

Polymer Chemistry

4C1
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Topics

- Introduction of polymers.
- Functionality of monomers
- Polymerisation - Addition polymerisation is also called as chain growth polymerisation.

Condensation polymerisation (step-growth polymerisation)
copolymerisation and coordination polymerisation.

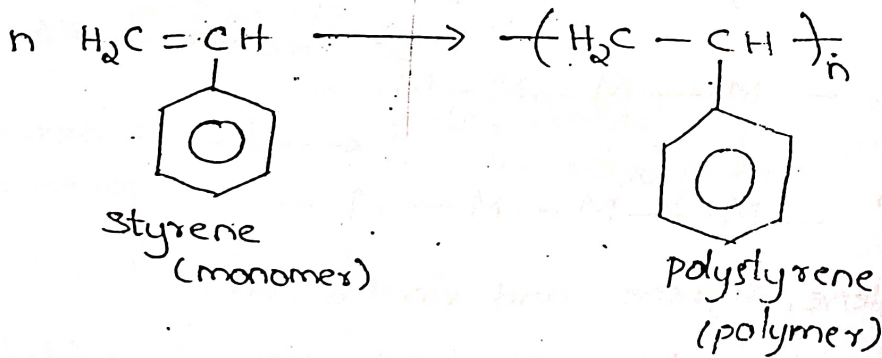
- Mechanism of polymer formation
- Plastics - Thermoplastics, Thermosetting plastics preparation, properties, applications of nylons (or) polyamides
- Bakelite (Phenol formaldehyde resin), Urea formaldehyde resin
- Elastomers - Buna-S, Buna-N preparation, properties and applications
- Conducting polymers - classification, definition and mechanism of conducting polymer, applications.

Introduction:

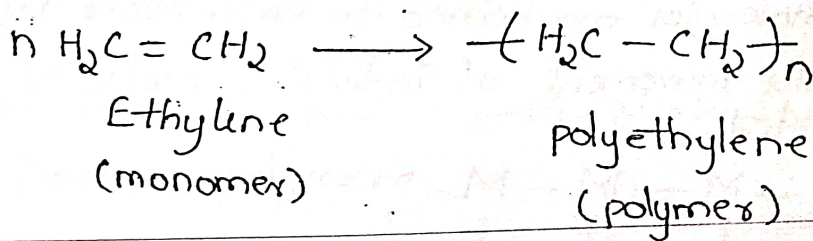
- * Every matter is composed of many small units called molecules.
- * Molecules are in different size and shapes and associated with atoms.
- * They are generally too small to be observed under a powerful microscope.
- * But polymers are giants or macromolecules. They play a vital role in our daily life.
- * The word polymer was derived from the Greek word 'Poly' = many and 'mers' = parts or units.
- * The repeating units in a polymer are called monomers.

Example

1. Polystyrene is a polymer of styrene



2. Polythene (or) Polyethylene is a polymer of ethylene



- * The number of repeating units in a polymer chain is called degree of polymerisation (DP). The properties of polymers are different from those of its monomers.

Molecular weight of polymer = Molecular weight of monomer

Polymers with high DP are called high polymers while the polymers with low DP are called oligopolymers. The DP

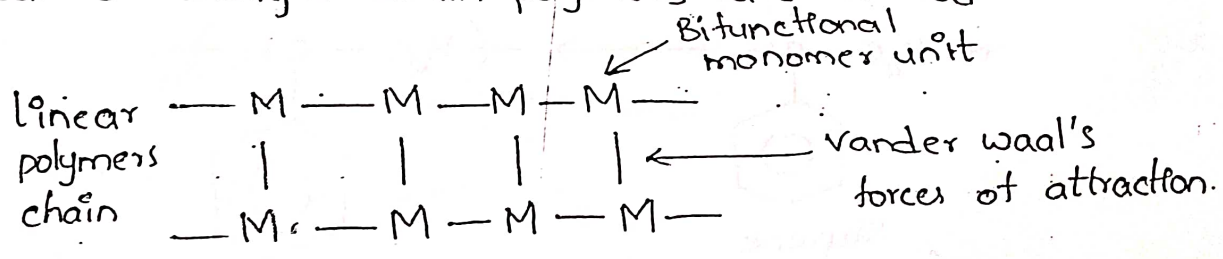
- * The molecular weight of high polymers range from 10,000-10,00,000
- * Polymers may be natural (e.g. cellulose, proteins, natural rubber, wool and silk) or synthetic (e.g. polythene, PVC, tetlon, nylon and bakelite.)

Basic Concepts:

i) Functionality: The number of bonding sites or reactive sites present in a monomer is called as its functionality.

* Every monomer must have minimum two bonding sites for polymerisation process.

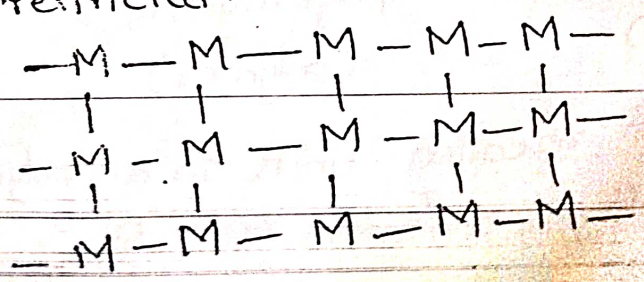
(a) If the functionality of monomer is two (bifunctional), i.e. two reactive groups attach side by side to each other, linear or straight chain polymers are formed.



e.g. Ethylene, styrene and vinyl chloride.

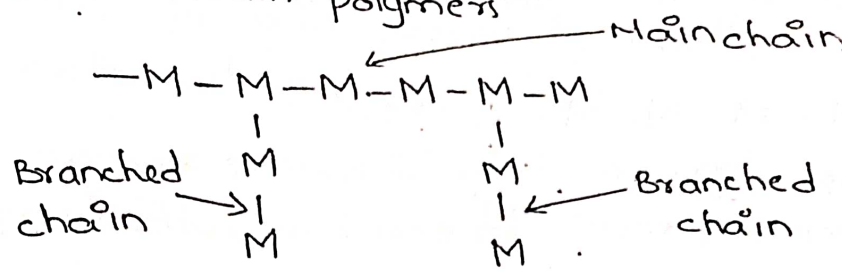
(b) If the functionality of monomer is three (tri-functional), cross-linked three-dimensional network polymers are formed.

* The monomer molecules are joined to each other by covalent bonds and the movement of individual molecules is totally restricted.



Eq: Bakelite

c) Mixture of bifunctional and trifunctional polymers give branched chain polymers

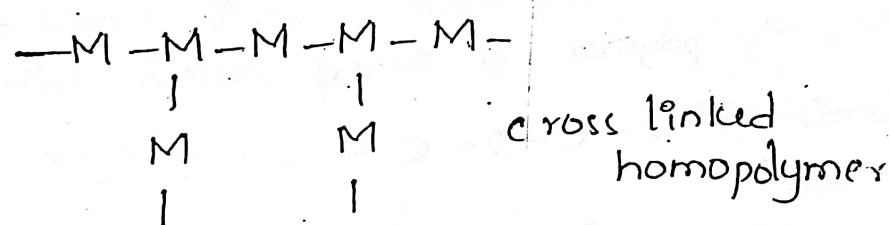
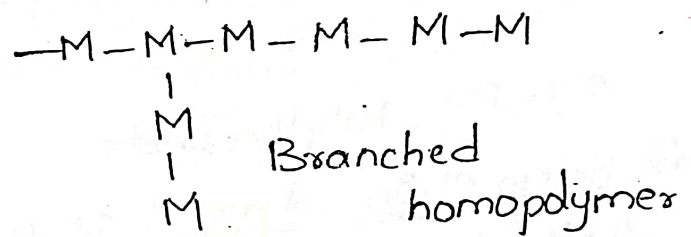
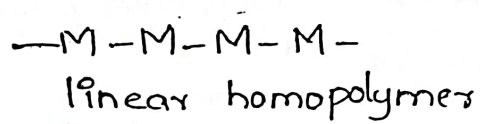


ii) Nomenclature of polymers:-

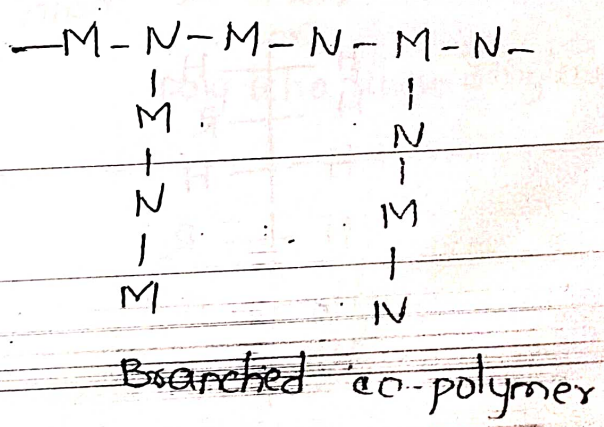
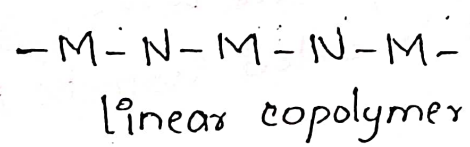
a) Homopolymers :- Polymers obtained from same type of monomers are called homopolymers.

e.g., PVC, polythene and teflon.

They may be linear branched or cross linked.



b) Heteropolymers (or) Copolymers :- Polymers obtained from different type of monomers are called copolymers. They may be generally linear or branched.

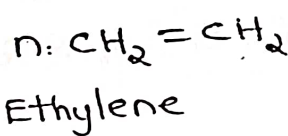


1) Addition Polymerisation (or) Chain Polymerisation:

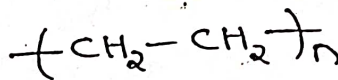
- * In addition polymerisation, several bifunctional monomers combine to form polymers by addition reaction without the elimination of any byproducts.
- * The monomers containing double bonds generally undergoes addition polymerisation and produce linear polymers.
- * The produced polymer contains the same ~~elemental~~ elemental composition as that of the monomer.
- * The molecular weight of polymer is an integral multiple of the monomer.

Example:

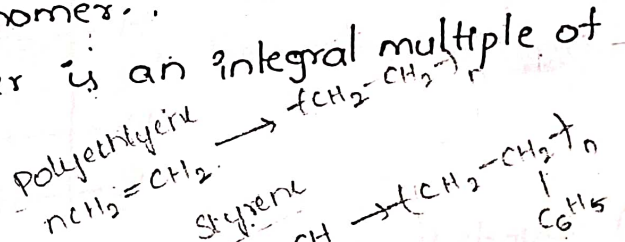
Polyethylene



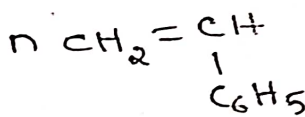
Addition
Polymerisation



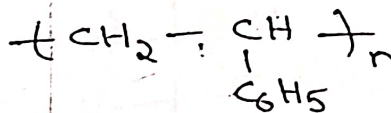
Polythene
(or)
polyethylene



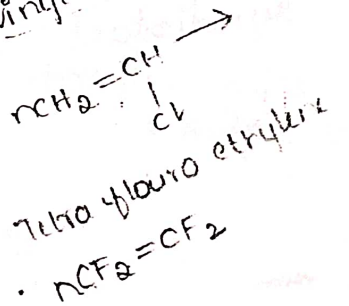
Styrene



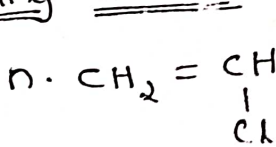
A.P



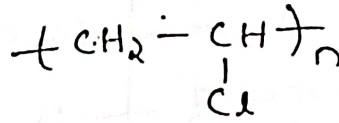
polystyrene



Vinyl chloride

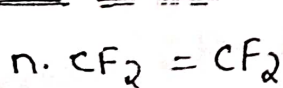


A.P

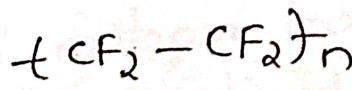


poly vinyl chloride

Tetra fluoro ethylene



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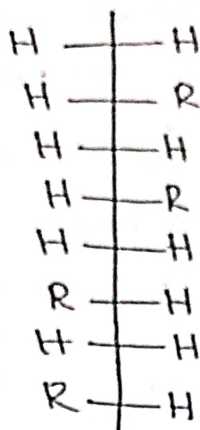
Teflon

(or)

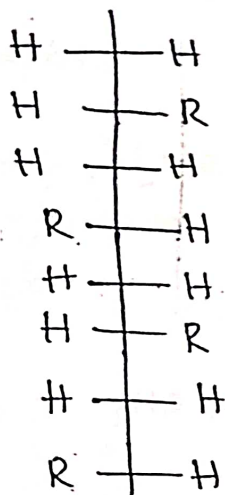
poly tetra fluoro ethylene

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b) Atactic Polymer: If the functional groups are arranged at random around the chain, it is called atactic polymer.



c) Syndiotactic Polymer: If the functional groups are arranged in alternative fashion with respect to the main chain, it is called syndiotactic polymer.



Polymerisation:

* The chemical reaction by which the monomers are combined to form polymers is called polymerisation.

Types of Polymerisation

i.) Addition Polymerisation

ii.) Condensation Polymerisation

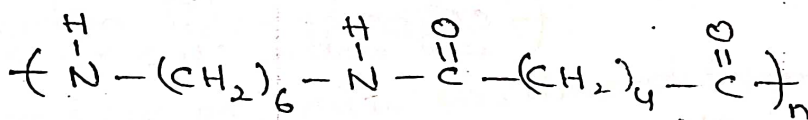
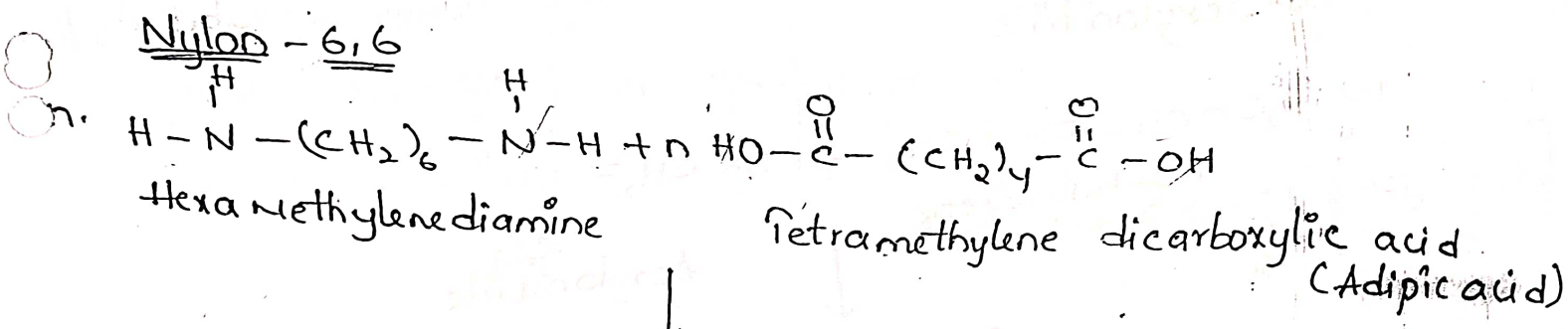
iii.) Co-polymerisation

iv.) Co-ordination polymerisation.

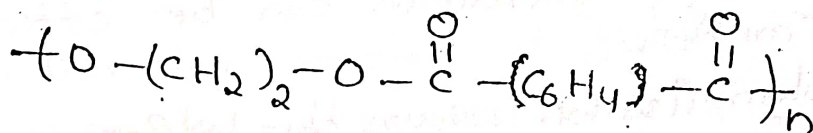
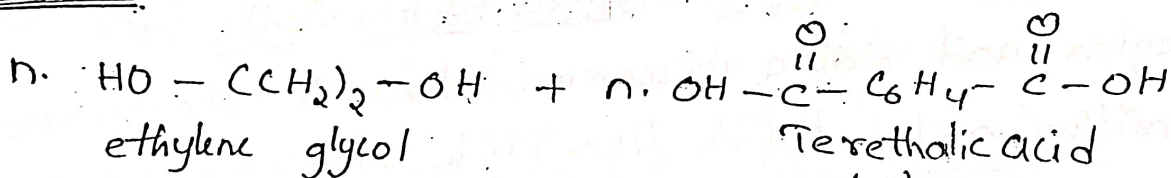
11/ Condensation Polymerisation (or) Stepwise Polymerisation:
 * In condensation polymerisation, the polymer is formed by stepwise reaction between the same or different polar groups containing monomers with the elimination of small molecules like H_2O , HCl and NH_3 .
 * Polymerisation proceeds through intermolecular condensation and forms linear or cross linked polymers. The molecular weight of a polymer is not an integral multiple of the molecular weight of monomers.

Example:

Nylon - 6,6



Polyester:-

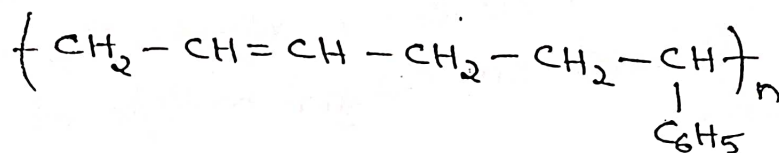
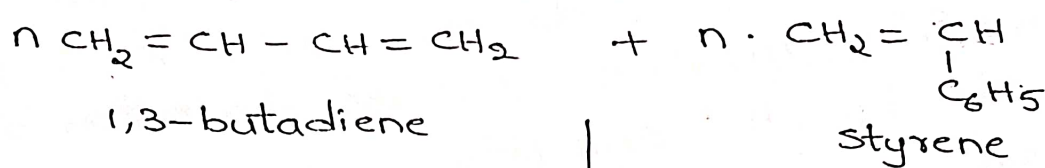


12/ Copolymerisation:- When two or more different types of monomers undergo simultaneous polymerisation, it is called copolymerisation.

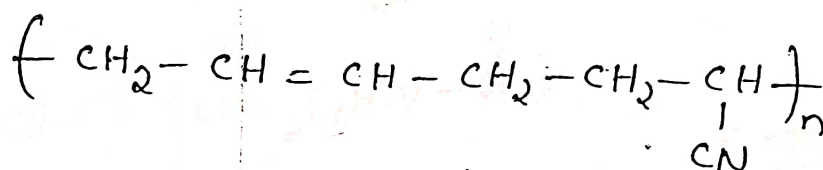
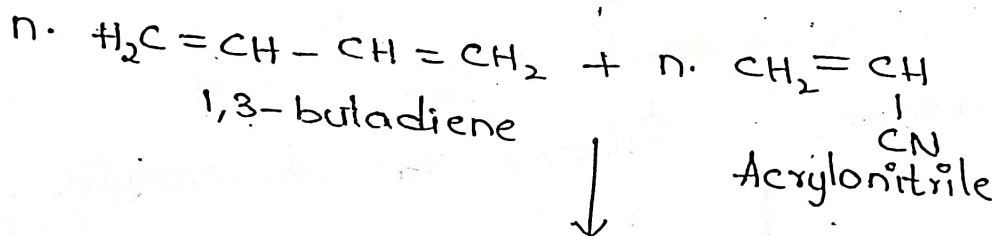
* The properties of copolymers are different from those of individual monomers.

* The copolymers may be alternating, random block and graft copolymers.

Eg: GRS-rubber (or) Styrene Butadiene Rubber (SBR) (or) Buna
(or) polybutadiene co-styrene



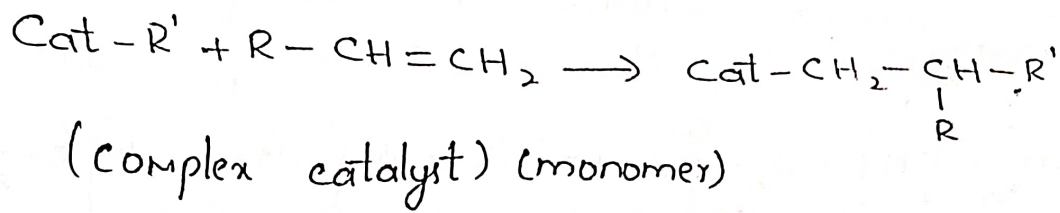
Buna-N (or) GRA Rubber (or) Nitrile rubber (or) polybutadiene
co-acrylonitrile



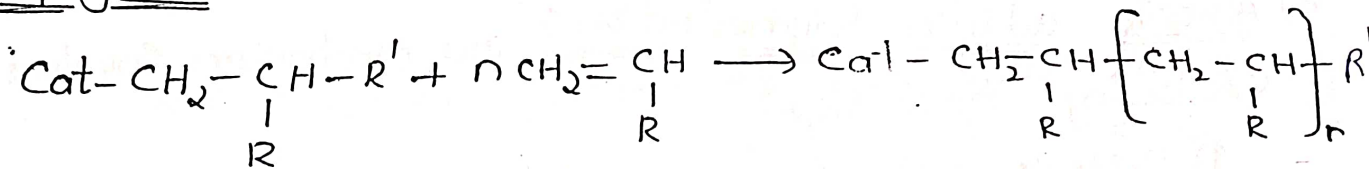
iv) Co-ordination or Ziegler-Natta Polymerisation:-

- * Ziegler and Natta discovered that in the presence of transition metal halide like TiCl_4 with an organometallic compound, triethyl aluminium (Ziegler-Natta catalyst), stereospecific polymerisation can be effected.
- * Polymerisation occurs due to insertion of alkane monomer molecules between the $\text{Ti}-\text{C}$ bond.
- * Mechanism of co-ordination polymerization involves the following three steps.

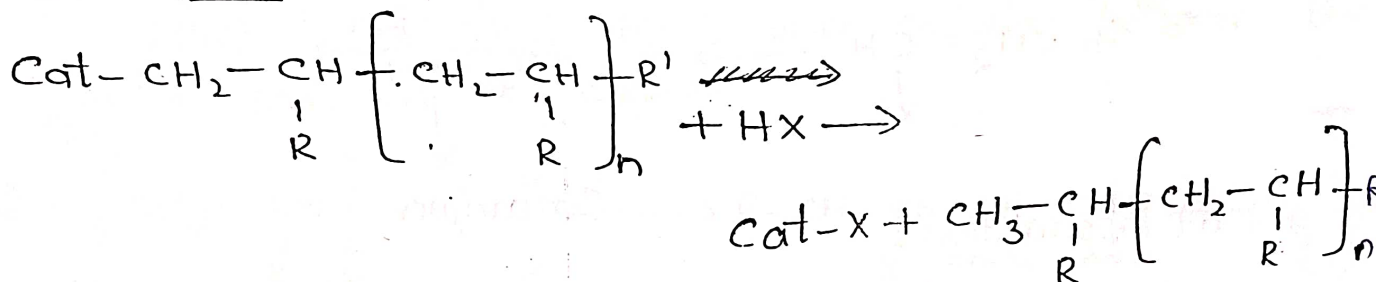
i) Initiation:



ii) Propagation:



iii) Termination:

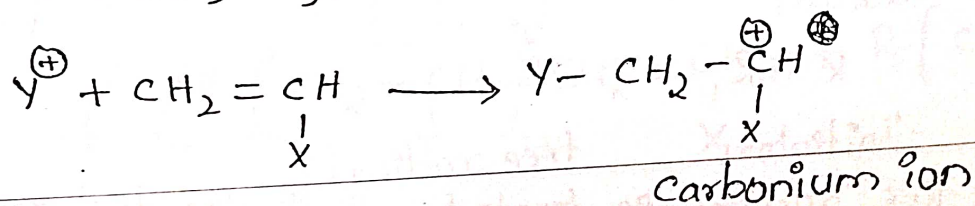


Mechanism of Addition Polymerisation:

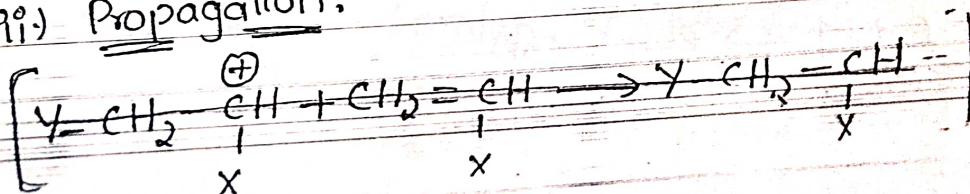
* During chain or addition polymerisation, three different types of active centres have been found to be formed. These are Carbonium ions, carbanions and free radicals.

a) Cationic addition Polymerisation: This involves the following three steps.

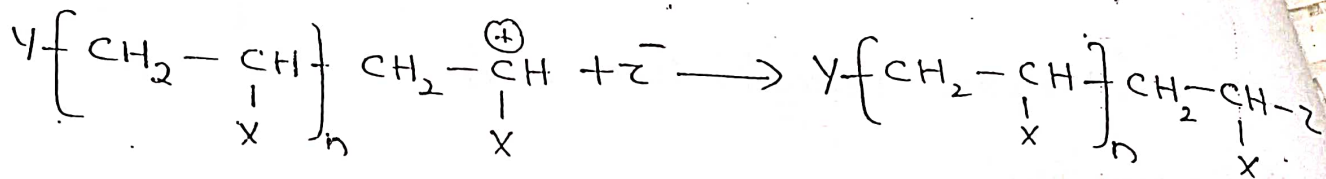
i) Initiation: In this step formation of carbonium ion takes place, usually by transfer of a proton.



ii) Propagation:

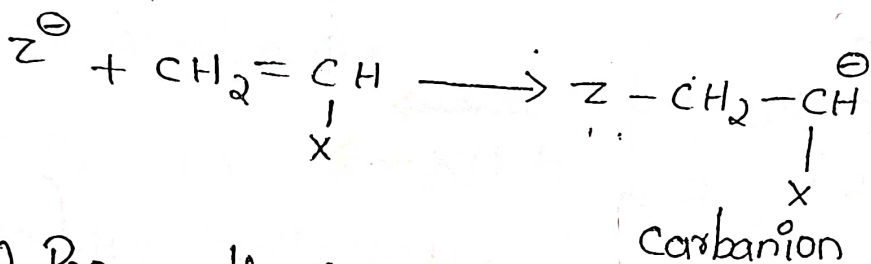


iii) Termination:

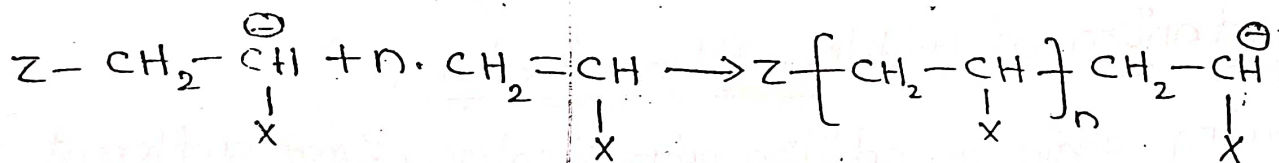


b) Anionic addition Polymerisation:- This mechanism involves the following three steps:

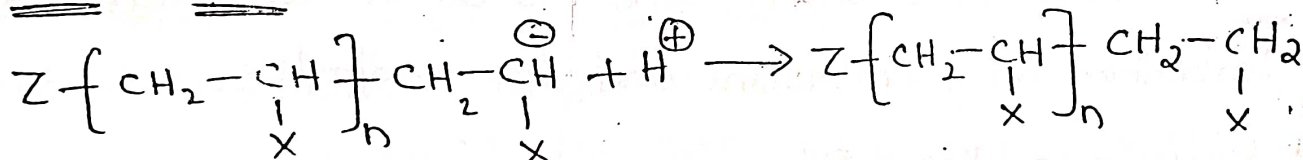
i) Initiation: In this step formation of carbanion takes place.



ii) Propagation:



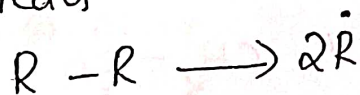
iii) Termination:



c) Free Radical Addition Polymerisation:-

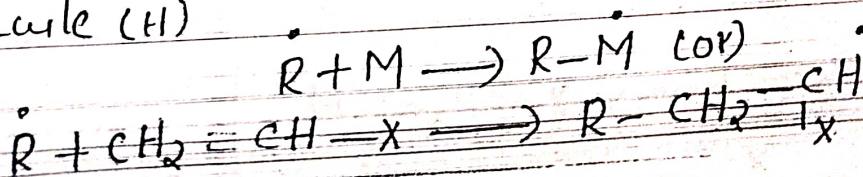
The mechanism involves the following three steps

i) Initiation: This involves the dissociation of an initiator into two free radicals



Initiators free radical

Then the free radical so formed adds to the first monomer molecule (M)



M-Monomer

Mechanism of Condensation Polymerisation:

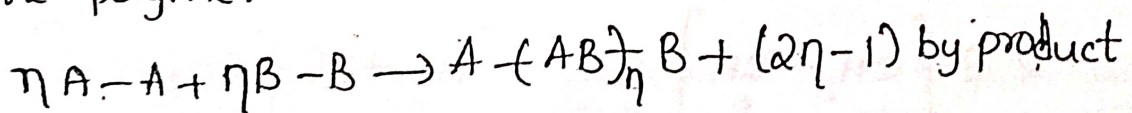
* Condensation reaction is rather slow and proceeds stepwise. Such polymerisation is often called step polymerization. It involves condensation reaction of two or more reactive functional groups of monomers with elimination of by products like H_2O , HCl , NH_3 etc.

The main features of condensation polymerization are:

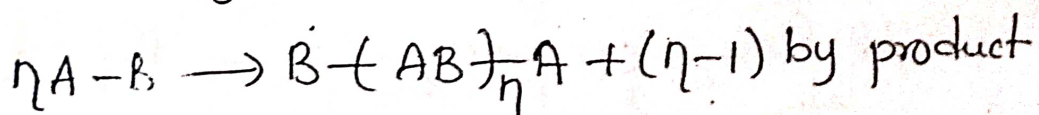
- the monomers having two or more reactive functional groups can undergo condensation polymerization
- There is continuous elimination of by products
- The polymer chain buildup is slow and stepwise.
- Linear or cross linked polymers are produced.
- Polymerization is catalyzed by acids or alkali

Two types of poly condensation are possible.

i) AA-BB type poly condensation: When a pair of bifunctional monomers undergoes poly condensation. One of the monomers is trifunctional the polymer obtained is a three dimensional network polymer.



ii) A-B type poly condensation: When a single bifunctional monomer undergoes self condensation.



Plastomers:

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- * Plastics are high polymers which can be moulded into any desired form by application of heat and pressure in presence of a catalyst.
- * There is no chemical change during the moulding process.
- * Resins are basic binding materials, which form a major part of the plastics and these two terms are used synonymously.
- * Plastics have very important position as engineering materials.
- * Some important use of plastics are for making electrical goods, handles for tools, paints, table tops, wind screens, radio and i.v. parts, overhead water tanks and floor tiles.

Properties of Plastics:

- * Now a days, plastics have attained great importance in everyday life because of their ~~cert~~ certain unique properties.
 - i) light in weight
 - ii) good thermal and electrical insulation
 - iii) low fabrication cost
 - iv) easy moulding
 - v) insect resistant
 - vi) chemical inertness
 - vii) low maintenance cost
 - viii) high resistance to abrasion - damage to a surface caused due to rubbing very hard.
 - ix) good dimensional stability
 - x) Corrosion resistance
 - xi) easy workability
 - xii) high refractive index, and soon.

Classification of Plastics,

* Plastics are classified into two types:

i) Thermoplastics

ii) Thermosetting plastics

i) Thermoplastics or Thermoplastic Resins: These are the polymers which

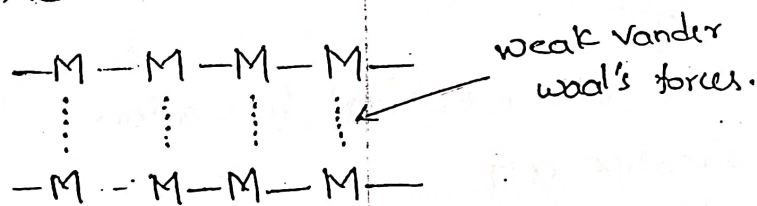
become soft on heating and hard on cooling.

* On reheating they become soft again and can be remoulded to any desired shape.

* They are formed by the addition polymerisation and have linear long chain polymeric structure.

* The chemical structure is not changed during heating or moulding operations.

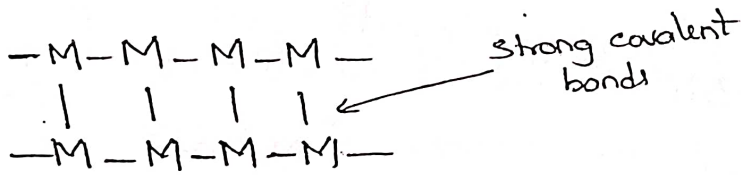
* The weak, secondary vander waal's forces act between the thermoplastic resin chains.



* During the heating, only secondary vander waal's forces are broken while on cooling, these secondary bonds are reestablished.

e.g. Polythene, PVC, teflon and polystyrene.

ii) Thermosetting Plastics (or) Thermosetting Resins: These are the polymers which are fusible on initial heating, but on further heating become set insoluble, infusible, rigid, hard and three dimensional network product, i.e. once they are set on heating, they cannot be reformed.



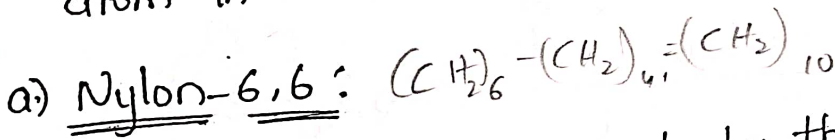
Thermosetting plastics

* They are formed by condensation polymerisation.

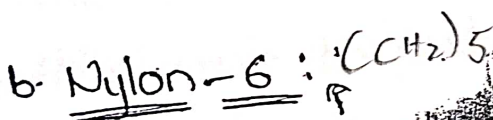
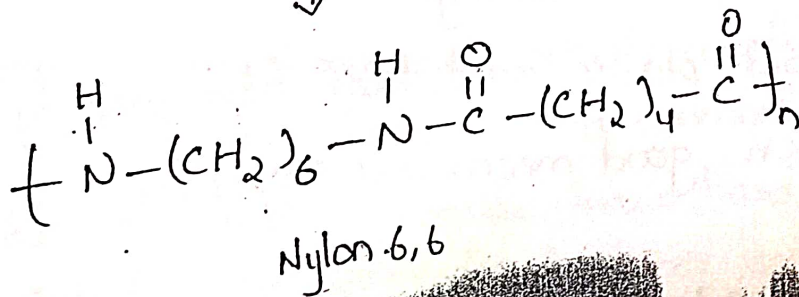
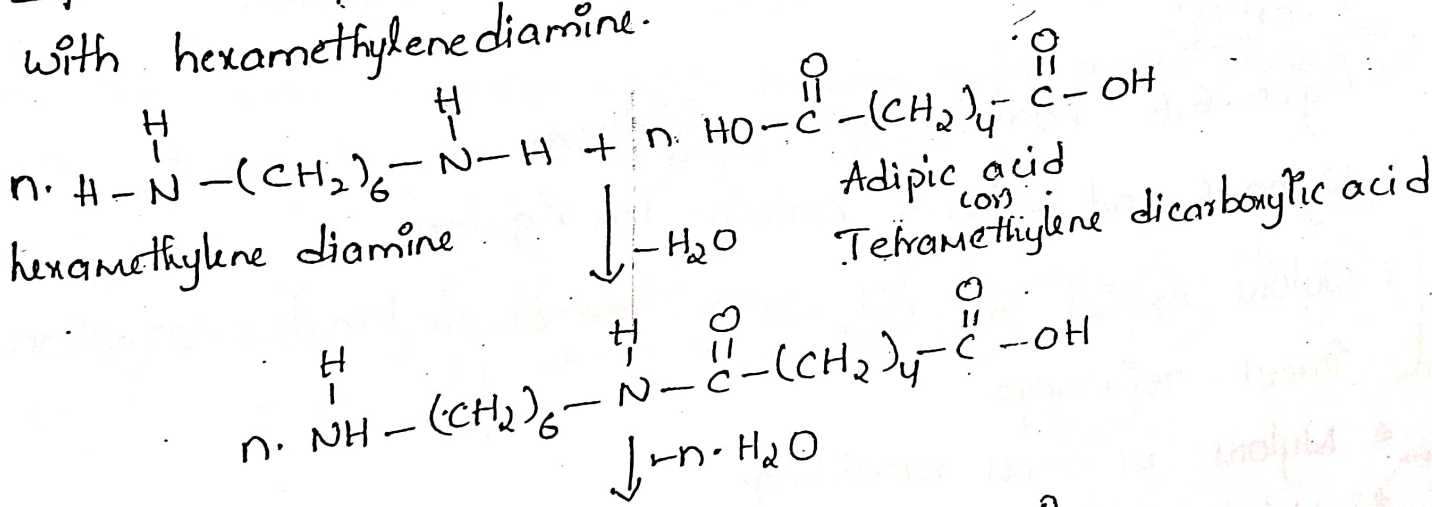
e.g. Bakelite, polyesters, urea formaldehyde resin, etc.

Nylons (or) Polyamides :-

* The nylons have been named on the basis of the number of carbon atom in monomer chain.

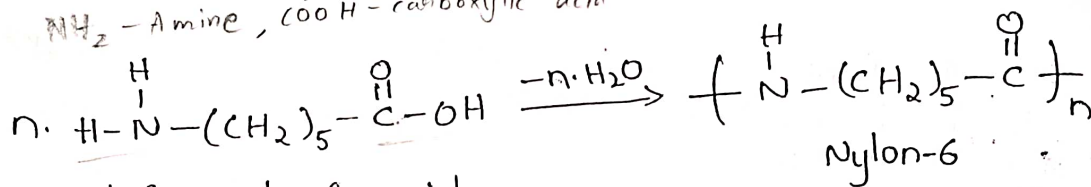


Preparation: It is obtained by the polymerisation of adipic acid with hexamethylenediamine.



Preparation: It is produced by the self condensation of caproic acid or diamine.

NH_2 - Amine, COOH - carboxylic acid

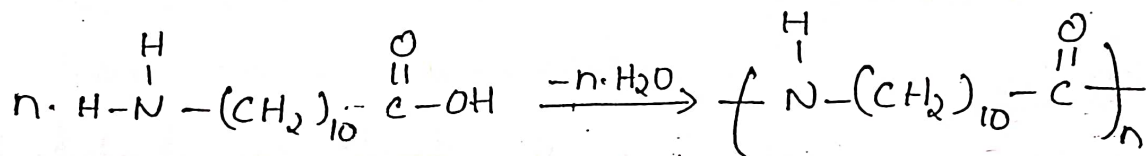


α -Amino pentanoic acid
(or)

α -Amino caproic acid

Nylon-11: $\text{(CH}_2\text{)}_{10}$

Preparation: It is obtained by the self condensation of ω -amino undecanoic acid.



ω -amino undecanoic acid.

Nylon-11

Properties:

- * Nylon-6,6 contains more rigidity
- * Nylon-6 and Nylon-11 contains less rigidity
- * Nylons consist of oil, water, thermal, electrical, corrosion and insect resistance.
- * Nylons undergoes remolding.
- * Nylons show plastic and fibre property.
- * They possess good mechanical properties.

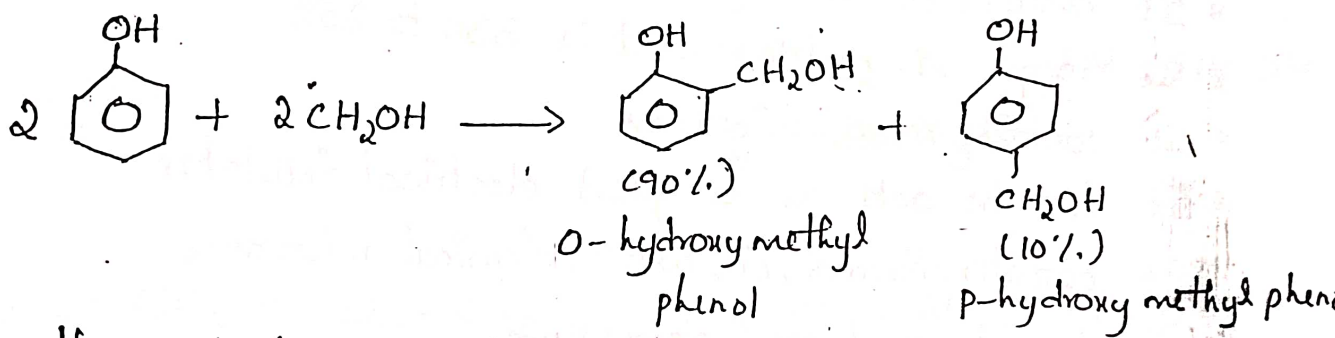
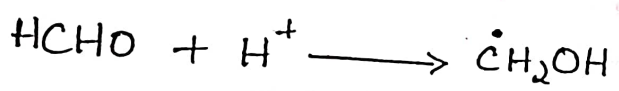
Applications:

- * Nylon-6,6 mainly takes place in the making of domestic items, automobile spare parts, radio and T.V compartment, and in the making of tyres etc.
- * Nylon-6 and nylon-11 mainly takes place in the making of film sheet, brush bristles, elastic garments (or) stretchable garments etc.

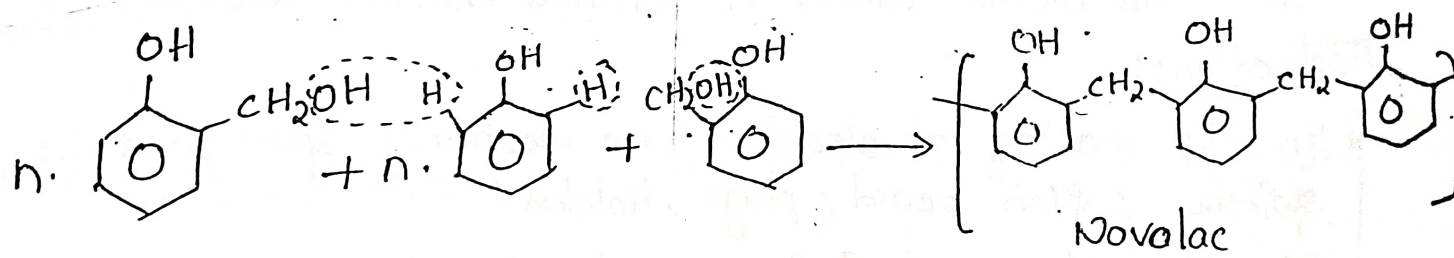
Formaldehyde resin :-

Preparation: Bakelite is obtained by the condensation polymerisation of phenol and formaldehyde in the presence of an acid or alkali catalyst. The following steps are involved:

a) In the first step, phenol reacts with formaldehyde to form o-hydroxymethyl phenol and p-hydroxymethyl phenol

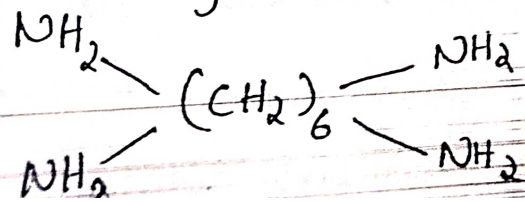


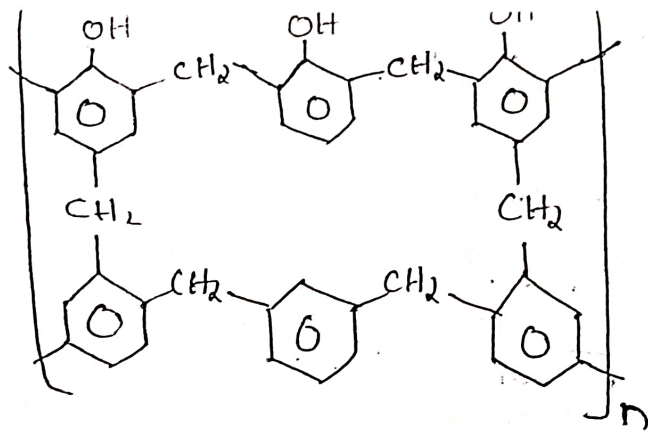
b) In the second step, condensation between hydroxymethyl phenol and phenol occurs to give linear polymer (Novolac)



c) In the third step a small amount of hexamethylene tetramine is added. It produces formaldehyde and ammonia. Formaldehyde converts the soluble and fusible novolac into a hard, infusible solid of cross-linked three-dimensional polymer called Bakelite while ammonia neutralizes the acid.

hexamethylene tetramine





Properties :-

- * It contains highest melting point.
- * It contains more rigidity
- * The range of melting point is 330 to 350
- * It contains more brightness
- * It can be acts as a good electrical insulator
- * It contains thermal, oil, water, chemical resistance
- * It doesnot undergoes remolding
- * It is a non-degradable plastic
- * In some organic solvents it contains chemical resistance

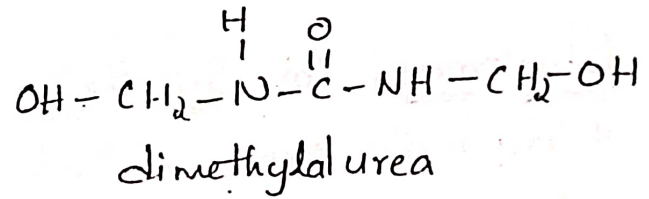
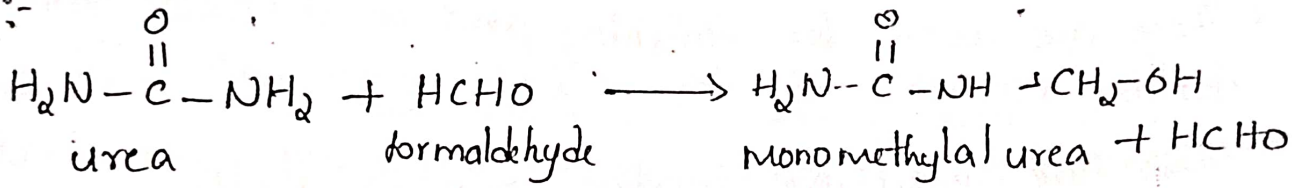
Applications :-

- * In the making of electrical and electronics spare parts like switches, switch board, plugs, holders.
- * In the making of frying pan handles, Iron box handle and pressure cooker handles.
- * In making of lubricant and paint
- * Coating on surface material.
- * It is used in the production of ion-exchange resin.

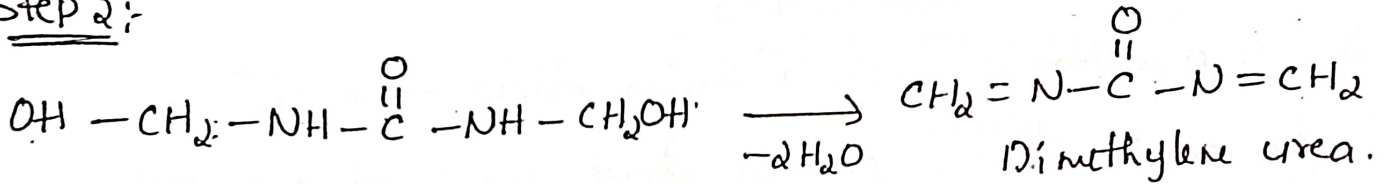
Urea-formaldehyde resin

Preparation :-

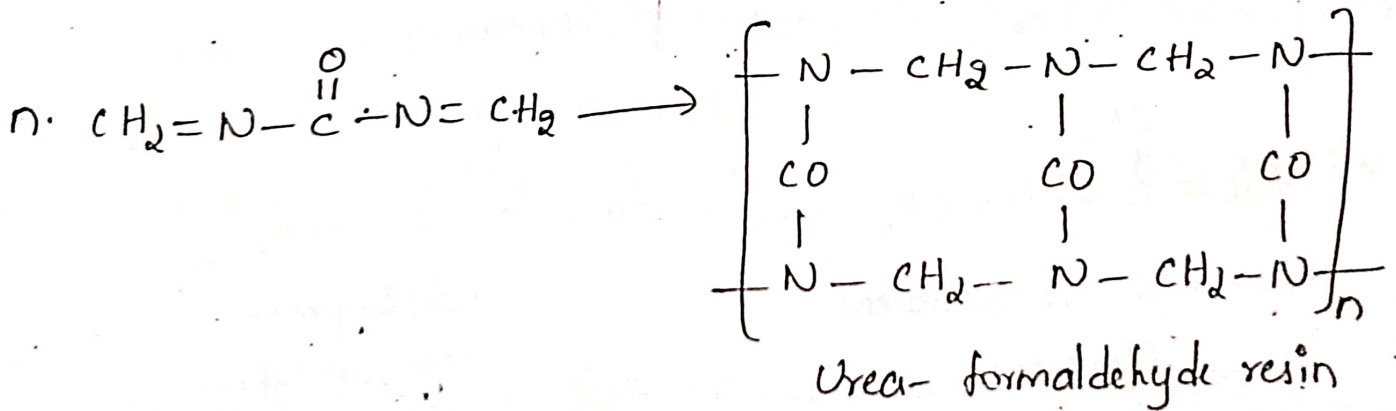
Step-1 :-



Step 2 :-



Step 3 :-



Properties :-

- * These are clear and colorless
- * These are resistance towards solvents, chemicals, grease, and moisture.
- * These exhibit excellent abrasion resistance
- * These are good electrical insulators.

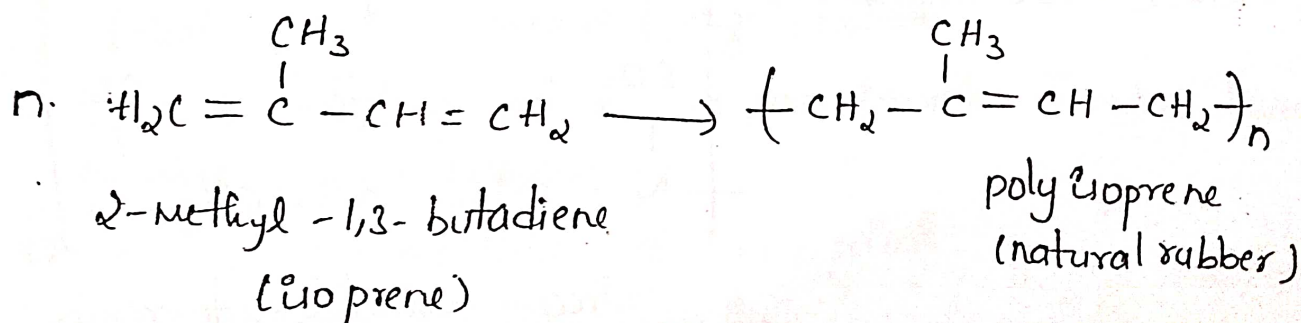
* These exhibits good tensile strength.

Applications:

- * These are used for finishing parts on the cotton garments, tentles
- * These are used for bonding, grinding wheels.
- * These are used in making of plates, glasses etc.
- * These are used as adhesive for plywood.

Elastomers; (or) Synthetic Rubber:

- * The main source of natural rubber is the species of tree known as *Hevea brasiliensis*.
- * It is a polymeric material having elastic character.
- * India ranks 5th and produces about 2.7% of the total world production.
- * Most of the Indian production comes from Kerala, Natural rubber is the polymer of isoprene.

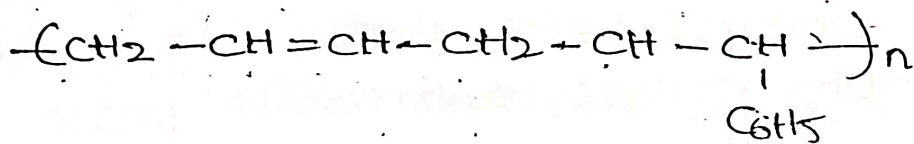
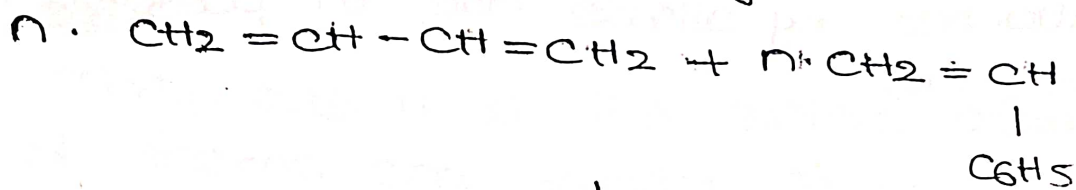


- * X-ray diffraction studies have shown that isoprene units are arranged in natural rubber in cis-form

synthetic rubbers (or) elastomers are divided into different types they are: Page no-12

1) Buna-S (a) Styrene Rubber (b) GR-S Rubber.

Preparation: The Buna-S rubber contains 1,3-butadiene (75%) and styrene (25%). It is produced by co-polymerisation of butadiene and styrene.



Properties :-

- It possesses high abrasion resistance and high load bearing capacity.
- It easily oxidises in presence of ozone atmosphere.
- It swells oils and solvents.
- It can be vulcanised in the same way as natural rubber.

Uses :-

- It is mainly used for manufacture of tyres.
- It is also used for floor tiles, shoe soles, gaskets, wire and cable insulations, adhesives, tank linings, etc.

2) Buna-N (a) Nitrile Rubber (b) GR-A Rubber.

Preparation :-

It is prepared by co-polymerisation of 1,3-butadiene and acrylonitrile.

Properties :-

- (a) It can be vulcanised in the same way as natural rubber.
- (b) It has good oil resistance, heat resistance and abrasion resistance.
- (c) It can be attacked by alkalis due to presence of cyanogroups (-CN)

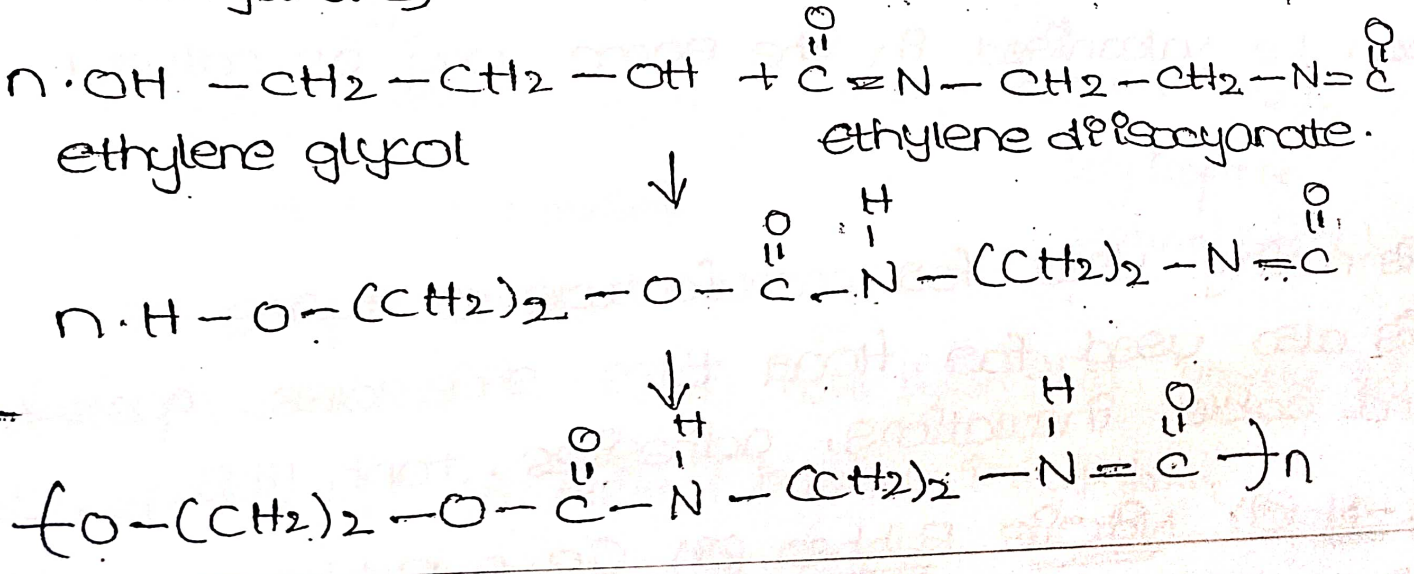
Uses :-

Nitrile rubber is used for making aircraft components, conveyor belts, tank linings, gaskets, hoses, printing rollers, automobile parts, etc.

(iii) polyurethane Rubber (iv) isocyanate Rubber :-

preparation :-

It is obtained by reaction polyalcohols (e.g, ethylene glycol) with diisocyanates (e.g, ethylene diisocyanate).



They are highly resistant to organic solvents but are attacked by acids and alkalis.

(b) They also show good resistance to oxidation because of their saturation character.

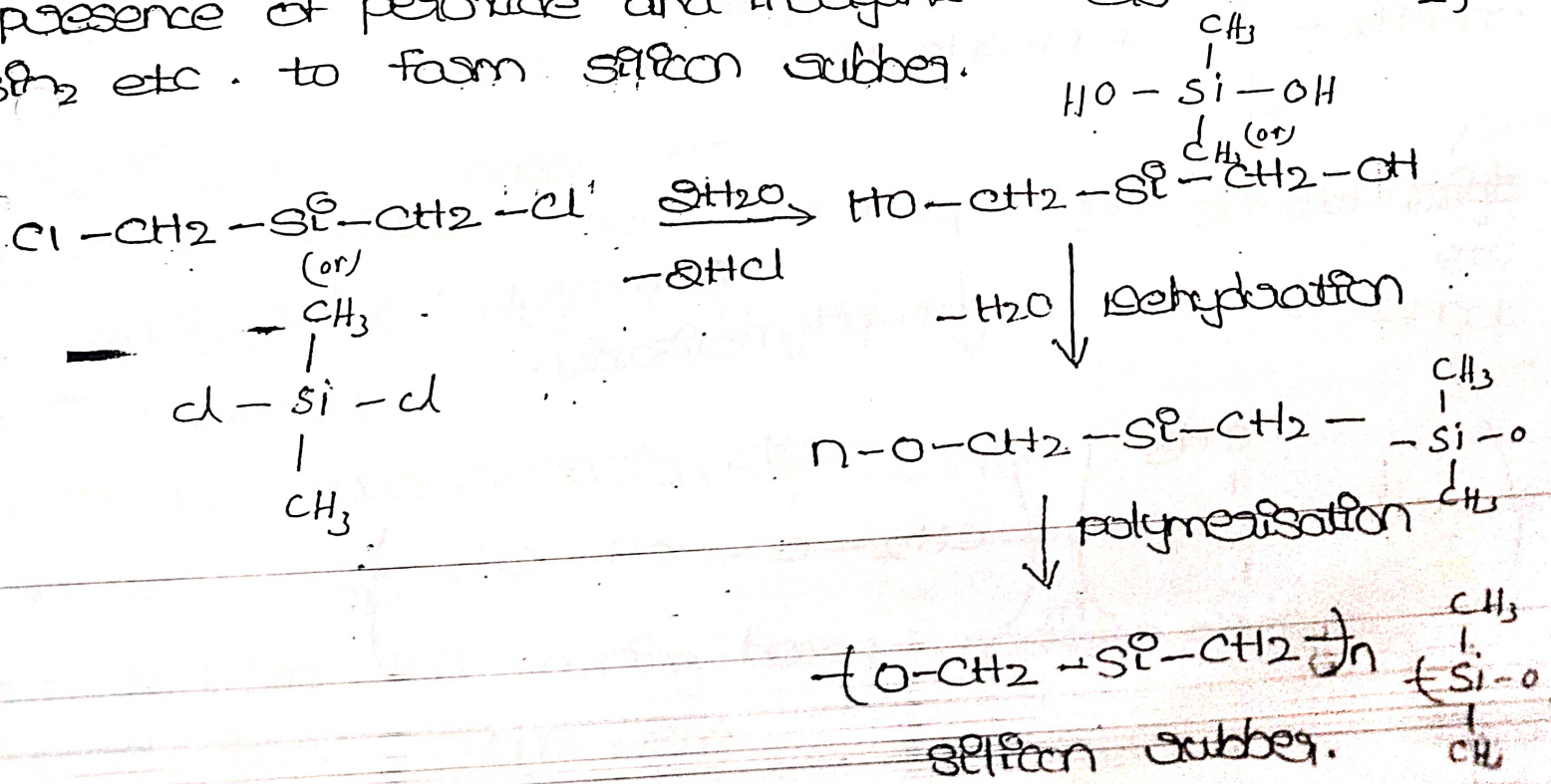
(c) Their foams are light, tough and resistant to heat, weathering, chemicals and abrasion.

uses:-

They are used for surface coatings, manufacture of foams and spandex fibres.

(iv) Silicone Rubber :-

Preparation :- It is obtained by the polymerisation of dihydroxy dimethyl silicon. In first step, dihydroxydimethyl silicon (monomer) is produced by hydrolysis of dimethyl silicon dichloride which on dehydration is followed by polymerisation in the presence of peroxide and inorganic fillers like TiO_2 , SnO_2 etc. to form silicon rubber.



a) It has good resistance to sunlight, oils, acids and alkalis.

b) It retains rubber properties over a much wider temperature range.

c) It is also resistant to air and ozone at high temperature range.

Uses:-

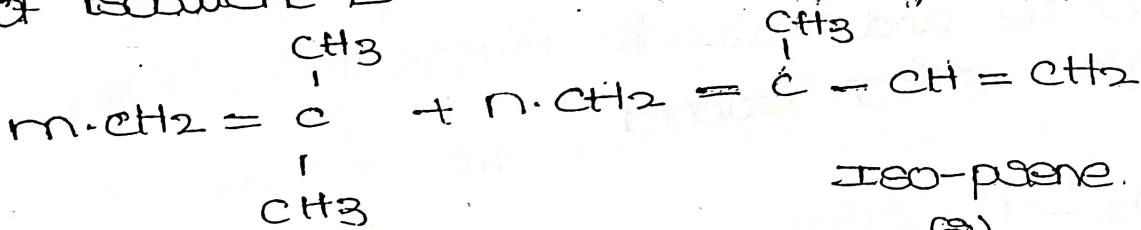
a) It is used in making lubricants, paints, etc.

b) For making artificial heart valves, transfusion tubings, for special boots to be used at low temperature, etc.

v) Butyl Rubber (B) GR-I Rubber

Preparation:-

Butyl rubber is obtained by co-polymerisation of Isobutene with small amount of Isoprene.



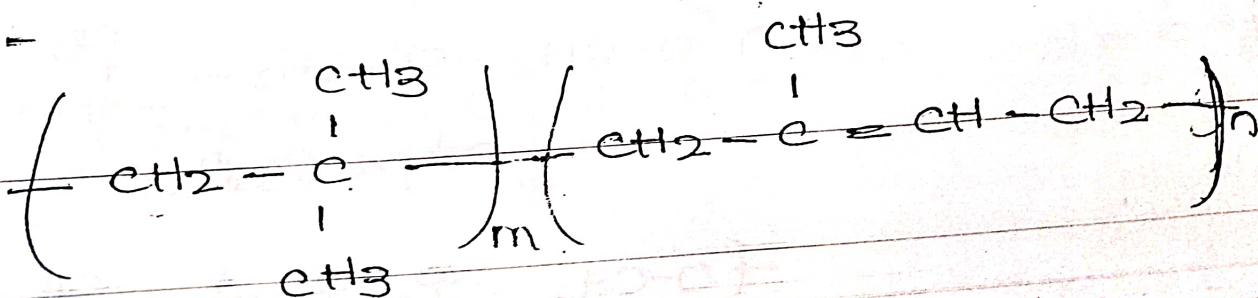
iso butene

iso-prene

(B)

2-methyl 1,3 butadiene

↓
co-polymerisation.



Properties :-

- It is a resistance to sunlight, air, heat, mineral acids, polar solvents, etc.
- (ii) It is non-resistant to flame and oil.

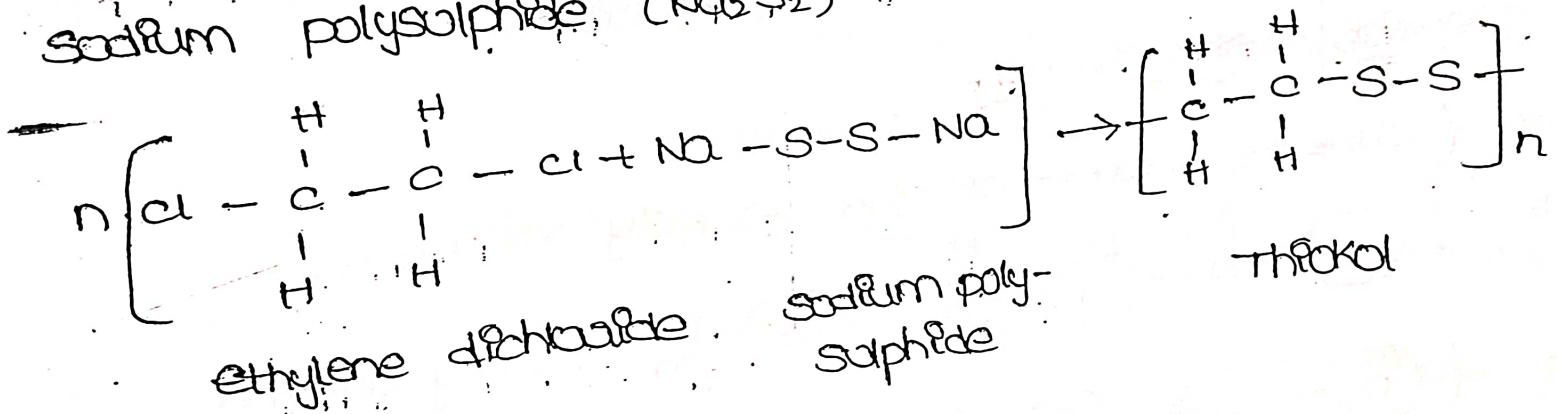
Uses :-

It is used in manufacture of cycle and automobile tubes, hoses, conveyor belts etc.

(vi) polysulphide rubber (a) Thiokol (b) GR-P.

Preparation :-

Thiokol is produced by condensation between sodium polysulphide (Na_2S_2) and 1,2-dichloroethane.



Properties :-

- (a) It is resistant to mineral oils oxygen, ozone, sunlight etc.
- (b) It does not foam hard rubber because it cannot be vulcanised.
- (c) It has poor abrasion resistance.

Uses :-

It is used for making hoses, gaskets, painting rollers, tank linings, etc.

conducting polymers :-

Polymers are poor conductors of electricity and generally used as electrical insulators and dielectric materials.

* However, there are polymers with improved electrical conductivity prepared by the addition of some additives such as conducting metals like copper and silver or other materials.

* An organic polymer with highly delocalised π -electronic system, having electrical conductance on par with metallic conductor is called a conducting polymer.

* For example :- polyacetylene, polythiophene, polyphenylene, polyphenylene sulphide and polyaniline.

chemical structures :-

* $(-CH=CH-CH=CH-)_n \rightarrow$ poly acetylene.

* $(\text{Benzene ring}-N^H-N^H-\text{Benzene ring})_n \rightarrow$ poly aniline

* $(\text{Benzene ring}-\text{Benzene ring}-\text{Benzene ring})_n \rightarrow$ poly phenylene

* $(\text{Thiophene ring}-\text{Thiophene ring}-\text{Thiophene ring}-\text{Thiophene ring})_n \rightarrow$ polythiophene

classification :-

i) π -electrons conducting polymers :- The polymer whose backbone is made up of molecules that contain conjugated π -electrons which extend the entire polymer and make it conducting.