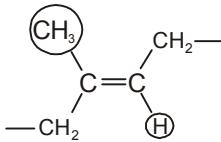


Here  $\text{CH}_3$  group and the H atom are positioned on the same side of the double bond. This is termed a **cis** structure, and the resulting polymer, cis-polyisoprene, is natural rubber shown in Fig.10.7.

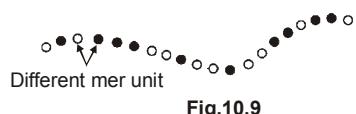


The **trans** structure, the  $\text{CH}_3$  and H reside on opposite sides of the double bond. Trans-polyisoprene, sometimes called gutta percha, has properties that are distinctly different from natural rubber as a result of this configurational alteration shown in Fig 10.8.

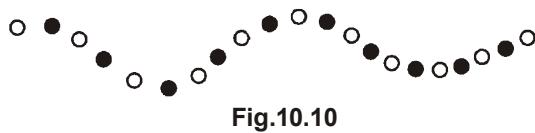
## 10.5 COPOLYMERS

Here different type of mer synthesised for obtaining better properties compared to homopolymers. Various sequencing arrangements along the polymer chains are possible. They are :

- ◀ **Random**



- ◀ **Alternating**



- ◀ **Block**

Identical mers are illustrated in blocks along the chain



Synthetic rubbers, are often copolymers; chemical repeat units that are employed. Styrene-butadiene rubber (SBR) is a common random copolymer from which automobile tyres are made. Nitrile butadiene rubber (NBR) is another random copolymer composed of acrylonitrile and butadiene. It is also highly elastic and, in addition, resistant to swelling in organic solvents; gasoline hoses are made of NBR.

## 10.6 POLYMER CRYSTALLINITY

### Crystallinity of Polymers

Polymers are normally partially crystalline. There will be crystalline regions dispersed within the remaining amorphous polymers. The degree of crystallinity of a polymer is controlled by amorphous polymers and by the fabrication processes. The density of crystalline polymers is greater than the totally amorphous polymer. The degree of crystallinity may be measured in terms of the density difference, as

$$\% \text{ crystallinity} = \frac{\rho_c (\rho_s - \rho_a)}{\rho_s (\rho_c - \rho_a)} \times 100$$

where  $\rho_a$  is the density of the totally amorphous polymer

$\rho_c$  is the density of the totally crystalline polymer

$\rho_s$  is the density of the partially crystalline polymer whose crystallinity is to be determined. It is easier to obtain high percent crystallinity in linear polymers than in branched or cross-linked polymers. In cross-linked polymers, the primary bond bridges between chains prevent easy alignment to form single crystals. Crystalline polymers are usually stronger and have higher softening temperatures than their amorphous counterparts.

- ◀ Linear polymer are easily crystallized as compared to branched polymers, as branches interfere in crystallization with regard to stereo-isomerism. Atactic polymers are difficult to crystallize because of random configuration.
- ◀ For copolymers, as a general rule, the more irregular and random the mer arrangements, the greater is non crystallinity.
- ◀ In general, the degree of crystallinity achievable in a solid polymer depends on the size of its molecules and the complexity of their basic shape.

**Example:** The unit cell of polyethylene molecules has an orthorhombic geometry. As a result to their large size and complexity, polymer molecules are only partially crystalline, having crystalline regions dispersed within the remaining amorphous material. Any chain disorder will result in an amorphous region since twisting and bending prevent strict ordering of chains.

### Degree of Polymerization

The degree of polymerization represents the average number of mer units in a molecular chain. There are two ways of specifying the degree of polymerization.

(I) Number average polymerization

(ii) Weight average polymerization.

Number average polymerization is given by

$$n_n = \frac{\bar{M}_n}{m}$$

where  $\bar{M}_n$  is the number average molecular weight and  $m$  is the average mer molecular weight defined by

$$m = \sum_j f_j m_j$$

$f_j$  is the chain fraction of mer  $j$  and  $m_j$  is the molecular weight of mer  $j$ .

Weight average polymerization is given by

$$n_w = \frac{\bar{M}_w}{\bar{m}}$$

where  $\bar{M}_w$  is the weight average molecular.

Table 10.1

Mol. wt.	State of polymer
> 100 g/mol	Liquids or gases
1000 g/mol	Waxy Solids or soft resins
<10,000 g/mol	Solid

## 10.7 POLYMERIZATION

The synthesis of larger molecular weight polymers is known as polymerization. It is the process by which monomer units are joined over and over to generate giant molecules. The reaction by which polymerization occur are grouped into two classification—

- (i) **Addition Polymerization:** It is a process by which monomer units are attached one at a time in chainlike fashion to form a linear macromolecule. There must be at least one double bond in the monomer. Generally, thermoplastic are made by this process (exception Nylon, PEEK etc.).
- (ii) **Condensation Polymerization:** It is the formation of polymer by stepwise inter molecular chemical reactions. There is usually a small molecular weight by product such as water that is eliminated. Generally, thermosetting are made by this process.

## 10.8 CLASSIFICATION OF POLYMERS

- (i) Plastics and resins
  - (a) Thermoplastics
  - (b) Thermosetting
- (ii) Rubber or elastomers
- (ii) Fibres

### 10.8.1 Plastics

Plastics are basically of two types which are as follows:

#### Thermoplastic

Thermoplastic materials are those which soften on the application of heat with or without pressure, but then require cooling to set them to shape.

They can be heated and cooled number of times, only they should not be heated above their decomposition temperatures.

- These polymers are primarily include long chain straight or slightly branched molecules and the chains are held close to each other by secondary weak forces like van der Waal's forces. During heating, as the temperature increases the secondary forces are reduced and the sliding of these long chain molecules can easily occur one over the other at a reduced stress level.
- They are highly plastic and are easy for moulding or shaping.
- They have low melting temperatures and are not so strong as the thermosetting plastics.
- Since they can be repeatedly used, they have a resale value.
- Some commercial thermosetting resins have three-dimensional molecular structure and have very high molecular weights.
- They can be recycled
- Here bond between the polymer chain are weak secondary bonds.

### 10.8.2 Thermosetting

Thermosetting materials are those plastics which require heat and pressure to mould them into shape.

- They cannot be resoftened once they have set and hardened.
- They are ideal for moulding into components which require rigidity, strength and some resistance to heat.
- In general, resins formed by condensation are thermosetting.
- Thermosetting resins have three-dimensional molecular structure and have very high molecular weights.
- Here mer are joined more than one direction with several branches.