

Polymer

The word 'polymer' is derived from Greek words, poly meaning 'many' & mere meaning parts.

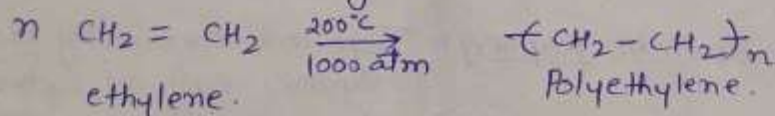
"Polymers may be defined as the high molecular weight compounds formed by the combination of a large number of one or more type of small molecules of low molecular weight."

or

High molecular weight compounds in which certain structural units repeat themselves in a regular fashion are called polymers. The simple molecules from which the repeating structural units are derived are called monomers.

"The overall reaction leading to formation of polymer from monomers is called polymerisation."

Degree of polymerization - The number of repeating units (monomers) combined to form polymer is known as degree of polymerization, it is denoted by 'n'.



Functionality - The number of binding sites present in a monomer is known as its functionality. For a substance to act as a monomer it must have two binding sites.

A compound possesses functionality because of the presence of reactive functional groups like -OH, -COOH, -NH₂, -SH etc. The number of functional groups present in a compound define its functionality e.g.

	functionality
CH ₃ COOH (acetic acid)	1
HOOC-CH ₂ -COOH (Malonic acid)	2
CH ₃ CH(OH)COOH (lactic acid)	2
HOOC(CH ₂ OH) ₂ COOH (Tartaric acid)	4

Some compounds, do not contain any reactive functional groups but the presence of double or triple bonds in the molecule makes them bifunctional or polyfunctional.

$\text{CH}_2=\text{CH}_2$	functionality
	2
$\text{CH}\equiv\text{CH}$	4

The structure of polymers formed depends upon the functionality. In case of bifunctional monomer linear or branched chain polymer is obtained. To get a crosslinked polymer the functionality of monomer will be three.

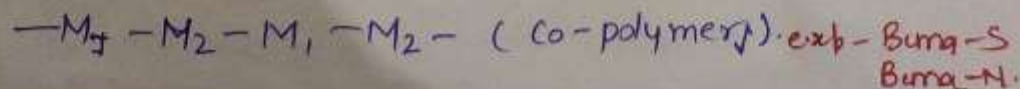
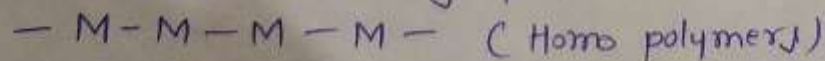
Classification of polymers

[a] On the basis of origin

- [1] Natural polymers - These are available in nature in polymeric form. e.g. - natural rubber, natural silk, starch, protein etc.
- [2] Semi-Synthetic polymers - These are chemically modified natural polymers such as hydrogenated, alkylated & nitrated polymers. e.g. nitrocellulose, methyl cellulose etc.
- [3] Synthetic polymers - These are synthetically prepared polymers. e.g. - polyethylene, PVC, phenol-formaldehyde resin, etc.

[b] On the basis of chemical structure of their backbone, polymers are of two types.

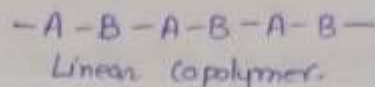
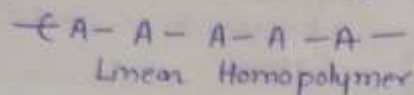
- [1] Homopolymers - The polymers which contain only one type of monomer units. e.g. - polyethylene.
- [2] Copolymers - When a mixture of two or more monomer units are allowed to undergo polymerization the resulting polymers are called copolymers.



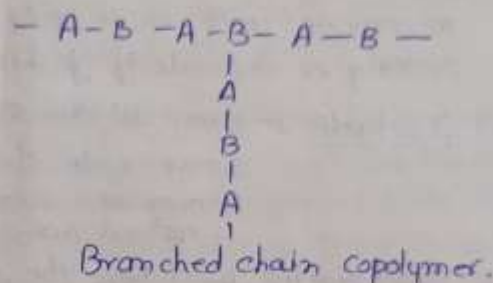
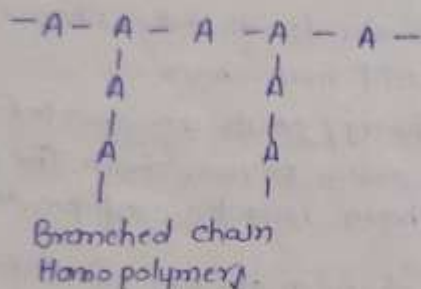
(3)

[C] On the basis of polymeric structure - Three types.

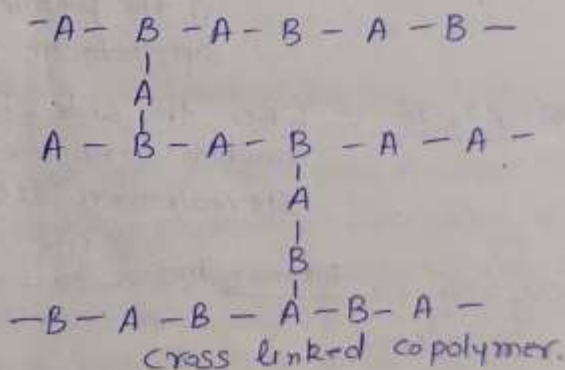
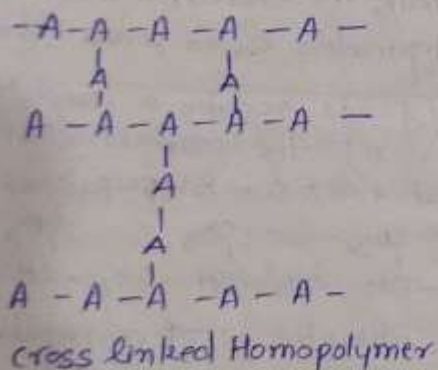
[1] Linear - In straight chain



[2] Branched chain - exp polyethylene at high temp & pressure



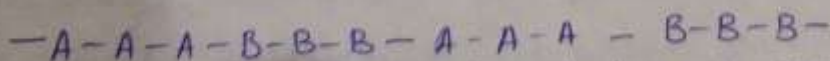
[3] Cross linked -



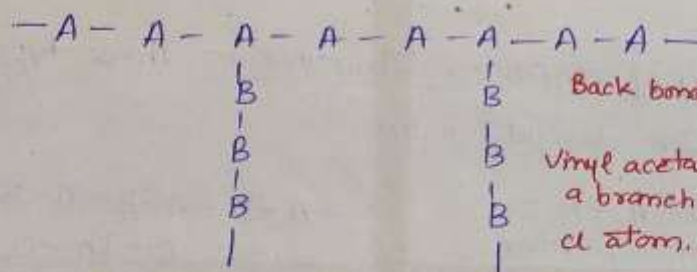
[d] On the basis of arrangement of monomers - ~~on the basis~~

Depending upon the arrangement of the monomers, in case of copolymers, the polymers are divided into block & graft copolymers

[1] Block copolymers - Linear polymers in which the identical monomer units occur in relatively long sequence are called block co-polymers. *Butyl-styrene*



[2] Graft co-polymers - Are branched copolymers in which the backbone is formed from one type of monomer and branches are formed of the other i.e. the monomer segments on the branches and backbone are not the same.



Back bone - styrene + vinyl chloride.

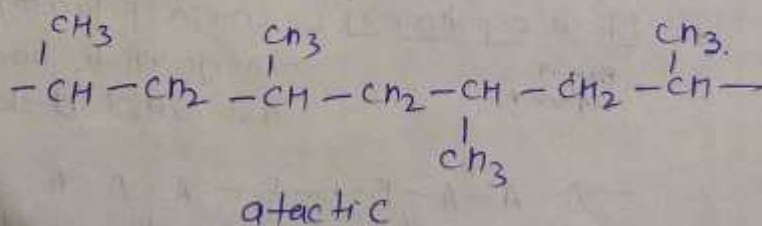
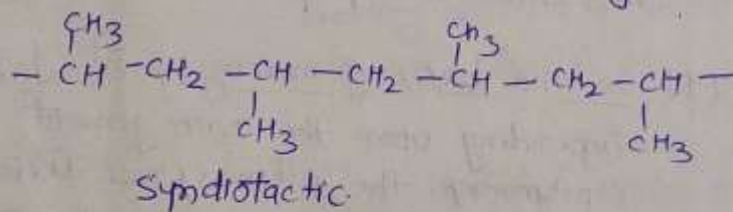
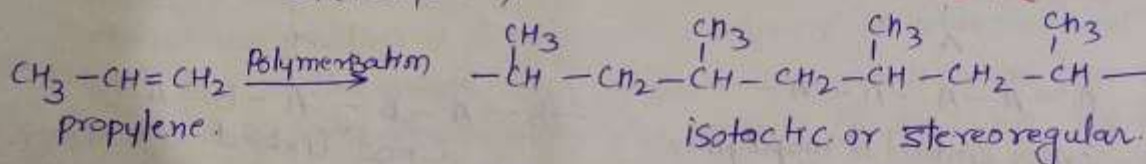
Vinyl acetate attached as a branch by replacing a atom.

[e] On the basis of orientation or tacticity - The orientation of monomeric unit in a polymer molecule can take place in an orderly or disorderly fashion w.r.t main chain.

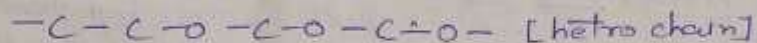
[1] Isotactic - When all the side chain/groups are oriented on the same side of the main polymer chain. The stereoisomer is said to have isotactic configuration.
- natural rubber.

[2] Syndiotactic - When the side chain/groups are oriented alternately on the one side and then on the other side of the polymer chain, the stereoisomer is called syndiotactic configuration. Gutta percha rubber.

[3] Atactic - When the side chain/groups occupy a completely random arrangement w.r.t the polymer chain, the stereoisomer is called atactic. - Polypropylene.



⇒ If the main chain (back bone) is composed of the atoms of the same specie, the polymer is called homochain and if the main chain is made up of different atoms, then they are called hetero-chain polymer.



[1] On the basis of thermal response - According to their behaviour on heating the polymers are divided into two groups.

[1] Thermoplastic - These are generally linear chain polymers and are soluble in organic solvents. These polymers soften on heating and harden again on cooling. In the molten or softened state these polymers can be moulded into different shapes. There is only physical changes in thermoplastic polymers on heating. The intermolecular force of attraction in thermoplastic polymers lie between those of elastomers & fibres. eg, PVC, polyethylene, etc.

[2] Thermosetting polymers - Thermosetting polymers when heated, undergo chemical changes and set to hard masses, since the change on heating a thermosetting polymer is irreversible, it can not be melted again. These polymers are normally made from relatively low molecular weight mass ~~mass~~ semi-fluid polymers. Thermosetting polymers have extensive cross-linking between different polymer chains forming 3-D network. eg - Bakelite.

[9] On the basis of ultimate form - addition

[1] Plastics - All the synthetic polymers (other than elastomers) are usually referred to as plastics. The polymers which are shaped into hard and tough utility articles by the application of heat and pressure are called plastics. They are mostly organic origin.

[2] Elastomers - In elastomers, the polymer chains are held together by weakest intermolecular forces. These weak force permit the polymer to stretched.

The polymers which are capable of being stretched rapidly at least 150 percent of their original length without breaking and return to their original shape on release of stress are known as elastomers. e.g. - rubber.

⇒ Fibrous polymers - These polymers are used for making fibres which possess high tensile strength. This can be due to the strong intermolecular forces like hydrogen bonding. e.g. - polyamides, nylon etc.

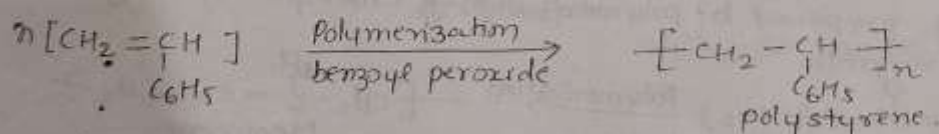
Addition Polymerization (Chain growth polymerization)

1. Monomer must have $=$ or \equiv bond.
2. No loss of small molecules
3. Produces Thermoplastics
4. Initiator will be radicals, Lewis acids & Lewis bases
5. High m.wt polymers are formed at once.

Condensation Polymerization (Step Growth polymerization)

1. Monomer must have at least two similar or different functional group
2. Produces by products such as H_2O , NH_3 , HCl etc.
3. Produces Thermosetting
4. Mineral acids & bases are catalyst.
5. m. wt of polymer rises slowly throughout the reaction.

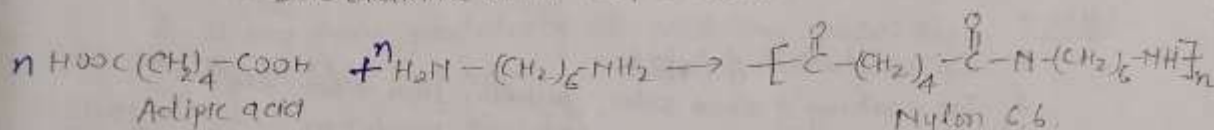
✓ Polystyrene - It is prepared by free radical addition polymerization of styrene in presence of benzoyl peroxide as catalyst.



Properties -

1. It is a transparent polymer and has a unique property of transmitting light all wave lengths.
2. It has very low heat distortion temp (85°C) hence articles made of polystyrene cannot be sterilized with steam.
3. It has got excellent moisture resistance.
4. It has good electrical insulating properties.
5. It can be dyed of different colours.

✓ -
7 Nylon 66 - It is prepared by the polycondensation of hexamethylene diamine with adipic acid.



Properties of Nylon -

1. High strength, elasticity, toughness.
2. They have very good moisture resistance.
3. Insoluble in common solvents.
4. They are very flexible and retain their original shape after use.

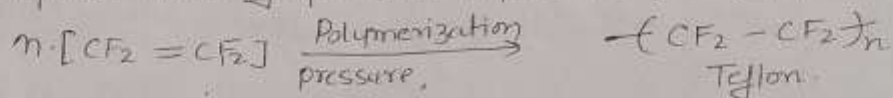
Uses -

1. Used as plastic as well as fiber.
2. In making of textile fibres for use in dresses, socks etc.
3. Nylon 66 is a tough plastic, and is used as a substitute for metal in gears and bearings etc.
4. Due to its high tenacity, nylon is suitably used for parachute fabric.
5. Nylon is also used for making insect screens because of their biological resistance.

Uses - used in making of -

1. Jars, bottles, combs, brush handles, radio & T.V. cabinets.
2. Containers of talcum powder.
3. Foam & bead for insulating & packaging material.

✓ [3] Teflon [Polytetrafluoro ethylene] PTFE - It is prepared by the polymerization of tetrafluoro-ethylene, under high pressure in presence of benzoyl peroxide catalyst.



Properties -

1. It has very high softening point ($327^\circ C$).
2. It is extremely resistant to attack by chemicals such as strong acids & base.
3. It has very good electrical insulating properties.
4. It is slippery & waxy to touch.

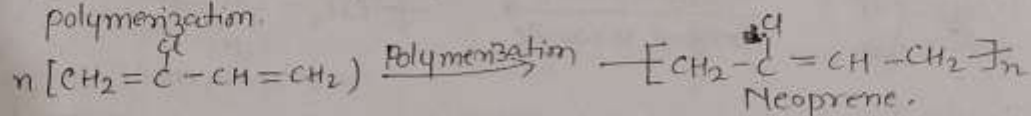
Uses -

1. Due to its chemical inertness it is used in chemical carrying pipes.
2. It is used as an insulating material for transformers, wires etc.
3. It is used as non-stick coating for pots & pans.
4. It is used in non lubricating bearings.

[4] ✓ Neoprene - or GR-M rubber - polychloroprene or duprene -

It was the first synthetic rubber developed in United States.

It is prepared by polymerization of chloroprene via free radical polymerization.



Properties -

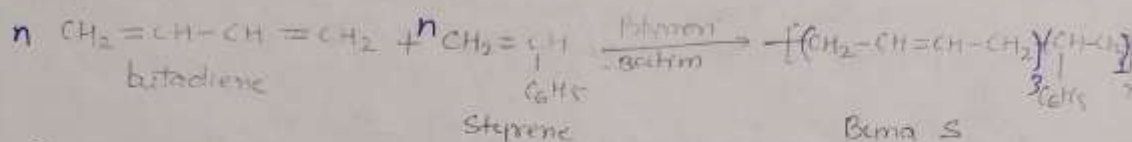
1. As H atom in the natural rubber is replaced by Cl atom, neoprene has superior resistance to vegetable & oils.
2. It is soluble in polar solvents.
3. It is superior to natural rubber as far as ageing is concerned.

Uses -

1. It is used in oil resistant wire & cable coatings.
2. It is used in making of sponges & linings of reaction vessels.
3. Used in making tubings for carrying corrosive gases & oils.

Buna S rubber (SBR) ✓

It is a copolymer obtained by free radical polymerization of two monomers, styrene & butadiene in presence of initiator such as cumene hydroperoxide.



Properties +

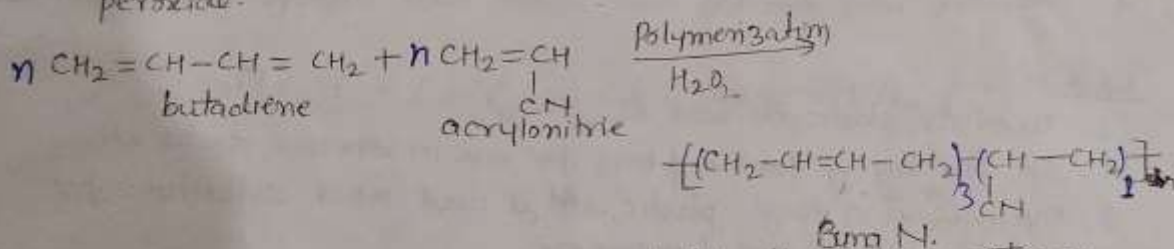
1. It has high load bearing capacity and has much more tensile strength than natural rubber.
2. Its resilience is poorer than that of natural rubber which restricts its use in tire industry.
3. It gets oxidized in presence of traces of ozone present in atm.

Uses +

1. In production of tyres.
2. In making of shoe soles, gaskets, floor tiles, etc.
3. It is widely used for electrical insulation.

Buna N rubber (NBR) ✓

The nitrile rubbers are polymers of butadiene & acrylonitrile in ratio of 75% & 25% respectively. Here initiator is H_2O_2 or cumene hydroperoxide.



Properties +

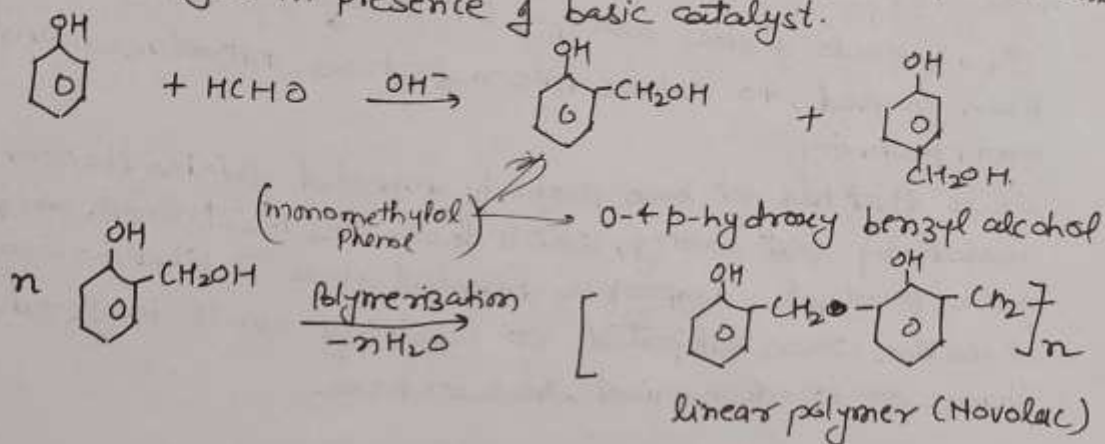
1. Nitrile rubbers are noted for their oil resistance.
2. It has excellent resistance to heat, sunlight acid & salts.
3. Because of the presence of CN group it has less resistance to alkali than natural rubber.
4. It shows resistance to oxidative degradation.

Uses +

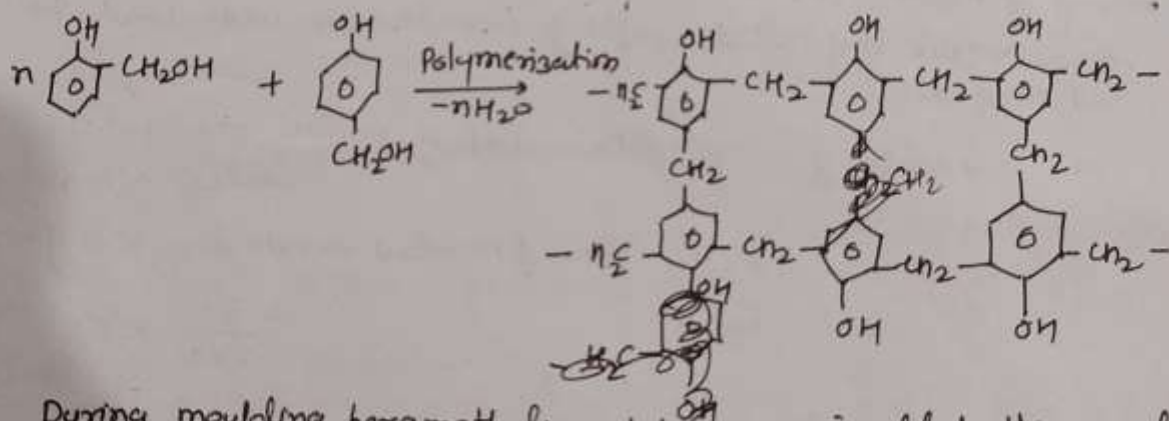
1. Nitrile rubber is used primarily for oil resistance. These are extensively used for oil tanks, gaskets, printing rollers.
2. Used in making of aircraft components.
3. Used as blend component in tyre manufacturing.

1. Phenol-Formaldehyde Resin or bakelite-

It is a condensation polymer obtained from phenol and formaldehyde in presence of basic catalyst.



2. The o + p-substituted phenols can undergo polymerization to produce a cross linked polymer known as bakelite.



During moulding hexamethylene tetraamine is added, this provides formaldehyde, which converts the soluble and fusible novolac into hard infusible solid of crosslinked str.

Properties -

1. hard, scratch resistant, water resistant, insoluble solid
2. Reacts with alkali, due to presence of OH group.
3. excellent electrical insulating properties.

Uses -

1. For making electric insulator parts like - switches, plugs etc.
2. for making glue for binding wooden plates and in varnishes
3. for impregnating fabric, wood & paper.
4. for making bearings.

Molecular Weight of polymer :- The molecular weight of the polymer depends upon the number of simple molecules joined together during the polymerisation reaction. The molar mass of a polymer increases continuously during the condensation reaction. ~~increased~~ However, since the polymerisation chains might be broken at different stages, the final product generally contains macromolecules of different masses i.e. the molecules of the polymer sample do not have identical molecular weight. Hence it is necessary to take an average molar mass in these substances. Two types of calculations are there.

[1] Number average Molecular Weight (M_n) :- For a sample consisting of N polymer molecules containing n_1 ~~molecules~~ molecules of molar mass M_1 , n_2 ~~molecules~~ molecules of molar mass M_2 , etc. then, Number average molar mass.

$$M_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}{n_1 + n_2 + n_3 + \dots} = \frac{\sum n_i M_i}{\sum n_i}$$

The number average molecular weight M_n assumes that each molecule makes an equal contribution to polymer.

[2] Weight average Molecular Weight (M_w) :- Weight average depends upon the masses of the material in different mol. wt. fraction. In this case, while taking average, the molecular weight of each species is multiplied by the weight of species and not with the number.

$$M_w = \frac{m_1 M_1 + m_2 M_2 + m_3 M_3 + \dots}{m_1 + m_2 + m_3 + \dots} \quad \text{where } m_i = n_i M_i$$

$$M_w = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \dots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}$$

In Weight average, molecule contributes according to their masses.

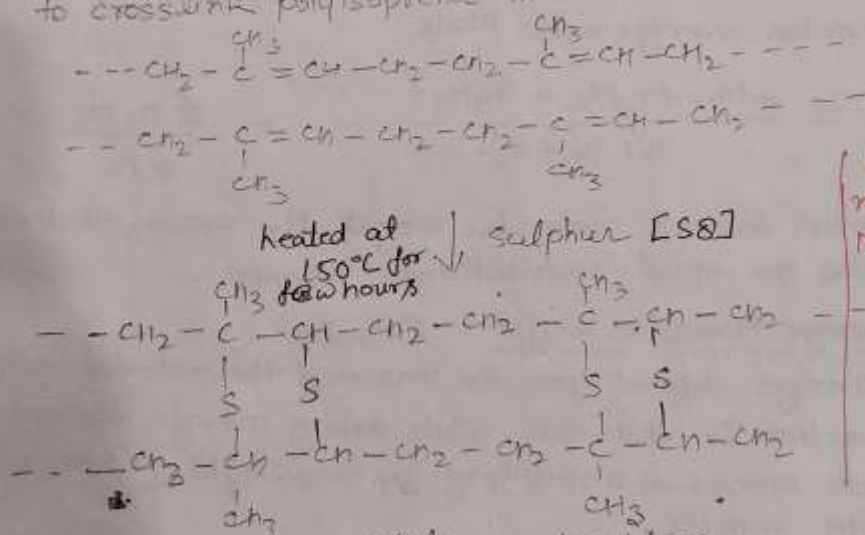
Drawbacks of Raw rubber

1. Crude rubber is soft at high temp but becomes brittle at low temp. So it can be used in a limited temperature range. $10-60^{\circ}\text{C}$
2. It has very low tensile strength.
3. It is not resistant to mineral oils & organic solvents.
4. It has very large absorption capacity.
5. It is also attacked by the oxidizing agents like HNO_3 , H_2O_2 , chromic acid etc.
6. It undergoes permanent deformation when stretched.

However, the above drawbacks can be overcome by the vulcanization of rubber.

Vulcanization

The process by which a network of crosslinks is introduced into an elastomer is called vulcanization. Some scientist used sulphur to crosslink polyisoprene molecules in natural rubber.



Vulcanization of neoprene is done by MgO or ZnO etc.

The tensile strength, stiffness, durability, resistance (temp), elasticity and chemical resistance of vulcanized rubber are increased manifold as compared to raw rubber. The extent of stiffness of vulcanized rubber depends upon the amount of sulphur added.

Properties	Raw rubber	Vulcanized rubber
1. Tensile strength	(Pulling stress)	More than raw rubber
2. Water absorption		lower " " "
3. Insulation		better insulator than raw rubber
4. Organic solvent		better resistance " " "
5. Temperature range	$-40-100^{\circ}\text{C}$	$10-60^{\circ}\text{C}$
6. Elasticity		is greatly reduced.

Biodegradable Polymers

The polymers which are degraded upon disposal by the action of living organisms (fungi & microbial agents) are called biodegradable polymers. The microbial organisms degrade the polymer through metabolic or enzymatic process.

Though most commercial polymers in use today are non biodegradable, interest among the researchers is to develop cheap biodegradable polymers which can replace those non biodegradable polymers.

Biodegradable ^{synthetic} polymers mostly have functional groups prevalent in proteins, polysaccharides & lipids.

Classification of Biodegradable Polymers

(a) Naturally occurring biodegradable polymers fall into four broad groups.

- (i) Polysaccharides eg starch & cellulose.
- (ii) Proteins eg. gelatin, casein, silk, wool.
- (iii) Polyesters eg. polyhydroxyalkanoates.
- (iv) Others eg. lignin, shellac, natural rubber.

(b) Synthesized Biodegradable polymers There are many polymers produced from feed stocks derived from petrochemical or biological resources that are biodegradable.

- (i) Polyalkylene esters.
- (ii) Polylactic acid.
- (iii) Polyamide esters.
- (iv) Polyvinyl esters.
- (v) Polyvinyl alcohols.
- (vi) Poly anhydrides.
- (vii) Poly glycolic acid.
- (viii) Poly β -hydroxy butyrate.
- (ix) Polycaprolactone.

poly lactic Acid or PLA - It is prepared by the condensation of lactic acid.



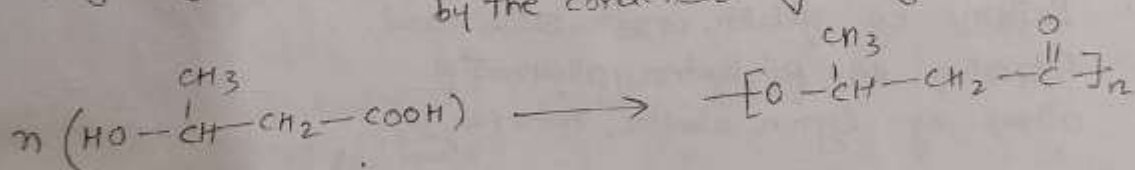
Properties

1. Its crystallinity, transparency & degradation rate depends on the composition of isomers of lactic acid.
2. PLA degrades primarily by hydrolysis, not by microbial attack.
3. It can be thermally processed with minimal changes to secondary-standard machinery.

Uses

1. PLA is currently used in packaging (film & short shelf life bottles).
2. used in formation of fibres for clothing & other uses.
- 3.

B-hydroxy butyrate - It is a biodegradable polyester formed by the condensation of B-hydroxy butyric acid.



Properties

1. Good ultra-violet resistance, but poor resistance to acids and bases.
2. Tensile strength close to that of polypropylene.
3. Less sticky when melted, making it a potentially good material for clothing in the future.

Uses

1. It is used as packaging material.
2. Orthopedic devices.
3. It is used as biodegradable plastic.