UNIT-3

POLYMERS

Polymers are high molecular weight compounds whose structures are made up of a large number of simple repeating units. The repeating units are usually obtained from low molecular weight simple compounds referred to as monomers. The reaction by which monomers are converted into polymers is known as polymerisation.

For example polyethylene formation from ethylene

$$n\,CH_2 = CH_2 \xrightarrow{\text{polymerisation}} -(CH_2\text{-}CH_2)-_n$$

Ethylene Polyethylene

The monomer is shown on the left hand side of the equation and products on the right hand side, the repeating polymer unit is enclosed in brackets and lines passing through the brackets show that the chain continues in both directions. The subscript n shows how many times the repeating unit appears.

Degree of polymerisation:-

The size of the polymer molecule is decided by the number of repeating units present in it. The number of repeating units (n) contained in the polymer is known as degree of polymerisation.

$$n\, CH_2 = CH_2 \xrightarrow{\text{polymerisation}} -(CH_2\text{-}CH_2)_n -$$

Ethylene Polyethylene

Where n is degree of polymerisation, it can be 10^4 or more.

Functionality:

The number of bonding sites in a monomer is termed as functionality. For a molecule to act as a monomer it must have at least two reactive sites i.e. its functionality should be two. When the double bond is broken, two single bonds become available for combination.

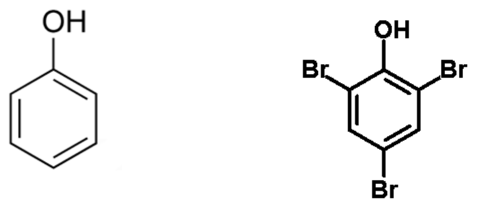
Eg:- 1) Ethylene can add two molecules of hydrogen or halogen.

Hence, it is bi-functional (functionality two)

$$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$$

Ethylene Ethane

2) Phenol has three reaction sites. Hence, it is tri-functional



$+ 3Br_2 \rightarrow \quad + 3HBr$

Phenol 2,4,6 Bromo phenol

3) Acetylene has a functionality of four (tetra functional), as it can react with four atoms of hydrogen or halogen.

$$CH \equiv CH + 2H_2 \rightarrow CH_3 - CH_3$$

Actylene Ethane

Mechanism of Polymerisation:

The process of joining together a large number of simple molecules to form a very big molecule is termed as polymerisation. There are two broad types of polymerisation reactions i.e.

1) Addition Polymerisation (or) Chain Growth Polymerisation
2) Condensation Polymerisation (or) Step Growth Polymerisation

1. Addition Polymerisation: [Chain Growth]

The self addition of monomers to form a large molecule without elimination of any by product is known as 'Addition Polymerisation'. As no by-product is formed the molecular weight of polymer is sum of molecular weight of monomers.

Addition Polymerisation can be carried out by two mechanisms.

i) Free radical mechanism
ii) Ionic mechanism
iii) Coordination mechanism

i) Free Radical Mechanism

The initiation of reaction is brought about by the free radicals produced by the initiator which undergo the homolytic fission in the presence of light (or) heat.

Step-1:

1. Chain Initiation

Organic peroxides undergo homolytic fission.

$$R - \overset{\overset{O}{\|}}{C} - O + O - \overset{\overset{O}{\|}}{C} - R \overset{\triangle}{\rightarrow} 2\left[R - \overset{\overset{O}{\|}}{C} - O\right] \dot{\rightarrow} 2R + 2CO_2 \uparrow$$

2. Chain Propagation:

$$R + CH_2 = CH_2 \rightarrow R - CH_2 - \dot{C}H_2$$

$$R - CH_2 - \dot{C}H_2 + n(CH_2 = CH_2) \rightarrow R(CH_2CH_2)nC\dot{H}_2CH_2$$

3. Chain Termination:

When two free radicals combine, chain termination takes place.

$$2R(CH_2CH_2)_n\ \dot{C}H_2CH_2 \rightarrow R(CH_2CH_2)_n\ CH_2CH_2 : CH_2CH_2(CH_2CH_2)_nR$$

$$\rightarrow R(CH_2CH_2)_n\ CH_2CH_2\ CH_2CH_2(CH_2CH_2)_nR$$

3) Condensation Polymerisation: [Step growth polymerisation]

In step growth polymerisation, polymers are formed by the stepwise reaction between the functional groups of monomers.

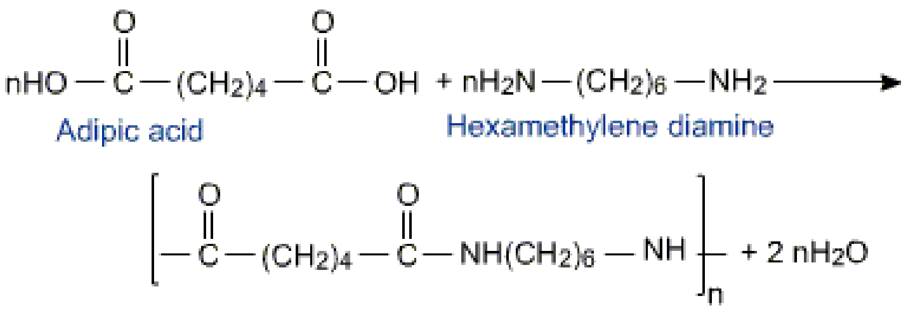
Main Features:

1) Monomers having two (or) more functional groups (-OH, -COOH, $-NH_2$) can undergo condensation.

2) Polymerisation proceeds through intermolecular condensation.

- Polymer chain growth is slow.
- Polymerisation is catalysed by acids and alkalies.
- Elemental composition of a polymer is different from that of its monomers.

Eg: Nylon 6, 6



Difference between Addition and Condensation Polymerisation

Addition Polymerisation	Condensation Polymerisation
1) Takes place in monomers having multiple bonds	1) It takes place in monomers having reactive functional group
2) Growth of chain is at one active chain	2) Chain growth occurs minimum at two active centers
3) No by product is formed	3) Generally a byproduct is formed
4) The molecular weight of polymer is sum of molecular weights of monomers.	4) Molecular weight of polymer is not sum of molecular weights of monomers.
Eg: Polyethylene, PVC, Polystyrene	Eg: Bakelite, Urea- Formaldehyde Resin.

Stereo Specific Polymersiation:

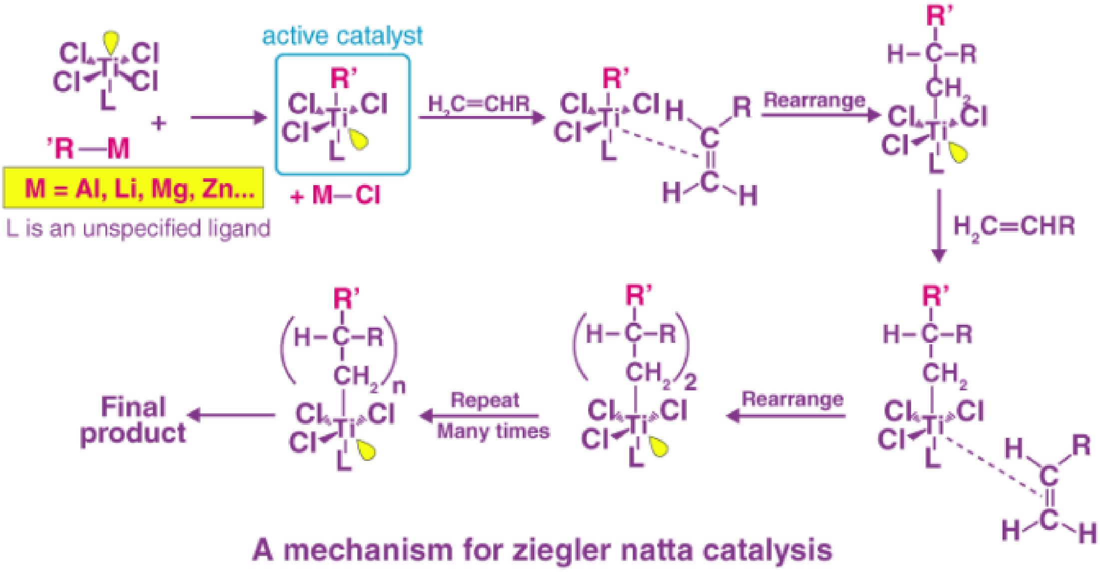
Coordination polymerisation is a form of polymerization that is catalysed by transition metal salts and complexes Known as Ziegler-Natta Catalyst.

Stereospecific polymerization is carried out as:

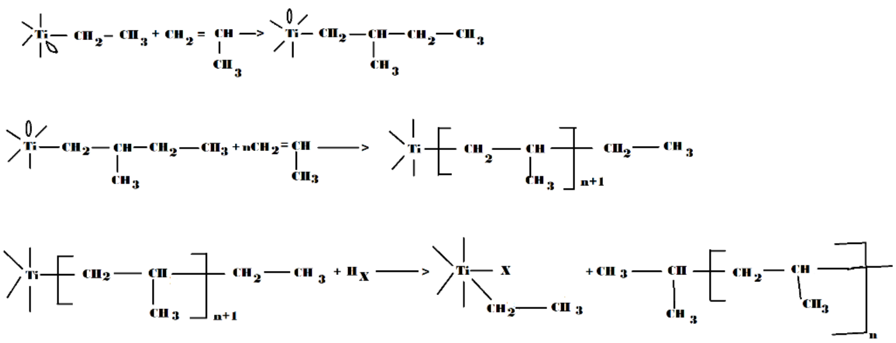
Initiation: In the initiation step, π – cloud of alkene overlaps with an empty orbital of titanium, then there is insertion of alkene molecule in between the Ti-C bond.

Propagation: As intra molecular rearrangement in carbon chain occurs again generate a vacant site on titanium, each time one monomer molecule can be added.

Termination: It can be done by the addition of molecules containing active hydrogen like hydrogenfluoride.



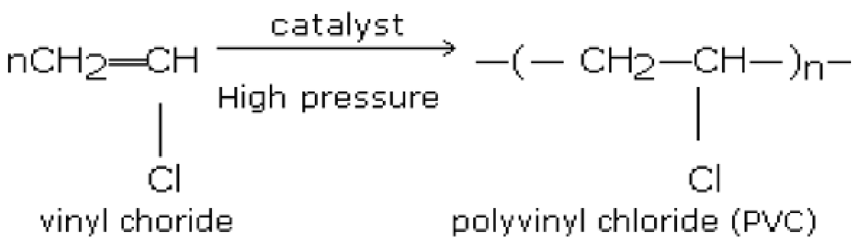
A mechanism for ziegler natta catalysis



Individual polymers

A. Polyvinyl Chloride: It is obtained by polymerizing vinyl chloride

$$CH \equiv CH + HCl \rightarrow CH_2 = \overset{\overset{Cl}{|}}{CH}$$



Properties

1) It is colourless, odourless, non-flammable, chemically inert powder.

2) It is resistant to light, atmospheric oxygen, inorganic acids and alkali.

3) It is soluble in hot ethyl chloride.

4) PVC posses a high softening point, greater stiffness and rigidity compared to polyethylene but brittle.

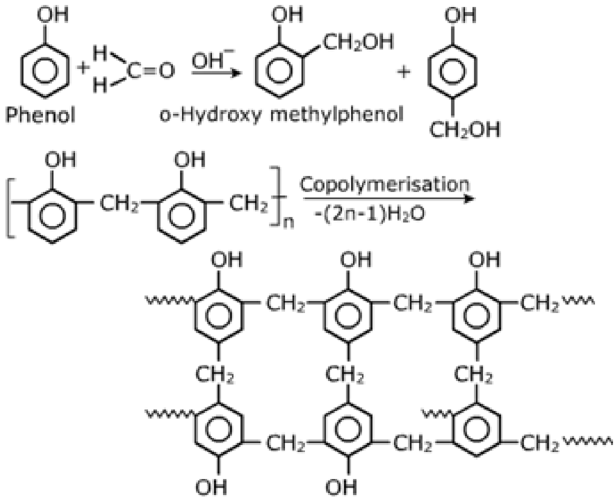
Uses:

1) Rigid PVC is used for making tyres of cycles, motor cycles and mud guards, refrigerator components tank linings of acids, alkalies and safety helmet.

2) Plasticized PVC is used for packing continuous sheets, employed for packing, rain coats, table cloths, curtains, electric insulation, covering electric cables.

B. Bakelite:

It is prepared by condensing phenol with formaldehyde in presence of acidic or alkaline catalyst.



Novolac which on further heating in presence of Hexamethylene tetramine produces Bakelite.

Properties:

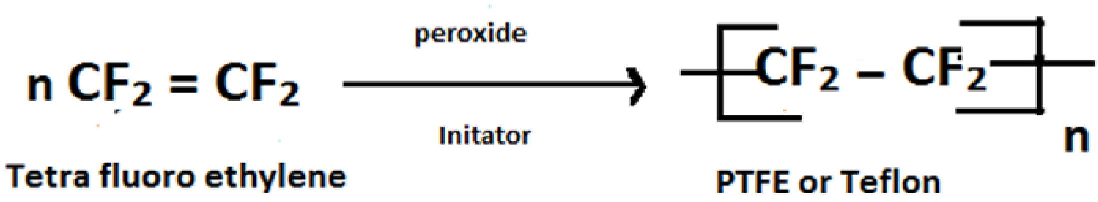
1) It is rigid, hard, scratch resistant, infusible, water resistant, insoluble solid.
2) Resistance to non-oxidizing acids (H_2SO_4), salts and many organic salts.
3) They are attacked by alkalies due to presence of free hydroxyl group.
4) They posses excellent electrical insulator.
5) It is a very good adhesive.

Applications:

1) For making electrical insulator parts like switches, switch boarders, etc.
2) For making moulded articles like telephone parts, cabinets for radio and television.
3) In paints and varnishes.
4) As hydrogen exchange resins in water softening
5) Used as adhesives for grinding wheels.

Poly tetra fluoro ethylene (PTFE) or Teflon :

Teflon is obtained by polymerization of tetra fluoro ethylene, under pressure in the presence of benzoyl peroxide as initiator.



Properties:

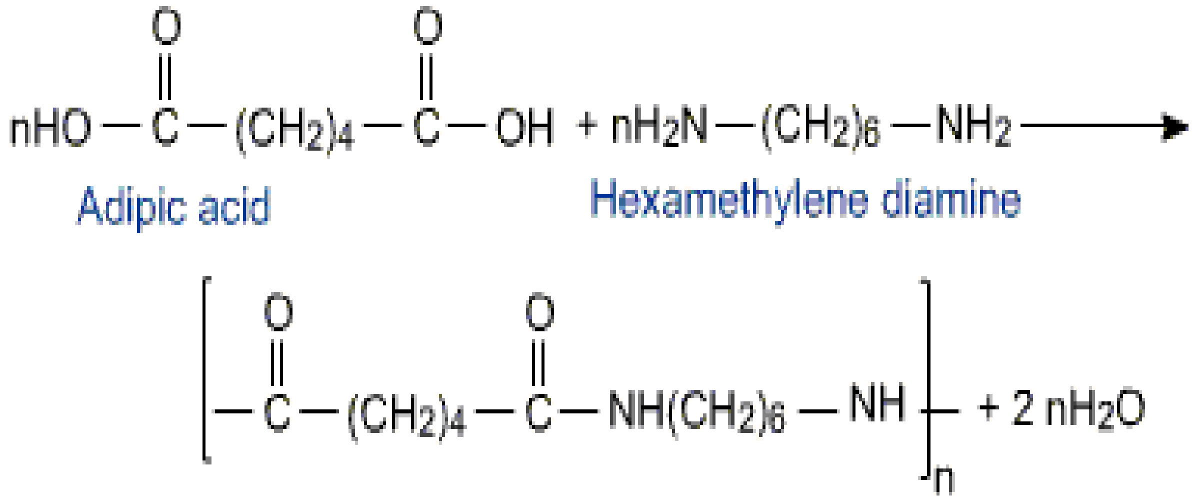
1. PTFE has extreme toughness, high softening point (327^0 C), high density (2.3 g/cm^2) and strength due to presence of high electronegative fluorine atoms.
2. It has excellent chemical resistance except towards alkali and hot fluorine.
3. PTFE has extreme toughness, high softening point (3270 C), high density (2.3 g/cm2) and strength due to presence of high electronegative fluorine atoms.
4. It has excellent chemical resistance except towards alkali and hot fluorine.

Uses :

1. It is used as non-sticky coating for pans.
2. It is used as insulating material for motors, generators, wires and cables.
3. It is used in non-lubricating bearings.
4. It is used in tank linings, gaskets, magnetic stirrer, coatings etc.

Nylon-6,6:

It is obtained by condensation polymerization of hexamethylene diamine and adipic acid.



1. They are translucent, whitish, horny, high melting point (160- 264 ^{0}C).

2. They are resistant to temperature and possess good abrasion resistance.

3.They are insoluble in common organic solvents (benzene, acetone) and soluble in phenol and formic acid.

4.They possess high physical strength and have high lubricating properties.

5.They are flexible and retain original shape after use.

Uses:

1. It is used for fibers which are used in making socks, under garments, dresses ,carpet etc.
2. They are used for making filaments, ropes, bristles of tooth brushes, films etc.
3. They are used in making gears, bearings, electrical mouldings.

Classification of Plastics (Resins):

Plastics are of two types.

1. Thermo Plastic resins are those which can be softened on heating and harden on cooling reversibly.

2. Thermosetting resin does not become soft on heating and they never melt once they set.

Thermoplastics	Thermosettings
1. They are formed by addition polymerisation only.	1. They are formed by condensation polymerisation.
2. They consists of long chain linear polymers with negligible cross links.	2. They have three dimensional network structures.
3. They soften on heating because secondary forces between the individual chains can break easily by heat, pressure, or both.	3. Their cross links and bonds retain their strength on heating and hence they do not soften on heating.
4. They can be softened, reshaped and reused.	4. They cannot be reshaped and reused.
5. They are usually soft, weak and less brittle.	5. They are usually hard strong and brittle.
6. They are soluble in some organic solvents	6. They are insoluble in almost all organic solvents.
Eg: Polyethylene, Polyvinyl Chloride, Cellulose, Cellulose Derivatives.	Eg: Bakelite, Polyester.

Individual Rubber:

1. Styrene Rubber or Buna-S:

Butadiene and styrene rubber is obtained from the monomers – styrene, Butadune.

$$n\,CH_2 = \underset{\underset{C_6H_5}{|}}{CH} + n\,CH_2 = CH - CH = CH_2$$

Styrene 1, 3 Butadeine

$$\downarrow$$

$$-[CH_2 - \underset{\underset{C_6H_5}{|}}{CH} - CH_2 - CH = CH - CH_2]-_n$$

Buna-S

Properties:

1) It posses high abrasion, resistance, high load bearing capacity and resilience.

2) It gets readily oxidized in presence of traces of ozone.

3) Swells in oils and organic solvents.

Applications:

1) Mainly used for the manufacture of motor tyres.

2) Floor tiles, shoe soles, gaskets etc.

3) Wires and cable insulation and adhesives.

2. Buna-N: (Nitrile Rubber)

It is a copolymer of Butadiene and Acrylonitrile

$$\underset{\text{1, 3 butadiene}}{H_2C = CH - CH = CH_2} + n\ \underset{\text{acryloritrile}}{H_2C = \underset{|\atop CN}{CH}}$$

$$\Big\downarrow \text{Polymerisation}$$

$$-[H_2C - CH = CH - CH_2 - CH_2 - \underset{|\atop CN}{CH}]-_n$$

Properties:

1) It possess excellent resistance to heat, sunlight, oils.

2) Less resistant to alkalis.

3) It is more resistant to ageing than natural rubber.

Uses:

Conveyor belts, high attitude aircraft components, tank linings, hoses, gaskets, printing rollers, adhesives, automobile parts etc.

STEEL

Steel is graded as a way of classification and is often categorized into four groups—Carbon, Alloy, Stainless, and Tool.

1. Carbon Steels only contain trace amounts of elements besides carbon and iron. This group is the most common, accounting for 90% of steel production. Carbon Steel is divided into three subgroups depending on the amount of carbon in the metal: Low Carbon Steels/Mild Steels (up to 0.3% carbon), Medium Carbon Steels (0.3–0.6% carbon), and High Carbon Steels (more than 0.6% carbon).

2. Alloy Steels contain alloying elements like nickel, copper, chromium, and/or aluminum. These additional elements are used to influence the metal's strength, ductility, corrosion resistance, and machinability.

3. Stainless Steels contain 10–20% chromium as their alloying element and are valued for their high corrosion resistance. These steels are commonly used in medical equipment, piping, cutting tools, and food processing equipment.

4. Tool Steels make excellent cutting and drilling equipment as they contain tungsten, molybdenum, cobalt, and vanadium to increase heat resistance and durability.

Applications of alloy steels:

Alloy steels are specifically produced for sophisticated engineering applications. An alloy steel finds its application in various areas:

1. Automotive: Transmission parts,Engine components,steering components,High tensile fasteners,Fuel injection pumps,bearings,axles,gears,crankshaft,transmission chains,springs,combustion chambers,axles,wheel hubs.

2. Engineering: Cutting tools, structural steel.

3. Industry: Mining machinery, Energy exploration machinery,food-processing units

4. Construction: Reinforcing bars.

5. Agriculture: Tractor parts.

6. Home: Utensils, decorative purposes.

7. Railways: Wagon axles, crankshafts, cushioning device components, steel liners, traction gears.

8. Military: Ordnance, gun barrels, projectiles , missile components.