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DEPARTMENT OF EDUCATION (S)
Government of Manipur

Chapter – 15

Polymers

1. **Polymers.** Polymers are macromolecules of relatively high molecular mass, whose structures are composed of a large number of simple repeating units.
2. **Monomers.** The small repeating units of a polymer usually obtained from low molecular mass simple compounds are known as monomers.
3. **Polymerisation.** The process of formation of polymers from monomers is known as **polymerization.**

Homo polymers and Copolymers :

Depending upon the nature of the repeating structural unit, polymers are divided into two categories : i) Homopolymers and ii) Copolymers.

i) Homopolymers : Polymers whose repeating structural units are derived from only one type of monomer units are called Homopolymers. For example in case of polythene (polyethylene) polymer which is obtained by polymerization of ethene (ethylene) molecules, the repeating structural unit, i.e., -CH2 – CH2 – is derived from only one type of monomer, i.e., ethene.

$$\underset{\substack{\text{Ethene}\\ \textit{(Monomer)}}}{{}_{n}\,CH_2 = CH_2} \xrightarrow{Polymerization} \underset{\substack{\text{Polythene}\\ \textit{(Polymer)}}}{[-CH_2 - CH_2-]_{n}}$$

Other examples of homopolymers are polypropene, polyvinylchloride (PVC), Polyisoprene, neoprene (Polychloroprene), polyacrylonitrile (PAN), nylon 6,6, polybutadiene, Teflon (polytetrafluoroethylene), cellulose, starch etc.

ii) Copolymers : Polymers whose repeating structural units are derived from two or more types of monomer are called copolymers. For example, is case of nylon 6,6, the repeating structural unit, i.e., $-NH-(CH_2)_6 - NH - CO - (CH_2)_4 - CO -$ is derived from two monomer units, i.e., hexamethylenediamine and adipic acid.

$$\underset{\substack{\text{Hexamethylenediamine}\\ \text{(Monomer)}}}{N\ H_2N - (CH_2)_6 - NH_2} + \underset{\substack{\text{Adipic acid}\\ \text{(Monomer)}}}{n\ HOOC - (CH_2)_4 - COOH} \xrightarrow{Polymerization}$$

$$\underset{\substack{\text{Nylon 6, 6}\\ \textit{(Polymer)}}}{[\,-NH - (CH_2)_6 - NH - CO - (CH_2)_4 - CO -\,]_n} + (2n - 1)\,H_2O$$

Other examples of copolymers are : Buna-S, Polyesters, alkyd resins, bakelite, melamine-formaldehyde polymer etc.

Classification of polymers base upon sources :

i) **Natural polymers.** The polymers which occur in nature i.e., which occur either in plants or **animals, are called** natural polymers. For example, natural rubber, proteins, cellulose, starch polysaccharides), wood, silk and nucleic acids are natural polymers.

ii) **Synthetic polymers.** Synthetic polymers are man-made polymers. These polymers are made in laboratories or factories. Typical examples of synthetic polymers include polyethene. PYC, nylon, terylene, teflon, synthetic rubber, bakelite and melamine.

iii) **Semi-synthetic polymers** Chemically modified natural polymers are called semi-synthetic polymers. For example, nitrocellulose, cellulose acetate etc. are termed semi-synthetic polymers. These polymers are also called chemically modified natural polymers.

CLASSIFICATIN ON THE BASIS OF STRUCTURE

- **Linear Chain Polymers :** The polymer in which the constituent monomers link with each other to form a long straight chain are called linear chain polymers, or straight chain polymers. Linear polymers are well packed and thus have high densities, high tensile strength and high melting points. For example, high-density polythene (HDPE) is a linear chain polymer.
- **Branched-Chain Polymers :** The polymers which have side chains attached to the linear chains consisting of monomers are called branch chain polymers. The branch chain polymers are irregularly packed and thus have lower tensile strength, lower melting point and lower density. For example, low density polythene (LDPE) has lower density, lower melting point and lower tensile strength than the linear high density polythene (HDPE).
- **Cross-Linked Polymers :** The polymers in which the adjacent polymeric chains are linked to each other directly or through a side chain are called cross linked polymers. The cross linking of polymeric chains leads to a network structure. So the cross linked polymers are also called network polymers. The cross linked polymers are hard, rigid and brittle.
  Examples: Bakelite, melamine-formaldehyde resins are cross- linked polymers.

Classification based upon Mode of Polymerization :

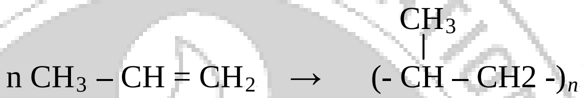
Polymers have been classified into the following two sub groups :

1. Addition polymers and
2. Condensation polymers

1. **Addition polymers and addition polymerization :** Addition polymers are formed by the repeated addition of a large number of same or different monomers possessing double and triple bonds and the process by which addition polymers are formed is called addition polymerization.

For example, $n\,CH_2 = CH_2 \rightarrow (-CH_2 - CH_2 -)_n$

Ethene or Ethylene (Monomer) → Polythene or Polyethylene (Polymer)



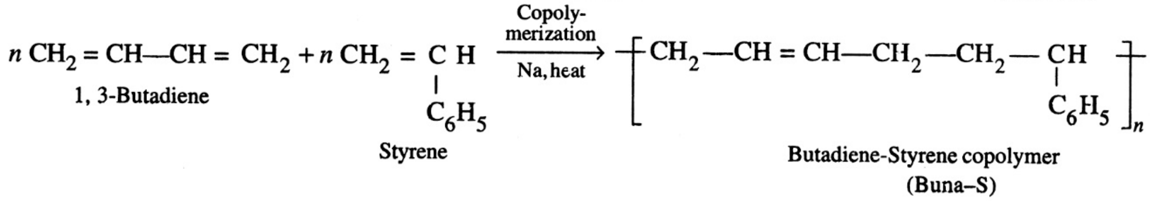
$$n\,CH_3 - CH = CH_2 \rightarrow (-\underset{}{\overset{CH_3}{\overset{|}{CH}}} - CH2 -)_n$$

Propene or Propylene (Monomer) → Polypropene or Polypropyiene (Polymer)

The addition polymers can be either addition hompolymers or addition copolymers. Both polythene and polypropene are addition hompolymers because they are formed by the addition polymerization of only one type of monomer units. Other examples of addition homopolymers are :

Sl. No.	Monomer	Polymer
i)	Butadiene	Polybutadiene
ii)	Tetrafluoroethylene	Polytetrafluoroethylene (PTFE) or Teflon
iii)	Vinyl chloride	Polyvinyl chloride (PVC)
iv)	Isoprene	*cis* – Polyisoprene (natural rubber)

Addition polymers formed by repeated addition of two or more types of monomer units, are called addition copolymers. For example, Buna-S is an addition polymer of 1, 3-butadiene and styrene.

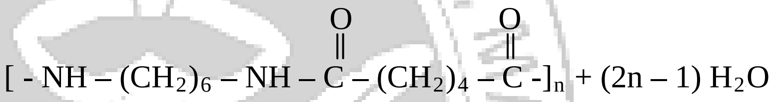


$$n\,CH_2 = CH-CH = CH_2 + n\,CH_2 = \underset{C_6H_5}{\underset{|}{CH}} \xrightarrow[\text{Na, heat}]{\text{Copoly-merization}} \left[CH_2-CH = CH-CH_2-CH_2-\underset{C_6H_5}{\underset{|}{CH}} \right]_n$$

Other examples of addition copolymers are : Buna-N (1, 3-butadiene and acrylonitrile), butyl rubber (isobutylene and isoprene), saran (vinyl chloride and vinylidene chloride), etc.

2. **Condensation polymers and condensation polymerization :** Condensation polymers are formed by repeated condensation reaction between two bifunctional or trifunctional monomer units usually with the elimination of small molecules like water, alcohol, ammonia, carbon dioxide, hydrogen chloride etc. and the process by which condensation polymers are formed is called condensation polymerization. For example, nylon 6, 6 is obtained by condensation polymerization, of two elements i.e., hexamethylenediamine and adipic acid, each containing two functional groups, with the loss of water molecules. Thus,

$$n\,\underset{\text{Hexamethylenediamine}}{H_2N-(CH_2)_6-NH_2} + n\,\underset{\text{Adipic acid}}{HOOC-(CH_2)_4-COOH} \xrightarrow{525\,K}$$



$$\underset{\text{Nylon-6,6}}{[-NH-(CH_2)_6-NH-\overset{\overset{\large O}{\|}}{C}-(CH_2)_4-\overset{\overset{\large O}{\|}}{C}-]_n} + (2n-1)\,H_2O$$

Like addition polymers, condensation polymers can be either condensation copolymers or condensation homopolymers. The polymer nylon 6, 6 discussed above is an example of condensation copolymer.

Some other examples of condensation copolumers are :

Polymer	Monomers
(i) Terylene or Dacorn	Ethylene glycol and terephthalic acid or its methyl ester
(ii) Alkyl resin	Ethylene glycol and phthalic acid
(iii) Bakelite	Phenol and formaldehyde
(iv) Melamine – formaldehyde resin	Melamine and formaldehyde
(v) Polyurethane	Ethylene glycol and toluene m-diisocyanate

Some examples of condensation hompolymers are :

Polymer	Monomers
(i) Nylon	Caprolactam
(ii) Starch (amylose, amylopectin) and glycogen	$\alpha - D - Glucose$
(iii) Cellulose	$\beta - D - Glucose$

Classification of polymers on the Basis of Molecular Forces

i) **Elastomers (rubber-like).** In elastromers, the polymer chains are held together by the weakest intermolecular forces which permit the polymer to stretch. Elastromers become soft on heating, and can be moulded into any desired shape. Natural rubber is an elastromer.

(ii) **Synthetic fibres (or Fibrous polymers).** These polymers have long linear chains, with very strong intermolecular forces between the chains. The forces which hold the chains together are strong intermolecular forces like hydrogen bonding or dipole-dipole interactions. Due to these strong intermolecular forces, the polymeric chains in fibrous polymers are closely packed and thus they have crystalline nature, sharp melting points and high tensile strength. Polyamides such as, nylon - 6, 6 show high tensile strength, high melting points etc., due to hydrogen bonding between their polymeric chains.

(iii) **Thermoplastic polymers.** Thermoplastic polymers show the following characteristics

(a) These are linear polymers, with no cross-links.

(b) These are generally soluble in organic solvents.

(c) The intermolecular forces of attraction in thermoplastic polymers are intermediatory to those in elastomers and fibrous polymers.

(d) Because of the not so strong intermolecular forces, thermoplastic polymers soften on heating and harden on cooling.

(d) To enhance the workability of thermoplastics at relatively lower temperatures, certain compounds called plasticizers are added during processing. Tricresyl phosphate, dioctylphthalate etc., are good plasticizers.

Examples: Typical thermoplastics are - polypropylene (PP), polyethene (PE), polyvinylchloride (PVC), and perspex etc.

(iv) **Thermosetting polymers.** When heated in a mould, thermosetting polymers become infusible and form an insoluble hard mass due to the formation of a three-dimensional network of bonds. Thus thermosetting plastics cannot be remelted, or reshaped by heating. Thus, thermosetting polymers can be processed only once.

Examples : Phenol-formaldehyde resins (bakelite) and Melamine-formaldehyde resins are typical thermosetting polymers.

Difference between Thermosetting and Thermoplastic Polymers

Property	Thermopastic	Thermosetting
1. Structure	Linear polymers with no cross-linking	Low molecular mass, semi-fluid polymers.
2. Effect of heating	Soften on heating and harden on cooling. Heating and cooling process can be carried out any number of times. No cross-links are developed on heating.	On heating, the low molecular mass polymeric material gets further polymerized due to extensive cross-linking on heating. On cooling. It becomes hard, and infusible. Once thermoset, these cannot be remelted / reshaped

Vulcanization : The modification in the properties of rubber by introducing some cross-linking between their polymeric chains is known as the vulcanization of rubber.

During vulcanization, -S-S- cross-links are introduced in the structure of natural rubber by heating with sulphur at 110_0C. Vulcanization is carried out by adding sulphur (3-5%) to the rubber-mix, and then heating the object at about 110^0 C for about 20-30 min.

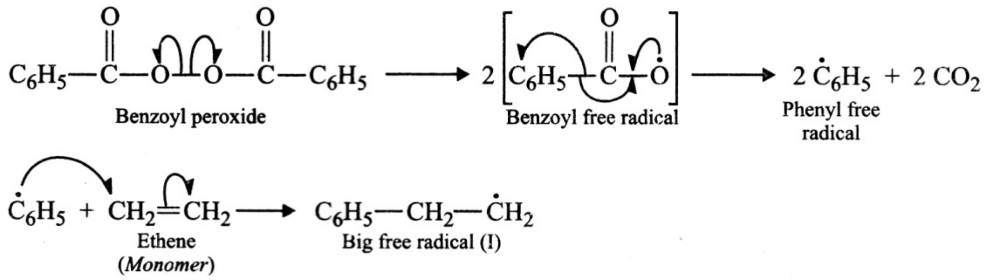
Classification based upon the type of Mechanism involved during Growth of Polymerisation Chain

Addition or Chain Growth Polymerisation : Chain growth polymerization is characterized by self-addition of the monomer molecules, to each other, very rapidly through a chain reaction. No by-product is formed; the product has the same elemental composition as that of the monomer. Chain polymerization consists of three major steps, namely, initiation, propagation and termination and the process can be brought about by a free radical, ionic or coordination mechanism.

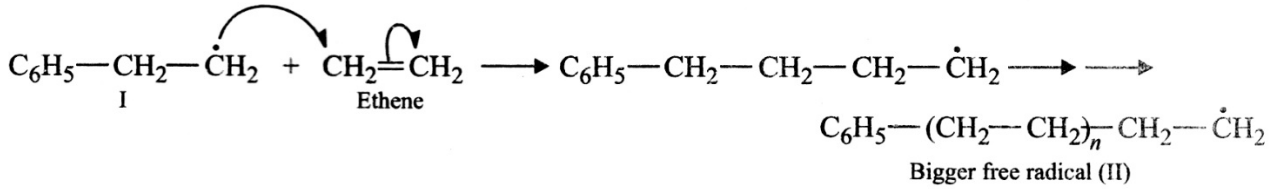
Chain growth : It is a process involving a continuous and very rapid addition of the monomer units to form polymer molecules or polymer chains.

Free-Radical Polymerization : The initiation of the polymer chain growth is brought about by free radicals produced by the decomposition of compounds called initiators.

Chain initiating steps :

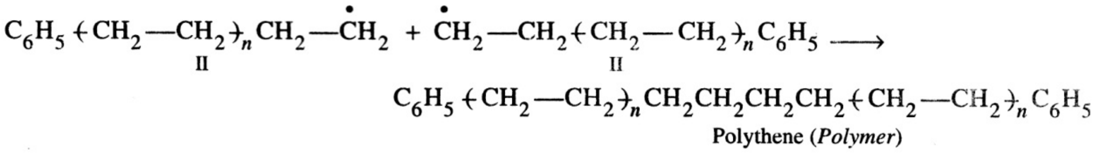


Chain propagation steps :

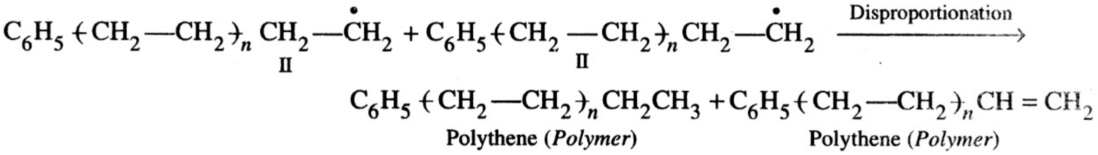


Chain terminating steps :

Step 1. By combination of free radicals (II) :



Step 2. By disproportionation of free radicals (II) :



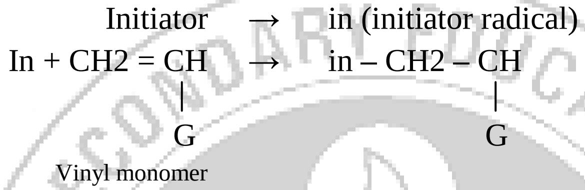
1. Vinyl polymers and vinyl polymerization

Most of the commercial addition polymers are derived from monomers containing a vinyl group (i.e., CH2 = CH-G where G = CH3, C6H5, Cl, CN, OCOCH3, COOCH3, etc.) by free radical polymerization. These are called vinyl polymers and the process is called vinyl polymerization.

Mechanism of free radical vinyl polymerization

Vinyl polymerization involves the same three steps, viz. chain initiating, chain propagation and chain terminating as discussed above for polymerization of ethene.

(i) Chain initiating steps :

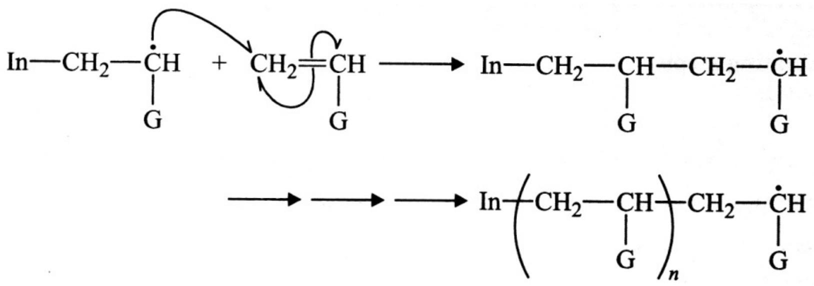


$$\text{Initiator} \rightarrow \text{in (initiator radical)}$$

$$\text{In} + \underset{\substack{|\\ \text{G}}}{\text{CH2} = \text{CH}} \rightarrow \text{in} - \text{CH2} - \underset{\substack{|\\ \text{G}}}{\text{CH}}$$

Vinyl monomer

(ii) Chain propagating step :

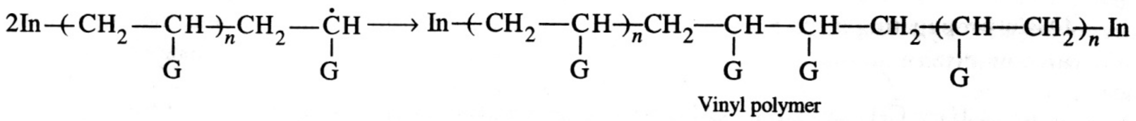


$$\text{In}-\text{CH}_2-\underset{\substack{|\\ \text{G}}}{\dot{\text{C}}\text{H}} + \text{CH}_2=\underset{\substack{|\\ \text{G}}}{\text{CH}} \longrightarrow \text{In}-\text{CH}_2-\underset{\substack{|\\ \text{G}}}{\text{CH}}-\text{CH}_2-\underset{\substack{|\\ \text{G}}}{\dot{\text{C}}\text{H}}$$

$$\longrightarrow \longrightarrow \longrightarrow \text{In}\left(\text{CH}_2-\underset{\substack{|\\ \text{G}}}{\text{CH}}\right)_n\text{CH}_2-\underset{\substack{|\\ \text{G}}}{\dot{\text{C}}\text{H}}$$

(iii) Chain termination steps :

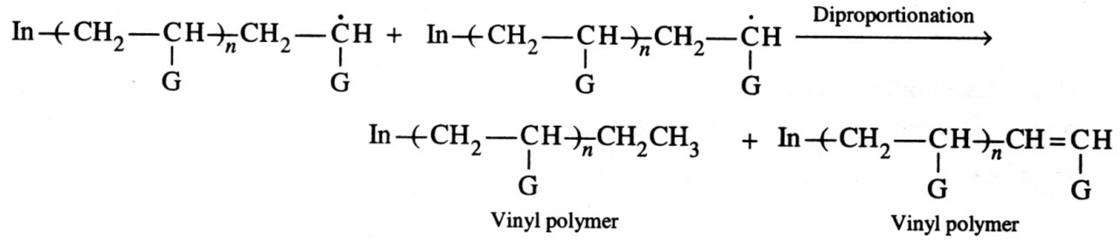
Step 1. By combination of free radicals



$$2\text{In}\left(\text{CH}_2-\underset{\substack{|\\ \text{G}}}{\text{CH}}\right)_n\text{CH}_2-\underset{\substack{|\\ \text{G}}}{\dot{\text{C}}\text{H}} \longrightarrow \text{In}\left(\text{CH}_2-\underset{\substack{|\\ \text{G}}}{\text{CH}}\right)_n\text{CH}_2-\underset{\substack{|\\ \text{G}}}{\text{CH}}-\underset{\substack{|\\ \text{G}}}{\text{CH}}-\text{CH}_2\left(\underset{\substack{|\\ \text{G}}}{\text{CH}}-\text{CH}_2\right)_n\text{In}$$

Vinyl polymer

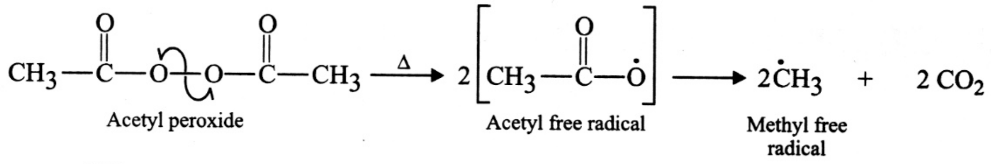
Step 2. By disproportionation of free radicals



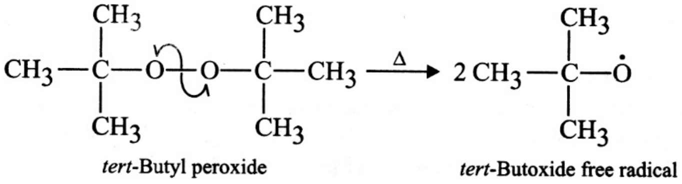
$$\mathrm{In}\!-\!(\mathrm{CH_2}-\underset{G}{\mathrm{CH}})_n\mathrm{CH_2}-\underset{G}{\dot{\mathrm{C}}\mathrm{H}} + \mathrm{In}\!-\!(\mathrm{CH_2}-\underset{G}{\mathrm{CH}})_n\mathrm{CH_2}-\underset{G}{\dot{\mathrm{C}}\mathrm{H}} \xrightarrow{\text{Diproportionation}} \mathrm{In}\!-\!(\mathrm{CH_2}-\underset{G}{\mathrm{CH}})_n\mathrm{CH_2CH_3} + \mathrm{In}\!-\!(\mathrm{CH_2}-\underset{G}{\mathrm{CH}})_n\mathrm{CH}=\underset{G}{\mathrm{CH}}$$

Initiators used in vinyl polymerization

The initiators commonly used in vinyl polymerization are benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. The initiator free radicals generated from them are discussed below :



$$\mathrm{CH_3}-\overset{O}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\mathrm{O}-\overset{O}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_3} \xrightarrow{\Delta} 2\left[\mathrm{CH_3}-\overset{O}{\overset{\|}{\mathrm{C}}}-\dot{\mathrm{O}}\right] \longrightarrow 2\dot{\mathrm{C}}\mathrm{H_3} + 2\,\mathrm{CO_2}$$



$$\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{O}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_3} \xrightarrow{\Delta} 2\,\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\dot{\mathrm{O}}$$

2. **Chain transfer reagents.** Compounds which bring termination of the original growing polymer chain with the simultaneous initiating of another polymer chain are called **chain transfer reagents.** For example CCl4 in the polymerization of styrene.

Preparationg of Some Addition Polymers :

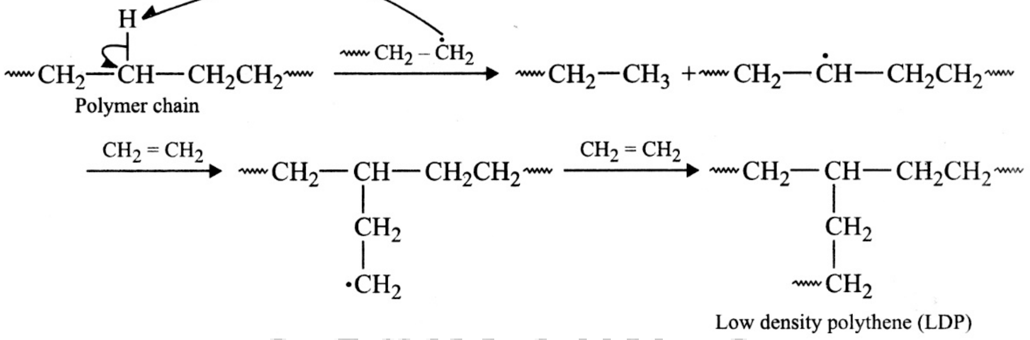
1. Polythene or Polyethylene

It is a widely used addition polymer and prepared by free radical or high-temperature polymerization of ethene. Two typees of polythenes are produced widely different properties. These are :

(a) Low density polythene (LDP) or Low density polyethylene (LDPE). It is manufactured by heating ethylene to 350-570 K under a pressure of 1000-2000 atmospheres and in presence of a trace of oxygen or peroxide. This polymerization occurs by a free radical mechanism which is initiated by oxygen or peroxide.

The Polythene thus produced has a molecular mass of about 20,000 and has highly branched structure. This branching occurs due to H abstraction.

At the high temperature at which this polymerization occurs, the growing free radicals not only add to the double bond of the monomer but also abstract hydrogen from a chain already formed. This abstraction generates a new free radical centre from which a chain can grow as shown below :



These branched polythene molecules do not pack well and hence this type of polythene has a low density (0.92 g/cm3) and a low melting point (384K). That is why polythene prepared by free radical polymerization is called low density polythene (LDP).

Properties and Used. Low density polythene is a transparent polymer of moderate tensile strength and high toughness. It is chemically inert, slightly flexible and is a poor conductor of electricity.

It is widely used as a packaging material (in the form of thin plastic films, bags, etc.) as insulation for electrical wires and cables, in manufacturing of squeeze bottles, toys and flexible pipes.

(b) High density polythene (HDP) or High density polyethylene (HDPE). It is prepared by co-ordination polymerization of ethene. In this process, ethene (in a hydrocarbon solvent) is heated by 333-343 K under a pressure of 6-7 atmospheres in presence of a catalyst consisting of triethylaluminium and titanium trichloride or tetrachloride *(Ziegler – Natta catalyst).*

$$n\ CH2 = CH2 \xrightarrow[(CH_3CH_3)_3Al + TiCl_4]{333-343K,\ 6-7atm} (-\ CH_2 - CH_2)n$$

Ethene

High density
Polythene (HDP)

Properites and Uses : High density polythene is a translucent polymer. It is also chemically inert but has greater toughness, hardness and tensile strength than low density polythene.

It is used in the manufacture of containers (buckets, tubs, etc.), housewares, pipes, bottles and toys, presence of peroxide or ammonium persulphate catalyst at high pressures.

$$n\ F_2C = CF_2 \xrightarrow[\text{Highpressure}]{(NH_4)_2S_2O_8} [-F2C - CF2-]_n$$

Tetrafluoroethene Polytetrafluoroethene or Teflon

Uses. Teflon is flexible and inert to solvents and to boiling acids even to aqua regia and is stable upto 598 K.

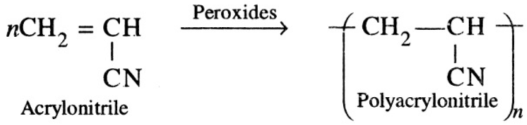
(i) Because of its great chemical inertness and high thermal stability, teflon is used for making non-stick utensils. For this purpose, a thin layer of teflon is coated on the inner side of the vessel.

(ii) It is also used for making gaskets, pump packings, valves, seals, non-lubricated bearings, filter cloth etc.

3. Polymacrylonitrile (PAN) or Orion

Starting material : Acrylonitrile ($CH_2 = CH - CN$)

Reaction. Addition polymerization of acrylonitrile in presence of a peroxide catalyst gives polyacrylonitrile.



$$2\ CH_3CH = CH_2 + 3O_2 + 2NH_3 \xrightarrow[\text{Mo, Co and Al, 723 K}]{\text{Oxides of}} 2\ CH_2 = CH - CN + 6H_2O$$

Uses. Polyacrlonitrile is a hard, horny and high melting material.

(i) It is used as a substitute for wool in the manufacture of Orion and Acrilan fibres which are used for making clothes, carpets and blankets.

(ii) It is also used in the preparation of other polymers to improve their qualities.

Condensation Polymerization or Step Growth Polymerization

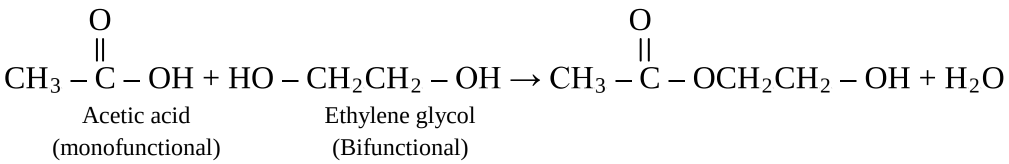
If two reacting molecules have one functional group each, the reaction stops after one step, For example, acetic acid reacts with ethyl alcohol to form ethyl acetate in one step :

$$CH_3 - \overset{\overset{O}{||}}{C} - OH + HO - CH_2CH_3 \rightarrow CH_3 - \overset{\overset{O}{||}}{C} - OCH_2CH_3 + H_2O$$

Acetic acid (monofunctional) Ethylene glycol (Bifunctional)

If, however, one of the reacting molecules has two functional groups and the other has one functional group, i.e. acetic acid and ethylene glycol, the reaction stops after two steps :

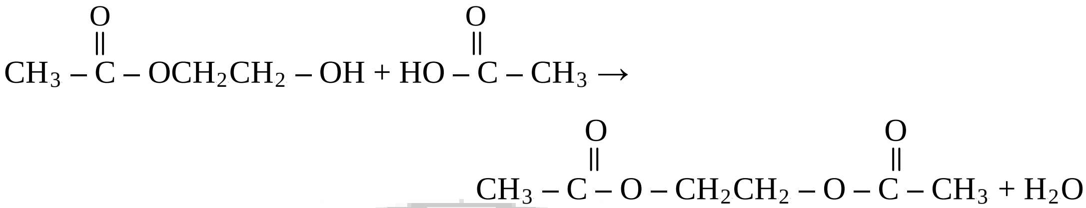
(i)



$$CH_3-\overset{\overset{O}{\|}}{C}-OH + HO-CH_2CH_2-OH \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_2-OH + H_2O$$

Acetic acid (monofunctional)   Ethylene glycol (Bifunctional)

(ii)



$$CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_2-OH + HO-\overset{\overset{O}{\|}}{C}-CH_3 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$$

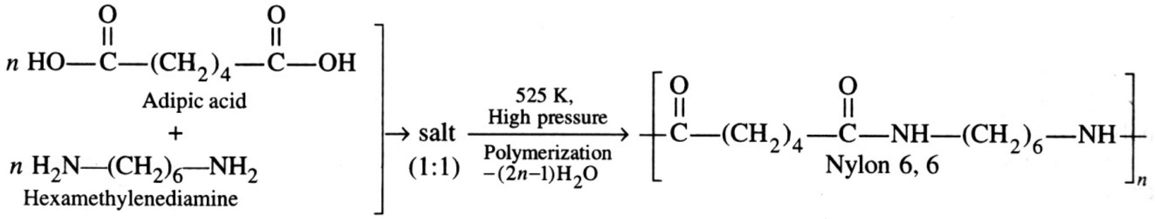
The formation of step-growth polymers does not occur through chain reactions involving free radicals, carbanions or carbocations as reactive chemical species.

Some Important condensation polymers are discussed below :

1. Polymers. Polymers which have amide linkages are called polyamides. These are prepared by the condensation polymerization of dibasic acids with diamines or their equivalents. These polymers are commonly called nylons. The name nylon(ny=New York and Ion – London) is given to these fibres since the most common nylons. i.e. nylon 6-6 was simultaneously prepared in New York and London.

(a) Nylon 6, 6. It is manufactured by the condensation polymerization of adipic acid and hexamethylenediamine. The acid and the amine first react to form a salt which when heated to 525 K under pressure undergoes polymerization with elimination of water as steam and the nylon is produced in the molten state. It can then be cast into a sheet of fibres by passing through a spinneret.

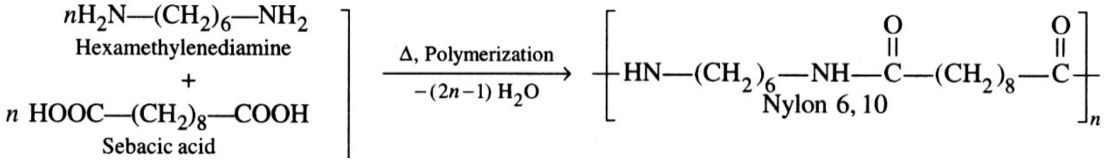
Reaction :



$$\left.\begin{array}{l} n\,HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH \\ \text{Adipic acid} \\ + \\ n\,H_2N-(CH_2)_6-NH_2 \\ \text{Hexamethylenediamine} \end{array}\right] \rightarrow \underset{(1:1)}{\text{salt}} \xrightarrow[\text{Polymerization}\ -(2n-1)H_2O]{525\text{ K, High pressure}} \left[\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-NH \right]_n$$

It is called nylon 6,6 (read as nylon six, six) since both adipic acid and hexamethylenediamine contain six carbon atom each.

(b) Nylon 6, 10. Another commonly used nylon is nylon-6, 10 (read as nylon six ten) which is obtained by the condensation of hexamethylenediamine (containing six carbon atoms) and sebaic acid [HOOC $(CH_2)_8$ COOH], a dibasic acid containing ten carbon atoms.



$$n\,H_2N{-}(CH_2)_6{-}NH_2 + n\,HOOC{-}(CH_2)_8{-}COOH \xrightarrow[-(2n-1)\,H_2O]{\Delta,\ \text{Polymerization}} \left[-HN-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-\right]_n$$

Uses. (i) Unlike cotton fibres, nylon fibres do not rot, have high tensile strength are tough, abrasion-resistant and somewhat elastic. These are therefore, used in manufacture of carpets, textile fibres and bristles for brushes.

Further, nylon fibres are so much stronger than the natural materials that these can be made much thinner. The availability of such a strong thin thread made possibly nearly invisible women's stockings called 'nylons'

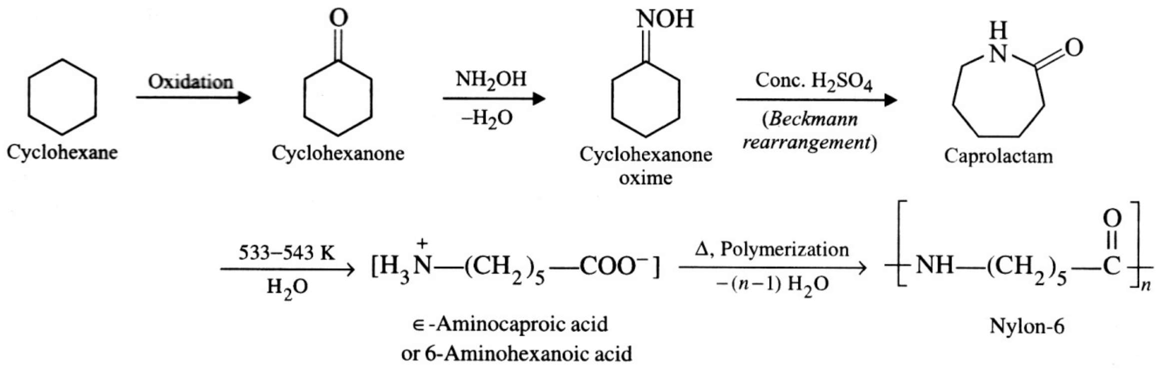
(ii) Being tough nylon is used as a substitute for metals in bearings and gears.

(iii) Crinkled nylon fibres are used for making elastic hosiery.

(c) Nylon 6 or Perlon. Nylons can also be prepared from a single monomer having a potential amino group at one end and a potential carboxyl group at the other. For example, the monomer caprolactam on heating with water at high temperature polymerization gives nylon 6.

Caprolactam needed for the purpose is manufactured from cyclohexane (a petrochemical) as described below :

When caprolactam is heated with a trace of water, it hydrolyses to ∈-aminocaproic acid (6-aminohexanoic acid) which upon continued heating undergoes polymerization to give nylon-6. It is manufactured by most of the industries in India. It is called the nylon-6 (read as nylon six) since the monomer (caprolactam) contains six carbon atoms.

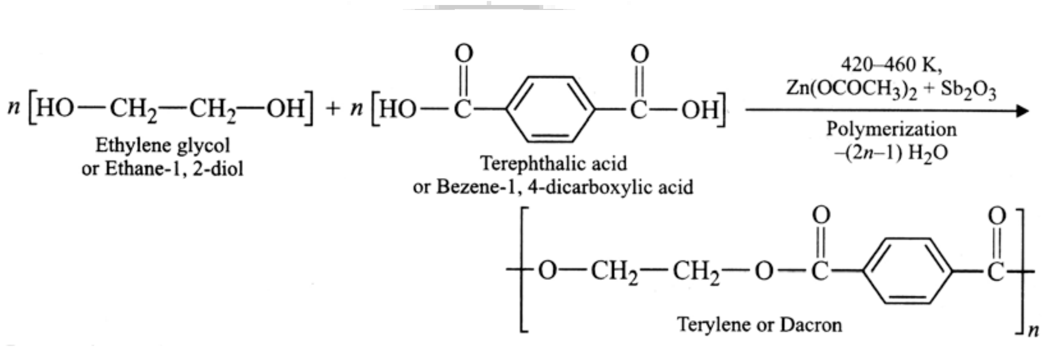


The filaments (fibres) of nylon 6 are obtained when molten polymer is forced through a spinneret and the fibres formed are cooled by a stream of air.

Uses. It is used for the manufacture of tyre cords, fabrics and mountaineering tropes.

2. Polyesters. Polymers which have ester linkages are called polyesters and are prepared by the condensation polymerization of diacids with diols.

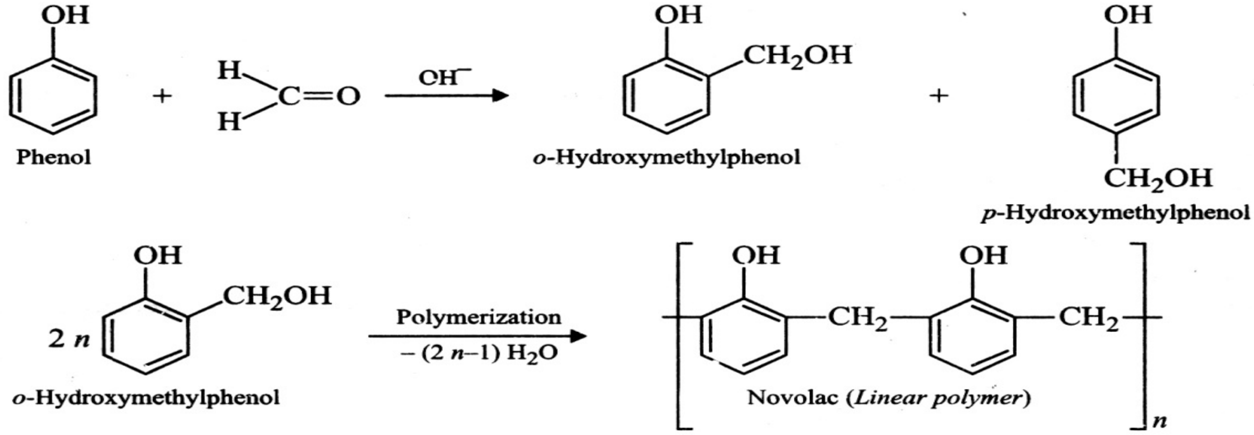
Terylene or Dacron is the best known example of polyesters. It is prepared by condensation polymerization of ethylene glycol and terephthalic acid with elimination of water. The reaction is carried out at about 420 – 460 K in presence of a catalyst consisting of a mixture of zinc acetate and antimony trioxide.



obtained is spun into Dacron fibres or cast into a film called Mylar.

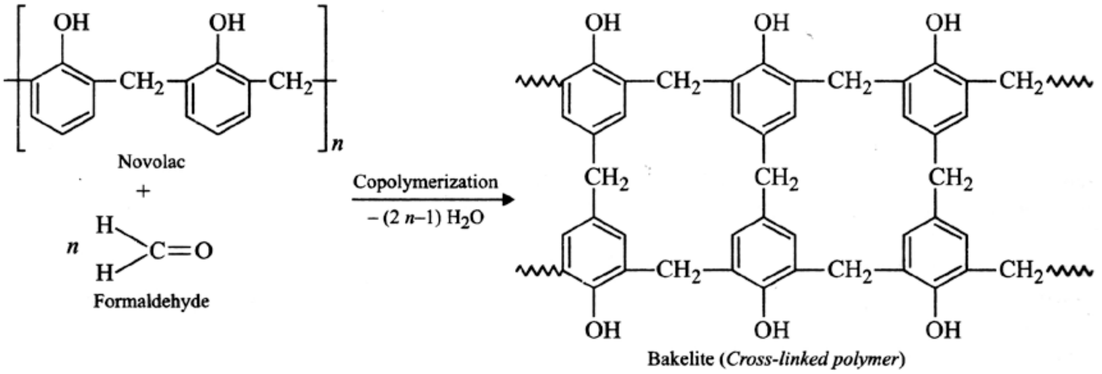
Uses. (i) The fibre of terylene is highly crease-resistant, durable and has low moisture content. It is also not damaged by pests like moths and mildew. It is, therefore, used for the manufacture of wash and wear fabrics, tyre cords, seat belts and sails. It is also bended with cotton and wool to increase their resistance to wear and tear. (ii) The Mylar film is extremely flexible, tear-resistant and resistant to ultraviolet degradation. It is, therefore, used for making magnetic recording tapes.

3. Phenol-formaldehyde Polymers (Bakelite and related polymers). Phenol formaldehyde polymers are the oldest synthetic polymers. These are obtained by condensation of phenol with formaldehyde in the presence of either and acid or a base catalyst. The reaction begins with the formation o- and/or p-hydroxymethylphenol derivatives which further react with phenol to form compounds containing rings joined to each other through methylene (- CH_2 -) bridges. The initial product is a linear polymer called novalac which is used in paints.



Reaction :

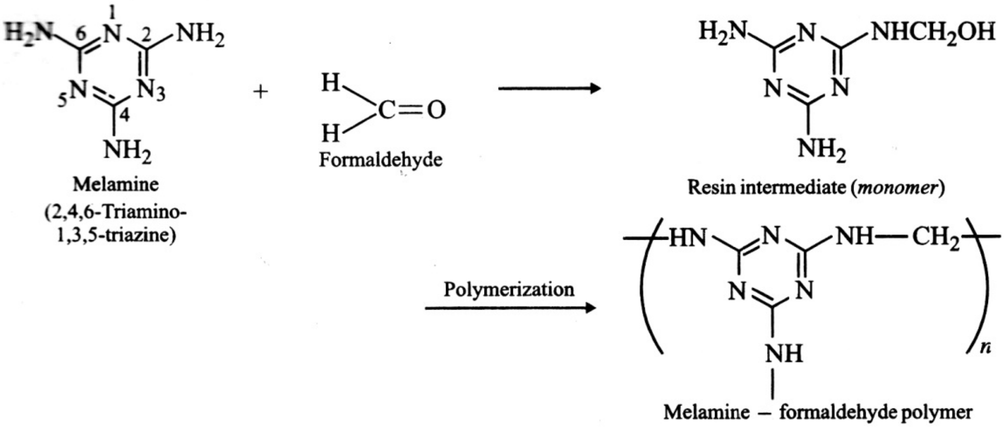
Novolac on further heating with formaldehyde undergoes cross-linkage to form an infusible solid called **bakelite.**



leads to the formation of a hard bakelite which is highly cross-linked and is a thermosetting polymer. It is a scratch and water resistant polymer and hence is used for the manufacture of combs, formica table-tops, fountain pen barrels, phonograph records, computer discs etc. It also possesses excellent electrical insulating properties and hence is widely used in making electrical goods (switches, plugs, handles of various utensils, etc.). Sulphonated bakelites are used as ion exchange resins.

4. Melamine-formaldehyde polymer. Melamine and formaldehyde undergo condensation copolymerization to form melamine-formaldehyde polymer are also called **melmac.**

Reaction :

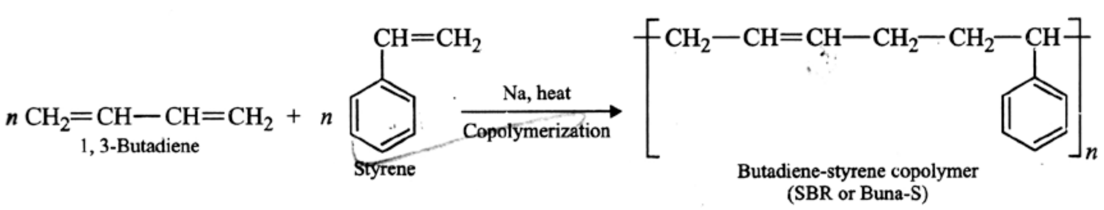


Uses. Melamine-formaldehyde copolymer is widely used for making non-breakable plastic crockery, i.e., cups and plates made from melamine polymer are hard and do not break or being dropped.

Copolymerization :

When two or more different monomers are allowed to polymeric together, the product formed is called a **copolymer** and the process is called copolymerization.

A copolymer can be made not only by chain growth polymerization but also by step growth polymerization. It contains a large number of units of each monomer used in the same polymeric chain. For example, copolymerization of a mixture of 1, 3-butadiene and styrene in the ratio 3 : 1 in presence of sodium gives styrenebutadiene copolymer commonly called as styrene-butadiene rubber (SBR) or Buna-S. In Buna-S, Bu stands for butadiene, na for sodium which is the polymerising agent and S stands for styrene.



example, maleic anhydride does not polymerize as such but undergoes copolymerization with styrene in a highly symmetrical manner to form styrene-maleic anhydride copolymer.

Properties and uses of copolymer. The properties of copolymers are usually quite different from those of homopolymers derived from each of the combining monomers.

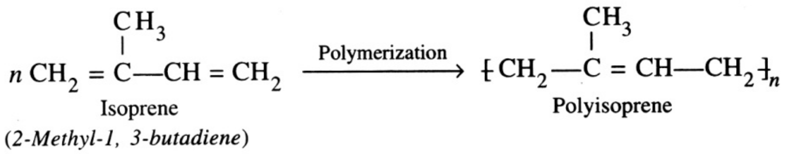
Actually, copolymers have better physical and mechanical properties. Copolymerization is similar to alloying in metallurgy. Just like alloys, various copolymers can be synthesized having desired properties. For example, polystyrene, is an homopolymer of styrene. It is a good electrical insulator and can be moulded into toys, combs, radio and television parts. In contract, SBR or Buna-S is a copolymer of styrene and butadiene. It is very tough and is a good substitute for natural rubber. It possesses high abrasion resistance, high load bearing capacity and its used for the manufacture of automobile tyres. It is also used for making floors tiles, footwear components, cable insulation, etc.

Rubbers :

Natural Rubber :

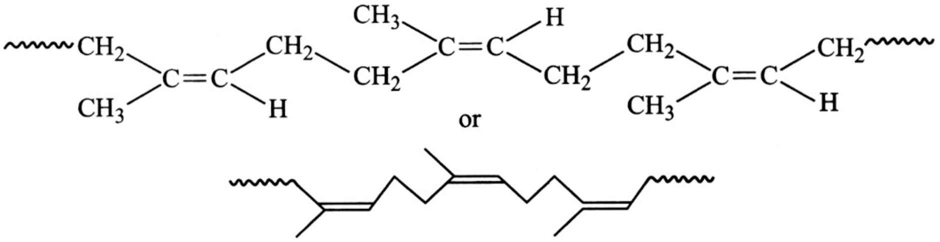
It is a natural polymer. It has remarkable elasticity and undergoes long range reversible extension even under relatively small applied force. That is why it is also called an elastromer. It is manufactured from latex which is colloidal solution of rubber particles in water. Latex is obtained by making incisions in the bark of rubber trees found in tropical and semitropical countries such as Southern India (Kerala, Tamil Nadu, Karnataka etc.) Indonesia Malaysia, Sri Lanka, South America, etc.

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

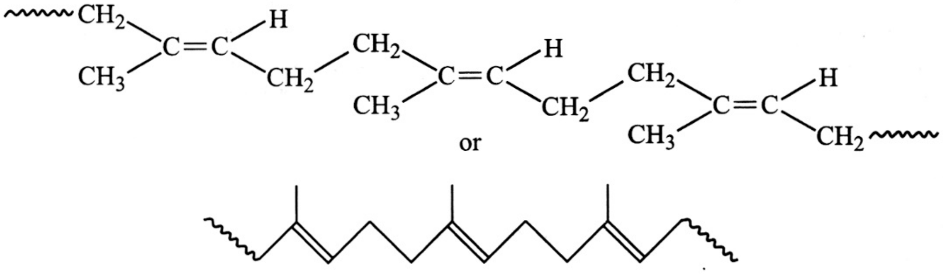


$$n\,CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2 \xrightarrow{\text{Polymerization}} \left[CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2\right]_n$$

Since each repeating unit is polyisoprene contains a double bond, it may have either a cis- or a trans-orientation. Actually, in natural rubber, all the bonds 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.



cis-Polyisoprene (*Natural rubber*)



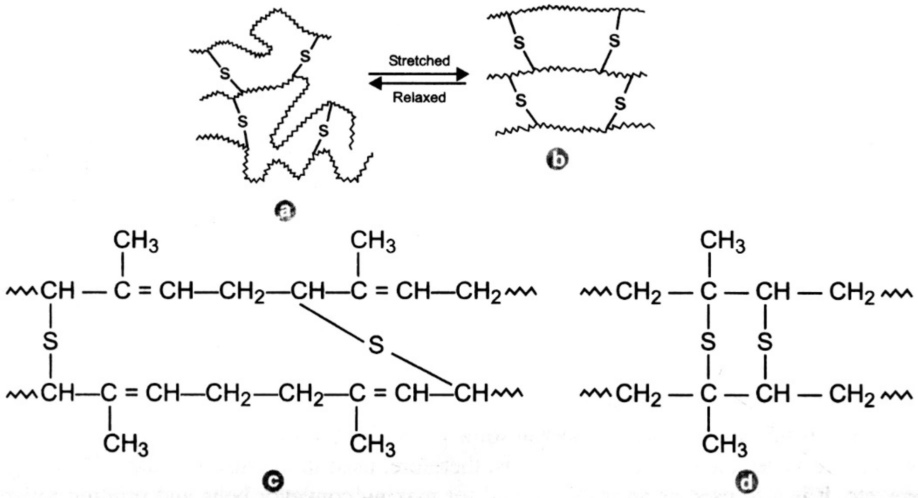
trans-Polyisoprene (*Gutta-Percha*)

Inspection of the structure of natural rubber reveals that there are no polar group/substitutes and hence intermolecular forces of attraction are only weak vandar 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 streched 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. Thus, natural rubber is elastic. In contrast, due to trans-orientation of double bonds, gutta percha has highly regular zig-zag chains which cannot be stretched much. Therefore, gutta percha is considered to be non-elastic.

Further, due to colid structure, natural rubber does not fit closely in the crystal lattice and hence is considered to be non-crystalline. In contrast, due to highly regular zig-zag structure, gutta percha fits closely in the crystal in the crystal lattice and hence is considered to be crystalline.

Vulcanized Rubber :

Natural rubber is soft and tacky (sticky) 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 low resistance to abrasion. It is also not-resistant to the action of organic solvents and is also easily attacked by oxidizing 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 etc. are used to accelerate the rate of vulcanization. The vulcanized rubber thus obtained has excellent elasticit, low water absorption tendency and is resistant to the action of organic solvents and oxidizing agents. During vulcanization, sulphur bridges or cross-links between polymer chains are introduced either at their reactive allylic positions or at the sites of the double bonds.



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 ebonite and 30% S for making battery case rubber. The process of vulcanization was discovered by Charles Goodyear in 1839.

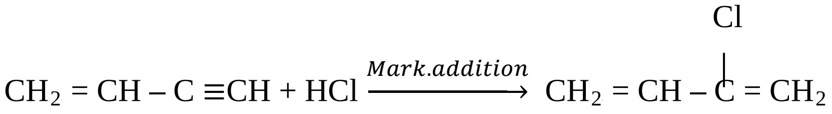
Synthetic Rubbers :

Synthetic rubber may be defined as any vulcanisable rubber like polymer which is capable of getting stretched to twice its length. However, it returns to its original size and shape when the stretching force is withdrawn.

Majority of these rubbers are derived from butadiene derivatives and contain carbon-carbon double stretched to twice its length. However, it returns to its original size and shape when the stretching force is withdrawn.

Some important synthetic rubbers are : Neoprene, Buna-S, Buna-N and Thiokol.

1. Neoprene. It is a polymer of chloroprene (2-chloro-1, 3-butadiene) and is also called polychloroprene. Chloroprene needed for the purpose is prepared by the addition of HCl to vinylacetylene. The addition takes place on the triple bond in accordance with Markovnikov’s rule.



$$CH_2 = CH - C \equiv CH + HCl \xrightarrow{Mark.addition} CH_2 = CH - \underset{}{\overset{Cl}{\overset{|}{C}}} = CH_2$$

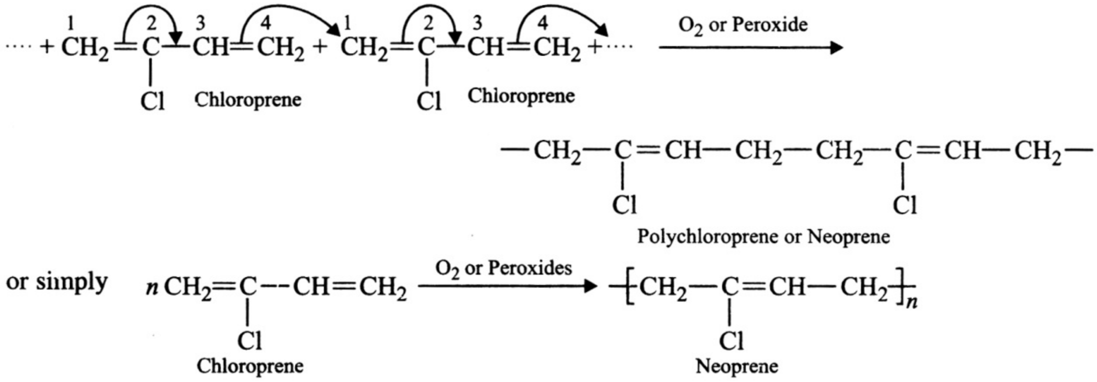
Vinylacetylene Chloroprene

Vinylacetylene needed for the purpose is prepared by dimerization of acetylene by passing it through an aqueous solution of ammonium chloride and cuprous chloride at 343 K.

$$CH \equiv CH + HC \equiv CH \xrightarrow[343K]{NH_4Cl, CuCl} CH_2 = CH - C \equiv CH$$

Acetylene (2 molecules) Vinylacetylene

Reaction. Chloroprene polymerises very rapidly (700 times faster than isoprene). No specific catalysts are needed but the polymerization is slower in absence of oxygen. The reaction occurs by 1, 4-addtion of one chloroprene molecule to the other as shown below :

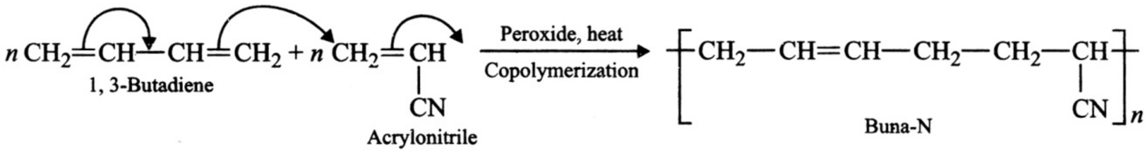


It is an excellent rubber like material.

Uses. Neoprene is inferior to natural rubber in some properties but superior in its stability to aerial oxidation and in its resistance to vegetable or mineral oils. It is, therefore, used in manufacture of hoses, gaskets, shoe heels, stoppers, etc. It is also used as an insulator and for making conveyor belts and printing rollaers.

2. Buna-S. It has already been discussed under copolymerization.

3. Buna-N or Nitrile rubber. Buta-N is obtained by copolymerization of 1, 3-butadiene and acrylonitrile in presence of a peroxide catalyst.



The letter ‘N’ in Buna-N stands for acrylonitrile.

Uses. It is resistant to the action of petrol, lubricating oils and organic solvents. It is, therefore, used in making oil seals, hoses and tank linings etc.

4. Thiokol. It is prepared by copolymerization of 1, 2-dichloroethene (ethylene dichloride) with sodium tetrasulphide (Na_2S_4) in presence of magnesium hydroxide.

$$n\,Cl-CH_2-CH_2-Cl + n\,Na_2S_4 \xrightarrow[\text{Polymerization}]{Mg(OH)_2} [-CH_2-CH_2-S-S-S-S-]_n + 2n\,NaCl$$

Properties and uses. It is also called polysulphide rubber. It has slightly less tensile strength than natural rubber but is exceptionally resistant to the action of mineral oils, solvents, oxygen and ozone.

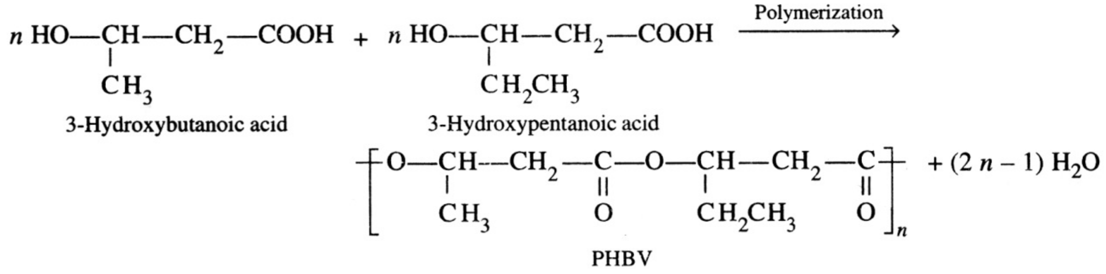
Biodegradable Polymers.

Polymers such as polysaccharides (starch, cellulose, etc.) proteins and nucleic acids which control the various life processes are called **biopolymers.**

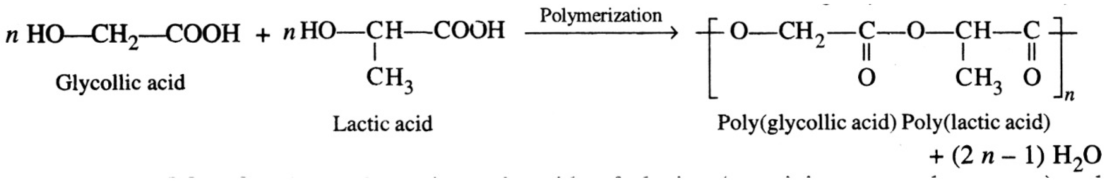
All these biopolymers disintegrate by themselves in biological systems during a certain period of time by enzymatic hydrolysis and to some extent by oxidation and hence are biodegradable. As a result, they do not cause any pollution.

The most important class of biodegradable polymers are aliphatic polyesters and polyamides as discussed below :

(i) Poly – $\boldsymbol{\beta}$ –hydroxybutyrate – co – $\boldsymbol{\beta}$ – hydroxyvalerate (PHBV). It is a thermoplastic copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid in which the two monomer units are connected by ester linkages.

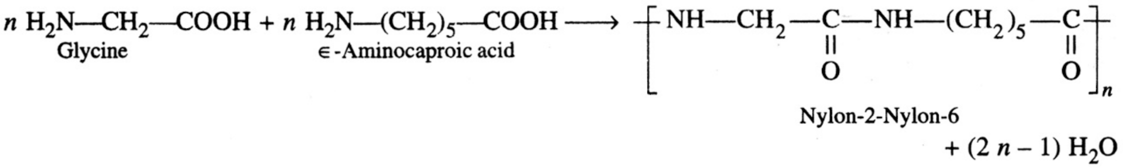


(ii) Poly (glycolic acid) Poly (lactic acid). This copolymer is commercially called dextron. This was the first biodegradable polyester used as sutures, i.e., for stitching of wounds after operation. This polymer gets degraded within the body in about a week's time. During this degradation, the polymer undergoes hydrolysis to form small non-toxic molecules which are excreted without causing any harm to the body.



$$n\,HO{-}CH_2{-}COOH + n\,HO{-}\underset{CH_3}{\underset{|}{CH}}{-}COOH \xrightarrow{\text{Polymerization}} \left[O{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}\underset{CH_3}{\underset{|}{CH}}{-}\underset{O}{\underset{\|}{C}} \right]_n + (2n-1)\,H_2O$$

(iii) Nylon – 2 – Nylon – 6. It is an alternating polyamide of glycine (containing two carbon atoms) and ∈ - aminocaproic acid or 6- aminohexanoic acid, (containing six carbon atoms)



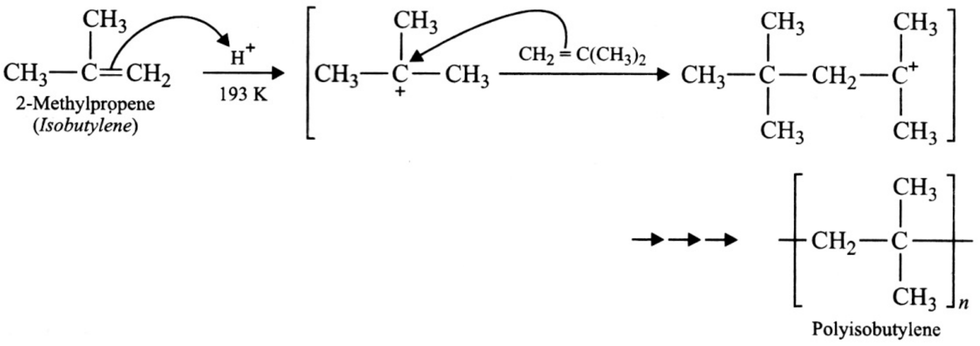
$$n\,H_2N{-}CH_2{-}COOH + n\,H_2N{-}(CH_2)_5{-}COOH \longrightarrow \left[NH{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}NH{-}(CH_2)_5{-}\underset{O}{\underset{\|}{C}} \right]_n + (2n-1)\,H_2O$$

It is a biodegradable step-growth copolymer.

About Polymers (For Advanced Competitions)

1. **Cationic Polymerization.** Certain alkene monomers can be polymerized by a cationic mechanism as well as by a free radical mechanism. Cationic polymerization, like free radical polymerization, occurs by a chain reaction pathway in presence of strong acids such as H_2SO_4 or Lewis acids such as $AlCl_3$, BF_3, etc. in presence of a trace of water as initiator.

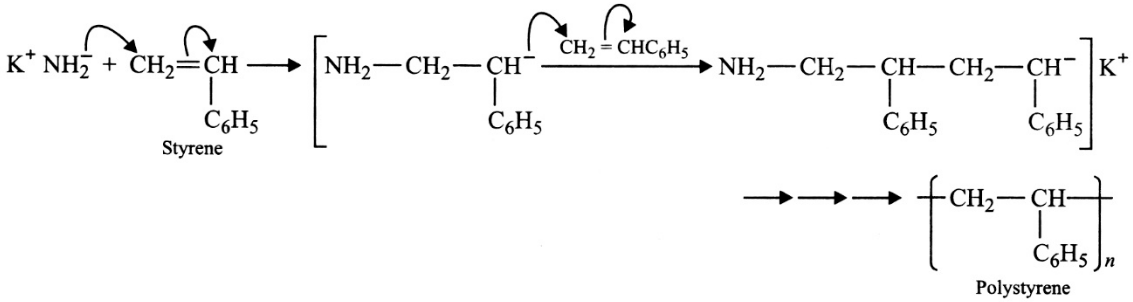
For example, isobutylene undergoes cationic polymerization easily since it has two electron-donating methyl groups that will stabilize the intermediate carbocation.



Polyisobutylene is a tacky material and hence it is used for making adhesives, tyre inner tubes.

2. Anionic polymerization. Alkene monomers with electron- withdrawing substitutents such as – C_6H_5, - CN, - COOR, etc. can be polymerized by an atomic mechanism as well as by a free radical mechanism. Anionic polymerization, like free radical polymerization, occurs by a chain reaction in presence of strong bases such Na, K, $K^+ \ NH_2^-$, $Li^+ \ NH_2^-$ etc.

For example formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerization reaction.



Evidently greater the stability of carbonion intermediate, more facile is the anionic polymerization. Thus, alkenes containing electron-withdrawing groups such as acrylonitrile, methyl methylacrylate, styrene, etc. can be polymerized under anionic conditions although free radical polymerization is commercially preferred.