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The Phase Rule

Phase Rule:- When a heterogeneous system in equilibrium at a definite temperature and pressure, the number of degrees of freedom is equal to by 2 the difference in the no. of components & the no. of phases provided the equilibrium is not influenced by external factors such as gravity, electrical & magnetic forces, surface tension etc.

Gibbs Phase Rule:

$$\boxed{F = C - P + 2}$$ where F : no. of degrees of freedom
C : no. of components
P : no. of phases of system

* "GREATER THE NO. OF PHASES, THE LESSER IS THE NO. OF DEGREE OF FREEDOM".

(i) System consists of only one phase then $C = 1$ & $P = 1$ so $\boxed{F = 2}$

(ii) System consists of two phases in equilibrium then $C = 1$ & $P = 2$ so $\boxed{F = 1}$ i.e. monovariant.

→ For one component system, the maximum no. of phases is three and degree of freedom → 0.

* "LARGER THE NO. OF COMPONENTS, GREATER WILL BE THE NO. OF DEGREE OF FREEDOM."

→ The two component system has a higher no. of degree of freedom.

Phase:- The part of system by means of a dynamic boundary. It is a physically distinct and mechanically separable part of a system.

For eg: System with H_2O & ice — Two phases
Mixture of gases such as He, H_2 & Ar — Single phase
Miscible liquids like Alcohol & H_2O — Single phase

COMPONENT:- Minimum no. of independently variable constituents in terms of which the composition of each phase of a heterogeneous system can be expressed directly or in the form of a chemical equation.

Eg: (a) System consisting of a solution of sugar in water ($P = 1$) is a two component system.

(b) Ice (s) ⇌ Water (l) ⇌ Vapour (g)
System consists of three phases ice, water & vapour but it is a one component system.

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DEGREE OF FREEDOM (F): Smallest no. of independently variable factors such as temperature, pressure & concentration which must be required in order to define the system completely. It is also known as the variance.

→ When a system having no degree of freedom
  F = 0 it is called non-variant system or invariant system

→ When a system having only one degree of freedom
  F = 1 it is called univariant or a monovariant system

→ When a system having two degrees of freedom
  F = 2 it is called bivariant system.

Eg: (a) ice ⇌ water ⇌ vapour , F = 0
  (b) Mixture of gases, F = 3
  (c) Saturated LiCl solution , F = 1

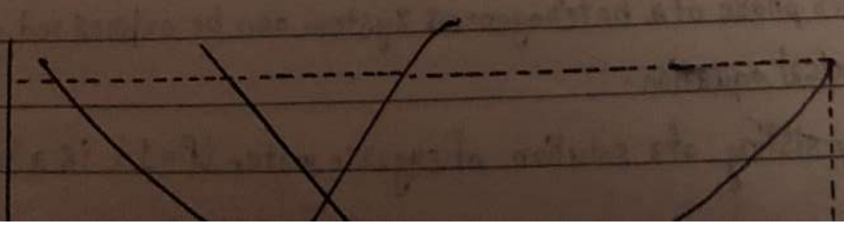
PHASE RULE FOR ONE COMPONENT SYSTEM

→ According to the Phase Rule equation, a one component system should have a maximum of two degrees of freedom and the least no. of phases possible in any system is one.

In case of a one-component system, phase diagram provide the following informations regarding the system:

(i) Point : Represents a non variant system i.e F = 0
(ii) AREA : Represents a bivariant system i.e. F = 2
(iii) CURVE : Represents a univariant system i.e. F = 1

Eg: Water System & Sulphur System



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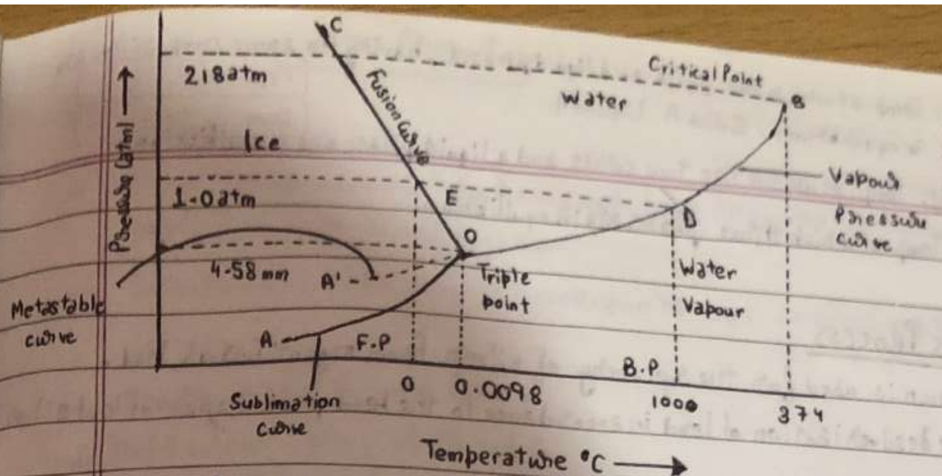


* Curve OB tells us about the vapour pressure of water at different temperatures. Along this curve, the two phases - water & vapour exist together in equilibrium. Represents univariant system.

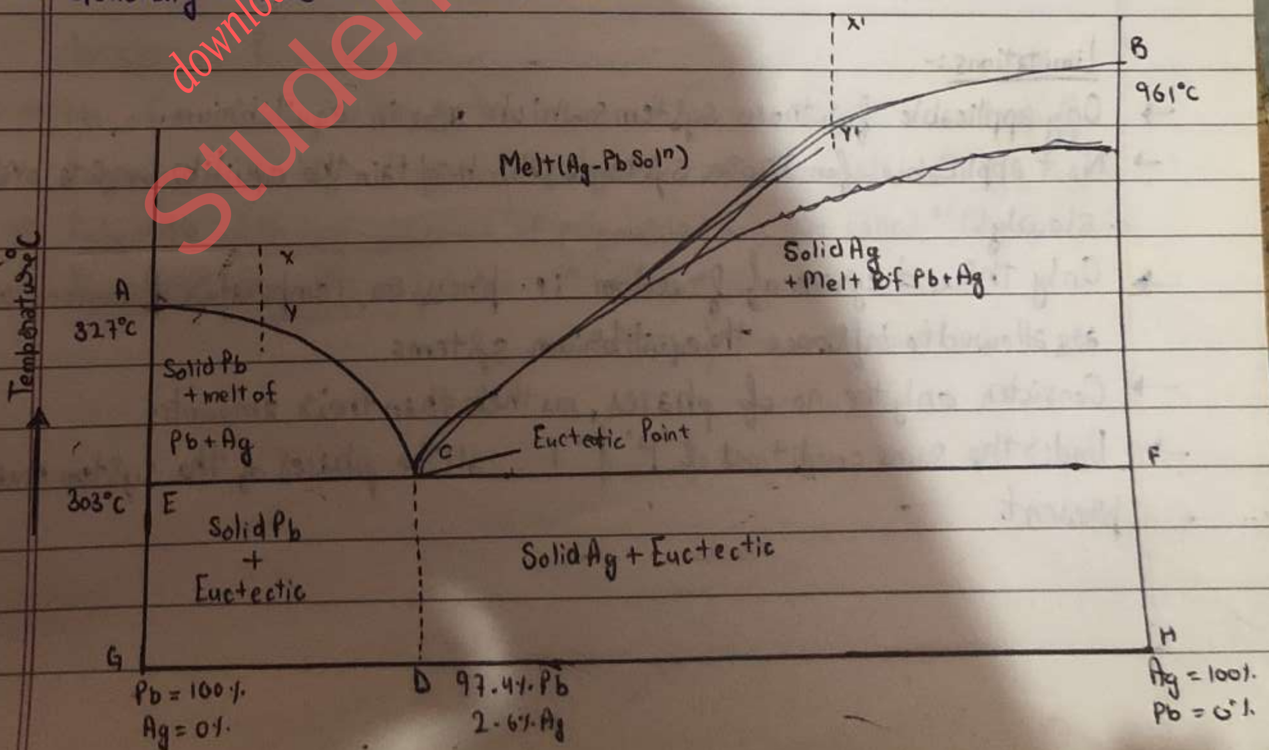
* Curve OA gives the vapour pressure of solid ice at diff. temperatures. Along this curve the phases ice & vapour exist together in equilibrium.

TWO COMPONENT SYSTEM : When two independent components are present in a heterogeneous system. The two component system having one phase will have three degrees of freedom.

LEAD-SILVER SYSTEM

→ Maximum of following four phases :- Solid lead, Solid Silver, Solution of molten silver & lead and Vapours.

- Bpt of Ag & Pb are high & vapour pressure of the system is very low.
- Generally studied at constant pressure.



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- **Melting Point**: Temp. at which the solid and liquid phases, having the same composition are in equilibrium. Solid A ⇌ Liquid A.
- **Eutectic Point**: Temp. at which the two solids and a liquid phase are in equilibrium.
- **Triple Point**: Temp. at which three phases are in equilibrium.

Pattinson's Process

1. Process which is used for the recovery of silver from argentiferrous lead.
2. Involves the desilverisation of lead in accordance to the ~~lead~~ phase diagram of lead silver system.
3. Argentiferrous lead ⟶ Small % of silver (less than 0.1%)
4. For recovery, argentiferrous lead is heated above its melting point when a liquid melt consisting of Ag-Pb solⁿ is obtained.
5. If the Ag-Pb solⁿ is cooled, then Pb continues to separate out and is regularly removed.
6. In the end, a eutectic solⁿ containing 2.6% Ag is obtained.
7. Above process increases the % of Ag in the argentiferrous lead.

Advantages of Phase Rule

→ Applicable to both chemical & physical equilibria
→ Applicable to macroscopic system
→ Conveniently classify equilibrium states in terms of phases, components & degrees of freedom.
→ Behaviour of system can be predicted under diffⁿ conditions.
→ Diff. systems behave similarly if they have same degree of freedom.

Limitations:-

→ Only applicable for those systems which are in equilibrium.
→ Not applicable for those systems which attain the equilibrium state very slowly.
→ Only three degrees of freedom i.e. pressure, temperature & concentration are allowed to influence the equilibrium systems
→ Consider only the no. of phases, rather than their amounts.
→ Under the same conditions of 'P' & 'T', all the phases of the system must be present.

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Applications of the Phase Rule :

[1] Solders :

→ Alloy, homogeneous mixture having mpt. lower than that of the corresponding metal pieces which have to be joined together.

→ Selection of solder alloy is based upon the mpt. desired and the pieces of metals to be joined.

→ Should spread in liquid form.

(i) "Soft solder" alloy of Pb and Sn.

(ii) "Plumber Alloy" → Pb = 67%; Sn = 33%.

(iii) "Half-half Alloy" → Pb = 50%; Sn = 50%.

[2] Safety Plug :

→ Alloy having low mpt.

→ Used to ensure the safe working & avoid accidents.

→ One alloy is wood metal, which is used in the safety fuses.

→ Melts at 65°C & consists of Bi = 50%; Pb = 25%; Sn = 12.5%; Cd = 12.5%.

POLYMER

- Combination of two Greek words, "Poly" means "many" & "Mers" meaning "parts" or "units"
- Large molecule which is formed by repeated linking of the small molecules called "monomers."

DEGREE OF POLYMERIZATION

→ No. of repeating units in the chains of which a polymer is made up of.

→ Polymers with high degree of polymerization are called "High Polymers".

→ Polymers with low degree of polymerization are called "Oligopolymers."

Formula, $P = M/m$ where M : Mass of polymer

m : Mass of monomeric unit

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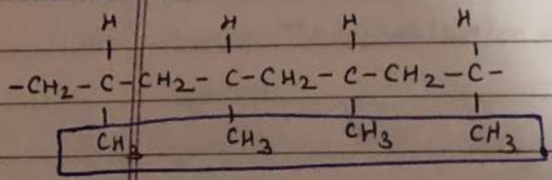
Classification of Polymers

A macromolecule may consists of monomer of identical or different chemical structure and accordingly they are called Homopolymers or copolymers (or Heteropolymers).

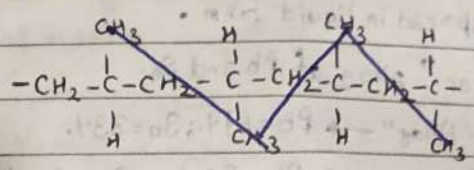
1. Isotactic polymers

Functional groups on the same side of the main carbon skeleton



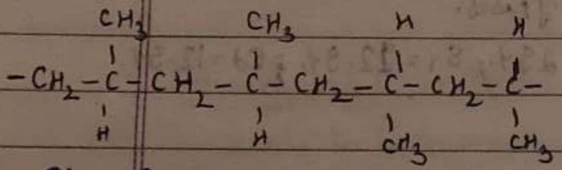
2. Syndiotactic Polymers

Functional groups arranged in the alternate fashion of the main carbon skeleton



3. Atactic Polymers

Functional groups arranged in a random manner around the main carbon skeleton



- Polymers can be linear, branched or cross linked. The monomer maybe arranged in the chain at random or regularly.

- Classification based on Source

1. Natural Polymers

Eg: Proteins, Cellulose, Starch, Rubber

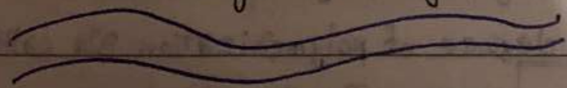
2. Semi-Synthetic polymers

Eg: Cellulose derivatives - Cellulose acetate (Rayon)

3. Synthetic Polymers

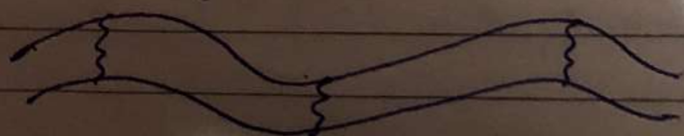
Eg: Buna-S, Buna-N, Nylon, Polyethene, Polyester

1. Linear Polymers: Consists of long and straight chains. Eg: Polyvinylchloride



2. Branched Chain Polymers: Contain linear chains having some branches

eg: low density polymer.



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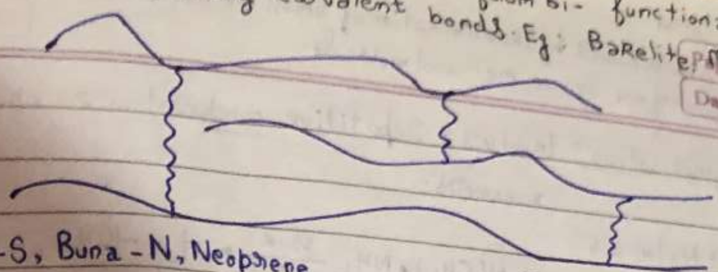
3. **Crosslinked or Network Polymers:** formed from bi-functional and tri-functional monomers and contain strong covalent bonds. Eg: Bakelite, Melamine



1. Elastomers : Buna-S, Buna-N, Neoprene
2. Fibers: Polyesters, Polyamides
3. Thermoplastic : Polyethene, Polystyrene, PVC
4. Thermosetting: Bakelite, Urea-formaldehyde resin

ORDER OF STRENGTH :- Thermosetting > Fibres > Thermoplastics > Elastomers

Mechanism of Polymerization :

1. **Addition Polymerization** : Formed by repeated addition of monomer molecules possessing double or triple bonds.

$$n(CH_2=CH_2) \longrightarrow -(CH_2-CH_2)-$$

Ethylene → Polyethylene

2. **Condensation Polymerization** : Formed by repeated condensation reaction between two different bifunctional or trifunctional monomeric units.
Eg: Terylene (dacron), nylon 6,6, nylon 6

$$n(H_2N(CH_2)_6NH_2) + n(HOOC(CH_2)_4COOH) \longrightarrow -[NH(CH_2)_6NHCO(CH_2)_4CO]-_n + nH_2O$$

(Nylon 6,6)

Addition Polymerization

1. **Free Radical Mechanism** : Alkenes or dienes and their derivatives are polymerized in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, t-bu peroxide etc.

This process involves 3 steps—

(a) Chain initiation step - addition of phenyl free radical formed by the peroxide to the ethene double bond, thereby forming a larger radical.

(b) Chain propogation step - repetition of this sequence with new and bigger radicals.

(c) Chain terminating step - the product radical thus formed reacts with another radical to form the polymerized product.

Eg: Polytetrafluroethene (Teflon), Polyacrylonitrile, Polyethylene etc.

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Condensation Polymerization

1. The chain growth is accompanied by the elimination of small molecules.
2. Molecules are in the form of water or methanol molecule.

(a) Step Growth Polymerisation: Involves a repetitive condensation rxn between two bifunctional monomers.

Eg: Formation of Nylon 6,6

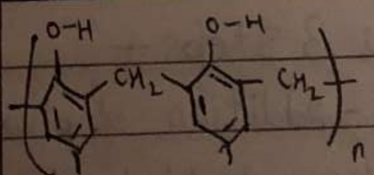
$$n\,HOOC(CH_2)_4COOH + n\,H_2N(CH_2)_6NH_2 \xrightarrow[HP]{550K} \left[\underset{H}{\underset{|}{N}} -(CH_2)_6- N - \underset{O}{\underset{\|}{C}} -(CH_2)_4- \underset{O}{\underset{\|}{C}} \right]$$

(b) Copolymerisation: Reaction in which a mixture of more than one monomeric species is allowed to polymerize and form a copolymer.

Eg:

$$n\,CH_2=CH-CH=CH_2 + n\,\underset{\text{Styrene}}{C_6H_5CH=CH_2} \longrightarrow \left[CH_2-CH=CH-CH_2-\underset{C_6H_5}{CH}-CH_2 \right]$$

1,3-butadiene + Styrene → Butadiene-Styrene

Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$-(CH_2-\underset{CH_3}{CH})_n-$	Manufacture of toys, ropes, pipes, fibres
Polystyrene	Styrene	$-(\underset{H}{C}H-\underset{H}{C}H(C_6H_5))_n-$	As insulator, wrapping material, manufacture of toys, radio & television cabinets
Polyvinyl Chloride (PVC)	Vinyl Chloride	$-(\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}})_n-$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea formaldehyde Resin	(a) Urea (b) Formaldehyde	$-(NH-CO-NH-CH_2)_n-$	For making unbreakable cups & laminated sheets.
Glyptal	(a) Ethylene Glycol (b) Pthalic Acid	$-(OCH_2-CH_2OOC-C_6H_4-CO)_n-$	Manufacture of paints & lacquers
Bakelite	(a) Phenol (b) Formaldehyde		For making combs, electrical switches, handles of utensils & computer discs.

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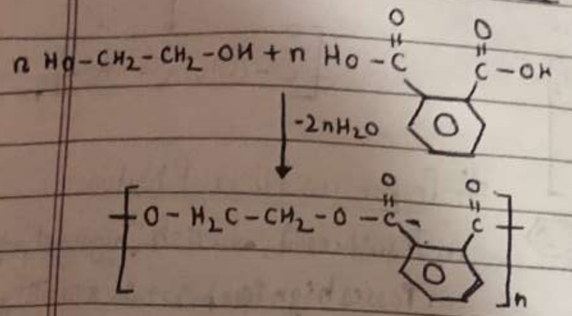
Glyptal or Alkyl Resin:

* General name of all polymers obtained by condensation of di basic acids & polyhydroxy alcohols.
* Simplest is polyethylene glycol pthalate which is obtained by a condensation rxn btw ethylene glycol & ortho pthalic acid.



Uses:

(a) 3D crosslinked polymers

(b) Dissolves in suitable solvents & the solution on evaporation leaves a tough & non flexible film

(c) Used in adherent paints & lacquers.

Ultra High Molecular Weight Polyethylene

→ Extremely tough plastic

→ High abrasion & wear resistance

→ Used where durability, low friction & chemical resistance

→ Uses: (i) Biomedical Applications

(ii) Guide rails & wear strips

(iii) High speed conveyors

(iv) Packaging machinery parts

(v) Bumbers, pileguards & dock fenders

Types of Polyethene

Low Density Polyethene	High density Polyethene
(i) $0.910 \leq \rho \leq 0.940\ g/cm^3$	(i) $\rho \geq 0.941\ g/cm^3$
(ii) Obtained by polymerisation of ethene under high pressure of 1000–2000 atm	(ii) Addition polymerisation of ethene in a hydrocarbon solvent under presence of catalyst Ziegler Natta at 333–343K, 6–7 atm
(iii) Temperature of 350–570K	(iii) Temperature of 333–343K
(iv) Insulation of electricity wires; manufacture of squeeze bottles; toys & flexible pipes	(iv) Manufacturing of buckets, dustbins, bottles, water pipes.

Linear Low Density Polyethylene (LLDPE)

→ Linear polymer

→ Significant no. of short branches made by copolymerization of ethylene with olefins longer chain

→ Differs from LDPE by absence of long chain branching.

PROPERTIES: (i) Unique melt flow

(ii) Lower viscosity in melt extension

USES: Plastic bags & Sheets; Plastic wrap, Pouches, Toys, covers, lid, pipes, flexible-tube etc.

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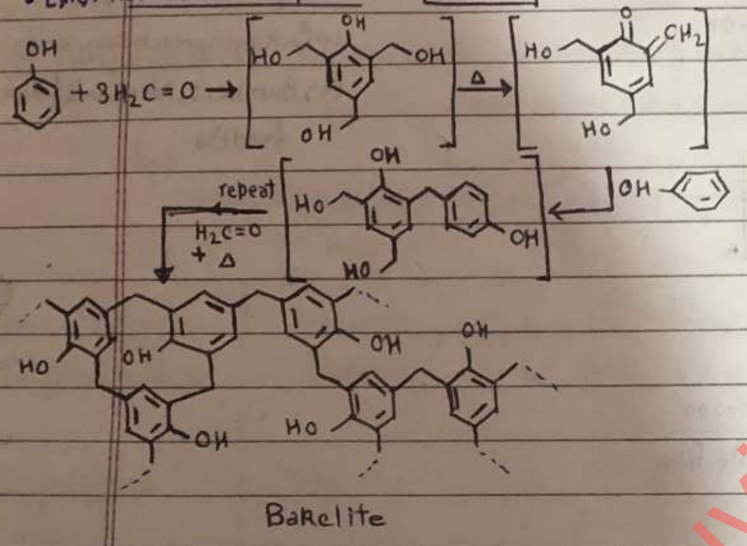
BAKELITE

- Condensation rxn of phenol with formaldehyde in the presence of either an acid or base catalyst.
- Rxn starts with initial formation of o or p-hydroxymethylphenol which further react with phenol to form compounds having rings joined to each other through a $-CH_2$ group.
- When Initial linear product - **Novolac** used in paints.



Uses: (i) Telephone parts; cabinets; heater handles
(ii) Phonograph records
(iii) Electric switches & bearings
(iv) For impregnating fabrics, wood & paper
(v) Soft Bakelite → Binding glue for laminated wooden plants
(vi) Sulphonated Bakelite → Ion exchange Resins.

Nylon-6,6

- Nylon → General name for all synthetic fibres forming polyamides i.e having a protein structure.
- Condensation polymers of diamines and dibasic acids.
- Polymerisation of adipic acid with hexamethylene diamine.

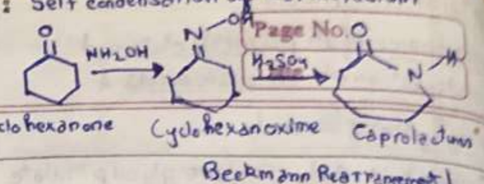
$$HO-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH + H-\underset{H}{\underset{|}{N}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{H}{\underset{|}{N}}-H$$

adipic acid   hexamethylene diamine

$$\xrightarrow{HCl} \left[\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{H}{\underset{|}{N}}\right]_n$$

amide group

Nylon-6: Self condensation of caprolactam



$$HOOC-(CH_2)_5-NH-CO-(CH_2)_5-...$$

$$\downarrow$$

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

Properties & Uses of Nylon

(i) Translucent, whitish, high mpt polymer
(ii) Possess high temperature stability
(iii) High abrasion resistance
(iv) Insoluble in common organic solvents like methylated spirit, benzene, acetone & soluble in phenol & HCOOH.

(a) Nylon-6,6: Used for fibres which are use in making socks, ladies hoses, dresses, carpets.
(b) Nylon-6: Moulding purposes for gears, bearings & electrical moulding. Bristles for tooth brush, Tyre cords.

★ Thermoplastics: So...
harden when coole...
★ structure are lin...
★ Polyethylene, pol...
- terephthalate ·
★ Thermosetting Pla...
- Made from ne...
resist motio...
- Epoxies, Phe...

■ Electrolumi...
★ Property i...
light of ...
electronic...
as electr...
★ Organic ...

Eg: Para...

1. Prepa...
pa...
2. Elim...
3. Use...
4. Al...

Appl...

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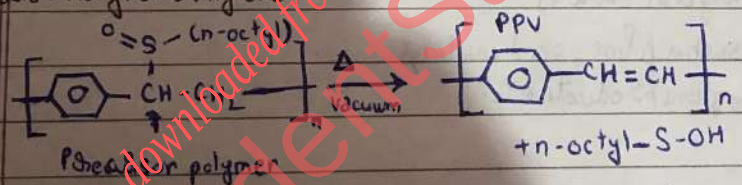
* Thermoplastics: Soften when heated & harden when cooled & vice versa.
* Structure are linear, branched
* Polyethylene, polystyrene, PVC, Polyethylene - terepthalate.

★ Thermosetting Plastics: Permanently hard
- Made from network polymers : covalent bond resist motion at high temp. prevent.
- Epoxies, Phenolics & some polyester resins.

Electroluminescent Polymers:

* Property in which a material produces bright light of different colours when stimulated electronically are electroluminescente, is called as electroluminescent material.
* Organic polymeric material ⟶ Self emitting device of high brightness; $\eta\uparrow$; DC low voltage operation; high speed response; no Δ

Eg: Para Phenylene vinylene (PPV)



1. Prepared from precursor polymer poly(α-n-octyl sulphinyl paraphenylene ethylene) by heating in vacuum.
2. Elimination of n-thiooctyl thiol introduces double bond in chain.
3. Used as mixture with (6,6) phenyl C_{60} - butyric acid methyl ester (PCBM)
4. Also prepared by chemical vapour deposition of dichloro-p-xylene at 500-700°C.

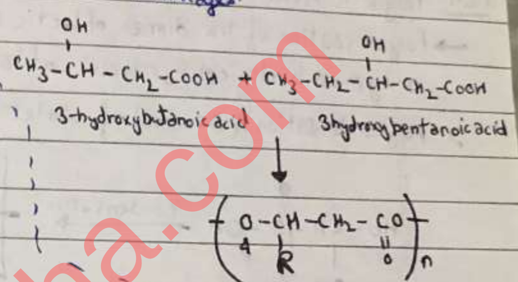
Application: Photovoltaic cells
→ Flat panel displays
→ Thin films for information display
→ Electroluminescence light lamp
→ Backlight for liquid crystal display.

Biodegradable Polymers

→ Expensive
→ Used in special situations when cost factor ignored
→ PHBV, PGA, PLA & PCL

Poly β-hydroxybutyrate-co-β-hydroxyvalerate (PHBV)

1. Copolymer of 3-hydroxybutanoic acid & 3-hydroxypentanoic acid
2. Monomer units are connected by ester linkages.



$R = -CH_3$ or $-CH_2-CH_3$

3. Properties vary acc. to ratio of both acids.
4. 3-hydroxybutanoic acid provides stiffness & 3-hydroxy pentanoic acid imparts the flexibility
5. Used in orthopaedic devices & in controlled drug disease.

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PGA: Polyglycolic acid

→ Chain polymerization of dimer of glycolic acid $HO-CH_2COOH$.

$$n\,HO-CH_2COOH \xrightarrow{\Delta} \left(O-CH_2-\overset{O}{\overset{\|}{C}}-O \right)_n$$

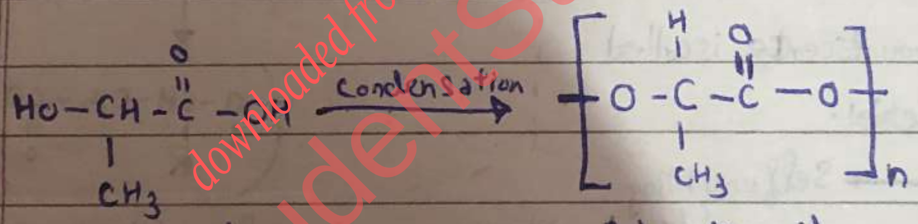
PCL: Poly E caprolactone

→ Chain polymerization of the lactone of 6-hydroxy hexanoic acid

$$\left(O-(CH_2)_5-\overset{O}{\overset{\|}{C}}-O \right)_n \xrightarrow{\text{Polymerization}} PCL$$

PLA: Polylactic Acid

→ Polymerization of the dimer of lactic acid ($HO-CH(CH_3)COOH$) or by microbiological synthesis of lactic acid followed by the polycondensation & removal of water by evaporation.



Lactic acid   Polylactic acid

Uses:

* Use in stitching wounds & cuts
* In medical goods such as surgical sutures
* In agriculture materials such as films, seed coatings
* In food wrappers, personal hygiene products etc.

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