

## UNIT-IV - POLYMERS

1. Polymers (In greek language poly means many and mer means units). It can be defined as the large molecules (macro molecular) formed by the linkage of small molecules called monomers.

2. Degree of polymerisation:

The degree is defined as the number of monomer units in the polymer.

$$\text{degree} = \frac{\text{Ratio of molecular wt of polymer}}{\text{molecular wt of repeat unit}}$$

e.g.: if 100 molecules of ethylene polymerize to give the polymer chain, the degree is 100.

3. The number of reactive sites in a molecule is termed as its functionality.

Molecule to act as a monomer it must have at least two reactive sites.

4. Types of Polymerisation:

Addition polymerisation:

The monomer molecules are added to each other without the formation of any byproduct.

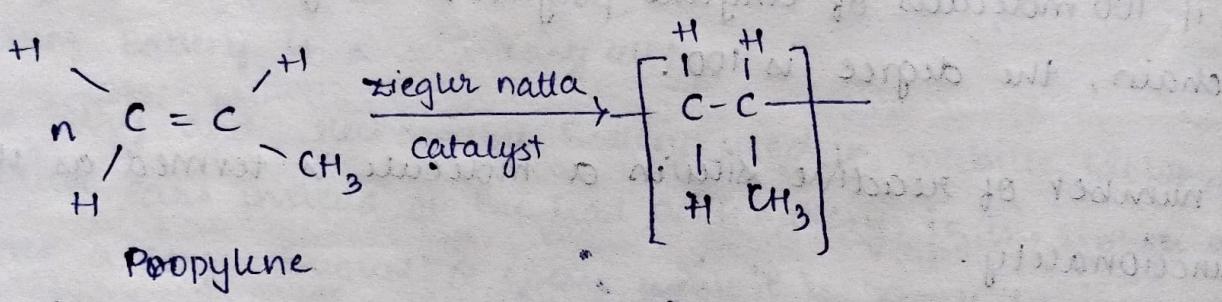
Condensation polymerisation:

The process in which a larger structure can form by the step-growth process by joining small monomers by the release of water molecules.

## Essay questions -

- 5) Addition polymerisation & types. steps involved with example.
- RVA free radical as example PVC synthesis properties & application
  - cationic polymerisation with example
  - Co-ordination with example.

ans) In addition polymerisation, the monomer molecules are added to each other without the formation of any byproduct. The elemental composition of polymer is similar to that of the monomer and its molecular weight is an exact multiple of the molecular weight of original monomeric molecule.

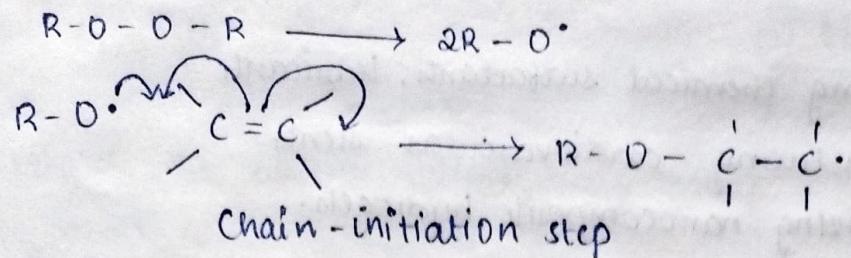


## Types of Addition polymerisation

- > the reactive initiation molecule can be a radical (free radical polymerization)
- > cation (cationic polymerization)
- > anion (anionic polymerization)
- > or an organometallic complex (coordination polymerization)

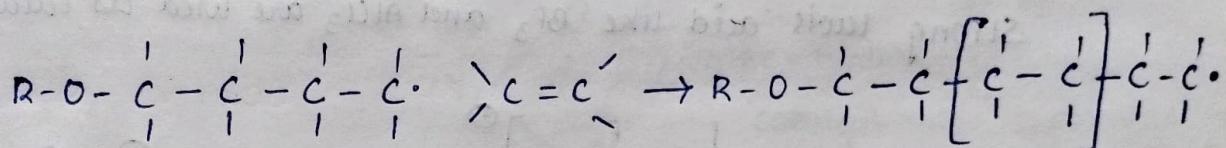
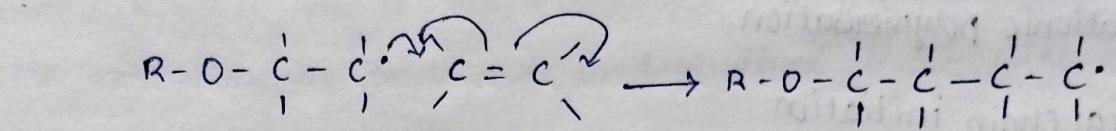
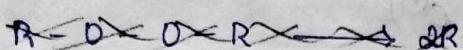
## Mechanism of Free Radical Polymerization.

- Initiation of Free Radical
- It is the foremost step, an active centre is generated in this process. All monomers are not liable for the initiation process.



propagat<sup>n</sup> of Free Radical

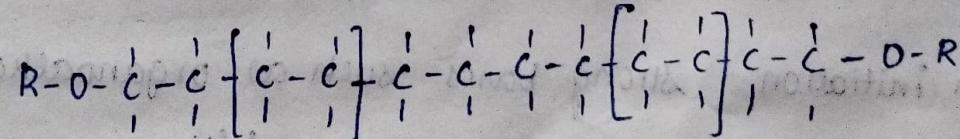
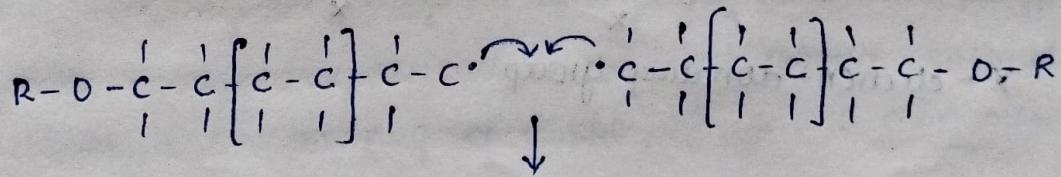
A polymer spends most of its time expanding its chain length or propagating. After initiation of free radical, it attacks another monomer subunit



Chain propagating step.

Termination of free radical

It is the final step in polymerization proc



Chain-terminating step

## Applications:

- It is used in synthesizing chemical surfactants, lubricants.
- It is used in manufacturing cardiovascular stents.
- It is used in synthesizing nanocomposite hydrogels.

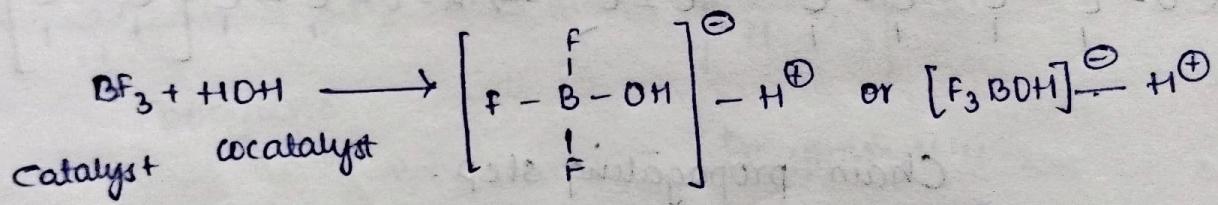
## (b) Ionic Polymerisation

Ionic polymerisations follow the same basic steps (initiation, propagation and termination). The chain is initiated either by a carbanion ( $c^-$ ) or carbocation ( $c^+$ )

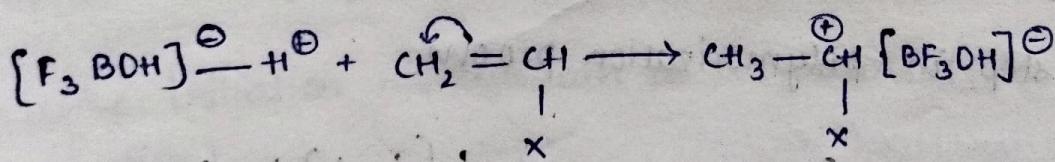
### (i) Cationic polymerisation

#### (a) Chain initiation

Strong Lewis acid like  $\text{BF}_3$  and  $\text{AlCl}_3$  are used as catalysts.



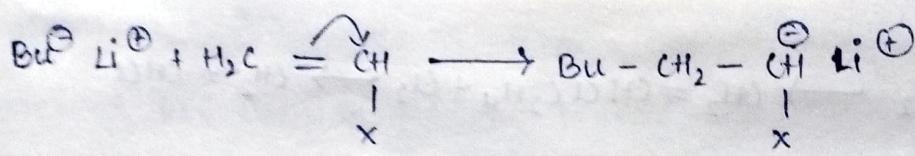
where  $\text{H}^+$  is the cationic initiator and  $[\text{F}_3\text{BDH}]^-$  is the counterion.



$x$  = electron-donating group.

### (ii) Anionic polymerisation

Chain initiation: Strong bases such as organoalkali compounds like n-butyllithium and ethyllithium initiate the anionic addition polymerisation.



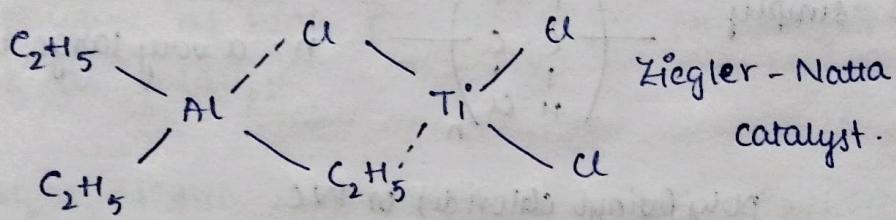
where  $\chi$  = electron-withdrawing group.

### (c) coordination mechanism

These are polymerisation reactions taking place in the presence of organometallic compounds as catalysts.

Ziegler and Natta discovered that an organometallic compound in combination with transition metal halide ( $\text{TiCl}_4$  and  $\text{TiCl}_3$ ) can be used to prepare stereospecific polymers.

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



### (d) PVC synthesis, properties & Applications:

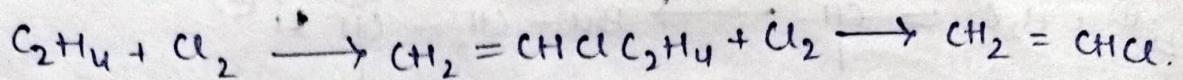
Polyvinyl chloride (PVC) is a synthetic polymer and the third most widely used thermoplastic polymer after polyethylene and polypropylene. It is prepared by radical polymerization of vinyl chloride to produce a material composed of an avg of 10,000 to 24,000 monomer units.

The monomer vinyl chloride is treated with peracid under pressure to obtain PVC.

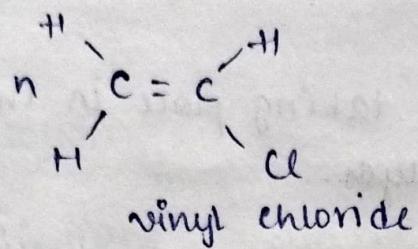
### The synthesis of PVC

#### Vinyl chloride production:

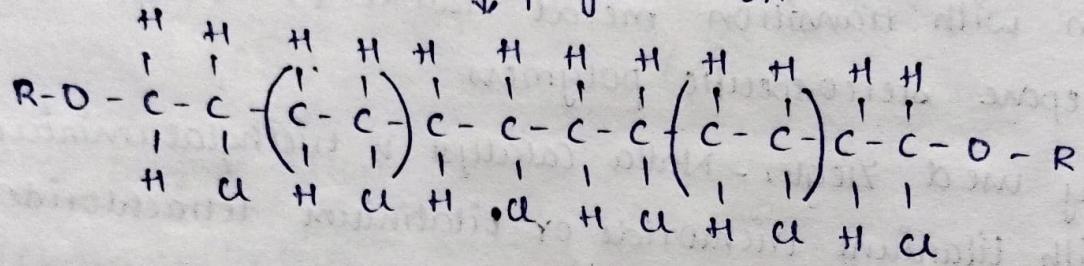
1. Vinyl chloride is typically produced through the chlorination of ethylene, which is derived from petroleum



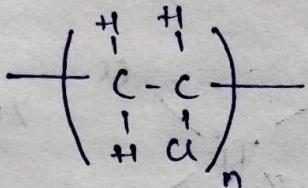
Polymerisation of Vinyl chloride:



↓ polymerisation



Or more simply



$n = \text{a very large integer}$

Poly(vinyl chloride) or PVC.

### Properties of PVC

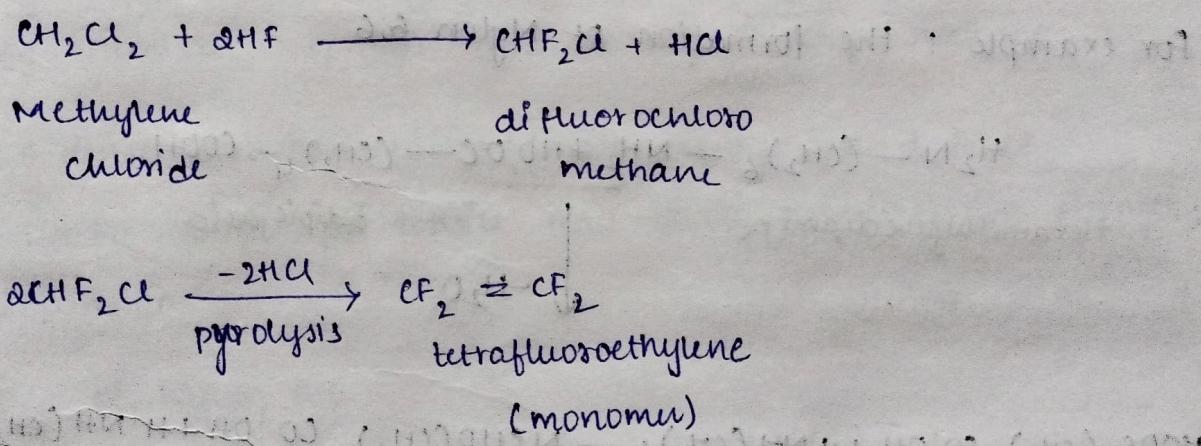
- It is a linear polymer and thermoplastic in nature.
- It is a white brittle solid, hard, rigid material which tends to stick to the metallic surface.
- It is insoluble in all hydrocarbon solvents.
- By nature, PVC is a lightweight, sturdy and abrasion-resistant material.
- This versatile thermoplastic polymer is resistant to the action of all inorganic chemicals.
- Since, the durability is more, long-life is assured.

## Applications of PVC

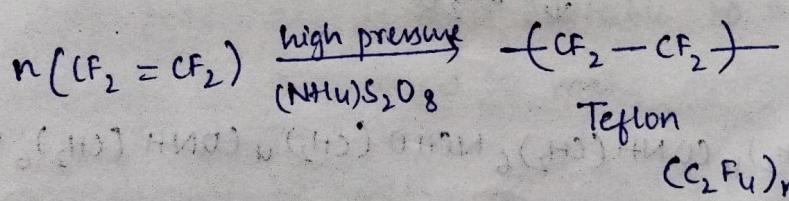
- Plasticized PVC used in flooring or (PVC-U) unplasticized PVC is used in making window frames.
- It is used in making sewage pipes and other pipe applications where cost or vulnerability to corrosion limit the use of metal.
- Used in construction fields for insulation on electrical wires or in flooring for hospitals, schools, homes and other areas where a sterile environment is a priority.
- It is used in the garden hose and imitation leather upholstery.

## 7) Teflon synthesis, properties & Applications:

Its trade name is teflon. It is prepared by the polymerisation of tetrafluoroethylene at high pressure in the presence of ammonium persulphate as catalyst



The monomer is polymerized using ammonium persulphate as initiation



## Properties:

- It is a linear polymer with practically no branching.
- Its softening temperature is high ( $350^{\circ}\text{C}$ )

\* It has high mechanical strength and is chemically inert.

### Applications :

#### Indirect :

- Non-stick pan coatings
- Cookware
- Carpet treating for stain resistance
- Paint
- Home and garden products

#### Direct

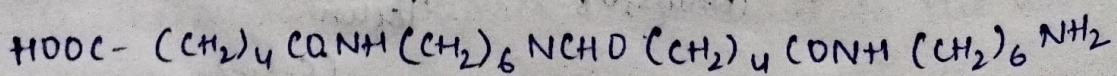
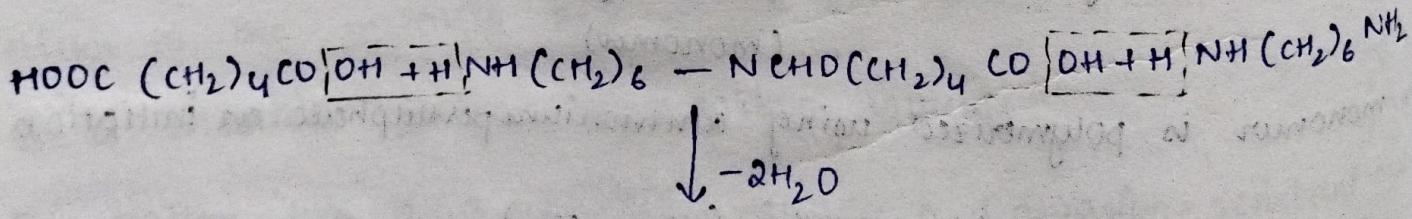
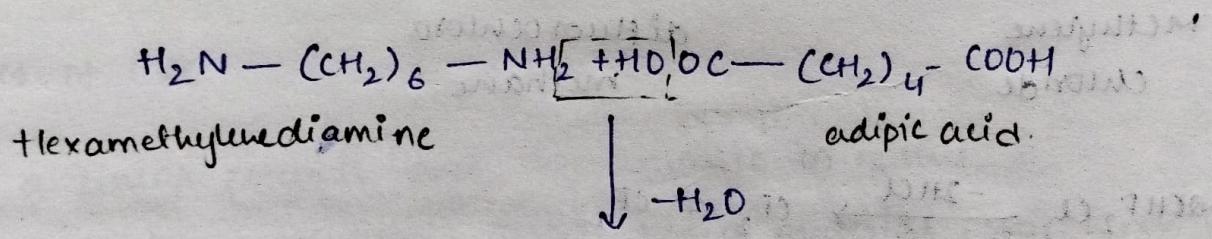
- Catheters
- Artificial limbs and body parts
- Surgical implants
- Coatings of surgical blades

### Q) Condensation polymerisation and Nylon 6,6 as example:

#### Step polymerisation:

In condensation polymerisation, the reaction proceeds step by step through reaction between the functional groups of the monomers with the removal of small molecules like water.

For example : the formation of Nylon 6,6



The reaction proceeds step by step and the chain elongates

Nylon 6,6 (polyhexamethylene diamine adipamide) is a polyamide made from adipic acid and hexamethylene dianiline by poly condensation.

The resulting polymer is extruded by polycondensation into a wide range of fiber types. The fibers are drawn, or stretched, in a process that increases their length and orients the material's molecules parallel to one another to produce a strong, elastic filament.

## 10) Nylon 6,6 synthesis, properties & applications

### Physical properties of Nylon 6,6

- It has melting point of  $265^{\circ}\text{C}$ , high for a synthetic fibre, though not a match for polyesters or amids such as Kevlar. This fact makes it the most resistant to heat and friction and enables it to withstand heat setting for twist retention.
- Its long molecular chain results in more sites for hydrogen bonds, creating chemical "springs" and making it very resilient.
- It has a dense structure with small, evenly spaced pores.
- It has up to 36000 psi tensile and 50,000 psi flexural strength; lower expansion.

### Applications of Nylon 6,6:

- Airbags, tires, ropes, conveyor belts, hoses.
- It is a light material so it is suitable to be used for parachutes.
- It is waterproof so it is used to make swimwear.
- It is also resistant to water, so it is used to make machine parts.

## ii) Thermosetting & Thermoplastic

### - Thermoplastics

i. Once moulded, they can be resoftened and reused

ii. They are softer & less strong

The polymeric chains are held together by weak van der waals forces

iii. Generally formed by addition polymerisation reaction

iv. As they soften again & again, can be recycled, reused and reclaimed from waste.

v. Examples:

Polythene, polypropylene, teflon, nylon, natural rubber.

### - Thermosetting plastics

Once moulded, they set permanently, do not soften again on heating.

They are strong and hard

There are cross-linkages and covalent bond formation b/w the adjacent polymeric chains

They are formed by condensation polymerisation reaction

Cannot be reused, recycled or reclaimed from waste.

Example :

Bakelite, melamine formaldehyde, epoxy resins, vulcanised rubber

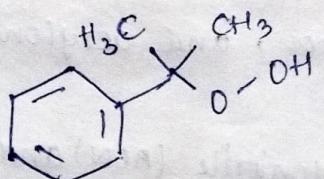
## 12) Synthesis, application, properties of Buna-S & Buna N (Elastomers)

### Synthetic rubbers

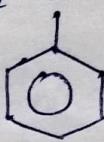
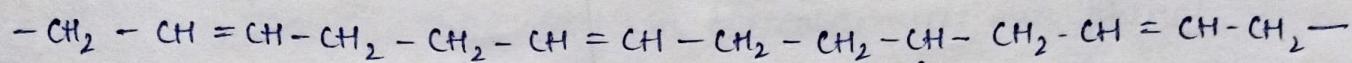
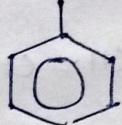
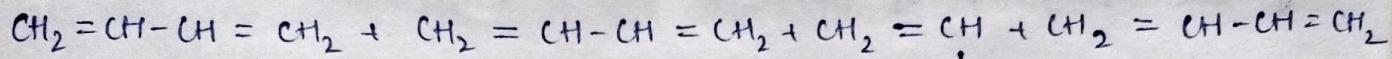
#### (i) Styrene Butadiene Rubber (Buna-S)

It is a random copolymer of butadiene and 10-25% styrene.

They are prepared by copolymerisation of butadiene (75%) and styrene (25%) in an emulsion system at 50°C in presence of cumene hydroperoxide as a catalyst.



cumene hydroperoxide



Buna-S

Vulcanisation of Buna-S is carried out by using either sulphur or sulphur monochloride ( $\text{S}_2\text{Cl}_2$ ).

#### Properties:

- > Like natural rubber, they are non-oil resistant and are generally poor in chemical resistance.
- > They have excellent impact and abrasion resistance.
- > Carbon black is generally added as a filler to improve its abrasion resistance.

#### Applications:

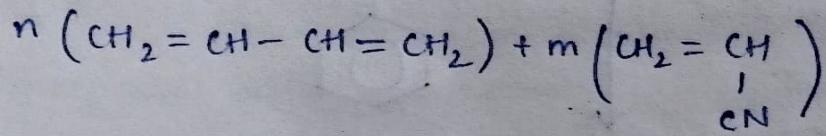
- > Their single largest use is in the manufacture of motor tyres.
- > They also find uses in the manufacture of footwear, components, carpet backing, gaskets, adhesives, tank lining.

## (ii) Nitrite Rubber (Buna-N):

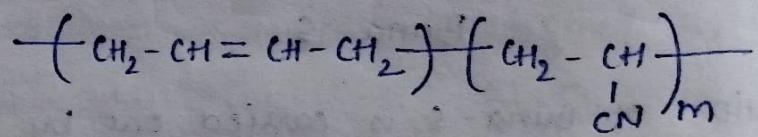
It is also known as nitrile butadiene rubber, and acrylonitrile butadiene rubber.

It is a synthetic rubber derived from acrylonitrile (ACN) and butadiene.

They are copolymers of butadiene and acrylonitrile



↓  
polymerisation



Compounding and vulcanisation are similar to natural rubber.

### Properties:

- > low in most mechanical properties
- > outstanding resistance to oil and fuels both at normal and elevated temperatures.
- > Their properties can be altered by varying the ratio of two monomers.

### Applications:

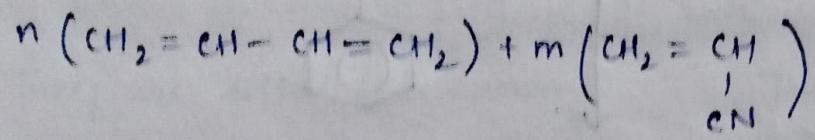
- Adhesives
- Fuel tanks
- Gasoline hoses
- Conveyor belts

### (ii) Nitrile Rubber (Buna-N):

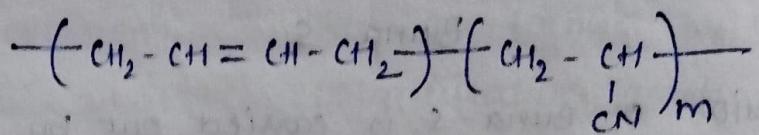
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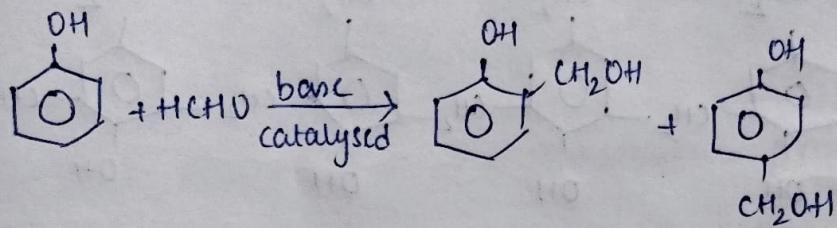
13) Synthesis, application, properties of Bakelite (Thermo-setting polymers)

Phenol formaldehyde resin (Bakelite):

Commercially known as bakelite, this polymer is formed by the condensation of phenol and formaldehyde in the presence of acidic/alkaline catalyst. They are also known as phenoplasts and PF resins.

They are prepared by two methods:

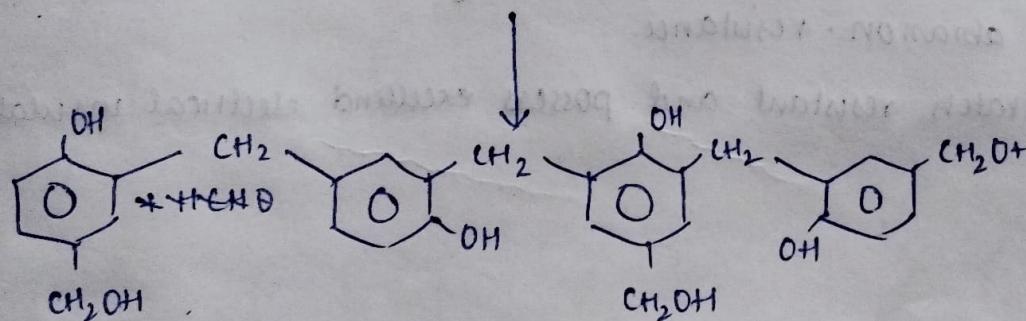
i) Base catalysed using excess of formaldehyde over phenol.



$\text{O}$ -monomethylol phenol

$\text{p}$ -monomethylol phenol

(diphenylmethanol and trimethylol phenols are also formed)

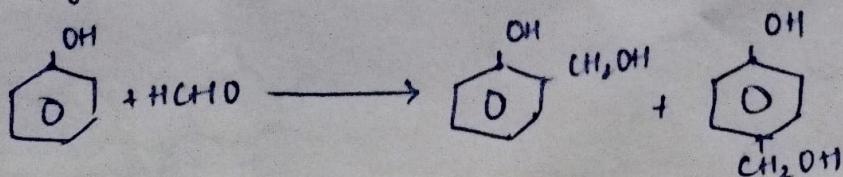


Resole

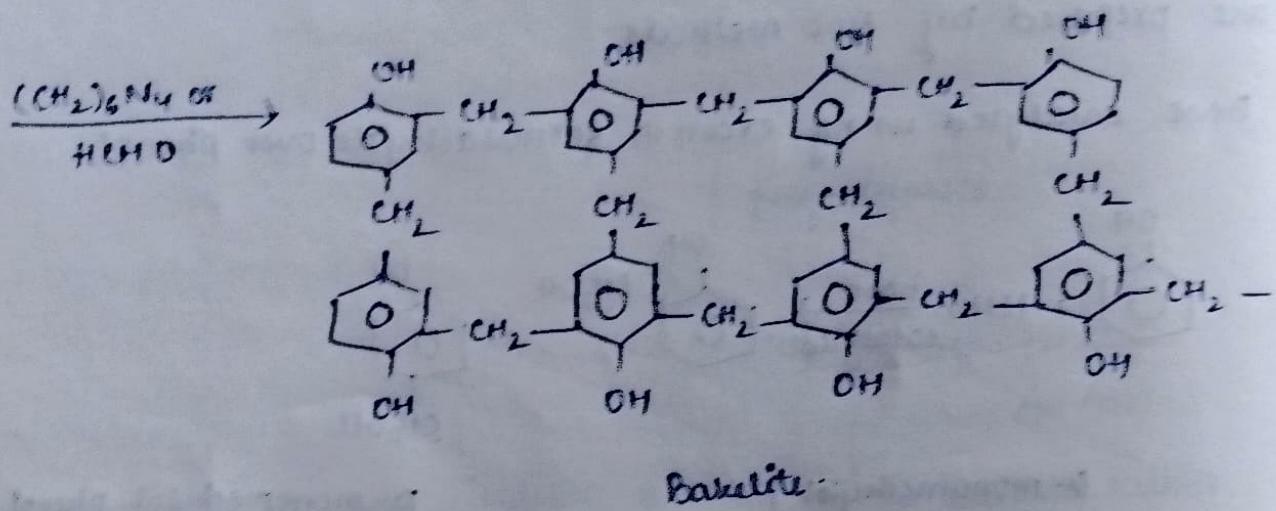
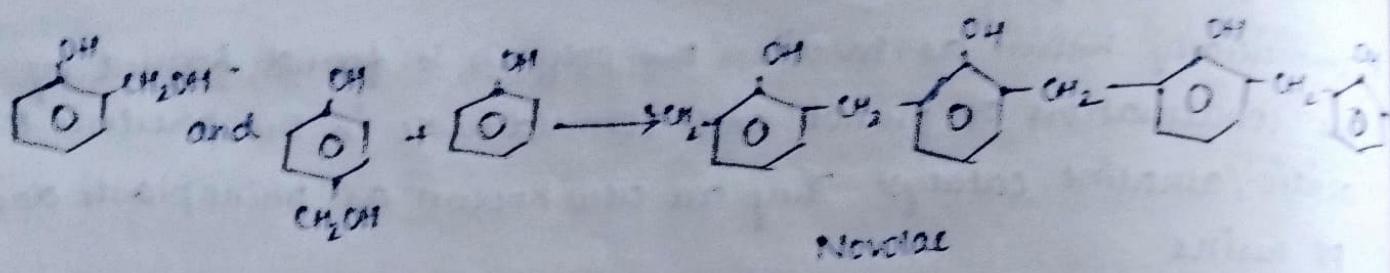
(low molecular wt. prepolymer)

Heat  $\longrightarrow$  Bakelite.

iii) Acid catalysed method using excess of phenol



This undergoes condensation to form a linear polymer novolac.



#### Properties:

- Phenolic resins are hard, rigid and strong with excellent heat, moisture, chemical and abrasion-resistance.
- They are scratch resistant and possess excellent electrical insulating properties.

#### Applications:

- They are used for making domestic switches, plugs, handles for pressure cookers, saucepans and frypans.
- used for making moulded articles like telephone parts, cabinets for radio and television.

#### 14) Synthesis of Carbon fibres:

carbon fibres are fibres about 5-10 micrometers in diameter and composed mostly of carbon atoms.

Carbon fibres have several advantages including high stiffness, high tensile strength, low weight, high chemical resistance, high temp tolerance and low thermal expansion.

These properties made carbon fiber very popular in aerospace, civil engineering, military and motorsports, along with other competition sports.

#### 1. Synthesis of Carbon fiber from polyacrylonitrile (PAN):

##### Polymerization of acrylonitrile to PAN

2. Enrol cyclization during the low temperature process.

3. High-temperature oxidative treatment of carbonization (hydrogen is removed). After this process of graphitization starts where nitrogen is removed and chains are joined into graphite planes

