- Chain termination :  $2R(CH_2CH_2)_nCH_2CH_2 \longrightarrow R(CH_2CH_2)_nCH_2CH_2CH_2CH_2CH_2(CH_2CH_2)_nR$
- > Ionic mechanism : (a) Cationic mechanism normally occurs in the acidic medium in the presence of protonic acids or Lewis acids.

$$H_2SO_4 = H^+ + HSO_4^-$$

- or  $BF_3 + H_2O \longrightarrow H^+ + BF_3(\bullet H)^-$
- Chain initiation :  $H^+ + CH_2 = CH_2 - \rightarrow CH_3 \overset{+}{C}H_2$
- Chain propagation :

$$CH_{3}CH_{2}+CH_{2}=CH_{2}--->CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}$$
  
 $CH_{3}CH_{2}CH_{2}CH_{2}+n(CH_{2}=CH_{2})$   
 $---->CH_{3}CH_{2}(CH_{2}CH_{2})nCH_{2}CH_{2}$ 

– Chain termination :

$$CH_{3}CH_{2}(CH_{2}CH_{2})_{n}CH_{7}CH_{2} \xrightarrow{T}H_{2} \longrightarrow H_{1}HSO_{4}$$
$$HSO_{4}$$
$$CH_{3}CH_{2}(CH_{2}CH_{2})_{n}CH = CH_{2} + H_{2}SO_{4}$$
Polymer

Cationic polymerization or acid catalysed mechanism is effective only with vinyl monomers containing electron releasing groups.

(b) Anionic mechanism occurs in alkenes having electron withdrawing groups in them and it is carried out in presence of a suitable base.

- Chain initiation :

$$B^{-} + CH_2 \stackrel{f}{=} CH_2 \longrightarrow B - CH_2 - \overline{CH}_2$$

– Chain propagation :

$$B - CH_2 - \overline{CH_2} + CH_2 \xrightarrow{\frown} CH_2 \xrightarrow{\frown} B - CH_2 CH_2 \overline{CH_2}$$

• Condensation or step growth polymerisation : A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, alcohol, etc. is called condensation polymer and the phenomenon is known as condensation polymerization.

$$nHOCH_{2}CH_{2}OH + nCH_{3}OOC - \swarrow - COOCH_{3}$$
  
Ethylene glycol Dimethyl terephthalate

$$\frac{\Delta}{-CH_3OH} \rightarrow -\left[ CH_2CH_2OOC - OO \right]_n$$

• **Copolymerisation :** A polymerization reaction in which a mixture of more than one monomeric species is allowed to polymerise to form a copolymer. Copolymers can be prepared by both chain growth and step growth polymerization. *e.g.*, Butadiene-styrene copolymer.

$$nCH_{2} = CH - CH = CH_{2} + \bigcup_{\text{Styrene}} Styrene$$

$$\longrightarrow -\left[CH_{2} - CH = CH - CH_{2} - CH - CH_{2}\right]_{n}$$

## SOME IMPORTANT POLYMERS

• **Rubber**: It is a common example of an elastomer. The rubber obtained from natural sources is called natural rubber and polymers prepared in laboratory which are similar to natural rubber are known as synthetic rubbers. Natural rubber is a hydrocarbon polymer. It has the composition  $(C_5H_8)_n$ . Destructive distillation of natural rubber gives mainly isoprene (2-methylbuta-1,3-diene). Isoprene is a monomer of natural rubber.

$$nCH_{2} = \overset{CH_{3}}{\overset{I}{\text{C}-CH}} = CH_{2} \xrightarrow{\text{Polymerisation}} \left[ \begin{array}{c} CH_{3} \\ CH_{2} - \overset{I}{\overset{C}{\text{C}}} = CH - CH_{2} \end{array} \right]_{n}$$

**Vulcanization** is a process in which natural rubber is treated with 3-5% sulphur. It introduces sulphur bridges between polymer chains thereby increasing its tensile strength, elasticity and resistance to abrasion. The rigidity of any vulcanized rubber depends upon the extent of sulphur cross-linking. The process of vulcanization was developed by Charles Goodyear in 1839.

The comparison of the main properties of natural rubber and vulcanized rubber is given below:

	Natural rubber	Vulcanized rubber (Synthetic)
1.	Natural rubber is soft and sticky.	Vulcanized rubber is hard and non-sticky.
2.	It has low tensile strength.	It has high tensile strength.
3.	It has low elasticity.	It has high elasticity.
4.	It can be used over a narrow range of temperature (from 10°C to 60°C).	It can be used over a wide range of temperature (-40°C to 100°C)
5.	It has low wear and tear resistance.	It has high wear and tear resistance.
6.	It is soluble in solvents like ether, carbon tetrachloride, petrol, etc.	It is insoluble in all the common solvents.

## • Homopolymers :

	Common name	Monomer	Uses
1.	Polyethylene	$\begin{array}{c} \mathrm{CH}_2 = \mathrm{CH}_2 \\ \mathrm{Ethylene} \end{array}$	In the manufacture of pipes, toys, bags, wire insulators, bottles, etc.
2.	Polyvinyl chloride (PVC)	CH <sub>2</sub> == CHCl Vinyl chloride	In the manufacture of sheets, water pipes, hoses, hand bags, etc.
3.	Polystyrene	$C_6H_5CH = CH_2$ Styrene	In the manufacture of combs, toys, radio and television cabinets, etc.
4.	Polyacrylonitrile (PAN)	$CH_2 = CH - CN$ Acrylonitrile	In the manufacture of orlon (fibre) and acrilon films.
5.	Teflon (Polytetrafluoroethylene)	$CF_2 = CF_2$ Tetrafluoroethylene	In the manufacture of insulators, gaskets, etc.

## • Copolymers :

	Common name	Monomers	Uses
1.	Dacron or Terylene	<ul> <li>(i) HOCH<sub>2</sub> - CH<sub>2</sub>OH Ethylene glycol</li> <li>(ii) H<sub>3</sub>COOC(C<sub>6</sub>H<sub>4</sub>)COOCH<sub>3</sub> Dimethyl terephthalate</li> </ul>	In the manufacture of fabrics and magnetic recording tapes.
4.	Nylon-66	<ul> <li>(i) H<sub>2</sub>N(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub> Hexamethylene diamine</li> <li>(ii) HOOC(CH<sub>2</sub>)<sub>4</sub>COOH Adipic acid</li> </ul>	In the manufacture of fabrics, tyre cords, ropes, carpets, etc.
5.	Bakelite	(i) HCHO Formaldehyde (ii) $C_6H_5OH$ Phenol	In the manufacture of electrical goods, phonograph records, fountain pen barrels, combs, etc.
6.	Melamine - formaldehyde resin	(i) HCHO Formaldehyde (ii) H <sub>2</sub> N N NH <sub>2</sub> N NH <sub>2</sub> Melamine	In the manufacture of plastic crockery.

## **BIODEGRADABLE POLYMERS**

The polymers are finding extensive use in our day to day life. Since ordinary polymers do not degrade naturally by light, oxygen, water or micro-organisms, there is serious problem for their disposal. The main option is to produce biodegradable polymers which can be broken down rapidly by soil micro-organisms and therefore, do not cause any serious effects on the environment. Thus, **biodegradable polymers** are the polymers which are degraded by microorganisms within a suitable period so that biodegradable polymers and their degraded products do not cause any serious effects on the environment.

In biological systems, biopolymers degrade mainly by enzymatic hydrolysis and to some extent by oxidation. Therefore, in view of the disposal problems of polymer waste and for developing polymers for other safe uses in human system, attempts have been made to develop biodegradable synthetic polymers. These synthetic polymers mostly have functional groups which are normally present in biopolymers and lipids.

The common examples of biodegradable polymers are polyhydroxy butyrate (PHB), polyhydroxy butyrate-co- $\beta$ -hydroxy valerate (PHBV), polyglycolic acid (PGA), polylactic acid (PLA), poly ( $\epsilon$ -caprolactone) (PCL) etc.

 Poly-β-hydroxybutyrate-co-β-hydroxy valerate (PHBV): It is copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid, in which the monomer units are joined by ester linkages.