

Synthetic Polymers

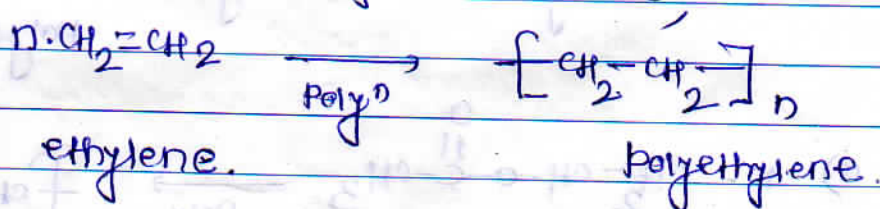
Introduction, Classification based on nature of synthesis (without mechanism) with examples. (Addition and condensation polymers). Properties, uses and synthesis of polyvinyl chloride, polyvinyl acetate, polystyrene, polyacrylonitrile, Nylon 6, Nylon 66. Introduction to synthetic and natural rubber, properties, uses and synthesis of Buna N., Neoprene and silicon rubber.

(a) **Introduction:-** In Polymer chemistry no. of chemist works & some typical man-made polymer in laboratory i.e. synthetic polymer i.e. PVC; Teflon; Polyethylene; Dacron; Ozlon etc. First Dunlop show rubber which is naturally occurs. Some natural polymers such as cellulose; starch; proteins & natural rubber etc.

Polymers synthetic or natural are high molecular wt compounds whose structure are made up of a large no. of simple repeating units; generally it is called as monomers. The reaction by which monomers are converted into polymer & process is polymerisation.

Polymer which is synthesized from same monomer are called as homopolymer. If it prepared from more than one kind of monomer are called as copolymers.

e.g. formation of wall from bricks; Railway track etc. short hand representation is,



(b) **Classification of polymers:-** based on nature of synthesis. Generally classification based on the nature of synthesis; so that polymers are classified in two types;

- a) Addition polymers or chain-growth polymers
- b) condensation polymers or step growth polymers.

a) **Addition polymer:-** (with out ~~example~~ Mechanism)

Addition polymers are made by combination of alkene monomer to produce a single huge molecule only. These reaction are catalysed by peroxides or acids, it require pressure of 1000 atm at 200°C & prepare polymers.

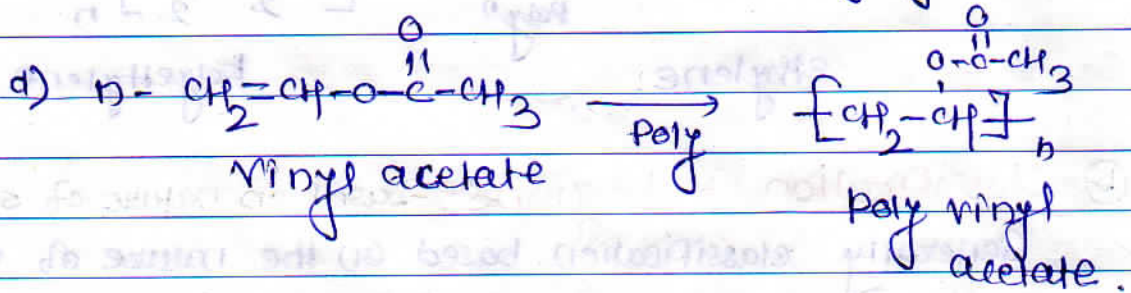
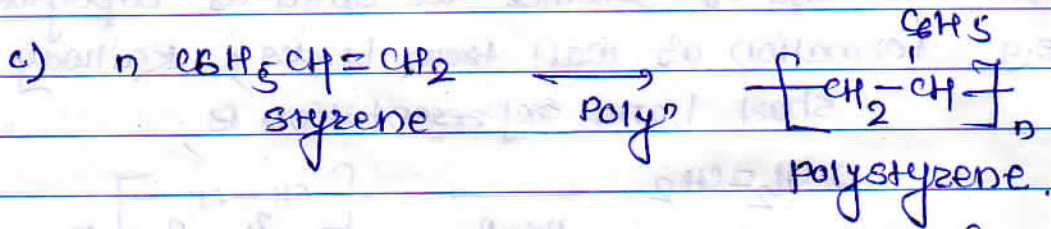
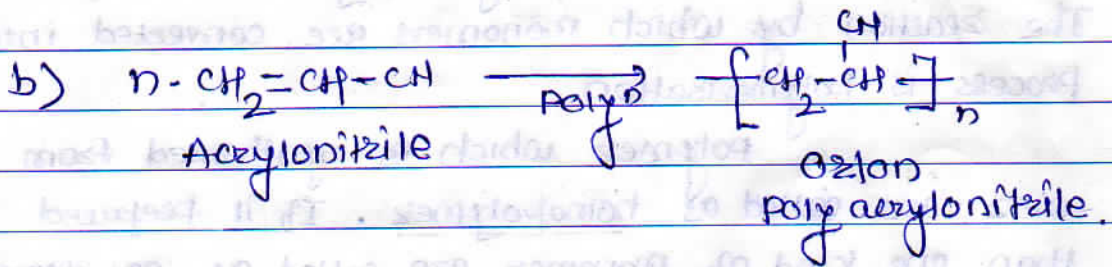
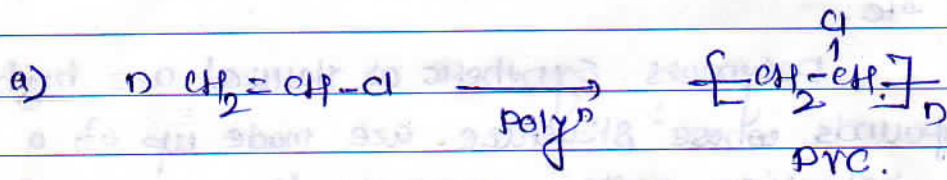
In some polymerization polymers prepared at much low pressure & temp called as Ziegler catalysts.

In Ziegler-Natta polymerization generally inert solvents used (Trialkyl-aluminium-titanium tetrachloride)

In vinyl polymerization no. of polymers are

prepared such PVC; Ozlon; P. Vinyl cyanide; P. Vinyl acetate
 Polyvinyl styrene etc.

e.g. PVC obtained by polymerising vinyl chloride gives PVC which is used for different purposes.



b) Condensation polymers :-

This type of polymerization normally employs in two difunctional monomers that are capable of undergoing typical organic reactions.

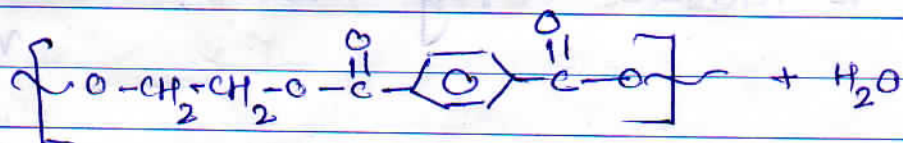
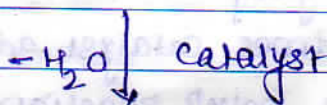
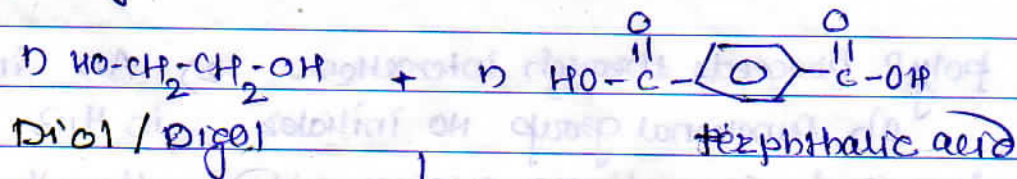
e.g. A diacid can be allowed to react with a diol in presence of an catalyst to offered a polyester. In this case chain growth is initiated by the reaction of one of the diacids carboxyl group with of the diols hydroxyl group. The free carboxyl or hydroxyl group of the resulting dimer can then reacts with an appropriate functional group in another monomer or dimer. This process is repeated throughout the polymerization mixture untill all of the monomers are converted to low molecules

wt species such as dimer; trimer; or tetramer.

e.g. Nylon-6; Nylon-6,6; Polyester etc.

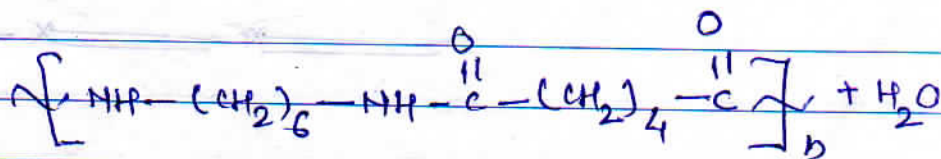
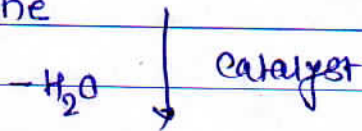
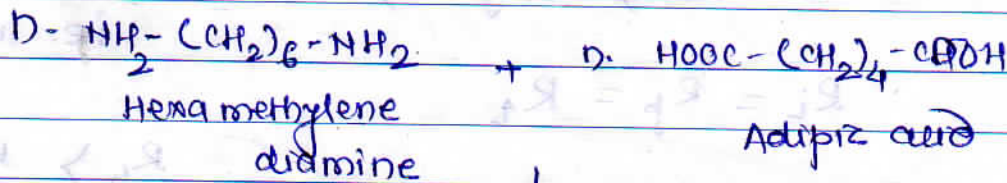
e.g. Examples as follows;

(a) Polyester



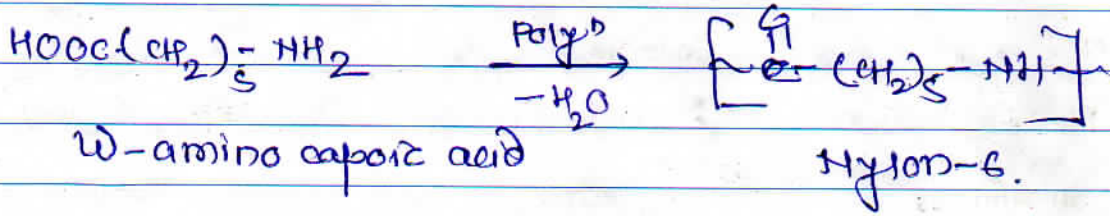
Polyester.

(b) Nylon-6,6 :-



Nylon-6,6.

② Nylon-6 -



Difference between condensation & Addition polymerisation

Ⓐ Condensation poly

Ⓑ Addition poly

1) Polymerization proceed through elimination of H₂O; alcohol etc.

1) No elimination takes place.

2) Polyⁿ proceeds through interaction of functional group NO initiator required. Some times catalyst added to facilitate the polyⁿ reaction.

2) An initiator required in this polyⁿ it proceeds through vinyl group & unsaturation. (initiate via double bond)

3) In this case polymer built up slowly by a sequence of discrete reaction i.e initiation; propagation; termination

3) In this case polymer molecule grows extremely rapidly once initiation occurs

i.e. initiation; propagation & termination.

R_i = R_p = R_t

R_p > R_i ≈ R_t



c) Properties, uses and synthesis of following Polymers -

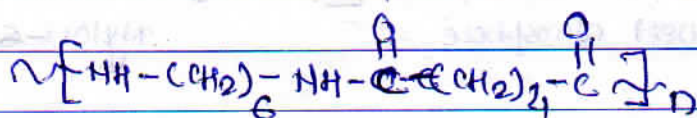
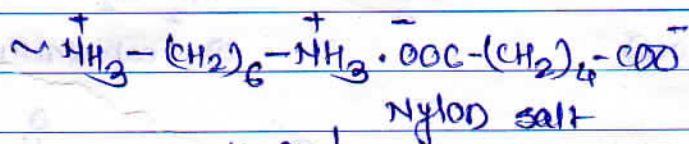
- $\left. \begin{array}{l} \text{Add}^{\circ} \\ \text{Poly} \end{array} \right\} \begin{array}{l} (1) \text{ Polyvinyl chloride } (CH_2=CH-Cl) \\ (2) \text{ Polyvinyl acetate } (CH_2=CH-\overset{\text{O}}{\parallel}{C}-CH_3) \\ (3) \text{ Polystyrene } (CH_2=CH-C_6H_5) \\ (4) \text{ Polyacrylonitrile } (CH_2=CH-CN) \end{array}$
- $\left. \begin{array}{l} \text{Cond}^{\circ} \\ \text{Poly} \end{array} \right\} \begin{array}{l} (5) \text{ Nylon-6 } (H_2N-(CH_2)_5-COOH) \text{ w. amino caproic acid.} \\ (6) \text{ Nylon-6,6 } NH_2-(CH_2)_6-NH_2 \text{ \& } HOOC-(CH_2)_4-COOH. \\ \text{Hexamethylene diamine.} \quad \text{Adipic acid} \end{array}$

Condensation Polymerization \rightarrow

① Nylon-66

Nylon is the first man made true synthetic fibre, It is made from long chain dibasic acids combine with long-chain diamines. They contain the amide groups $(-NH-CO-)$ in the polymer chain. Nylon is similar to silk in constitution & properties. Prepared firstly in 1930 by W.H. Carothers du Pont company as a substitute for silk.

Adipic acid & hexamethylene diamine are allowed to react in aq. solution in equimolar proportion to give a salt known as nylon salt. After purifying the salt it kept in to react & heated to about 543 K, when all moisture & air is removed, the reactor is sealed & ^{appl} pressure of about 250 pounds per square inch applied for few minutes/hrs, that time water is eliminated & ammonium salt is converted to polyamide by condⁿ polymerizatⁿ.



Nylon-66 (Polyamides)

On cooling the molten polymer forcing through capillary holes of spindles we get elongated threads.

- Properties -
- 1) It melts at about 537K
 - 2) It has high molecular wt ranging betⁿ 12000 to 15000.
 - 3) It is insoluble in water & in most of the organic solvents.
 - 4) It is resistant to abrasion; attack of chemical reagents as well as attack of moths & fungi.

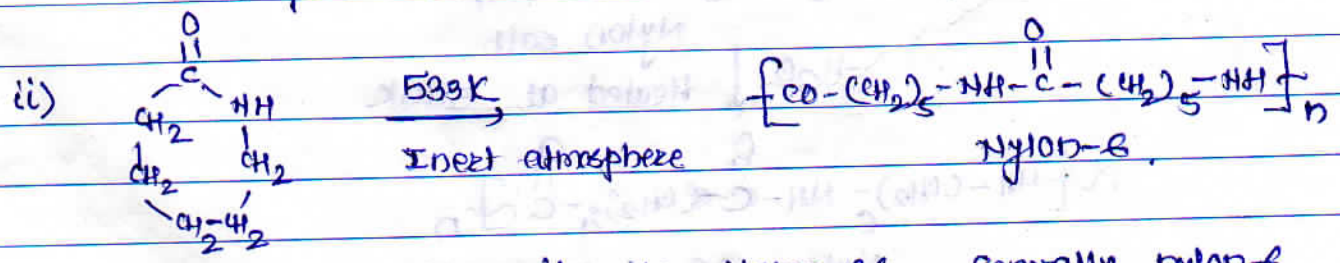
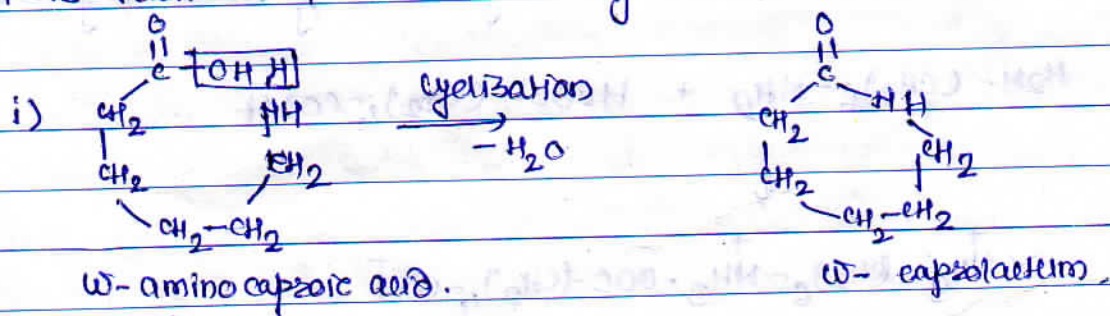
Uses - 1) It is extensively used for the manufacture of textile fabrics; carpet; ropes; brushes of tooth brushes; fishing net; surgical threads; tyre-cord machine part etc.



② Nylon-6 :- or (Perlon-L)

It is also a polyamide fibre obtained by the condensation process or polymerisation of ω -caprolactam. Since ω -caprolactam a monomer contains six carbon atoms in its molecule the name is Nylon-6.

It is prepared by polymerisation of ω -caprolactam, which is a lactam of ω -amino caproic acid $\text{NH}_2\text{-(CH}_2\text{)}_5\text{-COOH}$. The ω -caproic amino acid heated it eliminates H_2O molecule, then obtained ω -caprolactam is heated in a reactor, to about 533K in an inert atmosphere, when Nylon-6 polymer is obtained in a molten state it is further processed like Nylon-66.



uses of Nylon-6 similar to Nylon-66, generally nylon-6 is wrinkle free. They retain their shape well. Nylon-6 fibre has tenacity of 1.5-2.0 g/den & high tenacity continuous filament

The elasticity or elastic recovery is 100% upto about 2-5% strain.

The water absorbancy is 2.5-5% & the fibre does loose a small amount of strength when wet. The abrasion resistance is excellent.

Nylon-6 fibre soluble in mineral acid like HCl, H_2SO_4 & organic acid like acetic & formic acid.

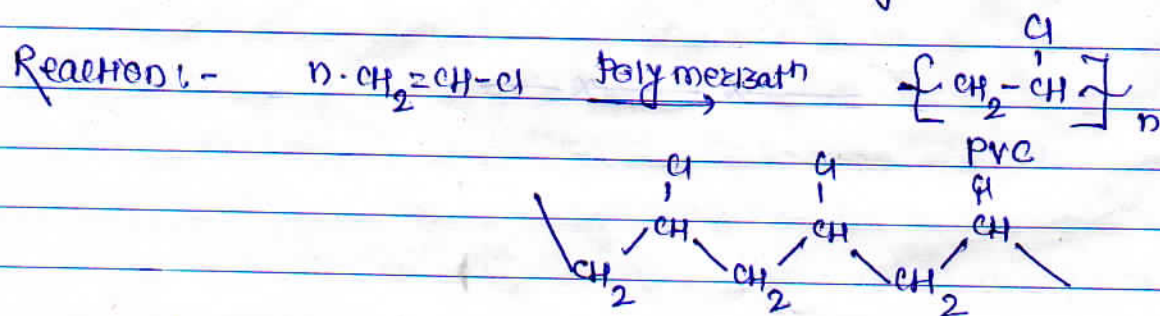


Addition Polymerization

③ Polyvinyl chloride :-

It is commonly called as PVC; obtained by the polymerisation of vinyl chloride (vinyl chloride is gas). PVC obtain by no. of methods i.e a) suspension b) bulk & c) emulsion polymerisation. Generally the suspension polymerisation method use for prepⁿ of PVC.

A mixture of vinyl chloride, water, polyvinyl alcohol, dichloroethylene & lauryl peroxide are mixed in a reactor fitted with a bursting disc & is also connected to vacuum line. The reactant are then heated to about 50°C & pressure in reactor increases upto 100 atm/in². This temp maintained for 15 hrs then pressure drops. The slurry is then discharged to a centrifuge where the polymer is separated & washed. Finally the polymer is dried in hot air at about 100°C we get product.



Properties - PVC is a colourless rigid material. It has high density & low softening point. It has higher dielectric constant. It is unaffected by acids; alkalis & aq. solution. Chemically it is an inert material.

Application :- In second world war there was great demand for PVC for cable insulation, for leather clothing, packing & toys. For making film, familiar handbags, rain coats; food covers; pipes; electrical insulation etc.

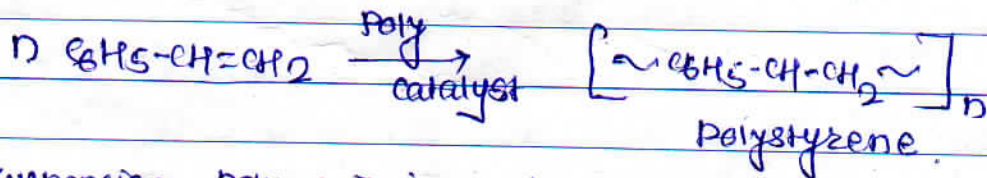
④ Polystyrene

Polystyrene is prepared from the vinyl monomer of styrene ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$). During 1930's the commercial interest of polystyrene began because of its good electrical insulation characteristics. During the second world war two companies namely I.G. Farben-Industries Germany & Dow chemical company U.S.A, started manufacturing this chemical, which is used for manufacture of synthetic rubber.

Preparation - Polystyrene can be manufactured by using the following four techniques;

- Bulk polymerisation
- Solution polymerisation
- Suspension polymerisation
- Emulsion polymerisation.

but bulk & suspension polymerisation are commercially used; styrene in presence of catalyst or initiator it gives polystyrene



In suspension polymerisation, this method is simple at time of polymerisation it run in batch wise in a stirred reactor, which has arrangements for heating & cooling. The suspending agents generally used as tricalcium phosphate & dodecyl benzene sulphate. Benzoyl peroxide is used as an initiator for the polymerisation of styrene. The reaction is carried out at 90°C in the form of slurry. After the polymerisation is completed it is washed with HCl & water to remove the suspending agent.

It is dried in warm air & used for further process.

Properties :-

The linear polystyrene is a hard rigid & brittle material. It has a relatively low softening points. Polystyrene is highly transparent; transmit about 90% of visible light. It also possesses good electrical insulation characteristics, It shows low moisture absorption & good mouldability.

Polystyrene is soluble in C_6H_6 ; toluene; CCl_4 ; $CHCl_3$ etc
 polystyrene is unaffected by acids & alkalis.

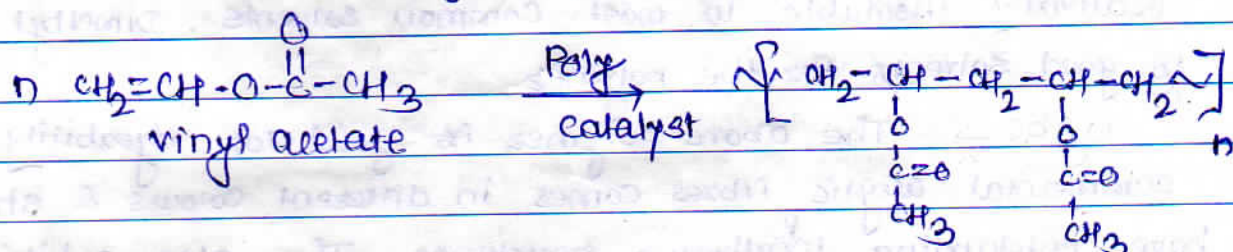
Applications or Uses :-

- 1) Polystyrene is used for manufacturing lens materials.
- 2) It is used as electrical insulation material in T.V & radio.
- 3) It is used for manufacturing packing materials.
- 4) It is also used for refrigerator lining & interior decoration coating.
- 5) ABS (acrylonitrile-butadiene-styrene) copolymer are used in automobile.

⑤ Polyvinyl acetate $(CH_2=CH-O-\overset{\overset{O}{\parallel}}{C}-CH_3)$

Polyvinyl acetate is prepared by the emulsion polymerisation of vinyl acetate. Polymerisation reaction is carried out by taking the following reactants, in a container & heating the mixture at $75-80^\circ C$ for two hrs. After the end of the reaction the polyvinyl acetate is filtered, dried & used for the preparation of polyvinyl alcohol or other application.

	Parts by weight
a) Vinyl acetate (monomer) -	100
b) H_2O -	100
c) Hydroxy cellulose -	2.5
d) Ethylene glycol -	2.5
e) sod. dodecyl benzene sulphonate -	0.1
f) sod. bicarbonate -	0.5
g) Pot. Peroxydisulphate (initiator) 0.5. etc.	

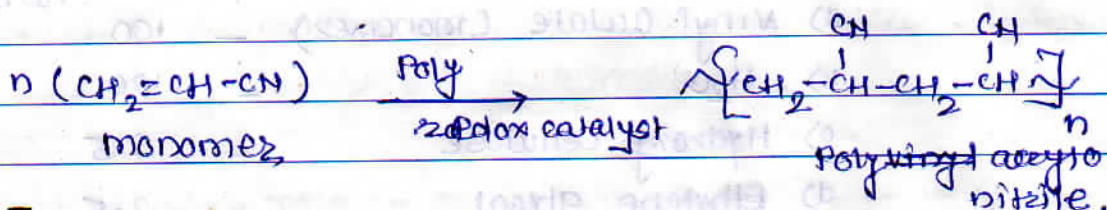


The polyvinyl acetate is generally used for manufacturing of polyvinyl alcohol by a mixture of vinyl acetate in 20% methanol along with small amount of sod. methoxide is taken in a high speed mixture (stirred) at $40^\circ C$ for 10-15 minutes. formed gel (PVA) is insoluble in methanol it is lastly neutralized by acetic acid to stop reaction. The solid obtained washed with methanol dried & pulverized.

This obtained PVA is used for making fibres, particularly used in Japan for manufacturing of dressess, Polyvinyl alcohol aq. solⁿ are used in the formation of adhesives, paper treatment & textile fibres.

⑥ Polyacrylonitrile ($\text{CH}_2=\text{CH}-\text{CN}$)

Polyacrylonitrile obtained by Bulk polymerisation, it is a heterogeneous polymerisation & is associated with high heat generation & consequent to that with hazardous of violent explosion. The acrylonitrile monomer is soluble in water to the extent of nearly 8% at room temp. For polymerisation $\text{K}_2\text{S}_2\text{O}_8$ catalyst is used & reaction run at room temp.



Properties -

Polyacrylonitrile is unstable for many conventional thermoplastic application as it suffers discolouration & infusibility on heating.

It starts yellowing on heating & finally turns black. It is ordinarily insoluble in most common solvents, Dimethyl formamide is good solvent for the polymer.

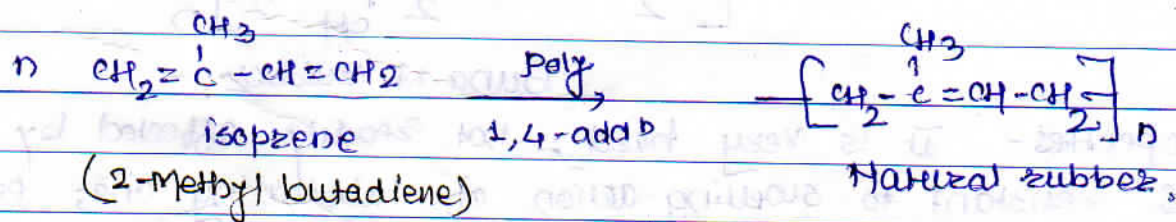
Uses → The above polymer is good for dyeability, now a day commercial acrylic fibres comes in different colours & shades. They have outstanding weathering resistance. They also exhibit good resistance to chemical, stain, insect & microorganism. The acrylic fibres are very much similar to wool.

(d) Introduction; Natural & Synthetic Rubber:-

(A) Natural Rubber:-

Rubber is a type of elastomer polymer. Natural rubber obtained from latex. The commercial natural rubber is obtained from a tree 'Hevea Brasiliensis'. Report of rubber firstly observe rubber in America. When the Cristopher Columbus arrived in the new world he saw native Americans play a game with balls made from the gum of rubber trees. The natives also coated outer garments with the material for protection against rain. They also knew how to prepare footwear & bottles by coating clay moulds with rubber & allowing them to dry. The name rubber was given to the substance by Joseph Priestley (Discover oxygen) who used it to rub out pencil marks.

Natural rubber is a hydrocarbon polymer built up from the monomer of isoprene.



Raw rubber obtained from milky sap (Latex) of the rubber tree does not possess the characteristics of the rubber with which we are familiar. In order to give it strength & elasticity ~~it is~~ by vulcanization

In vulcanization process raw rubber is mixed with small amount of sulphur & heated it, the sulphur reacts with the polymer molecules forming a cross-linked net work

unvulcanized rubber

vulcanized rubber.

This cross linking gives mechanical strength to the rubber. In addition fillers such as carbon black & zinc oxide are usually added to the crude rubber before vulcanization in order to improve its wearing characteristics.



Synthetic rubber :-

Synthetic rubber is prepared in laboratory which are similar to natural rubber. No. of synthetic rubbers are now a day available & it can be prepared by polymerisation of the conjugated dienes. Some of the commercially important synthetic rubbers as follows, e.g.

(1) Buna-N rubber

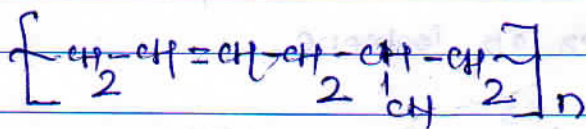
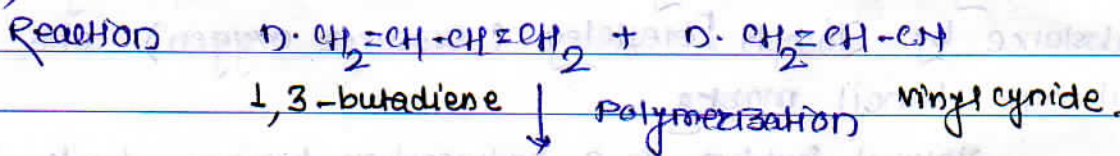
(2) Neoprene rubber

(3) Silcon rubber.

Synthesis; uses & properties of above synthetic rubbers as follow

(a) Buna-N rubber - (Properties; uses & synthesis)

Buna-N rubber is a copolymer of 75% butadiene & 25% vinyl cyanide.



Buna-N rubber

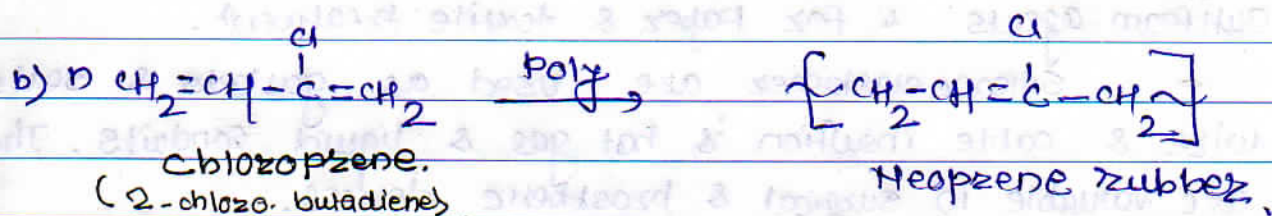
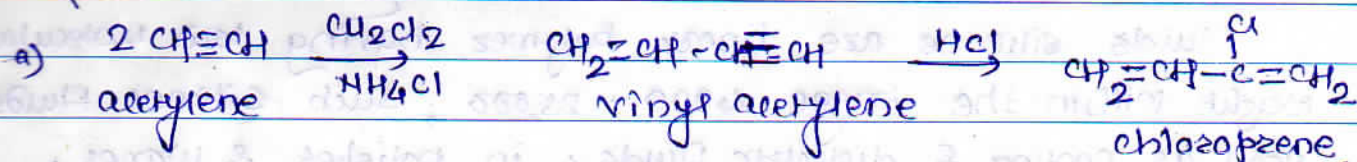
Properties - It is very hard; not readily affected by heat & resistant to swelling action of lubricating oils; petrol & chemicals. Hence used in fuel tanks.

(b) Neo-prene rubber -

It was the first synthetic rubber manufactured on large scale. The monomer chloroprene is prepared from acetylene. It gives intermediate product vinyl ~~acetate~~ acetylene lastly by action of HCl it gives the chloroprene. On polymerization of chloroprene

it yields the polymer (synthetic) i.e Neoprene rubber.

Reaction-

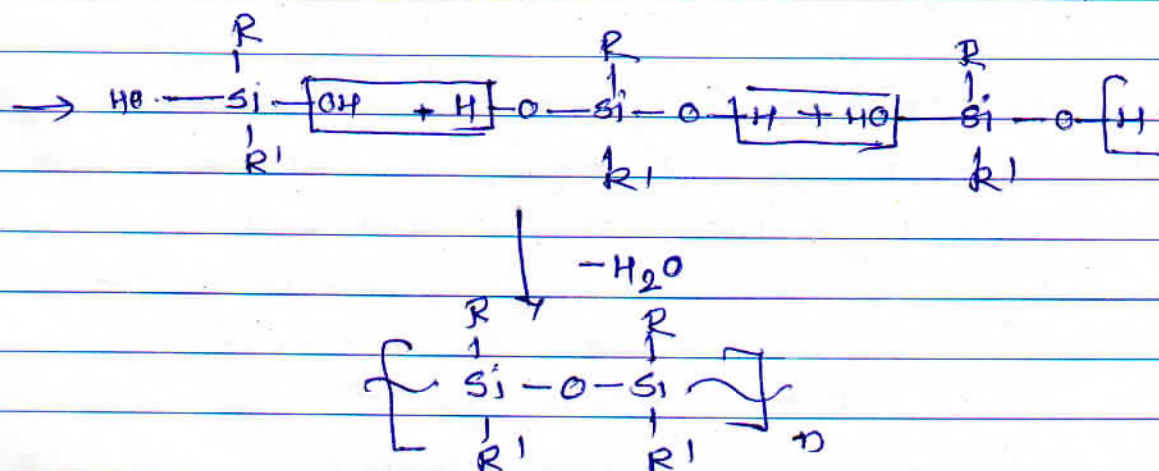
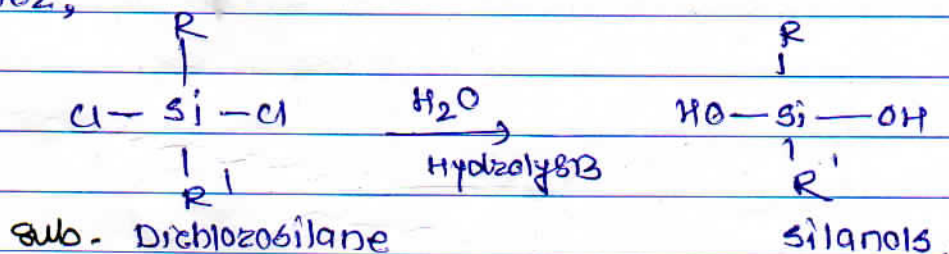


Neoprene rubber is resistant to chemical action & its there fore used in making hoses pipes for petrol & oils & in containers for corrosive chemical action.

(c) silicon rubber

Silicon polymer can formed by condensation reaction. The commercial interest in silicon polymers arose in 1930's during searches for heat resistant electrical insulating materials, silicon polymer were available during world war II. The manufacture of silicone polymers was started by the Dow Corning Corp (U.S.A) in 1943 & by the General Electric Co. (U.S.A) in 1946.

The monomer for silicon polymer is silanols. Silanols are very unstable compounds. They are formed by the hydrolysis of chlorosilanes & condense intermolecularly to give rise silicon polymer,



linear polysilicones.

Silicon polymer are three types or class or groups

- a) Fluids b) elastomers & c) resins etc.

Fluids silicone are linear polymer having low molecular weight within the range 4000 - 25,000, such silicone fluids are used as cooling & dielectric fluids; in polishes & waxes; Antifoam agents & for paper & textile treatment.

Silicone elastomers are used as gaskets & seals, wire & cable insulation & hot gas & liquid conduits. They are valuable in surgical & prosthetic devices.

