DR ROHIT BARGAH

POLYMER   CHEMISTRY

Introduction:

Polymers form very important components in our daily life. The polymers are highly useful in domestic industrial and medical fields. Polymers form a most important class of materials without which the life seems very difficult. They are all around us in everyday use; in rubber, in plastic, in resins, and in adhesives and adhesives tape.

The following are the reasons for the extensive use of polymers-

1) Most of the polymers are non-toxic and safe to use

2) They have low densities (light in weight) so transportation polymers will be easy.

3) They posses good mechanical strength.

4) These are resistant to corrosion and will not absorb moisture when exposed to the atmosphere.1

5) These can function as good thermal & electrical insulators.

6) These can be moulded and fabricate easily.

7) They posse's esthetic colors

POLYMERISATION:

The word "polymer" is derived from two Greek words, polys (= many) and mers (= parts or units). A polymer is a large molecule which is formed by repeated linking of small molecules called "monomers". Example: Polyethene is a polymer formed-by linking together of a large number of ethene (C_2H_4) molecules.

The process in which the simpler molecules combine together to form very large molecule having high molecular weight is known as polymerization". The molecule is known as polymer.

The reaction by which the monomers combine to form polymer is known as polymerization. The polymerization is a chemical reaction in which two or more substances combine together with or without evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight. The product is called polymer and the starting material is called monomer.

Example:- poly ethylene

The number of repeat units (or) monomeric units available in the polymer is known as degree of polymerization.

$$nCH_2 = CH_2 \xrightarrow{\text{polymerization}} -(CH_2-CH_2)n$$
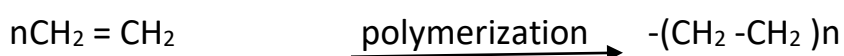
Thus the repeated unit of polymer is called monomer. The number of repeating units in a polymer chain is called degree of polymerization. For example if 100 molecules of ethylene polymerize to give the polymer chain, the degree of polymerization is 100. It is also interesting to note that many carbohydrates, Proteins and enzymes, DNA and RNA are natural polymers.

Degree of Polymerization (Dp)

It is the average number of repeating unit in a macromolecule.The degree of polymerization is obtained by dividing the molecular weight by the molecular weight of the monomer.

The subscript n in $[-CH_2-]$ n indicates the number of monomer units contained in the polymer and is known as degree o polymerization. Degree of polymerization is related to the molecular weight f the polymer[M] by the equation

$$Dp = M/m$$

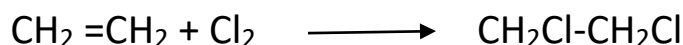Where m is the molecular weight of the monomer unit.
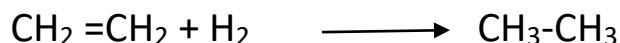
$$M = m.Dp$$

M = molecular weight of the polymer.

Dp = Degree of polymerization

Most of the polymers have molecular weights ranging from 5,000-2,00000.

Polymer Functionality: The number of reactive groups in a molecule. The number of active bonding sites in a monomer is referred to as its functionality. A compound assumes functionality because of the presence of reactive functional groups like –OH, -COOH, -SH, -NCO, etc. The concept of functionality can be better understood with the example in Table.

Some compounds, however, do not contain any reactive functional group, but the presence of double or triple bonds in these olecules bestows poly-functionality on them. For example ethylene ($CH_2= CH_2$), which can taken on two hydrogen or halogen, has a functionality of two (bifuntionality).Similarly, acetylene ($CH\equiv CH$) has a functionality of four (tetra –functionlity,since it can react with four atom of hydrogen or halogen.

$CH_2 = CH_2 + H_2 \longrightarrow CH_3\text{-}CH_3$

$CH_2 = CH_2 + Cl_2 \longrightarrow CH_2Cl\text{-}CH_2Cl$

(Bifunctionality)

$CH \equiv CH + 2H_2 \longrightarrow CH_3\text{-}CH_3$

$CH \equiv CH + 2Cl_2 \longrightarrow CCl_2 \text{–}CCl_2$

(Tetra –functionality)

Depending on the functionality of the monomers used ,we get linear, branched, and cross linked polymers.

Table: Functionality of compounds

Compound	Chemical formula	No of Functional groups present per molecule	functionality
Acetic acid	CH_3COOH	1 (-COOH)	Mono-functionality
Aniline	$C_6H_5NH_2$	1 (-NH2)	Mono-functionality
Lactic acid	$CH_3CH(OH)COOH$	2 (OH,-COOH)	Bi-functionality
Hexamethylene diamine	$H_2N(CH_2)_6NH_2$	2 (-NH2)	Bi-functionality
Ethylene glycol	$HOCH_2-CH_2OH$	2 (-OH)	Bi-functionality
Malonic acid	$HOOC-CH_2-COOH$	2 (-COOH)	Bi-functionality
Pentaerythritol	$C.(CHOH)_4$	4 (-OH)	Tetra-functionality

Characteristics of Polymers :

1. Polymeric molecules are very big molecules. There average molecular weights may approach 105 or more. That's why, they are also known as macromolecules.

2. Polymers are semi-crystalline materials. It means they have both amorphous and crystalline regions. In fact, polymers have regions of crystallinity, called crystallites, embedded in amorphous regions. Crystallites provide strength and hardness and the amorphous regions provide flexibility to the polymeric material.

3. The intermolecular forces in polymers can be Vander Waals' forces, dipole-dipole attractions or hydrogen bonding. These intermolecular forces are in addition to covalent bonds which connect the repeating units into a macromolecule.

4. The chemical, electrical, optical, mechanical and thermal properties of polymers depend on -

(i) Size and shape of polymers, and

(ii) The presence or absence of characteristic intermolecular forces.

These parameters not only determine the properties of the polymers, but also the performance of these materials in a given applications.

5. Polymers show time-dependent properties.

6. Polymers are combustible materials.

7. Polymers have low densities and they show excellent resistance to corrosion.

8. Generally, polymers are thermal and electrical insulators.

9. Polymeric materials are easily mouldable even into complex shapes with reproducible dimensions with a minimum of fabrication and finishing cost.

CLASSIFICATION OF POLYMERS :

Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless form and numbers because of very large number and type of atoms present in their molecule. Polymer can have different chemical structure, physical properties, mechanical behavior, thermal characteristics, etc., and on the basis of these properties polymer can be classified in different ways,

1. **Based on Number of Monomers :**
   Polymers can be homopolymer or copolymer when the number of monomers are one and two respectively.
   (i) **Co-polymers :** Molecules which are built up of at least two different kinds of monomer are known as co-polymers. Thus, a co-polymer is obtained when two or more suitable monomers are polymerised together. The chains of co-polymer consist of repeating units derived from each monomer.
   Following are some common types of co-polymers :

(a) Alternating co-polymers: In such Co-polymers, the different repeating units alternate in each chain. If A and B represent two different units then an alternating co-polymer will be represented as, -ABABABAB-

(b) Random Co-polymers: In this type of copolymers, the different repeating units are not arranged in a systematic manner but are randomly arranged, e.g. –ABAABABBAAABA

(c) Block Co-polymers: In such co-polymers, block of repeating units of one type alternate with block of another type, e.g. -AAAABBBBAAAABBBB-

(d) Graft Co-polymers : In such co-polymers, blocks of one repeating units are attached or grafted to a block of linear polymer, e.g.
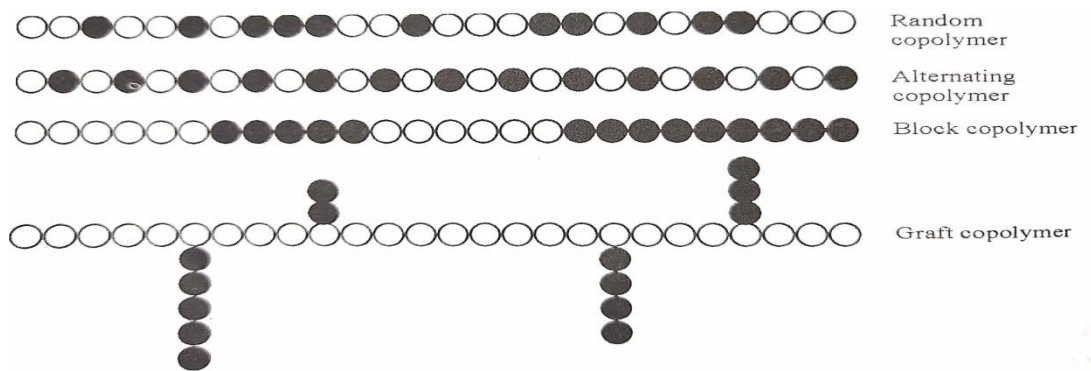

Fig: Schematic representation of different types of co-polymer structure

(ii) Homopolymers:

If the polymers consist of monomer of identical chemical structure then they are called homopolymers, eg., Polyethelene, Polyvinyl chloride etc.

2.Based on Tacticity :

The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain. The difference in configuration (tacticity) do affect their physical properties.

Based on tacticity they are classified as follows:

(i) **Isotactic Polymer:** The head-to-tail configuration, in which the functional groups are all on the same side of the chain, is called isotactic polymer, e.g.,
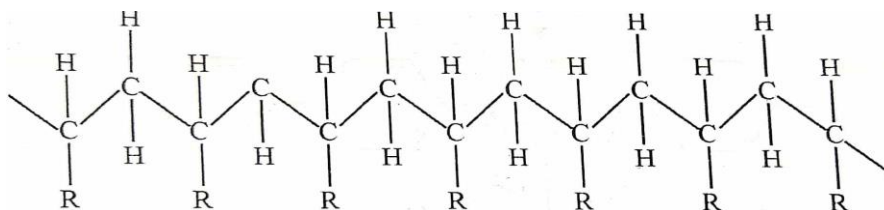
(ii) **Atactic Polymer:** If the arrangement of functional groups are at random around the main chain, it is called atactic polymer, e.g., polypropylene.
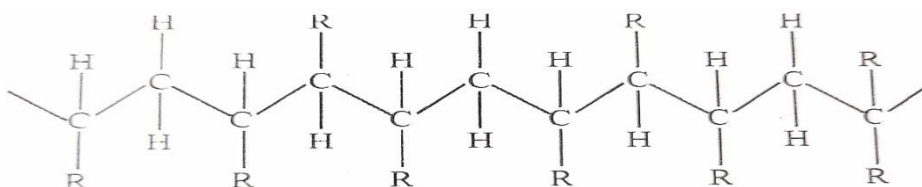
(iii) **Syndiotactic:** If the arrangement of side groups is in alternating fashion, it is called syndiotactic polymer, e.g., gutta percha.
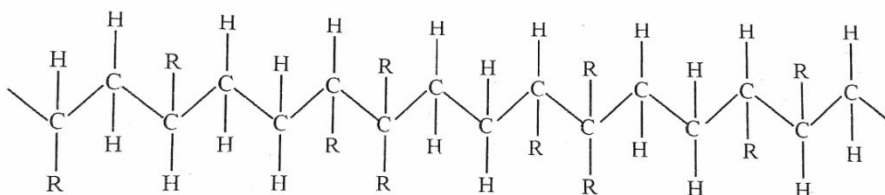
2. Depending upon Functionality Functionality:

For a substance to act as a monomer, it must have at least two reactive sites or bonding sites. The number of bonding sites in a monomer, is referred to as its functionality. In ethylene, 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.

(i) **Linear or Straight Chain Polymer:** In case of a bifunctional monomer, two reactive groups attach side by side to each other forming linear or straight chain polymer. Linear molecules consist of monomer units linked by primary covalent bonds, but the different chains are held together by secondary vander waals forces of molecular attraction. This gives the possibility of chain movement in one direction. Example-polyvinyl chloride (PVC).

(ii) **Branched Chain Polymers:** During the chain growth, side chains may also form, resulting in branched-chain polymers. Such a molecule is a linear, but the movement in brachedchain molecules is, generally, more restricted than that of simple straight-chain molecules. A branched-chain polymer also results, when a trifunc-tional monomer is mixed in small amounts with a bifunctional monomer and polymerised. Example: Low density polyethylene (LDPE)

(iii) **Cross-Linked Polymer (Network Polymer):** In case of polyfunctional groups, monomer molecules are connected to each other by covalent bonds, resulting in the formation of a three-dimensional netwrork polymer. In such polymeric molecules the movement of individual molecules is prevented by strong cross-links. eg. Bakelite.
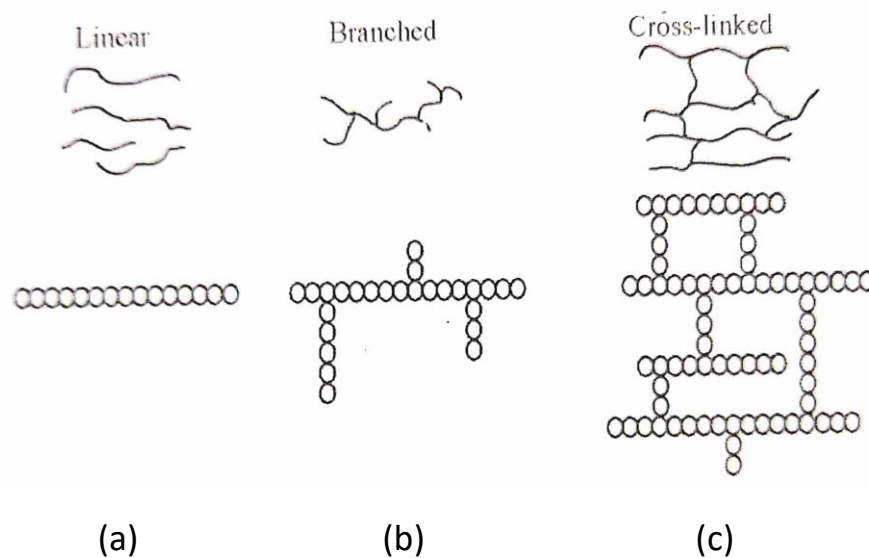

| Linear | Branched | Cross-linked |

(a)   (b)   (c)

Fig: Different structure of polymers: (a) Linear (b) Branched chain (c) Cross-linked structure

3. Based on Origin or Sources:

Based on origin, the polymer can be broadly classified into different groups:

(i) Natural Polymers: These polymer occur in nature, i.e., they have either vegitable or an animal origin. They include starch, cellulose, proteins, nucleic acids, natural rubbber etc. cellulose and starches are the polymers of glucose. Natural rubber contains isoprene (2-methyl-1, 3-butadiene) repeat unit.

(*ii) Synthetic Polymers:* Synthetic polymers are man made polymers. Most of the synthetic polymers are long-chain organic molecules containing thousands of monomer units. Most common synthetic polymers are : Polyethylene, Polyvinylchloride, polystyrene etc.

*(iii)Semi-synthetic polymers:*The polymers obtained by simple chemical treatment of natural fibers to improve their physical properties like lastrus nature, tensile strength are called semisynthetic fibers. e g. Acetate rayon, cupra ammonium silk, viscous rayon.

(iv)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 intermolecular forces act between the chains, e.g., Borazole, polysilane.

5.Classification Based on Molecular Forces :

(i)   Elastomers (Rubber): Held together by the weakest intermolecular forces e.g., Vulcanized Rubber. Vulcanization is a process of treating natural rubber with sulphur. Rubber is vulcanized to render it nonplastic and give it greater elasticity and ductility.

(ii) Fibres: They have strong inter-molecules forces between the chains giving them less elasticity and high tensile strength. The intermolecular forces may be hydrogen bonds or dipole-dipole interaction. Fibres have sharp and high melting points. e.g., Nylon-6,6.

(iii)Thermoplastics: 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' e.g., polyethylene, PVC, nylon and sealing wax.

(iv) Thermosetting: Some polymers undergo some chemical change on heating and convert themselves into infusible mass. They are like 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 e.g., bakelite.

(6) Based on Mode of Polymerisation:

Polymerization is the process by which monomer molecules are reacted together in a chemical reaction to form a polymer chain (or three-dimensional networks).

Based on the type of polymerization, polymers can be classified as:

(i)Condensation polymerization-eg.: Nylon-6,6

(ii) Addition polymerization-eg.: Polyethylene, PVC, Polystyrene

Types of Polymerisation :

There are two types of polymerization. They are

(**1**) **Condensation polymerization (Step reaction polymerization):** Condensation polymers are those in which two like or unlike monomers join each other by the elimination of small molecules such as H_2O, HCl, etc. When the same kind of monomers joins, the polymer is called homo polymer.eg.- Nylon -6

It is prepared by the self condensation of w-amino caproic acid which is produced from caprolactum.

(**2**) **Addition Polymerization(Chain reaction polymerization):**

In addition polymerization, the polymer is formed from the monomer, without the loss of any material and the product is an exact multiple of the original monomeric molecules.eg.Polyethylene, PVC, Polystyrene.

Example : (1) n $CH_2 = CH_2$ $\longrightarrow$ $[CH_2 - CH_2]$ n

             Ethylene   polyethylene

      (2) n $CH_2 = CH - Cl$ $\longrightarrow$ $[CH_2 - CH]$n -Cl

          Vinyl Chloride   Polyvinyl chloride

     Addition polymerization reactions proceed by a chain reaction mechanism consisting of three important steps,
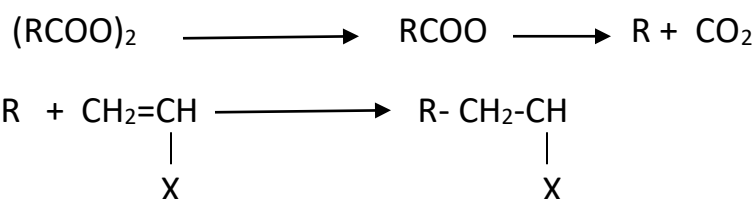
- (i)   Initiation or the formation of an active centre,
- (ii)   Propagation or the formation of a polymer having the active centre
- (iii)   Termination or removal of the active centre.

          The three different types of active centers have been found to be formed during the addition polymerization, viz., free radical, carbonium ion and carbanion. So the mechanisms involving these reactive species in polymerization constitute the mechanism of addition polymerization.
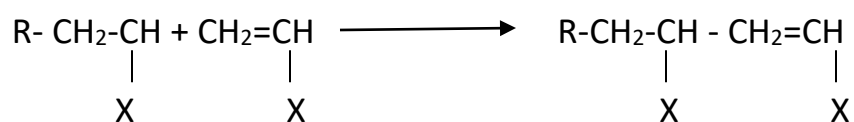
(a) Free radical polymerization :

Free-radical polymerization form only linear molecules.

(i) **Initiation step:** It involves the formation of a free-radical from a radical initiator such as benzoyl peroxides H_2O_2, and other materials that can generate free radicals. The radical so formed then adds to the monomer to form a new free radical, e.g., it adds to vinyl monomer in the following way-
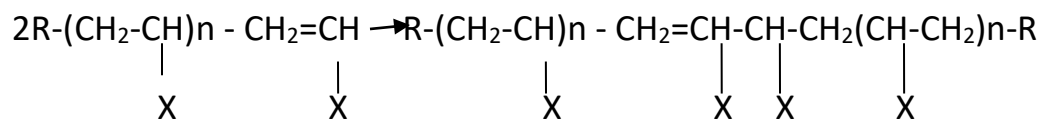
$$(RCOO)_2 \longrightarrow RCOO \longrightarrow R + CO_2$$

$$R + CH_2=CH \longrightarrow R-CH_2-CH$$
$$\qquad\qquad | \qquad\qquad\qquad\qquad |$$
$$\qquad\qquad X \qquad\qquad\qquad\qquad X$$

(ii) **Propagation step:** The new free radical now adds to another molecule of monomer to form another new free radical until a large free radical is formed . After the first few steps the addition of a monomer unit proceeds at a constant specific rate independent of the chain length of free radical formed.

$$R-CH_2-CH + CH_2=CH \longrightarrow R-CH_2-CH - CH_2=CH$$
$$\qquad\quad | \qquad\qquad | \qquad\qquad\qquad\qquad\qquad | \qquad\qquad |$$
$$\qquad\quad X \qquad\qquad X \qquad\qquad\qquad\qquad\qquad X \qquad\qquad X$$

(iii) **Termination step:** Termination of chains usually occurs by radical coupling or disproportionation reactions.
(a) **By coupling or combination,** *e.g.,*

$$2R-(CH_2-CH)n - CH_2=CH \longrightarrow R-(CH_2-CH)n - CH_2=CH-CH-CH_2(CH-CH_2)n-R$$
$$\qquad\qquad | \qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad | \qquad\qquad\quad | \quad | \qquad\quad |$$
$$\qquad\qquad X \qquad\qquad\quad X \qquad\qquad\qquad\qquad\qquad X \qquad\qquad\quad X \quad X \qquad\quad X$$

(b)Disproportionation: In which a hydrogen atom of one radical centre is transferred to another radical centre. This results in the formation of two polymer molecules, one saturated and other unsaturated, e.g.,

$$2R-(CH_2-CH)n - CH_2=CH \longrightarrow R-(CH_2-CH)n - CH_2-CH_2$$
$$X X X X$$

$$+ R-(CH_2-CH)n - CH_2=CH$$
$$ X X$$
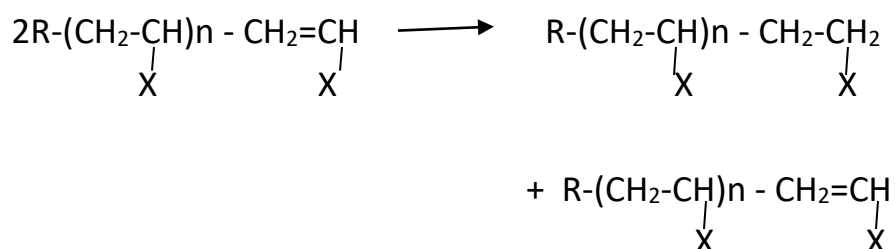
(b) **Chain Transfer reaction :** This leads to termination of the   original Chain but gives to a new free radicals which sets up a ew polymerization chain. For example

$$R-(CH_2-CH)n - CH_2=CH + R''-H \longrightarrow R-(CH_2-CH)n - CH_2-CH_2 + R''$$
$$X X X X$$
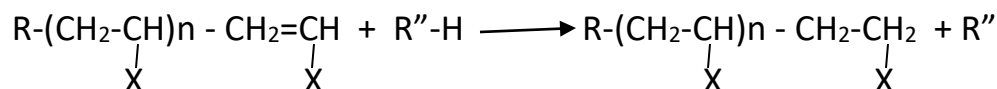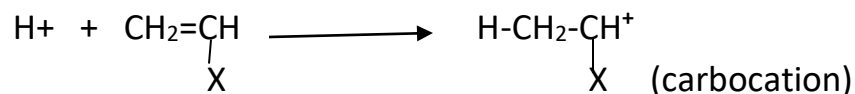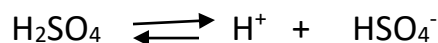
(b) Ionic Polymerization:

This type of polymerization takes plae through ionic species   instead f free radicals.If the ionic species are cations, it is called cationic polymerization If the ionic species anions, it is calledbanionic polymerization.
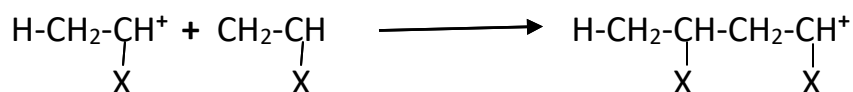
(i) Cationic Polymerization:

Cationic polymerization involves following steps:

(a)Initiation: This type of polymerization in initiated by acids. The commonly used acid catalysts being H_2SO_4, HF and Lewis acids such as $AlCl_3$, $SnCl_2$ and BF_3.
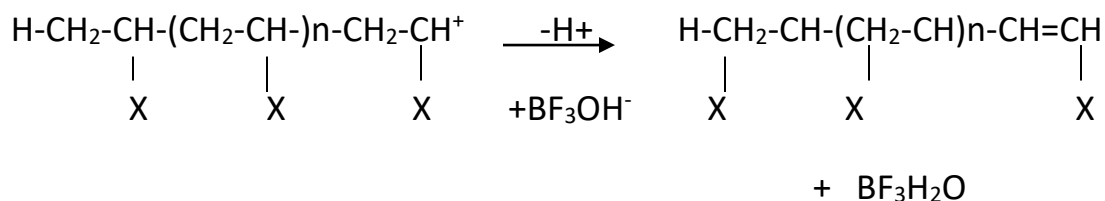
The process is initiatedby the rection of an acid with the monomer to from

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$H+ + CH_2=\underset{X}{CH} \longrightarrow H\text{-}CH_2\text{-}\underset{X}{CH^+} \quad \text{(carbocation)}$$

(b)Propagation : The carbocation formed abov being electrophilic addsto another molecule of the monomer to yield a second carbocation. Thisprocess continues till a large polymer molecule is formed.
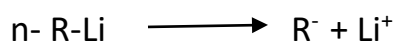
$$H\text{-}CH_2\text{-}\underset{X}{CH^+} + CH_2\text{-}\underset{X}{CH} \longrightarrow H\text{-}CH_2\text{-}\underset{X}{CH}\text{-}CH_2\text{-}\underset{X}{CH^+}$$

(c)Termination: The chain reaction is usually terminated by the loss of a hydrogen ion from the growing carbocation.

$$H\text{-}CH_2\text{-}\underset{X}{CH}\text{-}(CH_2\text{-}\underset{X}{CH}\text{-})n\text{-}CH_2\text{-}\underset{X}{CH^+} \xrightarrow[+BF_3OH^-]{-H+} H\text{-}CH_2\text{-}\underset{X}{CH}\text{-}(CH_2\text{-}\underset{X}{CH})n\text{-}CH=\underset{X}{CH}$$
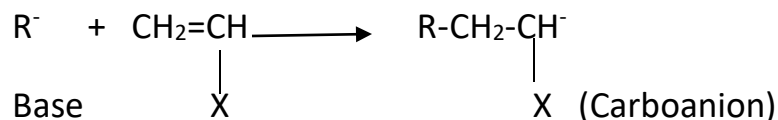
$$+ BF_3H_2O$$

(i) Anionic Polymerization:

Anionic polymerization involves following steps:

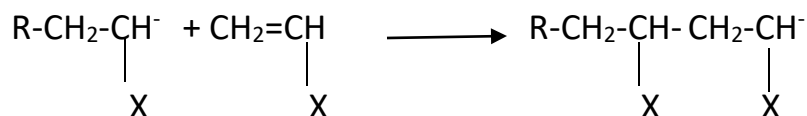*(a)Initiation:* A number of reagents are used to bring about initiation the most important being n-butyl lithium and lithium amide

$$n\text{-} R\text{-}Li \longrightarrow R^- + Li^+$$

$$(\text{Base} \quad R= C_4H_9)$$

R⁻ + CH₂=CH ⟶ R-CH₂-CH⁻

Base   X   X (Carboanion)

(ii)Propagation : The carbanion formed above reacts with another monomer molecule and this step is repeated unit a polymeric molecule is formed.

R-CH₂-CH⁻ + CH₂=CH ⟶ R-CH₂-CH- CH₂-CH⁻

     X   X   X   X

(iii)Termination : The chain reaction gets terminated by combination with proton (H^+) ion or some Lewis acid present in the reaction mixture.

R-CH₂-CH-(CH₂-CH-)n-CH₂-C̄H + H⁺ ⟶ R-CH₂-CH-(-CH₂-CH-)n-CH₂-CH₂

    X   X   X   X   X   X
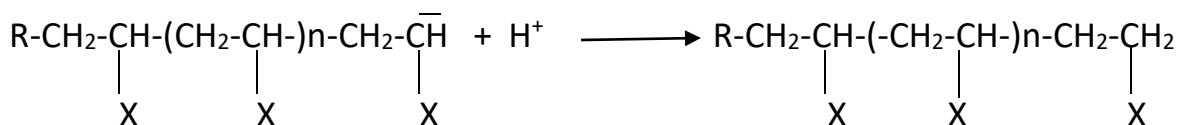
(C) Ziegler-Natta Polymerisation (Co-ordination polymerisation):

The coordination polymerization is invented by two Italian scientists: Karl Ziegler and Giulio Natta. They shared the nobel prize in chemistry in 1963 using Ziegler–Natta catalysts to polymerize nonpolar monomers: 1-alkene, cycloalkenes, dienes, and alkynes through coordination mechanism instead of common chain or step polymerization.
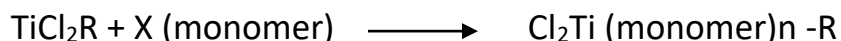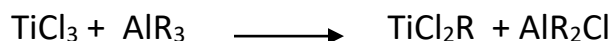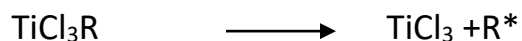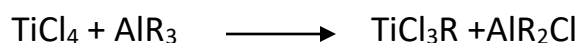
Coordination polymerization applies a novel class of transition-metal catalysts, called the Ziegler-Natta catalysts and produced of polymers with unsual stereospecific structures. The mechanism and the kinetics are complicated and the catalysts are usually solids to form heterogeneous polymerization systems. The most common catalyst of this type are composed of aluminium trialkyls and titanium or vanadium chloride.

Giulio Natta (Italy,1954) developed a stereochemical process to polymerize isotactic polypropylene (IPP). This IPP had degree of crystallinity comparable to LDPE and exhibited good mechanical properties in a wide range of temp. Karl Ziegler (Germany) developed a similar process to polymerize ethylene at lower

temp and pressure to produce HDPE. This HDPE had fewer branches and a higher degree of crystallinity.

A Ziegler-Natta catalyst is usually a metal-organic complex of a metal cation from groups I – III $\{Al_2(C_2H_5)_3\}$ and a metal compound from groups IV – VIII $\{TiCl_4\}$.

The following equations to best describe the reaction between titanium tetrachloride and a aluminium trialkyl.

$$TiCl_4 + AlR_3 \longrightarrow TiCl_3R + AlR_2Cl$$

$$TiCl_3R \longrightarrow TiCl_3 + R^*$$

$$TiCl_3 + AlR_3 \longrightarrow TiCl_2R + AlR_2Cl$$

$$TiCl_2R + X \text{ (monomer)} \longrightarrow Cl_2Ti \text{ (monomer)n -R}$$

Mechanism of coordination polymerization

The exact mechanism of coordination polymerization is still unclear. However, it is believed that the transition metal is the active site. The ethylene is coordinated to the free site at the transition metal and inserted between metal and the alkyl group R. The coordination process results in the stereospecificity of the polymerization. The rate of the reaction can be influenced by the nature of the other ligands present.

Several important points have to be kept in mind in order to propose an acceptable mechanism:

(i) The polymerization reaction is stereo-selective as shown by the fact that isotactic polymer of 1-olefins are formed.

(ii) The reaction has the characteristics of anionic polymerization.

(iii) The reaction takes place on a solid surface.

Organo-metallic co-catalyst ends up as the terminal group of the chain. Monomer activity decreases with increasing steric hindrance about the double bond as shown below:
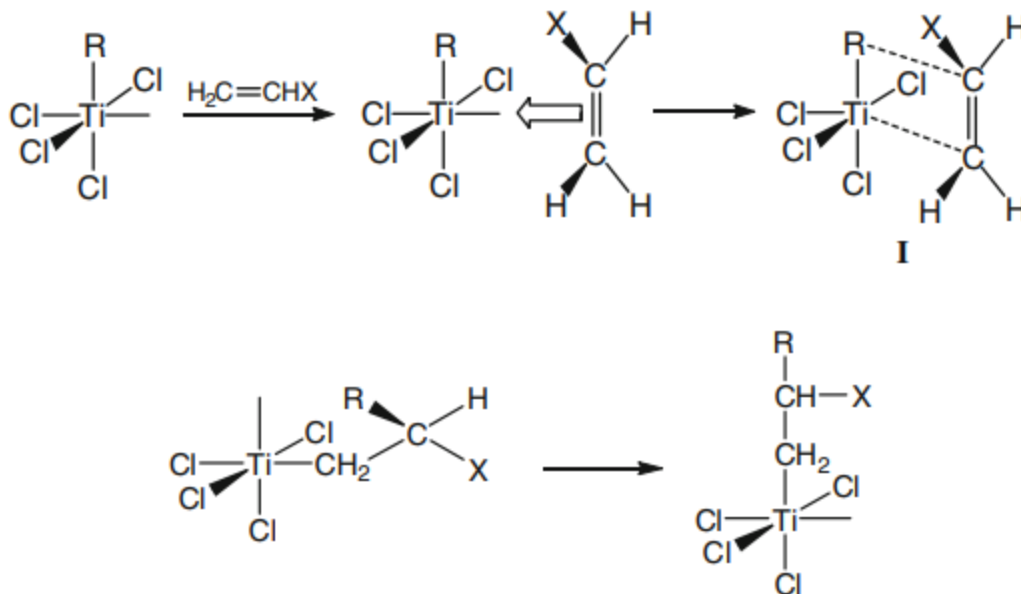
$CH_2 = CH_2 > CH_2 = CH\text{-}CH_3 > CH_2 = CH\text{-}CH_2\text{-}CH_3 > CH_2 = CH\text{-}CH_2\text{-}CH\text{-}(CH_3)_2 >$

$CH_2 = CH\text{-}CH(\text{-}CH_3)_2 > CH_2 = CH\text{-}CH\text{-}(CH_2CH_3)_2 > CH_2 = CH\ C(CH_3)_3$
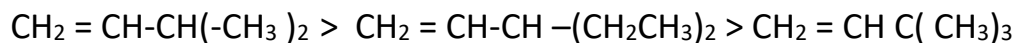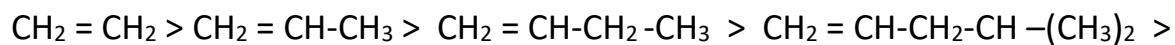

Fig: Monometallic mechanism of Ziegler–Natta polymerization of substituted alkene
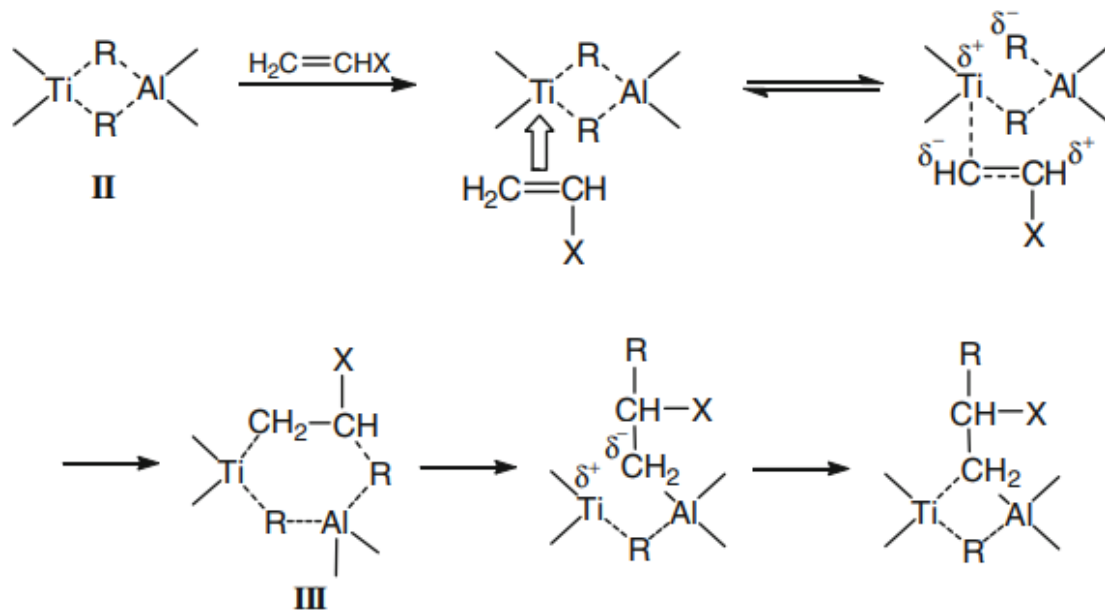
Fig: Bimetallic mechanism of Ziegler–Natta polymerization of substituted alkene

The relationship between the polymerization rate and time is shown in Figure. The decaying rate type is most common. That is due to structural changes from the reducing the number or activity of active centers. It is also due to the encapsulation of active centers by polymer which prevents approach by monomer
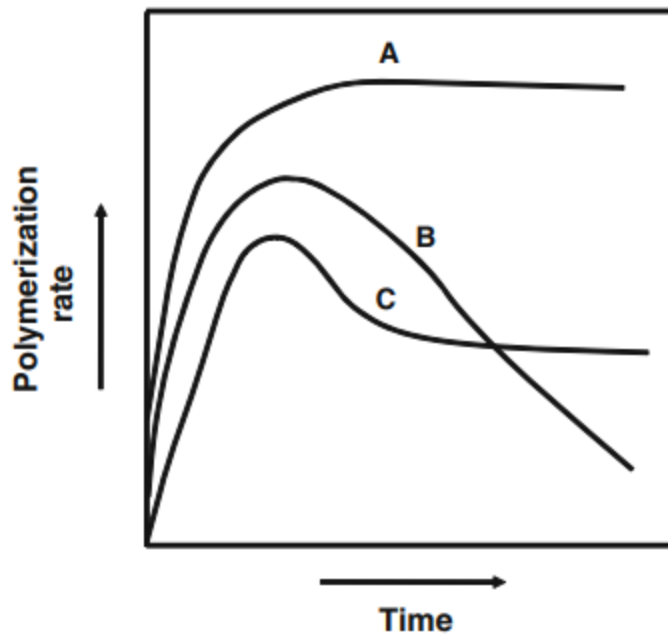
Fig: Three types of polymerization rate observed in Ziegler–Natta polymerization:

(A) Constant (B) Decaying (D) Decaying to constant

Table 1: Show some common addition polymers and their relevant monomers names and chemical structure

Name	Formula	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	Soft, waxy solid	Film wrap, plastic bags

Polyethylene density (HDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$	Rigid, translucent solid	Electrical insulation bottles, toys
Polyethylene (PP) different grades	$-[CH_2-CH(CH_3)_n-$	propylene $CH_2=CHCH_3$	Atactic, soft, elastic solid, isotactic, hard, strong solid	Similar to LDPE carpet, upholstery
Poly(vinyl chloride) (PVC)	$-(CH_2-CHCl)_n-$	Vinyl chloride $CH_2=CHCl$	Strong rigid solid	Pipes, siding, flooring
Poly(vinylidene chloride)(saran A)	$-(CH_2CCl_2)_n-$	Vinylidene chloride $CH_2=CCl_2$	Dense, high melting solid	Seat covers, films
Polystyrene (PS)	$-[CH_2-CH(C_6H_5)]_n-$	Styrene $CH_2=CHC_6H_5$	hard, rigid, clear solid, soluble in organic solvents	Toy, cabinets packaging (formed)
Polyacrylonitrile (PAN, Orlon, Acrilan)	$-(CH_2-CHCN)_n-$	Acrylonitrile $CH_2=CHC_6H_5$	High-melting solid soluble in organic solvents	Rugs, blankets clothing
Polytetrafluoro ethylene (PTFE,Teflone)	$-(CF_2-CF_2)_n-$	Trafluoro ethylene $CF_2=CF_2$	Resistant, smooth solid	Non-stick surface electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$-[CH_2C(CH_3)CO_2CH_3]_n-$	Methyl methacrylate $CH_2=C(CH_3)CO_2CH_3$	Hard, transparent solid	Lighting covers, Signs skylights
Poly(vinyl acetate)(PVAc)	$-(CH_2-CHOCOCH_3)_n-$	Vinyl acetate $CH_2=CHOCOCH_3$	Soft, sticky solid	Latex paints, adhesives
Cis-Polyisoprene (natural rubber)	$-[CH_2-CH=C(CH_3)-CH_2]_n-$	Isoprene $CH_2=CHC(CH_3)=CH_2$	Soft, sticky solid	Requires vulcanization for practical use
Polychloroprene (cis+trans) (neoprene)	$-[CH_2-CH=CCl-CH_2]_n-$	Chloroprene $CH_2=CH-CCl-CH_2$	Tough, rubbery solid	Synthetic rubber oil resistant

Co-polymerisation:

Addition polymerisation involving a mixture of two (or) more suitable or compatible monomers gives a copolymer and the process is known as co-polymerization.Examples:

1)Co-polymerisation of styrene and methyl methacrylate

2)Co-polymerisation of acrylo nitrile and vinyl chloride

3)Co-polymerisation of styrene and 1,3 – butadiene.

$mCH_2 = CH + n\ CH_2 = CH - CH = CH_2$ Co-polymerisation

Difference between condensation of additional polymerisation

Condensation polymerization	Additional polymerisation
(1) It is also known as step growth Polymerization	(1) It is also known as chain growth Polymerization
(2) It takes place in monomers having reactive functional groups.	(2) It takes place only in monomers having multiple bonds.
.(3) It takes place with elimination of simple molecule like H_2O, NH_3, HCl etc.,	(3) It takes place without elimination of simple molecule.
(4) Repeat units of monomers are different	(4) Repeat units & monomers are same.
(5) The polymer is formed in gradual steps	(5) Reaction is fast and polymer is formed at once.
(6) The molecular mass of polymer increases throughout the reaction	(6) There is very little change in the molecular mass throughout the reaction
(7) Product obtained may be thermosetting/thermoplastic	(7) Product obtained are thermoplastic
(8) Example- Bakelite, polyester,polyamides etc.,	(8) Eample-Polyethylene, PVC, poly styrene.

Plastics:- Plastic is a substance that can be easily formed or moulded into a desired shape. Plastic can be formed in a desired shape by the effect of mechanical force and heat. During molding process, there is no chemical change.

The plastics have linear structure.

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

Advantages of plastic:

(1) Low fabrication cost, low thermal and electrical conductivities, high resistance to corrosion and solvents.

(2) The stress – strain relationship of plastics is similar to that of the metals.

(3) Plastics reduce noise and vibration in machines.

(4) Plastics are bad conductors of heat are useful for making handles used for hot objects, most plastics are inflammable.

(5) Plastics are electrical insulators and find large scale use in the electrical industry.

(6) Plastics are resistance to chemicals.

(7) Plastics are clear and transparent so they can be given beautiful colours.

Types of Plastic: -

(1) Thermoplastics   (2)Thermosetting plastics.

(1) Thermoplastics: Thermo plastics 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, PMMA, PVA, HIDS.

Properties of Thermoplastics –

(i) Thermoplastics are formed by addition polymerisation

(ii) They are consists of linear polymer chains with negligible cross-linking

(iii) It is soft and less brittle.

(iv)It is soluble in organic solvents.

(v) soften on heating and hence are amenable for moulding into any shape in the hot condition on cooling, the resin becomes hard and rigid andretains the moulded shape.

(vi) It can be reheated and moulded into any other shape reversibly any number of times without any change in the chemical nature.

(2) 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, epoxyresins (araldite), melamine, Bakelite

Properties of Thermosets (Thermosetting resins):

(i)   They are mostly formed by condensation polymerisation.
(ii)   They are mostly branched polymer chains with potential to form a 3-dimensional structure.
(iii)   Thermosets become hard and rigid on heating during moulding process.

(iv)   It is not soluble in common organic solvents.

(v)   Thermosets exhibit their characteristic properties of non-softening and non- swelling nature, hardness and brittleness.

(vi) It cannot be softened, reformed, reshaped once they are set.

(vii) It cannot be reclaimed from wastes.

Difference between thermoplastic & thermosetting resins:

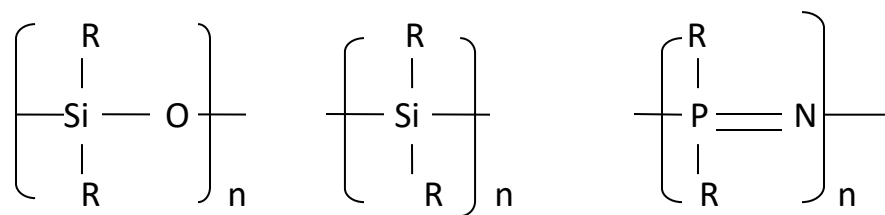| Thermoplastic (or) Polymers	Thermosetting resins
(1) These are produced by condensation polymerization.	(1) These are produced by condensation polymerization.
(2) The resins are made of long chains attached by weak Vander Waal's force of attraction	(2) The resins have three dimensional network structure connected bonds.
(3) On heating they soften and on cooling become stiff chemical nature won't change.	(3) On heating they become stiff & hard. No change on cooling. Chemical nature changes.
(4) They can be remoulded once set means they are permanently set.	(4) They cannot be remoulded because once set means they are permanently set.
(5) Scrap (waste product) can be used	(5) Scrap cannot be used
6) The resins are soft, weak and less Brittle.	(6) The resins are usually hard, strong tough & more brittle
(7) These are easily soluble in some organic substances Example:- PVC, polyethylene etc.,	(7) Resins are not soluble in organic solvents Example.:- Nylon, Bakelite etc.,
(8) Contain long chain polymer with no cross linkage.	(8) They have 3D network structure.

Table 2 General-purpose and speciality plastics

	Plastic	Comments
PMMA	acrylic, poly(methyl methacrylate)	Thermoplastic. A transparent rigid polymer.
ABS	acrylonitrile-butadiene-styrene	Based on SAN resin modified with polybutadiene rubber.
EP	Epoxy	Thermoset. Resins used for encapsulation, adhesives, surface coatings and high-strength fibre-reinforced composites.
GRP	glass-reinforced plastic (mainly polyester)	Thermoset. Reinforced with glass fibre in various forms, such as chopped strand mat (CSM) and woven rovings (WR). Used for pipes, tanks, boat hulls, etc. May be applied as SMC or DMC.
HDPE	high density polyethylene	Thermoplastic. Linear polyolefin widely used in blow moulding.
HIPS	high impact polystyrene	Thermoplastic. A polystyrene modified by copolymerization with butadiene to improve its toughness.
LDPE	low density polyethylene	Thermoplastic. Branched polyolefin used for film and as electrical insulator, made at high pressures.
MF	melamine formaldehyde	Thermoset. Used in domestic ware, switches, plugs, etc.
PA	nylon, polyamide	Thermoplastic. Used in bearings, gears, mouldings, wall plugs, etc.
PF	phenolic, phenol formaldehyde	Thermoset. Moulding material and laminating resin. Sometimes known as *Bakelite*.

PAN	Polyacrylonitrile	A fibre-forming thermoplastic polymer. One of the base polymers used to make carbon fibre.
UPR	polyester (unsaturated polyester resin)	Thermoset. A solution of polyester containing unsaturated groups in styrene or other polymerizable solvent. Matrix resin for GRP.
PET	poly(ethylene terephthalate)	Thermoplastic. A major fibre-forming polymer and a moulding material for beer bottles, etc. In competition with poly(butylene terephthalate) (PBT), a related thermoplastic polyester.
PVC	poly(vinyl chloride)	Thermoplastic. Can be plasticized to produce a leathery material. Unplasticized PVC (uPVC) used for rainwater goods, pipes, etc.
SAN	styrene-acrylonitrile	Thermoplastic. Rigid transparent material used for water jugs and beakers, etc.
SMC	sheet moulding compound	Thermoset. Sheets of glass fibre impregnated with polyester resin (td)

Applications of plastics:

1. Addition of china clay increases the electrical insulation property of PVC.

2. In textiles, for making shutters, filled polymer is used with nylon as polymer.

3. In electrical and electronic industries, filled polymers are used for making exhaust fans, computer tapes, insulators, wire and cable insulation, switch gear parts, etc.(using polypropylene, PET, nylon and SAN as base polymers).

4. In consumer goods like doors, windows, hinges, chairs, camera housing, etc. (polypropylene, ABS are used as base polymers).

5. In defense, for making nose cones, pistol grips and ripple bullets, filled polymers like polystyrene, nylon, etc. are used.

6. They are used in automobiles for making door handles and engine cooling fans.

Inorganic Polymers: Polymers having skeleton made up of atoms other than carbon are called inorganic polymers. Examples: polyphosphazines, polythiazyl, silicones, chalcogenide glass, etc. These compounds are of interest because they offer the opportunity to develop new technological applications due to their reactivity, structure, and physical properties. Inorganic polymers offer some properties not found in organic materials including low-temperature flexibility, electrical conductivity, and non-flammability. The term *inorganic polymer* refers generally to one-dimensional polymers, rather than to heavily cross-linked materials such as silicate minerals.The most widely developed contain silicon as polysiloxanes and polysilanes. Another common class are the polyphosphazenes.

$$\left(\begin{array}{c} R \\ | \\ -Si-O- \\ | \\ R \end{array}\right)_n \qquad \left(\begin{array}{c} R \\ | \\ -Si- \\ | \\ R \end{array}\right)_n \qquad \left(\begin{array}{c} R \\ | \\ -P=N- \\ | \\ R \end{array}\right)_n$$

Characteristics of Inorganic polymers:

(i)They have higher softening point as compared to organic polymers.

(ii)Inorganic polymers with cross-links are usually stiffer, harder and more brittle than organic polymers. The segments between the cross links are usually shorter; therefore, they do not allow intercalation with solvent molecules

(iii) These polymers have highly polar units, so dissolve in polar solvents.   They possess lesser tensile strength as compared to organic polymers.

(iv) Inorganic polymers do not burn. They soften or melt at high temperatures.

(v) Inorganic polymers having cross-linked structures with a high density of covalent bonds.
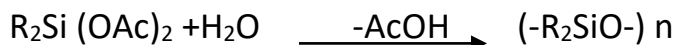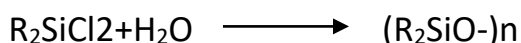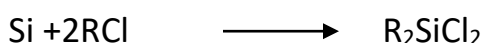
(vi) Inorganic polymers are generally much less ductile than organic polymers.

(vii) Inorganic polymers can usually be obtained n pure crystalline.

(viii)Most of the Inorganic polymers are built p of highly polar substances.

1. **Polysiloxane:** Most important inorganic polymers with regard to commercial applications. Medical: prosthetics, catheters, contact lenses, drug delivery capsules. Non medical: e.g. elastomers, adhesives, lubricants, water repellents, molds, cosmetics.

Preparation:

$Si + 2RCl \longrightarrow R_2SiCl_2$

$R_2SiCl2 + H_2O \longrightarrow (R_2SiO-)n$

$(R_2SiO)3 \text{ or } 4 \longrightarrow (-R_2SiO-) n$

$R_2Si (OAc)_2 + H_2O \xrightarrow{\text{-AcOH}} (-R_2SiO-) n$

PDMS (polydimethylsiloxane) is the most widely used.

2.Polysilanes :

The polymer backbone contains only silicon atoms. A silicon chain allows electron delocalisation of sigma electrons. Many uses of polysilanes derive from the electron mobility. Most uses are in the electronics industry as photoresists and precursors to silicon containing materials.

Preparation: Two general methods

(i)   Condensation of dichlorosilanes with alkali metals

$RR'SiCl_2 \xrightarrow{\text{Na, toluene } 100\,^{\circ}C} (RR'\,Si)n$
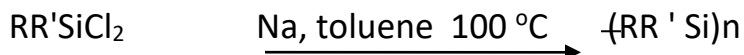
Product distribution indicates radicals are important intermediate
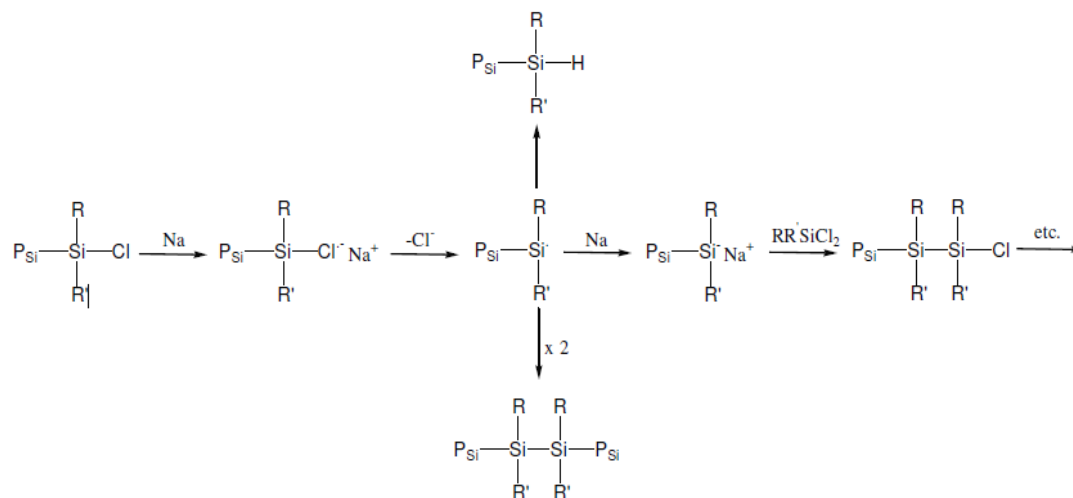
(ii)   *Dehydrogenative coupling of silanes*

$$n \; RR'SiH_2 \quad \xrightarrow{\text{catalyst}} \quad H(SiRR')nH \; + \; (n-1) \; H_2$$

Two proposed mechanisms : Mechanism is Step Growth Polymerisation. Si-Si bond formation can occur via s-bond metathesis or via a silylene if a hydride and a-hydrogen are present.

Via intermediate silylene
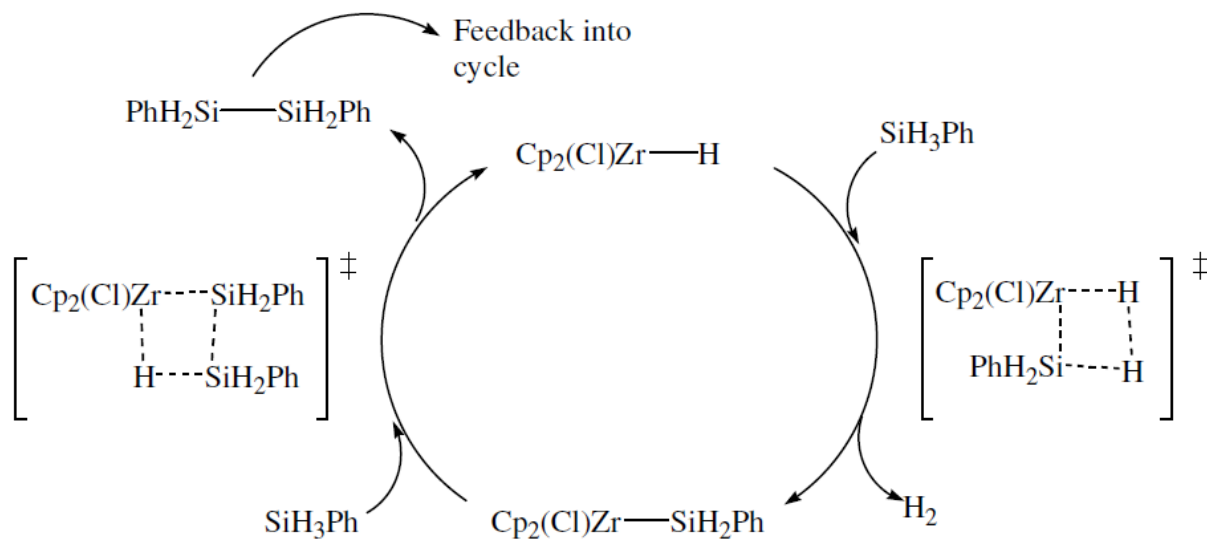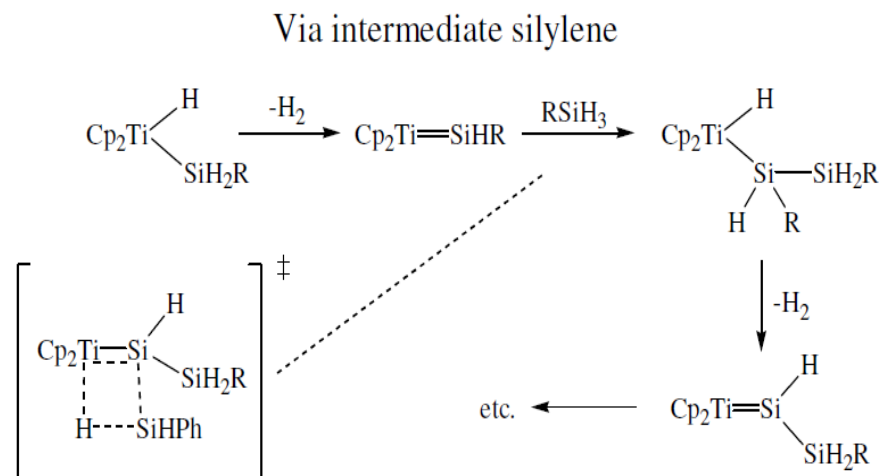
Chain length band gap decreases and absorption wavelength increases (lower energy). Reaches limit at ~ 30 Si atoms .Polysilanes can be used as photoresists.

3. Poly-phosphazenes (Inorganic Rubber) :

Largest class of inorganic polymers because of ease of side group modification. Backbone comprises alternate P and N atoms. Side groups (R) can be organic inorganic or organometallic. Method of synthesis allows modification of side groups. Uses include solid electrolytes (batteries), advanced elastomers (elastic at low temperature). Aerospace and automobile applications because of resistance to hydrocarbon solvents and oils, and flame resistance.

$n > 15000$
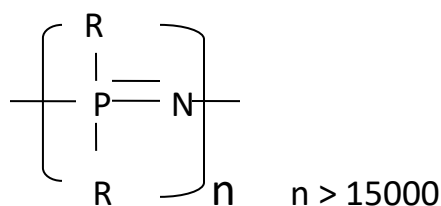
Poly phosphazenes (polyphosphonitrilic)

It may also be written as $(NPR_2)n$. They side group R, may be some alkyl, phenyl, or halogen group. On heating chloro-phasphazenes are transformed into an elastomeric material which is known as *Inorganic rubber.*

Preparation of poly-phosphazenes:

(i)   Phosphanitrilic chlorides can be obtained by heating a mixture of PCl_5 with a small excess of ammonium chloride in chloro benzene solvent at $120\text{-}140^0C$
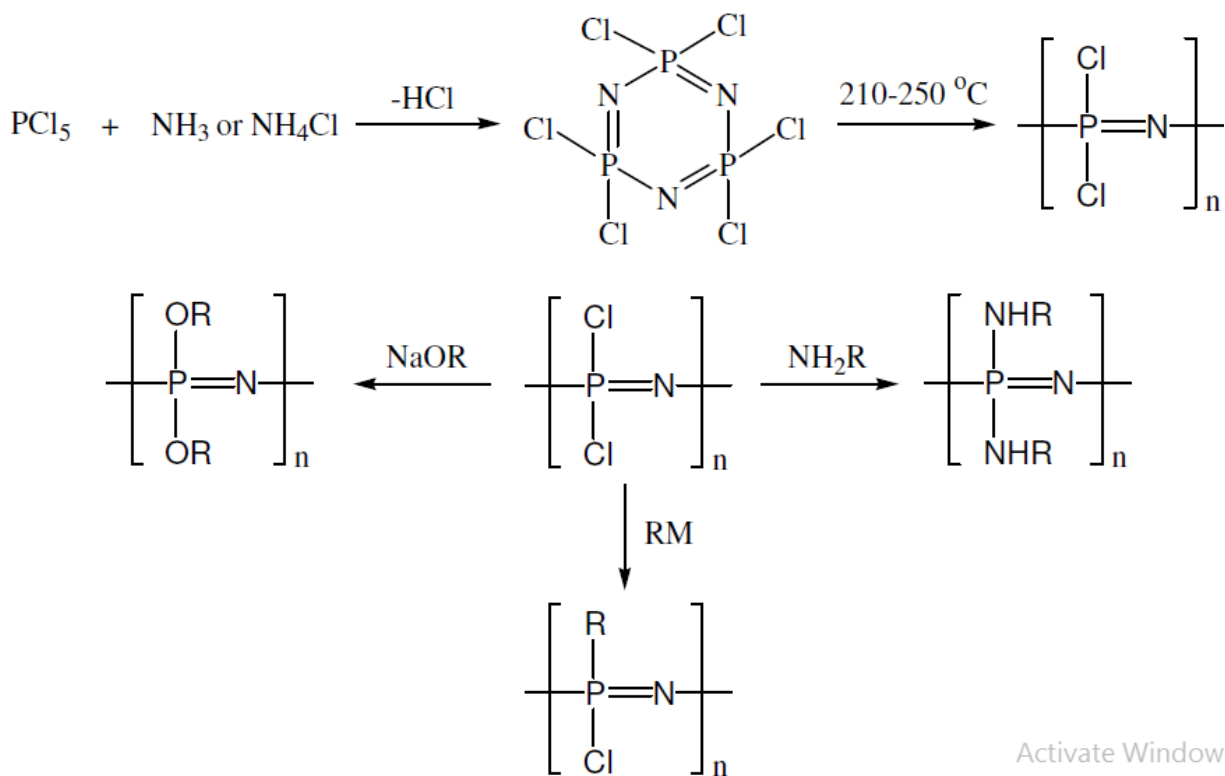
Can also functionalise the P-N precursor prior to polymerization.

Mechanism (ring opening polymerisation)
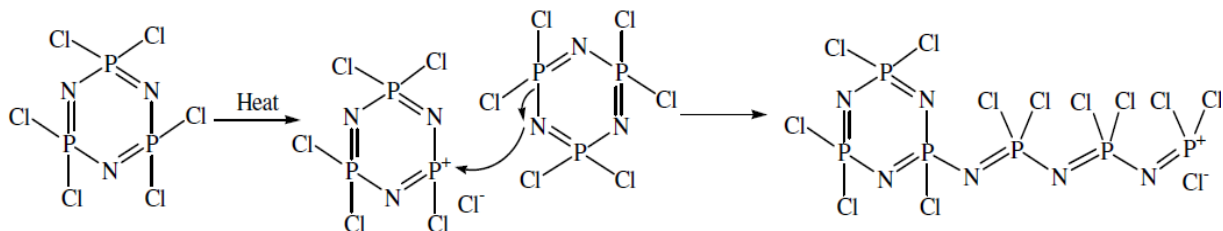
Cationic chain propagation.

Activate Windows

Properties of poly phosphazenes:

1. $(NPCl_2)_3$ has melting point 114^0C and boiling point 256^0C at 1 atm pressure.
2. It is readly soluble in ether,benzene and carbon tetra chloride.
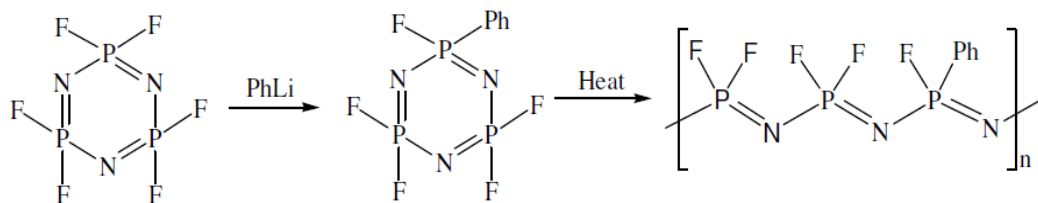3. On the other hand $(NPCl_2)_4$ has m.p 123.5^0C and b.p. 328.5^0C.
4. When the solutions are allowed to stand, the polymer get cross linked and slowly gel formation take place.

Use of poly- phosphazenes:

1. They are used as catalyst in manufacture of silicones.

2.The phosphonitrilic halides are used as rigid plastics, expanded foam and fibres because they are water proof, fire proof and are unaffected by oil ,petrol and other sovents.

3. They are also used as flexible plastics which are useful or fuel hoses and gaskets because they retain their elasticity at low temperatures.

4. Thin films of poly (aminophophazene) are used to cover severe burns and serious wounds because they prevent the loss of body fluids and keep germs out.

Bio-polymers(Biodegradable polymer) :

They are obtained by natural soueces such as animals and plants.The biopolymers DNA and RNA (polynucleotides), protein (polypeptide) , polymerized sugars (polysaccharide) and poly-isoprene(natural rubber) are winners of an evolutionary process that occurred during the earliest phases of life on Earth.

Properties of Biopolymers:

Biopolymers are-

(i) spontaneously fold and assemble into precise and highly elaborate yet fragile structures with meager stability.

(ii) pre-pay the free energy of folding and assembly during monomer synthesis and polymerization.

(iii) spontaneously degrade in the aqueous environments characteristic of biological systems, but can persist via kinetic trapping.

The three biopolymer types differ profoundly in their structures, properties, and functions. Polypeptide and polynucleotide dominate the functional and informational machineries of life, while polysaccharide is important in physical structure, energy storage, and recognition. Yet biopolymers share many critical properties including chirality, chain directionality, pre-organization and conditional self-complementarity, synthesis by condensation dehydration using phosphorylated intermediates, chemical instability in aqueous media, and persistence via kinetic traps whose depths are increased by folding and assembly. A recognition of the universalities and distinctive characteristics of DNA, RNA, protein, and polysaccharide is a necessary prerequisite for modeling their origins and early evolution.

Origins of Biopolymers: Darwinian processes require biopolymers, which must therefore pre-date natural selection. The universality of

(i)   Synthesis by condensation and degradation by hydrolysis,
(ii)   Self complementarity and pre-organization,

(iii)   Folding-conferred protection from chemical degradation, and

(iv)   Molecular mutualisms is consistent with biopolymer origins in a shared 20 milieu driven by 'self-interest' and co-evolution. Self-interest is equivalent to chemical persistence, a survival strategy with demonstrated utility in extant biological systems.
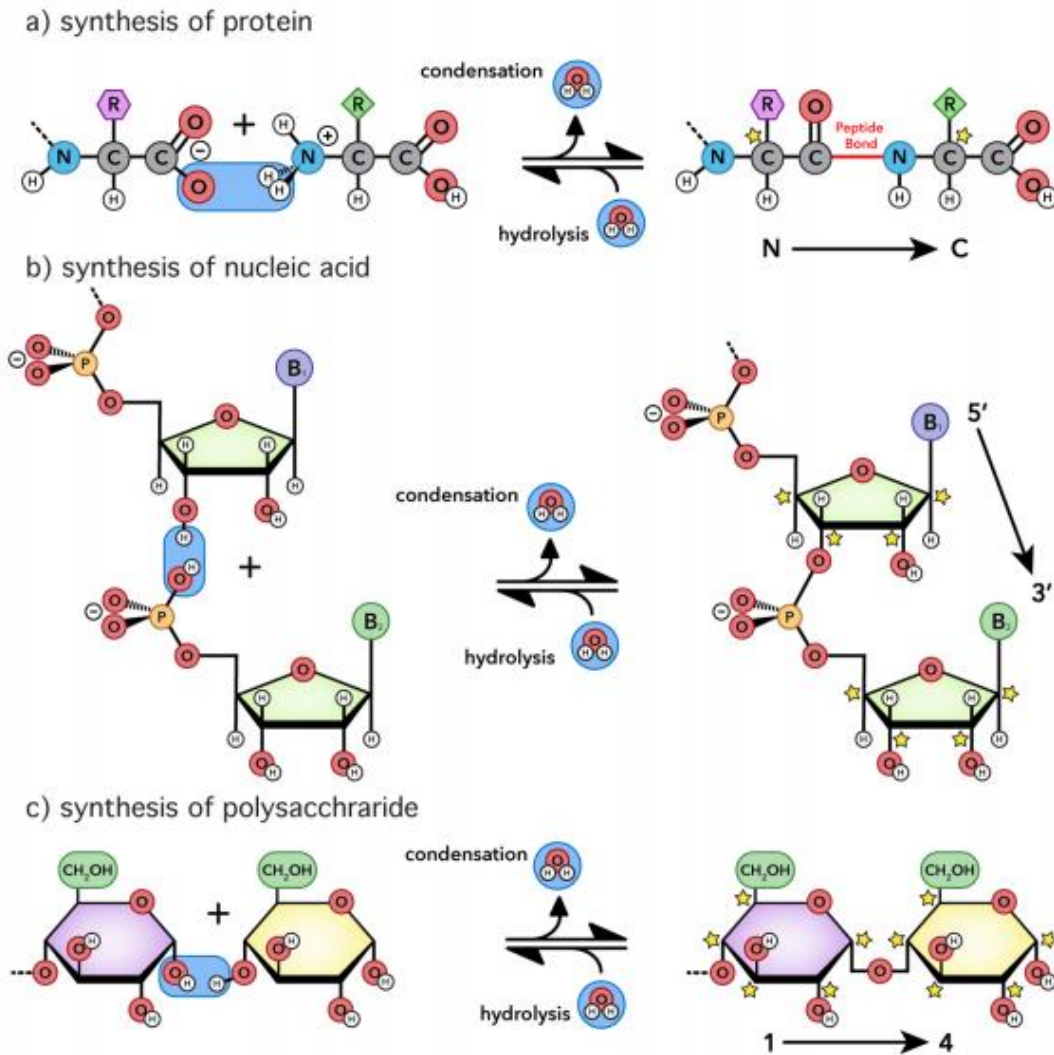

Fig: Net reactions for biopolymer formation by condensation dehydration and biopolymer degradation by hydrolysis. (a) Protein (b) RNA(c) Polysaccharide.

Table 1. Biopolymer Attributes

ATTRIBUTE	POLYNUCLEOTIDE	POLYPEPTIDE	POLYGLUCOSE
Primary proficiency	maintain, record, and transduce information,catalyze several chemical reactions	Catalyze and regulate chemical reactions, provide physical structure	provide physical structure, energy storage and recognition
Condition for complementarity	nucleotide sequence	Amino acid sequence	stereochemistry (b- vs. a-anomers)
Number of folding elements	four	One	One
Folding element(s)	nitrogenous bases	peptide linkage	cyclic glucose
Enzymatic capability	moderate	High	Low
Sidechain diversity	low: four planer nitrogenous bases	high: twenty amino acid side chains	N/A: no sidechains
Hydrogen bonding	unipolar, planar	unipolar, planar	bipolar, non-planar
Linearity	always linear	always linear	sometime linear
Secondary structure	helices, stem-loops, pseudoknots	a-helices and b-sheets	elongated fibers
Degradation by hydrolysis	yes	Yes	Yes

Table 1: Show some common addition polymers and their relevant monomers names and chemical structure

Molecular weight of Macromolecules :

A macromolecule is a iant molecule obtained by the polymerization of a large number of simple, low molecular weight molecules of similar structure. Polymerization may take place either by addition or by condensation reaction. Butadiene with molecular weight 54, polymerises to form poly-butadiene with molecular weight of 5 to 6 millions. It is, therefore, necessary to take an average molecular weight.

(i) Number Average Molecular Weight ($\bar{M}n$):

The number average molecular weight is defined as the total weight of the dispersed material divided by the total number of molecule present .If n_1, n_2, n_3............ represent the number of molecule having masse m_1, m_2, m_3.......... Then number average molecular weight ($\overline{Mn}$) is given by,

$$\overline{Mn} = \frac{n_1m_1+n_2m_2+n_3m_3+......}{n_1+n_2+n_3+........}$$

It may also be written as-

$$\overline{Mn} = \frac{\Sigma\, n_i m_i}{\Sigma\, n_i} \qquad\qquad ....(1)$$

where n_i =   number of momomer molecules

          m_i =   simple monomer of molecular weight.

(ii) Weight Average Molecular Weight ($\overline{Mw}$):

The weight average molecular weight gives representation to various molecular species in proportion to their weights in the given substance. Thus, in weight – average molecular weight, the molecular of each species is multiplied by the weight of that species and not by the number as in the case of number average molecular weight.

If w_1, w_2, w_3..... represent the weight of the species of masses m_1, m_2, m_3..........,then the weight average molecular weight (Mw) is given by,

$$\overline{Mw} = \frac{w_1m_1+w_2m_2+w_3m_3 +.......}{w_1+w_2+w_3+......}$$

$$\overline{Mw} = \frac{w_1m_1{}^2+w_2m_2{}^2+w_3m_3{}^2 +.......}{w_1+w_2+w_3+......}$$

$$\overline{Mw} \quad = \quad \frac{\Sigma\, n_i m_i^2}{\Sigma\, n_i m_i} \quad\quad\quad ....(2)$$

It will be seen from eqn.(1) and (2), that $\overline{Mw}$ always greater than $\overline{Mn}$.
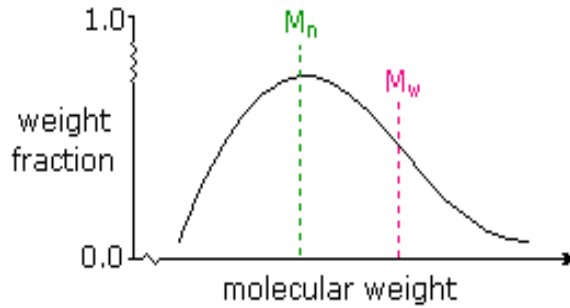
Fig: $\overline{Mn}$ and $\overline{Mw}$ in a typical sample of polydispersed macromolecules

Index of polydispersion (I) = $\overline{Mw}/\overline{Mn}$

Polymer Molecular Weight Determination:

Polymers like simple molecules can dissolve in common solvents. They are composed of functional groups that are chemically reactive; they exhibit colligative properties and at specific wavelength can absorb energy. However, unlike simple organic molecules, they are made up of smaller monomer units of different sizes. These changes in the degree of polymerization, give rise to molecules with different molecular weights and different molecular weight distributions.

Polymers can be characterized with respect to
    (i)   chemical identity of the repeat unit,
    (ii)   nature of the end group,
    (iii)   nature and extent of cross linking,
    (iv)   solubility, and
    (v)   colligative properties.

        Numerous methods abound for polymer characterizations and are classed under absolute (A), equivalent (E), and relative (R) (Table 1). Absolute methods allow the direct computation of polymer molecular weight from

measured quantities without assumptions about the chemical and/or physical properties of the tested polymer molecule. The equivalent techniques, although direct calculation of polymer molecular weight can be made from measured data requires knowledge of the chemical structure of the polymer molecule. The relative methods, on the other hand, measured properties that depend on the chemical and physical structure of the polymer structure; requiring molecular weight curves of polymer standards of the same chemical and physical structure as that of the characterized polymer to be established.

All synthetic polymers contain polymer chain of uneven length;they are polydispersed, and as such, molecular weight is not a single value but often described as average molecular weight. The average molecular weight can be expressed in different ways such as number average molecular weight (M_n), weight average molecular weight (Mw), viscosity average molecular weight (M_v), and higher average molecular weight (M_z, M_{z+1}).

The choice of method for polymer molecular weight determination is influenced by factors such as (i) information required, (ii) operative region, (iii) cost effectiveness, and (iv) experimental conditions and requirements. Information on some of the techniques used for molecular weight determination is given in

Table.1.1

Methods for Determining Molecular Weights of Polymers:

Some of the instruments used in the measurement of the molecular weights of larger molecules such as--
1. Osmometry: (a)Membrane osmometers (b). Vapor pressure osmometers
2. Viscometers
 3. Light-scattering photometers
4. Liquid chromatographs, gel-permeation
 5. End group determination

6. Electron microscopy
 7. Ultracentrifuge sedimentation

 1. **Osmometry Techniques** :

The two common osmometry techniques used for number average molecular weight determination are the(i) membrane omometry and (ii)vapour pressure osmometry. Vapour pressure osmometry is best suited for analyzing polymer samples with 20,000g/mol. The limiting factor in membrane osmometry is the diffusion problem of low molecular weight molecules through the membrane.

 (i)Membrane osmometry: Membrane osmometry depends to a large extent on the colligative properties of the polymer solution. These properties include osmotic pressure, boiling point elevation, vapour pressure reduction, and the freezing point depression. In this technique, polymer solution and pure solvent are separated by a membrane which is semi permeable only to the solvent and not to the polymer (solute). Because the chemical potential of the pure solvent is higher than that of the solvent in polymer solution, the solvent moves from the pure solvent side to the polymer solution side. If there is an applied pressure, this movement can be hindered such that the there is no net flow across the membrane. In this condition, the applied pressure is equal to the osmotic pressure.   However, osmotic pressure of a solution is a function of molecular weight and concentration; hence Eq. 12 is usually used in the evaluation of number average molecular weight .
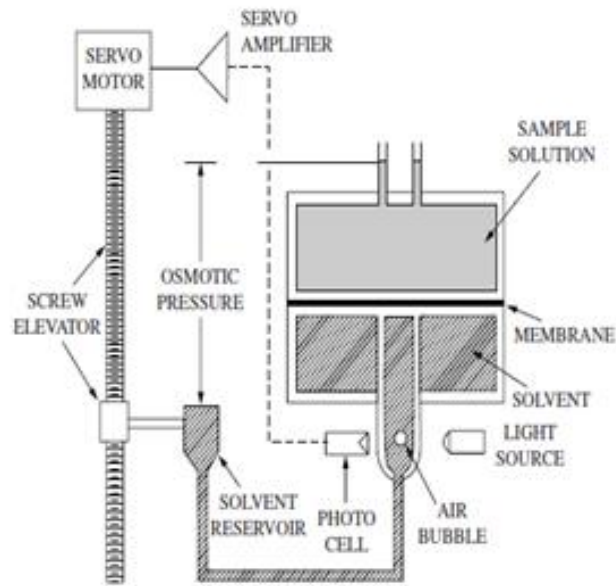
Fig: Schematic diagram of a high-speed membrane osmometer

The osmotic pressure (π) of a polymer solution is related to the number-average molecular weight of the polymer by the relations

$$\frac{\pi}{RTC} = \frac{1}{\overline{Mn}} + BC$$

$$\left[\frac{\pi}{RTC}\right]_{c \to o} = \frac{1}{\overline{Mn}}$$

We know that

$$(\pi/C)_{c \to o} = \frac{RT}{\overline{Mn}} = \frac{L.d}{1033}$$

$$Mn = \frac{1033.RT}{L.d} = \frac{1033 \times 0.8205T}{L.d}$$

A plot of (π/RTC) versus C therefore, gives a straight line, the ordinate intercept of which will gives 1/$\overline{Mn}$.

 Here, all the plots will have the same ordinate intercept since the molecular weight is the same. But as we have used different solvents, the plot will have different slopes as shown in figure.
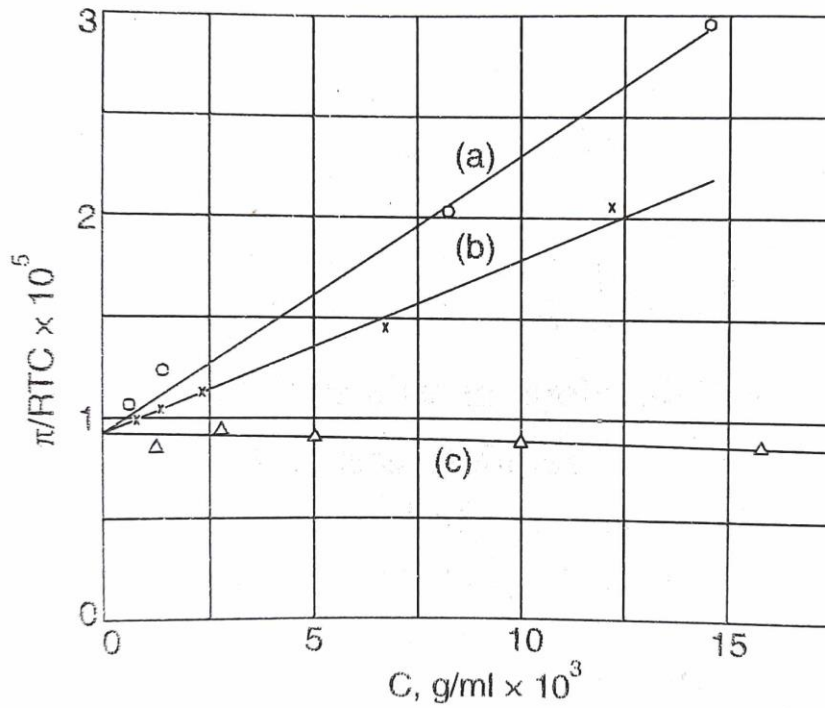
Fig: Plot of (л/RTC) versus C for one sample of nitro cellulose in(a) Acetone (b) Methanol (c) Nitrobenzene solution

Polymethyl acrylate
Benzene, 30°C
Pinner-Stabin glass osmometer
$(h/c)_{C \to 0} = L = 0.15$

$$\bar{M}_n = 1033R \, \frac{T}{Ld}$$

$$= \frac{1033 \times 0.8205 \times 303}{0.15 \times 0.8682}$$
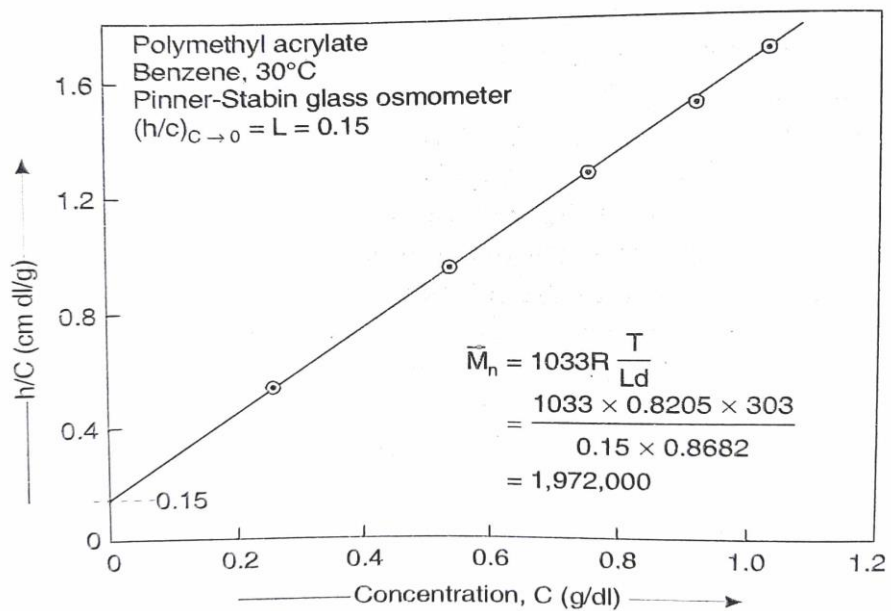
$$= 1,972,000$$

Fig: Plot of h/C versus C for a poly-methyl acrylate sample in benzene solution.

Limitations of membrane osmometry:

(i)Membrane osmometry measurements are best used for 30,000 M_n < 1,000,000 grams/mole. For M_n above 1,000,000 grams/mole, the solute is too dilute to create a measurable osmotic pressure. For M_n below 30,000 grams per mole, the solute permeates through the membrane and the measurements are inaccurate.

(ii)Another issue for membrane osmometer is the limited membrane types. The most common membrane used is cellulose acetate; however, cellulose acetate can only be used with toluene and water. While toluene and water are useful solvent for many compounds, not all polymers are miscible in toluene or water. Regenerated cellulose membranes can be used for many other solvents, but are hard to obtain.

(II)**Vapor Pressure Osmometers:**

The vapor pressure of any solvent is lowered by the addition of solute. If a pure solvent and a solution are placed in two containers and connected in a closed system, the pure solvent will evaporate and condense into the solution. The resultant temperature difference, due to the latent heat of evaporation of the solvent, can be detected as an indication of the molecular weight of the solute. In practice, the temperature difference is read as the output voltage of a resistance bridge using high-accuracy temperature sensors (Figur). The relationship between the bridge output voltage ΔV, the solution concentration c, and the average molecular weight Mn is given by Equation. where K is the calibration constant for the particular combination of solvent and type of thermistor used. Although the amount of drop in vapor pressure is only a function of the amount of solute in solution and of the solute molecular weight, ΔV is a relative quantity depending on the solvent, operating temperature, and temperature-sensing element used. The instrument, therefore, must be calibrated with a known solution.

The vapor-pressure osmometer consists of a thermostated chamber saturated with solvent vapor. Two thermistor beads are suspended in the chamber, and syringe guides are built into the chamber. Using the syringes, a

drop of solvent and a drop of solution are placed on the reference and measuring thermistor, respectively. As the solvent condenses, it warms the measuring thermistor. Therefore, its electrical resistance decreases. The thermistors are part of a resistance bridge whose output is in proportion to the temperature difference between measuring and reference thermistor. The resistance bridge output ΔV is plotted on a graph of ΔV/c vs. c.

The applicability of this instrument is limited because of the small difference in temperatures that need to be detected. Typically, for a 1% solution of 50,000 molecular weight polymer, the temperature difference is on the order of 0.001°F (0.0006°C).
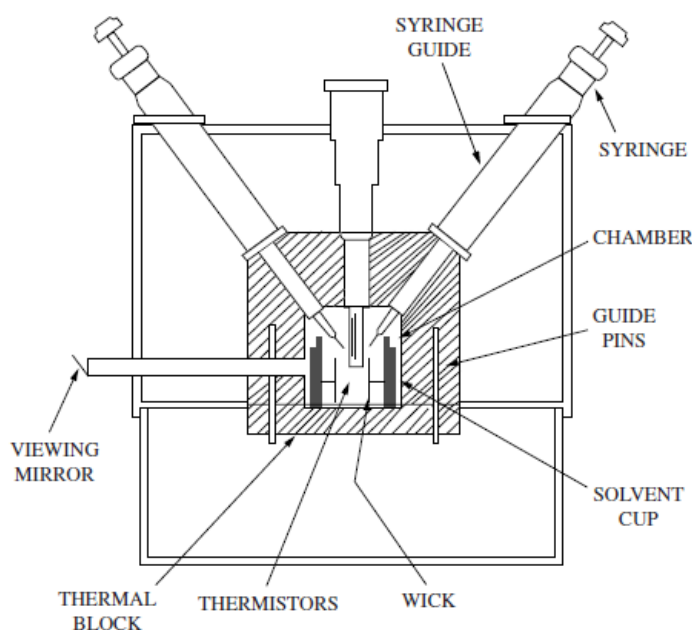

Fig: Schematic diagram of a vapour Pressur osmometer

2. Viscometry :(*Viscosity Average Molecular Weight (M_η) Determination*):

The solution viscosities of polymer are determined by viscometers. The Ostwald viscometer and the Ubbelohde suspended level viscometer(USLV) are the two popular viscometers used for this purpose. Polymers in general dissolve with

difficulty in solvents than their corresponding monomers probably due to increased number of methylene group. When a polymer dissolves in a solvent, the viscosity of the solvent increases and polymer chain has direct influence. In 1930, Hermann Staudinger reported a relationship existing between polymer molecular weight and the relative magnitude of increase in viscosity. The measurement of the viscosity of a solution is simple and in expensive, although somewhat time consuming. The Ubbelohde capillary viscometer is commonly used for polymer solution viscosity determination. The polymer solution is introduced into the reservoir of the viscometer and aspirated to the upper bulb. Air is then admitted which causes the solution to flow down the capillary by gravity. For η determination via this technique, the process is performed for pure solvent and polymer solution respectively. The solution flowing through the capillary obeys the Poiseuille's law for laminar flow and implies that the pressure drop (ΔP) varies as the viscosity (η) of the solutions.
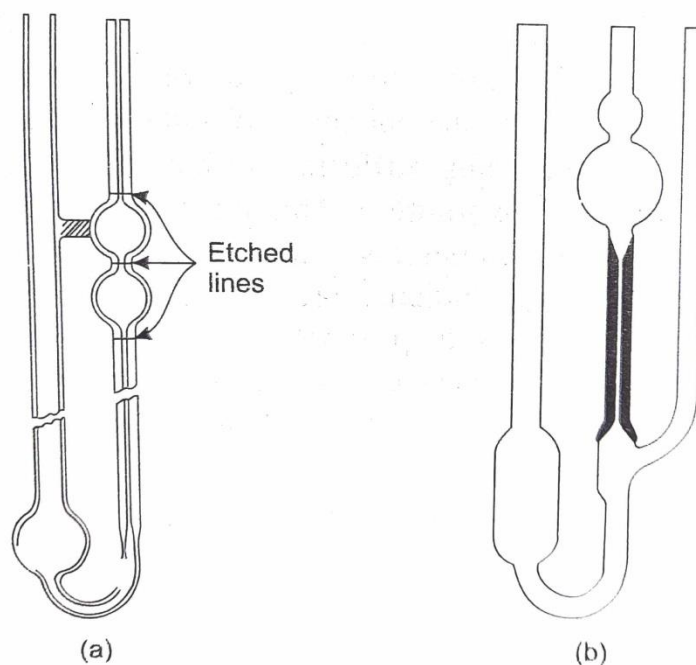

Fig: (a) The Ostwald viscometer (b) Ubbelohde suspended level viscometer(USLV)

From the Mark-Houwink equation the relationship among the molecular weight and viscosity are given below-

$$[\eta] = KM^{\alpha}$$

Where η is the intrinsic viscosity , M is Molecular weight, K and α are constants for a particular polymer solvent system. These constants are calculated by measuring the viscosities and molecular weight of a series of polymers over a wide range of molecular weights and fitting the best straight line to the following equation.

$$[\eta] = KM^a$$

$$\text{Log } [\eta] = \log K + a \log M$$

The limitation of this method is that the empirical relationship $[\eta] = KM^a$ is valid only for linear polymers.
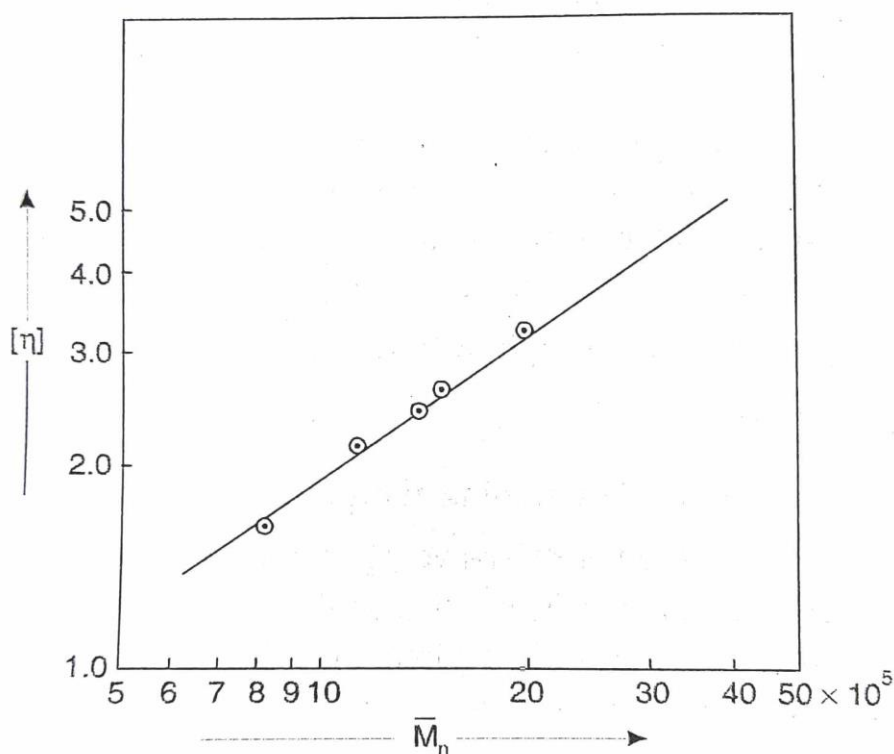
Fig: Plot of [η] versus $\overline{M}n$ for polymethyl acrylate in benzene solution

Polymer-solvent system	K x 10^3mL/g	α
PMMA-Acetone	7.70	0.70
PMMA-Benzene	5.20	0.76

PMMA-Toluene	7.0	0.71
Poly vinyl acetate-Acetone	10.2	0.72
Poly vinyl acetate-Benzene	56.3	0.62
Poly vinyl acetate-Acetonitrile	41.5	0.62
Poly vinyl alcohol-Water	45.3	0.64
Poly styrene-Benzene	10.6	0.735
Poly styrene-Toluene	11.0	0.725

S.N	Method					

Rubber:

Everyone must have come across rubber products. There are many rubber products which we come across in our daily life. For example rubber gloves, rubber band, footwear, etc. We all have seen that rubber items have the ability to recover their shapes after being stretched or distorted and hence rubber is referred to as elastomers. It is an elastic substance which can be obtained both by naturally (natural rubber) or they can also be synthesized chemically in laboratories (synthetic rubber-like butyl rubber, neoprene, etc.)

Types of rubber:

There are two types of rubber — Natural Rubber and Synthetic Rubber.

1.Natural rubber:

These are the elastomers which are obtained naturally. It is made up of solids particles suspended in milky white liquid, called latex that drips from the bark of tropical and subtropical trees. This latex rubber is mainly found in the countries like Brazil, India, Indonesia, Malaysia and Sri Lanka. It is made by the polymerization of isoprene (2 methyl-1, 3-butadiene) which has a chemical formula $(C_5H_8)_n$ and it is known as cis- 1, 4- polyisoprene. In simple words, we can say that they are made by loosely joining the monomers of isoprene (C_5H_8) in the form of a long tangled chain. In natural rubber, most of the double fonds formed in the polymer chain have the Z configuration, resulting in natural rubber's elastomer qualities.

Preparation of Natural Rubber:

- **Rubber tapping** – The milky white liquid latex is collected from the rubber trees in a cup by making a slight V-cut on the tree bark. The collected latex is washed, filtered and reacted with acids to congeal the rubber particles.

- **Mastication** – The rubber obtained from the tapping process is still not ready to be used. When it is cold it is very brittle in nature and when warmed up it becomes very gluey. To remove the brittle nature and strong odor of the rubber, it is allowed to pass through the rollers and is pressed to make it softer and flexible to work. This process is repeated based on the properties that are required for the rubber. In this process, extra chemical ingredients are also added to enhance the properties of rubber.

- Calendering is a process, which is mainly performed to provide shapes to rubber using rollers and proper mixing of the chemical ingredients.

- The final product obtained is then extruded to make hollow tubes by passing them through specially designed holes in an extrusion machine.

- Vulcanization – Even after performing all these steps rubber is not much stronger and harder to be used in various items like car tires and machinery. To enhance all these properties, sulphur is added to the rubber and it is heated at a temperature ranging 373 k to 415 k. This process is known as vulcanization. Sulphur acts as a cross-linking agent and after vulcanization, rubber gets cross-linked and becomes hard.

    Disadvantage of Natural Rubber:

- The natural rubber obtained from latex cannot be used in industries
- because it has the following defects.
- 1. It becomes soft and sticky during summer.
- 2. It becomes hard and brittle during winter.
- 3. It swells up in oils.
- 4. It flows plastically due to prolonged stress.
- 5. Chemicals easily affect natural rubber.

Vulcanization of rubber : Vulcanization is compounding of rubber with sulphur. Vulcanization is process of heating the natural rubber with sulphur at

140°C in CO_2 atmosphere. The double bonds present in rubber chain opened and cross linked through sulphur atoms. Hence the vulcanized rubber becomes very hard. The hardness of rubber increases as the percentage of sulphur increases. 2 to 4% sulphur addition gives soft elastic rubber. When sulphur content is more than 30%, hard rubber called 'Ebonite' is obtained.

Properties of vulcanized rubber :

1. Vulcanized rubber has very little electrical and thermal conductivity. Hence, it is mainly used for electrical insulation purposes.

2. It has high elasticity and tensile strength.

3. Corrosive chemicals and oils do not affect it.

4. It is also not affected by atmosphere.

2. Synthetic rubbers:

Synthetic rubbers are produced from petroleum and natural gas. It is obtained by polymerization of 1, 3 – butadiene derivatives or by copolymerization of 1, 3 – butadiene along with unsaturated monomer.

Preparation of synthetic rubbers:

(i)Neoprene (Polychloroprene): – It is a polymer of chloroprene, which formed by joining together the monomers of chloroprene.

(ii)***Buna- N:*** – It is a copolymer of 1, 3 – butadiene and acrylonitrile, it is formed in the presence of a peroxide catalyst.

(iii)Styrene-butadiene rubber (SBR) - which is a copolymer of 1,3-butadiene and styrene which is mixed in a 3 to 1 ratio, respectively. SBR rubber was developed

during World War II when important supplies of natural rubber were cut off. SBR is more resistant to abrasion and oxidation than natural rubber and can also be vulcanized. More than 40% of the synthetic rubber production is SBR and is used in tire production. A tiny amount is used for bubble-gum in the unvulcanized form.

(iv) **Nitrile rubber:** Nitrile rubber is copolymerized from butadiene and acrylonitrile ($H_2C=CH-CN$).

(v) **Butyl rubber :** Butyl rubber is copolymerized from isobutylene [which is methylpropene $H_2C=C(CH_3)_2$] and a small percentage of isoprene.

(vi) **Silicone rubber**: Silicone rubber and other compounds, chemically called polysiloxanes, are not from conjugated dienes but have repeating units like $-O-SiR_2-$ where R is some organic radical group like methyl. There is a separate page on Silicone Polymers.

Uses of Rubber:

Rubber can be used for various rubber and across various platforms, few of them are mentioned below;

(a) It is used for lining chutes, bins and industrial mixers. Because of its water-proof and resilient property it can be made into a good insulator.

(b) In clothing industry, it can be used as wetsuits and expandable clothes such as gym and cycling shorts etc.

(c) Rubbers are also used for flooring purposes it gives padding and prevents fatigue along with being waterproof and slip-resistant.

(d) In automobile industry, its use can be witnessed in tires, padding in brakes, airbags, seats, and roof etc

Table 1 General-purpose and speciality rubbers: properties and uses

	Rubber	General properties	Typical uses
BR	butadiene (polybutadiene)	Special-purpose rubbers of density 0.93 Mg m^{-3}. Good low-temperature properties and abrasion resistance. High resilience (low damping) and therefore low heat build-up at ordinary temperature. Poor resistance to oils and hydrocarbons.	Resilient mounts, tyre sidewalls (blended with NR)
CR	chloroprene *(Neoprene)*	Versatile special-purpose rubbers of density 1.20 Mg m^{-3} and good mechanical and electrical properties. Very good resistance to ozone oxidation, heat and flame.	Car radiator hose, gaskets, seals, conveyor belts, bridge bearings
EPM, EPDM	ethylene-propylene copolymer and terpolymer	The copolymer (EPM) and terpolymers (EPDM) are general-purpose rubbers of density about 0.85 Mg m^{-3} Good mechanical properties and resilience. Can accept very high loadings of oils and fillers. Very good resistance to ozone, oxidation, chemical, weathering and high and low temperatures.	Conveyor belts, hose, general goods
NR	natural rubber (*cis*-polyisoprene)	An excellent general-purpose rubber of density 0.93 Mg m^{-3} High resistance to tearing and abrasion. High resilience at 20 °C and thereforelow heat build-up under the action of dynamic stresses. Swells in mineral oils and degreasing solvents.	Tyres, suspension systems, bushes, bridge bearings
NBR	nitrile (acrylonitrile-butadiene copolymer)	Special-purpose rubbers of density 1.0 Mg m^{-3} and moderate mechanical properties. Poor cold resistance. Excellent resistance to swelling in hydrocarbons and alcohols. The greatest oil and alcohol resistance occurs in rubbers with a high acrylonitrile content.	Fuel lines and linings
SBR	styrene-butadiene copolymer	A good general-purpose rubber of density 0.94 Mg m^{-3}, competitive in properties with NR when reinforced with carbon black. Very good abrasion resistance. Swelling and adhesion properties similar to NR, ageing resistance better	Tyres, often in direct competition with NR

than NR.

Biomedical uses of polymers:

The mostly used polymers in medical applications are silicone rubber and polyurethane. Polymers used in specific medical applications in medicine are given below.

Sl.No.	Polymer	Applications
1.	Polyurethane	Heart valves, blood filters, artificial hearts, vascular tubes, etc.
2.	Polyvinyl chloride (PVC)	Disposable syringes, etc.
3.	Polypropylene	Heart valves, blood filters, etc.
4.	Polyethylene	Disposable syringes, etc.

QUESTIONS

1. What is polymerization?

2. What are the types of polymerization?

3. How polythene is formed?

4. How Bakelite is formed?

5. Define plastic.

6. What are the types of plastics?

7. What are reinforced plastics? 8. What are biomaterials?

PART – B

1. Explain addition polymerization with an example.

2. Explain condensation polymerization with an example.

3. What are thermoplastics? Give an example.

4. What are thermosetting plastics? Give an example.

5. Mention the advantages of reinforced plastics.

6. Give the applications of reinforced plastics.

PART – C

1. List the differences between thermoplastics and thermosetting plastics.

2. Explain the mechanical properties of plastics.

3. What are the advantages of plastics over traditional materials?

4. Write a note on reinforced plastics.

5. What are biomaterials? List the biomedical uses of the following.

a. Polyurethane b. PVC c. Polypropylene d. Polyethylene

QUESTIONS

PART – A

1. What is rubber? 2.
2. What is Latex?

3. What is compounding of rubber?

4. What is vulcanization?

5. Define reclaimed rubber.

6. Give any two defects of natural rubber.

PART – B

1. Give any three defects of natural rubber.

2. Mention the properties of reclaimed rubber.

3. Mention the uses of reclaimed rubber.

PART – C
1.How natural rubber is obtained from Latex? Explain.
2. What are the defects of natural rubber?
3. What is compounding of rubber? Mention the ingredients and their functions.
4. Explain vulcanization of rubber.
5. What is reclaimed rubber? Explain the process of reclamation of rubber.

1. Write the differences between
b) additional polymerization and condensation polymerization

c) thermoset and thermoplasts platics

2. Explain any one of the mechanism of additional polymerization, using suitable example

3. Write a note on thermo setting plastics? Write a note on properties and uses of Teflon.

4. Describe the manufacture , properties ,uses of a)polyethylene b) Teflon c) PVC

5.(a) How is HDPE is prepared? Give its properties and uses?

6.How is Bakelite manufactured? Discuss its important uses and properties.

7. Identify the thermosets & thermoplasts among the following: PVC, polyethylene, silicon, polyester fiber, bakelite.

8.What is Bakelite? How is it manufactured and mention its uses.

9(a) Differentiate between LDPE and HDPE.

(b) What are the drawbacks of raw rubber?

(c) Write the repeating unit for the following:

i. Nylon 6,6 ii. PVC

10..Describe the preparation, properties and engineering uses of Polythylene.

11. (a) Explain the preparation, properties and uses of Bakelite.

12. (a) How will you synthesis nylon 6,6 from 1,3 butadiene?

(b) Describe the method of preparation of polyester and mention its properties and uses.

(c) What is the repeating unit of (i). natural rubber ii. Teflon.

13. (a) What are elastomers? Give the preparation, properties and uses of Buna S.

14. (a) Differentiate between elastomer and plastic.

(b) Which rubbers are used in the preparation of automobile parts? Discuss their manufacture and vulcanization.

15. Write preparation, properties and uses of nylon, polyester, and polyurethanes.

(a) Why are Silicones called inorganic polymers? Discuss the synthesis of linear chain Silicones.

(b) Describe condensation polymerization with an example

Multiple choice questions:

1. Number of monomers in a polymer is (c)

(a) Tacticity
(b) Functionality
(c) Degree of polymerization
(d) All
2. Poly functional molecules can give the following type of polymer (d)
(a) Only linear
(b) Only straight
(c) Both (a) and (b)
(d) Only cross linked
3. In which of the following polymerization, the rate is fast (a)
(a) Addition polymerization
(b) Condensation polymerization
(c) Both equal
(d) None
4. Accelerators are added in which type of polymerization (c)
(a) Addition
(b) Condensation
(c) Both
(d) None
5. In which type of moulding, the continuous strips can be obtained (d)
(a) Compression
(b) Injection
(c) Transverse
(d) Extrusion
6. The polymer used in optical instruments is (c)
(a) PMMA
(b) PTFE
(c) PE
(d) Nylon
7. Urea formaldehyde resins are (b)
(a) Phenoplasts
(b) Amono plasts

(c) Both of these
(d) None of these
8. Adipic acid is _____ functional
(a) Mono
(b) Bi
(c) Tri
(d) Tetra

9. Vulcanization was first done by (d)
(a) MRF
(b) Ceat
(c) JK
(d) Good year
10. Isocyanate rubber is
(b)
(a) Polyamide
(b) Polyurethane
(c) Polyester
(d) Polythene
11. Which one among the following is a copolymer
(a) Nylon 6,6
(b) Teflon
(c) PVC
(d) Polybutadiene
12. Polyester belong to the following type of polymer
(a) Addition, thermoplastic
(b) Addition, thermosetting
(c) Condensation, thermoplastic
(d) Condensation, thermosetting
13. Bakelite is prepared by the condensation of
(a) Phenol and formaldehyde
(b) Phenol and acetaldehyde
(c) Cresol and formaldehyde
(d) Urea and formaldehyde
14. Chloroprene is the repeating unit in

(a) PVC
(b) SBR
(c) Neoprene
(d) Teflon
15. Cellulose acetate is a
(a) Thermoplastic
(b) Thermosetting plastic
(c) Both of these
(d) None of these