Polymers (or Polymeroz)

many units

n(Small units) $\xrightarrow{\text{Polymerisation is a chemical process}}$ Big unit

or n Microunits $\xrightarrow{\text{Polymerisation is a chemical process}}$ Macrounit

or n(Small mass) $\xrightarrow{\text{Polymerisation}}$ Big mass unit (10^3 to 10^7 amu)

or,

$\longrightarrow$ n(Monomers) $\xrightarrow{\text{Polymerisation}}$ polymer.

Polymers are high molecular mass substances consisting of large number of repeating structural units derived from simple molecules.

Polymerisation

The simple molecules which combine to give polymers are called monomers. The process by which the simple molecules (i.e. monomers) are converted into polymers is called polymerisation.

$n\,CH_2 \overset{\cdot\cdot}{=} CH_2 \xrightarrow{\text{polymerisation through free radical combination occurs.}} \left(CH_2-CH_2\right)_n$

n (monomers) — Ethylene — Polyethylene (polyethene)

it is a Homo (Polymer)

Classify polymers on the basis of types of monomers used

Homopolymer

- A polymer formed from one type of monomers is called homopolymer. For example – polythene is a homopolymer of monomer ethene. In this, the repeating structural unit is

eg: ① PVC ($CH_2=\underset{Cl}{CH}$, vinyl chloride)

② PAN (or Orlon) ($CH_2=\underset{CN}{CH}$, vinyl nitrile)

Copolymer

- A polymer formed from 2 or more different monomers is called copolymer or (mixed) polymer. As an example —

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

Hexamethylenediamine — Adipic acid

Two types of monomers

Polymerisation

$\left(NH-(CH_2)_6-NH-CO-(CH_2)_4-CO\right)_n + n H_2O$

Nylon-6,6 (Copolymer)

Classification of polymers

Polymers are classified in a number of ways as described below :

A. classification based on source of availability ① natural ② synthetic ③ semi synthetic

B. classification based upon (Structure)

HDPE = linear

LDPE = branched

C. classification based upon molecular forces.

D. classification based upon mode of synthesis

addition or condensation.

A. Classification based on source of availability

The polymers can be broadly classified as :-

① **Natural polymers** :- The polymers obtained from nature (plants & animals) are called natural polymers. eg :-

Biomolecules
- ➢ Starch ➢ Cellulose
- ➢ Proteins ➢ Nucleic acids
- ➢ Natural rubber.

② **Synthetic Polymers** :- The polymers which are prepared in the laboratories are called synthetic polymers. These are also called man-made polymers. eg :-

- ➢ Polyethylene ➢ Nylon
- ➢ PVC ➢ Teflon
- ➢ Bakelite ➢ Terylene

③ **Semisynthetic polymers**

These polymers are mostly derived from naturally occuring polymers by chemical modifications.

Example :- • Cellulose diacetate polymer
• Vulcanised rubber

B. **Classification of Polymers on the basis of Structure**

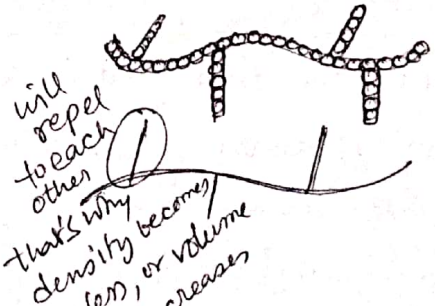
① Linear polymers
② Branched chain polymers
③ Cross-linked or network polymers

① **Linear polymers** These are polymers in which monomeric units are linked together to form long and linear chains.

Examples :-
- ➢ High density polyethene
- ➢ Polyvinylchloride
- ➢ Nylons
- ➢ Polyesters

② **Branched polymers** These are polymers in which the monomers are joined to form long chains with the side chains or branches of different lengths.

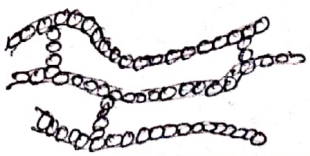
Examples :-
- ➢ Low density polyethene
- ➢ Glycogen } Biomolecules
- ➢ Starch }



③ **Cross-linked or network polymers**

These are polymers in which monomer units are crosslinked together to form a three-dimensional network.

Examples :
- ➢ Bakelite
- ➢ Melamine formaldehyde resin.



According to strength of polymers

Cross linked or network polymers > Linear polymers > Branched polymers

← Strength of polymer increases

C. **Classification of Polymers on the Basis of Molecular forces**

Depending upon the intermolecular forces, the polymers have been classified into four type :- 1. **Elastomers** :- Buna-S / Buna-N / Neoprene (rubber)

2. **Fibres** :- Nylon 66, Polyesters

3. **Thermoplastic** :- Polythene, PVC, Polystyrene On heating becomes soft, but on cooling it becomes hard.

4. **Thermosetting polymers** :- Bakelite, Urea-formaldehyde resins. ; it is not reusable.

D. **Classification of Polymers on the Basis of Mode of Synthesis**

1. Addition Polymers eg: polythene

2. Condensation Polymers eg:- Nylon 6,6.

Addition polymers	Condensation polymers
1. Different monomers add to form a polymer having same molecular formula of the repeating structural unit as that of starting monomer.	1. A large number of monomers combine with the loss of simple molecules (H_2O, NH_3, HCl, ROH) to form a polymer having molecular formula of the repeating structural unit different than that of starting monomers.
2. Nothing is lost during polymerisation	2. Small molecules like – H_2O, NH_3, HCl, ROH are lost.
3. Generally involves one monomer	3. Involves 2 monomers.
4. The monomers are generally unsaturated compounds.	4. The monomers generally contain two functional groups.
5. Common examples are polythene / polystyrene / polypropylene, PVC etc.	5. Common examples are – terylene, bakelite etc.

Types of polymerisation reactions

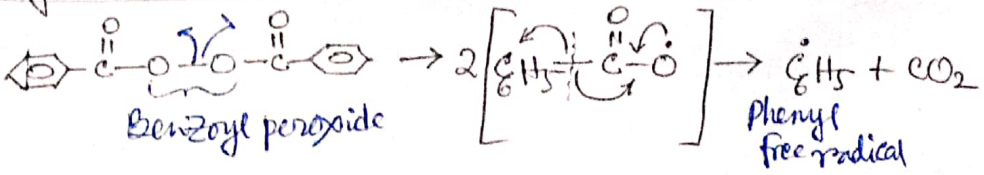
The polymerisation rxns occur in the following two principle types :-

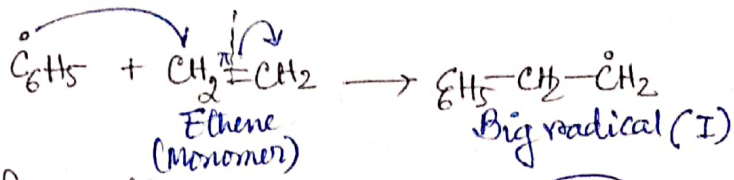
(i) Addition polymerisation or chain growth polymerisation

(ii) Condensation polymerisation or step growth polymerisation.

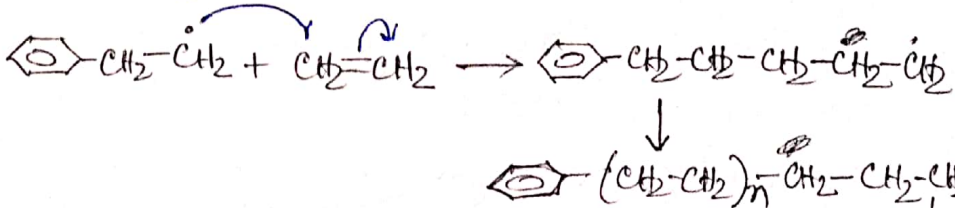
- Free radical addition polymerisation :-

Chain initiation Step :-

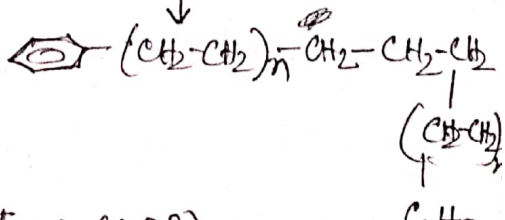




Chain Propagation Step :-



Chain Termination :-



Preparation of Some Important Addition Polymers

1. Polythene or Polyethylene → (2 types) → Low density polythene (LDP); High density polythene (HDP)

Low density polythene (LDP) It is manufactured by heating pure ethylene to 350–570K under high pressure (1000–2000 atm) in the presence of traces of oxygen (0·03 to 0·1%) or peroxide initiator (catalyst) which initiates polymerisation

$$n CH_2=CH_2 \xrightarrow[\text{(High pressure)}]{350-570K} \underset{\text{Polythene (Branched — LDPE)}}{(CH_2-CH_2)_n}$$

Ethylene (1000–2000 atm)

High density polythene (HDP) It is prepared by heating ethene in a hydrocarbon solvent at about 333–343K under a pressure of 6–7 atmosphere in the presences of a catalyst such as triethylaluminium and titanium tetrachloride (known as Ziegler-Natta catalyst.

$$n CH_2=CH_2 \xrightarrow[\text{Ziegler Natta catalyst}]{333-343K,\ (6-7\ atm.)\ \text{low pressure}} \underset{\text{Polythene (Linear — HDPE)}}{(CH_2-CH_2)_n}$$

$((C_2H_5)_3Al + TiCl_4)$

2. **Polytetrafluoroethylene (Teflon or PTEF)** It is an addition polymer of tetrafluoroethylene. It is obtained by heating tetrafluoroethylene with a free radical or persulphate catalyst (ammonium persulphate, $(NH_4)_2S_2O_8$) at high pressures.

$$n(F_2C=CF_2) \xrightarrow[\text{under High pressure}]{\text{Catalyst, Heat}} \underset{\text{Teflon}}{(F_2C-CF_2)_n}$$

Tetrafluoroethene (monomer)

3. **Polyacrylonitrile (PAN) or Orlon** → It is a polymerised product of vinyl cyanide (acrylonitrile). it is obtained by addition polymerisation of acrylonitrile in the presence of a peroxide catalyst.

$$n\,CH_2{=}CH{-}CN \xrightarrow{\text{Peroxide (catalyst)}} \left[CH_2{-}\underset{CN}{CH}\right]_n$$

Vinyl cyanide (acrylonitrile) → (Polyacrylonitrile)

4. **Condensation polymers or step growth polymers**

a. **Polyesters** –

These are poly condensation products of dicarboxylic acids and diols. These involve ester link ($-\overset{O}{\overset{\|}{C}}-O-$). Examples: Terylene, Glyptal etc.

$$n\,HOH_2C{-}CH_2OH + n\,HOOC{-}C_6H_4{-}COOH \xrightarrow[-H_2O]{} \left[O{-}CH_2CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}C_6H_4{-}\overset{O}{\overset{\|}{C}}\right]_n$$

Ethylene glycol + Terephthalic acid → Terylene or dacron

and

$$HOCH_2CH_2OH + C_6H_4(COOH)_2 \xrightarrow[\text{Polymerisation}]{-H_2O} \left[OCH_2CH_2O{-}\overset{O}{\overset{\|}{C}}{-}C_6H_4{-}\overset{O}{\overset{\|}{C}}\right]_n$$

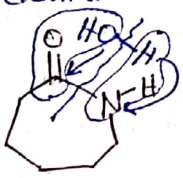
Ethylene glycol → Glyptal

b. **Polyamides**: These have amide linkages ($-\overset{O}{\overset{\|}{C}}-NH-$) in the chain. These polymers are popularly known as nylons. Examples: Nylon-6,6

$$n\,H_2N{-}(CH_2)_6{-}NH_2 + n\,HO{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}OH \longrightarrow \left[N{-}(CH_2)_6{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}O\right]_n$$

Hexamethylene diamine + Adipic acid

c. **Nylon 6**



caprolactum

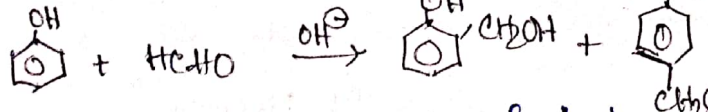
$\xrightarrow{\text{on Hydrolysis}}$ $\left[CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}\right]_n$ (nylon 6)

$$n\,HOOC{-}(CH_2)_5{-}NH_2 \xrightarrow{-H_2O} \left(\overset{O}{\overset{\|}{C}}{-}(CH_2)_5{-}NH\right)_n$$

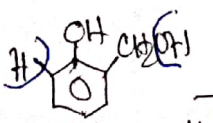
Monomer

4. **Formaldehyde resis** → These include polymers like bakelite and melamine polymers.

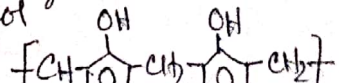
Example:- phenol formaldehyde resis or bakelite.



$\xrightarrow{OH^-}$ o-and p-hydroxymethylphenol (intermediate)

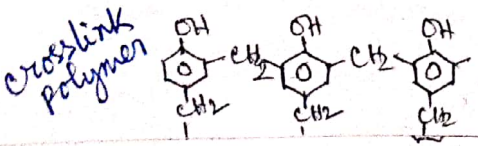


o-Hydroxymethyl phenol $\xrightarrow[-n\,H_2O]{\text{Polymerisation}}$



Novalac (linear polymer)

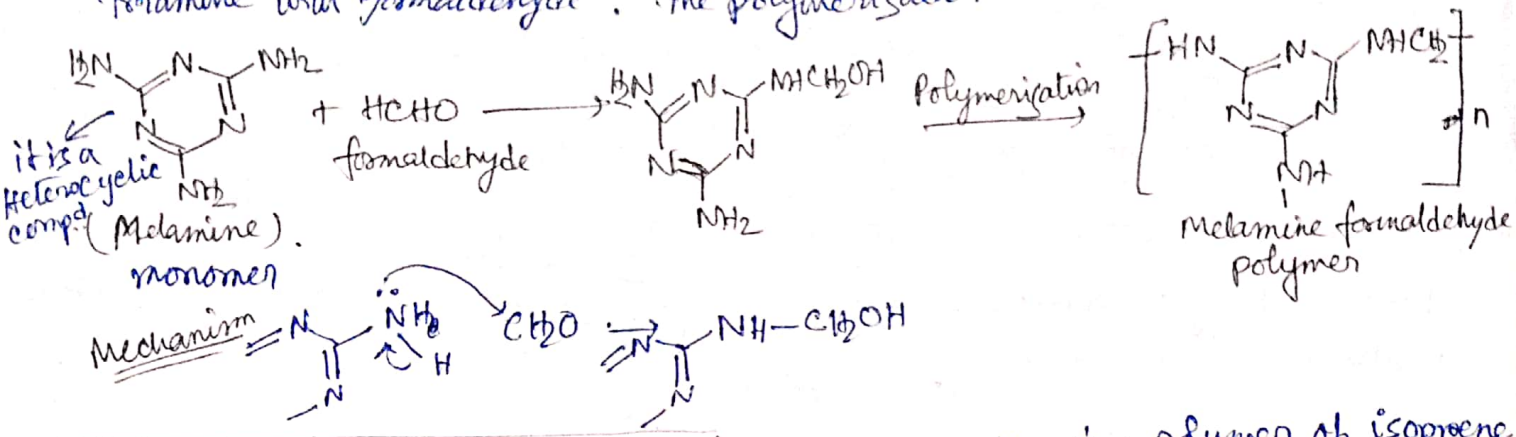
$\xrightarrow[HCHO]{\Delta}$



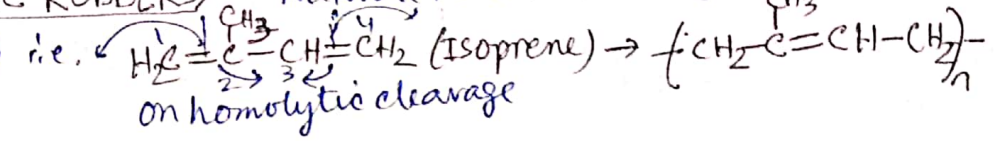
cross link polymer

5. **Melamine formaldehyde resin**

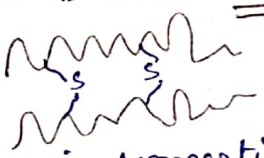
It is a polymer formed by the condensation of melamine which is a heterocyclic triamine with formaldehyde. The polymerisation occurs as :-



Mechanism

NATURAL AND SYNTHETIC RUBBERS : Natural rubber is a polymer of isoprene (2-methylbuta-1,3-diene) i.e. 

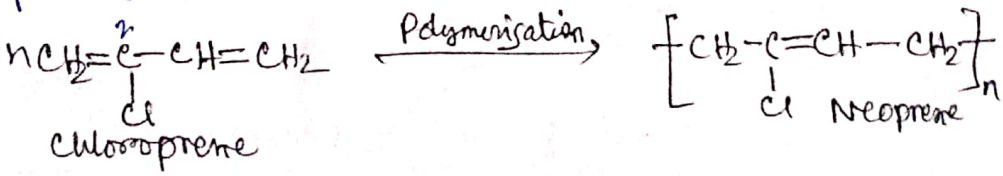
Vulcanisation of Rubber The process of heating natural rubber with Sulphur to improve its properties is called Vulcanisation



The comparison of the main properties of natural rubber and vulcanised rubber are given below :

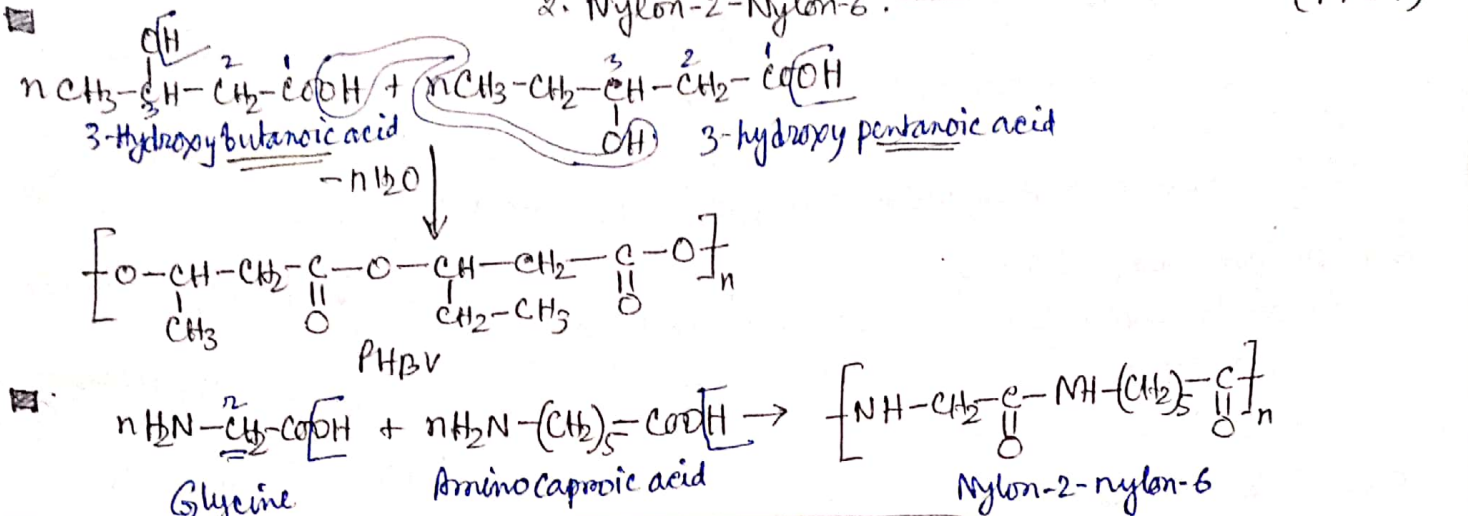
Natural rubber	Vulcanised rubber
1. It is soft & sticky.	1. It is hard and non-sticky.
2. It has low tensile strength.	2. It has high tensile strength.
3. It has elasticity.	3. It has high elasticity.
4. It can be used over a narrow range of temp. (from 10°C to 60°C)	4. It can be used over a wide range of temp. (−40°C to 100°C)
5. It has low wear & tear resistance	5. It has high wear & tear resistance.
6. It is soluble in solvents like-ether, CCl4, petrol etc.	6. It has insolubility in all the common solvents due to S-bonds.

SYNTHETIC RUBBERS like - Neoprene, it is prepared by free radical polymerisation of chloroprene (2-chlorobuta-1,3-diene)

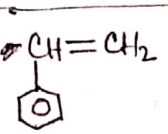
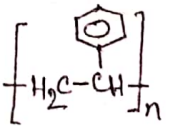
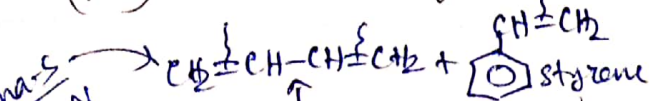
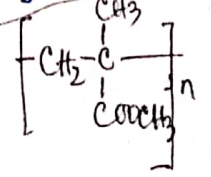
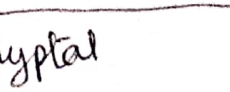
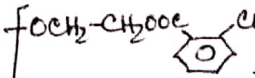


Biodegradable polymers

These are the polymers which are degraded by micro-organisms within a suitable period so that biodegradable polymers & their degraded products don't cause any serious affects on the environment. 1. poly-β-hydroxybutyrate-co-β-hydroxy valerate (PHBV)
2. Nylon-2-Nylon-6.

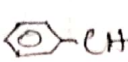


Biodegradable polymers, and their commercial importance

Name of the polymer	Monomers	Structure	Important uses
Polypropene	$CH_3-CH=CH_2$ Propene	$\left[CH(CH_3)-CH_2\right]_n$	• for packing of textiles & foods. • for mfg liners of bags, lining material for TV cabinets & refrigerators • for making ropes, fibres, heat shrinkable wraps for records & other articles. • for making automobile mouldings, seat covers, carpet fibres etc.
Polystyrene	 styrene		• for making hot drink cups, toys, combs, household articles etc. • for making radio and television bodies, refrigerator linings • as an insulator, wrapping material. • for making tiles to be used in covering ceilings and floors
Polyvinylchloride (PVC)	$CH_2=CH-Cl$ vinyl chloride	$\left[CH_2-CHCl\right]_n$	• in the mfg of raincoats, handbags curtain clothes, toys. • in artificial flooring • as a good insulator
Buna-S / Buna-N			
Polymethylmethacrylate (PMMA)	$CH_2=C(CH_3)-COOCH_3$ Methylmethacrylate		• used in the mfg of lenses, transparent domes & skylights, dentures, aircraft windows & protective coatings. • its commercial names are Lucite, Plexiglas, Acrylite & Perspex
Uses of formaldehyde resin	(i) NH_2CONH_2 (ii) $HCHO$	$\left[NH-CO-NH-CH_2\right]_n$	• For making unbreakable cups, plates & laminated sheets
Glyptal			• For mfg of paints & lacquers. • For mfg of building materials

Q1. Which of the following is a polyamide?
(A) Bakelite (B) Terylene (C) Nylon-66 (D) Teflon

Q2. Bakelite is obtained from phenol by reacting with:
(A) CH_3CHO (B) CH_3COCH_3 (C) $HCHO$ (D) $(CH_2OH)_2$

Q3. Buna-N synthetic rubber is a copolymer of:-
(A) $H_2C=CH-CH=CH_2$ and  (C) $CH_2=CH-CN$ & $H_2C=CH-$
(B) $H_2C=CH-CN$ and $H_2C=CH-CH=CH_2$ (D) $H_2C=CH-CH_3$ & $H_2C=CH-CH=CH_2$

Q4. The polymer containing strong intermolecular forces eg: hydrogen bonding is
(A) Teflon (B) nylon-6,6 (C) polystyrene
(D) natural rubber

Q5. Nylon-6,6 is made by using?
(A) phenol (B) Benzaldehyde
(C) Adipic acid
(D) Succinic acid

~~Q6. Which of the following is a~~

Q6. Ziegler-Natta catalyst is
(A) $K[PtCl_3(C_2H_4)]$ (B) $(Ph_3P)_3RhCl$
(C) $Al_2(C_2H_5)_3 + TiCl_4$ (D) $Fe(C_5H_5)_2$

7. Which of the following contains isoprene units?
(A) Natural rubber (C) Nylon-66
(B) Polyethylene (D) Dacron.

8. Which of the following is condensation polymer?
(A) Polystyrene (B) PVC (C) Polyester (or Dacron or Terylene) (D) Teflon

9. Repn of nylon from hexamethylene diamine & adipic acid is an example of
(A) addition polymerisation (C) condensation polymerisation
(B) homopolymerisation (D) copolymerisation.

10. Nylon threads are made up of:
(A) Polyvinyl polymer (B) Polyester polymer
(C) Polyamide polymer (D) Polyethylene polymer.

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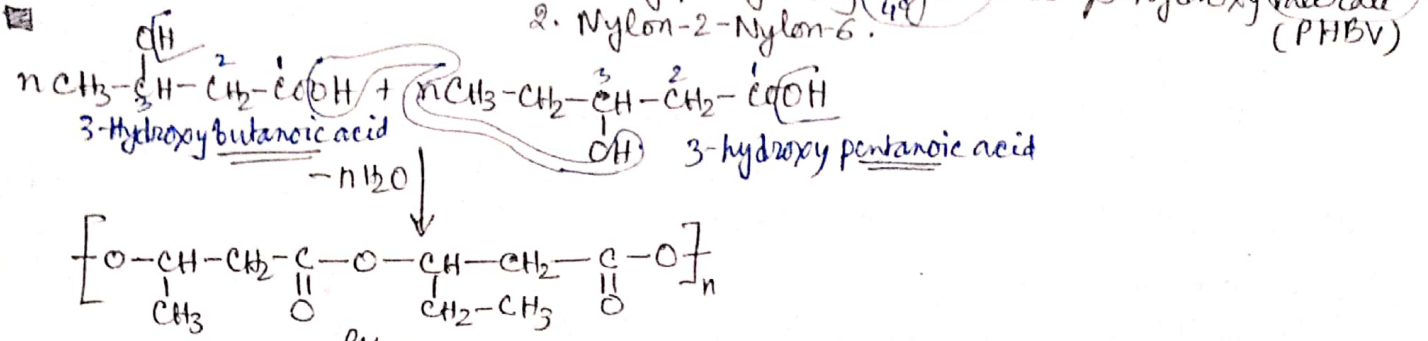

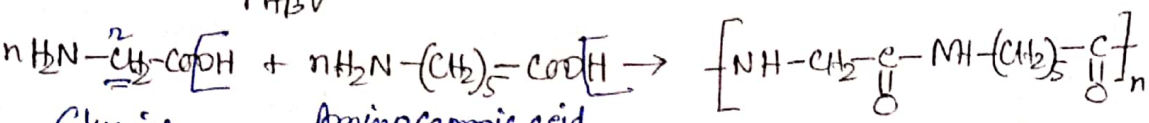

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Polystyrene	$C_6H_5-CH=CH_2$ Styrene	$\left[C_6H_5-CH-CH_2\right]_n$	• for making hot drink cups, toys, combs, household articles etc. • for making radio and television bodies, refrigerator linings • as an insulator, wrapping material. • for making tiles to be used in covering ceilings and floors
Polyvinylchloride (PVC)	$CH_2=CH-Cl$ Vinyl chloride	$\left[CH_2-CH(Cl)\right]_n$	• in the mfg of raincoats, handbags curtain clothes, toys. • in artificial flooring • as a good insulator
Buna-S: $CH_2=CH-CH=CH_2$ + styrene; Buna-N: $CH_2=CH-CH=CH_2$ + $CH_2=CH(CN)$ acrylonitrile			
Polymethylmethacrylate (PMMA)	$CH_2=C(CH_3)-COOCH_3$ Methylmethacrylate	$\left[CH_2-C(CH_3)(COOCH_3)\right]_n$	• used in the mfg of lenses, transparent domes & skylights, dentures, aircraft windows & protective coatings. • its commercial names are Lucite, Plexiglas, Acrylite & Perspex
Uses of formaldehyde resin	(i) NH_2CONH_2 (ii) HCHO	$\left[NH-CO-NH-CH_2\right]_n$	• For making unbreakable cups, plates & laminated sheets
Glyptal	$HOCH_2-CH_2OH$ + phthalic acid	$\left[OCH_2-CH_2OOC-C_6H_4-CO\right]_n$	• For mfg of paints & lacquers. • For mfg of building materials

Debdeep Mishra 19/11/17

Polymers Chemistry In Everyday Life

- Polymers are very large molecules having high molecular mass ($10^3 - 10^7$ u)
  - These are also referred to as macromolecules which are formed by joining of repeating structural units *monomers* on a large scale.
  - This process of formation of polymers from respective monomers is called *polymerisation*. $nM \xrightarrow[\text{(monomer)}]{\text{polymerisation}} \underset{\text{(polymer)}}{-M-M-M-M-M-}$
- All polymers are macromolecules but all macromolecules are not polymers.

Types of Polymers

- Depending upon the nature of the monomers.
  - **Homopolymers:** Polymer made up of only one type of monomer. e.g., Polythene, Polypropylene, PVC, etc.

$$n CH_2=CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2-CH_2\right]_n$$

Ethene → Polythene

  - **Copolymers:** Polymer made up of two or more types of monomers eg, Nylon 6,6, Buna-S, Bakelite, etc. The process of formation of copolymer is called *copolymerisation*.

– Copolymers have better physical and mechanical properties. The properties of copolymers could be changed by varying the amount of each monomer.

$$n NH_2-(CH_2)_6-NH_2 \text{ (Hexamethylene diamine)} + n HOOC-(CH_2)_4-COOH \text{ (Adipic acid)} \xrightarrow{\text{polymerisation}} \left[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO\right]_n$$

Nylon 6,6

- A polymer is a naturally occuring or synthetic macromolecule made up of a linked series of a large no. of repeated simple monomers.
- Naturally occuring polymers are proteins, starch, cellulose, rubber and DNA. Synthetic polymers are produced commercially on a very large scale and have a wide range of properties and uses, eg., plastics.
- Polymers are formed by chemical rxns in which a large no. of molecules called monomers are joined sequentially, forming a chain. This process is called polymerisation.

Classification Of Polymers

Classification based on

Source/Origin
1. Natural polymers
2. Synthetic polymers
3. Semi-synthetic polymers

Structure
1. Linear polymers
2. Branched chain
3. Cross-linked polymers

Molecular forces
1. Elastomers 2. Fibres
3. Thermoplastics 4. Thermosetting

Synthesis
1. Addition polymers
2. Condensation polymers

Classification

On the Basis Of Source

- **Natural**
  - Found in nature. eg., proteins, polysaccharides, etc.
- **Synthetic**
  - Man-made polymers. eg., nylon, polythene, etc.
- **Semi Synthetic**
  - Derived from naturally occuring polymers by chemical modification, eg., rayon, vulcanised rubber etc.

On the Basis of Structure

- **Linear**
  - Consisting of a single continuous chain of repeating units. eg., nylons, polyesters, high density polythene
- **Branched**
  - Includes side chains of repeating units connecting onto the main chain. eg., glycogen, amylopectin, low density polythene.
- **Cross-linked**
  - Includes interconnections between chains, either formed during polymerisation (by choice of monomer) or after polymerisation (by adding a specific reagent.
- **Network**
  - A cross-linked polymer that includes numerous interconnections between chains such that the entire sample is (or could be) a single molecule.
  - eg:
- **3D-network**
  - eg. bakelite, melmac, urea-formaldehyde polymer

On the Basis of Molecular Forces

- **Elastomers**
  - They're amorphous polymers having high degree of elasticity. Polymer chain is held up by the weakest attractive forces eg. synthetic rubber etc.
- **Fibres**
  - They've quite strong interparticle forces such as H-bond, high tensile strength and high modulus. eg., nylon 6,6, etc.
- **Thermoplastics**
  - They're linear, long chain addition polymers, which can be softened on heating and hardened on cooling reversibly. Interparticle forces of attraction are in between those of elastomer and fibres. eg., polythene (PE), polypropylene (PP), polyvinyl-chloride (PVC), nylons, polytetrafluoroethylene (PTFE or teflon), etc.
- **Thermosettings**
  - Become hard and infusible on heating, cannot be softened & are parmanent setting polymers obtained by condensation polymerisation. Heating results excessive cross-linking between the chain forming 3dimensional network. eg., polyester (terylene), bakelite, melamine, etc.

On the Basis Of Synthesis

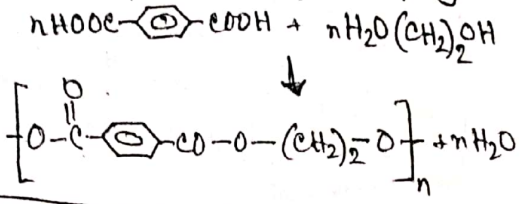
- **Chain growth or Addition polymers**
  - Formed by repeated addition of monomer molecules possessing double or triple bonds
  - **Homopolymers**
  - **Copolymers**
- **Step-growth or Condensation polymers**
  - Formed by repeated condensation rxn betwn 2 different bi-functional or tri-functional monomeric units. eg., nylon 6,6, terylene (dacron), nylon 6 etc.

...itensation (Step growth) polymerization

These are formed by the condensation of 2 or more bifunctional monomer units with the elimination of simple molecules like – H_2O, NH_3, CO_2 etc..

— The product of each step still contain 2 functional groups. Thus, the process proceeds by stepwise intermolecular condensation. eg., formation of nylon, terylene & bakelite etc.

for example, a dicarboxylic acids like terephthalic acids condense with a diol like ethylene glycol to give a polyester.

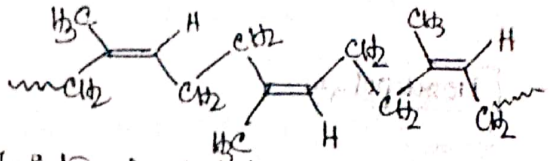


Natural Rubber:

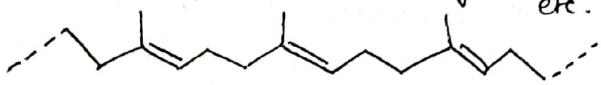
- Rubber is obtained as latex from rubber trees, a colloidal suspension of rubber. It is highly elastic, elasticity makes it valuable for a variety of uses.

  Natural rubber is a linear 1,4-addition polymer containing 11000 to 20,000 isoprene units are linked together. All the double bonds have cis-configuration, thus also known as cis-1,4-polyisoprene. All trans-configuration occurs naturally as gutta-percha, which is non-elastic and non-crystalline.

- The raw natural rubber is a soft, gummy and sticky mass. It is insoluble in H_2O, dilute acids and alkalies but soluble in benzene, Chloroform, ether, petrol and CS_2. It absorbs a large amount of H_2O. It has low elasticity and tensile strength. It breaks when too much stretched.



- The intermolecular forces present are weak vanderWaal's forces. The cis-configuration gives the polymeric chain of natural rubber a coiled structure, it can be stretched by the application of forces and returns back to original coiled shape when forces are removed. Thus the natural rubber is elastic & non-crystalline.
- Natural rubber is used for making shoes, water proof coats, golf balls etc.



Gutta-percha (trans-polyisoprene)

Vulcanisation of rubber:

- The process in which natural rubber is treated with sulphur or compounds containing sulphur (like – SF_6) to improve its properties is known as — vulcanization
- During vulcanisation, sulphur cross-links are formed which makes the rubber hard, tough with greater tensile strength. Some additives such as — carbon black, ZnO, etc. are added to accelerate the process & to improve wearing properties
- Cross links make rubber resistant to oxidn with greater absorption tendency and organic solvents. Sulphur forms cross-links at reactive sites. The extent of stiffness of vulcanised rubber depends upon the amount of Sulphur added.
- Vulcanised rubber is used for manufacturing rubber bands, gloves, conveyor belt, car tyres etc.

Homopolymers: They are formed from single monomeric species eg., polythene eg.,

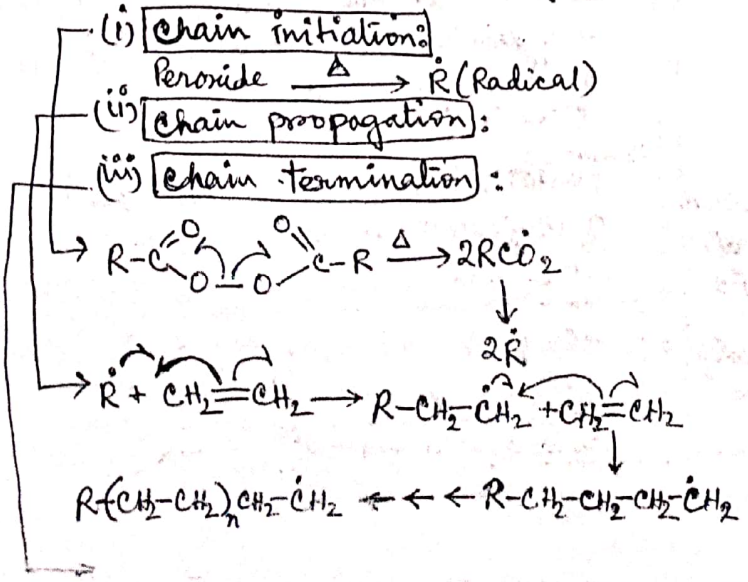
Copolymers: are formed from two different monomers. eg., Buna-S, Buna-N etc.

■ **Addition (chain-growth) polymerisation:**

A polymer formed by direct addition of repeated monomers without the elimination of by product molecules is called **addition polymer** and the phenomenon is known as **addition polymerization**.

The monomers used are unsaturated compds such as – alkenes and their derivatives. Depending upon the reactive particles formed these are of three types – free radical, cationic and anionic.

● **Free radical polymerization**: Many low molecular weight alkenes like – ethylene, propylene, styrene, vinyl chloride, tetrafluoro ethylene, acrylonitrile, methyl methacrylate etc. undergo rapid polymerization in presence of radical initiators such as – tert-butyl peroxide, benzoyl peroxide, azoisobutyronitrile (AIBN), etc. according to the following mechanism:



→ $2R\text{-}(CH_2\text{-}CH_2)_n\text{-}CH_2\text{-}\dot{C}H_2 \rightarrow$

$R\text{-}(CH_2CH_2)_n\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}(CH_2CH_2)_n\text{-}R$

or By disproportion of free radicals

$2R\text{-}(CH_2\text{-}CH_2)_n\text{-}CH_2\text{-}\dot{C}H_2 \rightarrow R\text{-}(CH_2\text{-}CH_2)_n\text{-}CH{=}$ Alkene

+

$R\text{-}(CH_2\text{-}CH_2)_n\text{-}CH_2\text{-}CH_3$ Alkane

eg. polythene, polystyrene.

Greater the stability of the intermediate free radical more is the reactivity of the alkene towards polymerization.

● **Mechanism of Cationic addition polymerisation**: Initiated by the use of strong Lewis acids such as – HF, $AlCl_3$, H_2SO_4 etc.

$H_2SO_4 \rightarrow H^{(+)} + HSO_4^{(-)}$

$H^{(+)} + CH_2{=}CH_2 \rightarrow CH_3\text{-}\overset{(+)}{C}H_2$

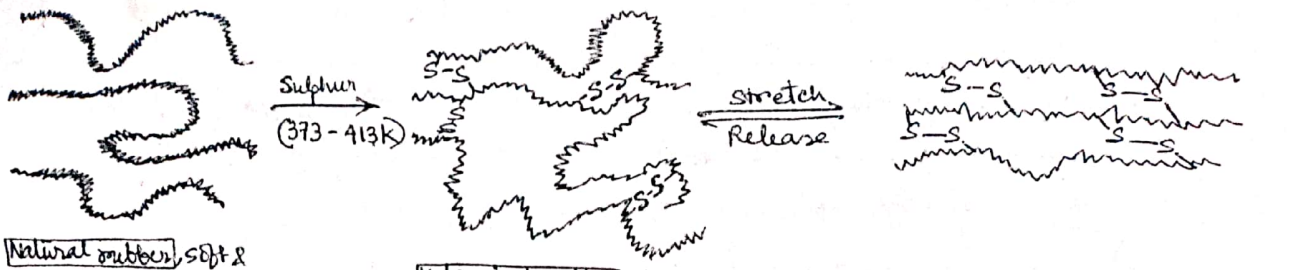
– The so formed carbocation undergoes addition with several monomers & finally the chain is terminated by combination with a negative ion or loss of a proton eg., polyvinyl ether, polyisobutylene, polystyrene etc.

● **Mechanism of anionic addition polymerisation**: Initiated by strong bases such as – $Na^{+}\bar{N}H_2$, C_4H_9Li and Grignard reagent etc.,

$B\text{:} + CH_2{=}CH_2 \rightarrow B\text{-}CH_2\text{-}\overset{(-)}{C}H_2$ carbanion

– The so formed carbanion undergoes addition with no. of monomers and finally terminates.

– This mechanism is more favourable when the monomer alkene have electron withdrawing group to stabilize the intermediate carbanion eg., polymerisation of acrylonitrile, vinyl chloride and methyl methacrylate etc.



Natural rubber: soft & sticky: no cross-links between the polymeric chains

Vulcanised rubber: the hydrocarbon chains are held together by cross-linking chains of sulphur atoms.

When stretched, the chains can straighten out but they cannot slip past each other b'cause of polysulphide bridges. Thus rubber can be stretched only to a limited extent. When the tension is removed, the chains tend to coil up again and the rubber resumes it original shape.

Natural rubber	Vulcanised rubber
It is soft & sticky	It is hard & nonsticky
It has low tensile strength	It has high tensile strength.
It has low elasticity	It has high elasticity
It can be used over a narrow range of temp. (from 10°C to 60°C)	It can be used over a wide range of temp. (-40°C to 100°C)
It has low wear & tear resistance	It has high wear and tear resistance
It is soluble in solvents like ether, carbon tetrachloride, petrol etc.	It is insoluble in all the common solvents

Synthetic rubber is obtained by polymerizing certain organic compds which may've properties similar to rubber & some additional desirable properties. Most of these polymers are derived from butadiene derivatives. These are also vulcanised. These are — neoprene, Styrene butadiene rubber (SBR) or Buna-S, thiokol, Silicones, polyurethane rubber.

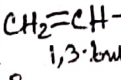
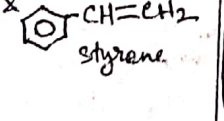
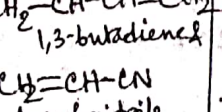
Key points:

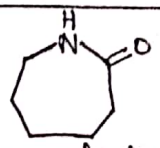
- Kevlar: A condensation copolymerisation polyamide is used in making bullet-proof vests.
- Nomex: A condensation polyamide used in protective clothing for fire resistance.
- Lexan: A condensation copolymerisation polycarbonate (polyester) with unusually high impact strength used for making bullet proof windows & safety helmets.
- Polydispersity Index (PDI) is the ratio of weight average molecular mass and number average molecular mass.

Synthetic Rubbers

- Neoprene or polychloroprene: It is prepared by free radical polymerization (polymerization of chloroprene) in presence of O_2 or peroxides.
  - Greater stability to aerial oxidation & in its resistance to action of vegetables or mineral oils.
- Styrene Butadiene Rubber (SBR) or Buna-S: polymer of buta-1,3-diene & Styrene. It has less tensile strength than natural rubber.
  - It is prepared by free radical copolymerisation.
  - It is very tough, possesses high abrasion resistance, high load bearing capacity.
- Buna-N: Prepared by copolymerisation in presence of a peroxide catalyst. It is a polymer of 1,3-butadiene and acrylonitrile. It is resistant to the action of petrol, lubricating organic solvents, etc. (Nitrile Rubber)
- Thiokol: Prepared by copolymerisation of ethylene dichloride with sodium tetrasulphide in presence of $Mg(OH)_2$.

- Rayon (artificial silk) is chemically similar to cotton but shine like silk. Artificial silk is a polysaccharide while natural silk is a protein (polyamide)

Polymer	Structure of monomer	Nature of polymer	properties	Uses
		A. Addition Polymers		
I. Polyolefins 1. Polyethylene or polythene	$CH_2=CH_2$	(a) Low density polyethylene (LDPE): An addition or chain growth homopolymer, highly branched polymer & is obtained by free radical polymerization (under a pressure of 1000–2000 atmosp at a temp of 350–570 K in presence of traces of oxygen or a peroxide. (b) High density polyethylene (HDPE) obtained by coordination polymerisation, it is a linear addition or chain growth homopolymer.	Transparent, moderate, tensile strength, chemically inert, tough but flexible and poor conductor of electricity. Translucent, chemically inert, greater toughness & tensile strength.	Packing material (plastic films, bags, etc.) insulation for electrical wires and cables, manufacture of squeeze bottles, toys & flexible pipes. Manufacture of containers, house wares (buckets, tubs), pipes, bottles and toys.
II. Polydienes 1. Neoprene	$CH_2=CH-\underset{Cl}{C}=CH_2$ Chloroprene or 2-chloro-1,3-butadiene	Addition homopolymer $[CH_2-\underset{Cl}{C}=CH-CH_2]_n$	Rubber like stability to aerial oxidation & its resistance to oils, gasolines etc.	As insulator, making conveyer belts, printing rollers, hoses & shoe heels, etc.
2. Buna-S or Styrene-Butadiene Rubber (SBR)	$CH_2=CH-CH=CH_2$ 1,3-butadiene &  Styrene	Addition copolymer 	Rubber like Stability to aerial oxidation & its resistance to oils, gasolines etc.	Manufacture of automobile tyres, rubber soles, water proof shoes etc.
3. Nitrile rubber (Buta-N)	$CH_2=CH-CH=CH_2$ 1,3-butadiene & $CH_2=CH-CN$ Acrylonitrile	Addition copolymer 	Rubber like	In making adhesives, oil seals, gasoline hoses and tank linings.
4. Natural rubber	$CH_2=CH-\underset{CH_3}{C}=CH_2$ Isoprene or cis-2-methyl-1,3 butadiene	1,4-free radical polymerization	Soft, low tensile strength low resistance to abrasion, organic solvents & oxidising agents	As insulator, manufacture of automobile tyres.

ymer	Structure of monomer	Nature of polymer	Properties	Uses
5. Synthetic rubber (Gutta percha)	$CH_2=CH-\overset{CH_3}{\overset{\vert}{C}}=CH_2$ Isoprene or trans-2-methyl-1,3-butadiene	1,4-free radical polymerization $[CH_2-\overset{CH_3}{\overset{\vert}{C}}-CH=CH_2]_n$	–	–
B. Condensation polymers				
I. polyesters 1. Terylene or Dacron	$HO-CH_2-CH_2-OH$ Ethylene glycol and $HO-C(=O)-C_6H_4-C(=O)-OH$ Terephthalic acid or Benzene-1,4-dicarboxylic acid.	Copolymer, slēp growth linear $[OOC-C_6H_4-COO-CH_2CH_2]_n$	Durable & low moisture content, not damaged by pests like moth and mildew, resistant to chemicals can be mixed with cotton & wool.	For making wash & wear fabrics, tyre cords, safety belts, tents, sea belts & sails.
2. Glyptal or alkyd resin	$HO-CH_2-CH_2-OH$ and $C_6H_4(COOH)_2$ Phthalic acid	Copolymer, linear slēp growth $[-OCH_2-CH_2-O-C(=O)-C_6H_4-C(=O)-]_n$ Glyptal	Dissolves in suitable solvents & its solns, on evaporation leave a tough but nonflexible film. It is thermosetting plastic having high degree of cross linking	For making paints and lacquers
II. Polyamides 1. Nylon-6,6	$HO-C(=O)-(CH_2)_4-C(=O)-OH$ Adipic acid & $H_2N-(CH_2)_6-NH_2$ Hexamethylene diamine	Copolymer, slēp growth, linear $[CO-(CH_2)_4-CONH-(CH_2)_6-NH]_n$	High tensile strength abrasion resistant, somewhat elastic, strong, flexible	(i) Textile fabrics, carpets, bristles for brushes, ropes & parachutes. (ii) Substitute for metals in bearings & gears.
2. Nylon-6,10	$H_2N(CH_2)_6NH_2$ Hexamethylene diamine and $HOOC-(CH_2)_8-COOH$ Sebacic acid	copolymer, slēp-growth, linear $[NH-(CH_2)_6-\overset{H}{N}-C(=O)-(CH_2)_8-C(=O)]_n$	Same as above	Same as above
3. Nylon-6 (Perlon L)	 caprolactum	Homopolymer, slēp-growth, linear $[C(=O)-(CH_2)_5-\overset{H}{N}]_n$	Same as above	Mountaineering ropes, tyre cords and fabrics. Carpets.
III. Formaldehyde 1. resins Phenol formaldehyde resin or bakelite	 & HCHO uses (i) Bakelite with high degree of polymerisation is used for making combs & mica table tops, fountain pen barrels, electrical goods (switches, gears & plugs, gramophone records etc.	$[CH_2-C_6H_3(OH)-CH_2-C_6H_3(OH)-CH_2]_n$ (i) Bakelite with low degree of polymerisation is used as binding glue for wooden planks and in varnishes & lacquers.	Copolymer, slēp-growth, highly branched thermosetting polymer	(iii) Bakelites are used as ion exchange resins.