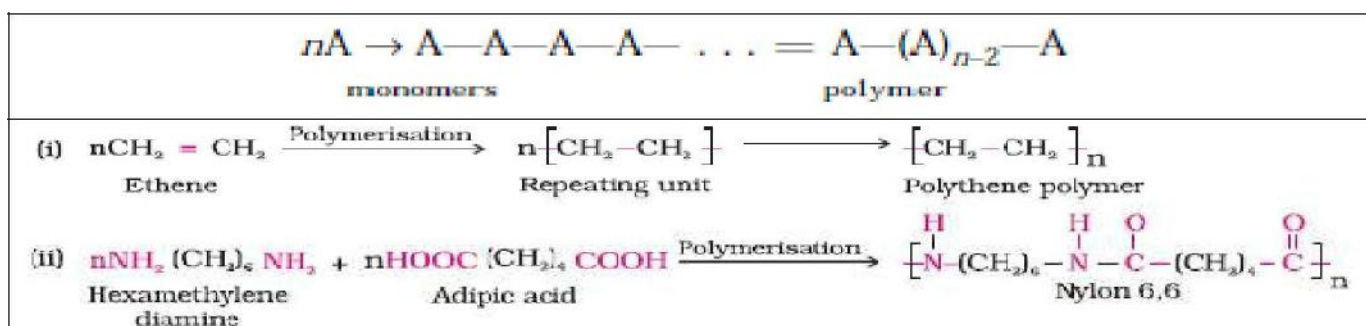


# POLYMERS

Polymers are the high molecular weight compounds obtained by repeated union of simple molecules. (Monomers). **Ex:** Starch, Polyvinyl chloride, Polyethylene, Nylon 6, 6 and etc.

The word '*Polymer*' is coined from two Greek words: *poly* means many and *mer* means unit or part. The term polymer is defined as very large molecules having high molecular mass. These are also referred to as *macromolecules*, which are formed by joining of repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as *monomers* and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called *polymerization*. The transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon 6, 6 are examples of two different types of polymerisation reactions.



## Monomers

Monomer is a simple repetitive unit which when joined together in large numbers which give rise to a polymer. These are the building blocks of Polymer

**Ex:** Vinyl chloride, ethene, propylene etc.

The number of repeating units (n) in the chain so formed is called the **Degree of polymerization(DP=n)**.

Polymers with a high degree of polymerization are called **High polymers** and those with low degree of polymerization are called **Oligopolymers**

### Degree of polymerization (DP).

Degree of polymerization is a number, which indicates the number of repetitive units (monomers) present in the polymer. By knowing the value of DP, the molecular weight of the polymer can be calculated.

[Molecular wt of the polymer] = DP x Molecular wt of each monomer. DP is represented as 'n'.

**Ex:**  $(CH_2 - CH_2)_n$  Polythene  
Here 'n' is the DP.

i) Calculate the molecular weight of the polythene polymer given DP is 100.

Molecular weight of the polythene = DP X Molecular weight of Polythene  
= 100 X 28 = **2800**.

## Basic Concepts:

### 1.Functionality

The **functionality of a monomer** is the number of sites it has for bonding to other monomers under the given conditions of the polymerization reaction. Thus, a bifunctional monomer, i.e., monomer with functionality two, can link to two other molecules under suitable conditions.

A polyfunctional monomer is one that can react with more than two molecules under the conditions of the polymerization reactions.

**Definition:** The number of bonding sites (or) reactive sites or functional groups present in the molecule.

Ex: The double bond in vinyl monomers ( $\text{CH}_2 = \text{CHX}$ ) can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination.



A). When the functionality of monomer is two bifunctional linear (or) straight chain polymer is formed.

Ex: (a) vinyl monomers (b) adipic acid (c) hexamethylene diamine

Example for polymer: HDPE (high density polythene)



B). When the functionality of monomer is three (tri-functional), three-dimensional net work polymer is formed. Ex: phenol, glycerol

Examples for polymers : Urea formaldehyde, phenol formaldehyde.



C). when a trifunctional monomer is mixed in small amounts with a bifunctional monomer, a branched chain polymer is formed.

Ex: LDPE (LOW density polyethene)



## 2. Nomenclature of Polymers

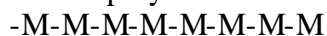
Polymers are classified in to four types

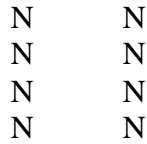
a) Homo Polymers b) Hetero polymers c) Homo chain Polymers d) Hetero chain polymers

**a) Homo Polymers** : Polymers made up of with same type of monomers are called homo polymers  
eg: Poly ethylene, PVC

**b) Hetero polymers** : Polymers made up of with different type of monomers are called hetero polymers  
eg: buna-s rubber

**Graft copolymers:** If main chain consists of one monomer and branched chain consists of another monomers are called Graft copolymers





**c) Homo chain Polymers** : If the main chain consists of only one type of atoms called Homo chain Polymers eg: polyethylene.  $-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-$

**d) Hetero chain polymers:** If the main chain consists of different type of atoms called Hetero chain Polymers eg: Polyester, Nylon-6.  $-\text{C}-\text{O}-\text{C}-\text{O}-\text{C}-\text{O}-\text{C}-\text{O}-$

### Copolymers

Homopolymer from a single monomer, copolymer from two (or more) monomers chain copolymerization (different monomers incorporated during the growth of the polymer chain) can lead to:

alternating copolymer – ABABABABABABABABABABABA

block copolymer - AAAAAAAAAABBBBBBBBBBBBBBAAA

random copolymer - BAABBAABABBABBBBAABBAB

graft copolymer - branches of a different polymer are attached to a polymer chain

AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAABBBBBBBBBBBBBBBBBBBBBB  
(generate reactive site on existing polymer chain, grow new chain)

**3. Tacticity** – The difference in configuration due to the orientation of different functional groups with respect to the main chain is called tacticity. It is of three types

**a). Isotactic** – If all the functional groups are arranged on the same side of main chain is called isotactic



**b). Syndiotactic** - If all the functional groups are arranged in the alternative fashion of main chain is called Syndiotactic



**c). Atactic** - If all the functional groups are arranged in random of main chain is called atactic



#### Basis of Classification

Origin

Thermal Response

Mode of formation

Line structure

Application and Physical Properties

Tacticity

Crystallinity

#### Polymer Type

- Natural, Semi synthetic, Synthetic

- Thermoplastic, Thermosetting

- Addition, Condensation

- Linear, Branched, Cross-linked

- Rubber, Plastic, Fibers

- Isotactic, Syndiotactic, Atactic

- Non crystalline(amorphous), Semi-crystalline, Crystalline

There are several ways of classification of polymers based on some special considerations. The following are some of the common classifications of polymers: [1] by Source [2] by Backbone of the chain [3] by Structure [4] by Composition [5] by Mode of Polymerization [6] by Molecular force

**Classification Based on Source:** [1] *Natural Polymers*: These polymers are found in plants and animals. Examples are proteins, cellulose, starch, resins and rubber. [2] *Semi-synthetic Polymers*: Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the usual examples of this sub category. [3] *Synthetic Polymers*: A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna - S) are examples of man-made polymers.

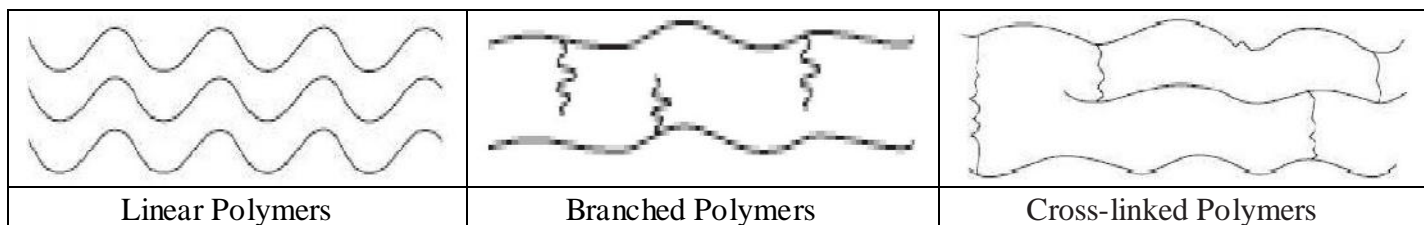
**Classification Based on Backbone of the polymer chain: *Organic and Inorganic Polymers*:**

A polymer whose backbone chain is essentially made of carbon atoms is termed as **organic polymer**. The atoms attached to the side valencies of the backbone carbon atoms are, however, usually those of hydrogen, oxygen, nitrogen, etc. The majority of synthetic polymers are organic. On the other hand, generally chain backbone contains no carbon atom is called **inorganic polymers**. Glass and silicone rubber are examples of it.

**Classification Based on Structure of Polymers:** [1] *Linear Polymers*: These polymers consist of long and straight chains. The examples are high density polythen, PVC, etc.

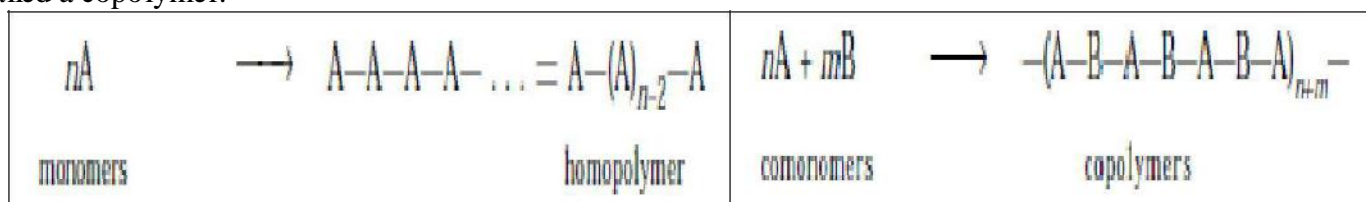
[2] *Branched Polymers*: These polymers contain linear chains having some branches, e.g., low density polythene.

[3] *Cross-linked Polymers*: These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains, e.g. vulcanized rubber, urea-formaldehyde resins, etc. Cross linked polymers are hard and do not melt, soften or dissolve in most cases.



**Classification Based on Composition of Polymers:** [1] *Homopolymer*: A polymer resulting from the polymerization of a single monomer; a polymer consisting substantially of a single type of repeating unit.

[2] *Copolymer*: When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer.



Lets imagine now two monomers(A and B) are made into a copolymer in many different ways

In an **alternating copolymer**, the two monomers are arranged in an alternating fashion

In a **random copolymer** the two monomers may follow in any order.

In a **block copolymer** all of one type of monomers are grouped together , and all of the other are grouped together

In **graft copolymer**, a block copolymer can be thought of as two homopolymers joined together at the ends: branched copolymers with one kind of monomers in their main chain and another kind of monomers in their side chains.

Alternating	
Random	
Block	
Graft	

**Copolymerization:** A *heteropolymer* or *copolymer* is a polymer derived from two

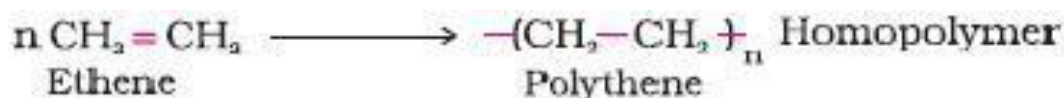
(or more) monomeric species, as opposed to a homopolymer where only one monomer is used.

Copolymerization refers to methods used to chemically synthesize a copolymer. Commercially

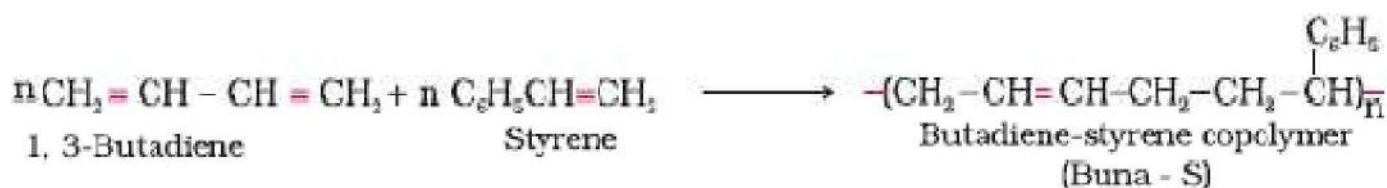
relevant copolymers include ABS plastic, SBR, Nitrile rubber, styrene-acrylonitrile,

**Classification Based on Mode of Polymerisation:** Polymers can also be classified on the basis of mode of polymerisation into two sub groups; (a) *Addition Polymers* and (b) *Condensation Polymers*.

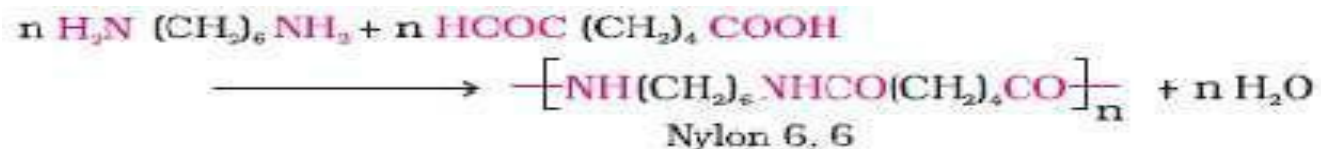
**Addition Polymers:** The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, *e.g.*, the formation of polythene from ethene and polypropene from propene. However, the addition polymers formed by the polymerisation of a single monomeric species are known as homopolymer, *e.g.*, polythene.



The polymers made by addition polymerisation from two different monomers are termed as copolymers, *e.g.*, Buna-S, Buna-N, etc.



**Condensation Polymers:** The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units. In these polymerisation reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. The examples are terylene (dacron), nylon 6, 6, nylon 6, etc. For e.g., nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid.



It is also possible, with three functional groups (or two different monomers at least one of which is tri-functional), to have long linkage sequences in two (or three) dimensions and such polymers are distinguished as *cross linked polymers*.

**Classification Based on Molecular Forces:** The mechanical properties of polymers are governed by intermolecular forces, e.g., van der Waals forces and hydrogen bonds, present in the polymer. These forces also bind the polymer chains. Under this category, the polymers are classified into the following groups on the basis of magnitude of intermolecular forces present in them. They are (i) *Elastomers* (ii) *Fibers* (iii) *Liquid resins* (iv) *Plastics* [(a) *Thermoplastic* and (b) *thermosetting plastic*].

**Elastomers:** These are rubber – like solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few ‘crosslinks’ are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc.

**Fibers:** If drawn into long filament like material whose length is at least 100 times its diameter, polymers are said to have been converted into ‘fibre’. Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. Examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

**Liquid Resins:** Polymers used as adhesives, potting compound sealants, etc. in a liquid form are described liquid resins. Examples are epoxy adhesives and polysulphide sealants.

#### Plastics

: A polymer is shaped into hard and tough utility articles by the application of heat and pressure; it is used as a ‘plastic’. Typical examples are polystyrene, PVC and polymethyl methacrylate.

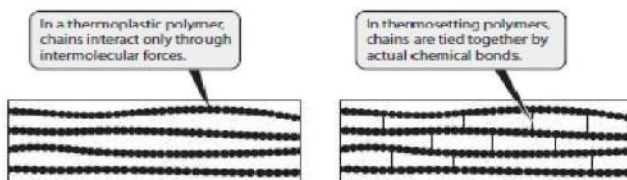
They are two types (a) thermoplastic and (b) thermosetting plastic.

**Thermoplastic Polymers:** Some polymers soften on heating and can be converted into any shape that they can retain on cooling. The process of heating, reshaping and retaining the same on cooling can be repeated several times. Such polymers, that soften on heating and stiffen on cooling, are termed ‘thermoplastics’. These are the



linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Polyethylene, PVC, nylon and sealing wax are examples of thermoplastic polymers.

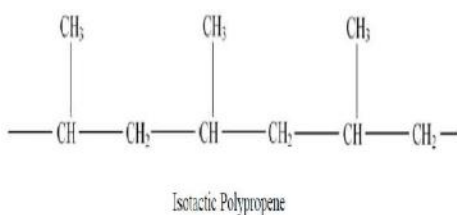
**Thermosetting Polymers:** Some polymers, on the other hand, undergo some chemical change on heating and convert themselves into an infusible mass. They are like the yolk of egg, which on heating sets into a mass, and, once set, cannot be reshaped. Such polymers, that become infusible and insoluble mass on heating, are called ‘thermosetting’ polymers. These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.



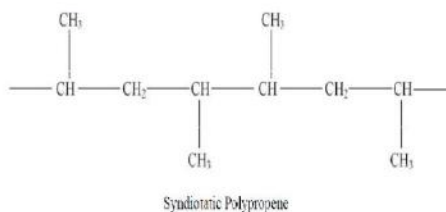
### 13.6 Tacticity:-

It may be defined as the geometric arrangement (orientation) of the characteristic group of monomer unit with respect to the main chain (backbone) of the polymers. On the basis of structure, polymer may be classified into three groups:-

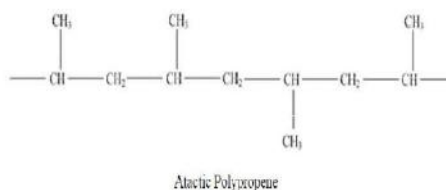
**A. Isotactic polymer:-** It is the type of polymer in which the characteristic group are arranged on the same side of the main chain.



**B. Syndiotactic polymer:-** A polymer is said to be syndiotactic if the side group (characteristic group) are arranged in an alternate fashion.



**C. Atactic polymer:-** A polymer is said to be atactic, if the characteristic groups (side group) are arranged in irregular fashion (randomness) around the main chain. It has proper strength and more elasticity.



## Types of Polymerization

There are four types of polymerisation reactions; (a) *Addition* or *chain growth* polymerisation (b) *Coordination* polymerisation (c) *Condensation* or *step growth* polymerisation and (d) *Copolymerization*

**Addition Polymerisation:** In this type of polymerisation, the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The monomers normally employed in this type of polymerization contain a carbon-carbon double bond (unsaturated compounds, *e.g.*, alkenes and their derivatives) that can participate in a *chain reaction*. A chain reaction consists of three stages, Initiation, Propagation and Termination.

In the *Initiation step* an initiator molecule is thermally decomposed or allowed to undergo a chemical reaction to generate an "active species." This "active species," which can be a free radical or a cation or an anion, then initiates the polymerization by adding to the monomer's carbon-carbon double bond. The reaction occurs in such a manner that a new free radical or cation or anion is generated. The initial monomer becomes the first repeat unit in the incipient polymer chain. In the *Propagation step*, the newly generated "active species" adds to another monomer in the same manner as in the initiation step. This procedure is repeated over and over again until the final step of the process, termination, occurs. In the *Termination step*, the growing chain terminates through reaction with another growing chain, by reaction with another species in the polymerization mixture, or by the spontaneous decomposition of the active site. Under certain conditions, anionic can be carried out without the termination step to generate so-called "living" polymers.

The following are several *general characteristics of addition polymerization*:

[1] Once initiation occurs, the polymer chain forms very quickly [2] The concentration of active species is very low. Hence, the polymerisation mixture consists of primarily of newly-formed polymer and unreacted monomer [3] Since the carbon-carbon double bonds in the monomers are, in effect, converted to two single carbon-carbon bonds in the polymer, so energy is released making the polymerization exothermic with cooling often required.

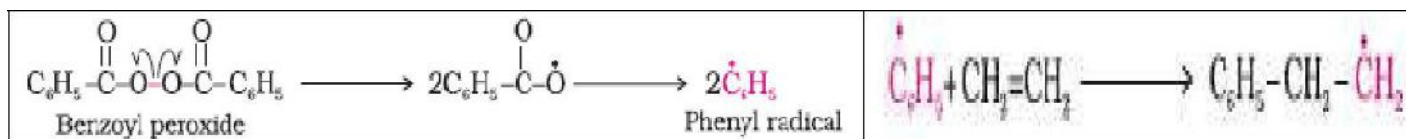
The mechanism of addition polymerisation can be divided broadly into two main classes, Free radical and Ionic polymerization and again Ionic is divided into two types Cationic and anionic Polymerisations

**Free radical polymerization:** A variety of alkenes or dienes and their derivatives are polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. A free radical may be defined as an intermediate compound containing an odd number of electrons, but which do not carry an electric charge and are not free ions. For example, the polymerization of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small



amount of benzoyl peroxide initiator.

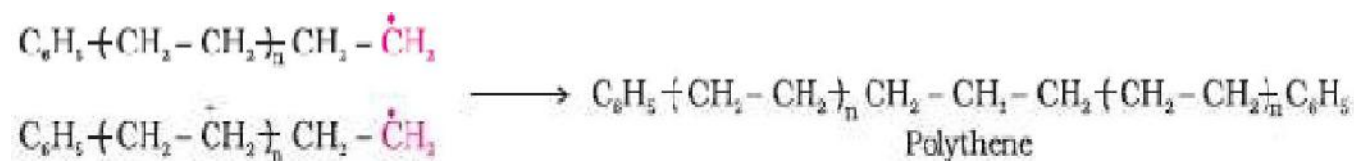
The first stage of the chain reaction is the **initiation process**; this process starts with the addition of phenyl free radical formed by the peroxide to the ethene double bond thus generating a new and larger free radical.



The second stage of the chain reaction is the **propagation process**, the radical reacts with another molecule of ethene, and another bigger sized radical is formed. The repetition of this sequence with new and bigger radicals carries the reaction forward and the step is chain propagating step



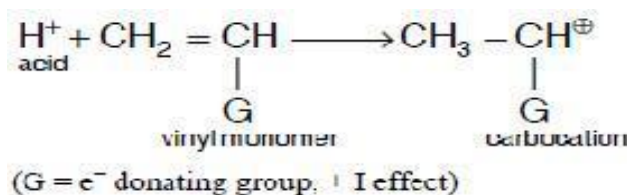
The final stage of the chain reaction is the **termination process**; the product radical formed reacts with another radical to form the polymerised product.



**Ionic Polymerisation:** The addition polymerization that takes place due to ionic intermediate is called ionic polymerization. Based on the nature of ions used for the initiation process ionic polymerization classified into two types; (a) Cationic polymerization and (b) Anionic polymerization

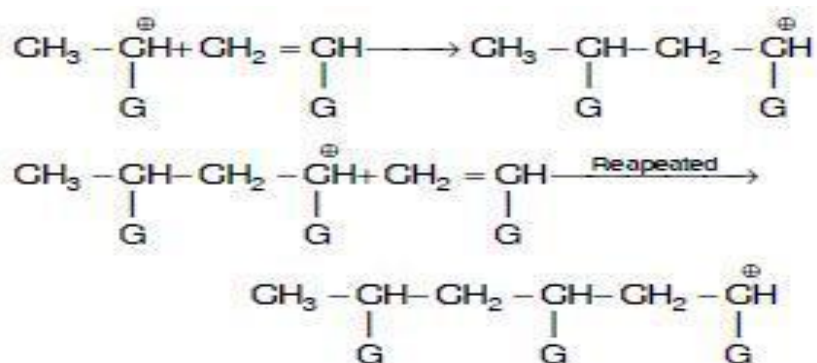
**Cationic polymerization** depends on the use of cationic initiators which include reagents capable of providing positive ions or  $\text{H}^+$  ions. Typical examples are aluminium chloride with water ( $\text{AlCl}_3 + \text{H}_2\text{O}$ ) or boron trifluoride with water ( $\text{BF}_3 + \text{H}_2\text{O}$ ). They are effective with monomers containing electron releasing groups like methyl ( $-\text{CH}_3$ ) or phenyl ( $-\text{C}_6\text{H}_5$ ) etc. They include propylene ( $\text{CH}_3\text{CH}=\text{CH}_2$ ) and the styrene ( $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ ).

i) **Chain Initiation:** Decomposition of the initiator is shown as  $\text{BF}_3 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{BF}_3(\text{OH}^-)$ . The proton ( $\text{H}^+$ ) adds to C - C double bond of alkene to form stable carbocation.

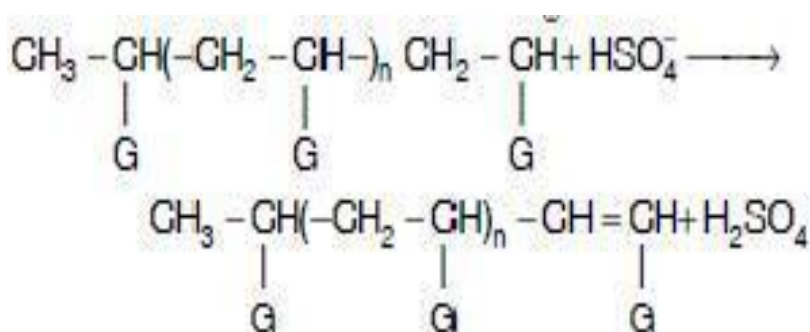


ii) **Chain Propagation:** Carbocation add to the C - C double bond of another monomer molecule to

from new carbocation.



**iii) Chain Termination:** Reaction is terminated by combination of carbocation with negative ion (or) by loss of proton



**Anionic polymerization** depends on the use of anionic initiators which include reagents capable of providing negative ions. Typical catalysts include sodium in liquid ammonia, alkali metal alkyls, Grignard reagents and triphenylmethyl sodium  $[(\text{C}_6\text{H}_5)_3\text{C-Na}]$ . They are effective with monomers containing electron withdrawing groups like nitrile ( $-\text{CN}$ ) or chloride ( $-\text{Cl}$ ), etc. They include acrylonitrile  $[\text{CH}_2=\text{C}(\text{CN})]$ , vinyl chloride  $[\text{CH}_2=\text{C}(\text{Cl})]$ , methyl methacrylate  $[\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3]$ , etc.

**i) Chain Initiation:** Potassium amide ( $\text{K}^+\text{NH}_2^-$ ) adds to C – C double bond of alkene to form stable carbanion.

where W is electron withdrawing group

**ii) Chain Propagation:** Carbanion adds to the C – C double bond of another monomer molecule to form new carbanion.

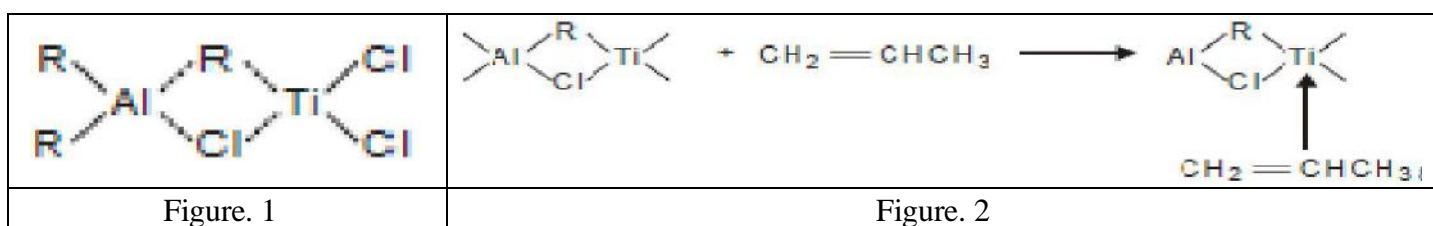
**iii)** Anionic polymerization has no chain termination reaction. So it is called living polymerization.

**Coordination polymerization:** It is also a subclass of addition polymerization. It usually involve

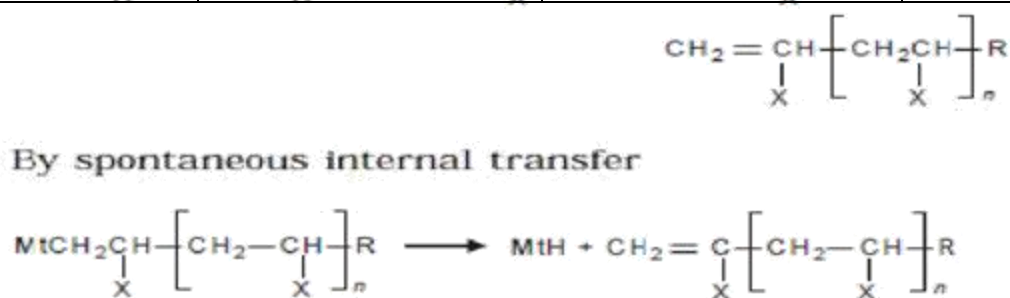
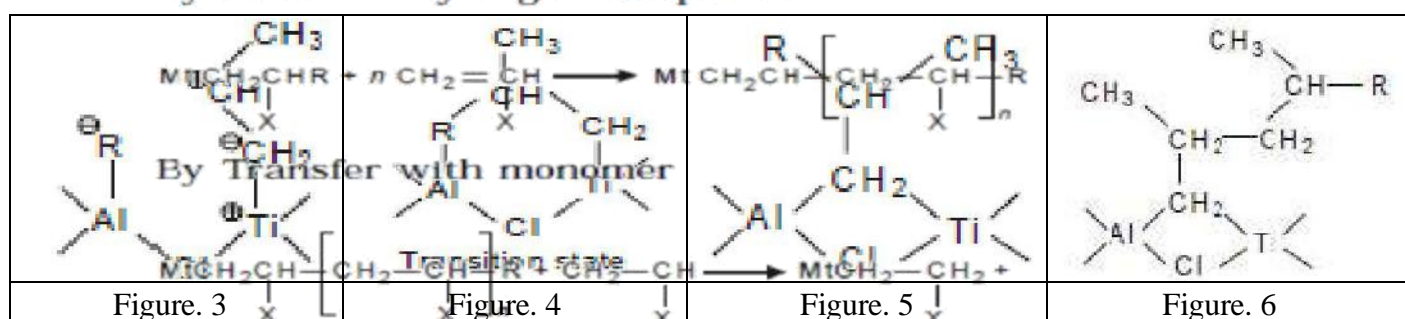
transition-metal catalysts. Here, the "active species" is a coordination complex, which initiates the polymerization by adding to the monomer's carbon-carbon double bond. The most important catalyst for coordination polymerization is so-called Ziegler-Natta catalyst discovered to be effective for alkene polymerization. Ziegler-Natta catalysts combine transition-metal compounds such as chlorides of titanium with organometallic compounds [TiCl<sub>3</sub> with Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]. An important property of these catalysts is that they yield stereoregular polymers when higher alkenes are polymerized, e.g., polymerization of propene produces polypropene with high selectivity. Branching will not occur through this mechanism since no radicals are involved; the active site of the growing chain is the carbon atom directly bonded to the metal.

**Ziegler-Natta catalysts:** These are a special type of coordination catalysts, comprising two components, which are generally referred to as the catalyst and the cocatalyst. The catalyst component consists of chlorides of titanium (TiCl<sub>3</sub> and TiCl<sub>4</sub>) and the cocatalysts are organometallic compound such as triethyl aluminium (Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>).

Triethyl aluminium [Al(R)<sub>3</sub>] act as the electron acceptor whereas the electron donor is titanium halides and the combination, therefore, readily forms coordination complexes (Fig. 1). The complex formed, now acts as the active centre. The monomer is complexed with the metal ion of the active centre in a way that the monomers attached towards the Ti—C bond (C from the alkyl group R) in the active centre, when it forms a π complex with the Ti ion (Fig. 2).



The bonds between R and Ti opens up producing an electron deficient Ti and a carbanion at R (Fig. 3). The Ti ion attracts the π electrons pair of the monomer and forms a bond (Fig. 4). This transition state now gives rise to the chain growth at the metal carbon bond, regenerating the active centre (Fig. 5). Repeating the whole sequence, with the addition of second monomer molecule, we will get the structure of the resultant chain growth as shown in Fig. 6.



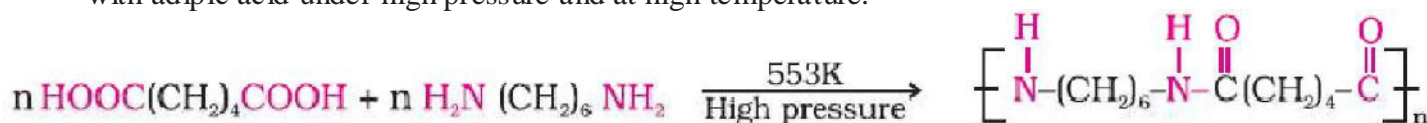
**Condensation Polymerisation:** This type of polymerisation generally involves a repetitive condensation reaction (two molecules join together, resulting loss of small molecules) between two bi-functional monomers. These polycondensation reactions may result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers. In these reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on. Since, each step produces a distinct functionalised species and is independent of each other; this process is also called as step growth polymerisation. The type of end polymer product resulting from a condensation polymerization is dependent on the number of functional end groups of the monomer which can react.

Monomers with only one reactive group terminate a growing chain, and thus give end products with a lower molecular weight. Linear polymers are created using monomers with two reactive end groups and monomers with more than two end groups give three dimensional polymers which are cross linked.

Polyester is created through ester linkages between monomers, which involve the functional groups carboxyl and hydroxyl (an organic acid and an alcohol monomer). The formation of polyester like terylene or dacron by the interaction of ethylene glycol and terephthalic acid is an example of this type of polymerisation.

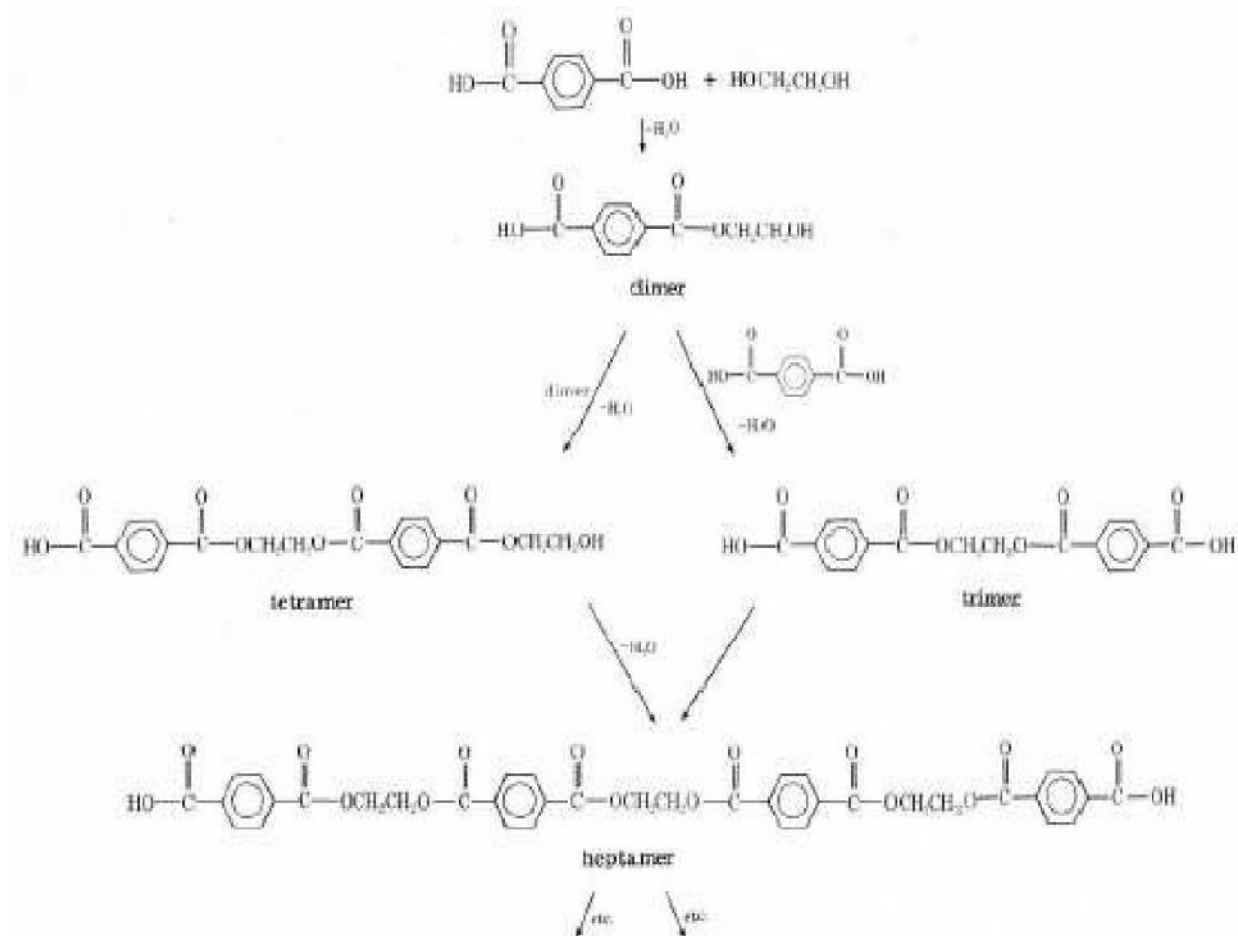


Polyamide is created through amide linkages between monomers, which involve the functional groups carboxyl and amine (an organic acid and an amine monomer). Nylon-6 is an example which can be manufactured by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.



This type of polymerization normally employs two bifunctional monomers that are capable of undergoing typical organic reactions. For example, a diacid can be allowed to react with a diol in the presence of an acid catalyst to afford polyester. In this case, chain growth is initiated by the reaction of one of the diacid's carboxyl groups with one of the diol's hydroxyl groups. The free carboxyl or hydroxyl group of the resulting dimer can then react with an appropriate functional group in another

monomer or dimer. This process is repeated throughout the polymerization mixture until all of the monomers are converted to low molecular weight species, such as dimers, trimers, tetramers, etc. These molecules, which are called oligomers, can then further react with each other through their free functional groups. Polymer chains that have moderate molecular weight can be built in this manner.



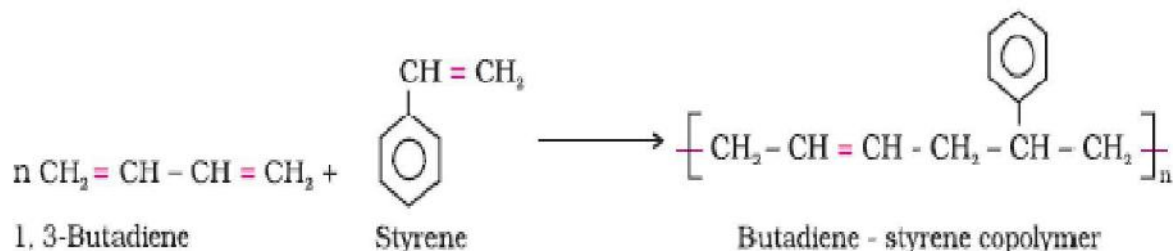
The following are several general characteristics of this type of polymerization

- 1) the polymer chain forms slowly, sometimes requiring several hours to several days
- (2) All of the monomers are quickly converted to oligomers, thus, the concentration of growing chains is high
- (3) Since most of the chemical reactions employed have relatively high energies of activation, the polymerization mixture is usually heated to high temperatures
- (4) Step-reaction polymerizations normally afford polymers with moderate molecular weights, i.e., <100,000
- (5) Branching or crosslinking does not occur unless a monomer with three or more functional groups is used.

**Copolymerization:** It is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerize and form a copolymer. The copolymer can be made not only by chain growth polymerisation but by step growth polymerisation also. It contains multiple units of each monomer used in the same polymeric chain. For example, a mixture of styrene and

1, 3 – butadiene can form a copolymer called styrene butadiene rubber (SBR).

A reaction in which a mixture of two (or) more monomers is allowed to undergo polymerisation is known as copolymerization. The polymer is known as copolymer.



<i>Addition polymerization</i>	<i>Condensation polymerization</i>
1. No by-product is formed.	1. Generally a by-product is obtained.
2. Homo-chain polymer is obtained.	2. Hetero-chain polymer is obtained.
3. Bifunctionality is provided due to the presence of double bond in the monomer.	3. Bifunctionality is provided due to the presence of reactive functional groups present at both ends of the monomer.
4. The chain growth is at one active centre.	4. The chain growth takes place at atleast two active centres.
5. Mostly thermoplastics are formed by this process.	5. Mostly thermosetting plastics are formed.
6. The polymer product is formed immediately.	6. The polymer product is formed stepwise steadily.
7. This follows a free radical or cationic or anionic mechanism.	7. This follows the mechanism of condensation reactions such as esterification and amide formation.

### Plastics(Plastomers)

Plastics are the high polymers that can be molded by the application of heat and pressure. During molding process, there is no chemical change. The plastics have linear structure.

Examples: Polythene, polyvinyl chloride, polystyrene, nylons, polyesters.



## Thermoplastics

Thermoplastics are the polymers that become soft on heating and hard on cooling and the process can be repeated for a number of times. They undergo reversible changes on heating.

Examples: Polythene (PE), polypropylene (PP), polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE or Teflon), polystyrene (PS), plexiglass, nylons, polyesters. (Polymethyl methacrylate)

**Thermoplastics –1.** These are formed by addition polymerisation

2. It consists of linear polymer chains with negligible cross-linking are soft and less brittle.
3. These are soluble in organic solvents.
4. soften on heating and hence are amenable for moulding into any shape in the hot condition on cooling, the resin becomes hard and rigid and retains the moulded shape.
5. These can be reheated and moulded into any other shape reversibly any number of times without any change in the chemical nature.

## Thermosetting polymers or, Thermosets:

Thermosets are the polymers that undergo chemical changes and cross-linking on heating and become permanently hard, rigid and infusible. They will not soften on heating, Once they are set.

Examples: Phenol-formaldehyde resin, urea-formaldehyde resin, epoxy resins (araldite), melamine, bakelite

**Thermosets (Thermosetting resins):**

1. Are mostly formed by condensation polymerisation.
2. Are mostly branched polymer chains with potential to form a 3-dimensional structure.
3. become hard and rigid on heating during moulding process. are not soluble in common organic solvents.
4. Exhibit their characteristic properties of non-softening and non-swelling nature, hardness and brittleness.
5. Cannot be softened, reformed, reshaped once they are set. cannot be reclaimed from wastes.

## Differences Between Thermoplastics and Thermosetting plastics

S.No	Thermoplastics	Thermosetting plastics
1	Formed either by addition or by Condensation polymerization reactions	Formed by Condensation polymerization reactions
2	They have either linear or branched structures.	They have three dimensional cross linked network structures
3	Adjacent polymer chains are held together by either vanderwaals forces, or by dipole-dipole forces or by hydrogen bonds	Adjacent polymer chains are held together by strong covalent bonds called crossed-links

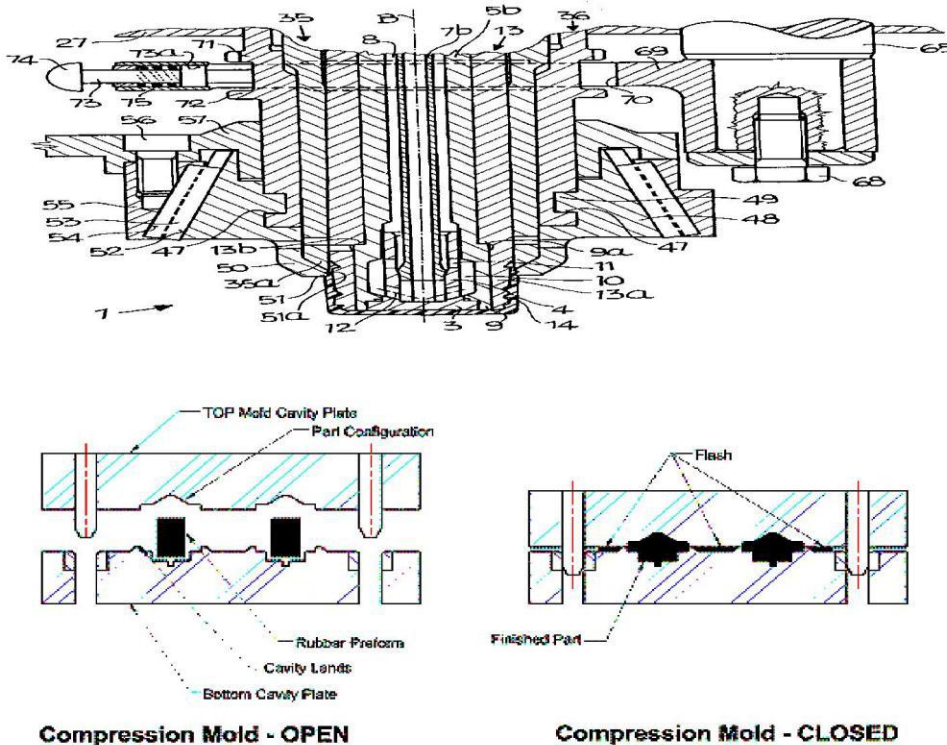
4	They soften on heating and stiffen on cooling	They do not soften on heating.
5	Low molecular weight thermoplastics are soluble in their suitable solvents.	They are insoluble in any solvent.
6	They can be remoulded, re-shaped and re-used.	They can be reclaimed from waste i.e., they can be recycled
7	There is no change in chemical composition and structure during moulding process.	They undergo chemical changes such as further polymerisation and cross-linking during moulding process.
8	They are soft and flexible	They are hard, rigid and infusible.
9	They can be reclaimed from waste i.e., they can be recycled.	They cannot be reclaimed from waste. They cannot be recycled.
10	They undergo reversible changes, on the application of heat.	They undergo irreversible changes on the application of heat.
11	They swell or dissolve in organic solvents.	They neither dissolve nor swell in organic solvents.
12	They are tough materials	They are brittle materials
13	The moulded articles are to be cooled to room temperature before taking out from the moulds to avoid deformation.	The moulded articles can be taken out of the moulds even when they are still hot without any deformations
14	Curing can be done by cooling.	Curing can be done by applying heat and pressure.
15	Examples: Polyethylene(PE), bakelite.	Examples: Phenol-formaldehyde resin (PF), urea-formaldehyde resin

## Moulding of Plastics

Moulding of plastics comprises of forming an article to the desired shape by application of heat and pressure to the moulding compounds in a suitable mould and hardening the material in the mould. The method of moulding depends upon the type of resins used. There are four types of moulding processes

### i) Compression moulding:

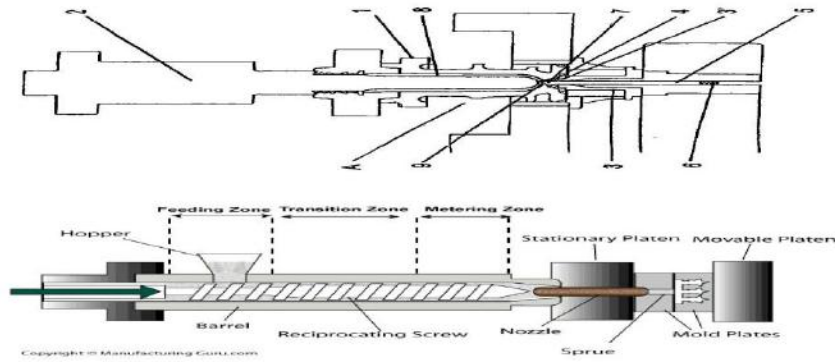
This method is applied to both thermoplastic and thermosetting resins. The predetermined quantity of plastic ingredients in proper properties are filled between the two half –pieces of mould which are capable of being moved relative to each other heat and pressure are then applied according to specifications. The containers filled with fluidized plastic. Two halves are closed very slowly. Finally curing is done either by heating or cooling. After curing the moulded article is taken out by opening the mould parts.



### ii) Injection moulding:

In this method, the moulding plastic powder is fed into a heated cylinder from where it is injected at a controlled rate into the tightly locked mould by means of a screw arrangement or by a piston plunger. The mould is kept cold to allow the hot plastic to cure and become rigid.

When the materials have been cured sufficiently, half of the mould is opened to allow the injection of the finished article without any deformation, etc. Heating is done by oil or electricity.



**iii) Transfer moulding:**

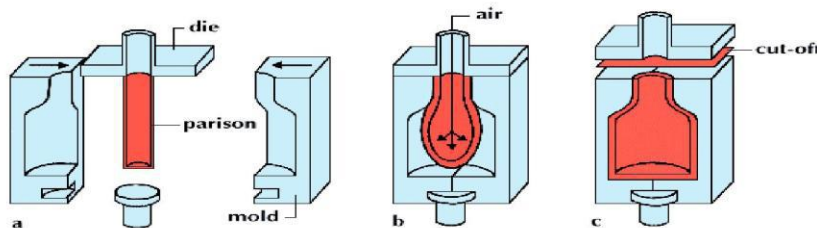
In this method, the principle is like injection moulding. The moulding powder is heated in a chamber to become plastic. Later it is injected into a mould by plunger working at high pressure through orifice. Due to this heat is developed and the plastic melts, takes the shape of the mould.

**iv) Extrusion moulding:**

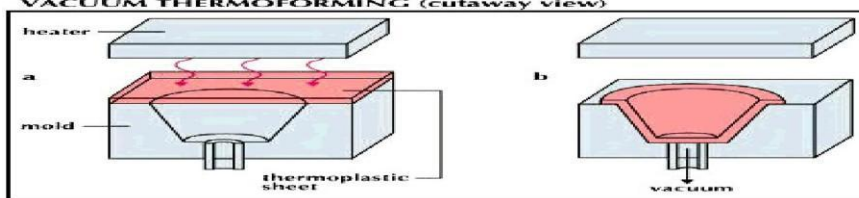
This process is useful in the preparation of continuous wires with uniform cross section. The heated plastic is pushed into the die with the help of screw conveyor. In the die, the plastic gets cooled due to the exposure to atmosphere and by artificial air jets.

Extrusion moulding is used mainly for continuous moulding of thermoplastic materials into articles of uniform cross section like tubes, rods, strips, insulated electric cables. The thermoplastic ingredients are heated to plastic condition and then pushed by means of a screw conveyor into a die, having the required outer shape of the article to be manufactured. Here the plastic mass gets cooled, due to the atmospheric exposure (or artificially by air jets). A long conveyor carries away continuously the cooled product.

**Extrusion Blow Molding (cutaway view)**



**VACUUM THERMOFORMING (cutaway view)**



## **Preparation, properties and engineering applications of some plastomers**

### **1. Bakelite:**

Preparation : It is prepared by condensing phenol with formaldehyde in presence of acidic/alkaline catalyst.

The initial reaction results in the formation of O- and P- hydroxyl methyl/phenol which reacts to form linear polymer. During modeling hexamethylene tetramine is added, which converts to insoluble solid of cross-linked structure Bakelite. Commercially these are available into two forms nova lacks & resols..

#### **i) Nova lacks.**

These are phenol formaldehyde resins obtained by condensation of phenol & formaldehyde in presence of acid as catalyst when phenol to formaldehyde ratio is greater than one

### **Properties.**

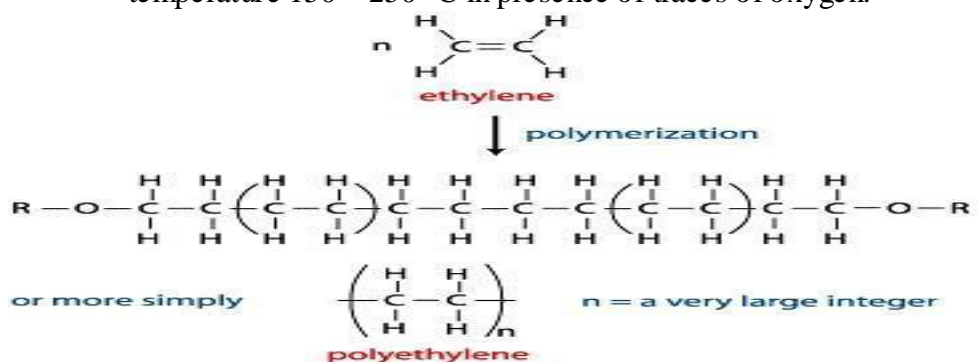
1. Phenolic resins are hard, rigid and strong materials They have excellent heat and moisture resistance.
2. They have good chemical resistance.
3. They have good abrasion resistance.
4. They have electrical insulation characteristics

5. They are usually dark coloured.
6. Lower molecular weight grades have excellent bonding strength and adhesive properties.

**Uses:** Phenol formaldehyde resins are used for

1. Domestic plugs and switches
2. Handles for cooker and saucepans.
3. Distributor heads for cars
4. Adhesives for grinding wheels and brake linings. Varnishes, electrical insulation and protective coatings.
5. The production of ion exchange resins.

**Polyethylene:** This can be obtained by the polymerization of ethylene at 1500 atm and a temperature 150 – 250 °C in presence of traces of oxygen.



### **Properties:**

1. Depending upon the density, they may be LDPE and HDPE.
2. If we use free radical initiator, LDPE is the product while use of ionic catalysts results in the formation of HDPE.
3. It is a rigid, waxy white solid. Translucent.
4. It is permeable to many organic solvents.
5. It crystallizes easily.

LDPE has a density 0.91 to 0.925 g/cm<sup>3</sup> HDPE has a density 0.941 to 0.965 g/cm<sup>3</sup>

HDPE is linear and has better chemical resistance.

**Uses:** 1. These are useful in the preparation of insulator parts, bottle caps, flexible bottles, pipes etc.

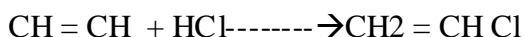
2. LDPE is used in making film and sheeting. Pipes made of LDPE are used for both agricultural, irrigation and domestic water line connections.

3. HDPE is used in manufacture of toys and other household articles.

### **PVC :**

Poly Vinyl Chloride is obtained by heating a water emulsion of vinyl chloride in presence of a small amount of benzoyl peroxide or hydrogen peroxide in an auto clave under pressure.

Vinyl chloride, so needed is generally prepared by treating acetylene at 1 to 1.5 atmospheres with hydrogen chloride at 60°C to 80°C in the presence of metal chloride as catalyst.



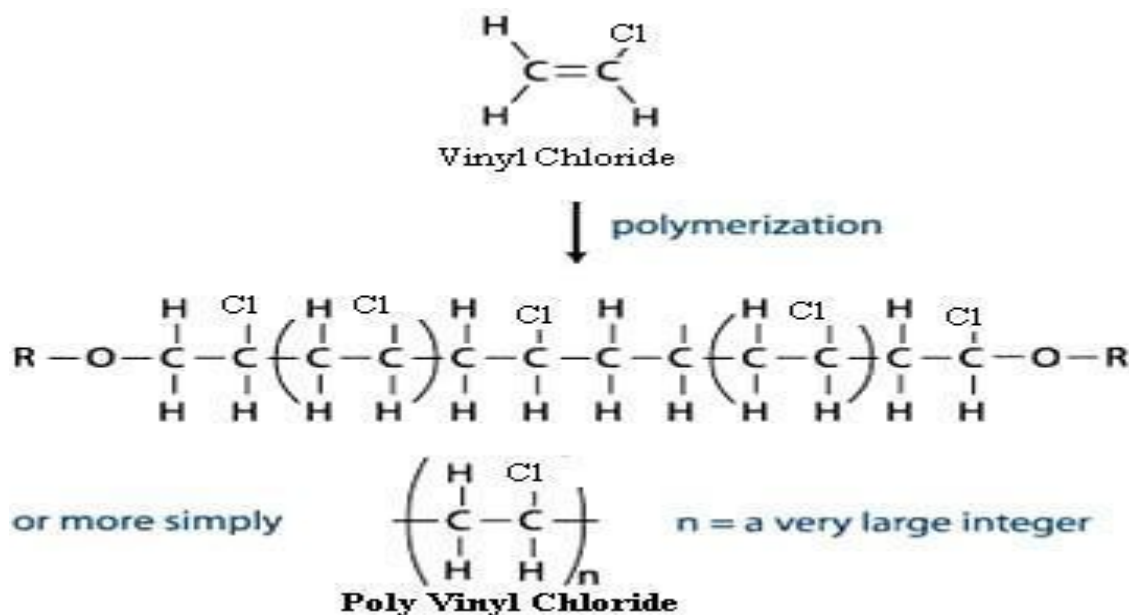


**Properties:**

1. It occurs as a colourless rigid mater
2. It is having high density and low softening point.
3. It is resistant to light, atmospheric oxygen, inorganic acids and alkalis.
4. It is most widely used synthetic plastic.

**Uses:**

1. It is mainly used as cable insulation, leather cloth, packing and toy
2. It is used for manufacturing of film, sheet and floor covering.
3. PVC pipes are used for carrying corrosive chemicals in petrochemical factories.

**Nylon:**

Synthetic fiber forming polyamides are termed as 'Nylons'.

**Preparation:** Nylon – 6 can be prepared by self-condensation of - amino caproic acid. Nylon-6 can be prepared by ring opening polymerisation of caprolactam.

- Uses:**
1. Nylon 6.6 is primarily used for fibers that find use in making socks, undergarments, carpets etc.,
  2. Nylon 6.6 is also used in mechanical engineering for well known applications like gears, bearings, bushes, cans etc.,
  3. Mouldings have application in medicine and pharmacy because of sterilisability.
  4. Durable but costly hair combs.
  5. Nylon 6.6 is also used for facketing electrical ware to provide a tough, abrasion resistant outer cover to protect the primary electrical insulation.
  6. Nylon 6 is mainly used for making tyre cords.
  7. Nylon 6.10 is suitable for monofilaments that are used for bristles, brushes etc.,
  8. Glass reinforced Nylon plastics are used in housings and cosings of domestic appliances, radiator parts of car and for relay coil formers.

### **Nylon-6,6:**

It is prepared by Hexamethylene diamine and Adipic acid are polymerized in 1:1 ratio.

**Properties:** This is linear polymer not resistant to alkali and mineral acids.

Oxidising agents like hydrogen peroxide, potassium permanganate etc. are able to degrade the fibres.

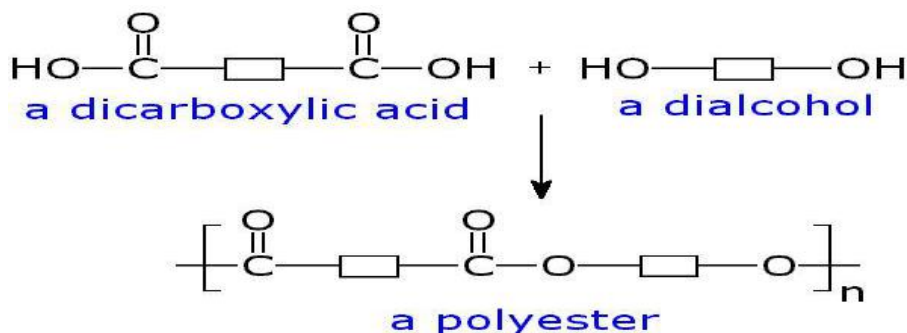
- Uses:**
1. Nylon-6,6 is mainly used for moulding purposes for gear bearings and making car tyres, used for fibres etc.
  2. This is mainly used in manufacture of tyre cord. Other uses include manufacture of carpets, rope, fibre cloth etc.

**Nylon-11:** Nylon – 11 can be prepared by self-condensation of w- amino undecanoic acid.

**Uses:** 1. Nylon 11 is used for making flexible tubing for conveying petrol

### POLYESTER

Terylene is a polyester fibre made from ethylene glycol and terephthalic acid. Terephthalic acid required for the manufacture of Terylene is produced by the catalytic atmospheric oxidation of p-xylene.



- Properties:**
1. This occurs as a colourless rigid substance.
  2. This is highly resistant to mineral and organic acids but is less resistant to alkalis.
  3. This is hydrophobic in nature. This has high melting point due to presence of aromatic ring.

- Uses:**
1. It is mostly used for making synthetic fibres.
  2. It can be blended with wool, cotton for better use and wrinkle resistance.
  3. Other application of polyethylene terephthalate film is in electrical insulation.

### TEFLON OR Poly tetra fluoro ethylene:

Teflon is obtained by polymerization of water-emulsion tetrafluoroethylene, under pressure in presence of benzoyl peroxide as catalyst.





1. It is hard and brittle at low temperature and soft and sticky at high temperature.
2. It is soft and soluble in many hydrocarbon solvents and carbon disulphide (CS<sub>2</sub>).
3. It has high water absorption power.
4. It is a sticky substance, rather difficult to handle It is readily attacked by acids and alkalies.
5. It has low tensile strength.
6. It has poor abrasion resistance.
7. It is sensitive to oxidative degradation

## **Vulcanization:**

Vulcanization is a process of heating the raw rubber at 100 – 140°C with sulfur for 1 – 4 hours. The sulfur combines chemically at the double bonds of different rubber molecules and provides cross-linking between the chains.

The degree of vulcanization depends on the amount of sulfur used. Tyre industry uses 3 – 5% sulfur. If the amount of sulfur is increased to 30%, a hard and rigid rubber called “ebonite” is produced.

## **Advantages of vulcanization:**

1. The tensile strength of vulcanized rubber is very good. It is 10 times the tensile strength of raw rubber.
2. It has excellent resilience i.e., articles made from it returns to the original shape when the deforming load is removed.
3. It has better resistance to moisture, oxidation, abrasion.
4. It has much higher resistance to wear and tear compared to raw rubber.
5. It has broader useful temperature range (-40 to 100°C) compared to raw rubber's useful temperature range (10 – 60°C).
6. It is a better electrical insulator Ex: Ebonite
7. It is resistant to i) Organic solvents like petrol, benzene, CCl<sub>4</sub>, ii) Fats and oils, but it swells in them.
8. It has only slight tackiness.
9. It has low elasticity. This property depends on the extent of vulcanization. Ebonite has practically no elasticity.
10. It is very easy to manipulate the vulcanized rubber to produce the desired shapes.

## **Vulcanization:**

Vulcanization discovered by Charles Goodyear in 1839.

It consists of heating the raw rubber at 100 – 140°C with sulphur. The combine chemically at the double bonds of different rubber spring and provides cross-linking between the chains. This cross-linking during vulcanization brings about a stiffening of the rubber by anchoring and consequently preventing intermolecular movement of rubber springs. The amount of sulphur added determines the extent of stiffness of vulcanized rubber. For example, ordinary rubber (say for battery case) may contain as much as 30% sulphur.



### **Compounding of rubber:**

Definition: "The process of mechanical mixing of various additives with polymers (without chemical reaction) to impart some special properties to the end product is known as compounding of plastics".

1. The additives get incorporated into the polymer to give a homogeneous mixture.
2. The functions of additives are To modify the properties of the polymer
3. To introduce new properties into the fabricated articles.
4. To assist polymer processing
5. To make the polymer products more pleasing and colourful. They should be cheap and sufficient in their functions.

6. They should be stable under processing and service conditions. They should not impart taste or odour.
7. They should be non-toxic for food grade application of final compound after processing.
8. They should not adversely affect the properties of polymer.

The principal additives used in compounding are

a) Fillers b) Plasticizers c) Lubricants d) Accelerators e) colouring agents f) Vulcanising agents

## **ELASTOMERS**

**Definition:** Elastomers are high polymers that undergo very long elongation (500 – 1000%) under stress, yet regain original size fully on released of stress.

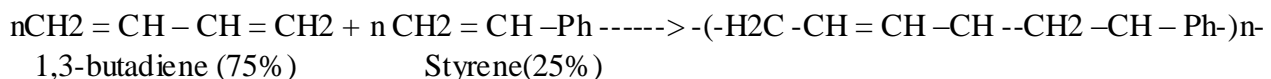
The property of elastomers is known as elasticity. This arises due to the coiled structure of elastomers.

### **Characteristics of Elastomers:**

Elastomers have linear but highly coiled structure. Inter chain cohesive forces are negligible because these are hydrocarbons. They have high degree of elasticity. They can retract rapidly.

### **Buna – S or STYRENE RUBBER:**

Buna-S rubber is probably the most important type of synthetic rubber, which is produced by copolymerization of butadiene (about 75% by weight) and styrene (25% by weight).



### **Properties:**

1. Styrene rubber resembles natural rubber in processing characteristics as well as quality of finished products.
2. It possesses high abrasion-resistance, high load-bearing capacity and resilience.
3. However, it gets readily oxidized, especially in presence of traces of ozone present in the atmosphere.
4. Moreover, it swells in oils and solvents.
5. It can be vulcanized in the same way as natural rubber either by sulphur or sulphur monochloride (S<sub>2</sub>Cl<sub>2</sub>).
6. However, It requires less sulphur, but more accelerators for vulcanization.

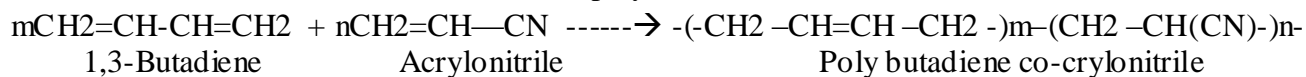
### Uses:

1. Mainly used for the manufacture of motor tyres.
2. Other uses of these elastomers are floor tiles, shoe soles, gaskets, foot-wear components, wire and cable insulations, carpet backing, adhesives, tank-linings, etc.

### Nitrile Rubber or GR-A or Buna – N or NBR:

**Preparation:** It is prepared by the copolymerization of butadiene and acrylonitrile in emulsion system.

#### Copolymerization



Compounding and vulcanization methods are similar to those of natural rubber.

### Properties:

1. Due to the presence of cyano group, nitrile rubber is less resistance to alkalis than natural rubber;
2. Excellent resistance to oils, chemicals, aging (sun light). As the acrylonitrile percentage is increased in nitrile rubber, its resistance to acids, salts, oils, solvents etc. increases. But the low temperature resilience suffers.
3. Compared to natural rubber, nitrile rubber (vulcanized) has more heat resistance and it may be exposed to high temperatures.
4. It has good abrasion resistance, even after immersion in gasoline or oils.

### USES:

1. For making Conveyor belts, Lining of tanks, Gaskets
2. Printing rollers, Oil-resistance foams
3. Automobile parts and high altitude air-craft components Hoses and adhesives.

### **Butyl rubber:**

Preparation:

Butyl rubber is prepared by the aluminum chloride initiated cationic copolymerisation of isobutene with small amount (1-5%) of isoprene.

### **Properties:**

1. Under normal conditions, it is amorphous but it crystallizes on stretching.
2. It is quite resistant to oxidation due to low degree of unsaturation. Due to very low unsaturation, it can be vulcanized but it cannot be hardened much.
3. It can be degraded by heat or light to sticky low-molecular weight products so stabilization is must.

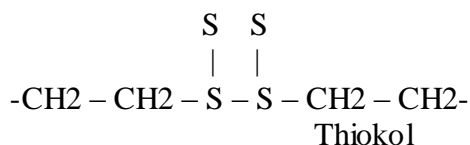
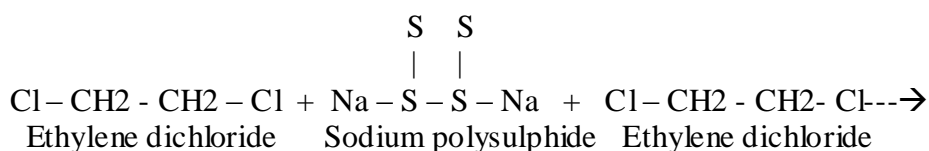
- Being non-polar, it has good electrical insulation properties.
- Compared to natural rubber it possesses outstanding low permeability to air and other gases.
- It does not crystallize on cooling and hence remains flexible down to  $-50^{\circ}\text{C}$
- Because of its hydrocarbon nature, butyl rubber is soluble in hydrocarbon solvents like benzene but has excellent resistance to polar solvents like alcohol, acetone and ageing chemicals (ex:  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  etc.)

**USES:**

- It is used for Insulation of high voltage wires and cables Inner tubes of automobile tyres.
- Conveyor belts for food and other materials.
- Lining of tanks Hoses

**Thiokol :**

This also called as polysulphide rubber (or Gr-P). It can be prepared by the condensation polymerization of sodium polysulphide ( $\text{Na}_2\text{S}_x$ ) and ethylene dichloride.

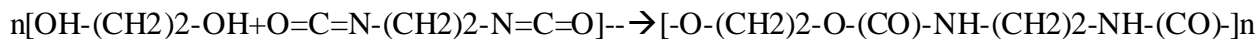


**USES:**

- It is used for the -
- Manufacture of oils hoses, chemically resistant tubing and engine gaskets;
- Diaphragms and seals in contact with solvents and Printing rolls, Containers for transporting solvents and Solid propellant fuels for rockets, etc.

**POLY URETHANES RUBBERS:**

Polyurethane or isocyanate rubber is produced by reacting polyalcohol with di-isocyanates.



### **Properties:**

1. Polyurethanes are highly resistant to oxidation, because of their saturated character.
2. They also show good resistance to many organic solvents, but are attacked by acids and alkalis, especially concentrated and hot.
3. The polyurethane foams are light, tough and resistant to heat, abrasion, chemicals and weathering

**Uses:** For surface coatings and manufacture of foams and spandex fibres.

### **Silicone resins:**

Silicone resins contain alternate silicon-oxygen structure, which has organic radicals attached to silicon atoms. Thus, their structure is: Where R= alkyl or phenyl radical

**Preparation:** reacting silicon with alkyl halide or silicon halide with Grignard reagent.

The reaction product is fractionally distilled to get different organo-silicon chlorides, which are then polymerized by carefully controlled hydrolysis.

1. Dimethyl-silicon dichloride is 'bifunctional' and can yield very long chain polymers,
2. Trimethyl silicon chloride is 'monofunctional' and hence, a 'chain-stopper'. This is, therefore, used in proportions to limit the chain-length.
3. Monomethyl silicon chlorides is 'trifunctional' and goes cross-linking to the final polymer. Its proportion used in polymerization, determines the amount of cross-linking that can be obtained.

### **Characteristics of silicones:**

1. Depending on the proportion of various alkyl silicon halides used during their preparation, silicones may be liquids, viscous liquids, semi-solid, rubber-like and solids.
2. Because of silicon-oxygen links, they exhibit outstanding-stability at high temperatures, good water resistance, good oxidation-stability, but their chemical-resistance is generally lower than that of other plastics.
3. Their specific gravity ranges from 1.03 to 2.1.
4. Their physical properties are much less affected by variations in temperature.
5. They are non-toxic in nature.

Different types of silicones and their uses: Liquid silicones or silicone oils are relatively low molecular-weight silicones, generally of dimethyl silicones. They possess great wetting-power for metals, Low surface tension and show very small changes in viscosity with temperature.

### **Uses:**

1. They are used as high temperature lubricants, antifoaming agents, water-repellent finishes for leather and textiles, heat transfer media, as damping and hydraulic fluids. They are also used in cosmetics and polishes.
2. Silicone greases are modified silicone oils, obtained by adding fillers like silica, carbon black, lithium soap, etc.
3. They are particularly used as lubricants in situations where very high and very low temperatures are encountered.

### **Conducting polymers:**

**Definition:** A polymer that can conduct electricity is known as conducting polymer.

**Classifi  
cation:  
Conduct**

ing polymers can be classified as follows.

### **I) Intrinsically conducting polymers:**

The polymers have extensive conjugation in the backbone which is responsible for conductance. These are of two types

- 1) **Conducting polymers** having conjugated - electrons in the backbone: Such polymers contain conjugated – electrons in the back bone which increases their conductivity to a large extent

**Explanation:** Overlapping of conjugated -electrons over the entire backbone results in the formation of valence bands as well as conduction bands that extends over the entire polymer molecule. The valence band and the conduction bands are separated by a significant band gap. Thus, electrical conduction occurs only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach into the lower levels of the conduction band.

All the three forms of polyanilines have conductivities of the order of  $10^{-10}$  Scm<sup>-1</sup>. Conductivity of these polymers having conjugated -electrons in the backbone is not sufficient for their use in different applications.

### **Applications of Conducting Polymers:-**

1. In rechargeable Light weight batteries based on perchlorate doped Polyacetylene-lithium Systems: These are about 10 times lighter than conventional lead storage batteries.
2. These can produce current density up to 50mA/cm<sup>2</sup>.
3. In electrochromic displays and optical filters: ICP's can absorb visible light to give coloured products so can be useful for electrochromic displays and optical filters.
4. Thus the conducting polymers can be used as electro chromic materials i.e., the materials that change colour reversibility during the electrochemical processes of charge and discharge.
5. In wiring in aircrafts and aerospace components.
6. In telecommunication systems.
7. In electromagnetic screening materials.
8. In electronic devices such as transistors and diodes.
9. IN solar cells, drug delivery system for human body etc., In photovoltaic devices.

aterials.

10. In molecular wires and molecular switches.
11. Membranes made up of conducting polymers can show boundary layer effects with selective permeability for ions, gases etc., Hence they are useful for ion-exchangers and controlled release of drugs

**4. ACCELERATORS:**  
These shorten the time required for vulcanization and give toughness to the rubber. For eg., 2-Mercaptothiazole.

**5. FILLERS:**  
These are added to give rigidity and strength to the rubber. For Eg., carbon black, zinc oxide and calcium carbonate

**6. COLORING MATTER:**

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The principal additives used in compounding are

- 1) Softeners and Plasticisers
- 2) Vulcanising Agents
- 3) Antioxidants
- 4) Accelerators
- 5) Fillers
- 6) Colouring Matter

**1. SOFTENERS AND PLASTICISERS:** These are added to give greater plasticity and flexibility to reduce the brittleness of the products eg. waxes, stearic acid and vegetable oils.

**2. VULCANISING AGENTS:** When rubber is heated with sulphur, its tensile strength, elasticity and resistance to swelling are increased. The sulphur atoms chemically bond with double bonded carbons of rubber chains and bring about excellent changes in their properties. The percentage of sulphur added varies from 0.15 to 32%.  $S_2Cl_2$ ,  $H_2S$ ,  $H_2O_2$ , benzoyl chloride etc., are other vulcanizing agents.

**3. ANTIOXIDANTS:** Natural rubber has tendency for oxidation. Antioxidants like phenyl naphthyl-amine and phosphites are added for preventing the oxidation of rubber.



These materials provide pleasing colour to the rubber product. For  
Titanium oxide- White

eg.,

Ferric oxide – Red

Lead chromate – Yellow

Antimony oxide – Crimson

Chromic oxide - Green