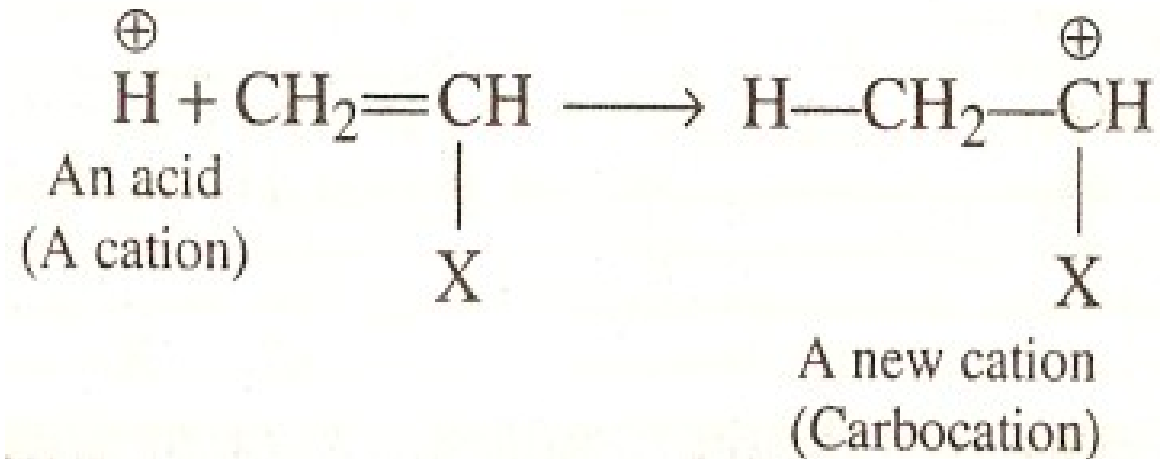


# POLYMERS

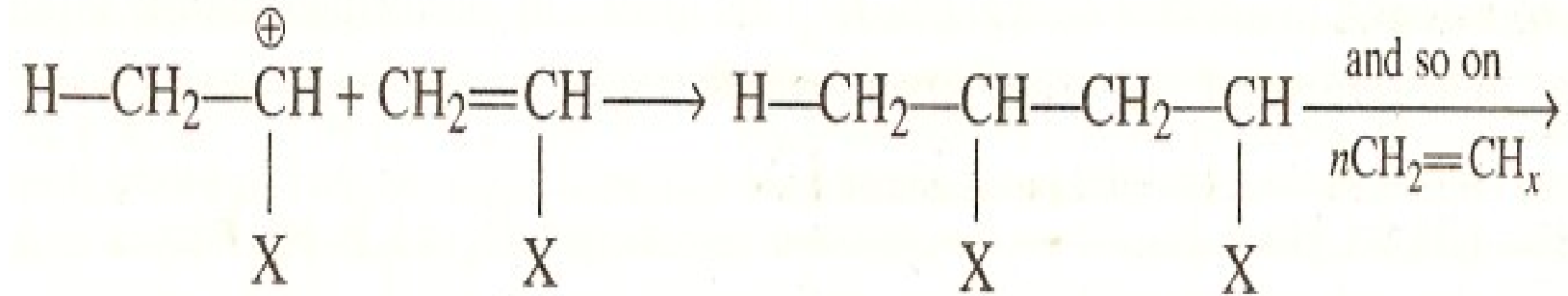
**(ii) Cationic Polymerization:** Cationic polymerization is initiated by acids and involves carbocationic centres. Monomers with electron-releasing substituents such as alkoxy or phenyl groups readily undergo this type of polymerization. The mechanism is as follows:

**Initiation:**

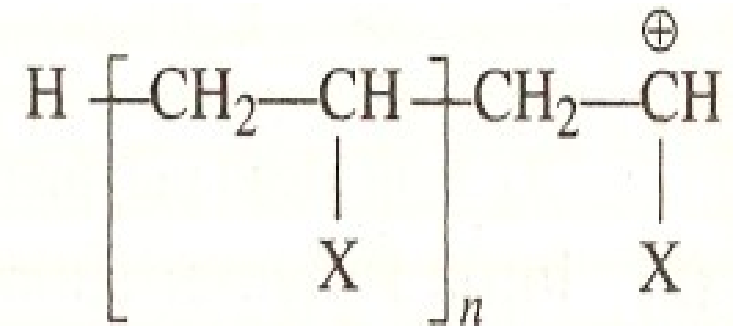


# POLYMERS

**Propagation :**

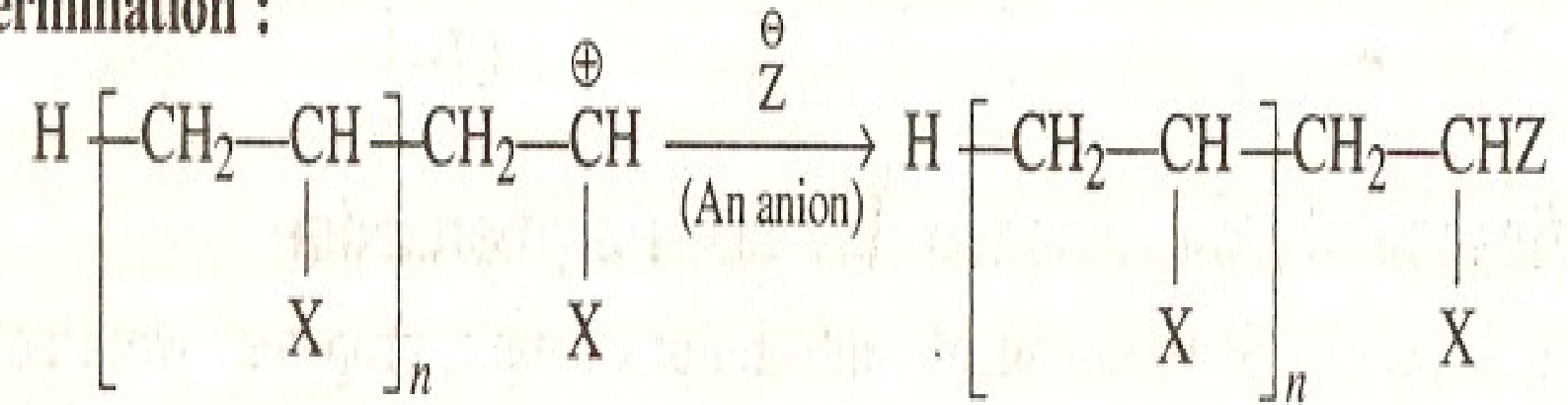


A new cation



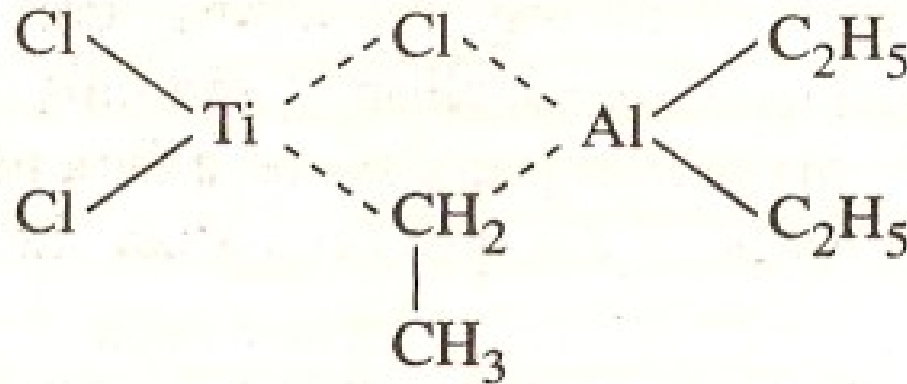
# POLYMERS

Termination :



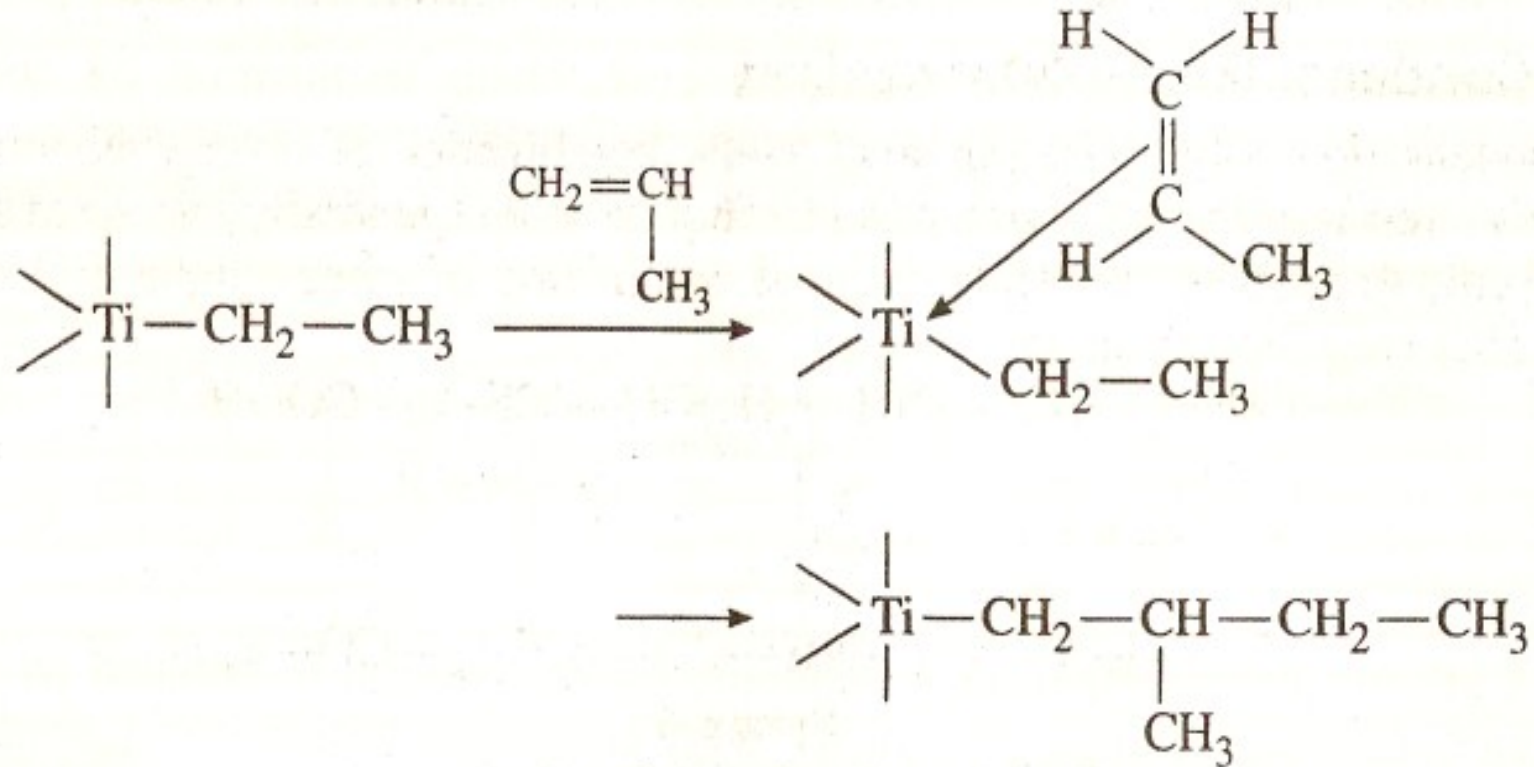
# POLYMERS

**(c) Co-ordination Polymerization :** Co-ordination addition polymerization are catalysed by a catalyst known as zeigler-Natta catalysts formed between triethyl aluminium  $\text{Al}(\text{C}_2\text{H}_5)_3$  and titanium halide  $\text{TiCl}_3$ . A co-ordination complex is formed between these two, in which the ethyl group is co-ordinated to titanium, this is an active catalyst and its structure is as :



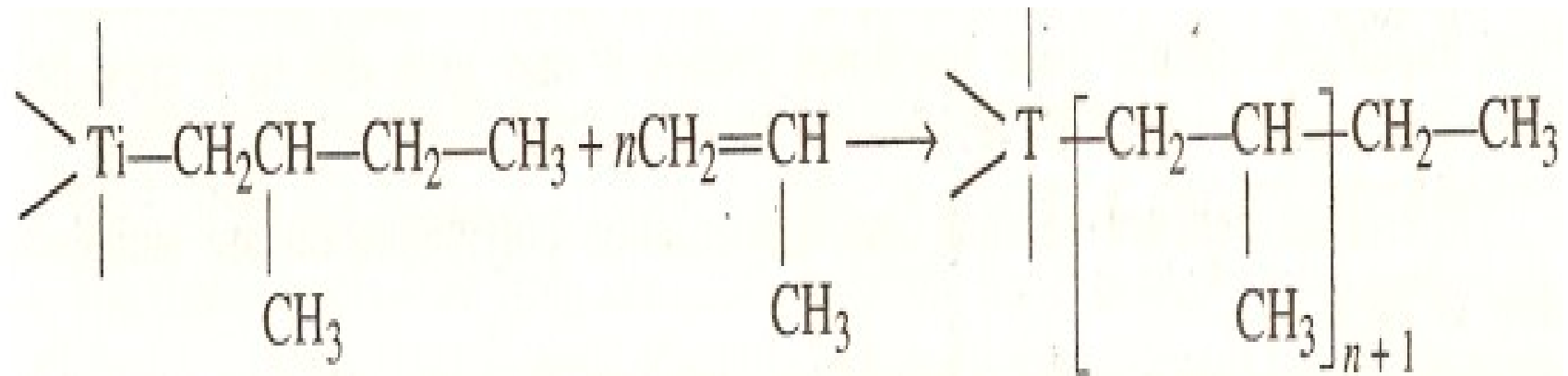
# POLYMERS

**Initiation:** In the initiation step,  $\pi$ -cloud of alkene overlaps with an empty orbital of titanium, then there is insertion of alkene molecules between the Ti-C bond.



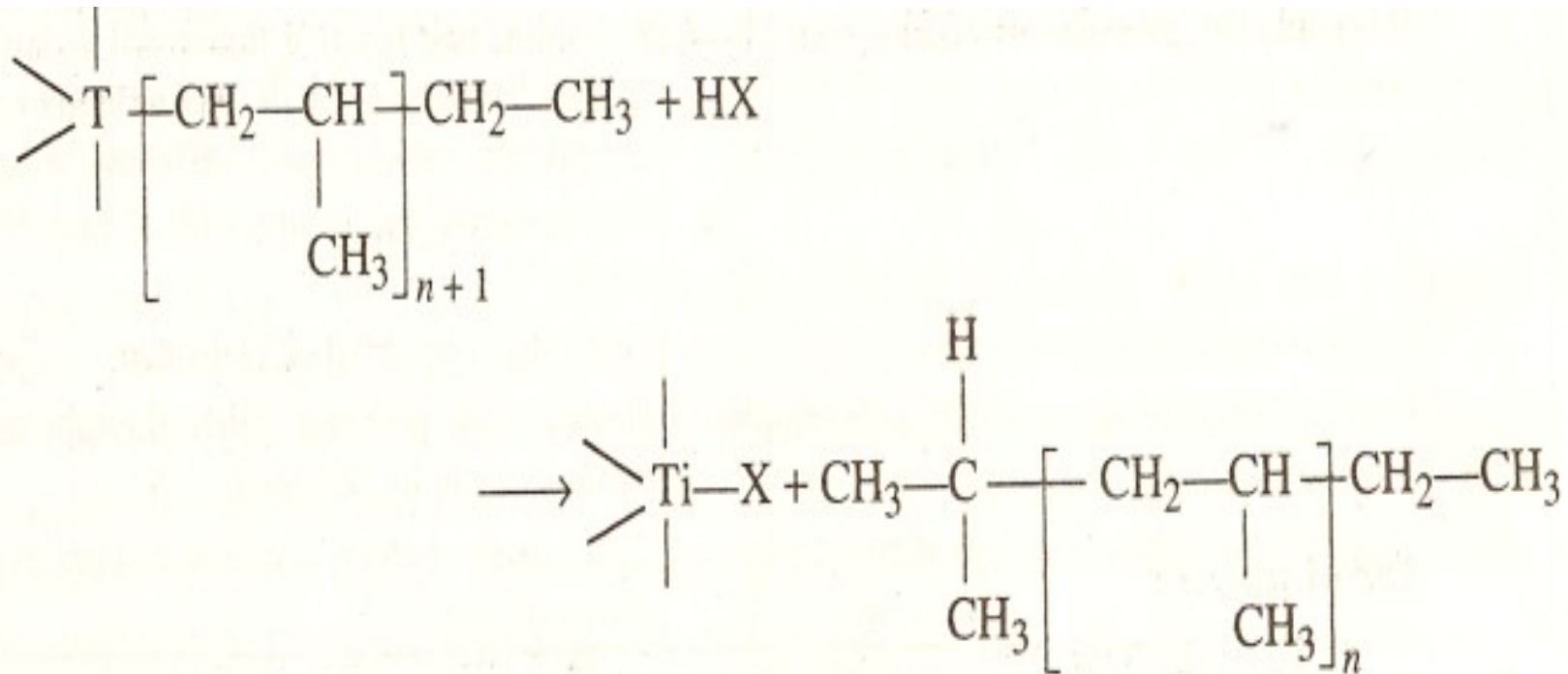
# POLYMERS

**Propagation:** As intermolecular rearrangement again generates a vacant site on titanium, each time one monomer molecule can be added in the same fashion.



# POLYMERS

**Termination:** It can be done by the addition of molecules containing active hydrogen like HX.

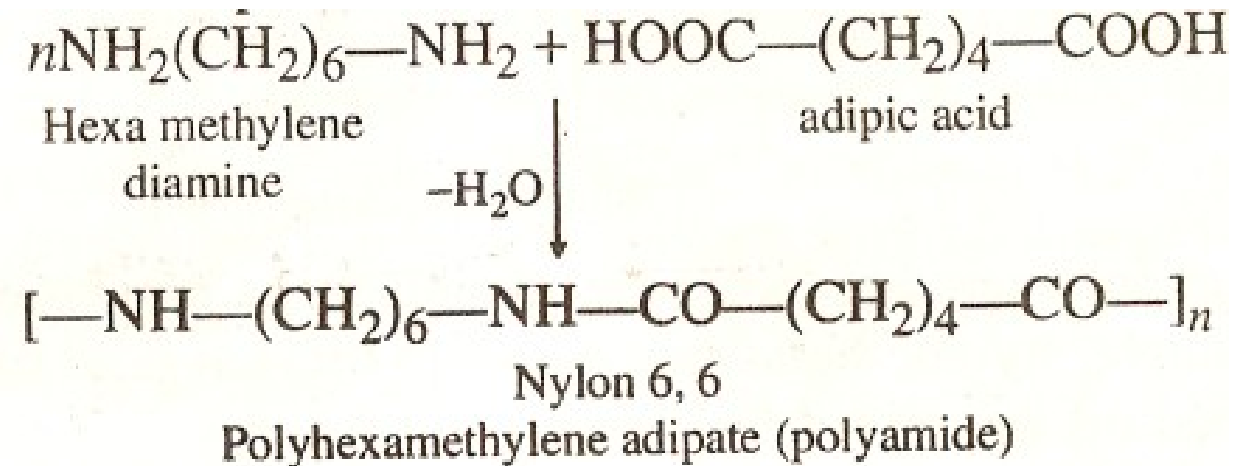


# POLYMERS

## 2. Condensation Polymerization :

Condensation polymerization involves the combination of several monomers to one another as a result of the migration of some mobile atom (generally hydrogen atom) from one molecule to another molecule with the elimination of some simple molecules (such as H<sub>2</sub>O, HCl etc.).

### Example :

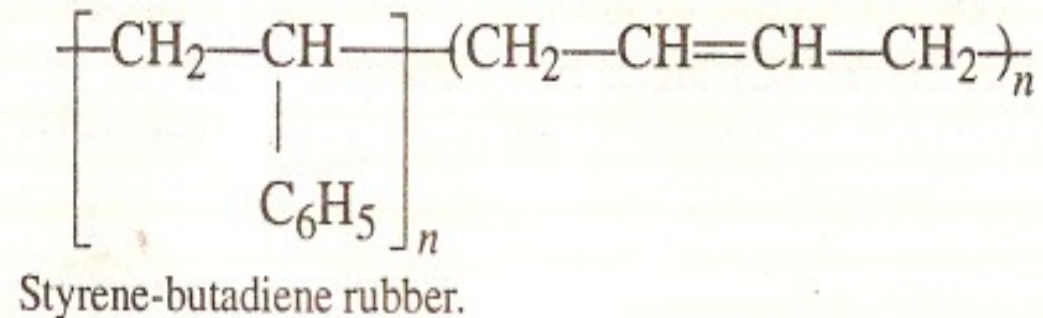
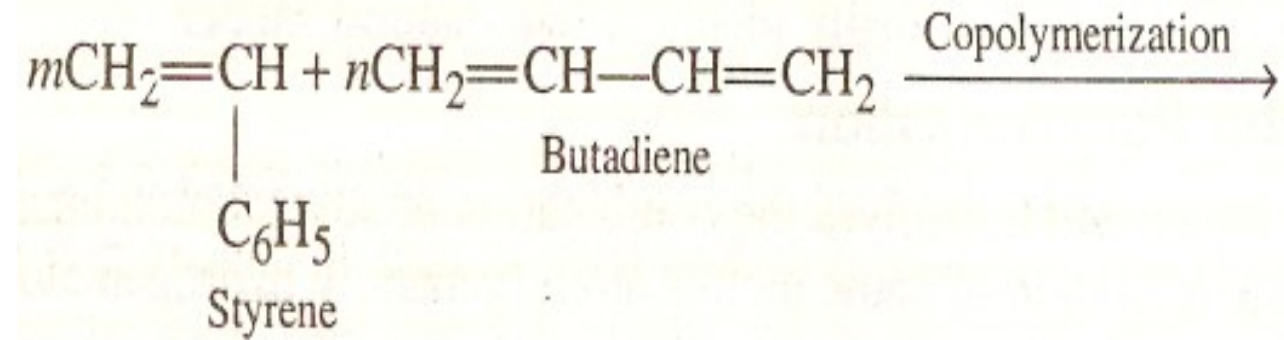




# POLYMERS

**3. Copolymerization :** Copolymerization has been used by nature in polypeptides which may contain as many as 20 different amino acids. Copolymerization is a polymerization of two or more monomeric species together.

**Example :**



# POLYMERS

## Natural Rubbers :

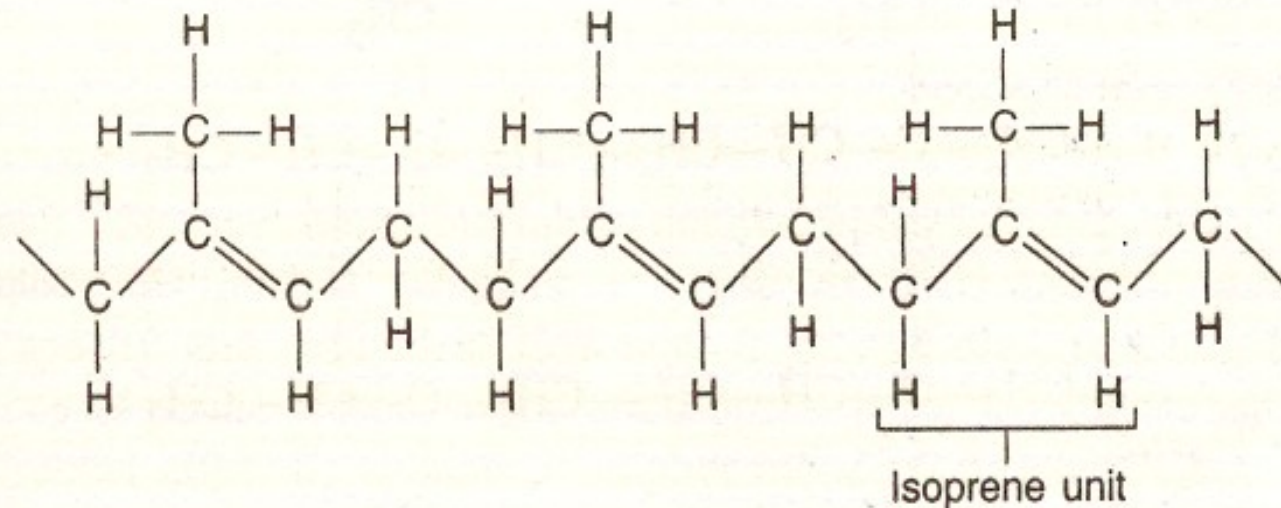
### 1. Caoutchouc or Hevea Rubber :

The main source from which the commercial natural rubber is obtained is the tree *hevea braziliensis*, The rubber is obtained from latex collected from the cuts made in the bark of the tree, The latex contains 25% to 40% of rubber hydrocarbon along with other impurities, such as fatty acids, proteins, resins, etc. The latex is treated with an acid such as acetic acid which coagulates the Crude rubber. The crude rubber is composed of 90-95% of rubber hydrocarbon, 2-4% of protein and 1 to 4% of resins. On destructive distillation, rubber gives isoprene as the main product which led to the suggestion that rubber is a polymer of isoprene,  $C_5H_8$  and hence can be represented  $(C_5H_8)_n$ .

# POLYMERS

**2. Gutta percha :** It is obtained from the mature leaves of *dichopsis gutta* and *palagum gutta* trees. Gutta percha may be recovered by solvent extraction, when insoluble resins and germs are separated. Alternatively, the mature leaves are ground carefully; treated with water at about 70°C for half an hour and then poured into cold-water when gutta percha floats on water surface and is removed.

**Structure :**



# POLYMERS

## **Properties:**

1. At room temperature, gutta percha is horny and tough, but it softens at about 100°C.
2. It is soluble in aliphatic hydrocarbons, but insoluble in aromatic and chlorinated hydrocarbons.
3. Structurally it is trans-poly-isoprene.

## **Uses:**

1. In the manufacture of golf-ball covers.
2. In the manufacture of submarine cables.
3. In the manufacture of adhesives and tissues for surgical purpose.

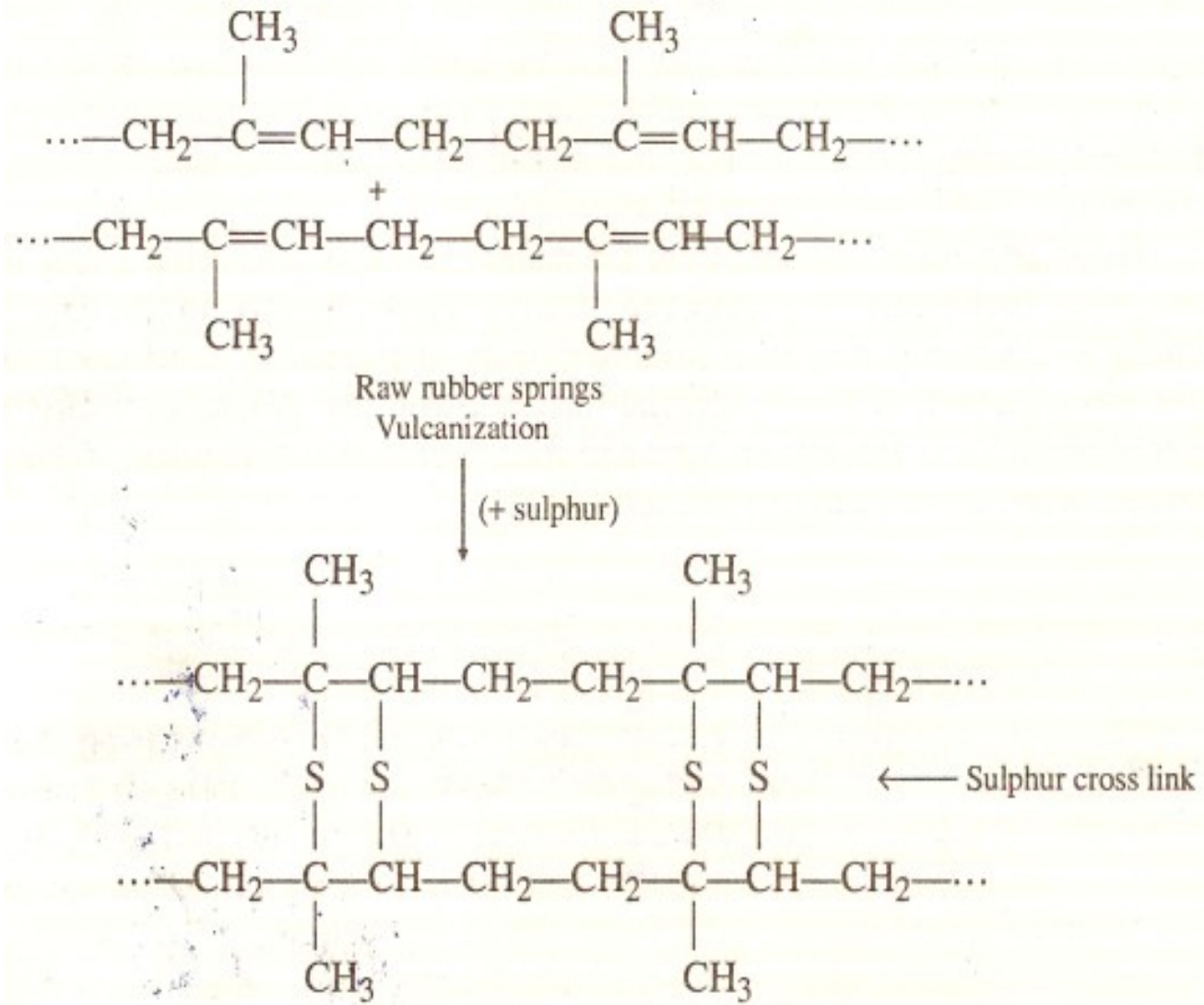
# POLYMERS

## **Vulcanization of Rubber :**

Raw rubber is of little use as such because it has very undesirable properties, e.g; it possesses elasticity only over a limited range of temperature, does not resume its original shape after being extended and becomes softer, more plastic and sticky on heating and brittle on cooling. The undesirable properties may be overcome by a process known as vulcanization.

**Process :** The process consists in heating the raw rubber with sulphur to 100-140°C. The added sulphur combines chemically at the double bonds of different rubber springs. Vulcanization thus serves to stiffen the material by a sort of anchoring and consequently, preventing intermolecular movement of rubber springs. The extent of stiffness of vulcanized rubber depends on the amount of sulphur added. The vulcanization can also be done by hydrogen sulphide and benzoyl chlorides.

# POLYMERS



# POLYMERS

## **Advantages of Vulcanization** Vulcanized rubber :

- (1) has good tensile strength and extensibility.
- (2) has excellent resilience, *i.e.*, article made from it returns to the original shape, when the deforming load is removed;
- (3) has higher resistance to oxidation .
- (4) has much higher resistance to wear and tear as compared to raw rubber.
- (5) is better electrical insulator, although it tends to absorb small amount of water.

Ebonite (raw rubber vulcanized with about 32% rubber) is better insulator.

- (6) is resistant to organic solvents (such as petrol, benzene, carbon tetrachloride), fats and oils. It swells in these liquids.

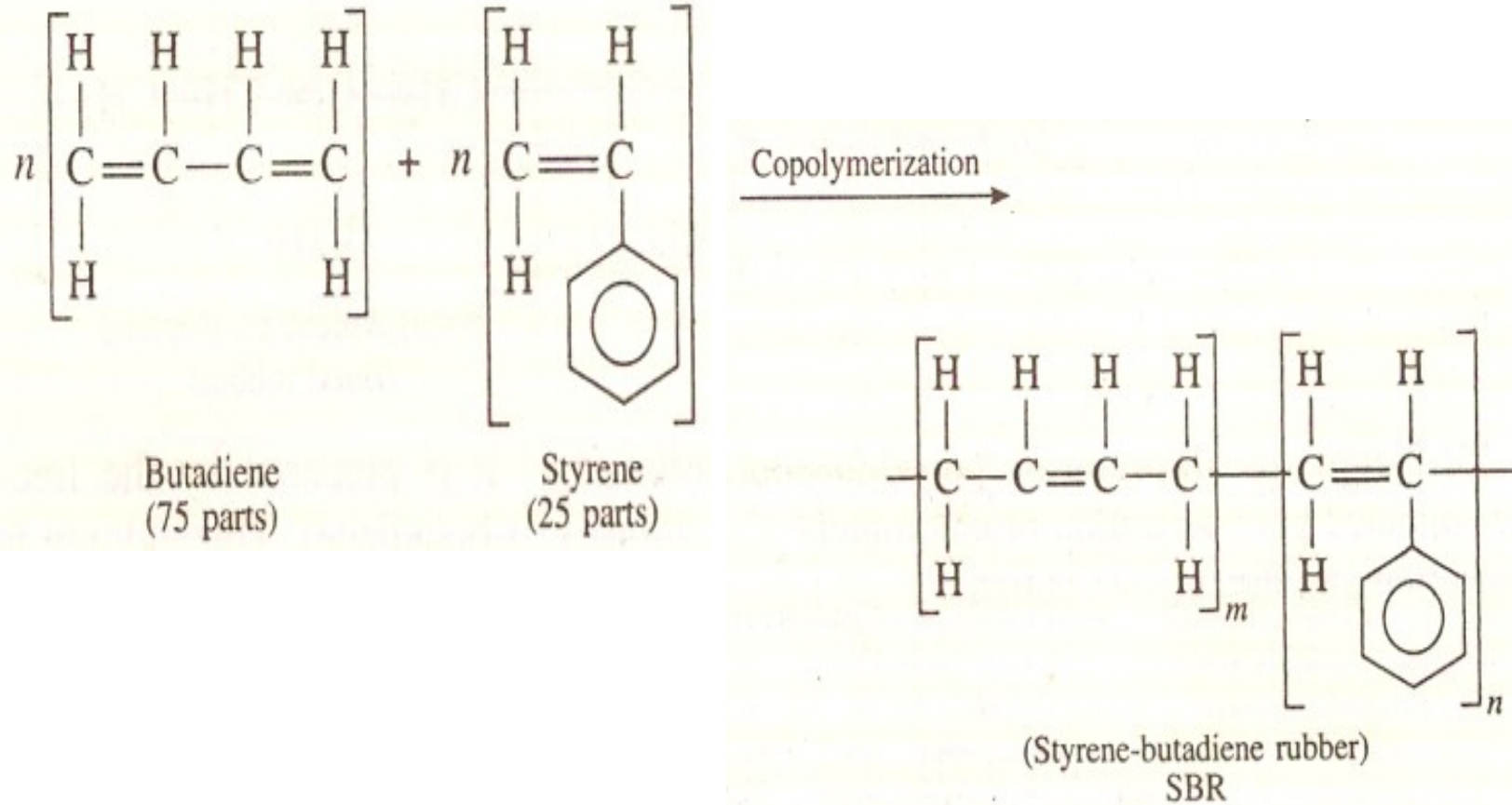
# POLYMERS

**Synthetic rubber** : Synthetic rubber is the term used for that rubber like material which is obtained by means of synthesis (i.e., in the laboratory) and can compete with natural rubber in its many uses.

**(a) Styrene Rubber or Buna-S** : Buna-S is copolymer of 75% butadiene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ) and 25% styrene ( $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ ). The polymerization is carried out in an emulsion system at  $50^\circ\text{C}$  in the presence of peroxide catalyst. The polymer consists of the repeating units of mainly 1, 4-addition product of butadiene along with a small amount of 1, 2-addition product.



# POLYMERS



# POLYMERS

- Properties:**
1. Styrene rubber resembles natural rubber in processing characteristics well as quality of finished products.
  2. It possesses high load-carrying capacity.
  3. It gets readily oxidized, especially in presence of traces of ozone present in the atmosphere.
  4. It can be vulcanized in the same way as natural rubber either by sulphur or sulphur monochloride ( $S_2Cl_2$ ).

- Uses:**
1. It is mainly used for the manufacture of motor tyres.
  2. Other uses of this elastomer are floor tiles, shoe soles, gaskets, footwear components, wire and cable insulations, adhesives etc.



# POLYMERS

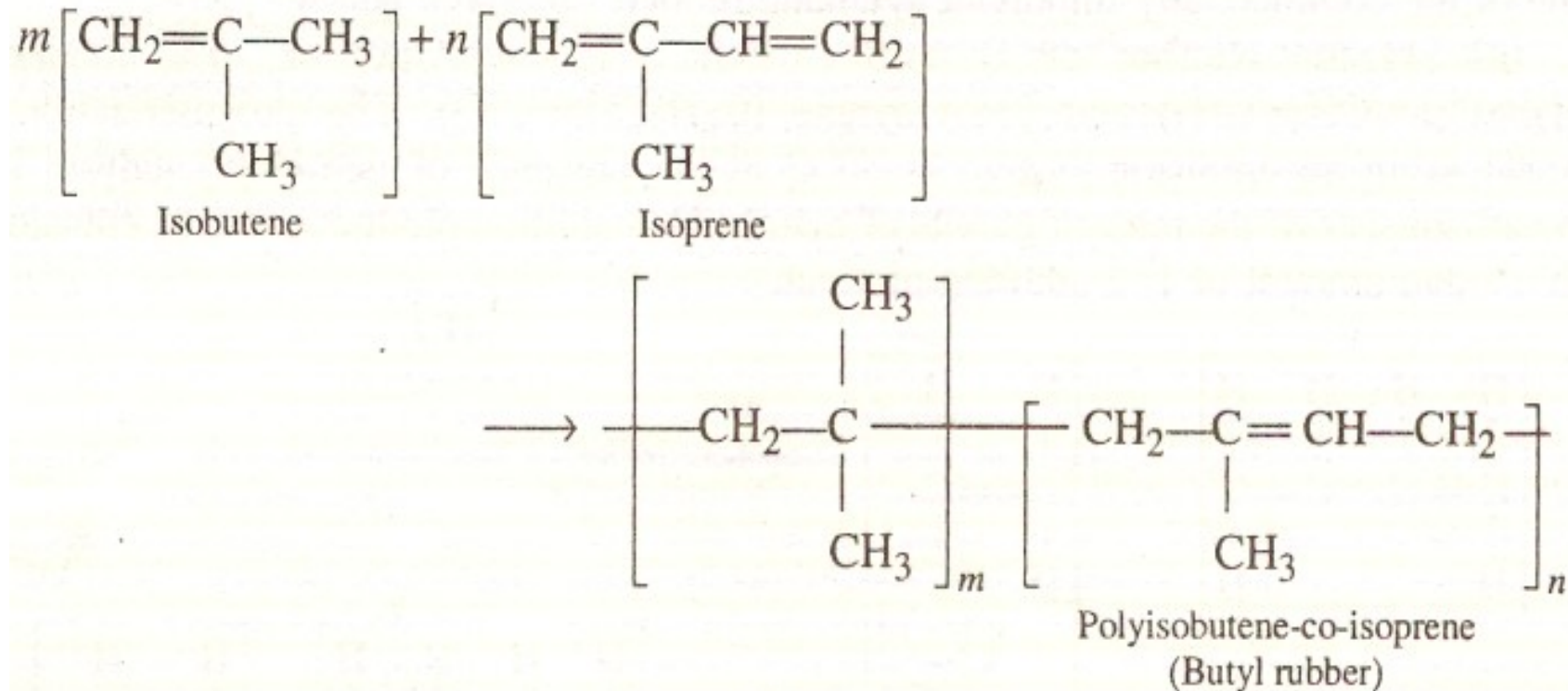
## Properties:

1. It possesses excellent resistance to heat, sunlight, oils, acids and salts, but it is less resistant to alkalis than natural rubber, because of the presence of cyano groups (-CN).
2. As the proportion of acrylonitrile is increased, the resistance to acids, salts, oils, solvents, etc., increases.
3. Vulcanized-nitrile rubber is more resistant to heat and ageing than natural rubber and may be exposed to high temperatures.

**Uses:** For making conveyor belts, high altitude aircraft components, tank-linings, printing rollers, adhesives, oil-resistant foams and automobile parts, etc.

# POLYMERS

**(c) Butyl Rubber:** It is a copolymer of 98% isobutene ( $\text{Me}_2\text{C}=\text{CH}_2$ ) and nearly 2% butadiene or isoprene ( $\text{CH}_2=\text{CMe}-\text{CH}=\text{CH}_2$ ); the latter is added to introduce the necessary ethylenic linkages for vulcanization.



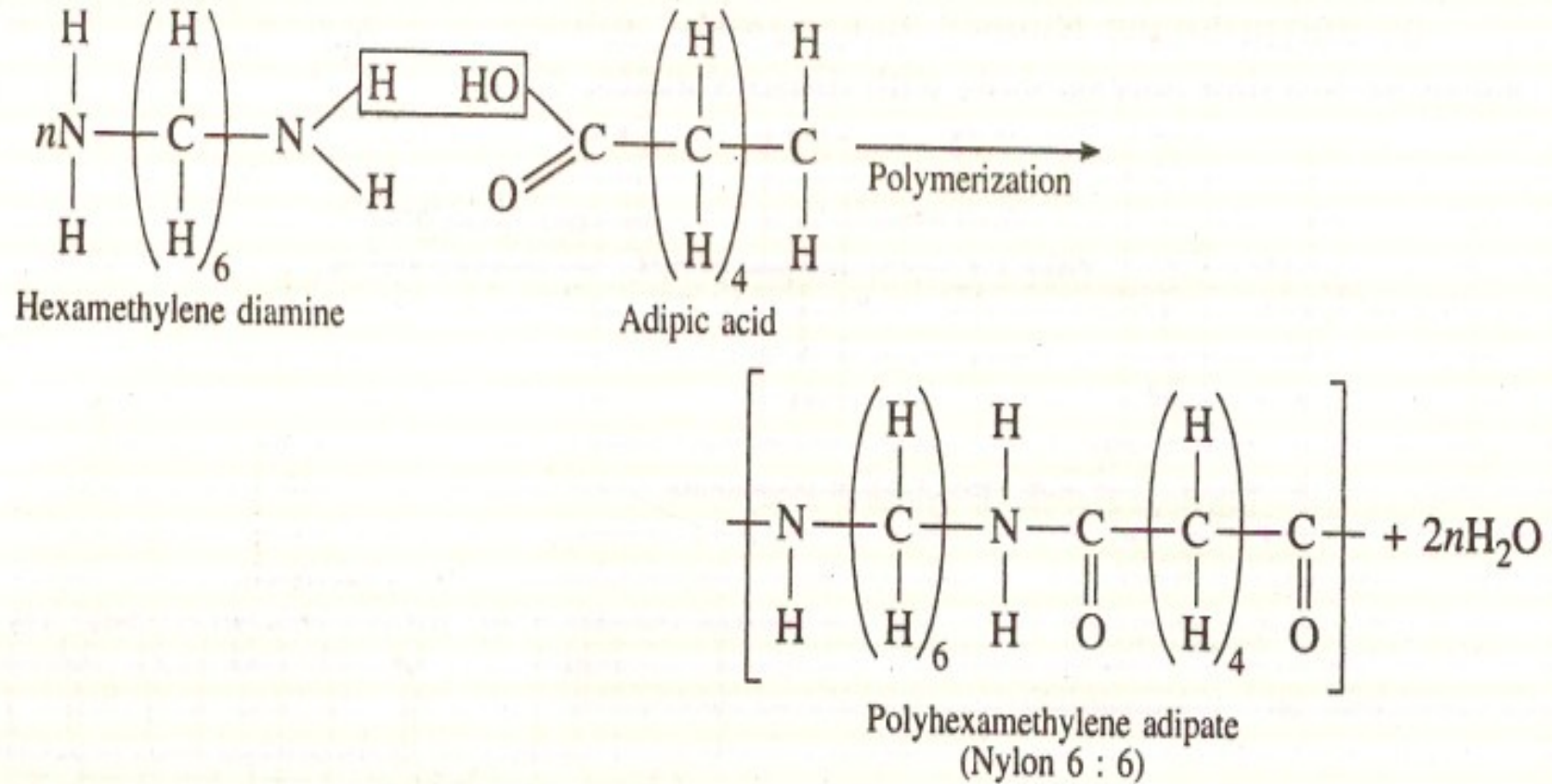
# POLYMERS

## **POLYAMIDES :**

Nylon is a generic term for synthetic polyamides capable of forming fibres. polyamides are synthetic polymers, which have recurring amide groups. Polyamides of commercial importance are Nylon 6; Nylon 6 : 6, Nylon 6 : 10 and Nylon 11.

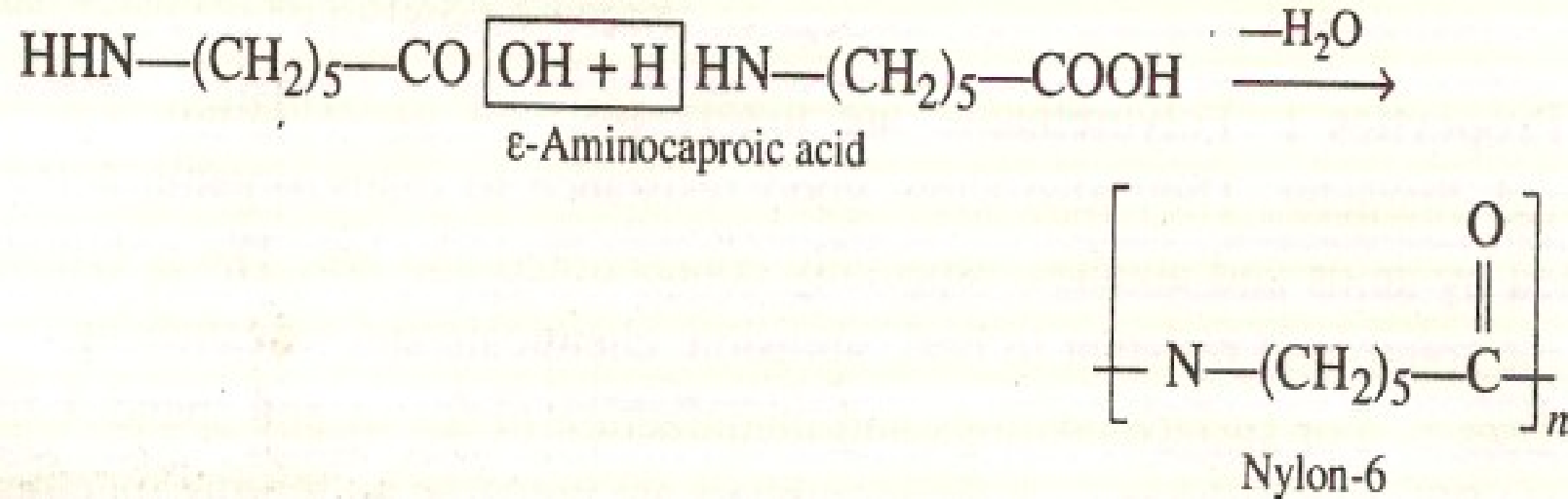
**Nylon 6 : 6** It is prepared by the condensation of adipic acid and hexamethylene diamine in the absence of air. The amine and carboxyl groups condense to form amide linkage with the evolution of water.

# POLYMERS



# POLYMERS

**Nylon 6** : It is produced by the self condensation of  $\epsilon$ -amino caproic acid.





# POLYMERS

**Nylon 6 : 10** It is prepared from reaction between hexamethylene diamine and sebacic acid to produce hexamethylene sebacamide (Nylon 6 : 10).

