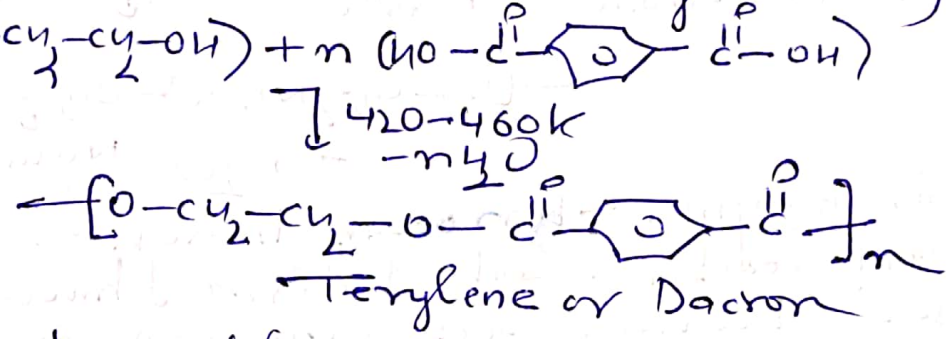
In contrast to chain growth polymers, the formation of step-growth polymers does not occur through chain reactions involving free radicals, carbanions or carbocations as reactive species

Polyesters

Polymers which have ester linkages are called polyesters and are prepared by the condensation polymerization of diacids with diols.

1. Polyethylene terephthalate (PETP) / Terylene / Dacron

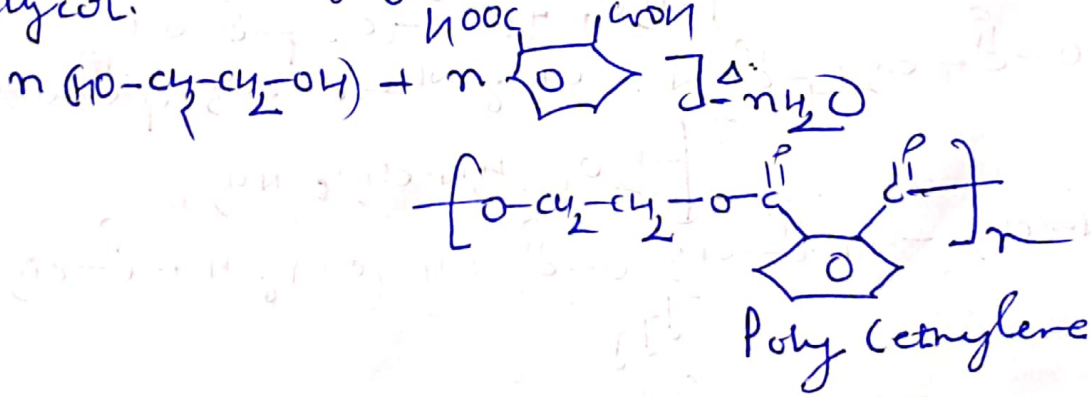
It is prepared by condensation polymerisation of ethylene glycol and terephthalic acid with elimination of water. The rxn is carried out at about 420–460K in the presence of catalyst mixture (Zinc acetate + antimony trioxide)



Use: It is used for the manufacture of wash and wear fabrics, tyre cords, seat belts. It is also blended with cotton and wool to increase their resistance to wear and tear.

2. Poly(ethylene phthalate) 'Glyptal'

Glyptal is obtained by the condensation of dibasic acids with polyhydric alcohol such as ethylene glycol.



Poly(ethylene phthalate)

Polyamides

Polymers which have amide linkages are called polyamides. These are prepared by the condensation polymerization of dibasic acids with diamines or their equivalents

1. Nylon-66

$$n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + n\,H_2N-(CH_2)_6-NH_2$$

$$\xrightarrow{525K,\ \text{Polymerization}} -\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\right]_n + n\,H_2O$$

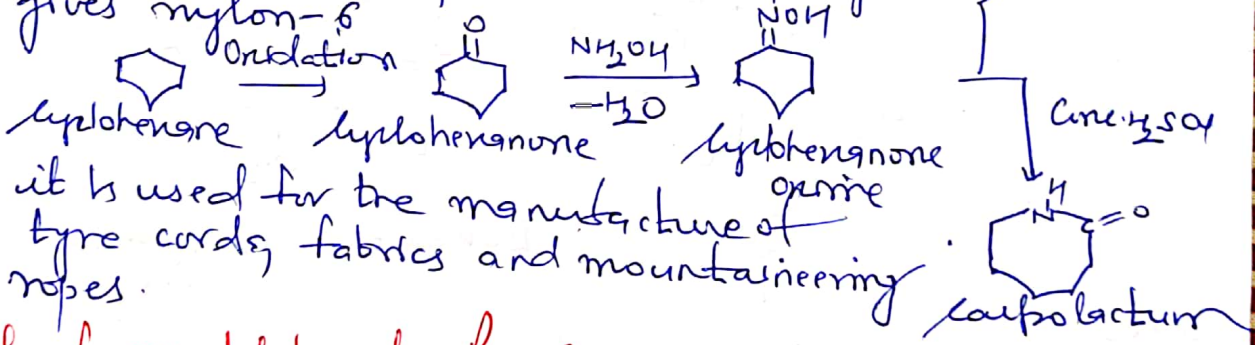
It is called nylon-66 since both adipic acid and hexamethylenediamine contain six carbon atom each.

Uses → it is used in the manufacture of carpets, bristles of brush, textile fibres

2. Nylon-6 or Perlon

Nylons can be prepared from a single monomer having a potential amino group at one end and a potential carbonyl group at the other

Eg: the monomer caprolactum on polymerization gives nylon-6



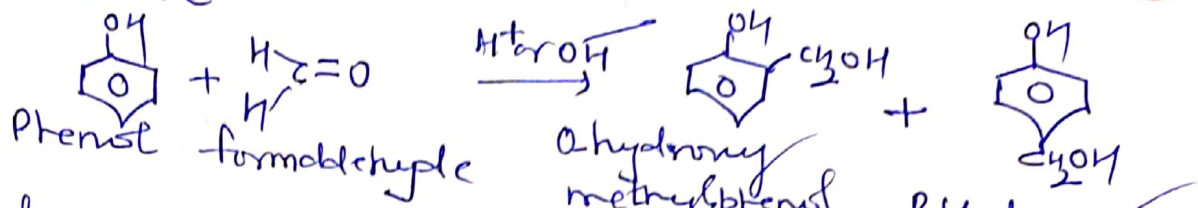
Uses → it is used for the manufacture of tyre cords, fabrics and mountaineering ropes.

Phenol-formaldehyde Resin

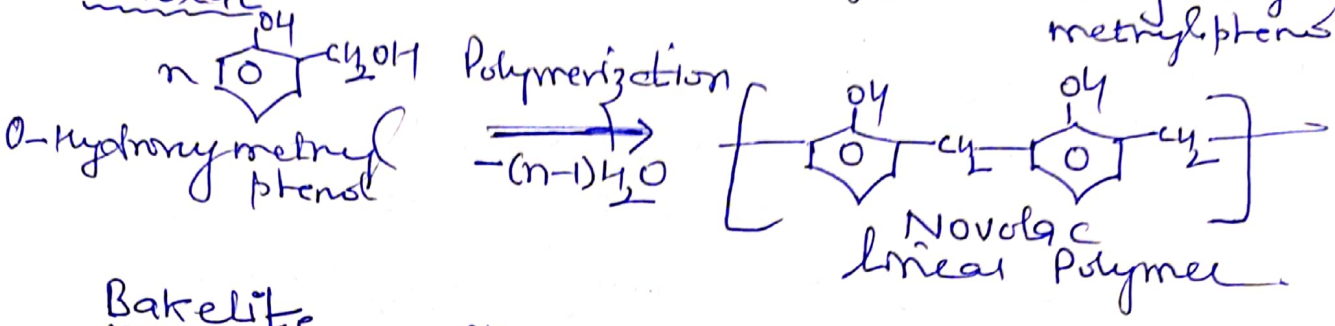
When phenol is treated with formaldehyde in presence of an acid or basic catalyst, it undergoes condensation polymerization to form either a linear or a cross-linked polymer called Phenol-formaldehyde resin or bakelite.

The process actually involves formation of methylene bridges either at ortho or para position or both wrt phenolic group. The initial product is a linear polymer called Novolac which upon further heating with the formaldehyde undergoes cross-linking to form an infusible solid called bakelite

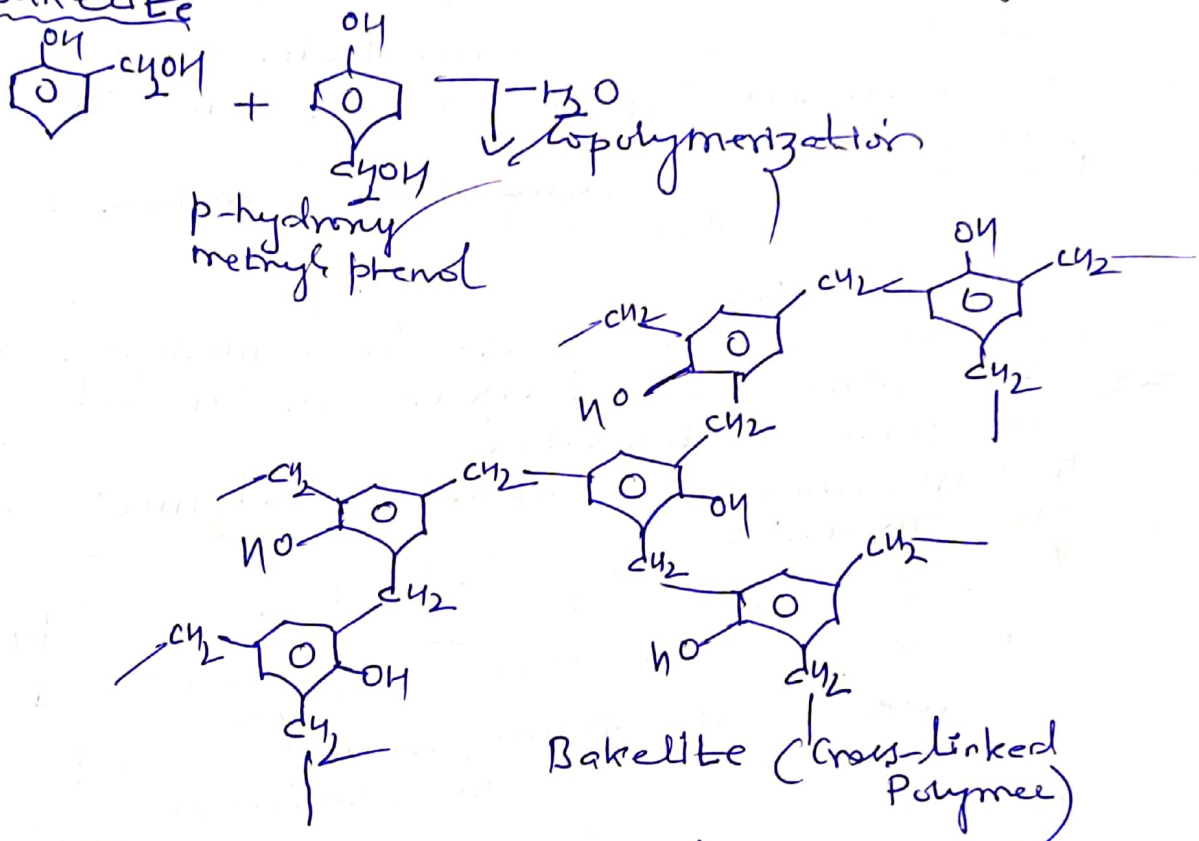
Reaction



Novolac



Bakelite



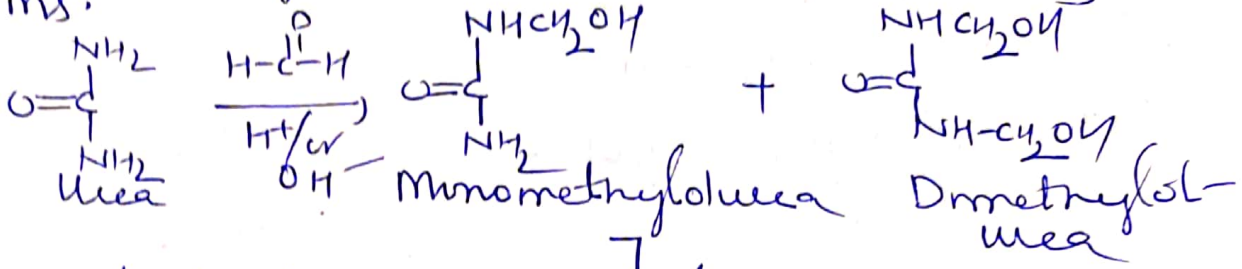
Uses

Soft bakelites with low degree of polymerization are used as binding glue and in Varnishes.

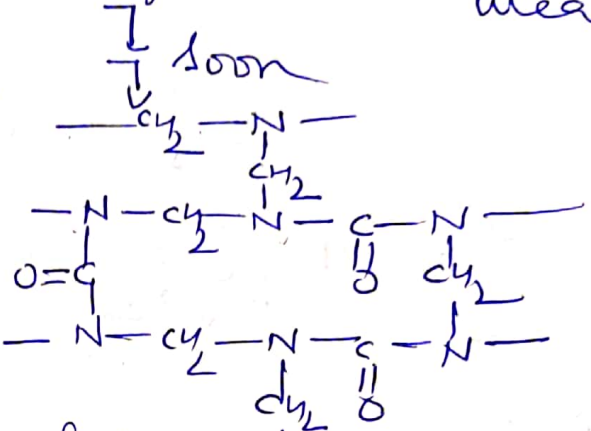
High degree polymerization leads to the formation of hard bakelite which is highly cross-linked & is a thermosetting polymer, it is a water resistant polymer & is used for the manufacture of combs, switches, plugs. Sulphonated bakelites are used as ion exchange resins

Urea-formaldehyde Resins

In the presence of either acid or basic catalysts, urea & formaldehyde undergo condensation to form 3-D polymer called urea-formaldehyde resins.



Urea-formaldehyde resins are superior to phenol-formaldehyde resins as they are colourless & do not discolour on exposure to light



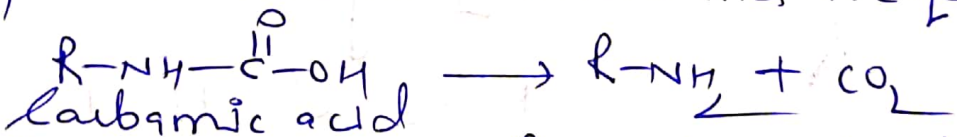
Uses:-

They are used in the manufacture of adhesive, tray, kitchenwares.

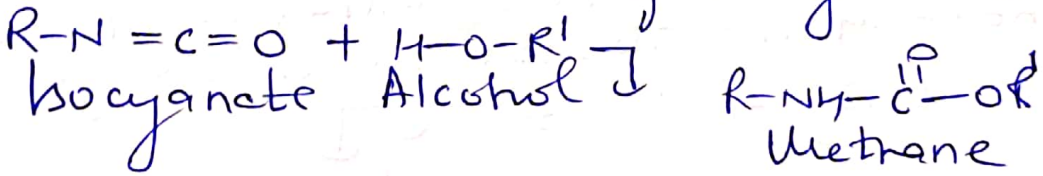
Polyurethanes

A urethane is an ester of carbamic acid (R-NH-COOH)

- The carbamic acids themselves are unstable, quickly decomposing to give amines and CO_2. However, their esters i.e. Urethanes are quite stable

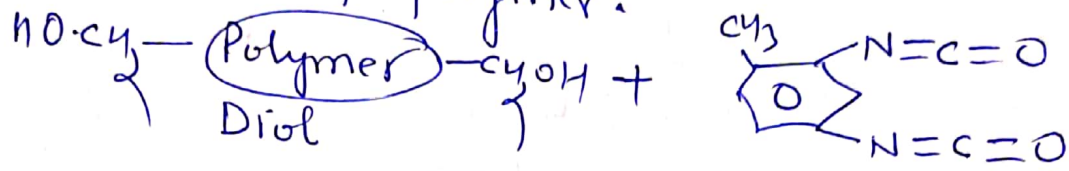


These are prepared by nucleophilic addition of alcohols to the org isocyanates



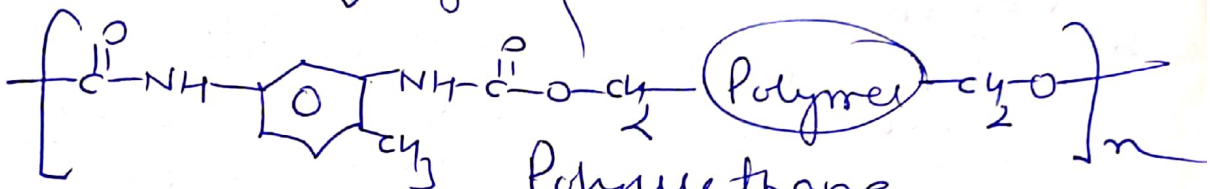
Preparation of Polyurethane

Polyurethane are condensation copolymers. These are prepared by the reaction b/w a diol and diisocyanate. The diol can be either ethylene glycol or some low m.wt polymer with CH_2OH groups at the ends called prepolymer.



Toulene-2,4-diisocyanate

Polymerization



Polyurethane

Polyurethane foams

Polyurethane foams are produced when small amount of water is added during polymerization. Water adds to isocyanate groups giving carbamic acid which spontaneously lose CO_2 thereby producing the foam.

$$R-N=C=O + H_2O \rightarrow R-NH-\overset{O}{\overset{\|}{C}}-OH$$

A carbamic acid

$$R-NH-\overset{O}{\overset{\|}{C}}-OH \rightarrow R-NH_2 + CO_2$$

The amines thus formed further react with isocyanate giving rise to urea linkages

$$R-NH_2 + R-N=C=O \rightarrow R-NH-\overset{O}{\overset{\|}{C}}-NH-R$$

Properties & uses

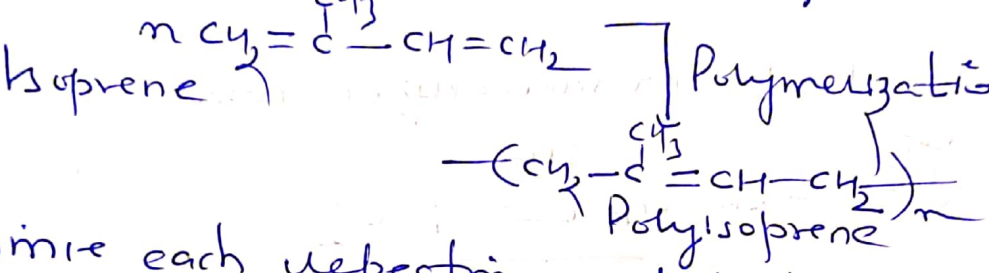
Polyurethanes having low degree of cross-linking are quite soft and elastic. Polyurethane foams are generally have a higher degree of cross-linking than do polyurethane foams. Polyurethane foams are used as thermal insulation. They are also used in pillows, car seats etc.

Natural and Synthetic Rubber

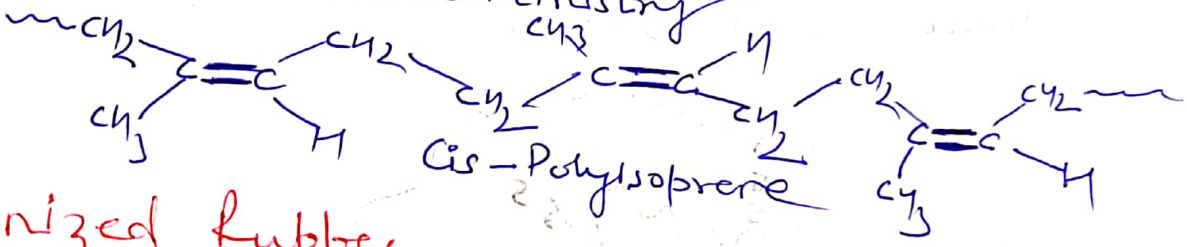
Natural Rubber

It is a natural polymer which is obtained from latex. Latex is a milky fluid which exudes from the rubber tree (Hevea brasiliensis) when an incision is made in the bark of the rubber trees found in tropical and semi-tropical countries (Kerala, Tamilnadu etc)

Chemically, natural rubber is a 1,4-addition polymer of isoprene (2-methyl-1,3-butadiene)



Since each repeating unit in polyisoprene contains a double bond, it may either a cis or a trans-Orientation. In a natural rubber, all the double bonds have cis-stereochemistry



Vulcanized Rubber

In natural rubber, there are no polar groups/substituents & hence intermolecular force of attraction are only weak Van-der Waal interactions. These forces are further weakened because of the cis configuration. As a result, it can be streched like a spring.

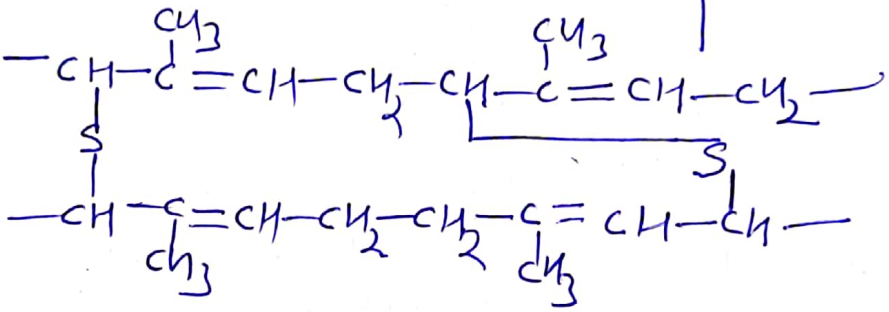
Natural rubber is soft & tacky and becomes even more so at high temperature and brittle at low temperature. Therefore rubber is generally used in the temp. 283-335K where its elasticity is maintained. It is also non-resistant to the action of organic solvents and is also easily attacked by oxidising agents. These

properties can be improved markedly by a process of Vulcanization

It consists of heating raw rubber with sulphur at 373-415K. Since this process is slow, therefore additives like ZnO, ~~2-Methyl~~ 2-Mercaptobenzothiazole are used to accelerate the Vulcanization.

→ The Vulcanized rubber has excellent elasticity, low water absorption & resistant to organic solvents and oxidising agent. During Vulcanization, sulphur bridges b/w polymeric chains are introduced through their reactive allylic positions.

Sulphur cross links in Vulcanized rubber



Vulcanized rubber

Properties of Vulcanized rubber

The cross links make rubber hard & stronger and remove the tackiness of natural rubber. The extent of hardness or toughness, however depends upon the amount of sulphur added. Thus about 5% sulphur is used for making tyre rubber, 30% for making battery case rubber.