- Unit -5

UNIT-5

Engineering chemistry (RAS-102)

Lecture NO. 12

(Basic Concepts of Polymer)

Polymer - The word 'Polymer' is derived from two greek words Poly (=many) and meros (= parts or units). Polymer may be defined as -

"when two compounds have the same emperical formulae but differ widely in their molecular masses, the compound having high molecula mass is termed as a polymer of the simple low-molecular mass molecule."

OR

"A polymer is a giant chain like molecule obtained by intermolecular combinations of the same are different type of smaller molecules." The phenomenon is known as polymerization.

eq. $$nCH_2=CH_2 \xrightarrow{Polymerization} {(CH_2-CH_2)}_n$$
Monomer Polymer

Repeat unit - The unit which repeat again and again in the polymer ($-CH_2-CH_2-$) is known as Repeat unit

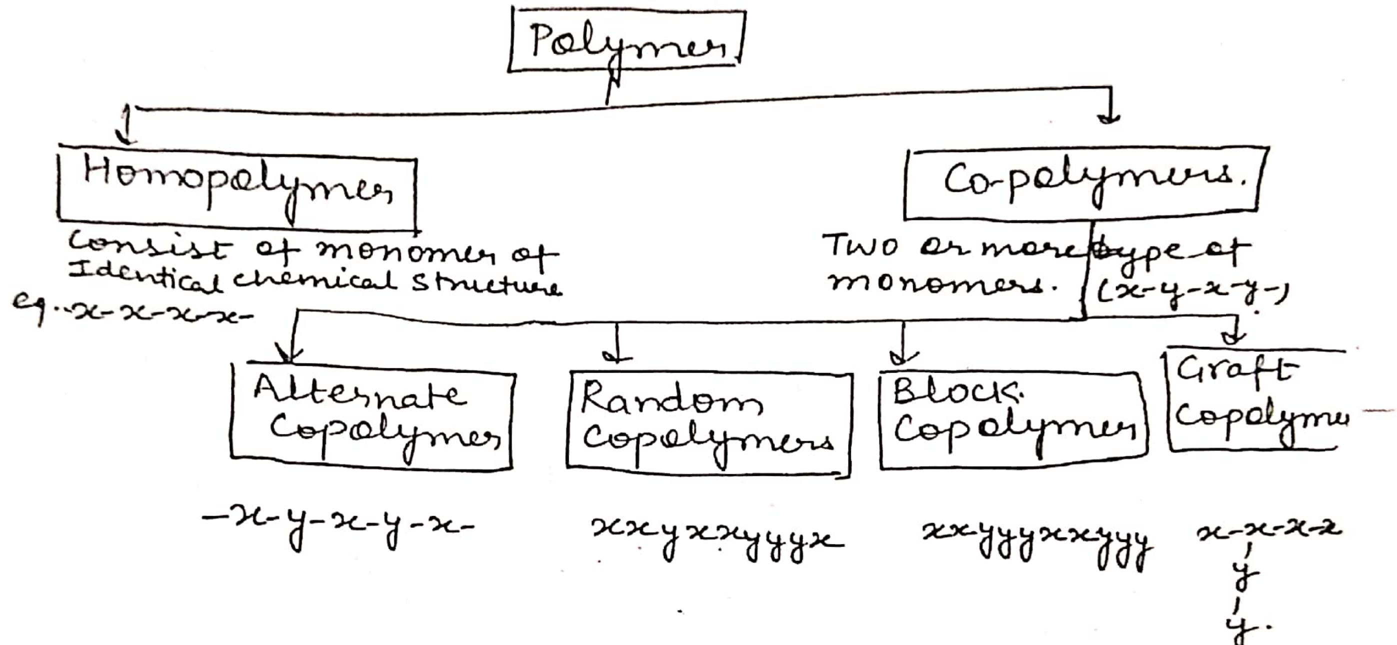
Degree of polymerization - The no. of Repeating unit in chain formed in a Polymer is known as 'degree of polymerization' (n).

Functionality - The no. of bonding sites present in a monomer is known as its functionality.

Classification of polymers

Polymer can be classified into several ways as described below -

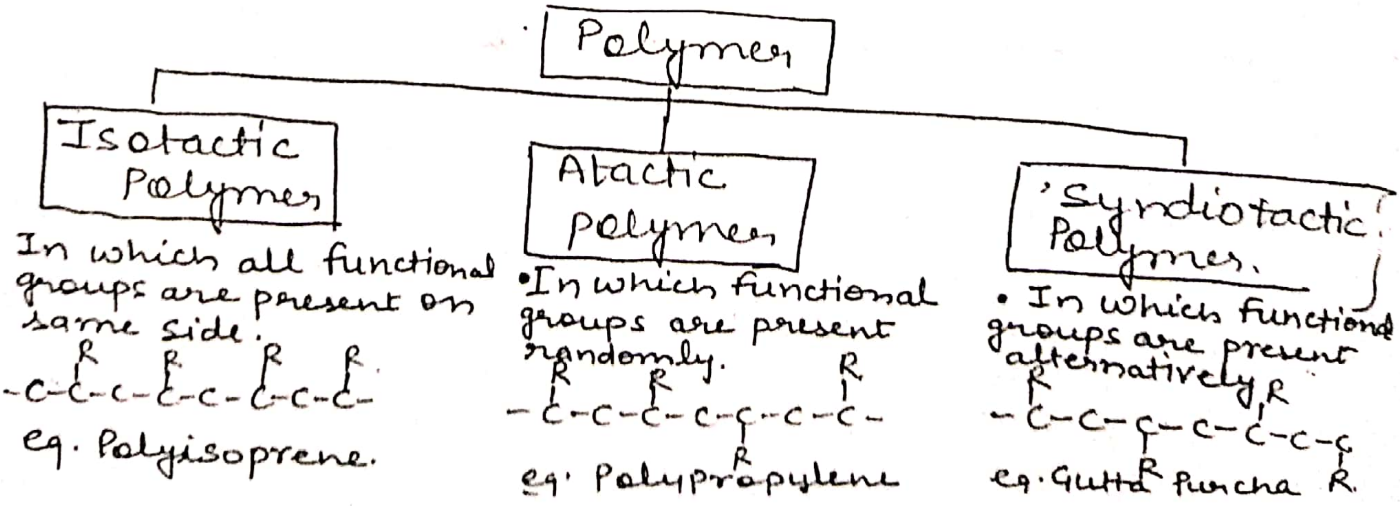
(1) Based on Number of Monomers -



Polymer
- Homopolymer – Consist of monomer of Identical chemical structure eg. -x-x-x-x-
- Co-polymers. – Two or more type of monomers. (x-y-x-y-)
  - Alternate Copolymer – -x-y-x-y-x-
  - Random Copolymers – xxyxxyyyx
  - Block Copolymer – xxyyyxxyyy
  - Graft Copolymer – x-x-x-x with -y-y branch

(2) Based on Tacticity -

The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to main chain. Due to difference in configuration (tacticity), the physical properties are affected.



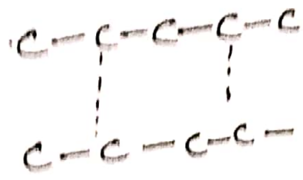
Polymer
- Isotactic Polymer – In which all functional groups are present on same side. eg. Polyisoprene.
- Atactic Polymer – In which functional groups are present randomly. eg. Polypropylene
- Syndiotactic Polymer. – In which functional groups are present alternatively. eg. Gutta Purcha

(3) Based on functionality

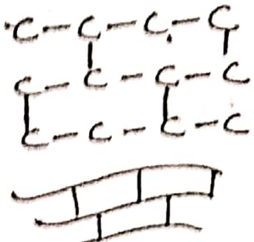
Polymer

- Linear or Straight chain polymer
- Branched chain Polymer
- Network polymer.

eg. HDPE
Polystyrene
Nylon



eg. LDPE



eg. Bakelite
Urea formalde-hyde.

(4) Based on source.

Polymer.

- Natural
  eg. Cellulose
- Artificial.
  eg. Nylone
  synthetic Rubber.

* Questions asked in university examination.

- * Define the term polymer and polymerization.
- * Define the term Repeat unit and degree of polymerization
- * Briefly explain polymer with their classification.
- * Give various types of polymers on the basis of tacticity.

UNIT-5

Eng. chemistry (RAS-102)

Lecture NO-13

(Basic concepts of Polymer)

Polymerization-

"The process of conversion of monomers into polymers are known as polymerization."

Types of polymerization- Polymerization is of two types-

(1) Addition polymerization
(2) Condensation polymerization.

(1) Addition polymerization-

" polymers which are formed by the polymerization of monomers without elimination of atoms or groups are known as addition polymers and the phenomenon is known as Addition polymerization"

Eg. PVC, PAN, PMMA, Teflon etc.

Eg. $nCH_2=CH_2 \xrightarrow[\text{catalyst}]{\text{heat, light}} -\!\!\left(CH_2-CH_2\right)\!\!-_n$

Ethylene → Polyethylene

$$nCH_2=\underset{\displaystyle Cl}{\underset{|}{CH}} \longrightarrow -\!\!\left(CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}\right)\!\!-_n$$

Vinyl chloride → Polyvinyl chloride (PVC)

Mechanism of Polymerization-

Polymerization takes place in following three steps-

(A) chain Initiation
(B) chain Propagation
(C) chain termination.

Types of polymerization mechanism depands on first step of polymerization i.e chain initiation; depanding on that Mechanism is of following three types -

(I) free Radical Polymerization

(II) Cationic polymerization

(III) Anionic polymerization.

(I) Free Radical Polymerization -

In this type of mechanism chain initiation takes place by free radical. This mechanism takes place in following steps -

(A) **Chain Initiation** - organic peroxides are generally used as initiators. These peroxides undergo homolytic cleavage to form free radical. Then free radical attack on monomer to initiate the chain reaction.

$$\underset{\substack{\text{(Initiator)} \\ \text{(Peroxides)}}}{I} \longrightarrow R^\circ$$

$$R^\bullet + CH_2 \overset{..}{=} CH_2 \longrightarrow \underset{\text{Free Radical.}}{R-CH_2-\dot{C}H_2}$$

(B) **chain propagation** - free radical formed in first step attacks another monomer to form new free radical which then attacks other molecule and the chain propagates.

$$R-CH_2-\dot{C}H_2 + CH_2 \overset{..}{=} CH_2 \longrightarrow R-(CH_2-CH_2)-CH_2-\dot{C}H_2$$

$$R(CH_2-CH_2)CH_2-\dot{C}H_2 + CH_2 \overset{..}{=} CH_2 \longrightarrow R(CH_2-CH_2)_2\,CH_2-CH_2^\bullet$$

In general

$$R-(CH_2-CH_2)^\bullet + nCH_2=CH_2 \longrightarrow R(CH_2-CH_2)_n\,CH_2-\dot{C}H_2$$

(C) **Chain termination** - Free radical formed in Step-II undergo chain termination.

$$R-(CH_2-CH_2)_n-CH_2-\dot{C}H_2 + R^{\circ} \longrightarrow R-(CH_2-CH_2)_n CH_2-CH_2-R$$

Polymer.

(II) **Cationic polymerization** - when chain initiation takes place by Cation, then mechanism is known as Cationic polymerization. Like free radical mechanism it also takes in three steps.

(A) **Chain initiation** - ~~eg~~. H_2SO_4, BF_3, $AlCl_3$ are the example of Cationic initiators.

$$H^+ + CH_2=CH_2 \longrightarrow CH_3-\overset{\oplus}{C}H_2$$

(B) **Chain propagation** -

$$CH_3-\overset{\oplus}{C}H_2 + CH_2=CH_2 \rightarrow CH_3-CH_2-CH_2-\overset{\oplus}{C}H_2$$

In general

$$\vdots$$

$$CH_3-CH_2-(CH_2-CH_2)_n CH_2-\overset{\oplus}{C}H_2$$

(C) **Chain termination** -

$$CH_3-CH_2-(CH_2-CH_2)_n CH_2-\overset{\oplus}{C}H_2 + B^{\ominus}.$$

$$\downarrow$$

$$CH_3-CH_2-(CH_2-CH_2)_n CH_2-CH_2-B$$

(III) Anionic polymerization- when chain initiation takes place by anion then mechanism is called as anionic polymerization. It also takes place in three steps -

(A) Chain Initiation- Initiator examples are bases and organometallic compounds.

$$CH_2=CH_2 + B^{\ominus} \longrightarrow B-CH_2-\overset{\ominus}{C}H_2$$

(B) Chain Propagation-

$$B-CH_2-\overset{\ominus}{C}H_2 + CH_2=CH_2 \longrightarrow B-CH_2-CH_2-CH_2-\overset{\ominus}{C}H_2$$

$$\vdots$$

$$B-(CH_2-CH_2)_n-CH_2-\overset{\ominus}{C}H_2$$

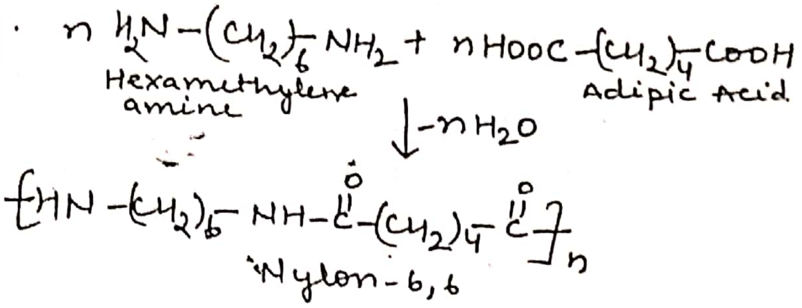
(C) Chain termination-

$$B-(CH_2-CH_2)_n-CH_2-\overset{\ominus}{C}H_2 + A^{\oplus} \longrightarrow B-(CH_2-CH_2)_n-CH_2-CH_2-A$$

(2) Condensation Polymerization- "Polymers which are formed by the polymerization of monomers with elimination of small molecules like NH_3, H_2O, HCl, CH_3OH etc are known as condensation polymers and the phenomenon is known as condensation Polymerization."

Eg. Nylon-6,6, Nylon-6,10, Terelene, Bakalite

Eg.



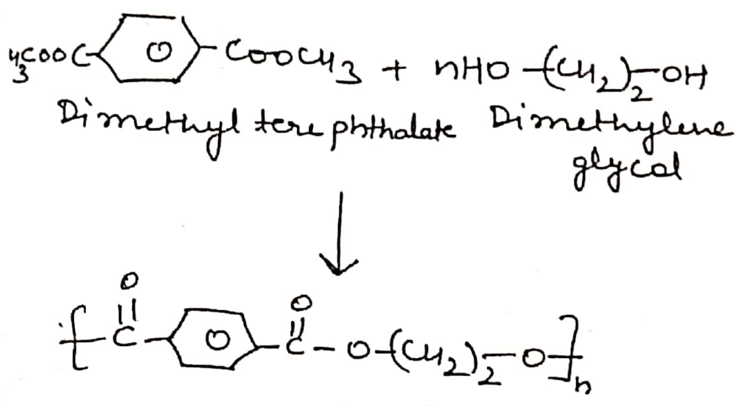
$$n\,H_2N-(CH_2)_6-NH_2 + n\,HOOC-(CH_2)_4-COOH \xrightarrow{-nH_2O} \left[HN-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n$$

Hexamethylene amine

Adipic Acid

Nylon-6,6

Eg.



$H_3COOC-C_6H_4-COOCH_3 + nHO-(CH_2)_2-OH$

Dimethyl terephthalate

Dimethylene glycol

Terylene.

Condensation polymerization can also take place in three types -

(1) Free Radical polymerization
(2) Cationic polymerization
(3) Anionic polymerization.

*<u>Questions asked in University examination</u>

- * Define the term polymer and polymerizatio
- * Explain polymerization with its mechanism.
- * Differentiate Addition and Condensation polymerization.

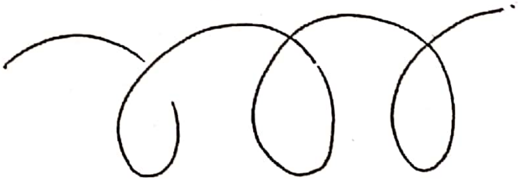
Eng. chemistry. (RAS-102) UNIT-5

Lecture NO. 15

(Preparation and Applications of BuNa-N, BuNa-S, Neoprene)

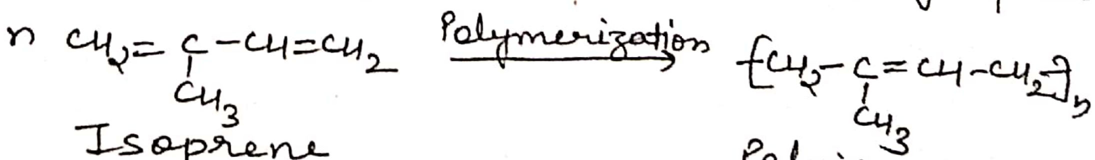
Elastomers or Rubber - "The group of polymers exhibiting high degree of elasticity, stretching at least twice of their Orignal length under the action of tensile force and recover their dimensions after the removal of the applied force, just like Rubber, are Known as elastomers."

They are cross linked are in the form of coils, when stress subjected, the coils open up and when stress releases it reverts back to its orignal shape.



Elastomer.

Natural Rubber - Natural Rubber occurs in plants as a milky latex, which is a dispersion of isoprene. During the treatment these isoprene molecule polymeri-se to form, long coiled chains of cis-polyisoprene



$$n\, CH_2=\underset{CH_3}{\underset{|}{C}}-CH=CH_2 \xrightarrow{\text{Polymerization}} \left[CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_2\right]_n$$

Isoprene

Polyisoprene (Natural Rubber

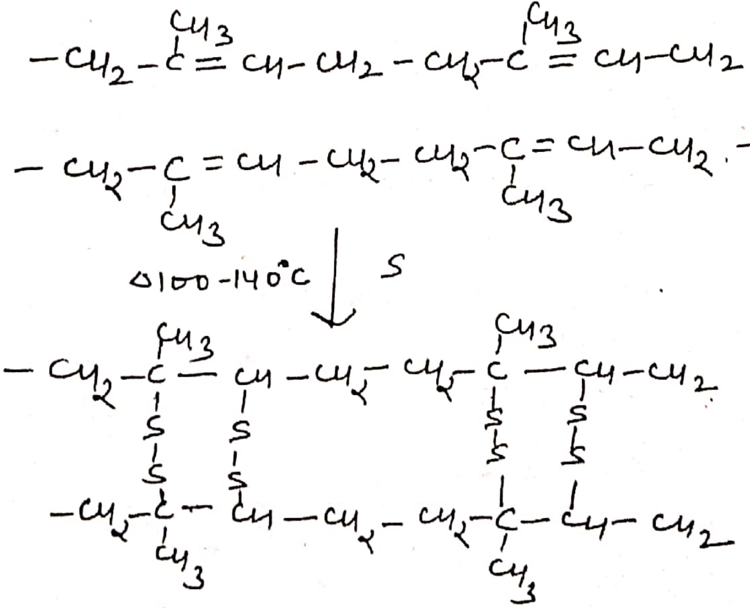
Drawbacks of Natural Rubber - Raw Rubber obtained is not of more use because it has very undesirable properties. eg -

(1) Its low resistance to frinction
(2) Tendency to oxidise
(3) Tendency to become sticky on heating
(4) Brittle on cooling and
(5) limited elasticity

Vulcanisation - In Vulcanisation, the raw Rubber is made to heat with sulphur or Sulphur Compounds at a temperature to 150°c for a few hours. This process gives rubber of improved quality.

Natural Rubber + S ⟶ Vulcanized Rubber
or
Cross-linked Rubber.

Chemistry of Vulcanisation - In vulcanisation there occurs the formation of cross-linkage between polymer chains.



'Structure of Vulcanised Rubber'.

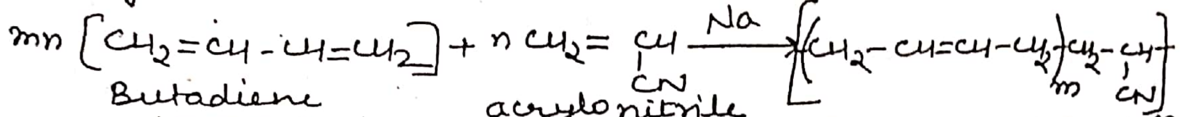
Synthetic Rubber - The term 'synthetic rubber' stands for rubber material which is prepared by synthesis. Eg. of synthetic Rubber are- BuNa-N ; BuNa-S , Neoprene, Butyl Rubber, Polyurethane.

BuNa-N or Nitrile Rubber -

It is a copolymer of Butadiene (75 parts) and acrylonitrile (25 parts.)

Monomer - Butadiene, acrylo nitrile.

Synthesis - Addition polymer, copolymer.



$$mn\left[CH_2=CH-CH=CH_2\right] + n\,CH_2=\underset{CN}{\underset{|}{CH}} \xrightarrow{Na} \left[(CH_2-CH=CH-CH_2)_m\,CH_2-\underset{CN}{\underset{|}{CH}}\right]_n$$

Butadiene (75 part)

acrylonitrile (25 part)

Poly acrylonitrile Butadiene (BuNa -N)

Properties -

(i) excellent resistance to heat, sunlight, oils, acids & salts.

(ii) Less resistant to alkalis, because of the presence of cyano group.

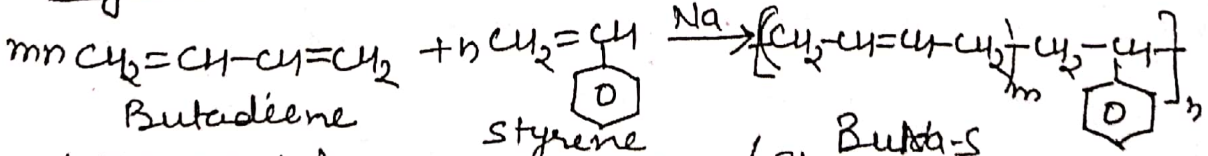
(iii) Vulcanized rubber is more resistant to heat than natural Rubber, i.e vulcanisation of BuNa-N is possible.

Uses - (i) For making conveyor belt
(ii) high altitude aircraft Components, tank linings, gaskets, printing rollers etc.

BuNa-S or styrene Rubber -

Monomers - Butadiene and styrene

Synthesis - Addition polymer, copolymer.



Butadiene (75 parts)

styrene (25 part

BuNa-S (Styrene Rubber) Poly butadiene styrene

Properties- Styrene butadiene Rubber(SBR) has following properties-

(i) High load bearing capacity
(ii) Pesses high abrasion ~~to~~ resistance.
(iii) It gets readily oxidized,
(iv) It can be Vulcanized.

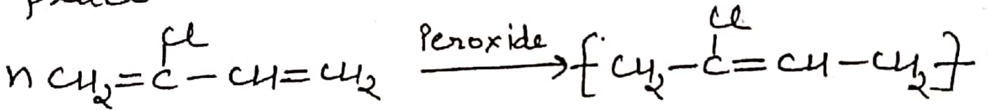
Uses-

(i) In Motor tyres (ii) shoes soles and foot wear component
(iii) Wire and Cable insulator (IV) Floor tiles.

Neoprene or GR-M Rubber

Monomer- chloroprene

Synthesis- Addition polymer, Homopolymer, syndiotattic i.e trans addition takes place.



$$n\,CH_2=\overset{Cl}{C}-CH=CH_2 \xrightarrow{Peroxide} \{CH_2-\overset{Cl}{C}=CH-CH_2\}$$

chloroprene

Polychloroprene or Neoprene.

Properties-

(i) Structure of Neoprene is closely related to Natural Rubber.
(ii) superior resistant to vegetable and mineral oils due to present of cl atom.
(iii) Can be vulcanized.

Uses-

(i) For making sponges, gaskets, tyres, shoes soles.
(ii) Linning of reaction vessel.
(iii) It is corrossion resistant

UNIT-5

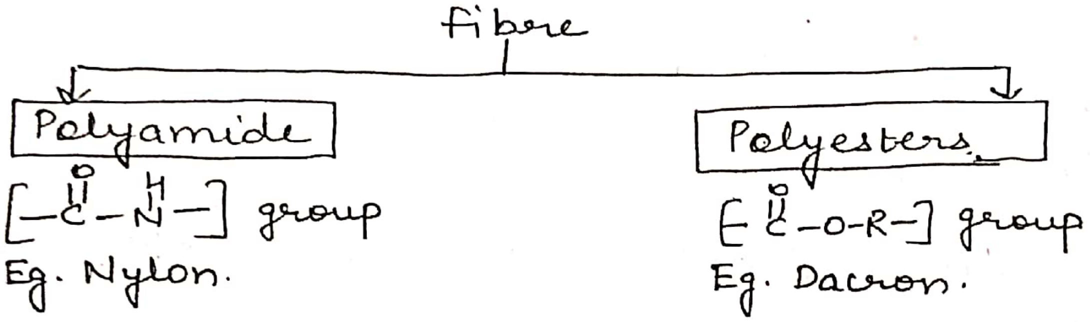
Eng. chemistry (RAS-102)

Lecture No. 16

(Preparations and applications of Nylon-6, Nylon-6,6, Terylene)

Fibres -

Fibres are polymers having thread-like structure with high aspect ratio (length to diameter ratio). They have high intermolecular forces.
Fibres have two categories -



$[-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-]$ group

$[-\overset{O}{\overset{\|}{C}}-O-R-]$ group

(1) **Polyamides** - Polyamides are the polymer obtained by condensation polymerisation of acids (bifunctional) and amines (bifunctional). They contain $[-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-]$ linkage.

Nylon is a generic term for synthetic polyamides capable of forming fibres. Polyamids of commercial importance are -
Nylon-6, Nylon-6,6, Nylon-6,10, Nylon-11

The numbering system represents the number of C-atom (first in amines, while second in acids.).

Nylon-6,6 - It is a copolymer.
It is prepared by the condensation polymerization.

Monomers - Adipic acid, Hexamethylene diamine.

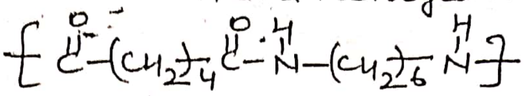
props - high strength, toughness & moisture resistant
insoluble in common solvent

Uses - 1 Substitute for metals to make plastic gears & bearings.
2. Textile fibres, 3. Making Tyre cords.

Synthesis-

$n\ HOOC-(CH_2)_4-COOH + n\ H_2N-(CH_2)_6-NH_2 \longrightarrow$

Adipic acid — Hexamethylene diamine



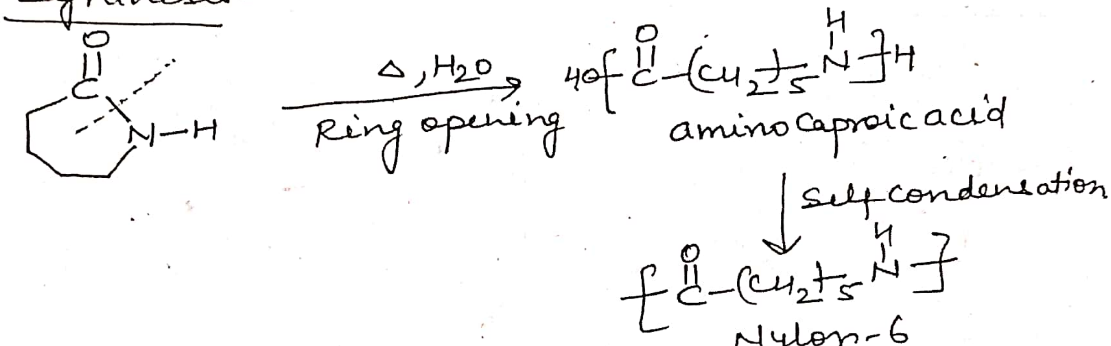
$$-\!\!\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}} \right]\!\!-$$

∴ Nylon 6,6

Nylon-6 -

It is a homopolymer. It is prepared by ring opening of ε-caprolactum or by self condensation of ε-amino caproic acid.

Synthesis -



$$HO-\!\left[\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}} \right]\!-H \xrightarrow{\text{Self condensation}} -\!\!\left[\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}} \right]\!\!-$$

Properties of Polyamides -

(i) They have high m.pt and possess high temperature stability

(ii) They are resistant to chemicals.

(iii) Their moulding and extrusions have good physical strength.

Uses -

(i) They are used for making socks, dresses, carpets etc.

(ii) In making filament for ropes, bristles for brushes, ~~tyre~~ tyre cords etc.

(2) Polyesters.

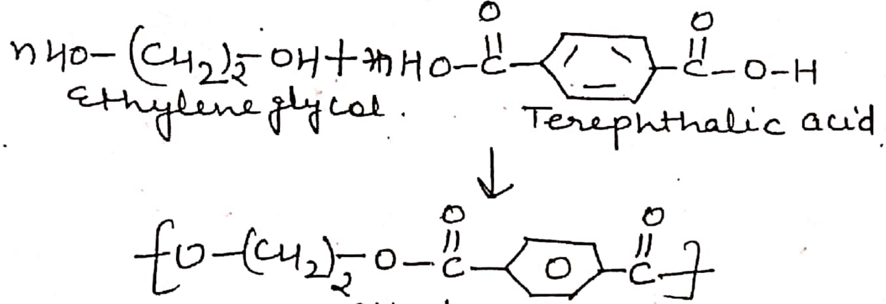
Polyesters are the polymers, obtained by the polycondensation of acid (bifunctional) and alcohol (bifunctional). They have $[\overset{\|}{C}-O-R]$ linkage.

Eg (A) Terelene (Dacron), (B) Glyptal.

Terelene- OR Dacron OR PET — It is a
- → condensation polymer
- → Copolymer
- → Thermosetting polymer.

Monomers- Ethylene glycol and Terephthalic acid.

Synthesis-



ethylene glycol.
[Poly tere phthalate]

(PET) or Dacron. or Terelene.

Properties-

(i) It is a polymer of high intermolecular forces.

(ii) It is resistant to chemicals & biologic substances and less resistant to alkalies

(iii) Low moisture absorbing capacity.

Application-

(i) It is used for making blended cloths with cotton or wool, which have superior property.

(ii) PET is used for making bottles.

UNIT-5

Eng. chemistry (RAS-102)

Lecture-17

(Blends & Composites)

Polymer Blends

"A polyblend or polymer blend is any physical mixture of two or more different polymers or copolymers that are not linked by covalent bonds."

Preparation of Polymer Blends-

(A) Mechanical Blends- For amorphous and semicrystalline polymers, mixing of polymer is done at temperature above Tg or Tm.

(B) Solution cast blends- Polymers are dissolved in common solvent and then solvent is removed.

(C) Latex Blend – Fine dispersions of polymers in water (latexes) are mixed and mixed polymers are coagulated.

(D) chemical Blend – Cross-linked polymer is swollen with different monomer, then monomer is polymerized and cross-linked. This is also known as Interpenetrating polymer Networks (IPN)-

Classification of Polymer blend-

(1) On the basis of Preparation- On the basis of preparation they are of four types –

(A) Mechanical Blend (B) Solution cast blend
(C) Latex Blend (D) chemical Blend.

(2) <u>On the basis of compatibility</u> - They are of two types -

(A) Miscible blend
(B) Immiscible blend.

	Miscible Blind	Immiscible Blend.
(1)	They exhibit a single glass transition tempera-ture (T_g), intermediate between those of the individual components.	(1) They exhibit separate Tg characteristic of each Component
(2)	They are usually clear	(2) They are opaque.
(3)	Eg. (1) Polyethylene tere-phthate (PET) & Polybutylene tere-phthalate (PBT)	(3) Eg. PS + PB Polystyrene and Poly Butadiene.

Properties of Polymer Blends - Properties of polymer blends can be predicted by following formulae -

$$P = P_1 V_1 + P_2 V_2 + I V_1 V_2$$

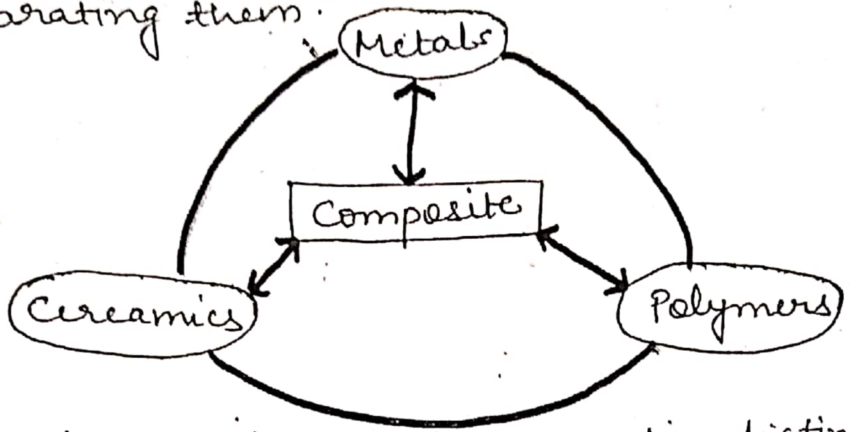
Where - P = Property of polymer blend.
P_1 = Property of A polymer.
P_2 = Property of B polymer
V_1 = Volumer of A polymer
V_2 = Volume of B polymer
I = Interaction term

If I = 0 (additive property
I = +ve (~~Non~~ synergetic property - favourable dipole-dipole attraction between components)
I = -ve (non-synergetic, Non-favourable intermolecular attraction)

Advantages of blending :- 1. Increment in desired properties. 2. Low Price, 3. Recycling easy 4. Scrap reduction

Polymeric Composite

A composite may be defined as "Any multiphase material which consist of two or more physically and/or chemically distinct phases with an interface separating them."



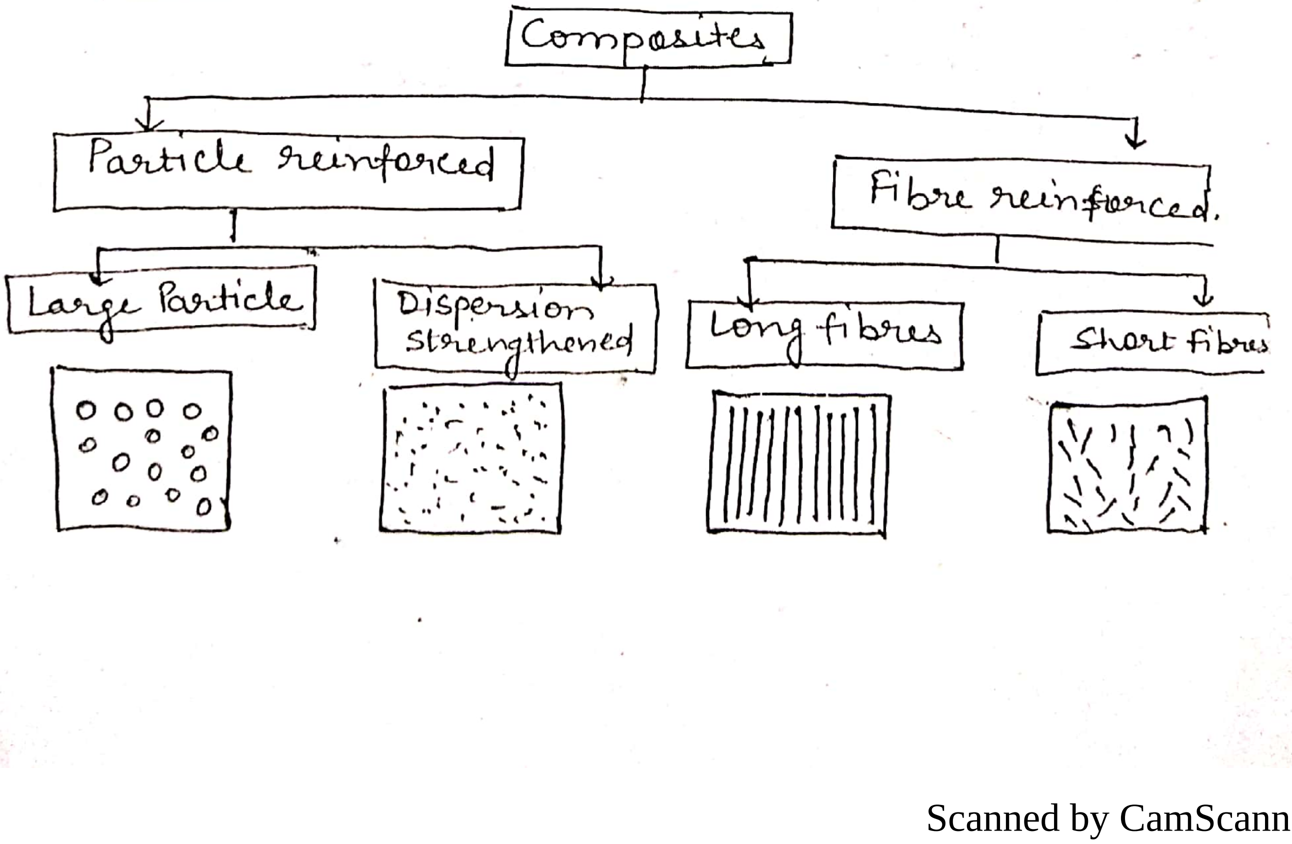
The composites shows properties distinctively (extra-ordinary) different from those of the individual materials of the composite.

Composites are made up of two phases-

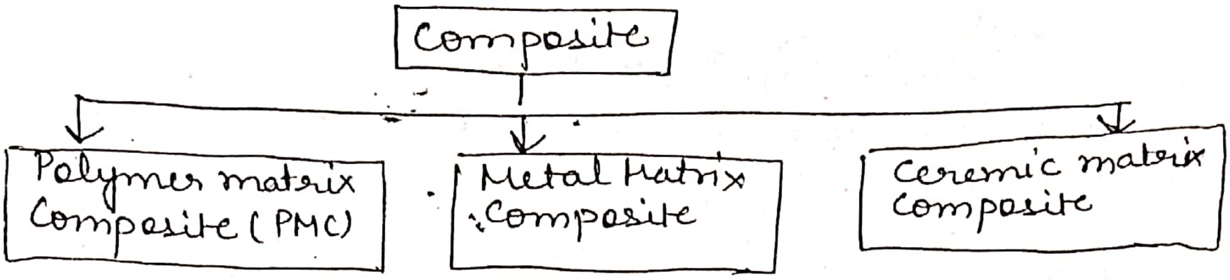
(i) Reinforcing phase - in form of fibres, Particles.
(ii) Matrix phase -

Classification of Composite materials-

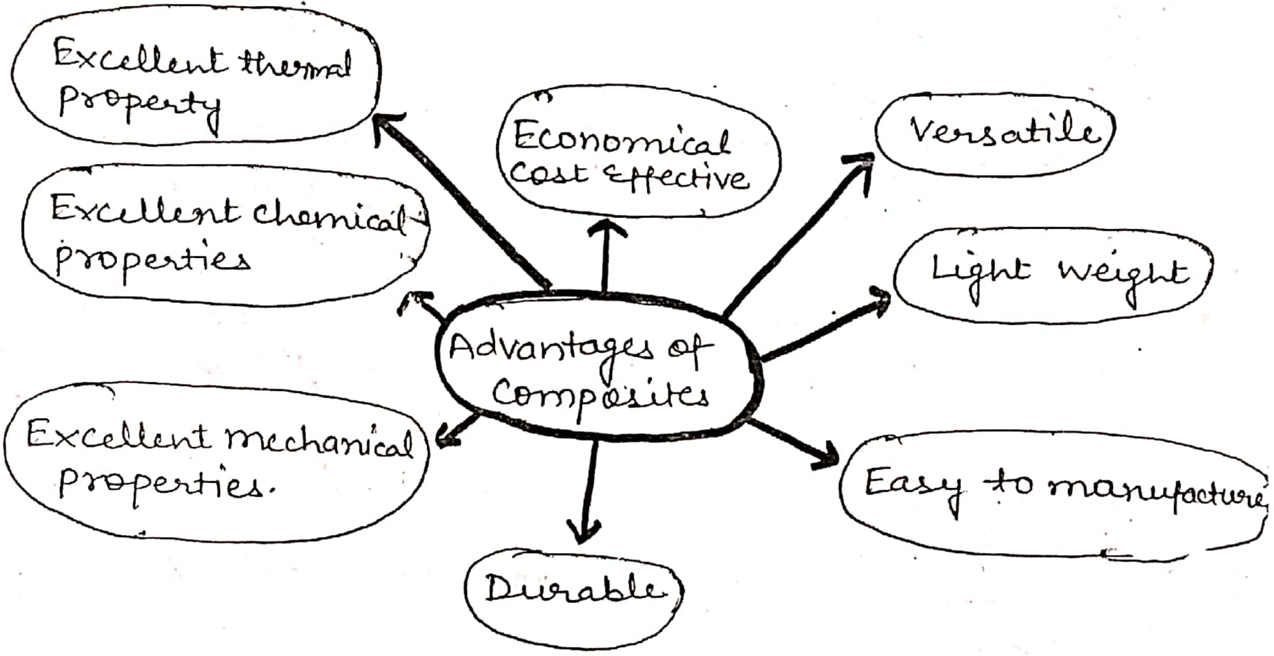
1) On the basis of Type of Reinforcement used in the Matrix



(2) On the basis of Type of Matrix



Advantages of composites-



Applications of Composite -

(1) In Transport industry - (Generally aromatic amide fibre reinforced composites are used).
→ Used in racing boats
→ used in Rocket component.
→ Used in military aircrafts
→ Used in engine components.

(2) In Consumer product - sporting goods (Lawn Tennis racket) and Musical instruments.

(3) In Industrial and scientific equipments - In high speed machinery, communication antennae.

UNIT-5

Eng. chemistry (RAS-102)
Lecture NO-18

(Conducting Polymers)

"A polymer which can conduct electricity is termed as conducting polymer."

Principles of conducting polymer-

(1) Polymers having extensive conjugation of π-bonds in the polymeric backbone to a large extent. This is because in such cases π-electrones get excited from valence band to conduction band as band gap decreases to 0.5 to 1 eV.

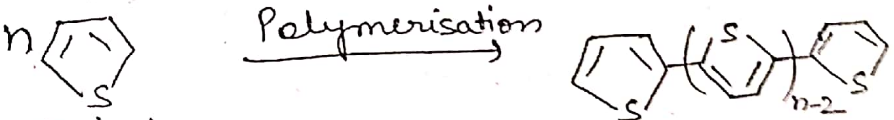
eg. n $CH\equiv CH$ $\xrightarrow{Polymerisation}$

acetylene

trans-polyacetylene

Pyrrole

Polypyrrole.



Thiophene

Polythiophene.

(2) Conducting polymer can easily be oxidised and Reduced. This can be fused for the purpose of doping.

Classification of Conducting polymer-

They are of two types - ICP, ECP

(A) Intrinsically Conducting Polymer - These polymer have extensive conjugation in their backbone. They are of two types -

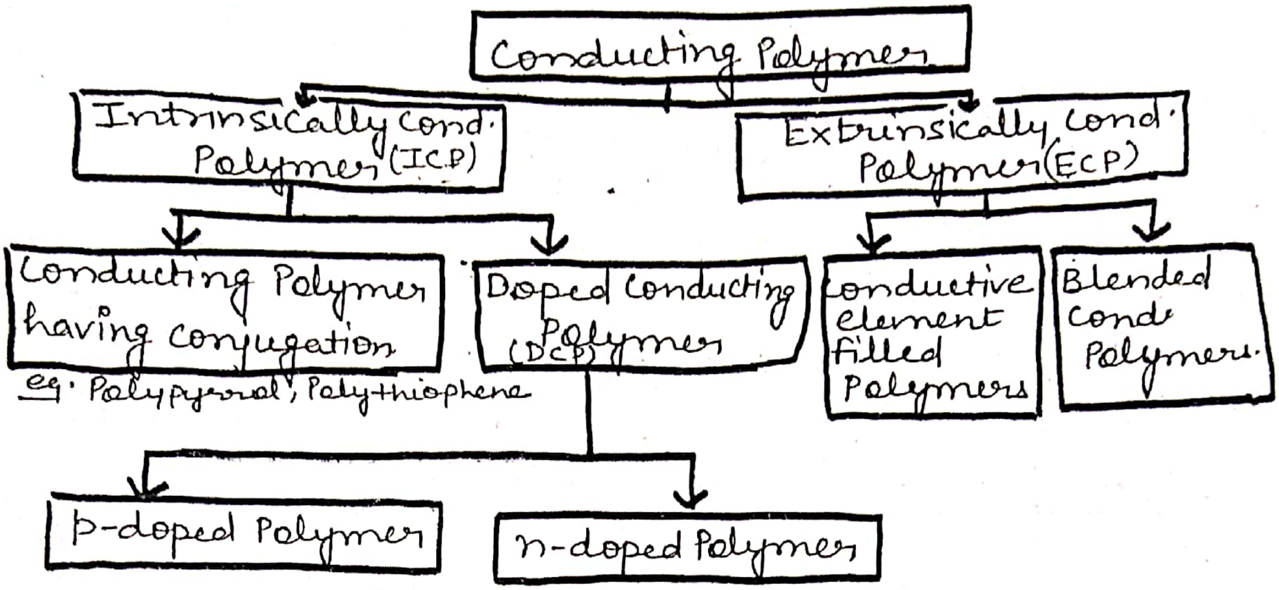


Chart showing classification of conducting polymer.

(A) Conducting polymer having conjugation –
Eg. Polypyrrole, Polythiophene

(B) Doped conducting polymer – (DCP) –
The conductiving of polymers with extensive conjugation can be increased by doping. Depanding upon the type of dopant used (Positive or Negative), conducting polymer may be of two types –

(i) p-doped conducting polymer – When dopant create positive charge on the backbone of polymer by oxidation, then polymer is known as p-dope polymer. They are holes dominating.

$$\underset{\text{(Lewis acid)}\ \text{(electron acceptor)}}{\text{Polymer} + A} \longrightarrow \underset{\text{(p-dope cond. polymer)}}{(\text{Polymer})^{n+} A^{n-}}$$

where $A = I_2$, Br_2, $FeCl_2$ etc.

(ii) n-doped conducting polymer - when dopant create negative charge on polymer backbone by reduction, they are known as n-doped conducting Polymer. They are free electron dominant.

$$\text{Polymer} + \underset{\substack{\text{Lewis} \\ \text{Base} \\ \text{(Electron donor}}}{B} \Longleftarrow \underset{\text{n-type doped cond. Poly.}}{(\text{Polymer})^{n-}} + B^{n+}$$

Where B = Na, Li.

(I) Extrinsically conducting polymer - These polymers ~~are~~ owe their conductivity due to the presence of externally added ingredients in them.

Properties of conducting polymer -

(1) Doped Polypyrrole and polythiophene are very stable in air.

Applications of conducting polymers -

(1) In rechargable batteries
(2) In Analytical sensors.
(3) for making ion exchangers.

Questions asked in university examinations.

- Explain conducting polymers with their properties and applications.
- Explain conductivity of doped polymers.

UNIT-5

- Eng. chemistry (RAS-102)

Lecture NO-19

(Biodegradable Polymers)

"Biodegradable polymers are those polymers which get decomposed by the process of biodegradation." Biodegradation is defined as the process carried out by biological systems wherein a polymer chain is cleaved via enzymatic activity.

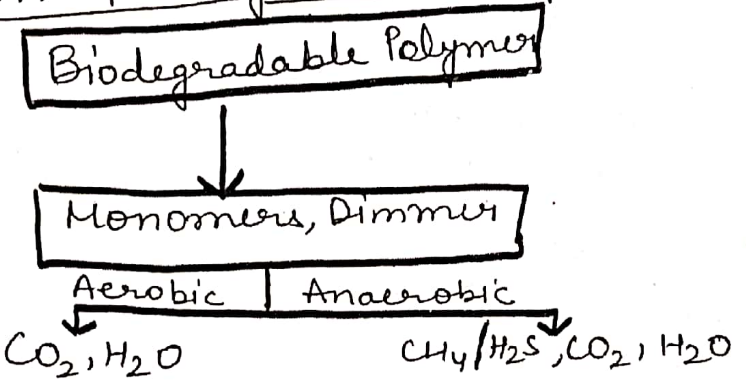
Requirement of Biodegradation-

(a) Micro-organisms

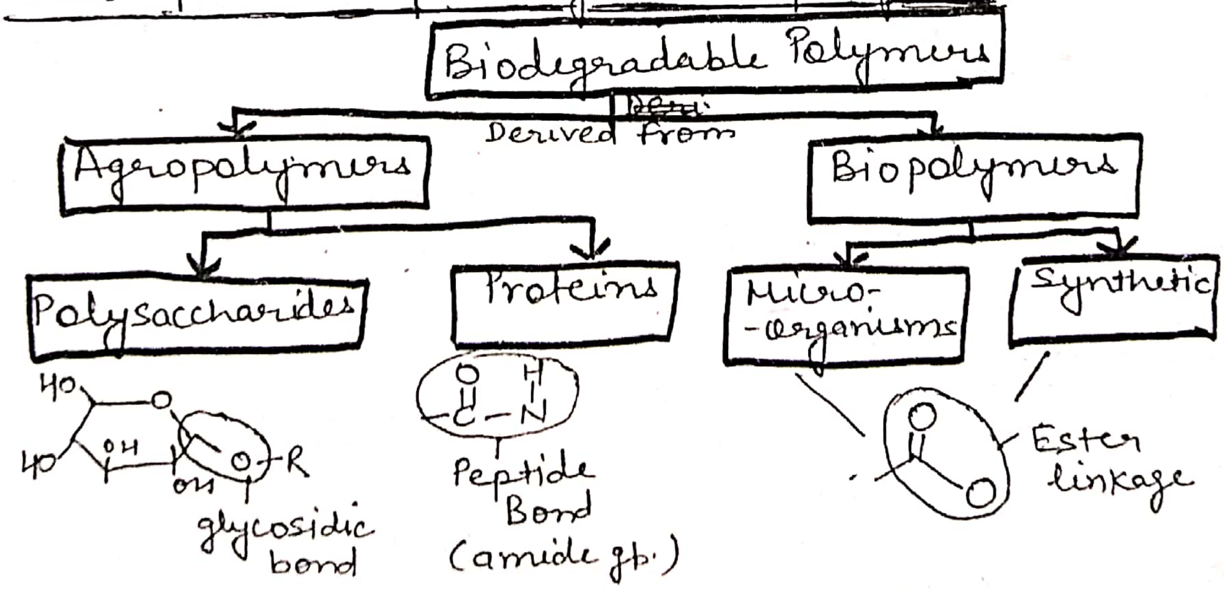
(b) Environment - Temp. , Pressure, Moisture, oxygen.

(c) Substrate.

Decomposition of Biodegradable Polymers-

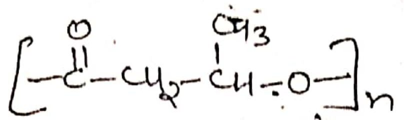


Classification of Biodegradable polymers-



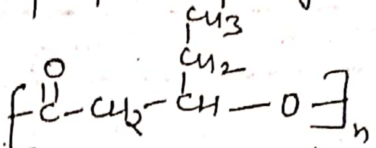
Examples of Biodegradable Polymers-

(1) **Biopol Resin**- made up of two polymers



$$[-\overset{O}{\overset{\|}{C}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-O-]_n$$

Polyhydroxy butyrate
(PHB)

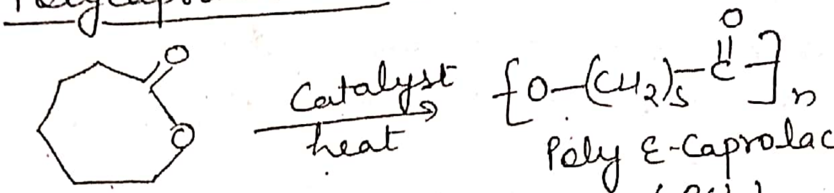


$$[-\overset{O}{\overset{\|}{C}}-CH_2-\overset{CH_3}{\overset{CH_2}{\overset{|}{CH}}}-O-]_n$$

Polyhydroxy Valenerate
(PHV)

It is chemical and moisture resistant.

(2) **Polycaprolactone** (PCL)

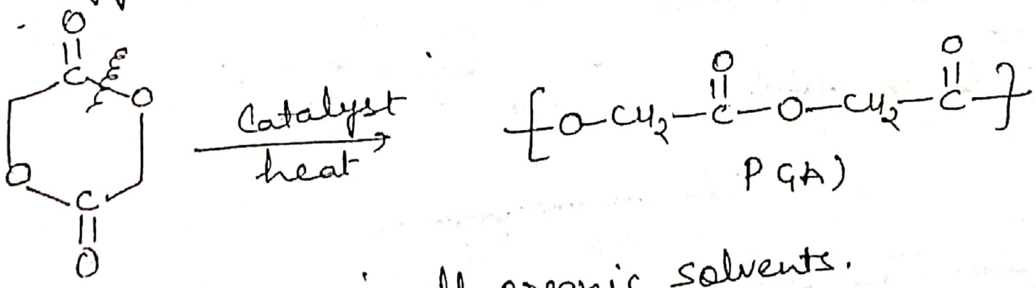


$[-O-(CH_2)_5-\overset{O}{\overset{\|}{C}}-]_n$

Poly ε-Caprolactone
(PCL)
(Tone polymer)

It is good resistant towards oil, water, chemical solvents.

(3) **Polyglycolide**- (PGA)



$[-O-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{O}{\overset{\|}{C}}-]$

PGA)

→ Insoluble in all organic solvents.

Applications- (1) Poly glycolic & lactic acid used for heart repair.

(2) Dextron - used for postoperative stitches contain polyglycolic acid.

(3) Bioplastic/Green plastic - Prepared by poly lactic acid (blend) contains ester, amide & ether functional group.

(4) Poly lactic acid - for drug deliverly.

UNIT-5

Eng. chemistry (RAS-102)

Lecture NO:- 20

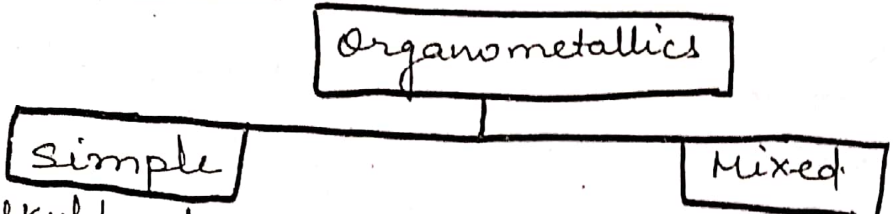
(General Methods of synthesis of Organometallic compounds-)

"Compounds in which Organic groups are linked directly to the metal through atleast one C-atom. eg- C_6H_5Ti, $(C_5H_5)_2Zn$, Grignard reagent etc are known as organometallic compounds."

CaC_2 is not organometallic compound.

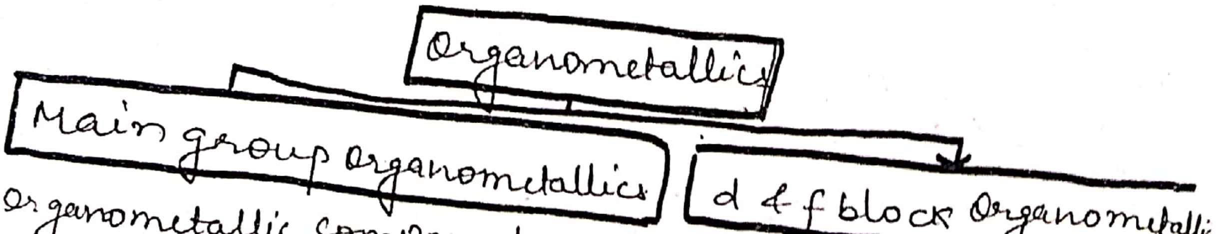
They are named after the name of the metal attached to the carbon centre as alkyl or aryl derivatives.

Classification-



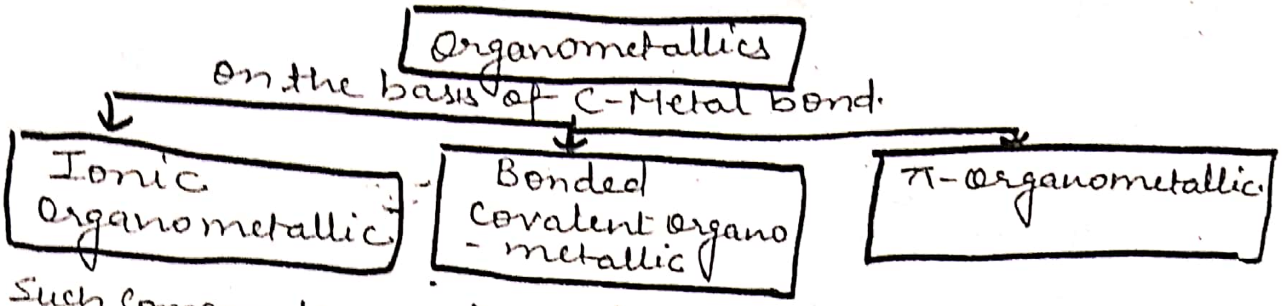
Simple: Alkyl/aryl group are attached to the metal atoms.
eg. $(C_2H_5)_4Pb$, H_3C-Li

Mixed: Groups other than alkyl are also attached directly to metal atoms.



Main group Organometallics: Organometallic compounds of s & p block elements are called main group organometallics.
$(CH_3)_4Si$, $(CH_3)_3As$, $(C_2H_5)_4Pb$.

d & f block Organometallics: Organometallic compounds of d & f block are π-bonded organometallics.
Eg. $K[PtCl_3(C_2H_4)]$ - zeise salt
$(C_5H_5)_2Fe$ - Ferrocene
(eg. of sandwitch bonded complex)



Ionic Organometallic

- Such compounds consist of hydro-carbon part (negatively charged) and positively charged metal ions held together by electrostatic force eg. $C_{10}H_8Na$.

Bonded Covalent organo-metallic

- Generally formed by non-transition metals with σ-Covalent bond. eg. $Al(CH_3)_3$

π-Organometallic

- Generally formed by transition metals.

Synthesis of organometallics.

I. Substitution Methods-

(i) By Compounds having acidic hydrogen-

$$RC\equiv CH + Na \longrightarrow RC\equiv C^-Na^+ + \tfrac{1}{2}H_2$$

$$C_5H_6 + K \longrightarrow C_5H_5^-K^+ + \tfrac{1}{2}H_2$$

$$Ph_3CH + Na \longrightarrow Ph_3C^-Na^+ + \tfrac{1}{2}H_2$$

(ii) By Reaction of Metals and Alkyl halides-

$$2Mg + 2RBr \xrightarrow{ether} \underset{\text{(Grignar reagent.}}{2RMgBr} \longrightarrow MgBr_2 + R_2Mg$$

$$2Li + EtI \longrightarrow EtLi + LiI$$

$$FeCl_2 + 2C_5H_5MgBr \longrightarrow \underset{\text{Ferrocene}}{Fe(C_5H_5)_2} + 2MgBrCl.$$

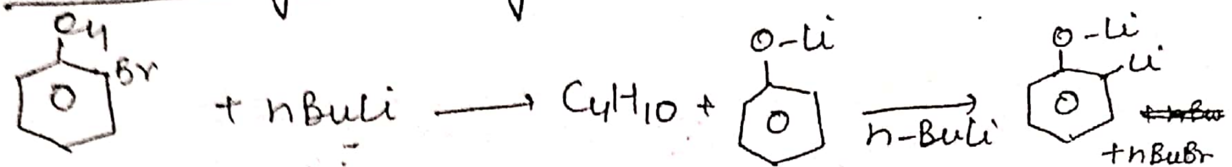
(iii) Metallation-

This term is usually restricted to metal-hydrogen exchange reaction.

$$C_5H_6 + RONa \longrightarrow C_5H_5^-Na^+ + ROH$$

$$RC\equiv CH + NaH \longrightarrow RC\equiv C.Na + H_2$$

(iv) Metal-halogen exchange Reactions -



Bromophenol

2. Addition Reaction or Methods.

(i) Reactions of Metals with CO, unsaturated hydrocarbons or radicals -

$Ni + 4CO \rightarrow Ni(CO)_4$

$Fe + 5CO \rightarrow Fe(CO)_5$ -

(ii) Ionization Reaction -

$B_2H_6 + 6CH_2=CH_2 \rightarrow 2(C_2H_5)_3B$

$Et_2AlH + CH_2=CH_2 \rightarrow Et_2Al$.

* Questions asked in University examination.

* what do you understand by organometallic compounds.

* Give general methods of synthesis of organometallic compounds.

Eng. chemistry

Lecture NO. 21

(Synthesis and application of Grignard Reagent).

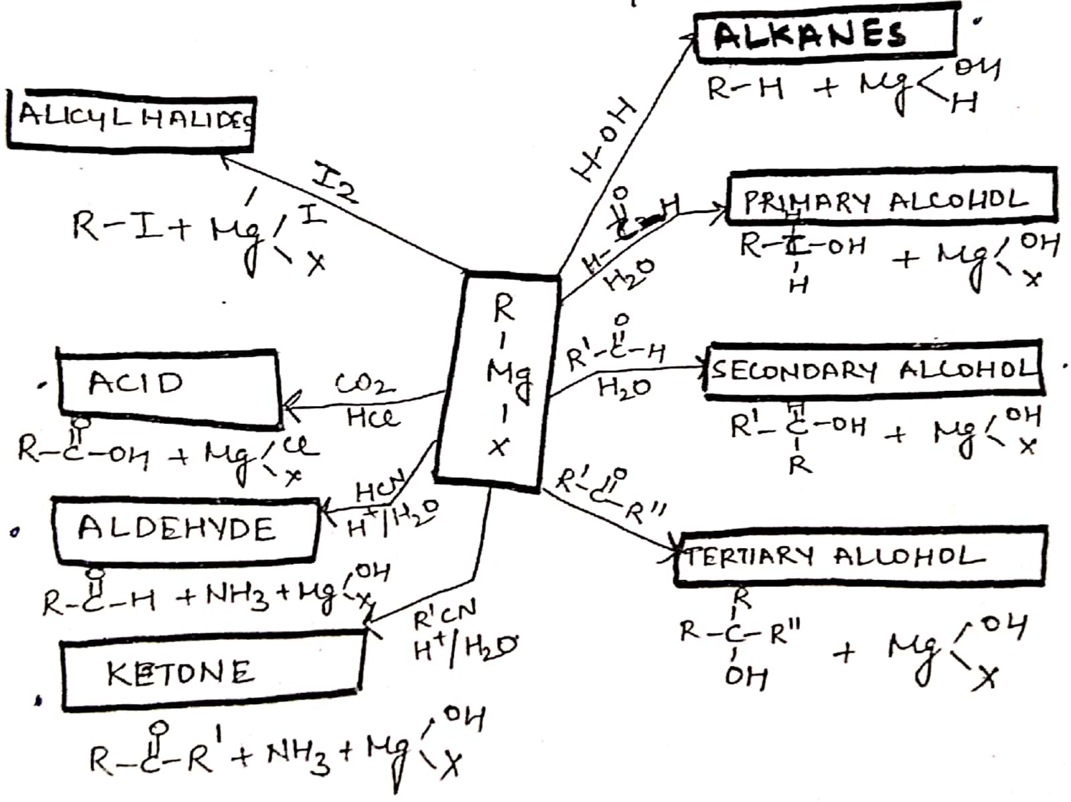
Synthesis of Grignard Reagent – These are prepared by reaction of Mg metal with alkyl halide in presence of dry ether.

$$Mg + R{-}X \xrightarrow[\text{ether}]{\text{dry}} R{-}MgX.$$

$$Mg + C_2H_5{-}Br \xrightarrow[\text{ether.}]{\text{dry}} C_2H_5{-}Mg{-}Br.$$

(Ethyl Magnesium Bromide)
(Grignard reagent.)

Application of Grignard Reagent – Grignard reagent is used in the synthesis of various classes of compounds.



UNIT-5

Eng. chemistry (RAS-102)

Lecture-22

Application of Organometallics in Polymerisation and Catalysis.)

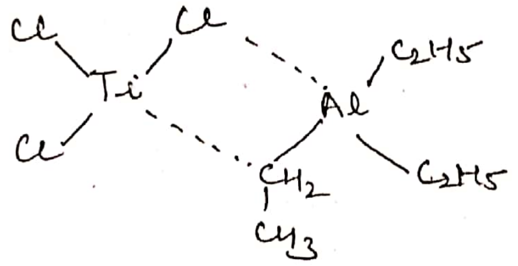
Application in polymerisation-

(1) Zigler Natta Catalyst-

Components-

(i) Catalyst - Halides of transition metal from IV to VIII (Ti, Fe, Mo, Ni, Rh etc.)

(ii) Organometallic Compound - hydrides of aryls, alkyls of gp. I to IV metals



Ziggler Natta Catalyst

Significance of Ziggler Natta Catalyst-

→ This polymerization is stereoselective hence permits stereochemical control. Therefore highly stereoregular polymers (preferentially Isotactic) are formed by this method. On the other hand conventional free radical polymerisation produces atactic polymers. The Isotactic polymers have superior quality than Atactic polymers.

→ Unlike free radical polymerisation, Ziggler Nata Catalyst leads the formation of Linear polymer devoid of Branched Polymers. Linear Polymer have high density & m.pt.

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Application in Catalysis -

(1) **Tetra ethyl lead (TEL)** - TEL is used as catalyst in Internal Combustion engines as '**antiknocking reagent**'.

Knocking is produced by $R^\bullet$, which is obtained by the combustion of fuel. TEL combine with $R^\bullet$, so that no knocking is produced.

$$\underset{\text{TLE}}{(C_2H_5)_4Pb} \rightleftharpoons 4C_2H_5^\bullet + Pb^\bullet$$

$$C_2H_5^\bullet + \underset{\text{(Produced by fuel)}}{R^\bullet} \longrightarrow R-C_2H_5-$$

(2) **Wilkinson Reagent** - Wilkinson Catalyst is used in **Homogenous hydrogenation of alkenes**. .

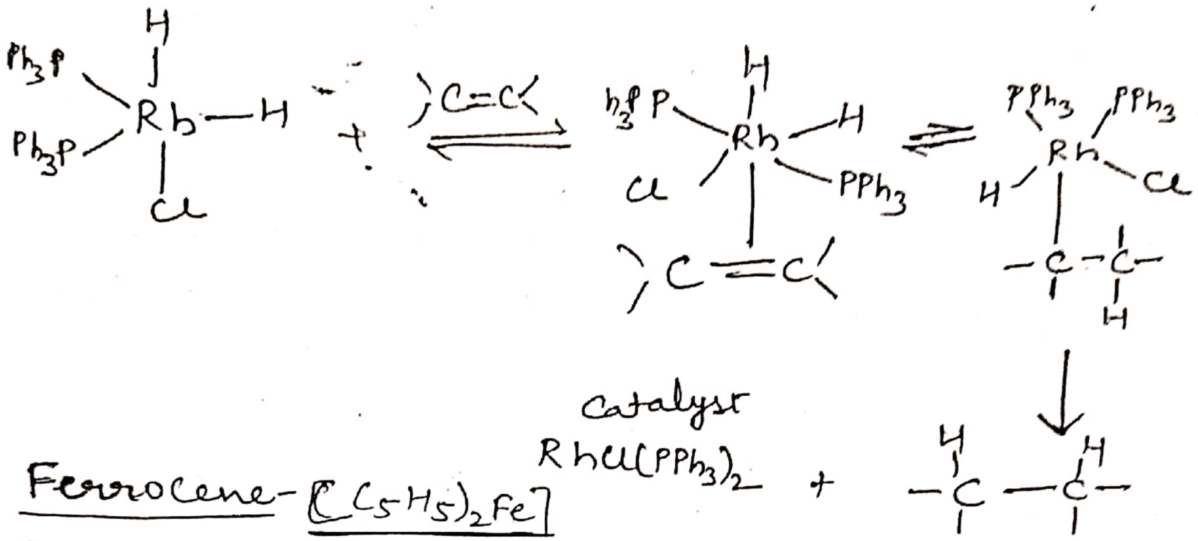
Chlotris(triphenyl phosphine) rhodium $[RhCl(PPh_3)_3]$ or Wilkinson catalyst is red-violet solid. It is used as a catalyst. It is obtained when an ethanolic solution of rhodium trichlorite is treated with an excess of triphenyl phosphine.

The rhodium complex is commonly used in benzene/ethanolic solution. In which it slightly dissociated as -

$$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3$$

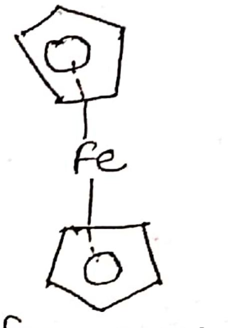
The mechanism of the process may be described as-

$RhCl(PPh_3)_2 + H_2 \rightleftharpoons RhClH_2(PPh_3)_2$



(3) **Ferrocene** - $[(C_5H_5)_2Fe]$

Ferrocene contains metal ion sandwitched between two C_5H_5 rings.

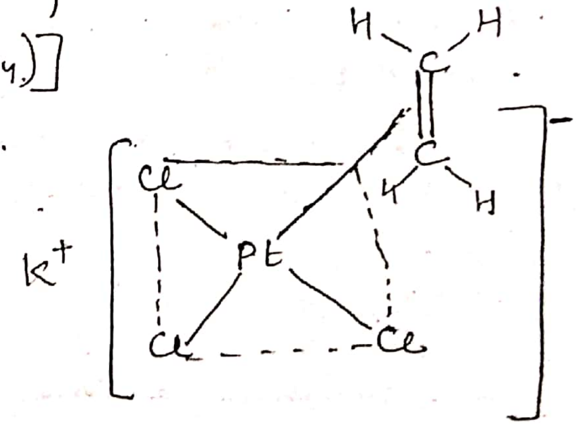


ferrocene

- It is better Anti knocking reagent than TEL.
- Can be used to deposit certain types of fullerene specially C-nanotubes.
- It shows anticancer activity.

(4) **Zeise salt** - $K[PtCl_3(C_2H_4)]$

Potassium trichloroethene Platinate (II)



$K_2[PtCl_4] + C_2H_4$

$\downarrow$

$K[PtCl_3(C_2H_4)] + KCl$

It is used, as a catalyst, in Water's process (conversion of ethylene into acrylaldehyde)