

## 6.13. NATURAL AND SYNTHETIC RUBBER

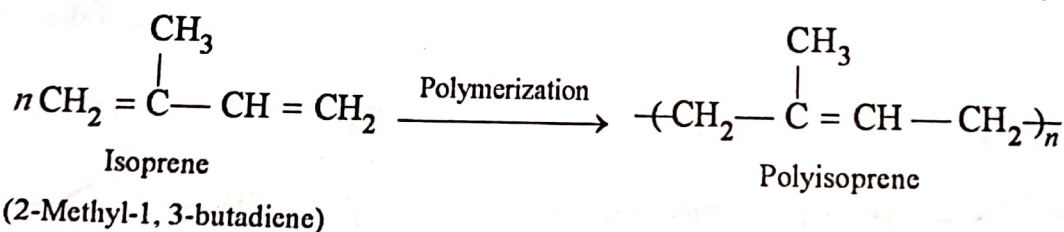
During the last 5-6 decades, the demand for rubber has increased tremendously. Therefore, apart from natural rubber a number of synthetic varieties of rubber have also been developed.

A brief description of the chemistry of natural and synthetic rubbers is given below :

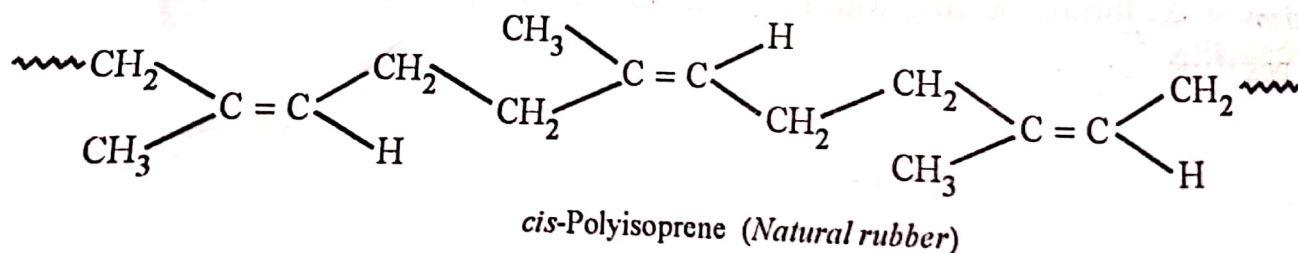
### 6.13.1. NATURAL RUBBER

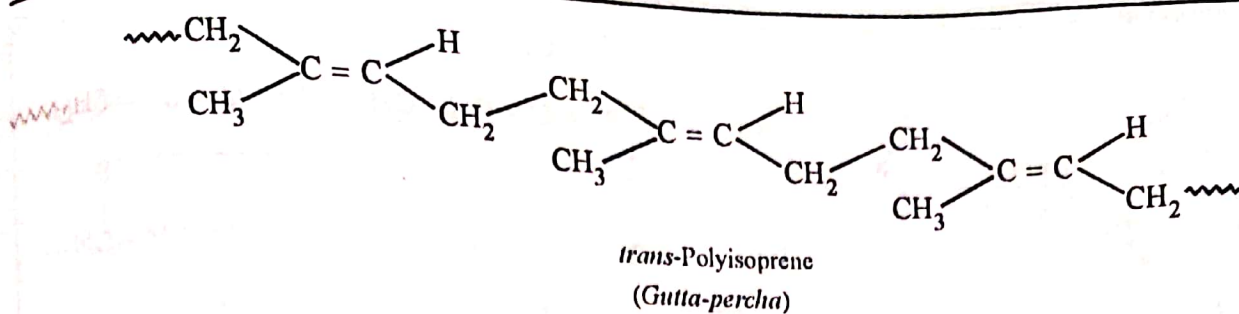
It is a natural polymer which is obtained from *latex*. Latex is a milky fluid which exudes from the rubber tree (*Hevea brasiliensis*) when an incision is made in the bark of the rubber trees found in tropical and semitropical countries such as Southern India (Kerala, Tamil Nadu, Karnatka, etc.), Indonesia, Malaysia, Sri Lanka, South America, etc. Latex is a colloidal solution of rubber particles (30-40%) which is coagulated by adding salts and acetic acid. The coagulated material is passed through rollers to make sheets.

**Structure.** Chemically, natural rubber is a 1, 4-addition, polymer of isoprene (*i.e.* 2-methyl-1, 3-butadiene)



Since each repeating unit in polyisoprene contains a double bond, it may have either a *cis*- or a *trans*-orientation. Actually, in natural rubber, all the double bonds have *cis*- stereochemistry. In other words, *natural rubber is cis-polyisoprene*. In contrast, synthetic rubber (*gutta percha*) obtained by free radical polymerization of isoprene has all *trans*-configuration.

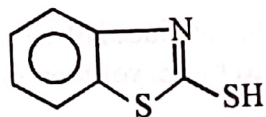




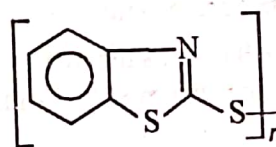
### 6.13.2. VULCANIZED RUBBER

Inspection of the structure of natural rubber reveals that there are no polar groups/substituents and hence intermolecular forces of attraction are only weak van der Waals interactions. These forces are further weakened because of the *cis*-configuration of all the double bonds which does not allow the polymer chains to come close enough for effective interactions. Thus, *cis*-polyisoprene does not have a straight chain but has a coiled structure. As a result, it can be stretched like a spring. On stretching, the molecules become partially aligned, w.r.t. each other and on withdrawing the force, the chains come back to their original coiled state.

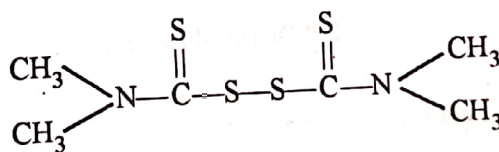
Natural rubber is soft and tacky and becomes even more so at high temperatures and brittle at low temperatures. Therefore, rubber is generally used in the temperature range 283-335 K where its elasticity is maintained. It has a large water absorption capacity, has low tensile strength and resistance to abrasion. It is also not-resistant to the action of organic solvents and is also easily attacked by oxidising agents. These properties can be improved markedly by a process called vulcanization. It consists of heating raw rubber with sulphur at 373-415 K. Since this process is slow, therefore, additives like zinc oxide, 2-mercaptobenzothiazole, 2, 2'-dithiobisbenzothiazole, tetramethylthiuram disulphide, etc.



2-Mercaptobenzothiazole



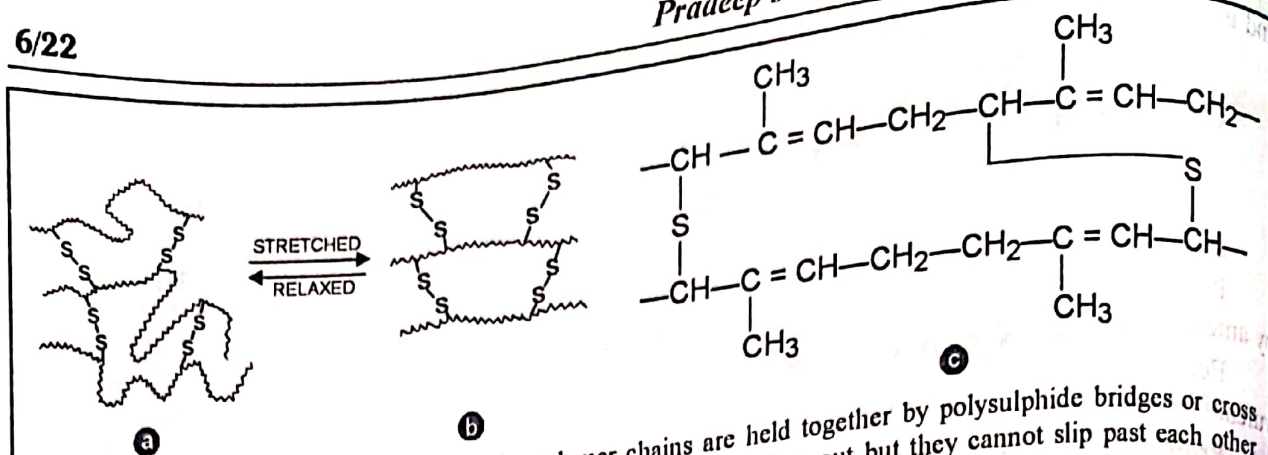
2, 2'-Dithiobisbenzothiazole



Tetramethylthiuram bisulphide

are used to accelerate the rate of vulcanization. The vulcanized rubber thus obtained has excellent elasticity, low water absorption tendency and resistant to the action of organic solvents and oxidising agents. During vulcanization, sulphur bridges or cross-links between polymeric chains are introduced through their reactive allylic positions (Fig. 6.2).





**FIGURE 6.2.** (a) In vulcanized rubber, the polymer chains are held together by polysulphide bridges or cross links. (b) When the stretching force is applied, the chains can straighten out but they cannot slip past each other because of polysulphide bridges. When the stretching force is withdrawn, the chains tend to coil up again and the rubber returns to its original shape. (c) Sulphur cross links at reactive allylic sites.

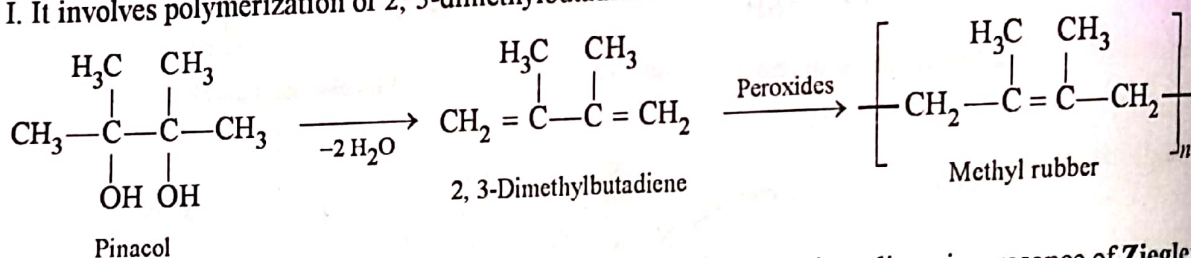
These cross links make rubber hard and stronger and remove the tackiness of natural rubber since the individual chains can no longer slip over the other but are instead locked together in a giant size molecule. The extent of hardness or toughness, however, depends upon the amount of sulphur added. Thus, about 5% sulphur is used for making tyre rubber, 20-25% S for making battery case rubber. The process of vulcanization was discovered by Charles Goodyear in 1839.

### 6.13.3. SYNTHETIC RUBBER

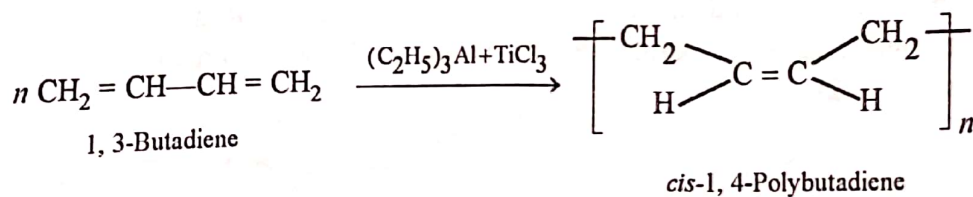
To improve the qualities of natural rubber and to meet the ever increasing demands of mankind, a number of forms of synthetic rubber have been prepared.

Majority of these rubbers are derived from butadiene derivatives and contain carbon-carbon double bonds so that they can also be vulcanized. Thus, synthetic rubbers are either homopolymers of 1, 3-butadiene or its derivatives or are copolymers in which one of the monomers is 1, 3-butadiene. Some important forms of synthetic rubbers are : Methyl rubber, *cis*-Polybutadiene, Buna-S, Buna-N, Neoprene and Butyl rubber.

**1. Methyl rubber.** This was the first commercial synthetic rubber produced by Germany during World War I. It involves polymerization of 2, 3-dimethylbutadiene obtained by dehydration of pinacol.

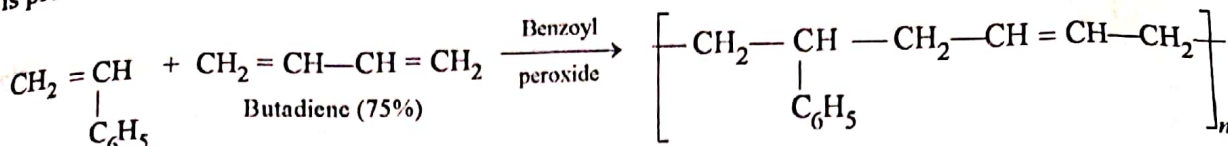


**2. *cis*-Polybutadiene and *cis*-polyisoprene.** Polymerization of 1, 3-butadiene in presence of Ziegler-Natta catalyst (*i.e.* a mixture of triethylaluminium and titanium trichloride or tetrachloride) gives *cis*-polybutadiene in which 1, 4-addition occurs in each butadiene molecule and the remaining double bonds are all *cis*. This polymer has properties similar to those of natural rubber and it can be vulcanized in the same way.



Similarly, all *cis*-polyisoprene can be prepared by Ziegler-Natta polymerization.

3. Styrene-butadiene rubber, SBR, Buna-S. It is a copolymer of butadiene (75%) and styrene (25%) and is produced by free-radical polymerization.



Styrene (25%)

Styrene-butadiene rubber (SBR).

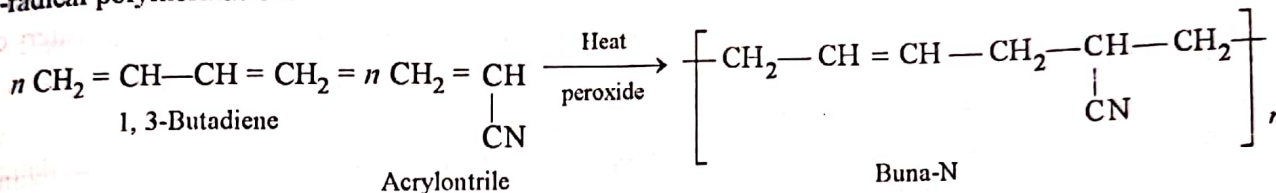
It is also called Buna-S (Bu = butadiene, na = natrium, S = styrene) because originally it was prepared by anionic copolymerization of butadiene and styrene in presence of sodium.

Because of the presence of double bonds, physical properties of SBR can be further improved by vulcanization.

**Properties and uses.** It is very tough and is a good substitute for natural rubber. It possesses high abrasion-resistance, high load bearing capacity and is used for the manufacture of auto tyres. It is also used for making floor tiles, footwear components, cable insulations, etc.

Bubble gum contains styrene-butadiene polymer.

4. Buna-N or Nitrile rubber. It is a copolymer of 1, 3-butadiene and acrylonitrile and is prepared by free-radical polymerization.



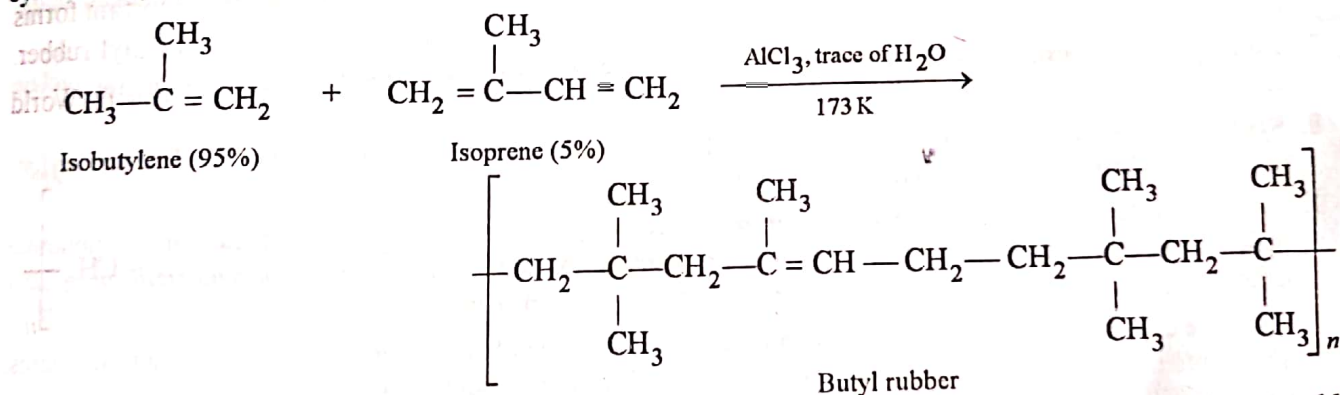
1, 3-Butadiene

Acrylonitrile

Buna-N

**Uses.** It is used in making oil seals, manufacture of hoses and tank linings.

5. Butyl rubber. It is an addition copolymer of isobutylene (95%) and isoprene (5%) and is prepared by cationic polymerization.



Isobutylene (95%)

Isoprene (5%)

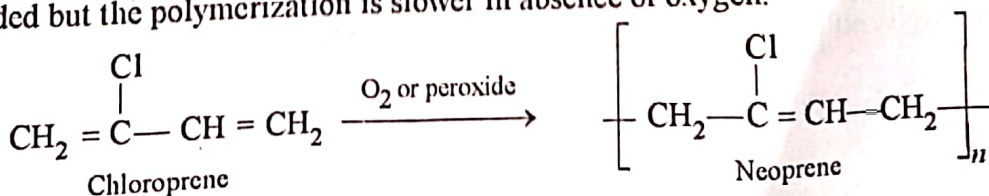
Butyl rubber

**Properties and uses.** The mechanical strength and resistance to abrasion can be further improved by vulcanization.

Butyl rubber is used to make automobile inner tubes and tyre liners.

6. Neoprene. It is a polymer of chloroprene, *i.e.*, 2-chloro-1, 3-butadiene.

**Preparation.** Chloroprene polymerises very readily (700 times faster than isoprene). No specific catalysts are needed but the polymerization is slower in absence of oxygen.

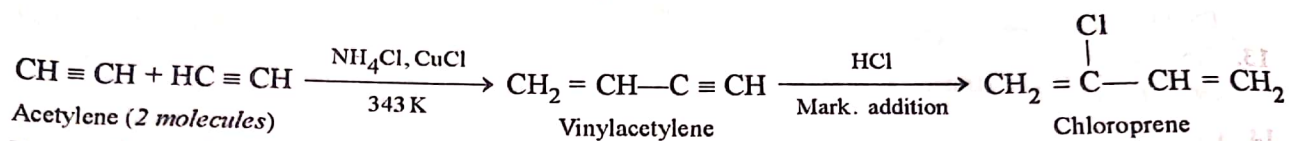


Chloroprene

Neoprene



Chloroprene needed for the purpose is obtained by the addition of HCl to vinylacetylene in accordance with *Markovnikov's rule*. Vinylacetylene itself, is prepared by dimerization of acetylene by passing it through an aqueous solution of ammonium chloride and cuprous chloride at 343 K.



**Properties and uses.** Neoprene is inferior to natural rubber in some properties but superior in its stability to aerial oxidation and in its resistance to oils, gasoline and other solvents. It is, therefore, used in the manufacture of hoses, shoe heels, stoppers, etc. It is also used as an insulator and for making conveyor belts and printing rollers.