ELASTOMERS OR RUBBER

All rubbers and Rubber like materials are called Elastomers.

- They get elongated on application of force and return back to their original position when force is removed.
- Rubber consist of spring shapped chains.
- They have high degree of free rotation about the bond in the chain.

Natural Rubber

- It is a polymer of high molecular weight hydro-carbon known as isoprene.
- The isoprene is in the milky latex of rubber trees Hevea brasileensis
- During the treatment of latex, these isoprene molecules polymerize to form long chain polyisoprene.

$$\cdots - CH_2 - \overset{\overset{CH_3}{|}}{C} = CH - CH_2 - CH_2 - \overset{\overset{CH_3}{|}}{C} = CH - CH_2 - \cdots$$

Vulcanization of Rubber

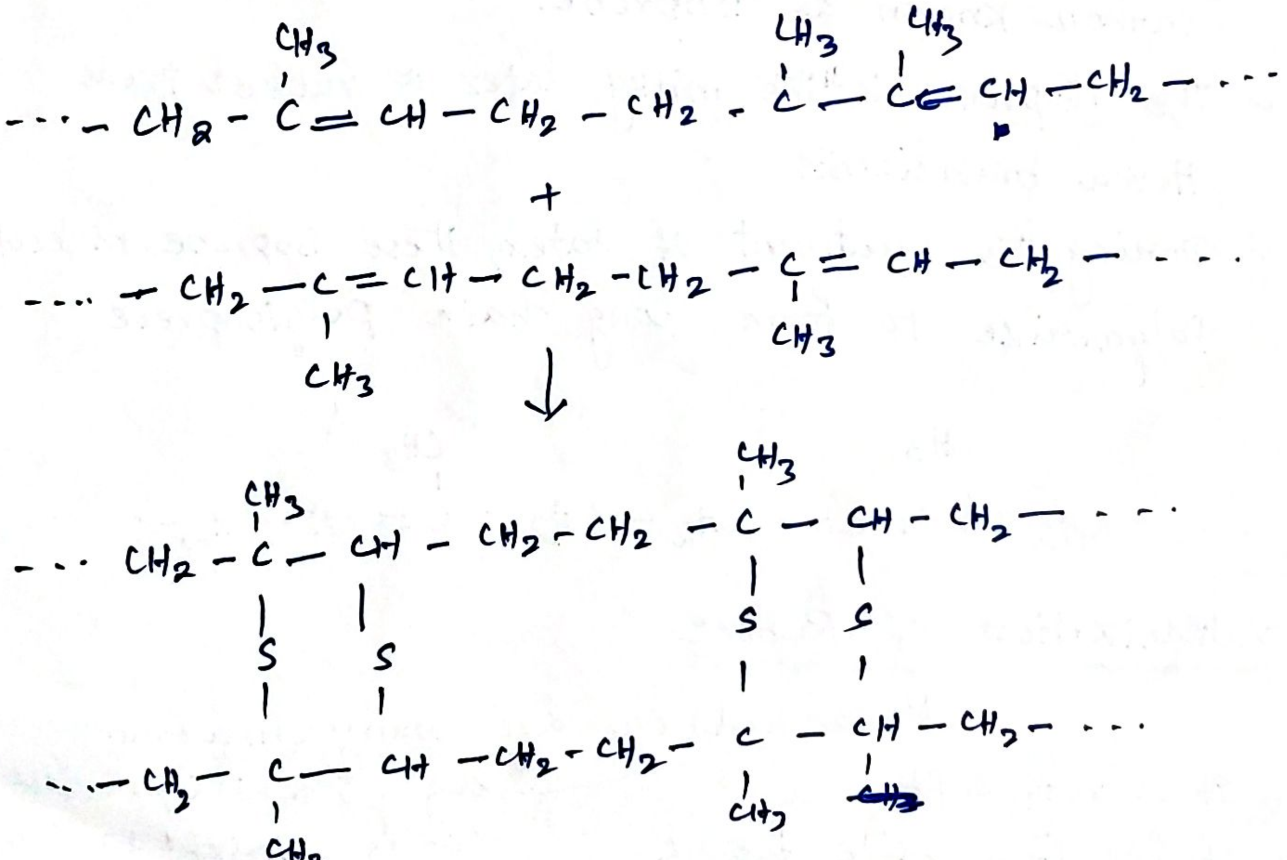
Raw Rubber has many disadvantages.

- It is very soft
- It has low tensile strength
- It swells in organic solvents and disintegrates gradually.
- high solubility in oils
- easily oxidized by HNO_3 & H_2SO_4

- ✓ It is easily soluble in non-polar solvents.
- ✓ It has little durability and suffers permanent deformation.

In order to rectify the above mentioned defects, Vulcanization of raw rubber is carried out.

- ✓ The raw rubber is compounded with chemicals such as sulphur, hydrogen sulphide and benzoyl chloride. Among all the chemicals sulphur is the important vulcanizing agent.
- ✓ When sulphur is heated with raw rubber at 110-140°C sulphur combines at the double bonds of different rubber layers and form cross-links (or) bridges between the layers.



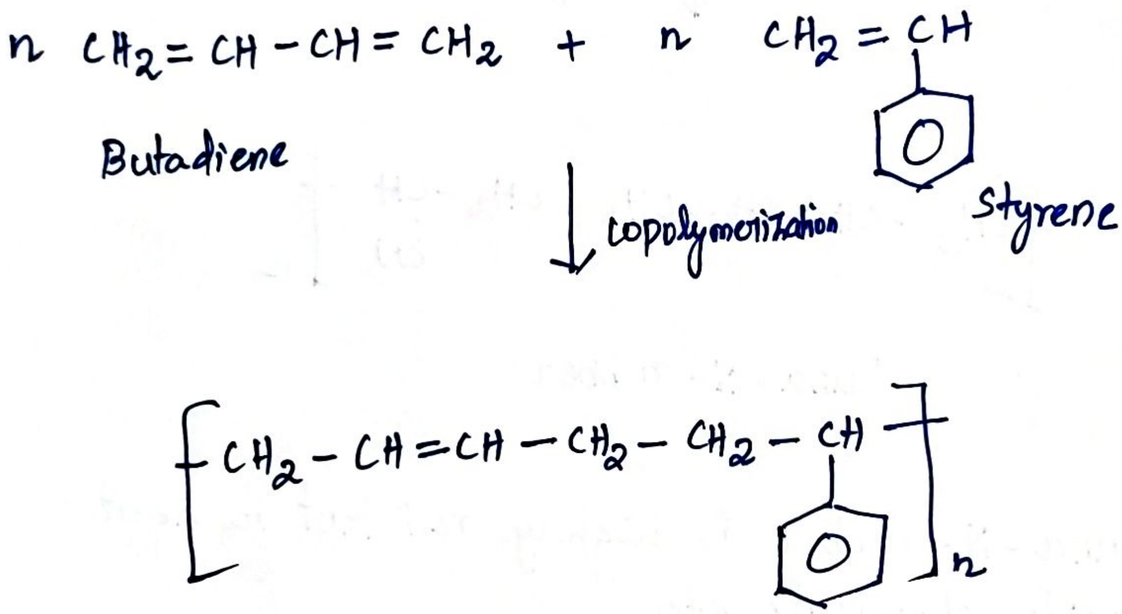
Vulcanized rubber.

Synthetic Rubbers

Synthetic rubbers are man-made rubbers. It is also called as artificial rubber.

(i) Styrene rubber or Buna-S-rubber

Buna-S-rubber is prepared by the copolymerization of butadiene (75%) and styrene (25%)



Buna-S-rubber

Properties

- ✓ It has high abrasion resistance
- ✓ high load bearing strength and resilience

Uses

* It is used for the manufacture of motor tyres.
* It is also used for making foot wear soles, gaskets, cable insulation, tank lining etc.

(ii) Nitrile rubber (or) Buna-N-rubber

Buna-N-rubber is prepared by the copolymerization of butadiene with acrylonitrile.

$$n\ CH_2{=}CH{-}CH{=}CH_2 \quad + \quad \underset{\displaystyle CN}{\overset{}{CH_2{=}\underset{|}{CH}}}$$

Butadiene

$$\Big\downarrow \text{copolymerization}$$

$$\left[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}} \right]_n$$

Buna-N-rubber

Properties:

Buna-N-rubber is highly resistant to heat, sunlight, acids, chemicals etc.

Uses:

It is used for making conveyer belts, aircraft components, tank linings, gaskets, adhesives etc.

(iii) Neoprene rubber

Neoprene rubber is produced by the addition Polymerization of chloroprene

$$n\ CH_2 - \overset{Cl}{\overset{|}{C}} - CH = CH_2] \xrightarrow{Poly} \left[CH_2 - \overset{Cl}{\overset{|}{C}} = CH - CH_2 \right]_n$$

chloroprene

Polychloroprene (Neoprene)

Properties

Neoprene is highly chemical resistant

Uses:

It is used for making hoses, gaskets, conveyor belt and tubing for corrosive oils and gas.

CONDUCTING POLYMERS

In 1977, in the plastic research Laboratory of BASE, Germany, a chemist by the name Shirakawa accidently discovered the conducting polymer.

During his experiment on polymerization reaction of acetylene, he mistakenly added a catalyst thousand times more than the required amount which resulted in a conducting polyacetylene.

organic polymer having conductance of the order of conductors are called as conducting polymers.

Classification of conducting polymers:

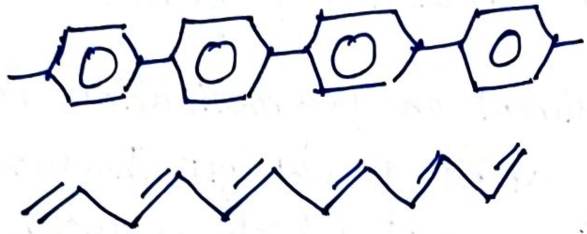
conducting polymers are classified into two types they are

i) Intrinsically conducting polymers and
ii) Extrinsically conducting polymers.

i) Intrinsically conducting polymers.

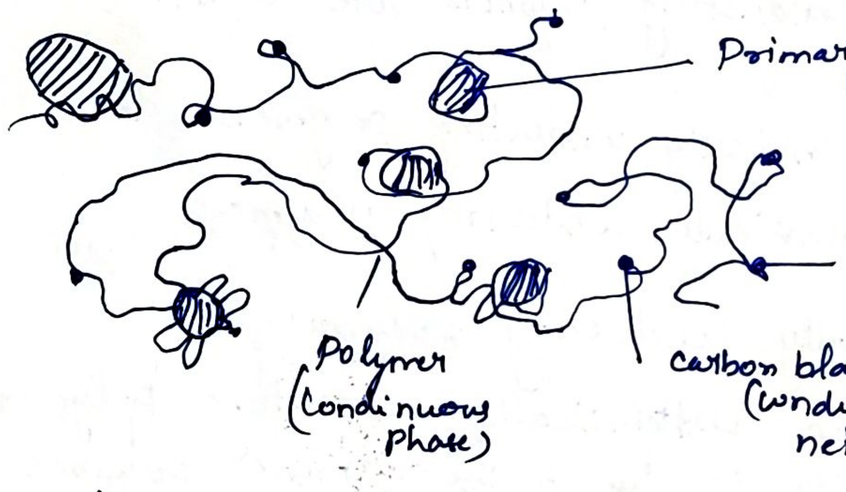
In Intrinsically conducting polymer the conductivity is due to the organic polymer themselves. They conduct electricity when dopped with oxidizing or reducing agents. The requirement for organic polymer to be conducting is the formation of continuous conjugation (alternate single and double bonds) through the polymer chain. The pi electrons are normally localised and donot take part in conductivity. However these electrons delocalise when dopant like oxidizing or reducing agents and protonic acids are added.

example



(ii) Extrinsically conducting polymers.

Extrinsically conducting polymers are prepared by mixing conducting fillers like metal fibers, metal oxides carbon black with insulating polymers. These are also called as conductive element filled polymers.



Electronic Behaviour of conducting polymer.

The electronic behaviour of conducting polymers are due to

1) Delocalization of conjugated π electrons
2) Incorporation of dopants in the polymer.

(ii) Incorporation of Dopants in the polymer.

Adding oxidizing or reducing agents in the structure of semiconducting polymer is known as doping.

There are two types of doping. They are.

(i) p-doping (electron acceptor) (or) oxidation doping.

(ii) N-doping (electron donor) or reduction doping.

P-Doping

- ✓ The oxidation method is used to perform p-doping.
- ✓ In p-doping the conducting polymer is treated with Lewis acids, which causes oxidation and the formation of positive electrons on the polymers backbone.
- ✓ The oxidation process produces a delocalized radical ion known as "polaron"
- ✓ A subsequent oxidation of this polaron, accompanied by radical recombination results in the formation of two mobile positive charges on the carbon chain. These delocalized positive charges act as current carriers.

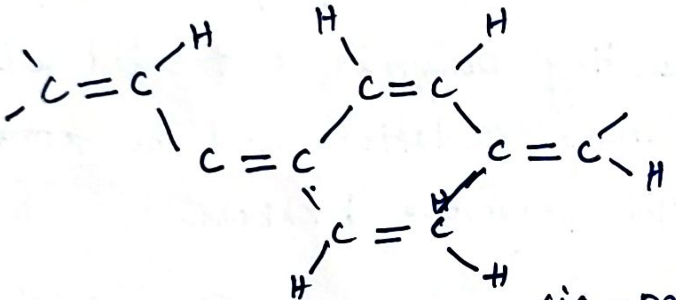
$$\text{Polymer} + X\ (\text{donor}) \longrightarrow (\text{Polymer})^{n+} + X^{n-}$$

where $X = I_2, Br_2, AsF_5, HClO_4$ etc.

i) Delocalisation of conjugated π Electrons.

Organic polymers have highly delocalised π electron system. These π electrons are responsible for conduction in the organic polymers.

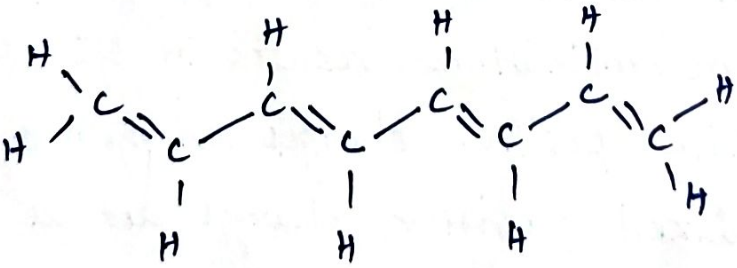
When an electron is excited to a free state, a positive hole is left behind in the molecule. These holes and the electrons are responsible for the conduction process.



→ conductivity of $1.7 \times 10^{-9}\ ohm^{-1}\ cm^{-1}$

cis-polyacetylene

$\Delta \downarrow 200^\circ C$



→ conductivity $4.4 \times 10^{-9}\ ohm^{-1}\ cm^{-1}$

Trans polyacetylene

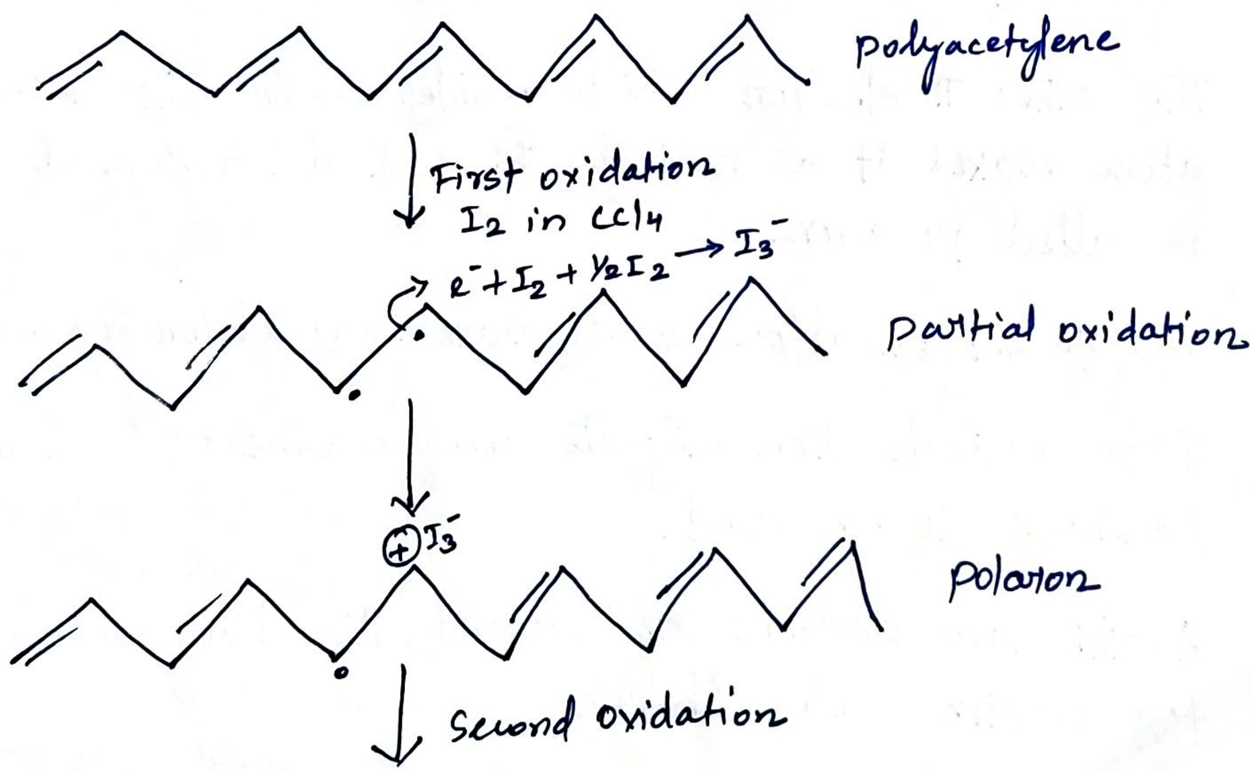
N - Doping

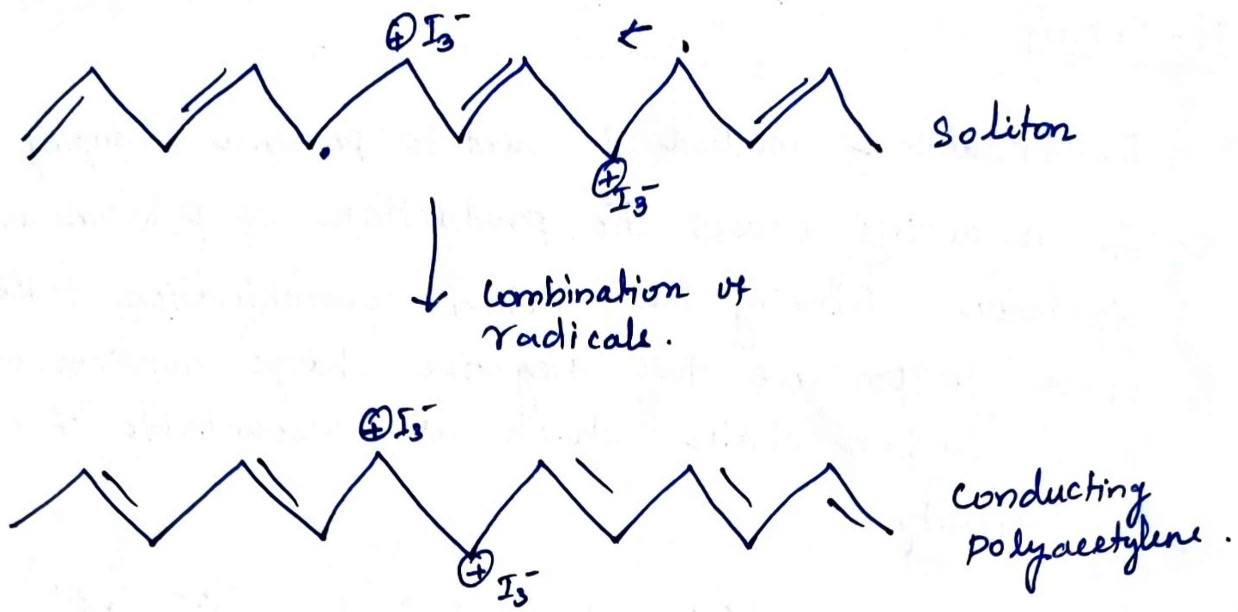
- The reduction method is used to perform n-doping.
- The n-doping causes the production of polaron and bipolaron. Following this radical recombination takes place to produce two negative charge carriers on each carbon chain which are accountable for conductivity.

$$\text{Polymer} + M\ (\text{donor}) \longrightarrow (\text{polymer})^{n-} + M^{n+}$$

where x = Li, Na etc.

Conductivity in polyacetylene





* When the oxidative dopant, such as I_2 is added, it takes away an electron from the π-backbone of the polyacetylene chain. This creates positive centre (hole) on one of the carbon.

* The other π electron which resides on the other carbon atom makes it a radical. The radical ion formed is called polaron.

* On further oxidation, a dipolaron (or) soliton is formed.

* These radicals then migrate and combine to form a backbone double bond.

* As the two electrons are removed, the chain will have two positive center (holes).

* The positive holes are mobile. When a potential is applied, the positive holes migrate from one carbon to another.

* The migration of positive holes account for the conductivity

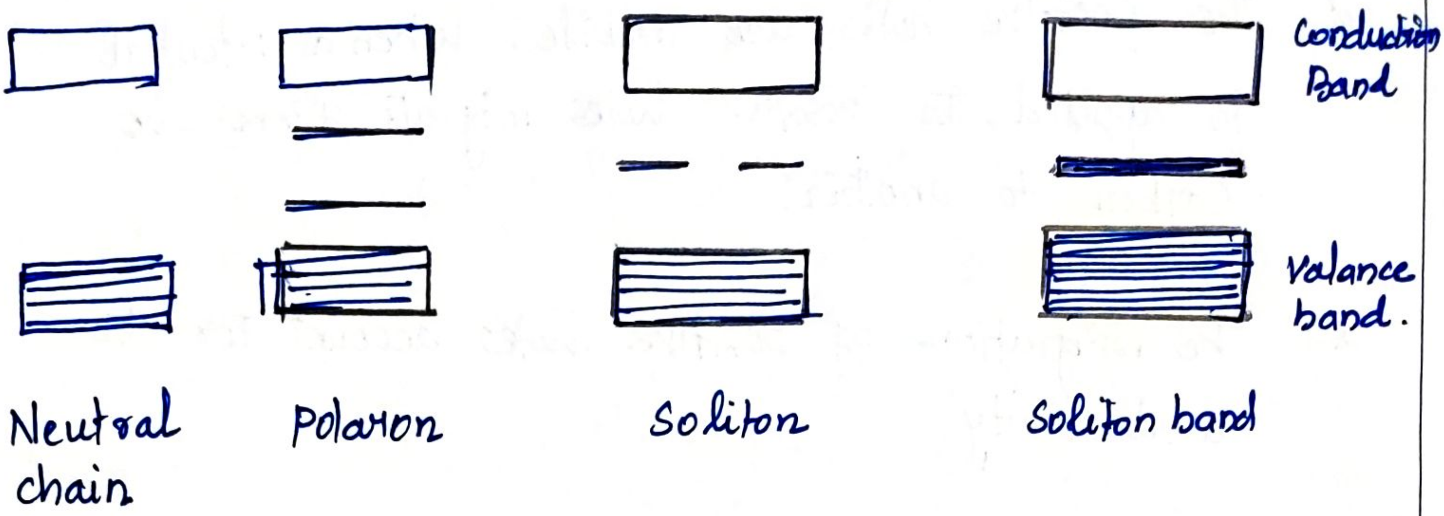
* When a π bond is formed, Valence Band (VB) and conduction Band (CB) are created.

* Before doping, there is sufficient energy gap between VB and CB, so that the electrons remain in VB and the polymer is an insulator.

* When dopant is added, polarons and solitons are formed resulting in the creation of new localized electronic states that fill the energy gap between VB and CB.

* When sufficient solitons are formed, a new mid gap energy band is created which overlaps with the VB and CB allowing electrons to flow.

* The charged solitons are responsible for making polyacetylene conducting in nature.


Conduction Band
Valance band.
Neutral chain
Polaron
Soliton
Soliton band