 to 0.965) and higher tensile strength.

(ii) It is much stiffer than LDPE and has high hardness.

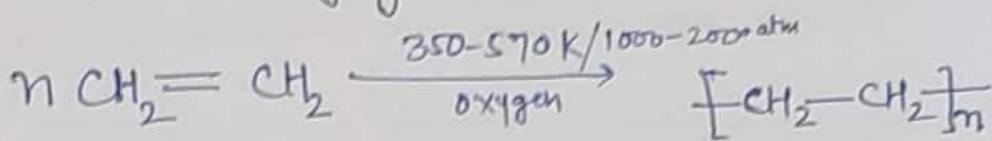
Uses: (i) Used in toys & housewares industries.

(ii) for wrapping food materials.

(iii) Use for strong plastic such as drums, pipes, tanks and crates etc.

(II) Low density Polyethylene (LDPE)

It is manufactured by heating ethylene to 350-570 K under a pressure of 1000-2000 atm and in the presence of trace of oxygen or peroxide. The polyethylene obtained by this method is highly branched.



LDPE.

Properties: ① It is a white, waxy translucent material.

② It has low density (0.91 g/cm^3).

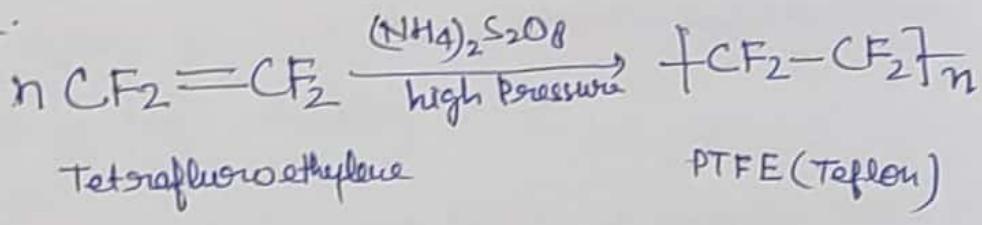
③ It shows moderate, ~~slightly inferior~~ tensile strength and high toughness.

Uses: ① It is used as film and sheet for packaging applications, including bags and wrapping etc.

② It is also used for insulation for electric wires.

2. TEFLO (Polytetrafluoro Ethylene)

Teflon is prepared by free-radical polymerisation of tetrafluoroethylene in the presence of ammonium peroxosulphate at high temperature under high pressure.



Tetrafluoroethylene

PTFE (Teflon)

Properties: ① It is extremely resistant to attack by ~~corrosive~~ ~~corrosive~~ corrosive reagent and solvents.

Except molten alkali metal and fluorine (it is inert— even to boiling aqua regia).

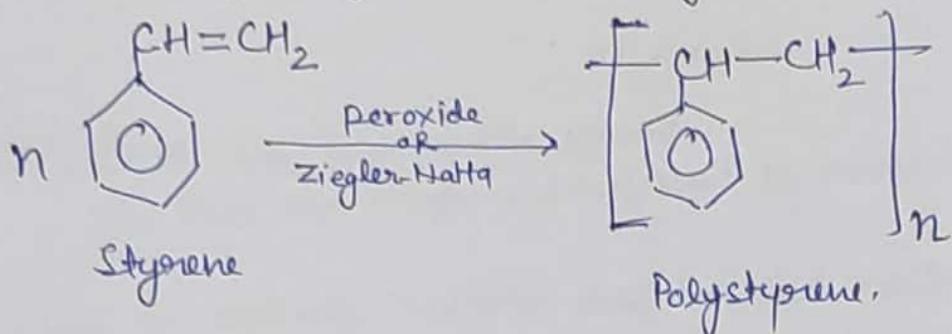
- ② It has high thermal stability (upto 360°C) and retains its properties over a wide temperature range.
- ③ Its density is unusually high (2.1 to 2.3)
- ④ Its refractive index is unusually low (1.375)

Uses: ① for wire coating, holders and spacers.

- ② for manufacturing gaskets, pump parts and laboratory equipments.

3. POLYSTYRENE

Polystyrene can be prepared by free radical polymerisation or by Ziegler-Natta polymerisation.



Properties: ① It is a linear polymer which is relatively inert chemically.

- ② It can be nitrated by fuming HNO_3 and sulfonated by conc. H_2SO_4 at 100°C to a water-soluble resin.
- ③ It has a poor stability.

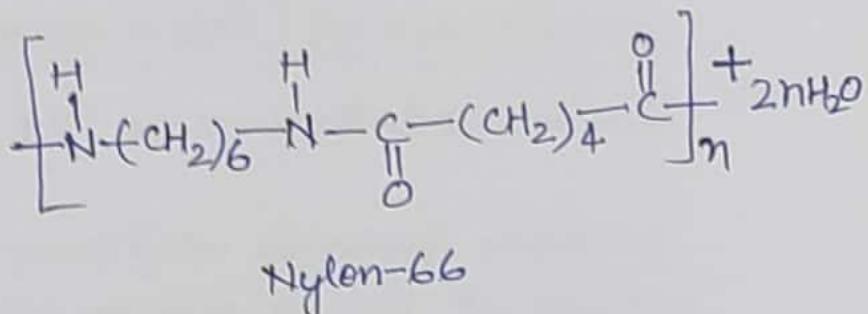
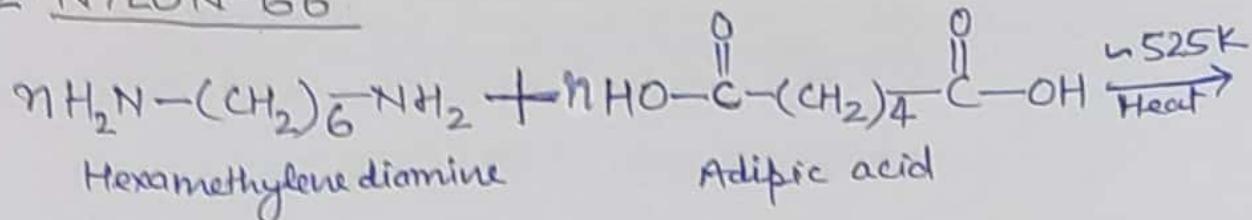
Uses: ① It is used for moulding of articles such as Comb, buttons, toys, buckets, lens, radio, T.V. etc.

- ② It is also used as high frequency insulator.

Properties: It is resistant to the action of chemical and biological substances and also low moisture absorbing power.
uses: used as a blend with cotton and wool in clothing.

uses: ① used as a blend with cotton and wool in clothing.
② it is also used in seat belts and for packing frozen food.

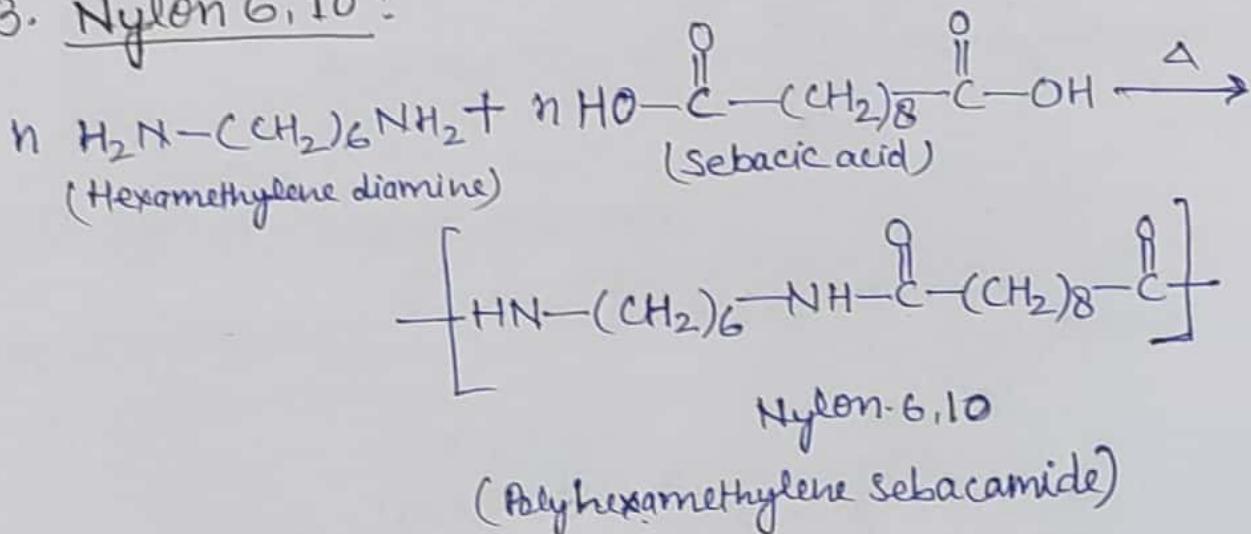
2. NYLON-66



Properties: ① It has high tensile strength.
② These are tough and resistant to abrasion.

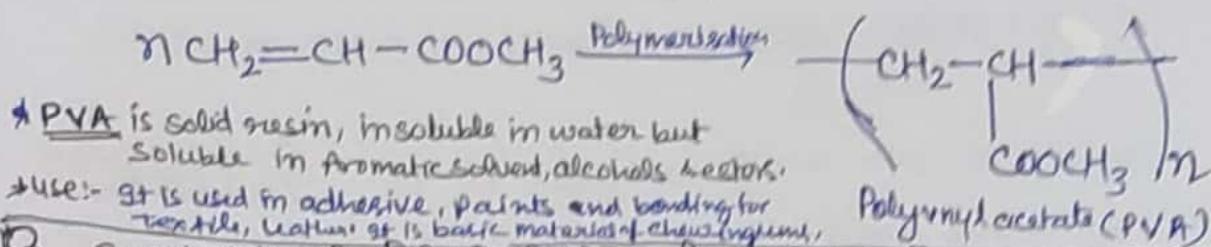
uses: Uses in making bristles and brushes, carpets and fabrics in textile industry.

3. Nylon 6, 10:



4. POLYVINYL ACETATE (PVA)

It is obtained by heating vinyl acetate in the presence of small amount of benzoyl peroxide.



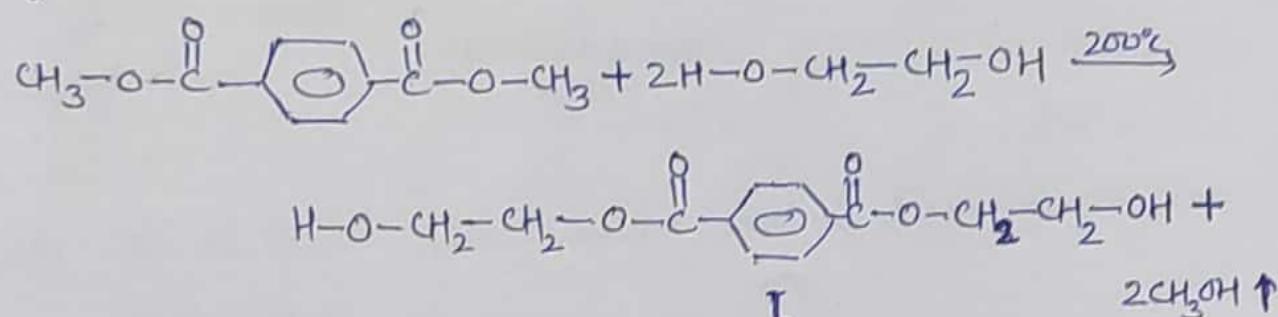
B. SYNTHESIS, PROPERTIES & USE OF CONDENSATION POLYMERS

1. Poly(ethylene terephthalate) PET or Dacron

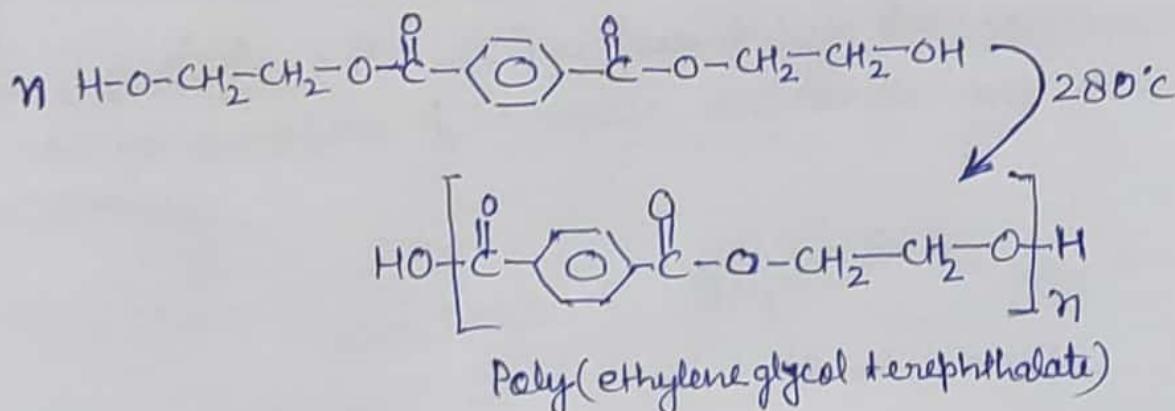
The monomers of PET is terephthalic acid and ethylene glycol.

PET is prepared from dimethyl ester of terephthalic acid and ethylene glycol. The reaction takes place in two steps:

Dimethylester of terephthalic acid and ethylene glycol gives products (I) at 200°C .



At 280°C (I) converts into PET.



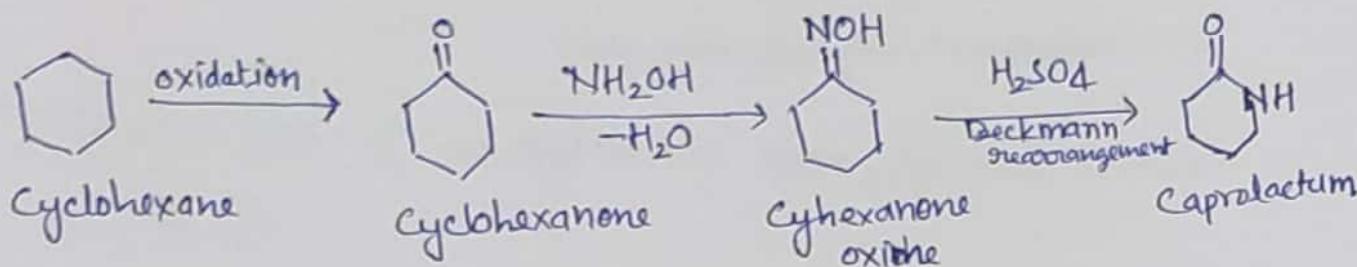
Properties: ① The polymer formed is extruded in the form of ribbon which is cut into chips.

Uses: ① It is not used as a fibre.

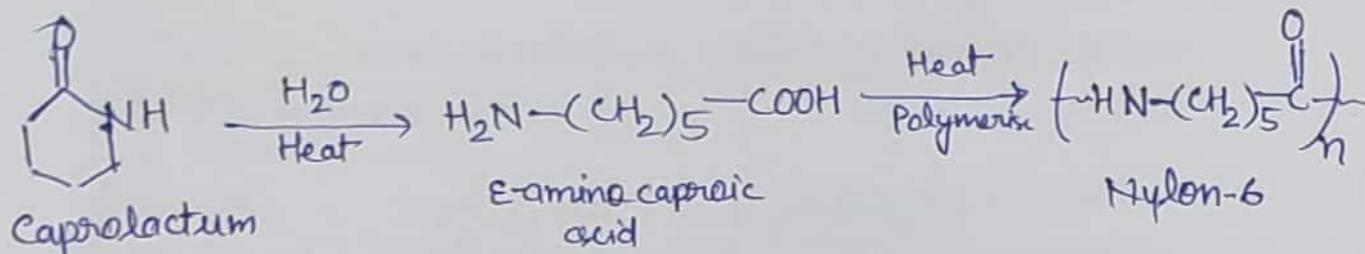
② It is used in brushes, bristles, sports equipment etc.

4. NYLON-6

It is obtained from the monomer Caprolactum. Caprolactum is obtained from cyclohexane.

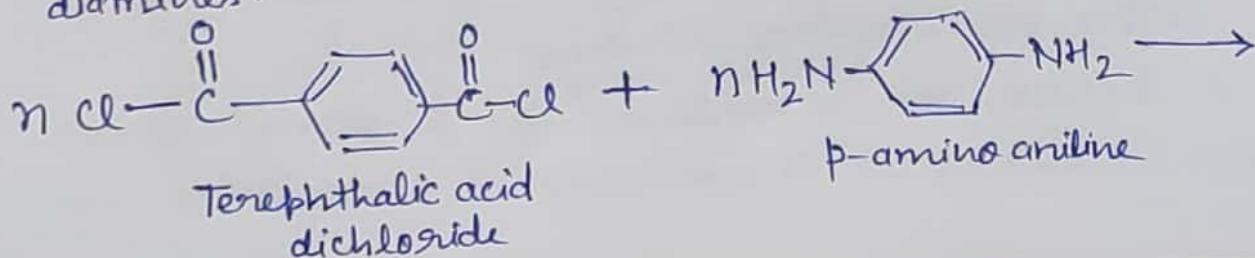


Caprolactum on heating with traces of water hydrolyses to ϵ -amino caproic acid which on continued heating undergoes self condensation and polymerises to give Nylon-6.

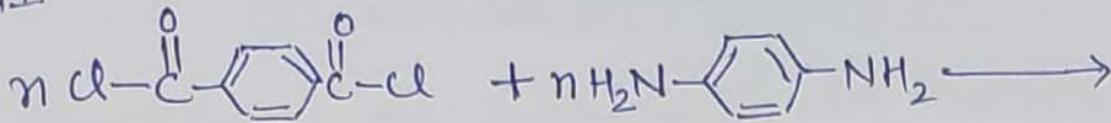


use: It is used for manufacture of tyre cords, fabrics, and ropes.

5. Kevlar: It is prepared by the condensation polymerization of aromatic dichloride and aromatic diamines.

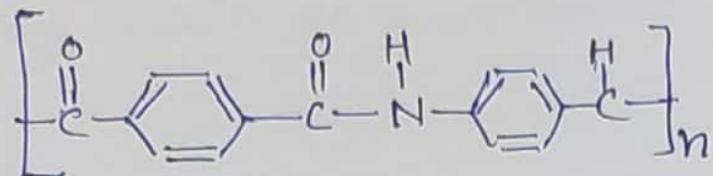


—Contd—



Terephthalic acid
dichloride

β -amino aniline



Kevlar

(Poly- ρ -para-phenylene terephthalamide)

Properties: It is exceptionally strong (5 times stronger than steel).

- ② It has high heat stability and flexibility.
- ③ The unique properties of 'Kevlar' are due to the delocalized bonding which causes the benzene rings to be inflexible.

Uses: It is used in aerospace and aircraft industries, ropes, cables, protective clothing, bullet proof vests, helmets etc.

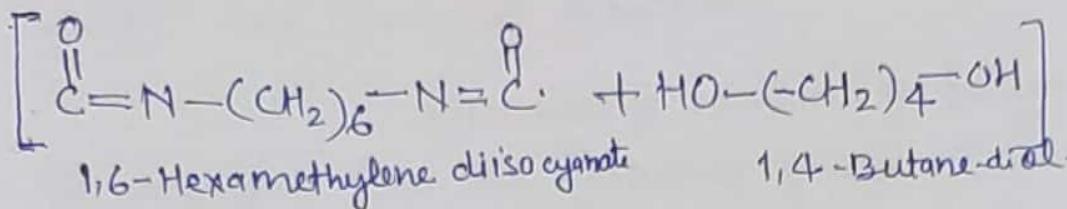
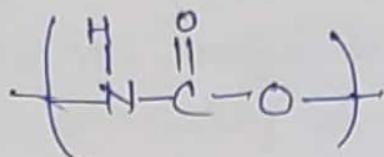
SYNTHETIC RUBBERS:

Synthetic rubber is the term used for that rubber like material which is obtained by means of synthesis and can compete with the natural rubber in its many uses. Synthetic rubbers are any vulcanisable man-made rubber like polymer which can be stretched to at least twice its length, but it returns to its original shape and dimensions as soon as stretching force is released.

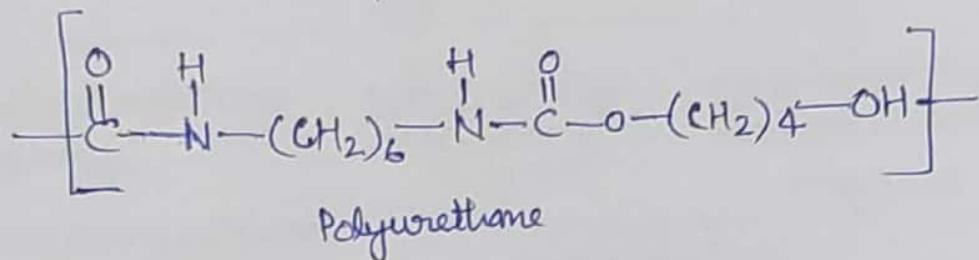
Synthetic rubbers are either homopolymers of 1,3-butadiene or its derivatives or are copolymers in which one of the monomers is 1,3-butadiene.

Example: Polyurethane (PU)

Polyurethanes are prepared by the rearrangement polymerization of di(α,β)-isocyanate with di(α,β)-hydroic alcohol, and they contain the characteristic — urethane linkages



↓
Rearrangement
Polymerization



- Properties:
- ① Polyurethane rubbers are highly resistance to oxidation.
 - ② They have good resistance to many organic solvents.
 - ③ Polyurethane are less stable at elevated temperature in comparison with Nylons.

uses: used in surface coating and manufacturing of foams and spandex fibres.

Conducting Polymers

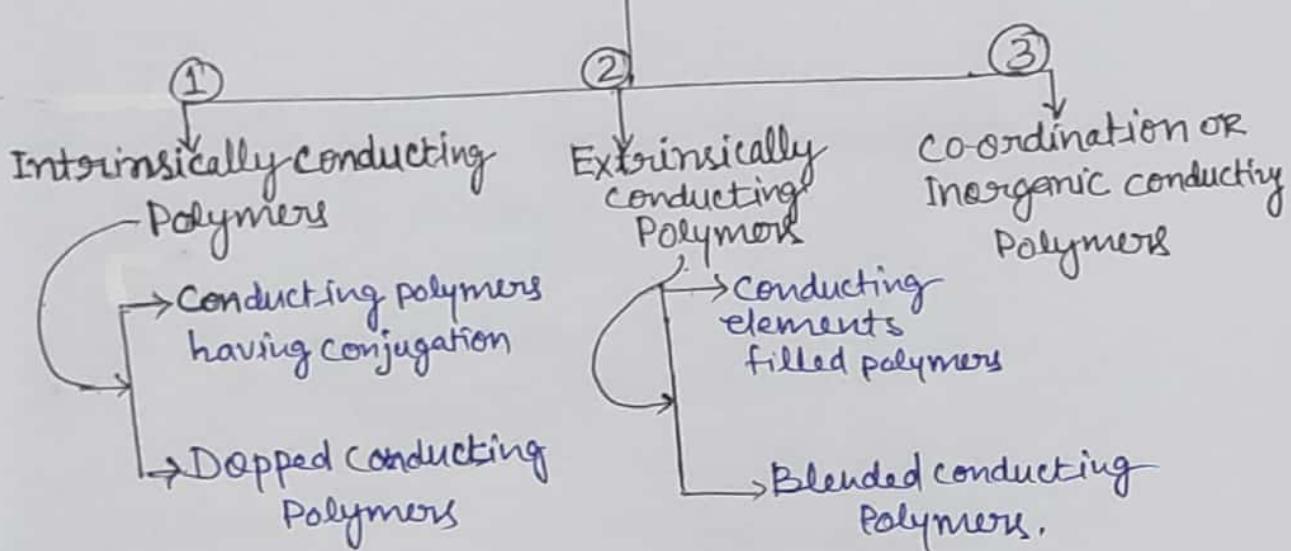
Polymers which can conduct electricity are called electrically conducting polymers.

Ordinary polymers obtained by usual methods are electrical insulators. However, some specific polymers may act as conductors.

Such polymers are useful because of their ease of fabrication, flexibility or strength, lightness of weight and chemical inertness.

Electrically conducting polymers can be classified into the following groups:

Electrically Conducting Polymer



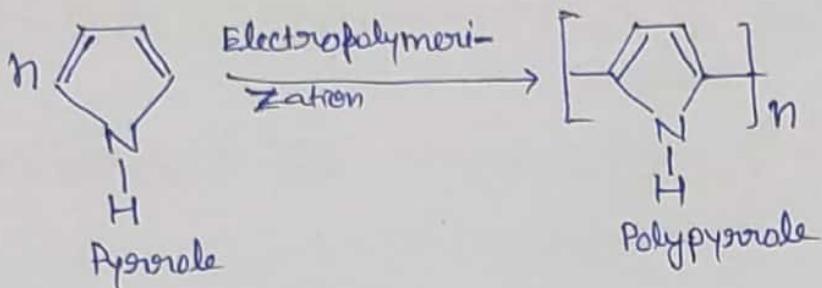
① INTRINSICALLY CONDUCTING POLYMERS:

(i) Conjugated Polymers having conjugated π -electrons:

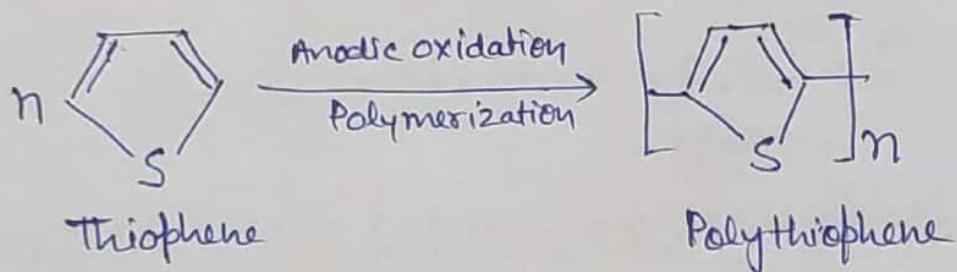
Such type of polymers essentially contain conjugated π -electrons backbone. These π -electrons are loosely held electrons and are responsible of electrical charge. Under the influence of electric field conjugated π -electrons of polymer get excited.

Then, they can be transported through the solid polymeric material. Overlapping of orbitals over the entire back-bone results in the formation of valence bonds as well as conduction bonds, which extend over the complete polymer molecule. Thus presence of conjugated π -electrons in a polymer increases its conductivity to a large extent.

Example: Polypyrrole is obtained by electropolymerization of pyrrole as a highly coloured, dense-conducting film.



Example: Polythiophene can be polymerized by oxidation of thiophene.



(ii) Doped Conducting Polymers:

Such kind of conducting polymers obtained by exposing the polymer to a charge transfer agent in either gas phase or in solution are called doped conducting polymers.

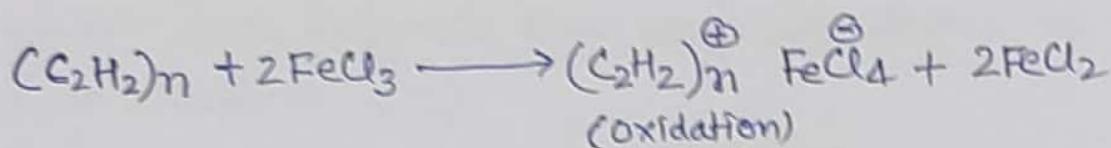
Dopping is the process by which conductivity of the polymers may be increased by creating negative or positive charge on the polymer.

--backbone by oxidation or reduction.

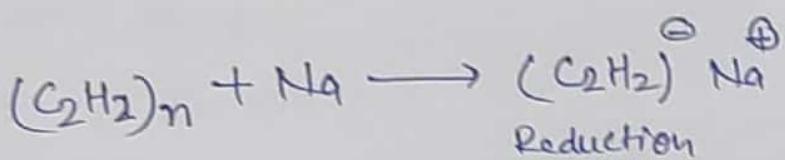
Dopping is of two types—

(a) P-dopping: It is a technique in which an ICP (intrinsically conducting polymer) is oxidised with Lewis acid (electron acceptor) creating the positive charge on the backbone of the polymer. Some of the common P-dopant are—

I_2 , Ber_2 , FeX_3 , PF_5 , AsF_5 etc.



(b) N-Dopping: This is a technique in which an ICP is reduced with Lewis bases creating the negative charge on the backbone of the polymer. Some of the common N-dopant used are Li, Na, K, Ca etc.



② EXTRINSICALLY CONDUTING POLYMERS(ECP) ?

This type of polymers own their conductivity due to the presence of externally added ingredients in them. It is of two types:

(a) Conductive element filled Polymers:

These polymers ~~are~~ act as the binder to hold the conducting material (i.e. carbon black, metallic fibres, metallic oxides etc.) together in the solid entity. These are usually low cost, light weight, mechanically sound and easily processable.

(b) Blended conducting Polymers: It is obtained by blending a conventional polymer with a conducting polymer. Such polymers possess better physical, chemical, electrical and mechanical properties and they can be easily processed.

③ CO-ordination or Inorganic polymers:

These polymers contain charge transfer complexes and are obtained by combining metal with polydentate ligands. Such polymers have very low degree of polymerisation (< 18).

- Application:
- (i) in rechargeable light weight batteries.
 - (ii) used in making button type batteries.
 - (iii) used as conductive paints.
 - (iv) used as electro-chemical accumulators
 - (v) used as biosensors and chemical sensors. Used for making sensors for pH, O₂, NO_x, SO₂, NH₃ and glucose as analytical sensors.
 - (vi) used in solar cells.
 - (vii) used in telecommunication systems.
 - (viii) used in smart windows.

Molecular Weight of Polymers,

Molecular weight of polymer increases continuously during the polymerization reaction (addition/condensation) depending upon the simple molecular units joined together to form macromolecules. Since the polymerization chains might be broken on various-

stages, the final product will not have macromolecules of same molecular weights. Thus, the molecular weight of the individual macromolecules in a particular sample of polymer are different.

Hence, an average value of molecular weight is taken. There are two types of average molecular weight of polymers—

(1) Number average molecular weight (\bar{M}_n)

(2) Weight average molecular weight (\bar{M}_w)

(1) Number Average Molecular weight (\bar{M}_n)

It may be defined as the weight of the sample divided by the number of moles n in the sample i.e.,

$$\bar{M}_n = \frac{\text{weight}}{n}$$

Suppose, n_1 monomer molecule (i.e. n_1 molecule) have MW = M_1

n_2 monomer molecule (i.e. n_2 molecule) have MW = M_2

n_3 monomer molecule (i.e. n_3 molecule) have MW = M_3

The number-average molar mass is defined as:

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

$$\bar{M}_n = \frac{\sum_i n_i M_i}{\sum n_i}$$

↑
number-average
molar mass.

(i) Weight Average Molecular Weight (\bar{M}_w)

Weight average depends upon the mass of the material in different molecular weight fraction. In this method, while taking average, the molecular weight of each species is multiplied by the weight of species and not the number.

Thus,

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2 + m_3 M_3 + \dots}{m_1 + m_2 + m_3 + \dots}$$

But $m_1 = n_1 M_1$, $M_2 = n_2 M_2$ and so on, where n_1 and n_2 are mole of molecular weight M_1 and M_2 respectively.

Hence,

$$\bar{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \dots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}$$

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

(iii) Degree of Polymerisation (D_p):

Degree of polymerisation represents the number of repeating units in a polymer. For example, if polymer molecule contain 1000 repeat units, the D_p is 1000. D_p is related with molecular weight of the polymer as:

$$M = D_p \cdot m$$

Where, M = molecular weight of the polymer

D_p = degree of polymerisation

m = molecular weight of repeat unit or monomer

D_p can expressed in terms of \bar{M}_n or \bar{M}_w .

$$\bar{M}_n = (D_p)n \cdot m$$

$$\bar{M}_w = (D_p)^w \cdot m$$