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KAMARAJ COLLEGE



**UNIT – I**  
**POLYMER CHEMISTRY**

The term polymer can be defined as a macromolecule with high molecular mass arising due to the joining of a large number of simpler / smaller molecules (called monomers)

Polymerization is the union of two or more simpler molecules (effected under the influence of heat, pressure, catalyst etc.), resulting in the formation of new macromolecule with the characteristic C-C linkages.

The resultant macromolecule is called polymer and the original / parent simpler molecule is called monomer.

Polymerization is classified as (i) the mechanism of the process and (ii) practical aspects of the process. Based on the mechanism, polymerization is broadly classified into two types namely (1) Addition or Chain polymerization and (2) Condensation or Step polymerization. Based on practical considerations, polymerization is of types such as solution polymerization, emulsion polymerization, bulk polymerization etc.

**Thermoplastics vs. Thermosetting plastics**

Thermoplastics	Thermosetting polymers
1. Soften on heating	1. Do not soften on heating
2. Long chain linear	2. 3-D structure
3. By addition polymerisation	3. By condensation polymerisation
4. Can be reshaped and reused	4. Can not be reshaped
5. Soft weak and less brittle	5. Hard and strong
6. Soluble in org. solvents	6. Insoluble in org. solvents.
7. Reclaimed for wastes	7. Can not be reclaimed

**Polymerisation Techniques**

**Bulk polymerization:**

In this method, the monomer is taken in the liquid state and the initiator is dissolved in the monomer. The chain transfer reagent, if required, is also dissolved in the monomer. The function of chain transfer reagent is to control the molecular weight of the final polymer and result in a homogenous phase. The resultant mass is heated or exposed to radiations of particular wavelength for the initiation of the polymerization. As the polymerization reaction proceeds, the viscosity of the medium increases and hence the mixing becomes progressively difficult, which is the disadvantage. Another disadvantage of this process is the restricted diffusibility of the growing polymer chain, because of the higher viscosity of the medium.

**Emulsion polymerization:**



Here, the monomer is dispersed in aqueous phase as emulsion. The emulsion is stabilized by the addition of surfactants (surface active agents), protective colloids and some buffers. Anionic surfactants such as sodium or potassium aryl sulphonates or cationic surfactants such as alkyl amino hydro chlorides or alkyl ammonium halides or non-ionic surfactants such as alkyl glycosides or saccharic esters of higher fatty acids are used. They function by lowering the surface tension at the water-monomer interface and hence facilitate the emulsion of monomer in water. Due to their low solubility, surfactants are molecularly dispersed even at low concentration. At a particular concentration, the excess un-dissolved ones form as molecular aggregates, called micelles and an equilibrium is established between the dissolved surfactant molecules and the aggregated micelles. The highest concentration of surfactants wherein all the molecules are in the dispersed state and the concentration beyond which the micelle formation is possible is termed as critical micelle concentration (CMC)

#### **Solution polymerization:**

In this technique, the monomer and the free radical initiator are dissolved in a suitable solvent, along with the ionic co-ordination catalyst and the chain transfer reagent, if any. The selection of some inert solvent enables viscosity control and prevents heat transfer. The advantage of this method lies in its use when the polymer is used in solution form or when the polymer is insoluble in monomer or any other solvent or precipitates out as slurry and is amenable for easy isolation.

#### **Suspension polymerization:**

Water-insoluble monomers are polymerized by this technique. The monomer is suspended in water in the form of fine droplets, which are then stabilized against coalescence, using stabilizers, surfactants, protective colloids and by stirring. But the initiators are monomer-soluble. Each monomer droplet is isolated and is independent of other droplets and hence acts as an independent bulk polymerization nucleus (where the polymer chain growth starts and proceeds). The continuous aqueous phase separating the monomer droplets, acts as the efficient heat transfer medium and hence the exothermicity is controlled. The size of the monomer droplets depends upon the monomer/water ratio, type and concentration of stabilizers and the mode and speed of agitation.

#### **Ionic polymerization**

Ionic polymerization is a type of chain reaction or addition polymerization involving cations or the anion intermediates as the chain initiators. The main steps are of course, chain initiation, chain propagation and chain termination. The type of polymerization reaction initiated by the proton and the chain propagated by the carbonium ion is called cationic polymerization.

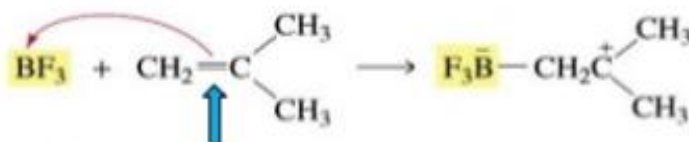
#### **Cationic polymerization**

The chain initiation of cationic polymerization involves the attack of the  $\pi$  electron pair of the monomer. A proton ( $H^+$ ) pulls the  $\pi$  electron pair towards it and the positive charge of the proton is transferred to the farther end of the monomer molecule, forming the carbonium ion or carbocation ( $C^+$ ), which acts as the cationic initiator. Here, a  $\sigma$  bond is formed between the proton, monomer unit and hence the polymeric chain further grows as a dimeric, trimetric, polymeric cation, which constitutes the chain propagation process. The chain termination may be effected by the collision between the growing polymeric cation and a counter-ion i.e. an



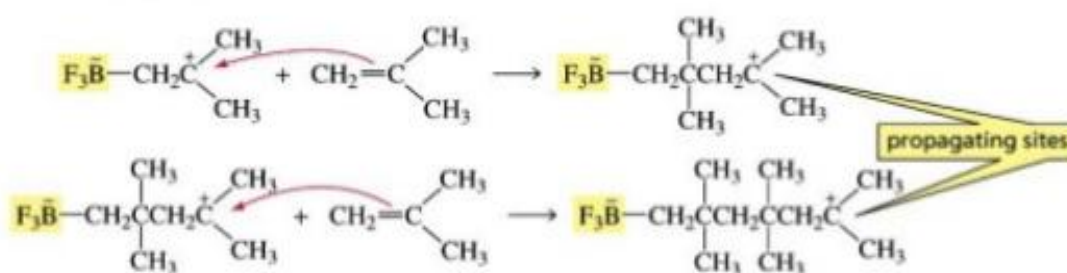
anion of other growing chain or a deliberately added anion. Lewis acids such as boron trifluoride (BF<sub>3</sub>), aluminium chloride (AlCl<sub>3</sub>), tin(IV)chloride (SnCl<sub>4</sub>), titanium(IV)chloride (TiCl<sub>4</sub>) etc. are used as the initiators / catalysts. Water is used as the cocatalyst. The catalyst and co-catalyst initially combine together forming the proton. The proton, in turn attacks the monomer, forming its cation which further acts as the chain carrier. The sequence of steps in this type of polymerization is represented below:

**chain-initiating step**

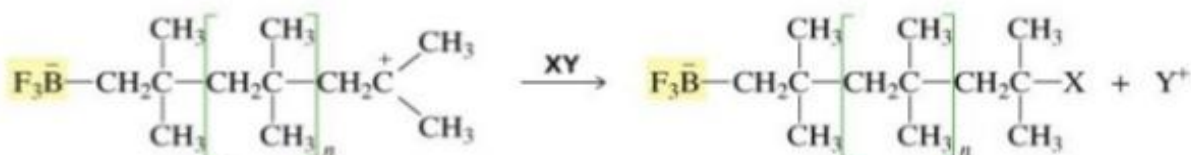
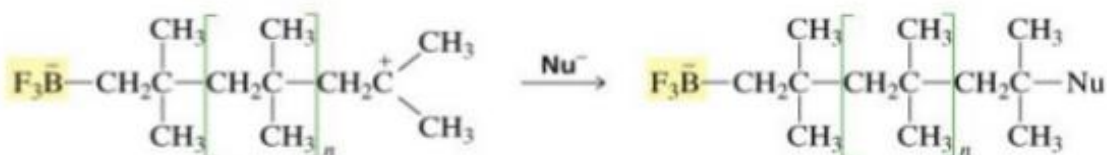
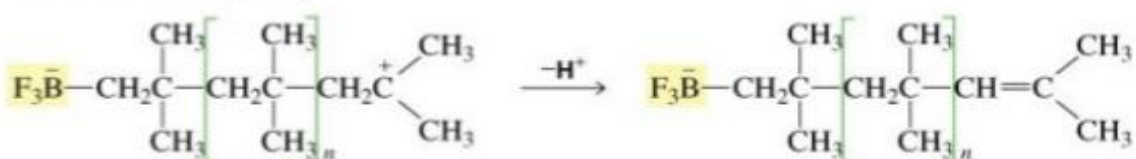


the alkene monomer  
reacts with an electrophile

**chain-propagating steps**



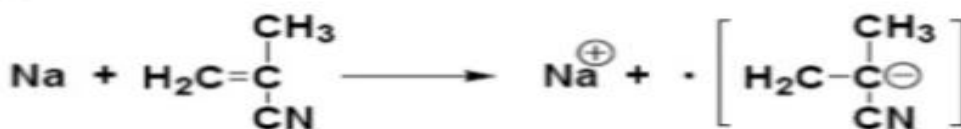
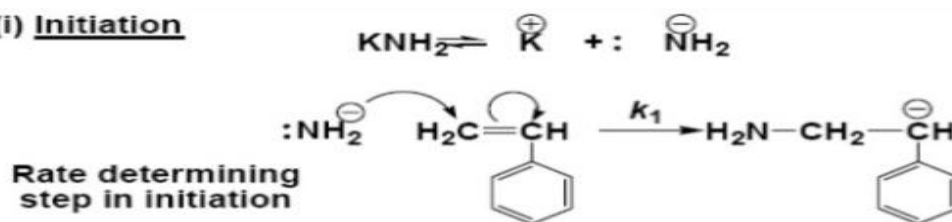
**chain-terminating steps**



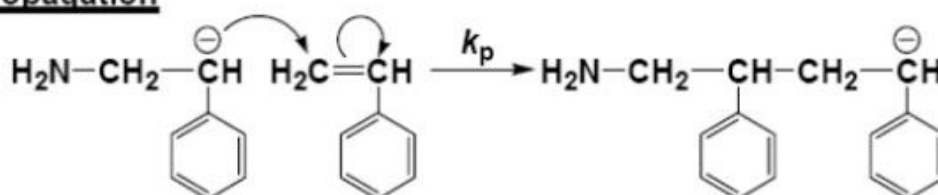


### Anionic polymerization

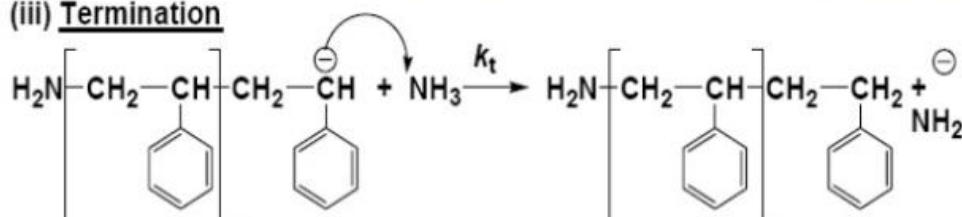
#### (i) Initiation



#### (ii) Propagation

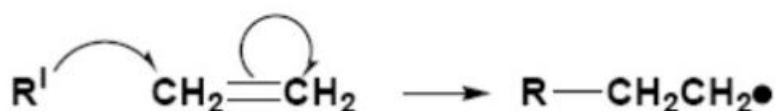


#### (iii) Termination

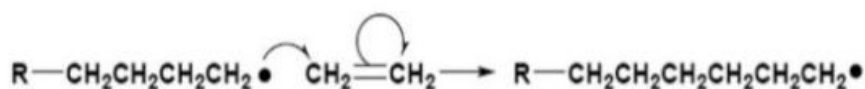
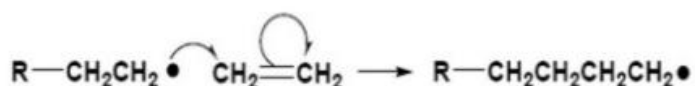


### Free Radical polymerization

#### step 1: Initiation

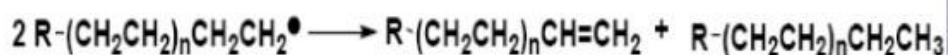
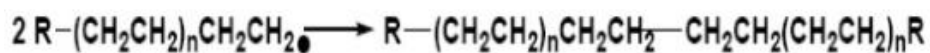


#### step 2: Propagation





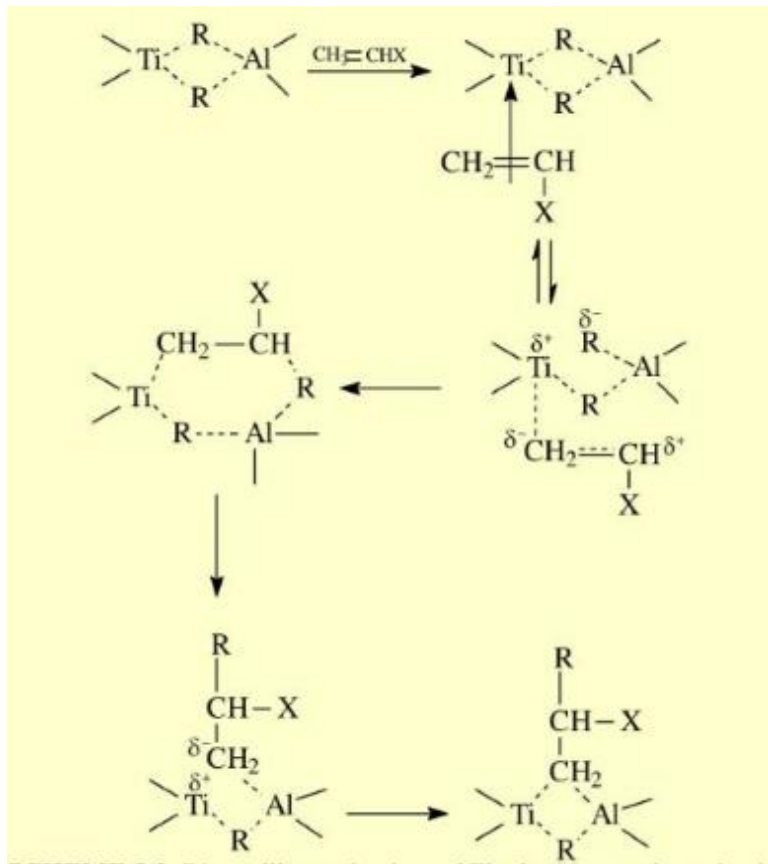
### step 3: Termination



	Addition polymerization	Condensation polymerization
1	Growth reaction adds repeating units one at a time to the polymeric chain.	Any two molecular species can react.
2	Number of monomer units increases steadily throughout the reaction.	Monomer disappears early in the reaction.
3	High polymer is formed at once.	Polymer molecular weight (degree of polymerization) rises steadily throughout the reaction.
4	Longer reaction times have very little effect on molecular weight but gives higher yields.	Longer reaction times are essential to obtain higher molecular weights i.e. reaction time influences molecular weight of the polymer.
5	The reaction mixture contains only monomers, high polymers and very small amount ( $10^{-8}$ ) of growing chains.	All types of molecular species are present at any stage.
6	E.g. polymerization of ethylene, styrene, vinyl chloride, propylene etc.	Polymerization to get nylon, PET, polycarbonate, polyurethane etc.

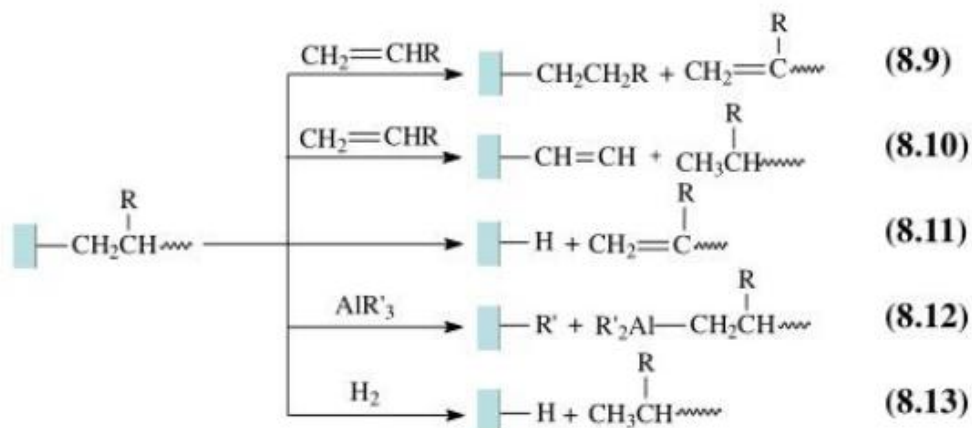


ZIEGLER NATA BI-METALLIC MECHANISM



■ Termination

- transfer to monomer (8.9 and 8.10)
- internal hydride transfer (8.11)
- transfer to cocatalyst or to an added alkylmetal compound (8.12)
- transfer to added hydrogen (8.13)





**UNIT - II**  
**CHARACTERISTICS OF POLYMERS**

Natural rubber is attacked by certain reactive chemicals which are present in the atmosphere must be considered

For the chemical degradation of these probably the most important are:

1. Oxygen – which leads to oxidative degradation
2. Ozone – which leads to Ozonolysis
3. Initiator residues (peroxides)

Other acids such as periodic acid and Sodium nitrite can attack the NR

**Oxidative Degradation**

Type of chemical degradation:

Oxidative degradation normally initiation by

1. Radiation e.g UV
2. Heat

**Basic Principle:**

Step - 1:

In NR, radical chain mechanism follow in which free radical in main backbone Chain is generated by some free radical produced by thermal decomposition of some additive

Step - 2:

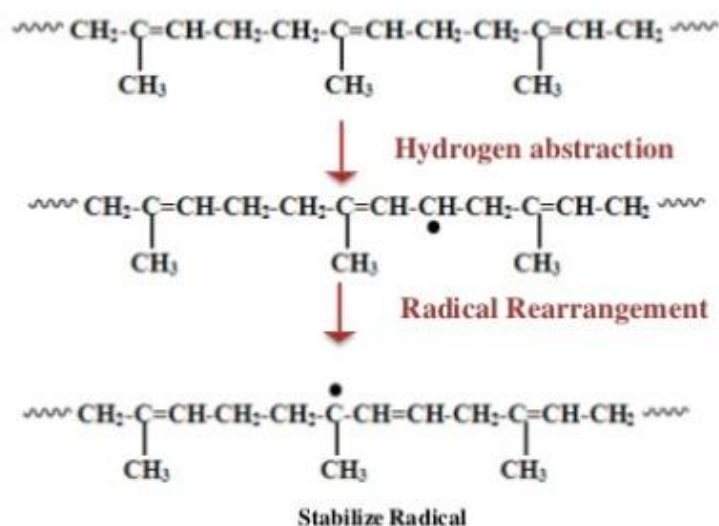
Then primarily attack of oxygen molecule leads to hydro peroxidation.

Step - 3:

Further they decomposes under heat, light results in chain degradation.  
Formation of – COOH, -CO-, -O-, and –OH occur.

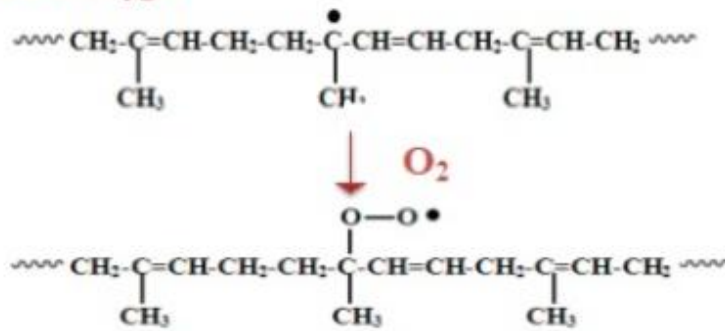
**Mechanism of oxidative degradation of Natural Rubber:**

**Step-1 : Abstraction of Hydrogen and rearrangement to stabilize radical.**

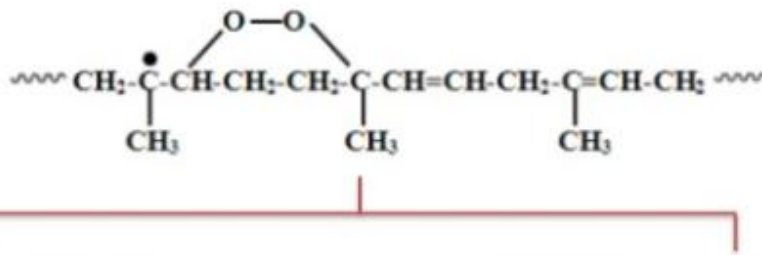




### Step-2 Attack of Oxygen



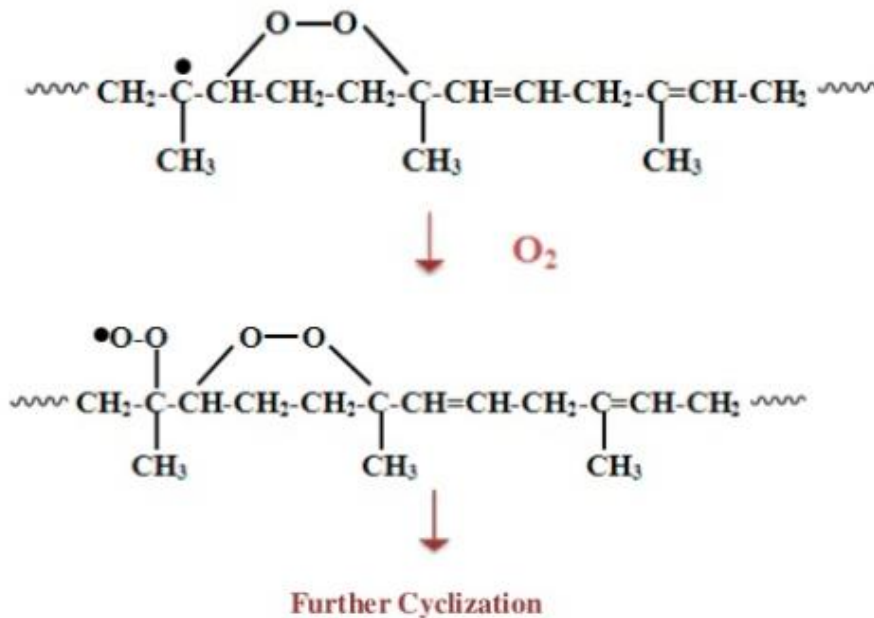
### Step-3 Cyclization



A) Further Cyclization

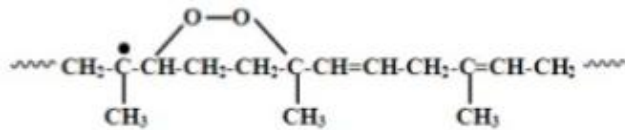
B) Hydro-peroxide Decomposition

### Possibility 1. Further Cyclization of previous product

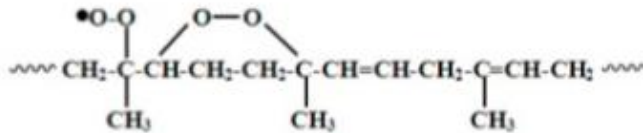
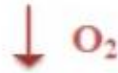




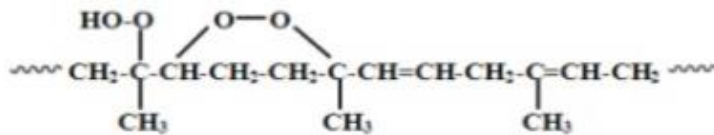
### Possibility 2. Hydro peroxide Decomposition



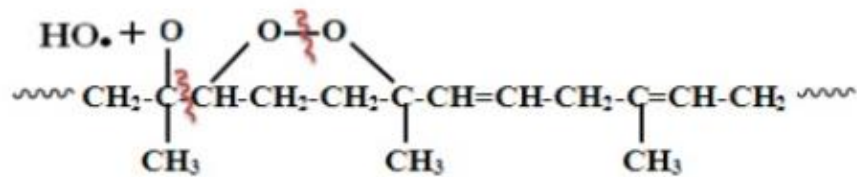
Sub Step-1. Attack of Oxygen



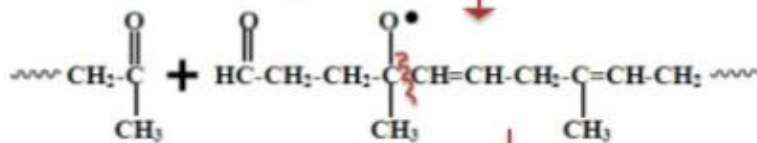
Sub Step-2. Per-oxy product



Sub Step-3. Hydro-peroxide Decomposition



Further Chain scission to produce stable products







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**UNIT – III**  
**TECHNIQUES OF POLYMERIZATION**

**Bulk polymerization**

Bulk polymerization or mass polymerization is carried out by adding a soluble initiator to pure monomer in liquid state. The initiator should dissolve in the monomer. The reaction is initiated by heating or exposing to radiation. As the reaction proceeds the mixture becomes more viscous. The reaction is exothermic and a wide range of molecular masses are produced.

**Advantages**

Bulk polymerization is carried out in the absence of any solvent or dispersant. Molecular weight distribution can be easily changed with the use of a chain transfer agent. The product obtained has high optical clarity.

**Disadvantages**

Heat transfer and mixing become difficult as the viscosity of reaction mass increases. The problem of heat transfer is compounded by the highly exothermic nature of free radical addition polymerization.

The polymerization is obtained with a broad molecular weight distribution due to the high viscosity and lack of good heat transfer.

Very low molecular weights are obtained.

Gel effect should be there for reducing the disadvantages of bulk polymerization, the process can be carried out in a solution. This is known as solution polymerization.

**Emulsion polymerization**

Emulsion polymerization is a type of radical polymerization that usually starts with an emulsion incorporating water, monomer, and surfactant. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified (with surfactants) in a continuous phase of water. Water-soluble polymers, such as certain polyvinyl alcohols or hydroxyethyl celluloses, can also be used to act as emulsifiers/stabilizers. The name “emulsion polymerization” is a misnomer that arises from a historical misconception. Rather than occurring in emulsion droplets, polymerization takes place in the latex particles that form spontaneously in the first few minutes of the process. These latex particles are typically 100 nm in size, and are made of many individual polymer chains. The particles are stopped from coagulating with each other because each particle is surrounded by the surfactant (‘soap’); the charge on the surfactant repels other particles electrostatically. When water-soluble polymers are used as stabilizers instead of soap, the repulsion between particles arises because these water-soluble polymers form a ‘hairy layer’ around a particle that repels other particles, because pushing particles together would involve compressing these chains.

**Advantages of emulsion polymerization include:**

High molecular weight polymers can be made at fast polymerization rates. By contrast, in bulk and solution free radical polymerization, there is a tradeoff between molecular weight and polymerization rate.

The continuous water phase is an excellent conductor of heat, enabling fast polymerization rates without loss of temperature control.



Since polymer molecules are contained within the particles, the viscosity of the reaction medium remains close to that of water and are not dependent on molecular weight.

The final product can be used as it is and does not generally need to be altered or processed.

#### **Disadvantages of emulsion polymerization include:**

Surfactants and other polymerization adjuvants remain in the polymer or are difficult to remove for dry (isolated) polymers, water removal is an energy-intensive process. Emulsion polymerizations are usually designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer, which cannot be used for condensation, ionic or Ziegler-Natta polymerization, although some exceptions are known.

#### **Solution Polymerization**

Solution polymerization is a method of industrial polymerization. In this procedure, a monomer is dissolved in a non-reactive solvent that contains a catalyst.

The reaction results in a polymer which is also soluble in the chosen solvent. Heat released by the reaction is absorbed by the solvent, and so the reaction rate is reduced. Moreover the viscosity of the reaction mixture is reduced, not allowing auto acceleration at high monomer concentrations. Once the maximum or desired conversion is reached, excess solvent has to be removed in order to obtain the pure polymer. Hence, solution polymerization is mainly used for applications where the presence of a solvent is desired anyway, as is the case for varnish and adhesives. It is not useful for the production of dry polymers because of the difficulty of complete solvent removal.

This process is used in the production of sodium polyacrylate, a super absorbent polymer used in disposable diapers.

Notable polymers produced using this method are polyacrylonitrile (PAN) and polyacrylic acid (PAA).

The process of solution polymerization offers a few advantages as well as one major disadvantage. The advantages include precise control of the chemical reaction, control of the resulting heat and viscosity, and control over auto acceleration of the process.

The disadvantage of the process is the difficulty involved in the removal of excess solvent from the finished polymer.

#### **Suspension Polymerization**

**Suspension polymerization** is used only in free radical type processes. The monomer is mechanically dispersed in a media, usually water. There are cases where an organic media is used in which neither the polymer nor the monomer are soluble in the organic media.

- styrene- a liquid
- vinyl chloride- a gas at room temperature

For **suspension polymerization**, there are two phases, water and organic, and the starting point may be 10 parts of the former, and 1 part of the latter. The initiator used can be water soluble or organic soluble [benzoyl peroxide, AIBN, or  $(\text{NH}_4)_2(\text{SxO}_4)_y$ .] Usually the initiator is organic soluble.

When using gases, pressure and containment concerns exist

1. There are two separate phases throughout the whole process.



2. The droplets must be kept far apart. This requires agitation: consistent, efficient, and controlled. A suspending agent can be used. Poly(vinyl alcohol) dissolved in the aqueous phase is a typical suspending agent.
3. The rate of suspension polymerization is similar to the rate of bulk polymerization, but the heat transfer is much better. For suspension polymerization, initiation, propagation, and termination take place inside the droplet.

Examples include the polymerization of methyl methacrylate, and vinyl chloride.

The solution polymerization of butadiene, isobutylene and isoprene require a pressure system.

The media to monomer ratio is 10:1. Is this wt/vol, wt/wt, or vol/vol? In an industrial setting it may be easier to combine chemical feedstocks on a per volume basis, asked Dr. Stoffer.

Particle size is affected by the following four factors:

1. stirring rate
2. ratio of reactants
3. suspension agent
4. temperature

#### **Limitations of suspension polymerization**

1. It only applies to free radical process.
2. Ionic catalysts don't work because they compete with water.
3. Agitation is critical because as the viscosity within the bead rises, the reaction rate increases suddenly (Tromsdorff effect.) This leads to a surge in heat generation which does not usually occur in solution or emulsion polymerization.

#### **Interfacial Polymerisation**

The characteristic for the interfacial polymerization occurs when the interfacial of two liquids and each of the liquid phase contains one reactant. Now, because reaction is very fast you saw the rate constant of the reaction is very high. So, the reaction is very fast, so you can do it at low temperature in room temperature and it is usually done at a temperature between 0 to 50 degree centigrade

#### **Processing Technologies**

##### **Introduction:**

All the processing stages between manufacture of the crude polymer and the final molding step are called the compounding processes. These include storage, transportation, metering, mixing, plastication and granulation. Sometimes additives may be added to the polymer mix to allow production on an industrial scale. Addition of plasticizers renders flexibility and ductility to rigid and brittle polymers. In a similar way, fillers can enable to enlarge the volume and also has influence upon the polymer properties.

##### **Processes:**

The various compounding processes are – 1. Mixing: Mixing allows obtaining a homogeneous mixture of polymer and additives. The additive is distributed uniformly



throughout the crude polymer, without any unnecessary stressing. Mixing can occur under the action of gravitational forces in a tumble mixer; or in a ribbon mixer, where materials are mixed in a horizontal barrel in a spiral manner. Such mixers are collectively known as cold mixers. Another class of mixers are the hot mixers, wherein the polymers are heated by contact with heated metal components. Such mixers are also known as high – speed or turbo mixers. This method is widely used in the plastic industry, especially in the compounding of poly vinyl chloride (PVC).

#### **Rolling and Kneading:**

Before processing, the plastics are compacted, melted, homogenized and modified with additives. These include rolling, in which the plastic is passed between two counterrotating, heated rolls wherein it is pressed into a thin layer. It is an open process in which additives can be added, and other scrap materials may be reintroduced. PVC is one plastic which extensively employs this process. Moreover, the material temperature can be controlled precisely and cleaning of the machine is easy.

#### **Pelletizing:**

It is the method of producing granules of equal size and shape. This enables the optimum feed behaviour on the processing equipment. Pelletizing can be done in hot or cold conditions. Using a pelletizing die, strands, ribbons or sheets are formed; and after solidification, they are chopped into the desired shapes. This is one procedure strictly followed in cold pelletizing. However, in hot pelletizing, the plasticated material is sent through a die, and a blade that rotates on the surface of the die plate chops the exiting strands. The melt is then cooled; and subsequently the water is removed.

#### **Shredding and Grinding:**

In thermoplastics processing, a variety of semi-finished and finished products are generated. These products, in order to be made suitable for processing, must be cut to produce a pellet form. A range of particle sizes is obtained in the process. Regranulating is achieved through cutting mills. The material is added through a feed system wherein a rotor revolves with high momentum. The system is further equipped with multiple cutting heads that operate against stationary cutting edges. The rotating cutting heads are divided and displaced with respect to each other in some other machines. As soon as the desired particle size is obtained, the material is ejected through a sieve, the pores of which determine the size of the particles. The housing and rotor may be equipped with water cooling apparatus to remove the excessive heat generated.

#### **Storage and Transportation:**

The storage and transportation of base polymers and intermediate products are achieved through automatic equipments. These equipments have an edge over the manually operated ones as they ensure improved working conditions, lower work place, lower contamination of materials and subsequent reduction losses. Moreover, accident hazards are also reduced. Large external silos are used for the storage of polymers, either in powder form, or in the pellet form. By incorporating vibrating frames, bunker cushions, slotted shelves or similar techniques as ventilation, the formation of granule bridges is avoided. The materials are transported via road or rail. Reserve materials and additives are transported in ships in bulk.



containers, drums or sacks. Pneumatic equipments are generally preferred for conveying powders and pellets. The conveyors used may be high pressure conveyors, medium pressure conveyors or low pressure conveyors. Fill level sensors help in controlling the transport interval. In order to meter liquids such as plasticizers or other additives for compounding, oscillating displacement pumps are used. Metering of solids can be done using gravimetric metering equipments or volumetric metering equipments

### Injection molding process

Injection molding process is a closed molding process. The process is suitable for both thermoplastic and thermosetting polymer based on short fiber reinforced composites. The schematic diagram of injection molding process is shown in figure 1. Fibers and polymer are either preblended or mixed manually and fed into the hopper. The mixture goes into the heated barrel where softening of the material takes place due to heating from the barrel. As the screw rotates, mixing of fiber and resin takes place and at the same time the blend is pushed towards the converging section of barrel where it is injected through nozzle into the mold cavity with high pressure. If natural fibers are used as reinforcement instead of synthetic fibers, sometimes, a separate hopper to feed the natural fibers into the barrel may be provided near the injection end of screw. Because, if natural fibers are mixed with resin and fed to the barrel, fibers have to travel the whole distance of the barrel and extensive fiber damage may take place due to high heating and shearing action for long time. Providing separate hopper, natural fibers will mix with soft resin and readily injected into the mold cavity.

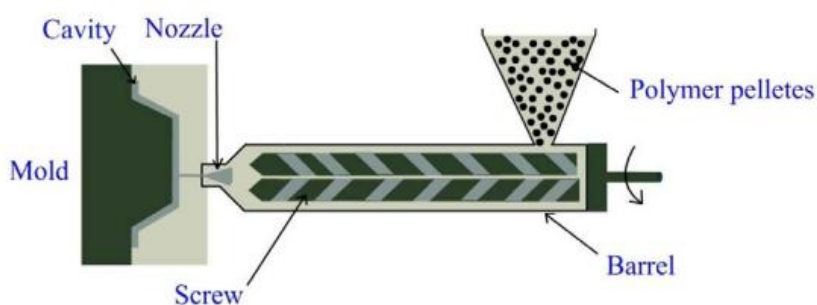


Figure 1 Injection molding process.

### Techniques for Pressureless Processing

The pressure less processing techniques are used for starting materials such as monomers, plastic solutions and dispersions that can flow and can be formed without application of external forces. The pressure less processing techniques include –

1. Casting
2. Dipping
3. Coating
4. Foaming

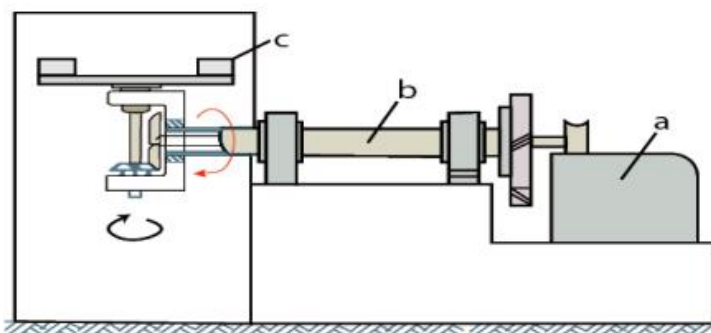
#### 1. Casting

By polymerizing monomers in molds, thick – walled articles, embeddings, sheets and blocks can be produced. These are preferentially made up of polystyrene, polyamides and polymethylmetacrylate. In order to avoid thermal stresses, adequate temperature regulation is required. The mold material choice is dependent upon the use and surface quality of the



moldings. Film casting is mainly used in the photographic industry for the manufacture of cellulose acetate films. In this method of casting, polymer solution, melts or dispersions are cast directly into a metal drum or a rotating belt ; and from a slot die into precipitation bath. Slush molding enables the production of hollow articles which are made from PVC pastes. These are made using two part metal molds, which are heated and filled with the paste. The paste gels on the outermost edges forming a skin ; and subsequently the excess paste is poured off. The remaining layer is gelled in an oven and after cooling, a hollow mold is obtained.

Slush molding can be further modified into Rotational casting for the production of hollow articles, made from PVC. The only difference is that in rotational casting, the amount of PVC paste is metered to the mold, which makes the removal of excess paste and post gelation techniques redundant. The mold is rotated about two perpendicular axes, while heating, and this enables uniform wetting of the cavity surface. Rotational casting has the advantage of low investment cost over slush,molding. In the manufacture of thick-walled, symmetrical structures such as pipes and sockets, centrifugal casting may be used. A partially filled mold is rotated rapidly about an central axis. Centrifugal force press the material outward in the mold, and in the process, the material gets compacted.



a) Motor b) Drive Shaft c) Molds

### Polymer Processing under pressure

Sometimes the molding process is carried under high pressure in which the solid thermoplastic materials are melted, molded and cooled subsequently. Some of the commonly used techniques for processing under pressure are –

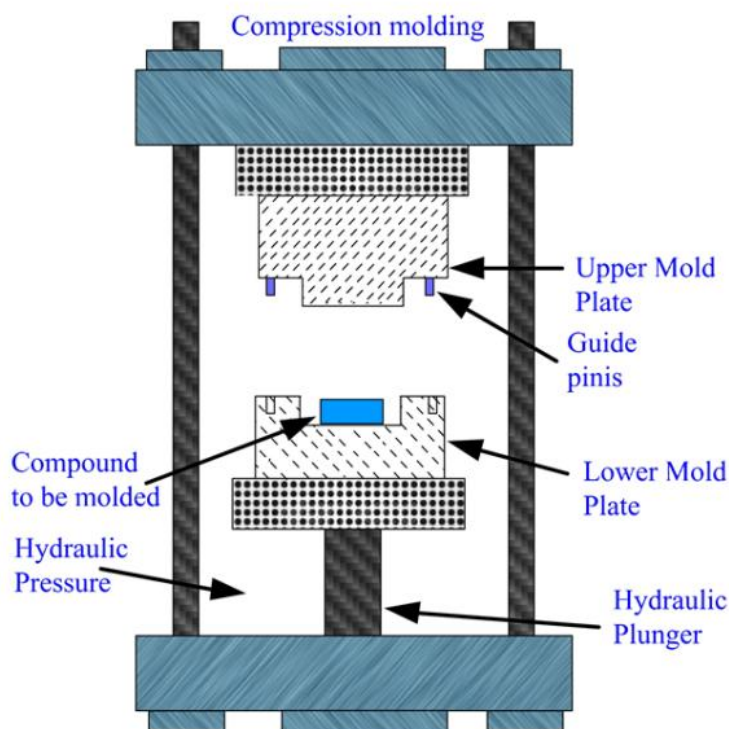
- Compression molding
- Rolling and Calendering
- Extrusion
- Blow Molding
- Injection Molding

#### a.Compression molding

Compression molding is a well-known technique to develop variety of composite products. It is a closed molding process with high pressure application. In this method, as shown in figure, two matched metal molds are used to fabricate composite product. In compression molder, base plate is stationary while upper plate is movable. Reinforcement and matrix are placed in the metallic mold and the whole assembly is kept in between the compression molder. Heat and pressure is applied as per the requirement of composite for a definite period of time. The material placed in between the molding plates flows due to



application of pressure and heat and acquires the shape of the mold cavity with high dimensional accuracy which depends upon mold design. Curing of the composite may be carried out either at room temperature or at some elevated temperature. After curing, mold is opened and composite product is removed for further processing. In principle, a compression molding machine is a kind of press which is oriented vertically with two molding halves (top and bottom halves). Generally, hydraulic mechanism is used for pressure application in compression molding. The controlling parameters in compression molding method to develop superior and desired properties of the composite are shown in figure. All the three dimensions of the model (pressure, temperature and time of application) are critical and have to be optimized effectively to achieve tailored composite product as every dimension of the model is equally important to other one. If applied pressure is not sufficient, it will lead to poor interfacial adhesion of fiber and matrix. If pressure is too high, it may cause fiber breakage, expulsion of enough resin from the composite system. If temperature is too high, properties of fibers and matrix may get changed. If temperature is low than desired, fibers may not get properly wetted due to high viscosity of polymers especially for thermoplastics. If time of application of these factors (pressure and temperature) is not sufficient (high or low), it may cause any of defects associated with insufficient pressure or temperature. The other manufacturing factors such as mold wall heating, closing rate of two matched plates of the plates and de-molding time also affect the production process.



Compression molding method



### Advantages of the Compression Molding Process

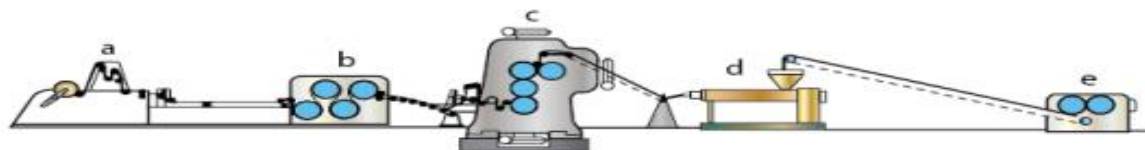
1. Production rate is high as the mold cycle time is in few minutes.
2. Good surface finish with different texture and styling can be achieved.
3. High part uniformity is achieved with compression molding process.
4. Good flexibility in part design is possible.
5. Extra features like inserts, bosses and attachment can be molded in during the processing.
6. Raw material wastage is minimum
7. Maintenance cost is low.
8. Residual stresses are absent or negligible in the molded component.
9. Twisting and shrinkage in product is reduced therefore dimensional accuracy is good.

### Disadvantages of compression molding process

1. Due to expensive machinery and parts, the initial capital investment associated with compression molding is high.
2. The process is suitable for high production volume. It is not economical for making a small number of parts or for prototyping applications.
3. It is a labour intensive process.
4. Sometimes secondary processing (trimming, machining) of product is required after compression molding.
5. Sometimes uneven parting lines are there.
6. There is limitation on mold depth.

### b.Rolling and Calendaring :

The rolling mills consist of two rolls that are used exclusively for the compounding of thermoplastics. The product that results from rolling is a sheet that can be granulated after cooling or fed in plasticized form directly into the processing equipment. PVC and rubber are processed using this process. When the rolls are more than two in number and the polymer is to be shaped using these rolls; then the machine is called a calendar. The number of rolls in a calendar can be up to seven; however, most commonly, four rolls are used. The rolls are made of polished cast iron, and are driven individually and heated. The heating medium is usually oil or water. The temperature and speed increases from one roll to the next. The roll mill must be able to withstand the extreme forces to which it is exposed, and hence, be made extremely rigid. The calendars are one of the most expensive types of processing equipments and are employed for the manufacture of a few special products like floor coverings and films made of plasticized PVC.



### Calendering Line

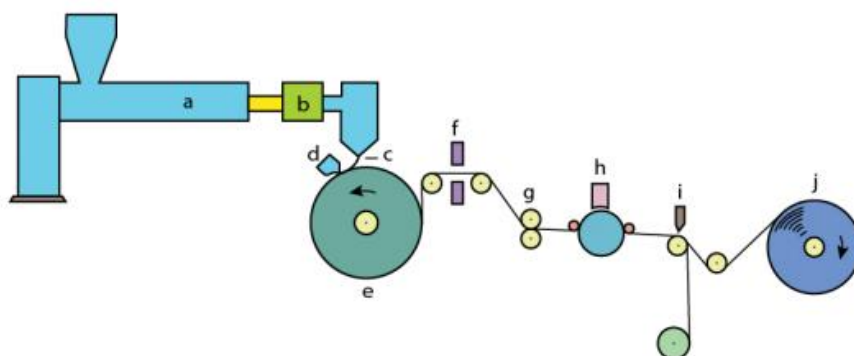
a)Winder and Edge Cutter b) Cooling Rolls c) Four-roll Calendar d)Extruder e)Mixing Roll Mill.



### c.Extrusion:

This method enables the attainment of a wide range of film thickness, and large scaling processing. Moreover, there is no necessity for expensive solvents in the recovery systems. A device known as extruder is used to melt the polymer, which is given the specific shape by a die. Later on, a cooling system is used to solidify it.

At the onset, the raw material is dried using heated air or vacuum, before it is melted in the extruder. The extruders may be single – screw extruders, or twin screw extruders, the single screw extruder being the most common. The melt is filtered depending upon the desired purity, and then the filtered raw materials are sent through the slot die. The width and thickness of the film are determined by the width of the die and the die gap respectively. The die gap can be further adjusted during production. The melt film emerging from the die is cast on to a highly polished roll. A vacuum device prevents the entrapment of air between the melt and the roller surface. The final film that is obtained is wound onto a roll after trimming off the edges. In a separate process, the film is cut into the designated width.



### d.BlowMolding

This is the most common method for manufacturing hollow articles from thermoplastics. The most simple products and articles that are made by blow molding are bottles, ventilation ducts, suit cases and fuel tanks for automobiles.

Two processes are generally followed for blow molding:

#### Extrusion Blow Molding:

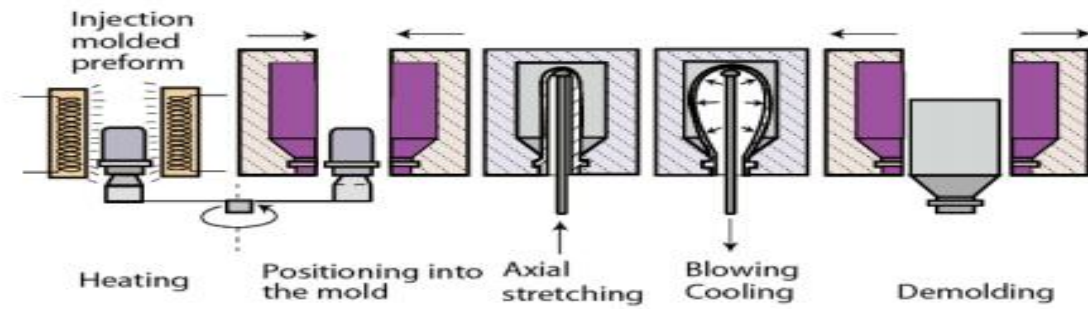
An extruded tube or parison is elongated to reach the required length. The parison is then enclosed by the mold, which is then cut by a blade. It is then conveyed to the blowing station. In the blowing station, a blow mandrel is inserted into the mold and the actual process is subsequently carried out. It is then cooled and the finished product is removed by opening the mold. The open mold is then transferred to the position below the extrusion die in order to receive a new parison. The process then continues.

#### Stretch Blow Molding:

This is a special form of blow molding in which the mechanical properties are considerably improved. A high degree of orientation is introduced in the plastics by drawing near the glass transition temperature or crystalline melting points. The molding material is drawn not only in the circumferential direction, but also in the machine direction. A mechanical ram is used for drawing in the longitudinal direction. The process is carried out under low



temperature with the application of high deformation forces. PVC, polypropylene and poly ethyl terephthalate are some of the materials used for this process.



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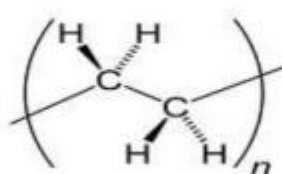
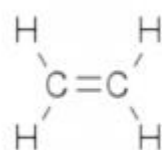


## UNIT - IV

### CHEMISTRY OF COMMERCIAL POLYMERS

#### **Polyethylene**

It is a polymer of ethylene, CH<sub>2</sub>-CH<sub>2</sub>, having the formula (-CH<sub>2</sub>-CH<sub>2</sub>-)<sub>n</sub>, and is produced at high pressures and temperatures in the presence of any one of several catalysts, depending on the desired properties for the finished product. Polyethylene is resistant to water, acids, alkalis, and most solvents. Its many applications include films or sheets for packaging, shower curtains, unbreakable bottles, pipes, pails, drinking glasses, and insulation for wire and cable. Polyethylene is a thermoplastic polymer consisting of long chains of the monomer ethylene (IUPAC name ethene). The ethene molecule (known almost universally by its common name ethylene) C<sub>2</sub>H<sub>4</sub> is CH<sub>2</sub>=CH<sub>2</sub>, Two CH<sub>2</sub> groups connected by a double bond, thus:



Polyethylene contains the chemical elements carbon and hydrogen. Polyethylene is created through polymerization of ethene. It can be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization.

#### **Classification:**

Polyethylene is classified into several different categories based mostly on its density and branching. 1. Ultra high molecular weight polyethylene (UHMWPE) 2. Ultra low molecular weight polyethylene (ULMWPE or PE-WAX) 3. High molecular weight polyethylene (HMWPE) 4. High density polyethylene (HDPE) 5. High density cross-linked polyethylene (HDXLPE) 6. Cross-linked polyethylene (PEX or XLPE) 7. Medium density polyethylene (MDPE) 8. Linear low density polyethylene (LLDPE) 9. Low density polyethylene (LDPE) 10. Very low density polyethylene (VLDPE) The most important polyethylene grades are HDPE, LLDPE and LDPE and here we will discuss two major classification, i.e., HDPE & LDPE.

#### **High-Density Polyethylene (HDPE)**

Polyethylene high-density (PEHD) is a polyethylene thermoplastic made from petroleum. It is defined by a density of greater or equal to 0.941 g/cm<sup>3</sup>. HDPE has a low degree of branching and thus stronger intermolecular forces and tensile strength. HDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts. HDPE is the strongest four times that of low density polyethylene, toughest, most chemical resistant, and least flexible of these four types of polyethylene. HDPE is used in products and packaging such as milk jugs, detergent bottles, margarine tubs, garbage containers and water pipes. One third of all toys are manufactured from HDPE.

Production of HDPE by addition polymerization with a supported metal oxide catalyst requires: o temperature ~300° C o 1 atmosphere pressure (101.3kPa) o aluminium-based metal oxide catalyst (metallocene catalyst) The catalyst can be used in a variety of operating modes including fixed-bed, moving-bed, fluid-bed or slurry processes. The ethene (ethylene) monomer is fed with a paraffin or cycloparaffin diluent (diluting agent). HDPE is now produced by catalytic



polymerisation of ethylene in either slurry (suspension), solution or gas phase reactors. Alpha-olefin comonomers, such as butene, hexene and octene, may be incorporated at low levels to modify the polymer's properties. Some processes can switch to linear low density polyethylene production ('swing' between HDPE and LLDPE). After polymerization the polymer (polythene) is recovered by cooling or by solvent evaporation.

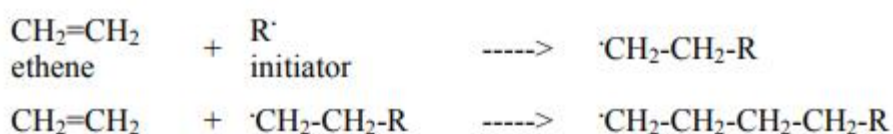
#### Properties:

Melting Point:-  $\sim 135^{\circ}\text{C}$ , Crystallinity:- Highly crystalline ( $>90\%$  crystalline). Contains less than 1 side chain per 200 carbon atoms in the main chain leading to long linear chains that result in regular packing and high crystallinity. Flexibility:- More rigid than LDPE due to higher crystallinity. Strength:- Strong as a result of regular packing of polymer chains. Heat Resistance:- Useful above  $100-110^{\circ}\text{C}$ . Transparency:- Less transparent than LDPE because it is more crystalline. Density:-  $0.95-0.97\text{ g/cm}^3$  higher density than LDPE. Chemical Properties:- Chemically inert. Tensile elongation at rupture (%):- 653, Molecular weight:- 90,000, Tensile strength (MPa):- 12.4

#### Low-Density Polyethylene (LDPE)

LDPE is a thermoplastic made from petroleum. LDPE is defined by a density range of  $0.910 - 0.940\text{ g/cc}$ . This results in a lower tensile strength and increased ductility. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap. It was the first grade of polyethylene, produced in 1933 by Imperial Chemical Industries (ICI) using a high pressure process via free radical polymerization. Its manufacture employs the same method today

Production of LDPE by addition polymerization requires: a temperature range of  $100-300^{\circ}\text{C}$  or very high pressure  $1500-3000$  atmospheres and oxygen or an organic peroxide such as dibutyl peroxide, benzoyl peroxide or diethyl peroxide as initiator or heat to produce a free radical ( $\text{R}\cdot$ ). A free radical is formed when a covalent bond is broken and a bonding electron is left on each part of the broken molecule. Since the O-O covalent bond is weak, free radicals are easily formed from oxygen or peroxides. Benzene or chlorobenzene used as the solvent since both polymer (polythene) and monomer (ethene) dissolve in these compounds at the temperature and pressure used. Water or other liquids may be added to dissipate the heat of reaction as the polymerization reaction is highly exothermic.



Process continues to form polythene (polyethylene)  $[-\text{CH}_2-\text{CH}_2-]_n$



**Tensile strength (MPa):-** 26.5

**Crystallinity:-** Low crystallinity (50-60% crystalline). Main chain contains many side chains of 2-4 carbon atoms leading to irregular packing and low crystallinity (amorphous).

**Flexibility:-** More flexible than HDPE due to lower crystallinity.

**Strength:-** Not as strong as HDPE due to irregular packing of polymer chains.

**Heat Resistance:-** Retains toughness & pliability over a wide temperature range, but density drops off dramatically above room temperature.

**Transparency:-** Good transparency, since it is more amorphous (has non-crystalline regions) than HDPE.

**Density:-** 0.91-0.94 g/cm<sup>3</sup>, lower density than HDPE.

**Chemical Properties:-** Chemically inert. Insolvent at room temperature in most solvents. Good resistance to acids and alkalis. Exposure to light and oxygen results in loss of strength and loss of tear resistance.

**Tensile elongation at rupture (%):-** 906

### Low-density polyethylene

LDPE is prepared from gaseous ethylene under very high pressures (up to about 350 megapascals, or 50,000 pounds per square inch) and high temperatures (up to about 350 °C [660 °F]) in the presence of oxide initiators. These processes yield a polymer structure with both long and short branches. Because the branches prevent the polyethylene molecules from packing closely together in hard, stiff, crystalline arrangements, LDPE is a very flexible material. Its melting point is approximately 110 °C (230 °F). Principal uses are in packaging film, trash and grocery bags, agricultural mulch, wire and cable insulation, squeeze bottles, toys, and housewares.

### Linear low-density polyethylene

LLDPE is structurally similar to LDPE. It is made by copolymerizing ethylene with 1-butene and smaller amounts of 1-hexene and 1-octene, using Ziegler-Natta or metallocene catalysts. The resultant structure has a linear backbone, but it has short, uniform branches that, like the longer branches of LDPE, prevent the polymer chains from packing closely together. Overall, LLDPE has similar properties to LDPE and competes for the same markets. The main advantages of LLDPE are that the polymerization conditions are less energy-intensive and that the polymer's properties may be altered by varying the type and amount of its chemical ingredients.

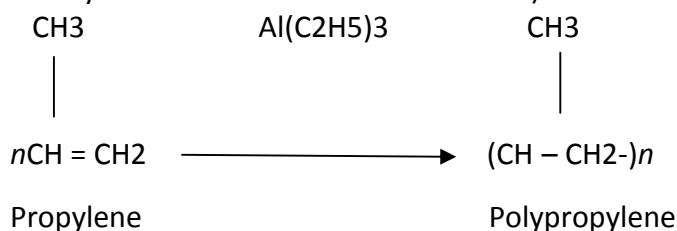
### High-density polyethylene

HDPE is manufactured at low temperatures and pressures, using Ziegler-Natta and metallocene catalysts or activated chromium oxide (known as a Phillips catalyst). The lack of branches in its structure allows the polymer chains to pack closely together, resulting in a dense, highly crystalline material of high strength and moderate stiffness. With a melting point more than 20 °C (36 °F) higher than LDPE, it can withstand repeated exposure to 120 °C (250 °F) so that it can be sterilized. Products include blow-molded bottles for milk and household cleaners; blow-extruded grocery bags, construction film, and agricultural mulch; and injection-molded pails, caps, appliance housings, and toys.



**Polypropylene:**

The monomer units are propylene molecules. It is generally manufactured by passing propylene through *n-hexane* (inert solvent) containing Ziegler-Natta catalyst (a mixture of triethylaluminium and titanium chloride).

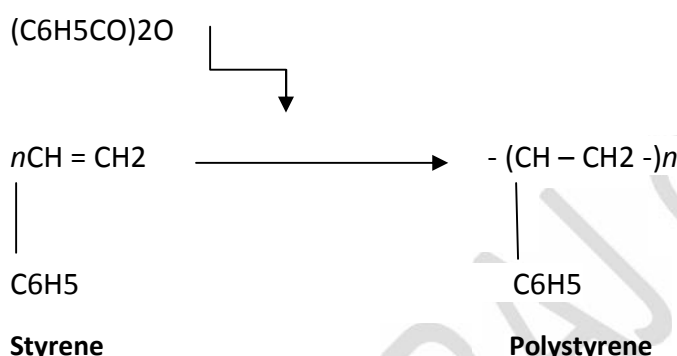


**Characteristics and uses**

It is harder, stronger and lighter than polyethene. It is used in: packing of textile material and food, liners of bags, gramophone records, ropes, carpet fibres etc.

**Polystyrene or Styron**

The monomer units are styrene molecules. It is prepared by free radical polymerisation of styrene in the presence of benzoyl peroxide.



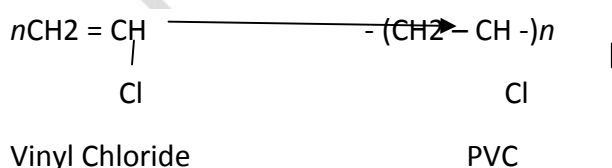
**Characteristics and uses**

It is a white thermoplastic material which is transparent and floats on water. It is used for making toys, combs, model construction kits, ceiling tiles, packing for delicate articles and lining material for refrigerators and TV cabinets. Polystyrene is sold under the name Styrofoam or Styron.

**Poly Vinyl Chloride (PVC)**

The monomer units are vinyl chloride molecules. It is prepared by heating vinyl chloride in an inert solvent in the presence of dibenzoyl peroxide.

Dibenzoyl peroxide



**Characteristics and uses**

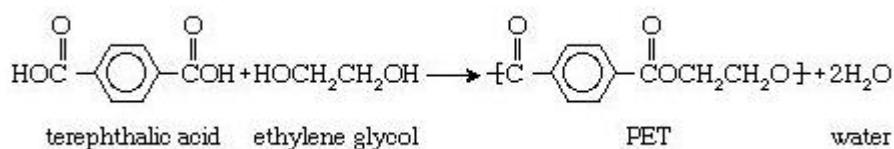
PVC is a hard horny material. However, it can be made to acquire any degree of pliability by the addition of a plasticizer. It is resistant to chemicals as well as heat. It is used for making: Rain coats, hand bags, toys, hoses, pipes, gramophone records, electrical insulations and floor covering.



### Polyethylene Terephthalate

Polyethylene terephthalate (PET or PETE), a strong, stiff synthetic fibre and resin, and a member of the polyester family of polymers. PET is spun into fibers for permanent-press fabrics, blow-molded into disposable beverage bottles, and extruded into photographic film and magnetic recording tape.

PET is produced by the polymerization of ethylene glycol and terephthalic acid. Ethylene glycol is a colourless liquid obtained from ethylene, and terephthalic acid is a crystalline solid obtained from xylene. When heated together under the influence of chemical catalysts, ethylene glycol and terephthalic acid produce PET in the form of a molten, viscous mass that can be spun directly to fibers or solidified for later processing as a plastic. In chemical terms, ethylene glycol is a diol, an alcohol with a molecular structure that contains two hydroxyl (OH) groups, and terephthalic acid is a dicarboxylic aromatic acid, an acid with a molecular structure that contains a large, six-sided carbon (or aromatic) ring and two carboxyl (CO<sub>2</sub>H) groups. Under the influence of heat and catalysts, the hydroxyl and carboxyl groups react to form ester (CO-O) groups, which serve as the chemical links joining multiple PET units together into long-chain polymers. Water is also produced as a by-product. The overall reaction can be represented as follows:



The presence of a large aromatic ring in the PET repeating units gives the polymer notable stiffness and strength, especially when the polymer chains are aligned with one another in an orderly arrangement by drawing (stretching).



**UNIT -V**  
**ADVANCES IN POLYMERS**

**Silicones**

Silicones are synthetic polymers with a silicon-oxygen backbone similar to that in silicon dioxide (silica), but with organic groups attached to the silicon atoms by C-Si bonds. The silicone chain exposes organic groups to the outside.

**Preparation**

Silicones are manufactured from pure silicon which has been obtained by the reduction of silicon dioxide (silica) in the form of sand with carbon at high temperatures:



The production of silicones from silicon takes place in three stages:

- Synthesis of chlorosilanes
- Hydrolysis of chlorosilanes
- Condensation polymerization

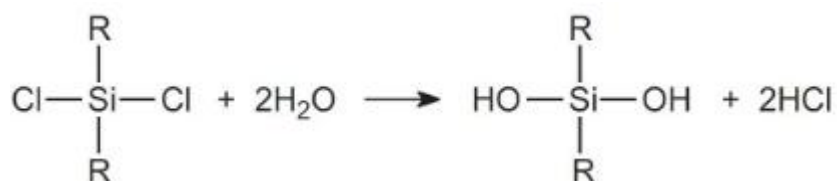
**a) Synthesis of chlorosilanes**

Silicon is first converted into chlorosilanes, e.g.  $\text{RSiCl}_3$ ,  $\text{R}_2\text{SiCl}_2$  and  $\text{R}_3\text{SiCl}$ , where R is an organic group. When chloromethane is passed through heated silicon at about 550 K under slight pressure and in the presence of a copper catalyst (often copper itself but other copper-containing materials can be used, for example, brass or copper(II) chloride) a volatile mixture of chlorosilanes distils over. For example:

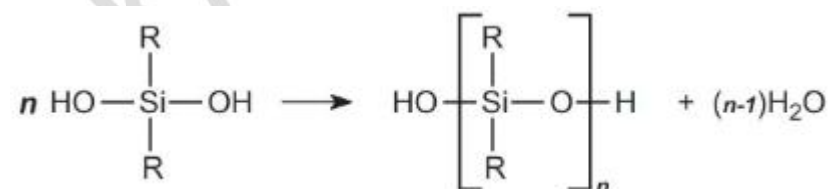


**b) Hydrolysis of chlorosilanes**

A dichlorosilane is hydrolyzed to a molecule with two hydroxyl groups:



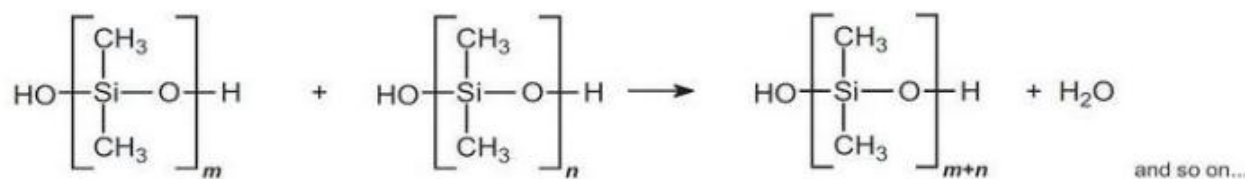
If R is a methyl group, the polymer is a poly(dimethylsiloxane).





### c) Condensation Polymerization

The oligomers condense rapidly in the presence of an acid catalyst to form long chain polymers:



These materials are silicone fluids.

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