

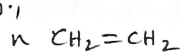
A Polymer is a giant molecule (or macromolecule) obtained by intermolecular combination of a large number of small molecules of the same or different type. (by covalent bonds).

The word polymer is derived from greek words 'poly' and or many, and 'meros' or parts.

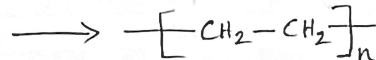
The starting material from which the molecule is formed is known as the monomer. (Simple short molecules)

The process by which the monomer molecules are linked to form a big polymer molecule is called Polymerisation

e.g.,



Ethylene (or) Ethene  
(Monomer)



polyethylene (or) Polyethene (PE)  
(Polymer)

### Nomenclature of Polymers:

Thermal properties,

Polymers according to their structure, mechanical properties, chemical properties, degree of polymerization, preparation methods, natural or synthetic etc, have been classified and named. They also classified into two main categories. ① natural polymers ② Synthetic polymers.

### ② Degree of polymerisation: (DP)

The number of repeating units (n) in the polymer chain is called degree of polymerization.

There may be hundreds or thousands or ten thousands or more monomer molecules are linked together in a polymer molecule.

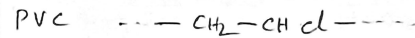
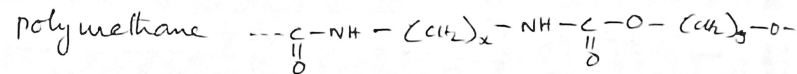
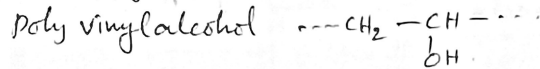
High Polymer Polymers with a high degree of polymerization ( $n$  is large) is called High Poly. High polymers generally have very high molecular weights ( $10^4$  to  $10^6$ ) and hence they are also called as 'macromolecules'.

Oligo Polymers: Polymers with low degree of polymerization are called 'oligopolymers'.

On the basis of chemical composition, polymers may be classified as <sup>mainly carbon atoms</sup>

i) Organic polymers: These polymers contains, apart from carbon atoms, then contains oxygen, nitrogen, sulphur and halogen atoms even in the main chain.

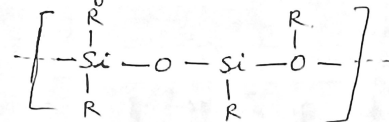
e.g.,



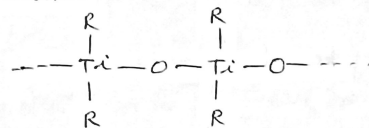
ii) Elemento-organic or hetero-organic polymers.

Polymers whose chains are composed of carbon atoms and hetero atoms (except N, S and O)

e.g., (i) Polysiloxanes



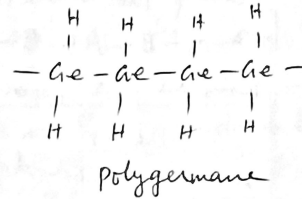
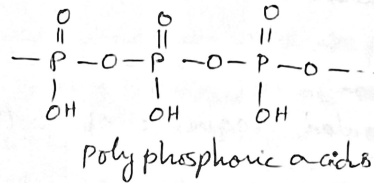
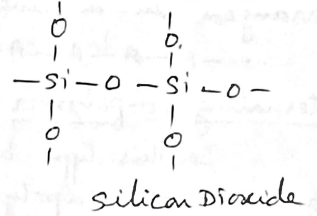
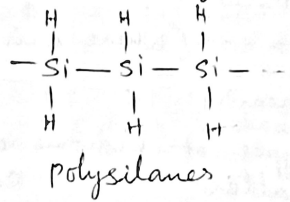
ii) Polytitanoxanes.



(iii) Polystannoxanes

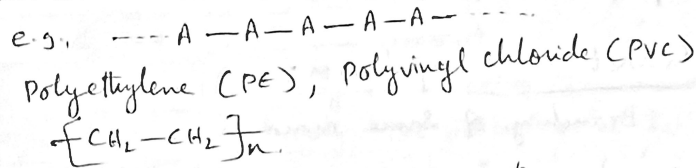
iii) Inorganic Polymers.

These are polymers containing no carbon atoms. The chains of these polymers are composed of different atoms joined by chemical bonds, while weaker inter-molecular forces act between the chains.

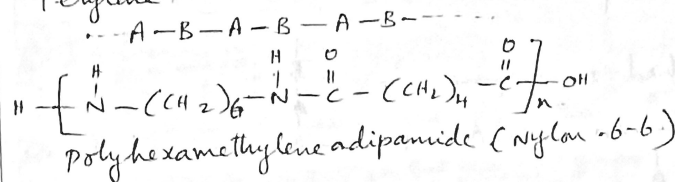


Homopolymers

A polymer formed from only one type of monomer is called homopolymer (ie, polymer consists of identical monomers).



Copolymer: A polymer formed from two or more different kinds of monomer is called a copolymer. e.g, Nylon-66, Terylene.





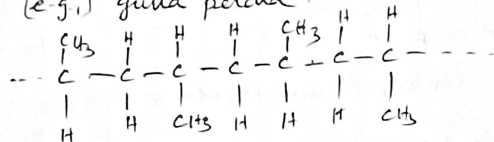




② Syndiotactic Polymer

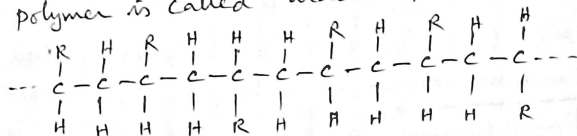
If the functional groups are located alternatively above and below the plane of the carbon-carbon chain, then that polymer is called syndiotactic polymer.

(e.g.) gutta percha



③ Atactic Polymer

If the functional groups are randomly arranged around the main chain, then that polymer is called atactic polymer (e.g.) Polypropylene



Because of their orderly arrangements, the chains of isotactic and syndiotactic polymers can lie closer and the polymers are more crystalline. On the otherhand, atactic polymer is soft and amorphous.

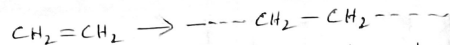
Functionality

The number of bonding sites (or reactive sites) present in a monomer is referred to as its functionality.

For a substance to act as a monomer, it must have at least two reactive sites or bonding sites.

In an olefin, the double bond can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination.

Thus,



Thus ethylene is considered to be bifunctional. (Functionality = 2).

Mrs. K. Anandhy (7)

Acetylene ( $\text{C}\equiv\text{CH}$ ) has a functionality of four.

Other reactive functional groups are  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NH}_2$ , amino acid, di-ol, polyalcohols, di-acids etc,

Depending upon the functionality of monomeric units, it is possible to obtain different types of structures for polymers.

For (e.s.), a bifunctional monomer polymerise to give linear or straight chain polymer.

If a trifunctional monomer is mixed in small amounts with a bifunctional monomer, they polymerise to give branched chain polymer.

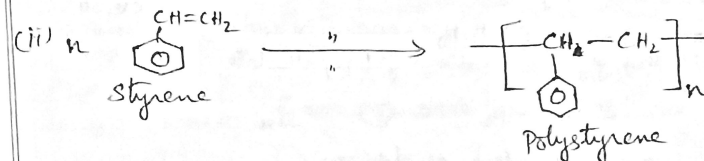
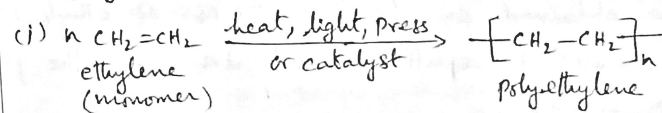
A polyfunctional monomer polymerise to give cross-linked polymer with three dimensional network.

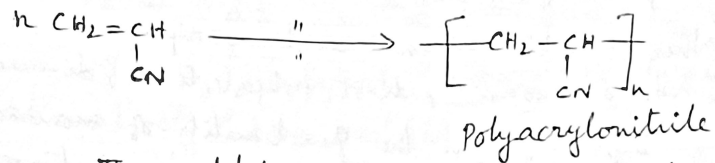
Types of Polymerisation: (There are 3 types of polymerisation)

- ① Addition or chain polymerisation
- ② Condensation polymerisation
- ③ Co-polymerisation.

① Addition or chain polymerisation.

In addition polymerisation, the monomers just add on to form the polymer without the loss of any smaller molecules. The polymer formed is an exact multiple of the original monomer. (ie. the monomer species retains its identity in a polymer). e.g., polyethylene, polystyrene, PVC, polyacrylonitrile, PVA, PMMA





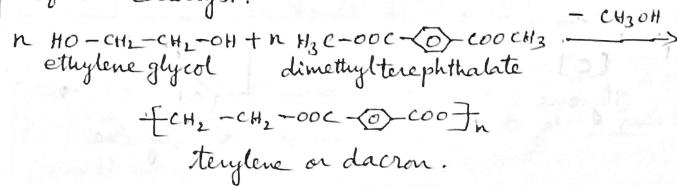
The addition polymerisation reaction must be initiated by the application of heat, light, pressure or a catalyst for breaking down the double bond of the monomers.

② Condensation or step polymerization:

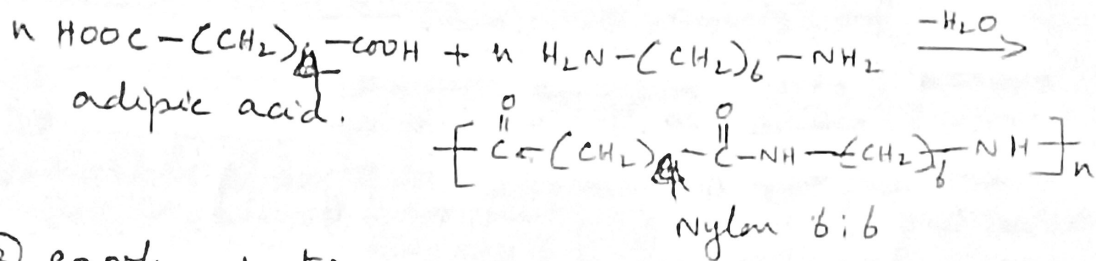
Condensation polymers are formed by the combination of monomers with the elimination of simple, small molecules such as H<sub>2</sub>O, CH<sub>3</sub>OH etc. The monomers involved in condensation polymerisation should have polar groups like -OH, -NH<sub>2</sub>, -COOH etc. The molecular weight of the polymers formed is lesser than the weight of simple monomers involved in the reaction. This is due to the elimination of smaller molecules. Condensation polymerisation results in the formation of thermosetting plastics.

e.g.) for condensation polymers are terylene, Nylon 6:6, Poly urethane, Bakelite.

(i) Terylene is the most important poly ester. It is obtained by heating excess of ethylene glycol with dimethyl terephthalate at 200°C in the presence of a catalyst.



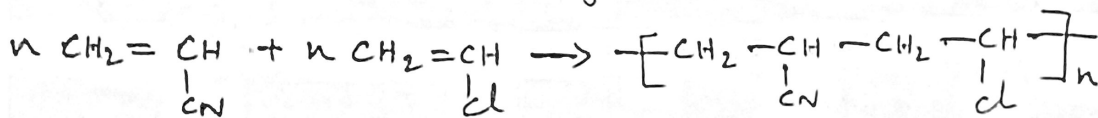
(ii) Nylon-6:6 is the most important polyamide. It is obtained by heating adipic acid and hexamethylene diamine.



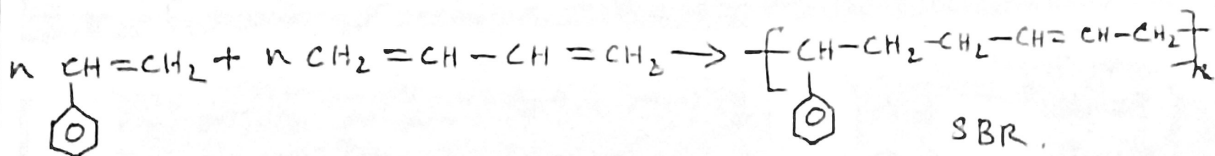
### ③ Copolymerisation.

The polymerisation of a mixture of two different monomers of equal reactivity is known as copolymerisation.

(e.g.) Acrylonitrile and vinyl chloride combine to give co-polymer of acrylonitrile vinyl chloride.



b) styrene and butadiene combine to give a copolymer of styrene-butadiene rubber. (SBR) or GR-S rubber.



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Differences between addition and condensation

polymerisation.

Addition Polymerisation	Condensation Polymerisation.
1. Monomers just add on to give a polymer without the loss of any small molecules.	① Monomers undergo condensation reaction among themselves to form the polymer with the loss of small molecules such as $H_2O$ , $CH_3OH$ etc.
2. In addition polymerisation, the monomer should contain at least one double bond or triple bond. (double bond - active centre)	② In condensation polymerisation the monomers should have the functional groups like $-OH$ , $-NH_2$ , $-COOH$ etc. (functional gps - active centres)
3. The chain growth is at one active centre	③ The chain growth takes place at a minimum of two active centres.
4. Homo-chain polymer is formed.	④ Hetero chain polymer is formed.
5. The polymer product is formed immediately.	⑤ The polymer product is formed stepwise steadily.
6. The molecular weight of the polymer is an integral multiple of the monomer weight.	⑥ The molecular weight of the polymer is always less than the integral multiple of the monomer weight.
7. Mostly thermoplastics are formed by this process.	⑦ Thermosetting plastics are formed by this process.
8. This follows a free radical or cationic or anionic mechanism.	⑧ This follows the mechanism of condensation reaction such as esterification, amide formation etc.
9. e.g., Polyethylene, Polystyrene, PVC etc.	⑨ Nylon 6:6, Terylene, Bakelite etc.

## Mechanism of Addition Polymerisation.

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Addition Polymerisation is classified into 4 types depending upon the reagents used.

- ① Free-radical addition polymerisation.
- ② Cationic addition polymerisation.
- ③ Anionic addition polymerisation.
- ④ Zeigler-Natta (or) Co-ordination polymerisation.

### ① Mechanism of Free radical polymerisation.

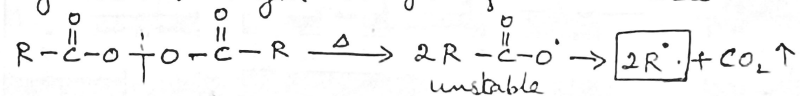
It takes place in 3 steps.

- (a) chain-initiation step.
- (b) " propagation step.
- (c) " termination step.

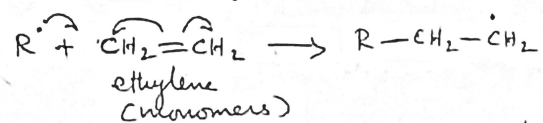
#### (a) chain-initiation step.

Chain-initiators are used to activate the monomer molecules. Chain initiators are usually organic peroxides or other reagents which decompose to give free radicals. Then the free radical adds with the first monomer molecule to produce the chain initiating monomer species.

For e.g., organic peroxides undergo homolytic fission by heat or light to give free radicals.



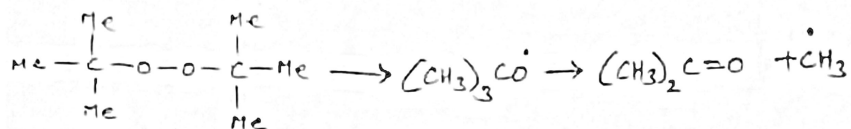
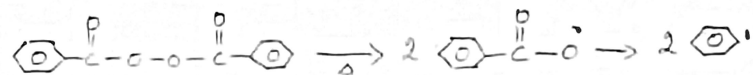
The  $\text{R}\cdot$  free radical contains an unpaired electron which is highly reactive. This attacks the monomer easily.



Now the free radical site is transferred to the monomer.

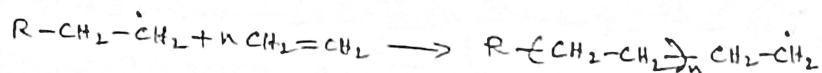
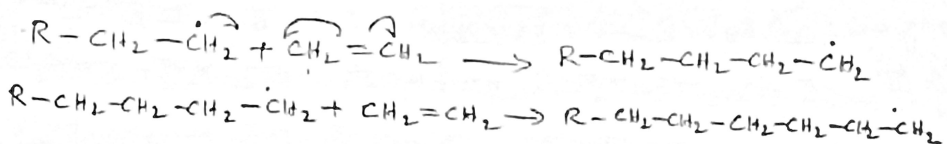


Note: Benzoyl peroxides (or) t-butyl peroxides are common initiators for free radical polymerisation.



(b) Chain propagation step

In the propagation step, the radical site at the first monomer attacks the double bond of the second monomer and results in the linking up of the second monomer and thus the radical chain continues.



Like this the chain grows and a macro radical is produced.

(c) Chain termination step

Chain termination results due to deactivation of the macro radical. This occurs by (i) combination of free radicals (ii) disproportionation of free radicals.

(i) Combination of free radicals.

Two growing macro radicals may combine by the coupling of the lone electron present in each chain atom and the reactivity of the radical is arrested.