Classification of lubricant on the basis of

- Liquid (oil)
- Semi-solid (greases)
- Solid

Polymers

Degree of polymerization

Which combines to get polymer.

When degree of polymerization is low the obtained polymer is oligopolymer.

When degree of polymer is high, resultant is high polymer.

Characteristics of polymers

Macromolecules

Semi-crystalline nature

Main bonding is covalent & but secondary forces are hydrogen bonding, dipole-dipole attraction, Vander-Wall forces.

Low density

Resistance to corrosion

Thermal & Electrical Insulators

Moldable

Combustible.

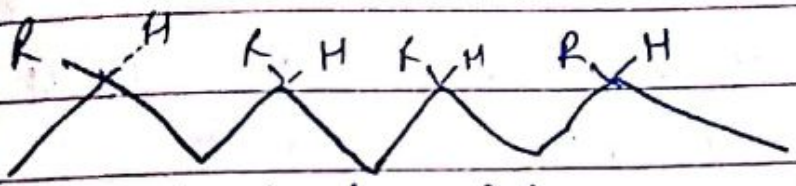
1) Homo & copolymers
2) Linear, Branched, Cross linked
Graft Polymers → In this type of polymers mo
of main chain & branches are different.
3) Homo chain & Hetero chain.

On the basis of tacticity.

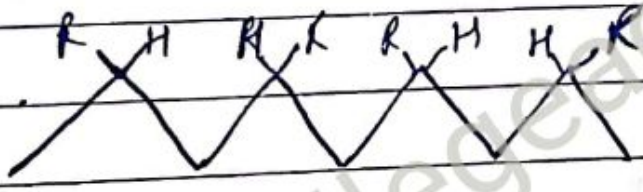
Orientation of monomeric unit in polymers is called tacticity.

This is the configuration of monomers.

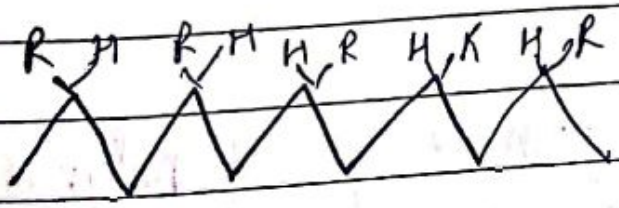
1. Isotactic polymers
All functional groups are arranged on the same side of main chain It is called Isotactic polymers.



Syndiotactic Polymer
When the functional groups are arranged in alternate order.



Atactic
random arrangement



Type of polymerization

Addition

In this type of polymerisation the exact multiple of monomers is should have double or triple bond.

Resultant polymer is linear in shape.

PVC, PVA, PMMA, PAN, Teflon,

$$n(CH_2=CH_2) \rightarrow (-CH_2-CH_2-)_n$$

Condensation polymerisation

In this process the formation of polymer & elimination of small molecules of HCl, H_2O occurs simultaneously. The monomers should have functional groups & the resultant polymer is ~~exact~~ not exact multiple of monomers.

E

$$H_2N-(CH_2)_6-NH_2 + nHOOC-(CH_2)_4-COOH$$

$$\downarrow$$

$$(HN-(CH_2)_6-NH-OC-(CH_2)_4-CO)_n$$

Nylon (6,6)

Polymethylene adipate.

$H_2N-(CH_2)_5-COOH \xrightarrow{-n(H_2O)} [HN-(CH_2)_5-CO]_n$

Nylon 6

ε-amino caproic Acid.

Co-polymerisation.

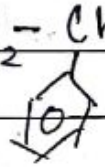
When 2 or more types of monomers combine togethers to give polymers. The process is called co-polymerisation.

$CH_2=CH-CH=CH_2$ + m 

75%

1,3 Butadiene

25%

$[CH_2-CH=CH-CH_2]_n[CH_2-CH]_m$ 

Buna-S

SBR

$CH_2=CH-CH=CH_2 + CH_2=\underset{CN}{CH} \rightarrow$

$[CH_2-CH=CH-CH_2]_n[CH_2-\underset{CN}{CH}]$

Comparison among addition, condensation & copolymerisation.

Mechanism of Polymerization.

1) Free radical
2) Anionic
3) Cationic
4) Co-ordination or Zeigler-Natta

Free Radical
This is done by homolytic fission in the presence of peroxides (catalyst). Linear polymers are formed.
It forms 3 steps

1) Initiation
a) Production of free radical.

$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \rightarrow 2\,C_6H_5COO^{\bullet} \rightarrow 2\,C_6H_5^{\bullet} + 2CO_2$$

b) Addition of phenyl free radical to monomers.

$$C_6H_5^{\bullet} = R^{\bullet}$$

$$R^{\bullet} + CH_2=\underset{X}{CH_2} \longrightarrow R-CH_2-\underset{X}{CH^{\bullet}}$$

free radical,

Propagation step or formation of polymers having free radical

In this step successive addition of monomers are added to give polymer having active centre free radical.

$$R-H_2C-\underset{X}{\overset{\cdot}{C}}H + H_2C=\underset{X}{CH_2} \longrightarrow R-CH_2-\underset{X}{CH}-CH_2-\underset{X}{\overset{\cdot}{C}}H$$

$$\xrightarrow{(n-2)\ CH_2=CH_2} R\left[CH_2-\underset{X}{CH}\right]_{(n-1)}-H_2C-\underset{X}{\overset{\cdot}{C}}H$$

a) By combination or coupling

$$R-\left[CH_2-\underset{X}{CH}\right]_{n-1}-CH_2-\underset{X}{\overset{\cdot}{C}}H + \underset{X}{\overset{\cdot}{C}}H-CH_2-$$

b) by disproportionation.

$$-H_2C-\underset{X}{\overset{\cdot}{C}}H + \underset{X}{\overset{\cdot}{C}}H-CH_2-$$

$$-H_2C-\underset{X}{\overset{H}{C}}H + \underset{X}{\overset{\cdot}{C}}=CH-$$

Thermoplastic	Thermosetting
formed by addition or condensation	formed by condensation
Either linear or branched structure	They have 3-D cross-linked structure
They soften on heating and becomes hard on cooling.	They do not soften on heating and becomes charred on cool
These are soluble in organic solvents	These are insoluble in organic solvents
Thermo plastics can be remoulded, re-shaped reclaimed	They cannot be remoulded or re-used.
Recycled from waste	Cannot be re-cycled.
Soft and weak	Hard and brittle.
Polymer chain are held together by Vanderwaal forces or H-B bond.	Polymers chains are held together by strong covalent bond.
Eg - PVC, PVA, PMMA, Teflon Nylon 6, Nylon 6,6	Bakelite, Urea formaldehyde resin Glyptal.

Addition	Condn
• It requires the presence of double bond	2 reactive functional groups
• No by product is formed.	Usually a by product is formed.
• Polymer is exact multiple of monomers.	Molecular weight of Polymer is always is always less than monomers
• Homo chain polymers of usually thermoplastic	Hetro chain either thermoplastic or thermosetting.
• PVC, PVA, Poly-styrene, Poly-thene, PMMA, Teflon	Nylon 6,6, Nylon 6, Bakelite, Novolac, Glyptal, Dacron

Cationic Polymerization mechanism

1) Initiation step (formation of carbonium ion)
It is ~~present~~ initiated by heterolytic fission in presence of lewis acid, electron deficit species.

$$H^+ + CH_2=\underset{X}{CH} \longrightarrow CH_3-\overset{\oplus}{\underset{X}{CH}}$$

carbonium (chain initiation species)

2) Propagation step →

$$CH_3-\overset{\oplus}{\underset{X}{CH}} + CH_2=\underset{X}{CH} \longrightarrow CH_3-\underset{X}{CH}-CH_2-\overset{\oplus}{\underset{X}{CH}}$$

$$\downarrow (n-2)\ CH_2=\underset{X}{CH}$$

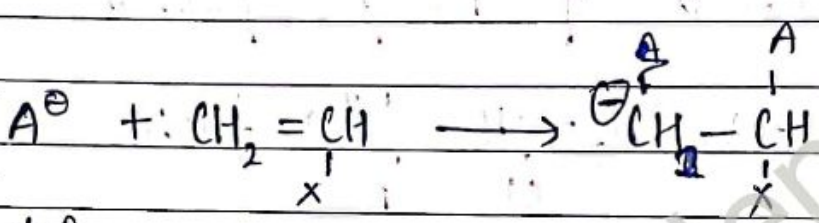
$$H_3C-\left[\underset{X}{HC}-CH_2\right]_{n-1}-\overset{+}{\underset{X}{CH}}$$

3) Termination
By addition of anion

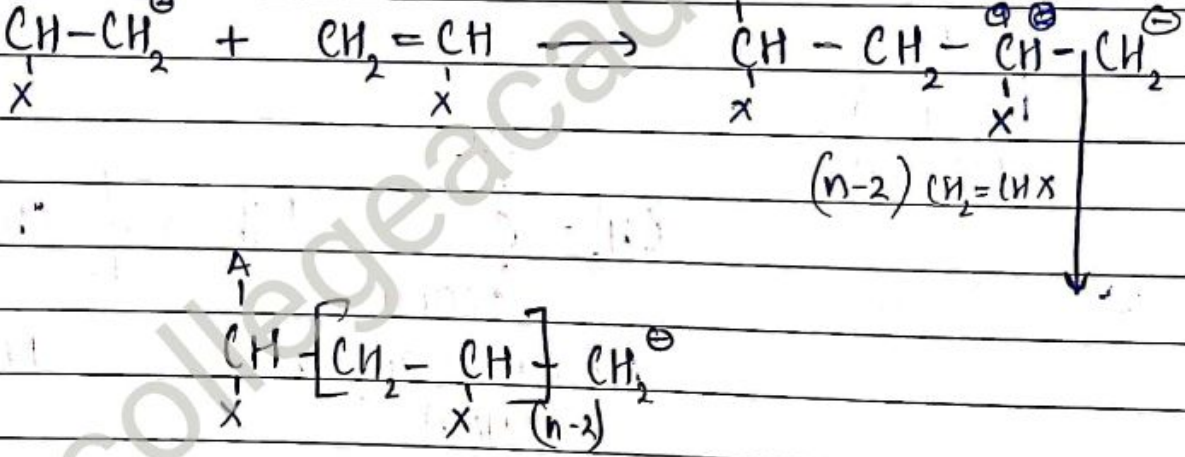
$$+ A^{\ominus} \longrightarrow H_3C-\left[\underset{X}{HC}-CH_2\right]-\underset{X}{CH}-A$$

Anionic Polymerization mechanism

1) Initiation step (formation of ~~carbanium~~ carbanion ion)

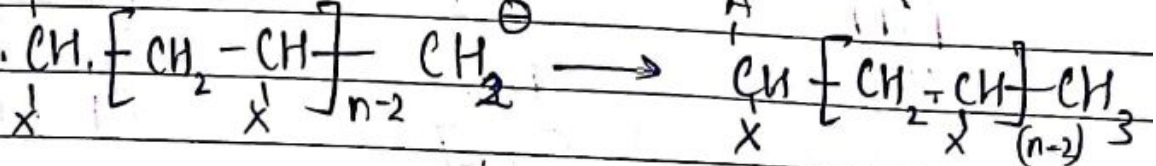


2) Propogation



3) Termination

By addition of $H^{\oplus}$ + A. cation



PVC

Poly Vinyl chloride

obtained by addition of Vinyl chloride in the presence of Benzoyl peroxide.

$$n\,CH_2=\underset{Cl}{\underset{|}{CH}} \xrightarrow[\text{Benzoyl Peroxide}]{\text{Poly}} \left[CH_2-\underset{Cl}{\underset{|}{CH}}\right]_n$$

PMMA

(Plexiglass)

(Lucite)

$$CH_2=\underset{OCOCH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} \xrightarrow{\text{Poly}} \left[CH_2-\underset{OCOCH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\right]_n$$

Methyl methacrylate

MMA

PMMA

Teflon

PTFE

(Fluricon)

$$F_2C=CF_2 \longrightarrow \left[F_2C-CF_2\right]_n$$

TFE

PTFE

4) Nylon 6,6 (Polyamide)

$NH_2-(CH_2)_6-NH_2 + HOOC-(CH_2)_4-COOH \xrightarrow[-2H_2O]{}$

Hexamethylene diamine — Adipic acid.

$-[NH-(CH_2)_6-NH-CO-(CH_2)_4-C$

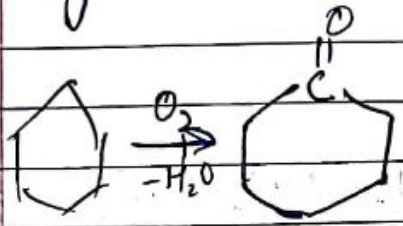
5) $NH_2-(CH_2)_5-COOH \xrightarrow{\Delta} -[HN-(CH_2)_5-CO]-_n$

ε Amino caproic acid. — Nylon-6

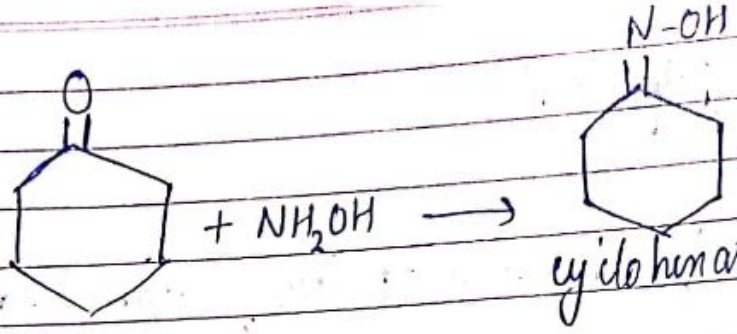
~~Urea formaldehyde~~

Synthesis of Nylon 6

1) Cyclohexane is oxidized in to cyclohexanone.

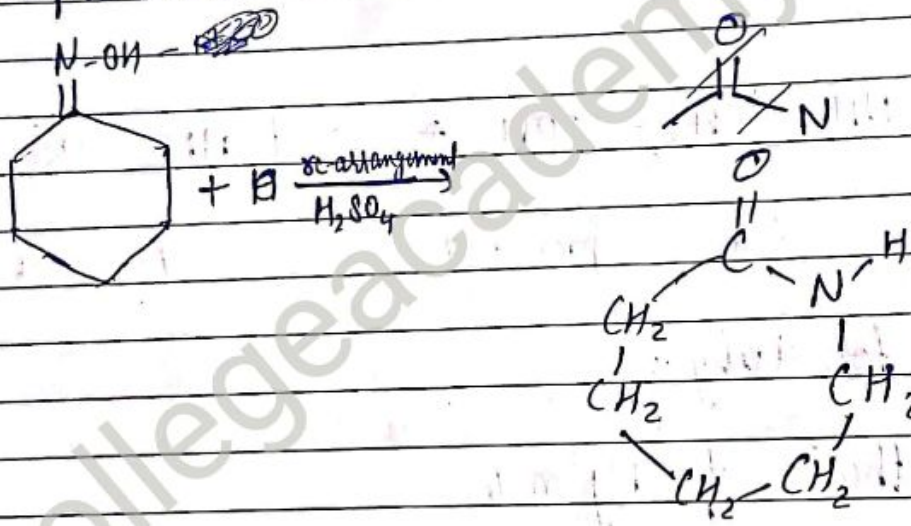


2) Cyclohexanone is reacted with NH_2OH to give oxime

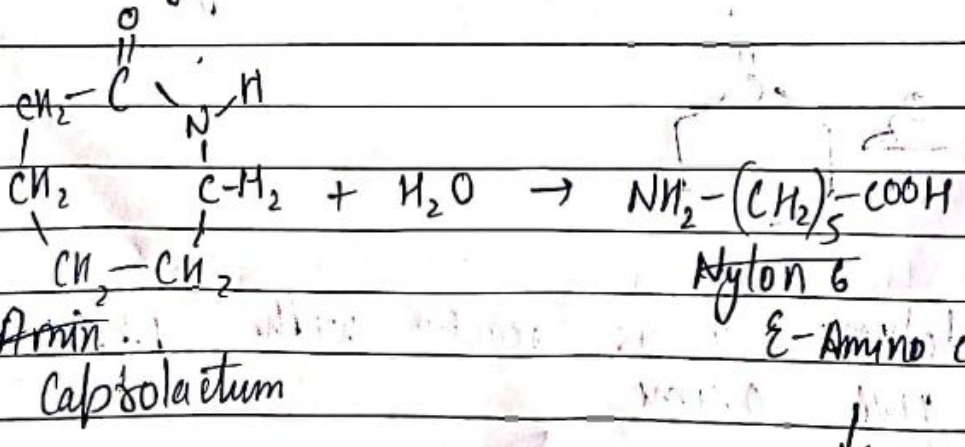


cyclohexanone - oxime

3) Cyclohexanone - oxime on Beckmann re-arrangement in the presence of H_2SO_4 gives Caprolactum:



4) On hydrolysis & polymerization caprolactum gives Nylon-6.



Amin..

Caprolactum

Nylon 6

ε-Amino caproic acid.

↓

$\left[NH-(CH_2)_5-CO\right]_n$

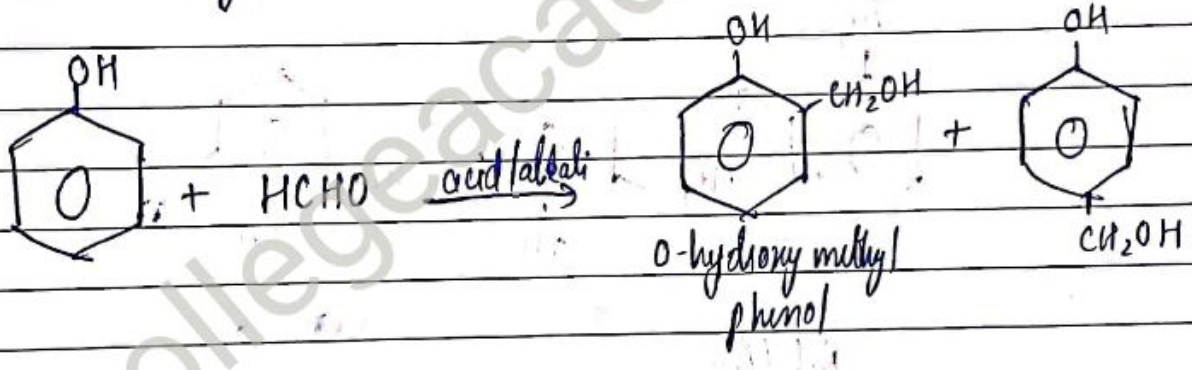
Nylon-6.

H-C(=O)-H

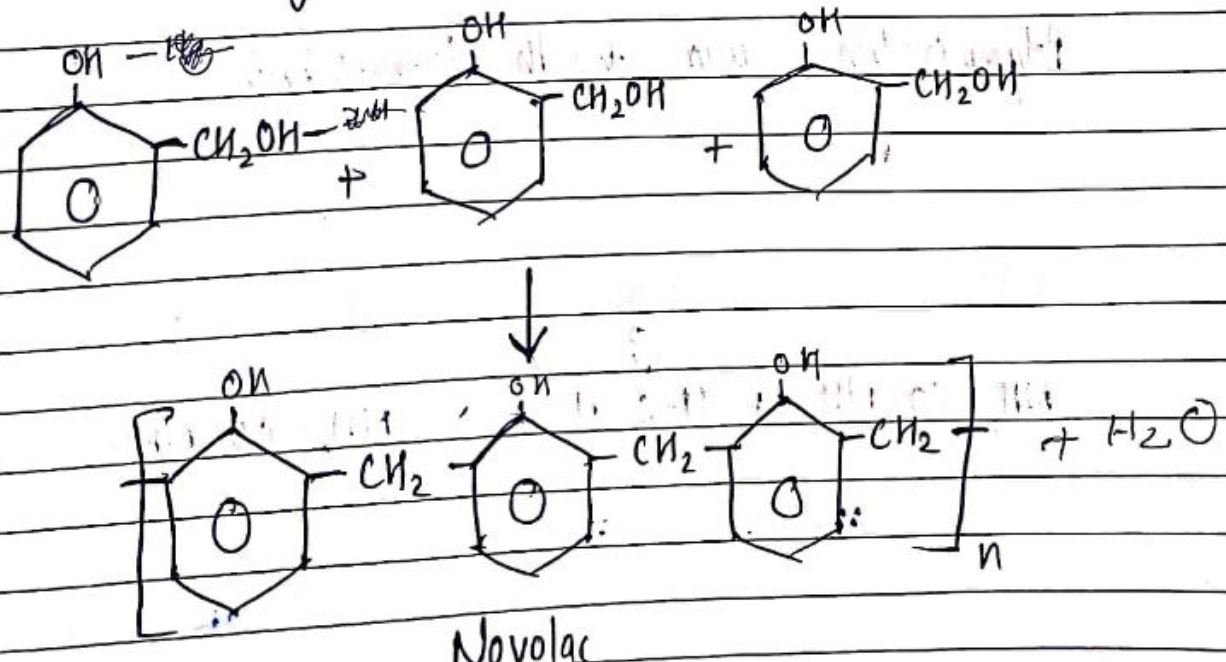
HOD ; Basic Sciences to request him to make arrangements for sports activities.

Bakelite

is obtained by condensation of phenol with formaldehyde in the presence of acid ~~or~~ or alkaline catalyst

1) 

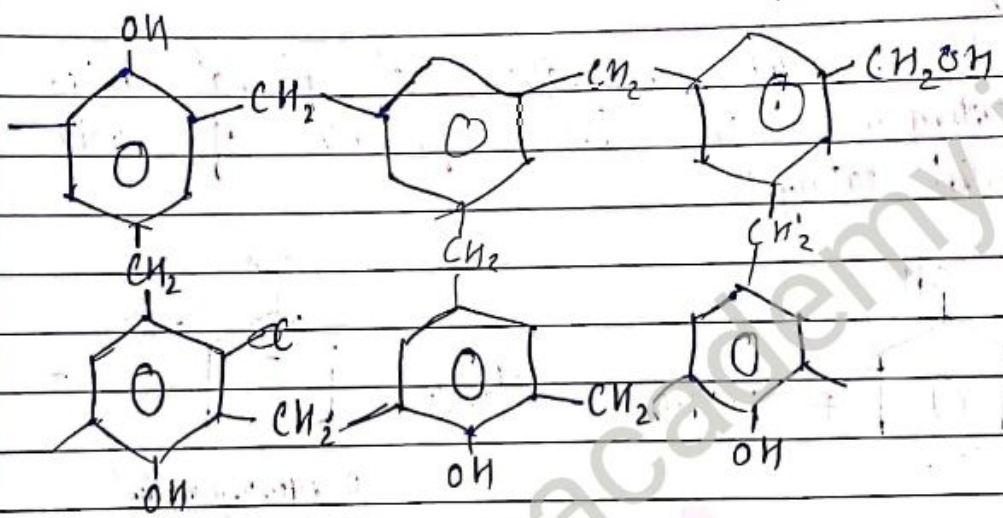
2) Polymerization of o-hydroxymethyl phenol gives linear polymer Novolac which contains OH and $-CH_2$ group in alternate order.



Novolac

$(CH_2)_2$-

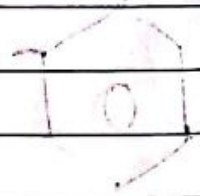
3) In the presence of Hexamethylene tetra amine on further heating it gives bakelite which is crossed linked polymer.

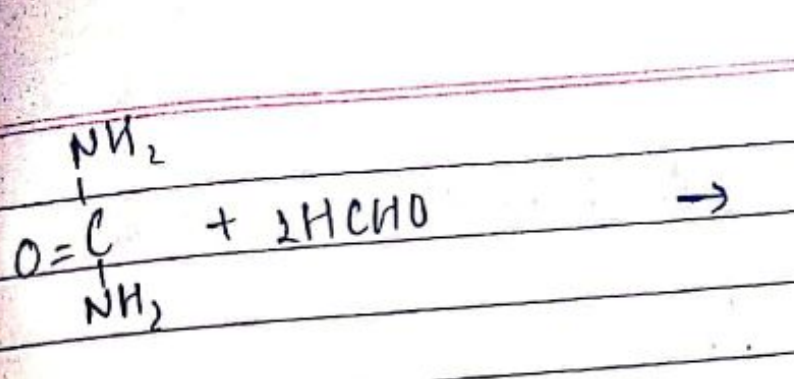


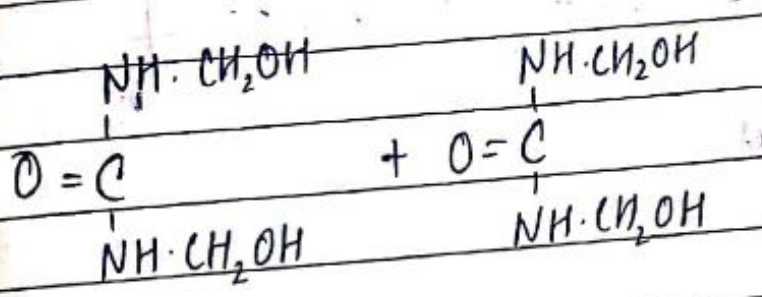
Bakellite

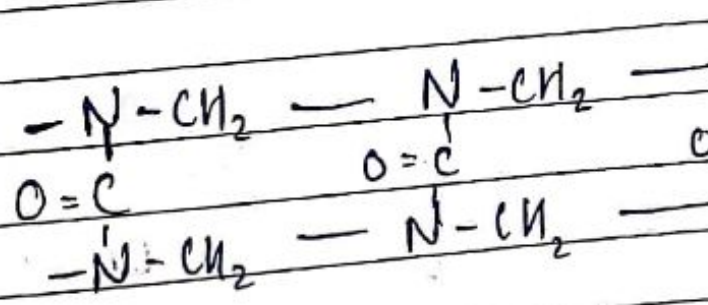
4) $NH_2-CO-NH_2$ (urea formaldehyde resin)
Amino plastic.

Polymerization urea with formaldehyde.



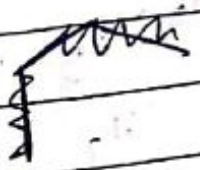




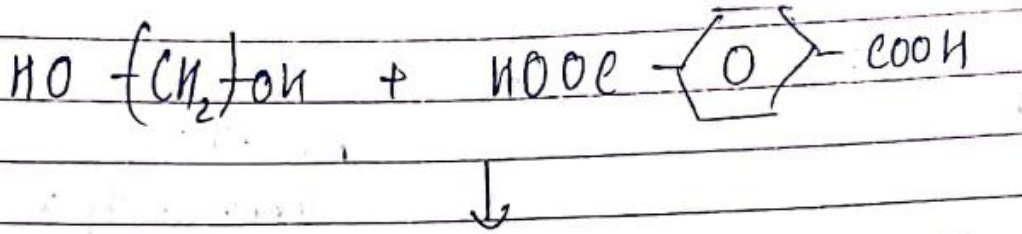


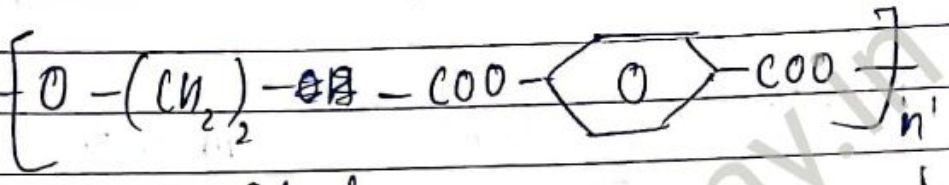
colourless

Polyesters (PET, Polyethylene terephthalate, Dacron, Terylene, Terene)



It is obtained by condensation of diol (ethylene glycol) and dicarboxylic acid: (Terephthalic acid)





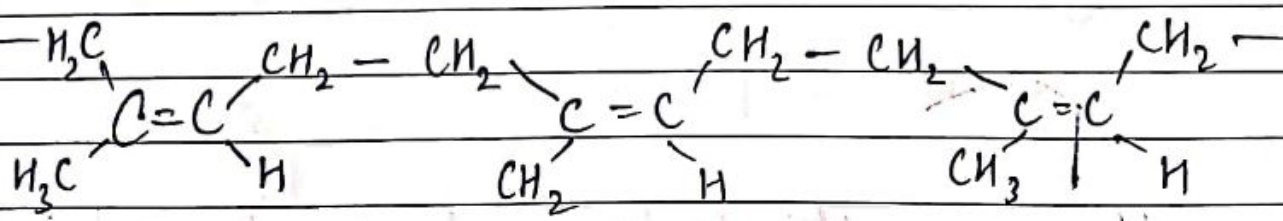
Polyester

Dacron.

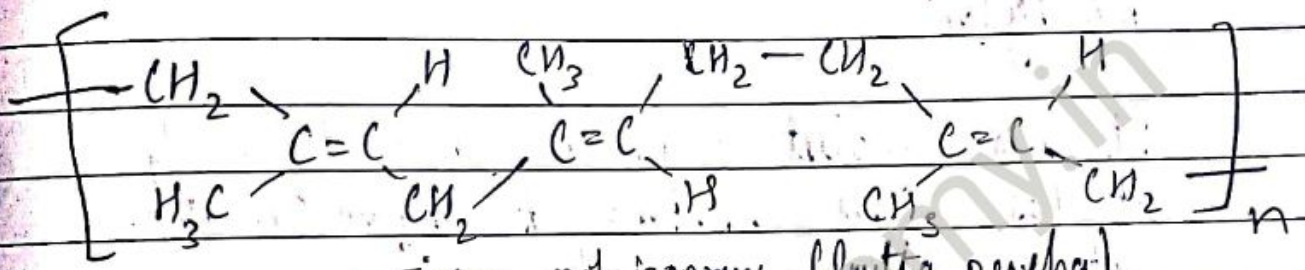
Natural Rubber

cis poly isoprene → Hevea brazi liensis

Trans poly isoprene → Palagum gutta (Gutta-Percha) Dichopsis gutta



cis polyisoprene (Hevea & guaguk rubber)



Trans polyisoprene (Gutta percha).

Vulcanisation of Rubber

Drawback of natural rubber. It is plastic in nature. It becomes soft at high temperature and brittle at low temperature so it can use at range of 10°-60°C. It is weak. Its tensile strength is 200 Kg per m^2.

It has large water absorption capacity. It is easily attacked by acids and organics solvents It has little durablity. All these undesirable properties can be overcome by a process known as vulcanization.

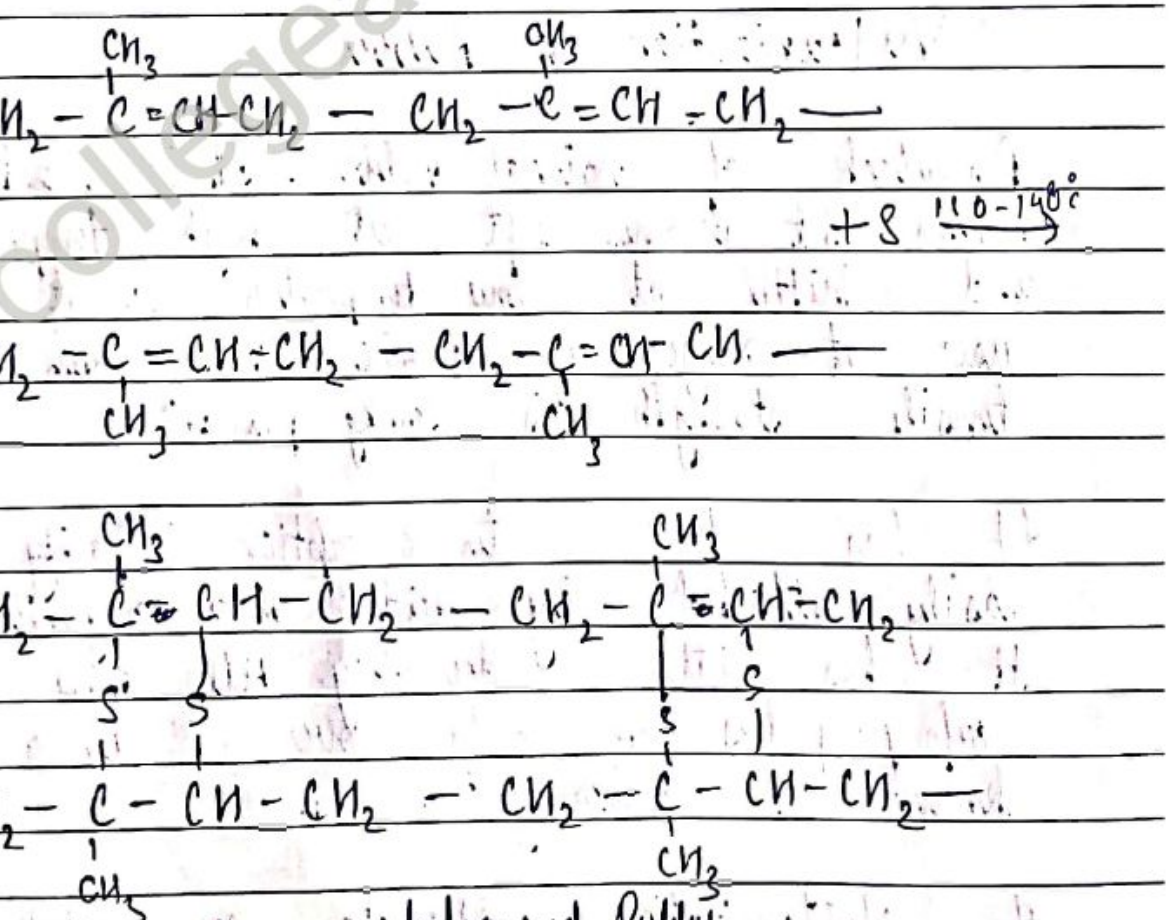
In Vulcanization rubber is compounded with some chemicals at 100°-140° C. for one hour. The added sulfur combines chemically at double bond. Vulcanization serves to stiffen the material

The extent of stiffness of vulcanized rubber depends on the amount of ~~sulfur~~ sulfur added.

- Advantages of Vulcanization.

Vulcanized rubber has good tensile strength 2000 kg/m².

It has excellent resilience and extensibility.
It has higher resistance to ~~Oxygen~~ Oxidation.
It is better electrical insulator.



Vulcanized Rubber

Ebonite Rubber

Synthetic Rubbers.

1) Bu Na-S GR-S (Good real - nobel prize for Bunas)

It obtained by copolymerization of Butadiene (75%) Styrene (25%) in the presence of Peroxide catalyst.

$$n\,CH_2=CH-CH=CH_2 \;(75\%) + m\,CH_2=CH\text{-}C_6H_5 \;(25\%)$$

Butadiene Styrene

$$\left[CH_2-CH=CH-CH_2\right]_n\left[CH_2-CH(C_6H_5)\right]_m$$

Corossion

Corossion is the process of gradual deterioation of a mutal from its surface due to the unwanted chemical, electrochemical interation of mutal with its environment.
eg → rusting of iron, tarnishing of silver.

Cause of corrosion :- Corrosion is to be considered as the reverse of the process of mutal extraction.

Ore of mutal (stable) $\xrightarrow[\text{operation}]{\text{metallurgical}}$ Pure mutal (unstable) $\xrightarrow{\text{Environment}}$ corroded mutal

Effect of corrosion →

1) loss of useful property of mutal.
2) Efficiency becomes less and replacement is time-consuming.
3) Increase is maintanance and production cost.
4) Contamination of product.
5) failure of machinery, loss of life leakage of gases.

Thermodynamics of corrosion – It depends on magnitude of gibbs free energy change (ΔG_T)

1) If $\Delta G_T < 0$ (-ve), the reaction is spontaneous & feasible.

2) If $\Delta G_T > 0$ (+ve), non spontaneous and not feasible.

Types of mechanism of corrosion

Chemical or dry corrosion

When metal surface is in corroded by atmospheric gases or anhydrous liquid, it is dry corrosion.

Wagner's theory of oxidation of metals.

Step - 1 Oxidation of metal (at anode)

$[M \rightarrow M^{n+} + ne^-] \times 2$

Step - 2 liberated e^- are transported to cathode.

Step - 3 Combination between the electrons and oxide

$[\frac{1}{2}O_2 + e^- \longrightarrow O^{2-}] \times 2$

Step 4 Formation of metal oxide by direct chemical interaction

$$2M^{n+} + nO^{2-} \rightarrow M_2O_n \text{ (metal oxide)}$$

Electrochemical or wet corrosion

When corrosion takes place by the transfer of e from anodic part of metal to cathodic part through conductive solution it is called electrochemical corrosion. It takes place mostly under wet or moist conditions.

Mechanism of corrosion → Corrosion starts by the flow of electricity between certain areas of a metal surface through a solution capable of conducting an electric current. Corrosion takes place at anode.

Oxidation at anode

a) atom of Fe oxides to form ferrous ~~oxides~~ ion with liberation of e^-

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

Fe^{2+} ion go into sol^n & e move from oxide to cathode

3) Corrosion by metal contact

In this type of corrosion different metal are in contact & jointly exposed to corrosive atmosphere. The metal which is higher in electrochemical series, more negative electrode potential will form anode which undergoes corrosion

Cu-Zn
Zn-Ag
Fe-Cu

Cu-Zn
Zn is more reactive than copper Zn is placed higher in the electrochemical series so when 2 metals are in direct contact, the electron flows from the anodic metal Zn to the cathodic metal Cu

$$Zn \longrightarrow Zn^{2+} + 2e$$

(oxidation at anode)

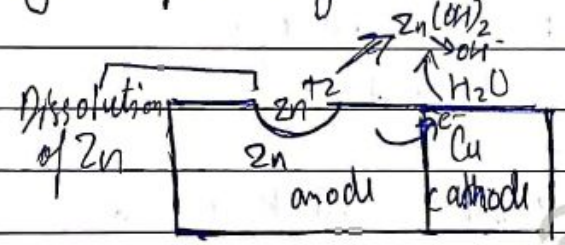
corrosion occurs at anode, while the cathodic part is protected from the attack.

Content of galvanic corrosion is more if

1. Potential difference 2 metals is large
2. Cathodic area is large.

It can be minimized by

1. Avoiding galvanic couple
2. By providing insulation b/w 2 metal.



4) Pitting Corrosion

due to

1. Heterogeneity in the metal surface resulting in the formation of pits and cavities is called pitting cavities.

Consider a drop of water resting on metal surface covered by the drop has low oxygen concentration and acts at anode and suffers corrosion. The uncovered metal surface due to high oxygen concentration act acts as cathode.

At anode → $Fe \longrightarrow Fe^{2+} + 2e^-$

At cathode – $\frac{1}{2}O_2 + H_2O + 2e \longrightarrow 2OH^-$

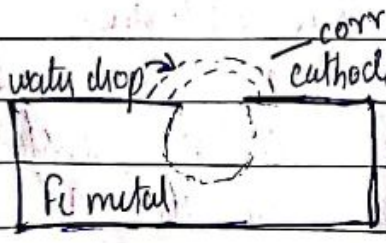
$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \xrightarrow{O} Fe(OH)_3$

Formation of small anodic & large cathodic area setup differences of potential at localized spots. to pit. Thus metal under water drop undergoes corrosion while it is submerged in water corrosion is less.

Pitting of the metal occurs when there is a break in the protective layer Once a small pit is formed rate of corrosion will be increased.

Preventions

1. Proper polishing of metal surface
2. Proper designing of metal surface.
3.



Phase Rule

It is given by Willard Gibb's applicable to all heterogenous systems in equilibrium. It is assumed that the equilibrium is not influenced by gravity, electrical & mechanical forces or by surface action & is influenced by only Temp, pressure & concentration

More number of degree of freedom is taken as 3, so phase rule is

$$F + P = C + 2$$

F = degree of freedom or variance
P = phase
C = component

True and metastable equilibrium

Thermodynamically true equilibrium is state when free energy content of the system is minimum for given variables

Solid ice $\rightleftharpoons$ water (l)

This equilibrium is maintained at 1atm pressure and 0°C.
This state can be achieved from either of the 2 direction. It is called true equilibrium.

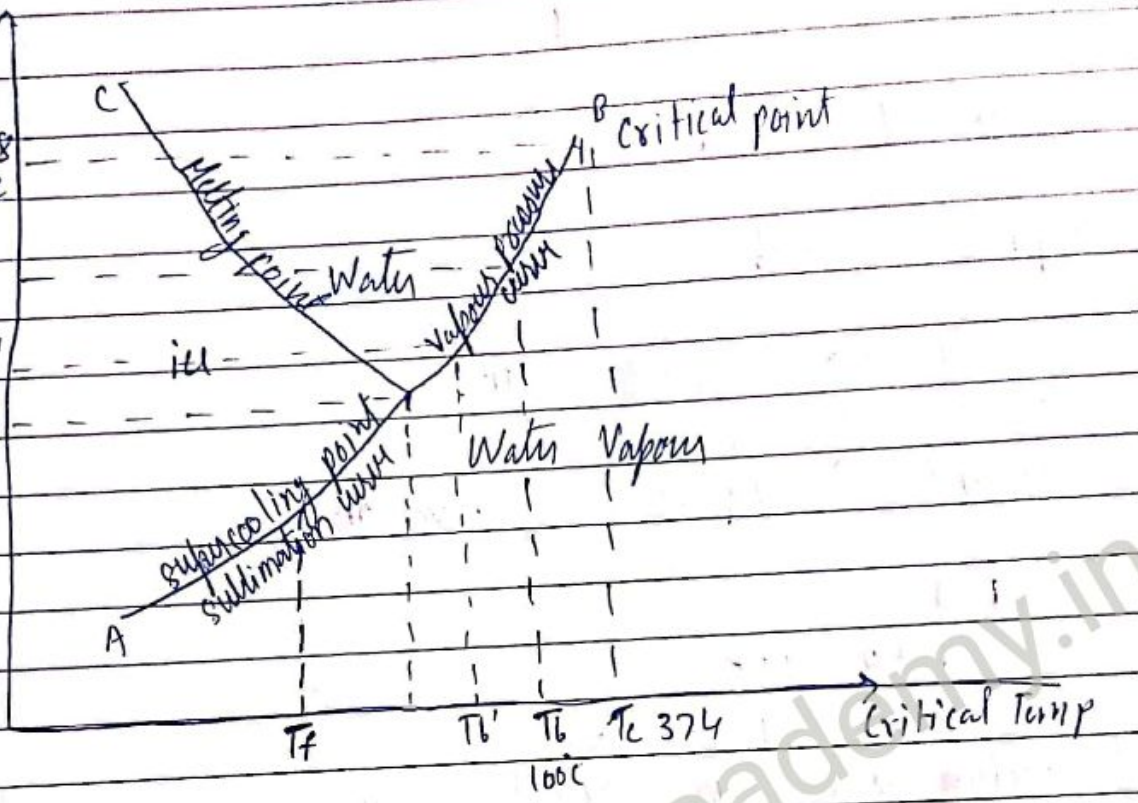
Water at -5°C is said to be in a meta stable equilibrium such a state can be achieved only by careful approach from one direction

In other words water can be cooled up to -5°C because it will normally freeze to ice at 0°C. and below this temperature it will adjust as solid but the water at -20°C can be maintained by careful approach. It is called meta stable equilibrium But a sudden shock, stirring or crystall of ice is introduced solidification starts.

Phase
Any part of the system which is homogenous in itself, physically distinct can mechanically separated from other part of system is called phase.

Two liquid - completely miscible - 1 phase
Solute completely dissolved in solvent = 1 phase
Benzene + Water = 2 phase
gaseous mixture = 1 phase
No. of Solids = No. of phase.

One component system (water System)



Tf = freezing point
Tb = boiling point
Tc = critical point
Tb' = boiling point of water (decreases & with external pressure decrease)

Study of areas (one phase equilibrium)
AOC = Ice
AOB = water Vapours
BOC = water

C = 1
f + P = 1 + 2
f = 3 - P
f = 2

System is bivariant

Study of curves

2 phase equilibrium

Solid ⇌ liquid : (curve OC)
Solid ⇌ vapour { curve OA }
Liquid ⇌ vapour { curve OB }

$P = 2$

$F + 2 = 1 + 2$

$F = 1$

System is univariant only one variant is sufficient to specify the system

Triple point (3 phase equilibrium)

: ice ⇌ water ⇌ vapour

$P = 3$

$F + 3 = 1 + 2$

$F = 0$

This is invariant system at 0.0098°C and 0.006 atm pressure.
Temp & pressure cannot be changed. When 3 phases ice, water, water vapours exists in equilibrium. So system is invariant at triple point

If pressure or temperature or both are changed, the 3 phases would no longer co-exist and atleast one of them would disappear.

It is the characteristic physical property of pure substance. It marks the lowest temperature at which the liquid can exist. as for water the solid liquid phase slope in the opposite direction so the triple point criteria is not applicable with respect to temperature but with respect to pressure a liquid can exist as stable phase if the pressure is above the triple point.

Study of points (Point O)

solid ⇌ liquid ⇌ vapour

P = 3 F = 0 − 3 + 2 = 0

∴ invariant

Water system is therefore invariant at the triple point O (0.0098°C and 0.006 atm)

The point O - It is called triple point because at this point all the 3 phases, ice, water and water vapour co-exist in equilibrium. So system is invariant at triple point. If either temperature or

pressure or both are changed. The phases would no longer co-exist in equilibrium. So system is invariant and atleast one of them would disappear.

Significance of triple point → It is a

Curve OA →
: sublimation curve
ice ⇌ : water vapour

Curve OB →
This is known as vapour pressure curve of water. With rise in temp, the vapour pressure increases. For any given vapour pressure on the curve, there is only one value of temp. and vice-versa. Above OB liquid is stable while below it gas is stable.

Curve OB extends up to the critical point of water. The liquid and vapour phases are no longer distinguishable from each other at and beyond critical temperature.

Critical point is a characteristic property of pure substance. Critical point marks the highest temp at which the liquid can exist.

Along the curve Oc.

ice $\rightleftharpoons$ water (l)

This curve is known as freezing point or fusion curve of ice.

The curve Oc shows how the melting temp of water depends pressure. The line slopes down from left to right. It means as the P is raised the melting point of ice falls.

ice melts at 0°C at 1 atm

but at -1°C at 130 atm

Liquid - solid system (Two component system) Binary System

Condensed Rule

$C = 2$ [2 metals]

$F + P = 2 + 2$

$F = 4 - P$

If $P = 1$ [least value of $P = 1$]

$F = 3$ [Temp, Press, Comp]

We need to make 1 variable const

Pressure - const

$F + P = C + 1$ — Isobaric or condensed Phase Rule.

For a 2 component system composition of components is also important for only solid liquid phase. In 2 component system pressure has little effect on the system so in this equilibrium pressure will not have considerable effect. because only gaseous system is affected by pressure. So pressure can kept constant and such systems are called isobaric or condensed system. Degree of freedom in such cases is reduced by one so we use reduced or condensed phase rule equation.

Eutectic system

A binary system consisting of 2 substances which are miscible in all proportions in the liquid phase but do not react chemically is known as eutectic system. For example Cas-Ag, Pb-Ag, are eutectic system.

Solid solution of 2 component system which has lowest freezing point of all the possible mixture of the component is known as eutectic mixture.

Minimum freezing point of eutectic mixture is known as eutectic point. It is an invariant point.

Characteristic of eutectic point.

Eutectic point represents the lowest temperature at which a liquid phase can adjust In this system no other mixture containing the 2 components will have a melting point lower than eutectic mixture.

Eutectic system is a mixture of components But not these compounds. Eutectic point has definite value of temperature & composition

and it represents an invariant system. If the molten state is cooled to just below the eutectic point both the components of eutectic mixture simultaneously solidify without any change in the composition or temperature of liquid phase.