LECTURE -34

FUNDAMENTALS

- **POLYMERS:** are the macromolecules with very high molecular mass. They are made of repeating structural units. (Poly = many ; merose = molecules) eg- Polythene.
- **MONOMERS:** are the repeating structural units. They join together through covalent bonds to form polymers. eg- ethene units join to form polythene.
- **POLYMERISATION:** Process through which monomers join together to form polymers under specific conditions
- **DEGREE OF POLYMERISATION:** The number of monomers that combine to form a polymer is known as its degree of polymerisation.

$$n\,CH_2=CH_2 \xrightarrow{\text{Polymerisation}} \left(CH_2-CH_2\right)_n$$

n = degree of polymerisation.

- The exact molecular weight of polymers cannot be calculated as they are polydisperse in nature. Their average molecular weight is calculated using either of the two methods :
  - → Number average molecular weight.
  - → Weight average molecular weight.

Q1. Equal number of molecules (say 10) with $M_1 =$ and $M_2 = 100,000$ are mixed. Calculate M_n and (2013-14), (2010-11)

Sol. Here, $n_1 = n_2 = 10$.

So,
$$\boxed{\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2}}$$

$$= \frac{10 \times 10000 + 10 \times 100,000}{10+10}$$

$$= \frac{10^5 + 10^6}{20} = \frac{10^5 (1+10)}{20}$$

$$= \frac{11}{2} \times 10^4 = \boxed{55,000}$$

To calculate M_w following formula is used:

$$\boxed{M_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}}$$

$$= \frac{N_1 M_1^2 + N_2 M_2^2}{N_1 M_1 + N_2 M_2} = \frac{10 \times (10000)^2 + 10 \times}{10 \times 10000 + 10 \times}$$

$$= \frac{10^9 + 10^{11}}{10^5 + 10^6} = \frac{10^9 (1+100)}{10^5 (1+10)} = \frac{101}{11} \times 10^4$$

$$= \boxed{91,818}$$

Imp

Q2. What is the necessary condition for a monomer to undergo condensation polymerisation? (2014-

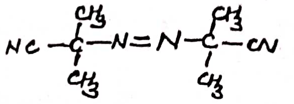
Ans. For any monomer to undergo condensation polymerisation :

a) It must contain two or more functional
b) There must be elimination of small molecules during polymerisation process.

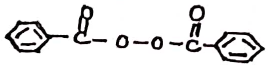
c) They must undergo polymerisation in steps.

Q3. Give two examples of initiators used for free radical polymerisation (2014-15)

Ans. Organic peroxides such as benzoyl peroxide (BPO) and azo compounds such as 2,2' - azo bis (iso butyronitrile) (AIBN) are used for free radical polymerisation.



AIBN



BPO.

Q4. Define chain growth polymers with examples (2014-15)

Ans. Chain growth polymers or addition polymers are the polymers that are formed by the addition poly-merisation. Here monomers simply add on without any elimination. It generally requires an initiator like organic peroxide to form a free radical. The process results in the formation of chain and ultimately a polymer is formed. Example - Buna-N, Buna-S, Polyethylene, PVC etc.

Q5. In a particular sample of polymer, 100 molecules have a molecular mass 10^3 each, 200 molecules have molecular mass 10^4 each and 200 molecules have molecular mass 10^5 each. Calculate M_n and M_w. (2014-15)

Sol.
$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} = \frac{N_1M_1 + N_2M_2 + N_3M_3}{N_1 + N_2 + N_3}$$

$$= \frac{100\times10^3 + 200\times10^4 + 200\times10^5}{100 + 200 + 200.}$$

$$= 200 \times 221 = 44,200.$$

$$\boxed{\overline{M}_w = \frac{\Sigma w_i M_i}{\Sigma w_i} = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2}{N_1M_1 + N_2M_2 + N_3M_3}}$$

$$= \frac{100\times(10^3)^2 + 200\times(10^4)^2 + 200\times(10^5)^2}{100\times10^3 + 200\times10^4 + 200\times10^5}$$

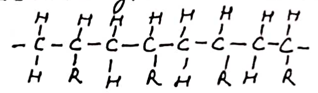
$$= \frac{20201\times10^8}{221\times10^5} = \boxed{91407.2}$$

Imp

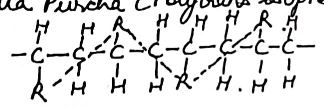
Q6. What is meant by tacticity. With suitable examples explain Isotactic, Syndiotact and atactic polymers

Ans. Tacticity means the order of arrangement or orientation of side chains/groups on both the sides of main carbon skeleton. (2016-17, 2014-15)

a) Isotactic: In these types of polymers the side groups are arranged on the same side of the polymeric backbone. eg: Natural rubber (poly cis-isoprene).



b) Syndiotactic: Here the functional groups are arranged on both the sides of the main polymeric backbone, but in the alternate manner. eg- Gutta Purcha (Polytrans isoprene).



c) A-tactic; Here the functional groups are arranged in a random manner around the main carbon skeleton eg- Poly vinyl chloride.

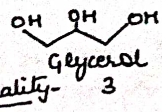
Imp
Q7. Differentiate between addition & condensation polymerisation (2015-16) (2014-15), (2017-18)

Ans.

CONDENSATION POLYMERISATION	ADDITION POLYMERISATION
① Also known as step growth polymerisation	① Also known as chain growth polymerisation.
② It takes place in monomers with reactive functional groups	② It takes place in monomers having multiple bonds.
③ It takes place with the elimination of simple molecules like H_2O, HCl etc.	③ No elimination of simple molecules.
④ Repeating units of monomers are different	④ Repeating units of monomers are same.
⑤ Molecular mass of polymers increases throughout the reaction.	⑤ Molecular mass of the polymers changes very little during the reaction.
⑥ Products obtained may be thermosetting / thermoplastic.	⑥ Products obtained are thermoplastic.
⑦ Example:- Bakelite, polyester, Polyamides etc.	⑦ Example :- Polyethylene, PVC, Polystyrene.

Imp
Q8. What do you understand by term functionality of polymer.

Ans. The number of binding sites in a monomer is known as its functionality. For example: functionality of ethene and propene is 2 as they can form two new bonds. functionality of glycerol is 3 as it has 3 -OH groups, so it has three binding sites. (2017-18)



$CH_2=CH_2$
ethene

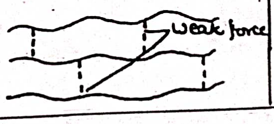
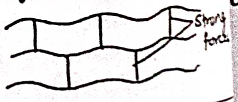
$CH_3-CH=CH_2$
propene

Functionality- 3 2 1

Q9. Simple molecules do not polymerise. Why (201

Ans. A molecule can act as a monomer only if it is at bifunctional in nature i.e. it must either be unsaturated or must contain atleast two reactive functional groups. Simple molecules are not bi-functional and so do not satisfy the criteria to act as a monomer. So, they do not polymerise.

Imp
Q10. Differentiate between thermoplastic & thermosetting polymers. (2014-15), (2017-18).

THERMOPLASTIC POLYMERS	THERMOSETTING POLYMERS
① formed by addition polymerisation	① Formed by condensation polymerisation.
②. Long chain polymers with no cross linkage.	② They have three dimension network structure.
③ chains are linked by weak Vanderwaal's forces.	③ chains are held together by strong cross links.
④ on heating they soften, and on cooling becomes hard.	④ on heating become sti hard as they undergo furth polymerisation of partic
⑤ can be remoulded & reused.	⑤ can't be remoulded & re
⑥ soft, weak & less brittle.	⑥ Hard, strong, Tough & more b
⑦ soluble in organic solvents	⑦ Insoluble in organic solve
⑧ Eg- PVC, 	⑧ Eg - bakelite, epoxy resi 

Q11. Write the properties or characteristics of polymers ... various methods for determination of molecular w of polymers. (2014-15)

Ans. **Characteristics of Polymers:**

a) All the polymers are macromolecules with very high molecular weight.

b) Polymers are semicrystalline materials.

c) They have high resistance towards corrosion.

d) They have low density.

e) Polymers are generally insulators, few are conductors.

f) Primary bond (in main polymeric backbone) in polymers are covalent bonds, whereas secondary bonds, holding different chains together are weak forces like Vander-waal's forces, dipole-dipole interaction or hydrogen bond.

g) Exact molecular weight of polymers cannot be determined as they are polydisperse in nature.

h) The molecular weight of polymers is determined as average mol. wt.

Molecular Weight Determination of Polymers:

There are two ways to calculate the average molecular weight of polymers:

(i) **Number average Molecular Weight ($\bar{M}_n$)**

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \ldots N_iM_i}{N_1 + N_2 + N_3 + \ldots N_i}$$

M_i = total molecular weight of monomer

N_i = Number of monomers.

$\bar{M}_n$ - Number average molecular weight.

(ii) **Weight average molecular weight ($\bar{M}_w$)**

$$\bar{M}_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{N_1M_1^2 + N_2M_2^2 + \ldots N_iM_i^2}{N_1M_1 + N_2M_2 + \ldots N_iM_i}$$

W_i = weight of monomers. ($W = N \times M$)

M_i = Total molecular weight of monomers.

$\bar{M}_w$ = weight average molecular weight.

Q12. What are fibres and their important properties? Give different type of fibres with examples. (2014-15)

Ans. Fibres are thin, long, thread like polymers which have strong intermolecular forces between the chains and therefore have high tensile strength.

Important properties of fibres.

a) Have high tensile strength.

b) Elastic nature

c) High length to width ratio

d) Tenacity

e) Flexibility.

There are two types of fibres:

i) **Natural fibres:** These fibres are derived from nature. example: cotton, wool, silk, Nylon-6.

ii) **Artificial or synthetic fibres:** These fibres are synthesized in factories etc. examples - Nylon-6,6, Dacron etc.

The synthetic fibres can be further classified as:

i) **Polyesters:** The polyesters are the fibres which contain ester linkage i.e $-\overset{O}{\overset{\parallel}{C}}-O-$ linkage. example: Terylene.

ii) **Polyamides:** These are the fibres containing amide linkage. ($-\overset{O}{\overset{\parallel}{C}}-NH-$) example - All the nylon fibres.

LECTURE-35

FUNDAMENTALS:

Polymerisation Mechanism: There are two types of polymerisation mechanisms: Addition (chain growth) & condensation (step growth) polymerisation.

Addition polymerisation can proceed through either of the two mechanisms:

i) **Free radical mechanism**:- Here free radical acts as an initiator.

ii) **Ionic Mechanism**:- Here either cation or an anion acts as initiator and so they are known as cationic polymerisation and anionic polymerisation respectively.

Every polymerisation process proceeds through 3 steps:

a) chain initiation
b) chain propagation
c) chain termination

- In the chain initiation the initiator molecule reacts with one monomer and starts or initiates the polymerisation process. In case of free radical polymerisation initiator is a free radical and in case of cationic and anionic polymerisation the initiators are cation and anion respectively.
- During chain propogation the polymerisation process continues where monomers react with each other & keep increasing the polymer chain.
- Chain termination involves the termination of polymerisation process, whereby either the growing chain reacts with a free radical, anion or cation.

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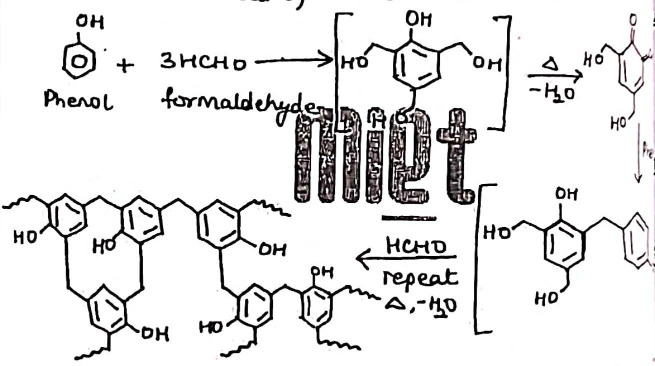
Q1. Explain the synthesis of phenol-formaldehy (2014-15).

Ans. Phenol formaldehyde resin or Bakelite is p by condensing phenol with formaldehyde in presen acidic / alkaline catalyst. First step involves the formation of ortho and para hydroxy methyl p which reacts to form linear polymer Novola During moulding $[(CH_2)_4NH_4]$ is added which soluble & fusible novolac into a hard, infus insoluble solid of cross linked structure.



Bakelite [cross linked polymer

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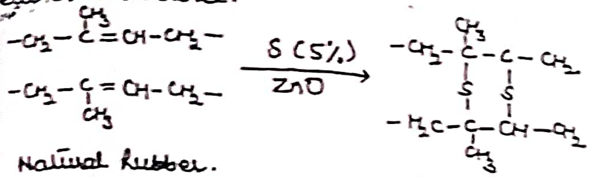
Q2. What is vulcanisation? How does it improve the properties of raw rubber? [2014-15], [2015-16]

Ans. Vulcanisation is a chemical process in which rubber is heated with sulphur, accelerator a activator at 140°C - 160°C. The added sulphur co chemically at the double bonds of different rubbe springs. The process involves the formation of cros between long rubber molecules so as to achieve improved elasticity, resilience, tensile strength and weather resistance.



Natural Rubber.

Vulcanised Rubber

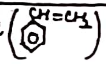
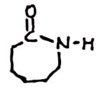
3. Explain why Teflon is highly chemical resistant? (2015-16) (2020-21).

Ans. In teflon $\{CF_2-CF_2\}_n$, the fluorine atoms surround the carbon chain like a protective sheat, creating a chemically inert and relatively dense molecule with very strong C-F bonds.

M.Imp.

4. What are the monomers of Buna-S, Buna-N, Nylon-6, Nylon-6,6, Dacron and Neoprene. [2015-16, 2018-19, 2020-21].

Ans.

Polymers	Monomers
Buna-S ⟶	styrene  & 1,3-Butadiene ($CH_2=CH-CH=CH_2$)
Buna-N ⟶	acrylonitrile & 1,3-Butadiene. ($CH_2=\underset{CN}{CH}$) ($CH_2=CH-CH=CH_2$)
Nylon-6. ⟶	caprolactum. 
Nylon-6,6 ⟶	Adipic acid & Hexamethylene diamine. $HOOC-(CH_2)_4-COOH$ $H_2N-(CH_2)_6-NH_2$

Polymers	Monomers
Dacron. ⟶	Ethylene glycol ($\begin{matrix}CH_2-OH\\ \vert\\ CH_2-OH\end{matrix}$) and Terephthalic acid.  (HOOC-C6H4-COOH)
Neoprene. ⟶	Chloroprene ($CH_2=\overset{Cl}{C}-CH=CH_2$)

Q5. What are copolymers? How does Buna-S differ from Buna-N? (2015-16).

Ans. Coplymers are the polymers that are formed by the combination of two or more different type of monomers. Example Nylon-6,6 is a copolymer of adipic acid & Hexamethylene-di-ammine.

Buna-S	Buna-N.
1) Formed by polymerisation of 1,3-Butadiene and styrene	1) formed by polymerisation of 1,3-Butadiene & acrylonitrile
2) Swells in oils & solvents	2) Oil resistant.
3) Non polar	3) Highly Polar.

M.M.Imp.

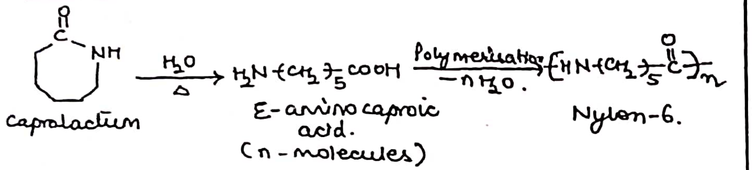
Q6. How would you prepare the following polymers? Give their properties and applications. (2014-15), (2015-16), (2016-17), (2017-18), (2018-19), (2019-2020), (2020-21).

1) Bakelite 2) Nylon-6 3) Nylon-6,6 4) Dacron
5) Buna-N 6) Buna-S 7) Neoprene 8) Butyl rubber
9) HDPE 10) Kevlar 11) PMMA 12) PVC 13) Polyethylene

Ans. **Bakelite**: Preparation - discussed in Q1.
Properties: It is very hard & has high melting point. Resistant to several destructive solvents

Uses: a) In manufacturing electrical switches.
b) In making handles of utensils.
c) In making machine parts of various electrical systems.

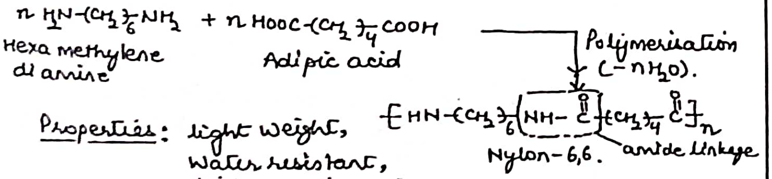
2 **Nylon-6** - Polyamide, condensation polymer, homo polymer
Monomer - caprolactum.



Properties: Tough, elastic in nature, high tensile strength have lustre.

Applications: Used in automotive industries.
Used as string in guitars, sitars, violins etc.
Used in making ropes, nets, filaments etc.

3. **Nylon-6,6** : Polyamide, condensation polymer, copolymer
Monomers: Hexamethylene diamine and adipic acid.



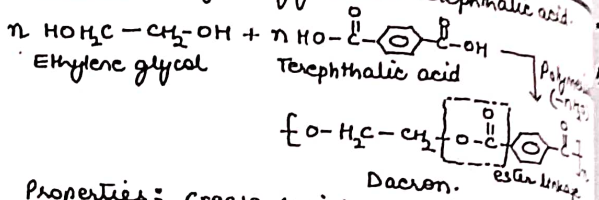
$$n\,H_2N{-}(CH_2)_6{-}NH_2 + n\,HOOC{-}(CH_2)_4{-}COOH \xrightarrow[(-nH_2O)]{\text{Polymerisation}} [HN{-}(CH_2)_6{-}NH{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}]_n$$

Properties: light weight,
Water resistant,
High melting point.

Uses: To make swim suits, sleeping bags.
To make carpets, socks, ropes etc.
Used in making parachutes.

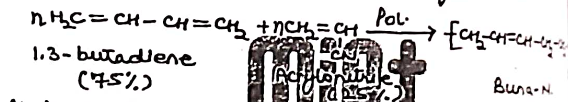
4. **Dacron or Terylene or Polyethylene Phthalate**:
Polyester, condensation polymer, copolymer.

Monomers: Ethylene glycol and Terephthalic acid.



Properties: Crease resistant, weightless, water
highly resistant to minerals and organic acids
Uses: In making ropes, nets, raincoats, clothing
textiles, fleece jackets, quilts.

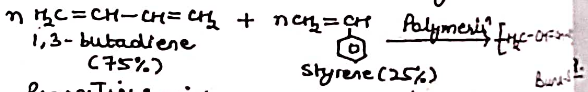
5. **Buna-N**: Elastomer, addition polymer, copolymer
Monomers: 1,3-Butadiene and acrylonitrile.



$$n\,H_2C{=}CH{-}CH{=}CH_2 + n\,CH_2{=}\underset{CN}{\underset{|}{CH}} \xrightarrow{\text{Pol.}} [CH_2{-}CH{=}CH{-}CH_2{-}$$

It is also known as NBR or nitrile rubber.
Properties: Highly polar, oil resistant.
Uses: Used in making seals, gaskets, protective glove
nuclear industry tank lining, used as adhesive.

6. **Buna-S or SBR**: Elastomer, addition polymer,
Monomers: 1,3-Butadiene and styrene.

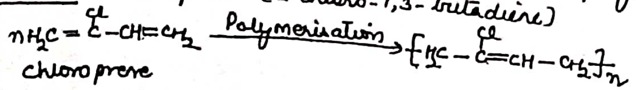


Properties: High abrasion resistance
High load bearing capacity
Swells in oils and solvents

Applications: Used in shoe soles.
Used in chewing gums
Used for electrical insulation.
Used for making tyres of scooter, motor

Neoprene : Elastomer, addition polymer, homopolymer

Monomer: chloroprene (2-chloro-1,3-butadiene)



$$n\,H_2C=\overset{Cl}{C}-CH=CH_2 \xrightarrow{Polymerisation} \{H_2C-\overset{Cl}{C}=CH-CH_2\}_n$$

chloroprene
(2-chloro-1,3-butadiene)

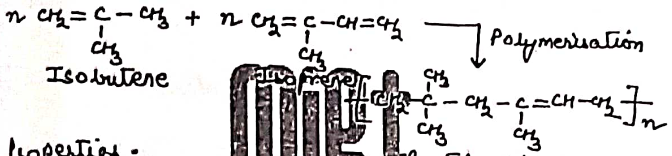
Neoprene

Properties: Fire resistant, water resistant, corrosion resistant, inert to chemicals.

Uses: In making swim suits, diving suits.
In making gloves and coated fabrics.
used for Halloween masks.

Butyl Rubber : Rubber, addition polymer, copolymer.

Monomers: Isobutene and Isoprene.



$$n\,CH_2=\underset{CH_3}{C}-CH_3 + n\,CH_2=\underset{CH_3}{C}-CH=CH_2 \xrightarrow{Polymerisation} [CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{C}=CH-CH_2]_n$$

Isobutene

Isoprene

Butyl rubber.

Properties:
Impermeable to air and other gases.
Highly resistant to heat, abrasion, ageing, chemicals, ozone, tearing, have good electrical insulation properties.

Applications: used for making cycle & automobile tyres, Used in tank linings, Used in conveyor belts, Used in insulation for high voltage wires & cables.

9. HDPE - High density polyethylene

Addition polymer, Homopolymer.

Monomer: ethylene.

Catalyst used: Zeigler Natta Catalyst.

$$n\ H_2C=CH_2 \xrightarrow[5\text{-}7\,atm/\ 60\text{-}70^\circ C]{Zeigler\ Natta\ catalyst} \{CH_2-CH_2\}_n$$

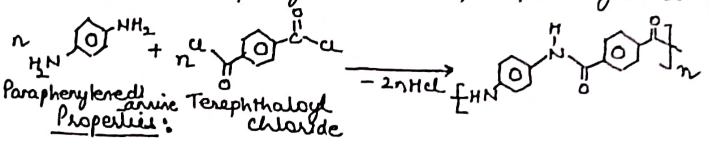
HDPE (no branching)

Properties: Highly crystalline (80-90%), very tough but flexible, chemically inert, non polar.

Uses: used for storage of H_2SO_4, used in 3D printer filament and banners, used in chemical resistant pipings, used in far-IR lenses, used in bottle caps, folding chairs, tables.

10 Kevlar : Polyamide, condensation polymer, copolymer.

Monomers: Paraphenylene diamine & Terephthaloyl chloride



Paraphenylenediamine Terephthaloyl chloride

Properties:

- very strong (about 5 times more stronger than steel)
- High tensile strength, low weight and high chemical inertness.
- High cut resistance, flame resistance & fracture resistance

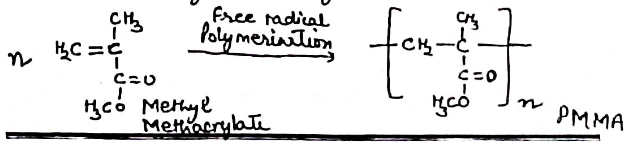
Applications:

- Heat or flame resistant fabrics.
- Bulletproof clothing
- for aircraft panels.
- Motorcycle helmets.

11 PMMA - Poly methyl methacrylate or Perspex or Plexiglass or acrylic glass : Also known as Lucite.

ThermoPlastic, addition polymer, homopolymer.

Monomer: Methyl methacrylate.



Methyl Methacrylate

PMMA

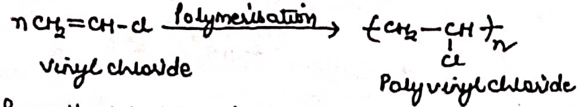
Properties: High resistance to UV light & weathering.
Excellent light transmission, durable, light weight
Unlimited colouring options, scratch resistant

Applications: Used in smart phone screens.
Used in car windows.
Used as wind screen in motorbikes.

12 **PVC** - (**Polyvinyl chloride**)

Thermoplastic, addition homopolymer.

Monomer: vinyl chloride ($CH_2=CHCl$)



$$n\,CH_2=CH-Cl \xrightarrow{Polymerisation} \left[CH_2-\underset{\underset{Cl}{|}}{C}H\right]_n$$

vinyl chloride — Polyvinyl chloride

Properties: light weight, durable, low cost, easy processibility.

Applications: used for refrigerator components.
Used in safety helmets, window Frames, drainage pipes, Water service pipe, medical devices

13. **Polyethylene** Thermoplastic, addition homopolymer.

Monomer: Ethylene.

$$n\ CH_2=CH_2 \longrightarrow \left[CH_2-CH_2\right]_n$$

Ethene. — Polythene

Properties: light weight, durable, excellent electrical insulating properties, good processibility.

Applications: Used to prepare Tubes, pipes, toys, bottles, bags.

Q7. Differentiate between elastomers and Fibres. [2018-19]

Ans. Elastomers are rubbery material composed of long chain like polymers that are capable of recovering

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1.) **Thiokol Rubber** or
Poly sulphide Rubber :-

Thiokol is prepared by the condensation polymeizat
sodium poly sulphide (Na_2S_x) and ethylene dic
($Cl\,CH_2CH_2\,Cl$).

In these elastomers, sulphur forms a part of t
polymer chain.

$$Cl-CH_2-CH_2-Cl + Na-S-S-Na + Cl-CH_2-CH_2-Cl$$

1,2-dichloro-ethane — sodium poly-sulphide — 1,2-dichloro et

$$\Big\downarrow \text{polymeization}$$

$$-\!\!\left(CH_2-CH_2-S-S-CH_2-CH_2\right)\!\!-_n \quad + NaCl$$

Thiokol (ethylene poly sulphide polymer) — sodium

Properties :-

1.) These rubbers possess strength and impe
gases.

2.) This rubber can't be vulcanized because i
is not similar to natural rubber and it ca
hard rubber.

3.) It possess extremely good resistance to mine
fuels, Oxygen, Solvent ozone and sun lig

Applications :-

1. Fabrics coated with Thiokol are used for barrage balloons.
2. It is mainly used as solid propellant fuel for rocket.
3. It is also used for making gaskets, hoses, cable linings, tank lining etc.
4. It is also used for printing rolls.
5. Containers for transporting solvents.
6. Diaphragms and seats in contact with solvents.

---

their original shape after being stretched.
Fibres are long thread like polymer which have strong intermolecular forces between chain and therefore have high tensile strength.

LECTURE - 36

FUNDAMENTALS:

Conventional polymers, also called plastics have been considered as insulators for a long time. At the begining, polymers were used in clothes, tools, plastic bags, wire shielding and many other applications. The majority of polymers are insulators due to unavailability of free electrons to create the conductivity. In the covalent bond, electrons are locked in these strong and directional bonds. So, these type of materials show poor conductivity.

In 1970, when first intrinsic conducting polymer was produced by Shirakawa, Heegar and Mac Diarmid, which resulted in noble prize in 2000. The polymer was produced by the exposure of the polyacetylene to dopant compounds: oxidising or reducing agents, electron donor or electron acceptor.

The structure of these materials has <u>conjugated chain</u> i.e (<u>an alternating single and double bond between atoms</u>). The process of doping becomes easier due to these conjugated bonds.

Polyacetylene is synthesized by the reaction of the ethyne, commercially known as acetylene with Zeigler Natta Catalyst.

M.Imp

Q1. How do natural biodegradable polymers undergo biodegrad
(2014-15).

Ans. Biodegradable polymers are those polymers which und decomposition or degradation in nature by the acti of microbes, enzymes etc. They undergo biodegradation by the following process:

Step 1:→ The long polymer molecules are reduced to shor lengths and undergo oxidation. The molecules become hyd philic (water attracting) and small.

Step 2:→ Biodegradation occurs in the presence of moll and micro organisms. The polymer is completely brok down into the residual product.

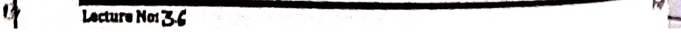
Step 3:→ Micro organisms consume the degraded polym CO_2, H_2O and bio mass are produced and returned to nature by the way of biocycle.

M.Imp

Q2. What are conducting polymers? Classify conducting poly and mention their important applications. How can conductivity of polymers be increased? (2015-16)

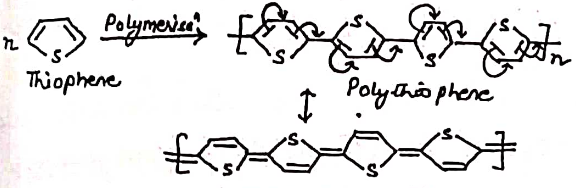
Ans. Conducting polymers are the organic polymers that conduct electricity due to extensive conjugation in their backbone. Examples - polypyrrole, polythiophen polyparaphenylene etc.

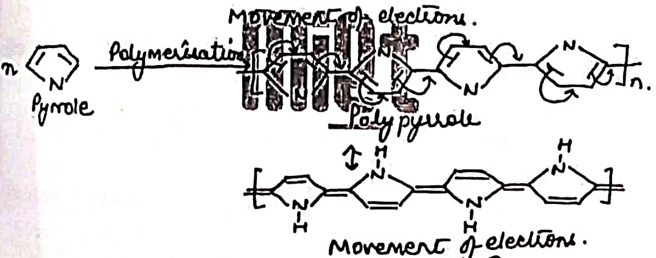
Conducting polymers can be classified as:

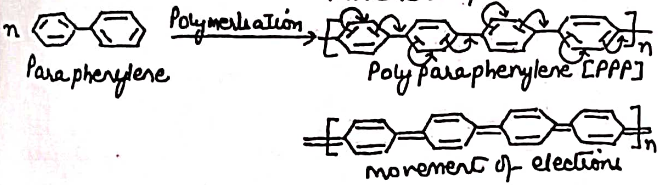


1) Intrinsically Conducting Polymers These polymers have pie conjugation in the main chain and can conduct the electricity either normally or on doping. They can be further classified as:

a) conjugated conducting Polymers: They contain conjugated pie bonds in their backbone which help them to form the valence band and conduction band. So, there is movement of electrons. Example:







b) Doped conducting polymers:
These are the intrinsically conducting polymers which have gap between valance and conduction band and cannot conduct electricity normally. They are doped

with electron donor or electron acceptor to make them conducting. Doping can be of two types:

i) P-doping - done by removal of electrons, by using Lewis acid.

$$\underset{\text{Acetylene}}{(CH)_x} + \underset{\text{lewis acid}}{A} \xrightarrow{\text{oxidation}} (CH)_x^+ A^- \quad [A = FeCl_3]$$

ii) n-doping - done by addition of electrons, by using Lewis base.

$$\underset{\text{Acetylene}}{(CH)_x} + \underset{\text{lewis base}}{B} \xrightarrow{\text{Reduction}} (CH)_x^- B^+ \quad [B = Na, Li \text{ etc}]$$

2) Extrinsically conducting Polymers: They do not contain the factors responsible for conduction and are made conducting by adding external factor in them. They are of two types:

i) Polymers with conducting elements: In these type of polymers conductive elements such as carbon black, metal oxide etc are added. The polymer act as a binder and hold these elements.

ii) Blended conducting polymers: In these polymers there is blending of conventional polymer with conducting polymer. As a result of this blending the conventional polymer gains conductivity.

conductivity of a polymer can be increased by: Doping, blending or filling the polymer with conductive element.

Applications of conducting Polymers

i) used in rechargeable batteries.
ii) used as antistatic material.
iii) used in optical filters & sensors.
iv) Used in electromagnetic screening material.

N.Imp

Q4. What are biodegradable polymers? Write a short note on them. Also give the preparation, properties and uses of some biodegradable polymers. [2015-16], [2016-17], [2018-19].

Ans. The polymers which can degrade in nature by the action of enzymes and microbes are called biodegradable polymers.

Factors affecting biodegradation:

i) **Size and shape:** The size of the polymer should not be too large and it should not be too branched. Simple polymers with minimum branching or no branching undergoes biodegradation easily.

ii) **Crystallinity:** Polymers are semicrystalline materials. The polymers with low crystallinity can degrade easily.

iii) **Hydrophilicity:** The biodegradable polymers are hydrophilic in nature. They generally dissolve in water.

iv) **Presence of functional groups:** Polymers based only on carbon chains are non biodegradable. The presence of a functional group is required as the enzymes and microbes start their action from these functional groups.

v) **Presence of suitable micro organisms:** For the polymers to undergo biodegradation, presence of suitable microbes, enzymes etc is required.

vi) **Presence of suitable conditions:** The microorganisms require a suitable temperature, moisture, pH etc for their survival and proper functioning.

Biodegradation Process: discussed in Q1.

Importance of biodegradable polymers:

i) Improper disposal and failure to recycle the polym results in overflowing landfills. Biodegradable polym are the best solution to this problem.

ii) Biodegradable polymers can be easily recycled and even burned without producing toxic products.

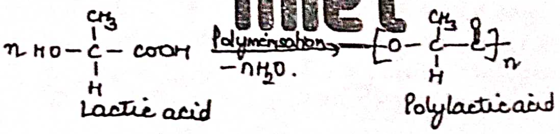
iii) Used in localized drug delivery.

iv) Biodegradable polymers reduces the risk of side effects.

v) They undergo degradation with a controlled ra

Formation, properties & uses of some biodegradable polymers

a) **Polylactic acid (PLA)** is formed by polymerisation of l acid.



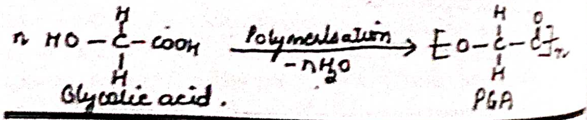
$$n\,HO-\underset{H}{\overset{CH_3}{C}}-COOH \xrightarrow[-nH_2O.]{Polymerisation} \left[O-\underset{H}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}\right]_n$$

Lactic acid Polylactic acid

Properties: Resistant to grease and moisture. It compostable & biodegradable

Uses: Used in plastic surgery, biodegradable sutu food packaging and drug delivery systems.

b) **Polyglycolic acid (PGA):** It was the first synthe absorbable suture.



$$n\,HO-\underset{H}{\overset{H}{C}}-COOH \xrightarrow[-nH_2O]{Polymerisation} \left[O-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}\right]_n$$

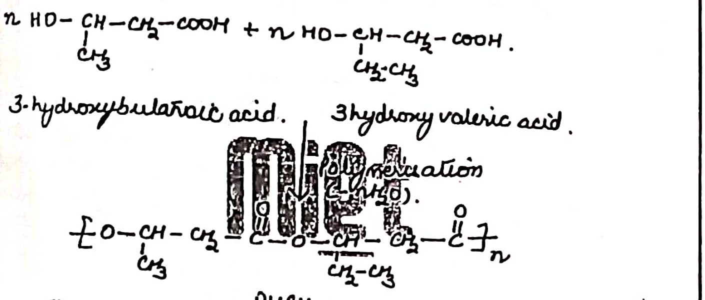
Glycolic acid. PGA

Properties: Highly crystalline, has high melting point, low solubility in organic solvents.

Uses: Used in tissue engineering, controlled drug delivery, biodegradable sutures.

This polymer was used to develop the first synthetic absorbable suture which was marketed under the trade name of **Dexon**.

c. PHBV (Poly-β-hydroxybutyrate-co-β-hydroxyvalarate) or BIOPOL or Biomer-L



$$n\,HO-\underset{CH_3}{CH}-CH_2-COOH + n\,HO-\underset{CH_2-CH_3}{CH}-CH_2-COOH \xrightarrow[(-nH_2O)]{Polymerisation} -\!\!\left[O-\underset{CH_3}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-O-\underset{CH_2-CH_3}{CH}-CH_2-\overset{O}{\overset{\|}{C}}\right]\!\!-_n$$

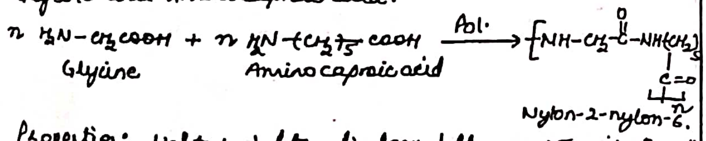
3-hydroxybutanoic acid. 3hydroxy valeric acid.

PHBV.

Properties: It is a thermoplastic polymer, brittle in nature

Uses: Used in controlled drug delivery, medical implants and repairs, orthopedic devices, for manufacturing shampoo bottles etc.

1) **Nylon-2-nylon-6:** formed by copolymerisation of Glycine and Aminocaproic acid.



$$n\,H_2N-CH_2COOH + n\,H_2N-(CH_2)_5-COOH \xrightarrow{Pol.} -\!\!\left[NH-CH_2-\overset{O}{\overset{\|}{C}}-NH(CH_2)_5-C{=}O\right]\!\!-_n$$

Glycine Aminocaproic acid

Nylon-2-nylon-6.

Properties: light weight, biodegradable, high Tensile strength

Uses: To make ropes, parachutes, tooth brush bristles, dress materials.

Environmental Impacts of Polymers —

The polymer industry is linked with the following environmental problems regarding manufacturing, use and synthetic polymers disposal.

Air Pollution :—

The non-biodegradable nature of synthetic polymers makes them a permanent waste. The used polymeric products like plastic bags and bottles can not be dumped in sanitary landfills.

These synthetic waste items are then combust in the incinerators which results in release of harmful gases and cause air pollution. The gases that are produced during combustion include carbon dioxide, nitrogen oxides and carbon monoxide. All these gases are toxic in nature and are cause of global warming and formation of acid rain.

Water Pollution :—

When the polymeric wastes are introduced to marine environment they are rapidly broken down into smaller particulates. The tiny plastic particles are ingested by sea organisms and results in the intestinal blockage in larva fishes.

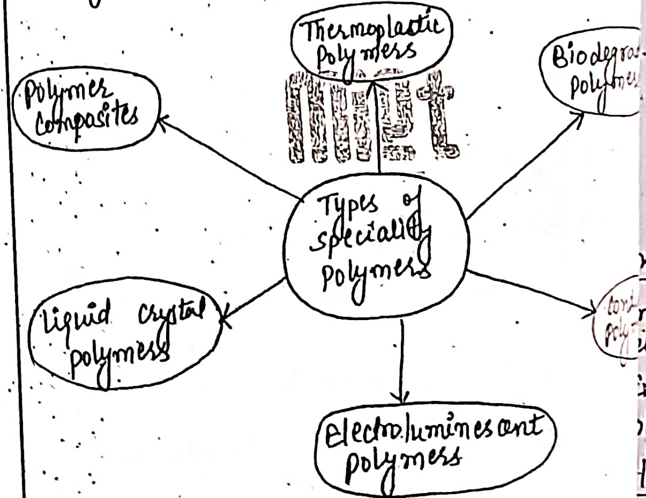
Health hazards due to Polymers–

- The additives used for hardening of plastic i.e. plasticizer mainly causes health hazards in humans. For example, phthalate ester plasticizers are taken out by the blood from the plastic bags which are used for the storage of blood.

- The health problems concerned with polychlorinated biphenyl are more dangerous.
- They are fat soluble polymers and therefore they concentrate in the aquatic organisms.
- When human consume contaminated fish they are base to headache, fatigue and pains in joint.
- If the polychlorinated biphenyl concentration increases to 12 ppm it results in blindness.

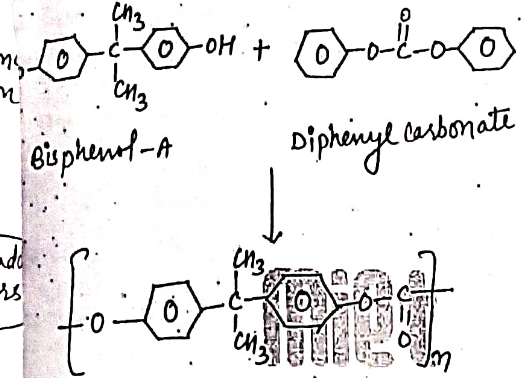
SPECIALITY POLYMERS

Speciality polymers are the class of some High Performance Polymers (HPP), including plastics, fluids, membranes, smart hydrogels and elastom that are designed to meet the critical requi that engineers face every day in key industries including plastics, Automobiles, Aeronautics, Sm Devices, Healthcare, Pharmacy, Energy Production storage.



Thermoplastic Polymers :-

Polycarbonate or Engineering Thermoplastics are speciality polymers made up of polyesters of Phenol and Carbonic acid.



Poly Carbonate

Conducting Polymers :-

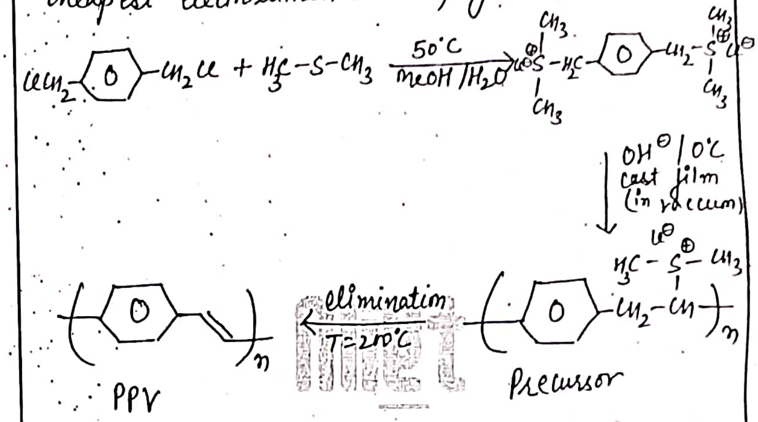
Conducting polymers find use in electronics, solar cells, displays, illumination sources and micro chips. Examples of conducting polymers – Poly acetylene (PAC), Poly (phenylene sulfide) (PPS), Poly (pyrrole) (PPY).

Electroluminescent Polymers :-

Electroluminescence is light emission stimulated by electric current. This property has led to the development

of flat Panel displays using organic LED's, solar panels and optical amplifiers.

e.g. Polyphenylene vinylene is the simplest and cheapest electroluminescent polymer.

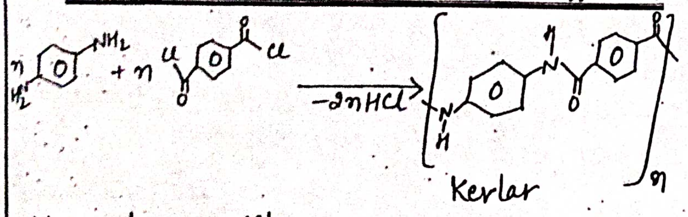


- Electroluminescent polymers are organic polymers that emit light upon application of an electric field.

Liquid Crystalline Polymers :-

Liquid crystalline polymers are those polymers that are capable of forming regions of highly ordered structure while in liquid phase.

A very commonly known liquid crystalline polymer is Kevlar.



Kerlar

Uses of Speciality Polymess :-

* It is used for mouldings for computeses, calculating machines, for making hair driers, electric razors, CDs and DVDs etc.
* It is used in automobile industry for making motor cycle windshields, police shields, head light covers, car bumpers, front panels, safety helmets, etc.
* It is used for making blenders, food processing bowls, coffee maker, food mixers housings etc.
* It finds use in the manufacture of baby bottles, syringes etc.
* It is also used for making water dispensers, vacuum cleaner bases, cord hooks, spectacles, cameras.

LECTURE - 37

Composites, the wonder materials are becoming an essential part of today's materials due to advantages such as low weight, corrosion resistance, high fatig. strength and faster assembly.
The different systems are combined sensibly to achie a system with more useful structural and functio properties which would be impossible to attain by any of the single constituent. They find extensive applic in aircraft structures, electronic packaging, medic equipments, space vehicles, home building etc.

Polymer blend is a mixture of at least two differ polymers to create a new material with different ph properties. The first polymer blend was patented in 1 by Parkes. This blend of natural rubber with gutta-pe resulted in partially cross linked material whose mech was controlled by composition of each monomer a comes. Most blends have been developed for improvem of specific properties and also the modification of alre existing polymer is more economically viable than development of new monomers for production of n type of polymers.

* The basic difference between a polymer blend an composite is that the two main constituents in composites remain recognisable while these may be recognisable in blends.
* Composite comprises of a polymeric and a non p material whereas polymer blend is made of 2 or more p

M.Imp

1. What do you understand by polymer blends? (2016-17)

ns. Polymer blend is a mixture of two or more than two polymers having physical properties different from the component polymers. The components of polymer blends should be friendly with each other.

Example: Mixture of wool $-(CONH)-$ and Terylene $-(\overset{O}{\overset{\|}{C}}-O)-$ form a polymer blend.

Types of Polymer blends:

a) **Miscible Polymer blend:**
- Homogeneous
- Negative value of free energy of mixing
- It is a single phase structure
- Has one Tg (glass transition temperature).
- Example :- PS/PPO

b) **Immiscible polymer blend:**
- Heterogeneous
- ΔG_{mix} and $\Delta H_{mix} > 0$
- Poor adhesion between phases of blend
- Example :- PA/PPO, PA/PP, PA/ABS

c) **Homologous polymer blend:**
Mixture of two or more fractions of the same polymer each having different molecular weight distribution.

d) **Isomorphic polymer blend:**
Polymer blend of two or more different semicrystalline polymer that are miscible in crystalline as well as molten state.

e) **Compatible Polymer blends:**
Blends which are miscible in a certain useful range of composition and temperature but immiscible in others.

Applications of Polymer blends-
Used in fabrics, textiles, sports materials, cold drink bottles.

Advantages of blending
1) Production of desired materials which are low in cost.
2) It improves solvent and chemical resistance.
3) It improves flame resistance
4) Plastic wastes are recycled.
5) Blending reduces material cost.

M.Imp

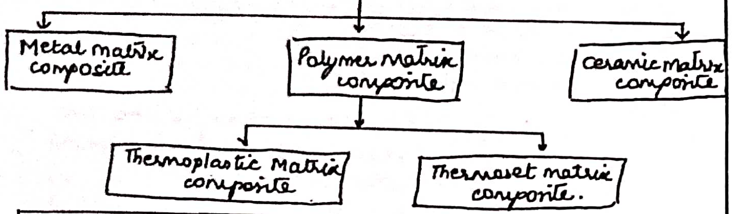
Q3. What are composites? Give their classification and advantages. Illustrate various applications of polymer composites. (2016-17), (2019-20), (2020-21).

Ans. Composite material is a material composed of two or more phases known as matrix phase and dispersed phase, and an interface seperating them. The combination results in a material with enhanced structural and functional properties which are different from any of the constituent phases.

MATRIX PHASE	DISPERSED/REINFORCING PHASE
1. It is a primary phase	It is a secondary phase.
2. It is continious form.	It is discontinious form.
3. It holds dispersed phase & share load with it.	It is embedded in matrix.
4. Weaker than dispersed phase	It is stronger than matrix phase

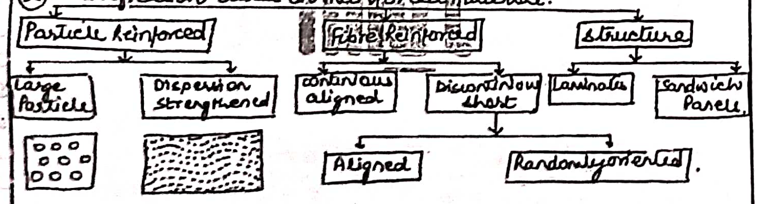
Classification of composite Materials
1) Based on Matrix phase
2) Based on reinforcement phase.

① composite material based on matrix



Polymer matrix comp.	Metal Matrix comp	Ceramic metal comp
•Matrix is made up of polymer. • Low cost • Low density • Low thermal stability	•Matrix is made up of metal • High cost • High density • Resist thermal shock	•Matrix is made up of ceramic material. • High cost • High density • High thermal stability

② classification based on Reinforced material.

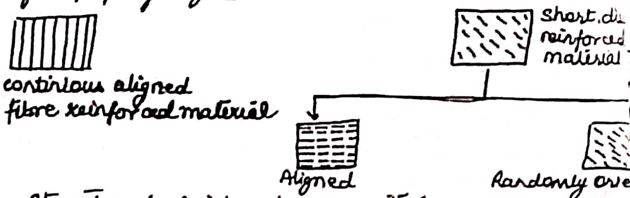


a) Particle Reinforced composite: these are the composites in which dispersed phase is made of particles.

- The particles used can be metallic or non metallic.
- Distribution of particles is random so these are isotropic.
- Hard and have high load bearing capacity.

b) Fibre Reinforced composite

- The dispersed phase consists of fibres, which may be continuous and aligned or may short & discontinuous.
- Short discontinuous fibres can be randomly oriented or may be properly aligned.

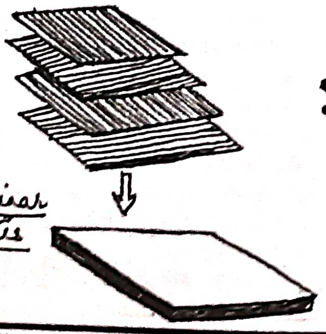


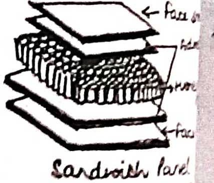
c Structural Reinforced composite:

The properties of these composites depends upon the con -tuent materials and on the geometric designs of vario structural elements. The most common structural com -osite types are: laminare and Sandwich panels.

i) Laminar: Laminare can be described as materials m of layers of materials bonded together. The layers can be same or different materials occuring alternately or an other order as per the requirement. Example - Plyw

ii) Sandwich Panels: They consist of two outer strong called face sheets which may be made of aluminium fibre reinforced plastics, steel etc. These face sheets carry of the load & stress. The core has less density and m a honeycomb. The core provides shear rigidity. Sandwich are used in floors, walls of buildings, roofs etc.


Laminar composites



Sandwich Panel

LECTURE - 38

The discovery of Zeigler-Natta represents the first and most significant step in the synthesis of crystalline poly olefines.

The German chemist Karl Zeigler (1898 - 1973) discovered in 1953 that when $TiCl_3$ and $(C_2H_5)_3Al$ are combined together, they produce an extremely active heterogeneous catalyst for polymerisation of ethylene at atmospheric pressure.

Giulio Natta (1903 - 1979) an Italian chemist developed variations of Zeigler catalyst and extended the method to produce stereoregular polypropylenes.

The Zeigler Natta catalyst include many mixtures of halides of transition metals especially Ti, Cr, V, Zr with organometallic compounds of a metal from group I to III

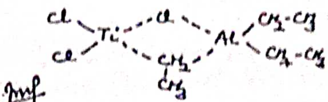
Vanadium based catalyst allows the formation of Syndiotactic polypropene. Efficiency of such a heterogeneous catalyst can be improved significantly by impregnating the catalyst on solid support such as $MgCl_2$ or MgO.

Zeigler Natta catalysts are now used worldwide to produce different classes of polymers from α-olefins

Example : • Polybutene (PB)
- Thermoplastic polyolefins
- Polyethylenes : HDPE, LDPE

Q1. Write down the structure of Zeigler Natta Catalyst.

Ans.



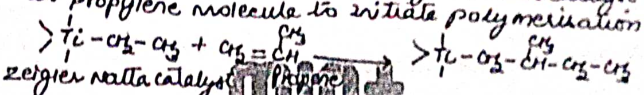
M.Imp

Q2. Discuss the mechanism of preparation of polypropylene using Zeigler Natta catalyst. Give the preparation & applications of PTFE and butyl rubber. [2014-15]

Ans. By using Zeigler Natta catalyst during the preparation of polypropylene, stereoregular (Isotactic) polypropylene is produced.

Mechanism for the preparation of Isotactic polypropylene

Step I : Initiation : In this step Zeigler Natta Catalyst react with propylene molecule to initiate polymerisation.

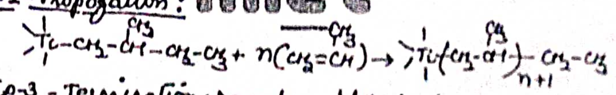


$$>\underset{|}{\overset{|}{Ti}}-CH_2-CH_3 + CH_2=\overset{CH_3}{\overset{|}{CH}} \longrightarrow >\underset{|}{\overset{|}{Ti}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$$

Zeigler Natta catalyst Propene

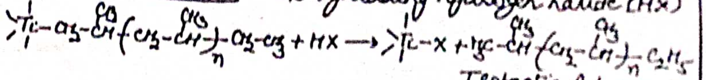
* Propene molecule inserts between Ti-C bond.

Step 2 - Propogation :



$$>\underset{|}{\overset{|}{Ti}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3 + n(CH_2=\overset{CH_3}{\overset{|}{CH}}) \rightarrow >\underset{|}{\overset{|}{Ti}}(CH_2-\overset{CH_3}{\overset{|}{CH}})_{n+1}-CH_2-CH_3$$

Step-3 - Termination : Done by adding hydrogen halide (HX)



$$>\underset{|}{\overset{|}{Ti}}-CH_2-\overset{CH_3}{\overset{|}{CH}}(CH_2-\overset{CH_3}{\overset{|}{CH}})_n-CH_2-CH_3 + HX \longrightarrow >\underset{|}{\overset{|}{Ti}}-X + H_3C-\overset{CH_3}{\overset{|}{CH}}(CH_2-\overset{CH_3}{\overset{|}{CH}})_n C_2H_5$$

Isotactic Polypropylene

TEPLON - It is obtained by polymerisation of water emulsion Tetrafluoroethene, under pressure in presence of benzoyl peroxide as catalyst.

$$n\,F_2C=CF_2 \xrightarrow[\text{under pressure}]{\text{Benzoyl peroxide}} \underset{\text{TEFLON}}{(F_2C-CF_2)_n}$$

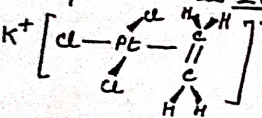
Applications :
- Used for making non stick cookwares.
- Used for making water proof fabrics.
- Used for coating medical appliances.

LECTURE -39

Organometallic Compounds

These are the class of compounds containing atleast one metal – carbon bond in which carbon is a part of organic group.

The first synthetic organometallic compound $K[PtCl_3(C_2H_4)]$ was prepared by the Danish pharmacist William C. Zeise in 1827 and is referred to as Zeise's Salt.



$K[PtCl_3(C_2H_4)]$ – Zeise's Salt

- Organo Magnesium halide (Grignard Reagent) is used widely in synthetic organic chemistry.
- Alkyl aluminium compounds are employed in organic synthesis.
- Organo tin compounds are used as pharmaceuticals, pesticides and fire retardants.
- Tetra carbonyl Nickel is employed in a process for nickel purification.
- Metal Carbonyls are employed as catalyst in many reactions of petrochemical industry

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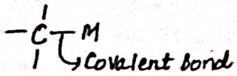
Lecture-39

M.Imp

Q What are organometallic compounds. Write their classification, preparation and applications. [2017-1

Ans The compounds in which Carbon atom is directly li to metal atom are known as organometallic comp



where $M = Mg, Li, Na, Ca, Al$

Based on groups attached to Metal atom

1) Simple Organometallic Compounds:– Metal atom bonded to carbon and hydrogen atoms. E.g $(C_2H_5)_4Pb$. They are of 2 types

a) Symmetrical: Metal atom is bonded to same type of gro e.g – $(C_2H_5)_2Hg$

b) Unsymmetrical: Metal atom is bonded to different hydr radical. Eg $C_2H_5HgC_4H_9$

2) Mixed Organometallic Compounds ⟹ In addition to Carbon, metal atom is attached to other groups also. E.g C_2H_5

On the Basis of type of C–M bond

① Ionic Organometallic Compound ⟹ Ionic Bond between me atom and carbon atom. Eg: Organo Sodium Compound (C_5H_5

② Covalent Organometallic Compound ⟹ Covalent Bond betwe Carbon and atom. Eg Metal alkyl compound – $Pb(C_2H_5)_4$,

③ Electron Deficient Organometallic Compound ⟹ These inclu the compounds having bridge alkyl groups. Eg: Dimeric t aluminium $[Al_2(CH_3)_6]$

④ Organometallics involving π Bonds: Have metal-ligand between metal and π orbitals of organic ligands. E.g Ferrocene – $(C_5H_5)_2Fe$

General Synthesis

1) Direct reaction of metal with alkyl/aryl halide in presence of ether or THF

$$M + RX \longrightarrow RMX$$

2) Metal-Exchange Reactions.

$RC\equiv CH + C_2H_5MgBr \longrightarrow RC\equiv CMgBr + C_2H_6$

Applications

- Used as homogenous catalyst in some chemical Reactions
- Used as stoichiometric reagents in both industrial and research oriented chemical reactions.
- Used in manufacturing of semiconductors.
- Used in production of LEDs
- Used in bulk hydrogenation process

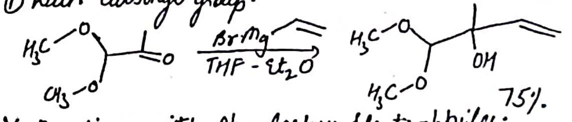
Lecture - 40

Fundamentals

- Grignard reagents are extremely useful organometallic compounds in the field of organic chemistry.
- They exhibit strong nucleophilic qualities and also have the ability to form Carbon-Carbon bond.
- When alkyl group replaced by an amido group, the resulting compound is Hauser Base.
- Grignard reagents are known for their ability to quickly target carbonyl at their carbon level.
- Grignard reagents do not function in presence of protic solvent.
- The reagents were discovered by French Chemist Victor Grignard who won the noble prize in chemistry for his discovery of new sequence of reactions resulting in creation of new C-C Bonds.

* Reactions of Grignard Reagent

① With Carbonyl group.



* Reaction with Non-Carbon Electrophiles.

$2R-Mg-X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$

Lecture-40

Imp

Q1 Why dry ether solvent is important for the preparation of Grignard reagent? [2018-19]

Ans The preparation of G.R is carried out in presence of diethyl ether or tetrahydrofuran to avoid the presence of moisture, as G.R reacts with water to form alkane

Q2 Give the preparations of Grignard Reagent. [2020-21]

Ans ① Prepared by reaction of organic halide with Mg in presence of THF or dry ether

$RX + Mg \xrightarrow{ether} RMgX$

$ArX + Mg \xrightarrow{ether} ArMgX$

② Metal Exchange Reaction

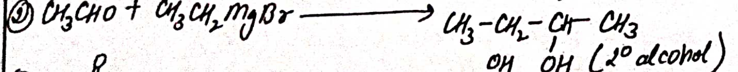
$RC\equiv CH + C_2H_5MgBr \longrightarrow RC\equiv CMgBr + C_2H_6$

M.Imp

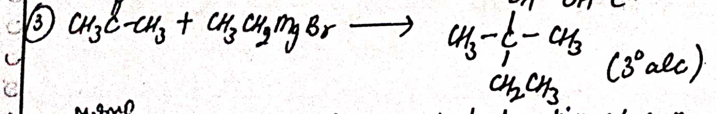
Q3 How is grignard Reagent prepared? How will CH_3CH_2MgBr reacts with $HCHO, CH_3CHO$ + $(CH_3)_2CO$ [2014-2015] [2016-2017]

Ans G.R Preparation → same as Ans 2.

① $HCHO + CH_3CH_2MgBr \xrightarrow{Dry\ ether} CH_3CH_2CH_2OH$ (1° Alc)



② $CH_3CHO + CH_3CH_2MgBr \longrightarrow CH_3-CH_2-\underset{OH}{CH}-CH_3$ OH (2° alcohol)



③ $CH_3\overset{O}{C}-CH_3 + CH_3CH_2MgBr \longrightarrow CH_3-\underset{CH_2CH_3}{C}-CH_3$ (3° alc)

M.Imp

Q4 ⇒ Explain various methods of preparation of G.R and also write its at least 5 applications. [2015-16] [2016-17] [2019-20]

Ans Preparation → same as Ans 2

Application of Grignard Reagent

① Formation of alkanes on reaction with acidic hy

With Water: $C_2H_5MgBr + H_2O \longrightarrow C_2H_6 + Mg($

With alcohol: $C_2H_5MgBr + C_2H_5OH \longrightarrow C_2H_6 + Mg($

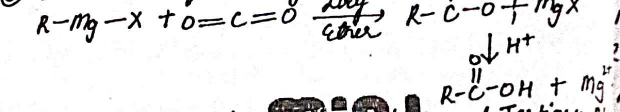
With Ammonia: $CH_3MgBr + HNH_2 \longrightarrow CH_4 + MgBr$

② Formation of Amines

$CH_3MgX + ClNH_2 \longrightarrow CH_3NH_2 + ClMgX$

chloramine methanamine

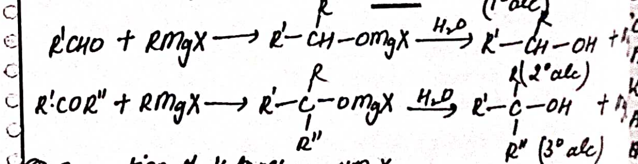
③ Formation of Carboxylic Acid



$R-Mg-X + O=C=O \xrightarrow[ether]{Dry} R-\overset{O}{C}-O-MgX \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-OH + Mg^{2+}$

④ Formation of Primary, Secondary and Tertiary Alc

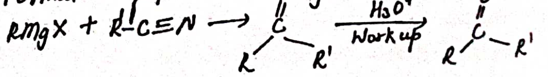
$HCHO + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg($ (1° alc)



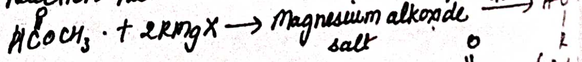
$R'CHO + RMgX \longrightarrow R'-\overset{R}{CH}-OMgX \xrightarrow{H_2O} R'-\overset{R}{CH}-OH$ + (2° alc)

$R'COR'' + RMgX \longrightarrow R'-\underset{R''}{\overset{R}{C}}-OMgX \xrightarrow{H_2O} R'-\underset{R''}{\overset{R}{C}}-OH$ + (3° alc)

⑤ Formation of Ketones

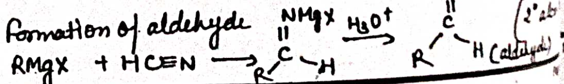


⑥ Reaction with ester



$H\overset{O}{C}OCH_3 + 2RMgX \longrightarrow$ Magnesium alkoxide salt $\xrightarrow{H_2O} H-\underset{R}{\overset{R}{C}}-OH$ (2° alc

⑦ Formation of aldehyde



Q5 What are organometallic compounds. Explain various methods of preparation of grignard Reagent and also write reaction of G.R with HCHO, R_2NH, CO_2, CH_3CH_2OH & ester.

Ans The compounds in which Carbon atom of organic group are bonded to metal atom directly are known as Organometallic Compounds. [2018-19]

Preparation of G.R → Same as Ans 2

$$RMgX + HCHO \xrightarrow[\text{② } H_2O]{\text{① Dry ether}} RCH_2OH + Mg(OH)X$$

$$RMgX + R'_2NH \xrightarrow[\text{"}]{\text{"}} R-H + MgBr(NR'_2)$$

$$RMgX + CO_2 \xrightarrow[\text{"}]{\text{"}} R-COOH + Mg^{2+} + X^-$$

$$RMgX + CH_3CH_2OH \xrightarrow[\text{"}]{\text{"}} R-H + Mg(OC_2H_5)Br$$

$$H_3MgBr + R-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \longrightarrow R-\underset{CH_3}{\overset{CH_3}{C}}-OH \ (3^\circ \text{ alc})$$

⇒ Explain ~~with~~ equations preparations of Acid, Ketone, alcohol, alkanes and Organometallic Compound from grignard reagent. [2020-21]

- Acid from CO_2
- Ketone from Alkyl cyanides
- Alcohols from aldehydes & Ketones.
- Alkanes from NH_2, H_2O

Already Done in Answer 4

Preparation of Organometallic Compounds from G.R

$$2R-Mg-X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

$$RC\equiv CH + C_2H_5MgBr \longrightarrow RC\equiv CMgBr + C_2H_6$$

Lithium Aluminium Hydride ($LiAlH_4$)

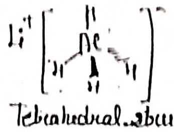
- * Lithium aluminium hydride, $LiAlH_4$ also abbreviated as LAH is a reducing agent commonly employed in modern organic synthesis.
- * It is a nucleophillic reducing agent, best used to reduce polar multiple bonds like C=O
- * $LiAlH_4$ reagent can reduce aldehydes to primary alcohols, ketones to secondary alcohols, carboxylic acids and esters to primary alcohols, amide and nitriles to amines and epoxides to alcohols
- * Lithium aluminium hydride. LAH reagent cannot reduce an isolated non-polar multiple bond like C=C. However the double bond in conjugation with the polar multiple bonds can be reduced.

Structure of $LiAlH_4$:-

- * There is a tetrahedral arrangement of hydrogens around Al^{3+} in aluminium hydride, AlH_4^- ion.

It is formed by coordination of hydride. H^- ions to Al^{3+} ion

* The hybridisation in central Al is sp^3



Tetrahedral structure of $LiAlH_4$

Preparation of $LiAlH_4$

Method 1 conventional method

$LiAlH_4$ was first prepared from the reaction between lithium hydride (LiH) and aluminium chloride.

$$4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$$

Method-2 Industrial method

In addition to above method, the industrial synthesis entails the initial preparation of sodium aluminium hydride from the elements under high pressure and temperature.

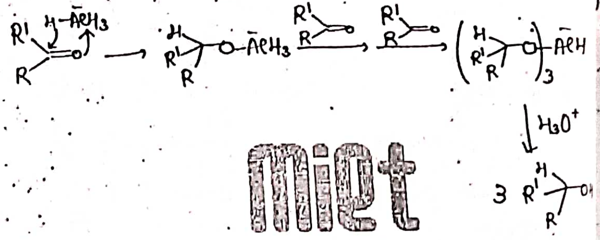
$$Na + Al + 2H_2 \longrightarrow NaAlH_4$$

$LiAlH_4$ is then prepared by a salt metathesis reaction

$$NaAlH_4 + LiCl \longrightarrow LiAlH_4 + NaCl$$

Mechanism of reduction by $LiAlH_4$:-

Initially, a hydride ion is transferred onto the carb
carbon and the oxygen atom coordinates to the rem
aluminium hydride species to furnish an alkoxytr
-aluminate ion, which can reduce the next carbonyl m
Thus, three of the hydride ions are used up in red



Applications of $LiAlH_4$ in organic synthesis :-

The summary chart of application of $LiAlH_4$ in the re
of different types of functional groups.

Functional group conversion

Aldehydes, ketones ----> Alcohols
Carboxylic acid ---> Alcohols
Esters, acid halides ---> Alcohols.
Amides ---> amines
Nitrile ----> amines
oxiranes (epoxides) ----> alcohols

lactones ---> diols

haloalkanes, haloarenes --- > alkanes, arenes

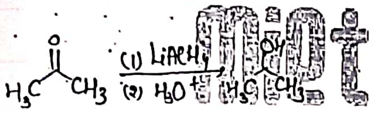
Reduction of carbonyl compounds using LiAlH4 :-

① The aldehydes or ketones are reduced by LiAlH4 to the corresponding primary or secondary alcohols respectively.

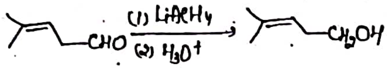
eg Acetaldehyde is reduced to ethyl alcohol and acetone is reduced to isopropyl alcohol.

LiAlH4 Reduction of carbonyl compounds

$$H_3C{-}CHO \xrightarrow[(2)\ H_3O^+]{(1)\ LiAlH_4} H_3C{-}CH_2OH$$



LiAlH4 does not affect the isolated carbon-carbon double or triple bonds



② The carboxylic acids, esters and acid halides are reduced to corresponding primary alcohols by LiAlH4.

eg. The reduction of acetic acid, methyl acetate and acetyl chloride by LiAlH4 furnish the same ethyl alcohol.

$$H_3C{-}COOH \xrightarrow[(2)\ H_3O^+]{(1)\ 3equiv.\ LiAlH_4} H_3C{-}CH_2OH$$

$$H_3C{-}COOMe \xrightarrow[(2)\ H_3O^+]{(1)\ 2equiv\ LiAlH_4} H_3C{-}CH_2OH + MeOH$$

$$H_3C{-}COCl \xrightarrow[(2)\ H_3O^+]{(1)\ 2equiv\ LiAlH_4} H_3C{-}CH_2OH$$

③ The amides are reduced to amines by LiAlH4. This method is used to get secondary amines.

eg. Diethylamine can be prepared starting from acetyl chloride as follows:-

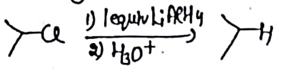
$$H_3C{-}COCl \xrightarrow[-HCl]{EtNH_2} H_3C{-}CONHEt \xrightarrow[2)\ H_3O^+]{1)\ 2equiv\ LiAlH_4} H_3C{-}CH_2NHEt$$

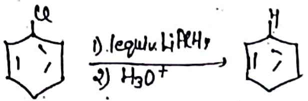
④ The nitriles are reduced to primary amines by LiAlH4.

eg. Acetonitrile is reduced to ethyl amine by LiAlH4.

$$H_3C{-}C{\equiv}N \xrightarrow[2)\ H_3O^+]{1)\ 2equiv.\ LiAlH_4} H_3C{-}CH_2NH_2$$

⑤ The haloalkanes and haloarenes are reduced to corresponding hydrocarbons by LiAlH4





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Topic-Wise Important Questions for AKTU End Semester Examinations

Code: BAS102		Subject Name : Engg. Chemistry	Taught In :	I Yea
Topics	**Q. No.**	**Question (Statement) - As Appeared In AKTU**	**Year**	**Mar**
POLYMER & CLASSIFICATION	42	Differentiate between:- (I) Homopolymers and co-polymers (II) Thermoplastic and Thermosetting polymers (III) Addition and condensation polymers.	2017-2018, 2019-2020	5,5
	43	Why polymers have average molecular weight? In a polymer, there are 100 molecules of molecular weight 10^3 each, 200 molecules of molecular weight 10^4 each and 200 molecules of molecular weight 10^5 each. Find out the number average and weight average molecular weight.	2014-2015	10
YNTHESIS OF POLYMER	44	Give the preparation, properties and uses of: Teflon, Lucite, Bakelite, Kelvar, Dacron, Thiokol, Nylon, Buna-N and Buna-S	2018-2019, 2019-2020, 2020-2021, 2021-2022	1
CONDUCTING and BIODEGRADABLE POLYMER	45	Write short notes on conducting and biodegradable polymers.	2015-2016, 2018-2019, 2019-2020	5
COMPOSITES and POLYMER BLENDS	46	Write short notes on polymer composites and polymer blends.	2018-2019, 2021-2022	1
ORGANOMATTELIC COMPOUNDS & APPLICATION	47	What are Zeigler Natta catalysts? Give the mechanism of preparation of iso-poly-propylene.	2014-2015	1
	48	What are organo-metallic compounds? Give their preparation and classification.	2018-2019, 2021-2022	5,
	49	Give the preparation of Grignards Reagent. Why do we use THF or dry ether in preparation of Grignard's reagent? Write 5 uses of Grignard's reagent.	2018-2019, 2020-2021, 2021-2022	2,
	50	General methods of preparation and applications of Organometallic compounds LiAlH4.		