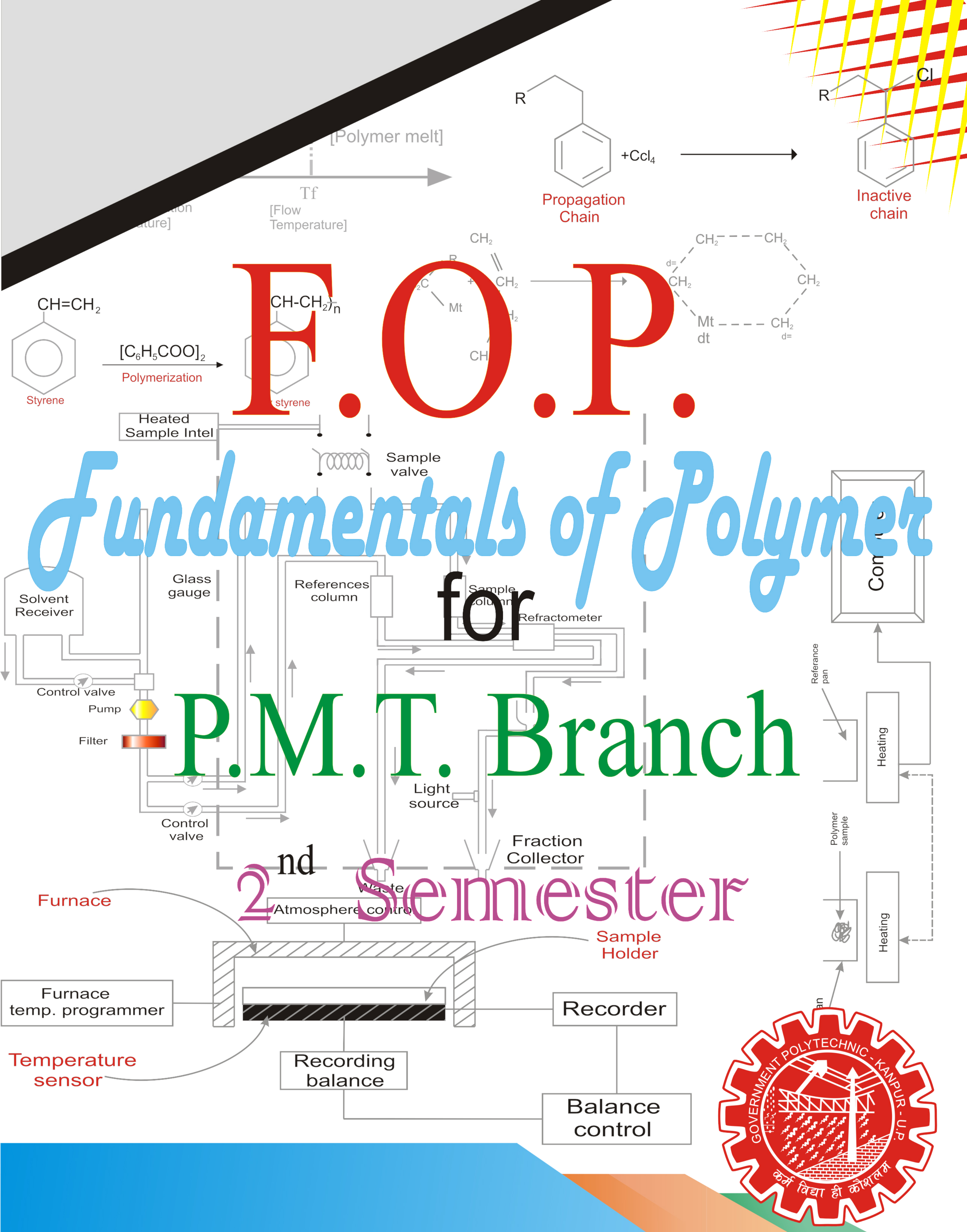
F.O.P.

Fundamentals of Polymer

for

P.M.T. Branch

2nd Semester



GOVERNMENT POLYTECHNIC - KANPUR - U.P.

कर्म विद्या ही कौशलम्

Unit -I Introduction to Polymer Science (24 Periods)

The science of large molecules - Definitions - Monomers & its requirement- Broad Classifications of Polymers - Types based on Structure- Processing and Applications - Molecular Force and Chemical Bonding in Polymers -Polymer structure - Homo Polymers and Copolymers - Geometric Isomerism - Tacticity - Nomenclature - Molecular Weight and Distribution and its effect on Properties and Processing of Polymers- Thermal Transition - Tg and Tm.

Unit -II Polymerization (24 Periods)

Chain growth Polymerization - Addition Polymerization - Reaction Mechanism - Free Radical Reaction - Ionic Reaction - Coordination Polymerization - Ring Opening Polymerization - Condensation Polymerization - Degree of Polymerization - Polymerization Techniques - Bulk, Solution, Suspension and Emulsion Polymerization - Co-polymerization.

Unit -III Polymer Structure and Properties (18 Periods)

Structure - Property Relationship - Molecular Weight and Poly Dispersity Index (PDI) - Effect of Polymerization on PDI - Polymer solutions and solubility - General Rules for Polymer solubility - solubility Parameters, Properties of Dilute solutions - Solid state properties - State of Polymer - Crystalline, Amorphous, Semi-crystalline, Liquid crystalline
- Requirement of Crystallinity - factors affecting crystallinity. Deformations in Polymer
- Mechanical properties - Stress - Strain behavior - Polymer Fracture and Toughness
- Cracking & Crazing - Thermal & Electrical properties.

Unit -IV Polymer Characterization (18 Periods)

Identification of Polymers - Simple Spectroscopic Methods - Molecular Weight Determination - Measuring Dilute Solution Viscosity - Gas Chromatography - Gel Permeation Chromatography - Melt Flow Characteristics - Thermal Analysis DSC and TGA
- Dynamic Mechanical Analysis.

SUGGESTED DISTRIBUTION OF MARKS

Topic no.	Time Allotted (Hrs)	Marks Allotted (%)
1.	24	30
2.	24	30
3.	18	20
4.	18	20
Total	84	100

UNIT -I Introduction to Polymer Science

Polymer:-

The polymer is high molecular weight compound form by the combination of small molecule of low molecular weight compound.

POLYMER

POLY [Many] — MER [unit]

Polymerization:-

The process by which monomer combine to form of polymer is known as polymerization .

POLYMERIZATION

ADDITION POLYMERIZATION — CONDENSATION POLYMERIZATION

Classification of Polymer

1.Based on Origin

- Natural Polymer
- Synthetic Polymer

2.Based on monomer

- Copolymer
- Homo polymer

3.Based on Structure

- Linear
- Branched
- Network

4.Thermal Behaviors

- Thermosetting
- Thermoplastic

Fun Fact – "Leo Hendrik Baekland" invented "Bakelite" [first plastic] in 1907

Natural polymer :-

Polymer which are isolated from natural origin is called Natural polymer. This polymer found in plant and animal.

Example- Protein, Cellulose, starch, natural rubber, casein etc.

Synthetic Polymer :-

Polymer are synthethyzed in lab from monomer called synthetic polymer.

Example – Poly Ethylene(PE),Poly Propylene(PP),Poly vinyl Chloride(PVC),Poly Carbonate(PC) etc.

Sami Synthetic Polymer:-

These polymer are obtained by chemical treatment of natural polymer to improve their physical properties are called Sami Synthetic Polymer.

Example- Cellulose acetate (Rayon), Cellulose Nitrate.

Homo polymer:-

Homo polymer is polymer that is made up of only one type of monomer unit.

Example-poly Ethylene (PE), PVC etc.

Copolymer:-

Co polymer is a polymer formed when two different types of monomer are linked in the same polymer chain.

Example- Nitrile Rubber, ABS etc.

Linear Polymer:-

The polymer made up of long continues chain without any branch called Linear Polymer.

Example- HDPE (High Density Poly Ethylene).

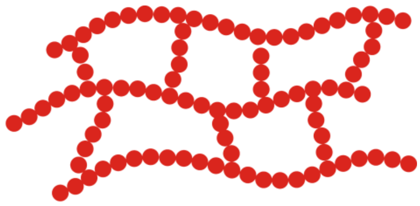
Branched Polymer:-

The Polymer Chain contain linear polymer having some branches called Branch polymer. They have low tesile strength low density and lower melting point.

Example- LDPE (Low Density Poly Ethylene).

Cross Linked/Network Polymer:-

These are usually formed by Bi-functional & Tri-functional monomer and contain strong covalent bond between various linear chain. They are hard and rigid.



Thermoplastic Polymer:-

Thermoplastic Polymer are resins that repeatedly soften when heating and harden when cooled.

Example- Poly propylene , poly vinyl chloride , poly ethylene etc.

They are usually formed by addition and condensation polymerization.

Thermosetting Polymer:-

Thermosets are resins that undergo reaction during processing to become permanently insoluble and infusible due to they formed three-dimensional cross linked network structure when heat is applied.

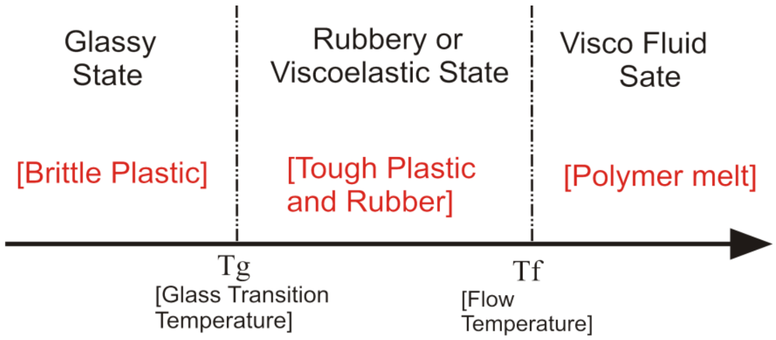
Example : Phenolic Resin, Polyester resin, Epoxy resin etc.

Difference between Thermoplastic and Thermosetting polymer.

Thermoplastic	Thermosetting
They are usually formed by addition and condensation polymerization.	They are usually formed by condensation polymerization.
They consist of long chain linear polymer with negligible cross links.	They have three dimensional network structure.
They soften on heating readily, because secondary forces between the individual chain can break easily by heat or pressure or both.	They cross link and bonds retain their strength on heating and hence they do not soften on heating.
By reheating to a suitable to a suitable temperature, they can be softening, reshaped and thus reused.	They retain their shape and structure, even on heating hence , they cannot be reshaped and reused.
They are usually soft, weak and less brittle.	They are usually hard, strong and more brittle.
These can be reclaimed from waste.	They cannot reclaimed from waste.
They are usually soluble in some organic solvents.	Due to strong bonds and cross link they are insoluble in almost all organic solvent.
Example- Poly Ethylene , poly propylene etc.	**Example-** Phenolic resin, epoxy resin, Polyesters etc.

Glass Transition temperature (Tg):-

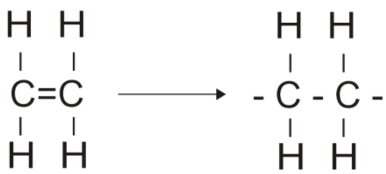
The temperature below, which a polymer is hard and above which it is soft, is called the Glass transition temperature (Tg). The hard, brittle state is known as the glassy state and the soft flexible state as rubbery or viscous state.



Functionality:-

Functionality of a monomer is defined as "the number of bonds that a monomers repeating unit forms in a polymer with other monomers".

In olefins the double bond can be considered as a side for two free valancies when double bond is broken, two single bond become available for combination.

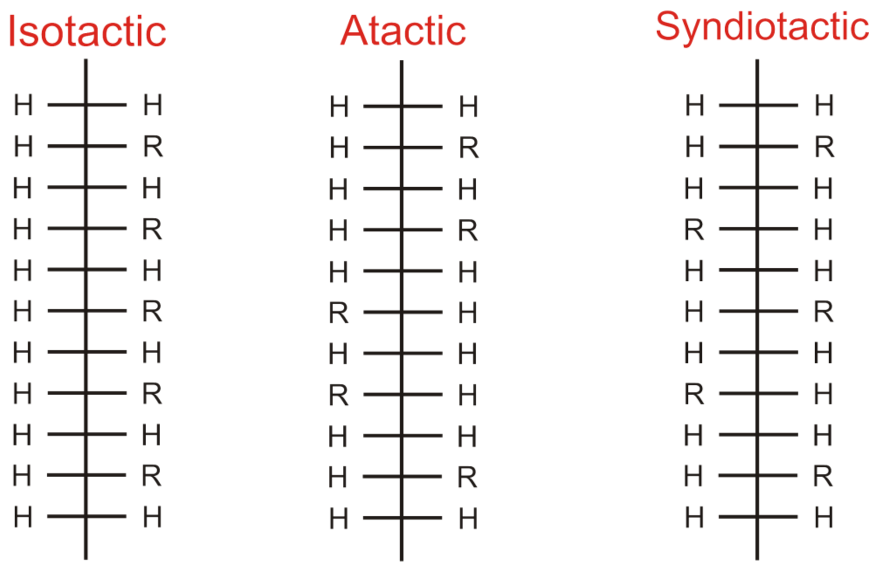


Tacticity:-

Tacticity is a property of polymer that refers to the monomer in which pendent groups are arranged along the hydrocarbon chain.

"The arrangement of stereochemical configuration in a polymer chain.

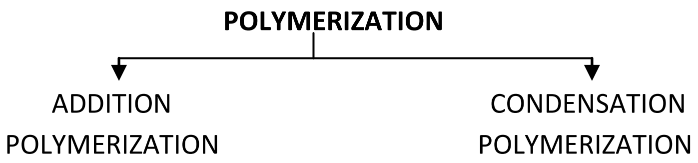
Example-



UNIT–II Polymerization

Polymerization:-

The process by which monomer combine to form of polymer is known as polymerization . They are two method of Polymerization.

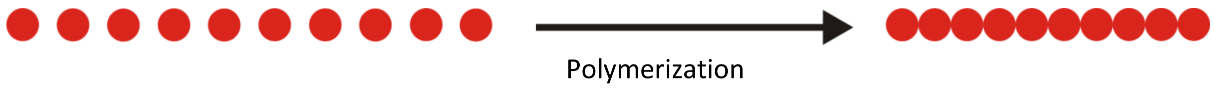


Addition Polymerization:-

When the monomer molecules just add in the form of polymer without the loss of any other atoms.

The process is called the Addition polymerization.

The molecular weight of polymer is roughly equal to that of all the molecule ,which combine to form the polymer.



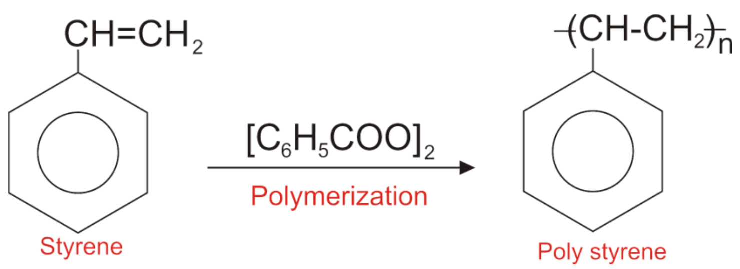
Example:- Poly ethylene (PE) , Poly propylene (PP) etc.

Reaction Mechanism:-

The sequence of elementary steps by which a chemical reaction occurs.

Free radical Polymerization:-

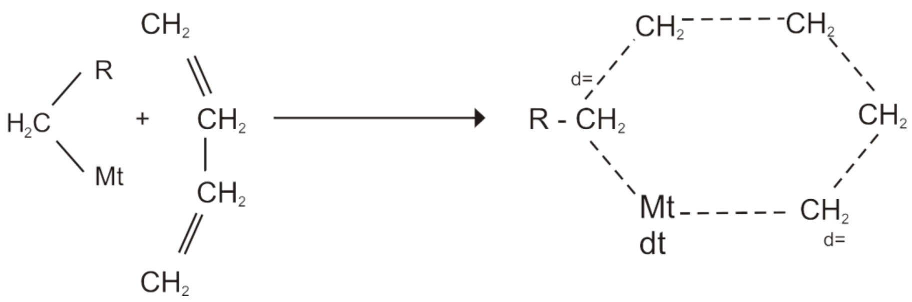
Free radical; polymerization is a method of polymerization by which a polymer form by the successive addition of free radical building blocks.



Co-ordination Polymerization:-

Co-ordination or stereo specific polymerization involves directing the monomer in their approach to the growing polymer chain.

Example- Special Ziegler-Natta catalysts are used in the polymerization process.



Condensation polymerization:-

When the monomer combine with elimination of any single molecule like water etc. the process is called condensation polymerization.

Example:- Poly Carbonate(PC) , Nylon , Poly ethylene terepthelate(PET)etc.

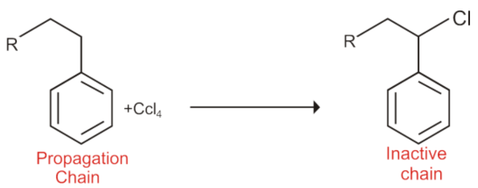
D.P. [Degree of Polymerization:-

The number of repeating unit present in it call degree of polymerization.

Chain Growth Polymerization:-

In chain growth polymerization "The molecules of monomer are added to form a large chain".

Monomer added may be, same type or different. Generally, alkenes, alkedienes and their derivatives are used.



Polymerization Techniques:-

- Bulk Polymerization
- Solution Polymerization
- Suspension Polymerization
- Emulsion Polymerization

Bulk Polymerization:-

- Carried out by adding a soluble initiator to pure monomer in liquid state.
- If necessary the chain transfer agent can be used.
- Initiating by heating and exposing to radiation.
- **Example-** Styrene, PVC resin etc.

Advantages-

- The polymer obtained is pure
- The system is simple.
- Long casting may be prepared diseatly.
- Molecular weight distribution can be easily changed with the use of a chain transfer agent.
- The product obtained has high optical clarity.

Limitation-

- High exothermic.
- Heat transfer and mixing become difficult as the viscosity of reaction mass increases.
- The polymer obtained is with broad molecular weight distribution due to the high viscosity and lack of good heat transfer.
- Very low molecular weight are obtained.

Solution polymerization:-

Solvent+Monomer ⟶ Polymerization ⟶ Polymer+Solvent

- The monomer is dissolved in a suitable inert solvent.
- The free redical initiator is also dissolved in the solvent medium.
- Reducing the viscosity and promotes proper heat transfer.
- The polymer is used as such in the form of polymer solution.
- **Example-** production of Poly acylo nitrile (PAN), Poly vinyl alchol (PVOH) etc.

Advantages-

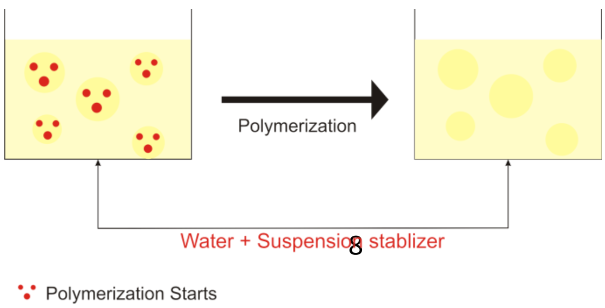
- Temperature control is easy.
- Viscosity build up is negligible.
- Solvent also facilitates the ease of removal of polymer form the seactor.

Limitations-

- Evaporate the solvent to get pure polymer.
- The method is costly since it uses costly solvents.
- Very low molecular weight are obtained.
- The purity of product is also not as high as that a bulk polymerization.

Suspension Polymerization:-

- Only water insoluble monomer can be polymerized.



- The monomer is suspended in the form of fine droplets in water.
- Each of these droplets act as tiny bulk reactor.
- The product is obtain as a spherical beads or pearl.
- Example- Poly vinyl Acetate, Polystyrene etc.

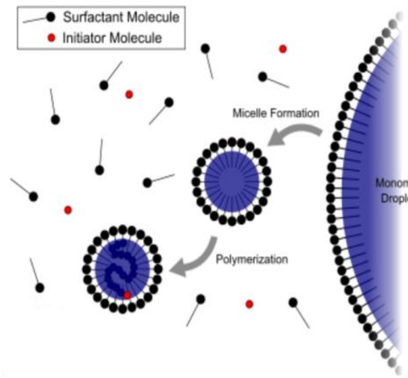
Advantages-

- The process is comparatively cheep as it involves only water instead of solvents.
- Viscosity increase in negligible.
- Agitation and temperature control is easy.
- Product insulation is easy sine the product is insoluble in water.

Limitation-

- The method can be adopted only for water insoluble monomer.
- It is difficult to control polymerization.
- The method cannot be used for tacky polymer.
- It is difficult to control polymer.
- Cannot run continuosly.

Emulsion Polymerization:-



- The Monomer is dispersed in an aqneous phase as tine droplets. Which are the stabilized [Emulsified] by surface active agents.
- A soluble water initiator are used.
- The surfactant will from micelles.
- The milky white disperision is called latex.
- Emulsion polymerization is a free redical polymerization in which a monomer or mixture of monomer is polymerized in an aqueous surfactant solution to form a latex.
- **Example-** synthetic Rubber-styrene butadiene , poly chlorphene etc.

Advantages-

- High molecular weight polymers.
- Fast polymerization rate.
- Easy heat control and easy agitation.
- Efficient heat transfer.

Limitations-

- Difficult separation and purification.
- Limited control over polymer size.
- Limited monomer selection.
- High energy consumption.

Co-Polymerization:-

The process of forming polymer from two or more different monomeric units is called Co-Polymerization .

$$A+B \longrightarrow -\!\!(A\text{-}B\text{-}A\text{-}B\text{-}A\text{-}B\text{-}A\text{-}B)\!\!-$$

Example- Buna-S, styrene etc.

Unit -III Polymer Structure and Properties

Molecular weight of Polymer:-

Molecular weight of a polymer is defined as sum of the atomic weight of each of the atoms in the molecules, which is presenting in the polymer.

Example- CH_4 = 12+1X4
= 16

CH_4-CH_4-CH_4 = 16+16+16
= 48

Poly Dispersity Index (PDI):-

The ratio of weight average molecular weight to number average of molecular weight is called Poly dispersity Index(PDI).

$$\textbf{PDI}= \frac{\sum Mw}{\sum Mn}$$

$$\therefore \sum \boldsymbol{Mw = Weight\ average\ molecular\ weight}$$
$$\therefore \sum \boldsymbol{Mn = Number\ average\ of\ molecular\ weight}$$

Relationship between PDI and molecular weight:-

Poly dispersity index [PDI] is used as a measure of the breadth of the molecular weight distribution.

Polymer Solution:-

Polymer solutions are "solutions containing dissolved polymers".
Polymer solution contains viscosity and elasticity both properties.

Polymer Solubility:-

Polymer solubility defines their ability to be dissolved in liquid solutions, through the aid of a solvent.

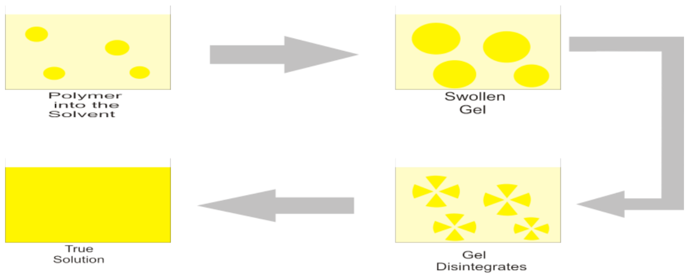
- Solubility well decrease with increasing molecular weight at const tempreture.
- Crystallinity decreases solubility.
- Cross linking eliminates solubility.

Solubility process of polymer:-

The dissolving process in polymer is very slow and occurs in two steps as

1. The solvent dissolves into the polymer to give a swollen gel. This process is slow because of cross linking and crystallity.
2. The gel gradually disintegrates into true solution. Agitation can speed up this process.

For very high molecular weight, the solution process takes day or weeks.



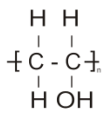
General Rules for Polymer solubility:-

1. Like dissolve like

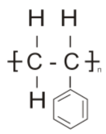
   Polar polymer   polar polymer

   Non polar polymer   Non polar polymer

   Example- Poly Vinyl Alcohol-

   Polystyrene-

2. Solubility will decrease with increasing molecular weight at const tempreture.
3. Crystallinity decreases solubility.
4. Cross link eliminates solubility.
5. The rate of solubility increases with short branches, allowing the solvent molecules to penetrate more easily.

Solubility parameters:-

The solubility parameters is a numerical value that indicates the relative solvency behavior of specific solvent.

A polymer dissolve in a given solvent when the free energy of mixing is negative.

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G = Free\ energy\ of\ mixing\ [< 0]$.

$\Delta H = Heat\ of\ mixing$.

$T = Tempature\ of\ mixing$.

$\Delta S = Entropy\ of\ mixing\ [> 0]$.

Properties of dilute solutions:-

- Lowering of the vapour pressure.
- Elevation of the boiling point.
- Depression of the freezing point.
- Osmotic pressure.

State of Polymer-

Crystalline polymer:-

The molecules are arranged in regular way called crystalline polymer.

Crystalline polymer are usually non transparent.

Example- Polyethylene, Polypropylene, Nylon etc.

Amorphous Polymer:-

An amorphous polymer is characterized by the completely random arrangement of molecule is called a Amorphous polymer.

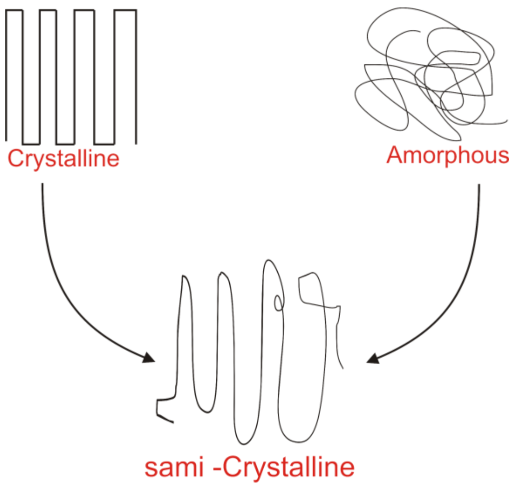
Amorphous polymer are usually transparent.

Example- Poly ethylene terepthelate(PET), Poly Carbonate(PC), PMMA etc.

Sami Crystalline Polymer:-

Sami crystalline polymer are a type of compound with a highly ordered molecular structure. With sharp melting point.

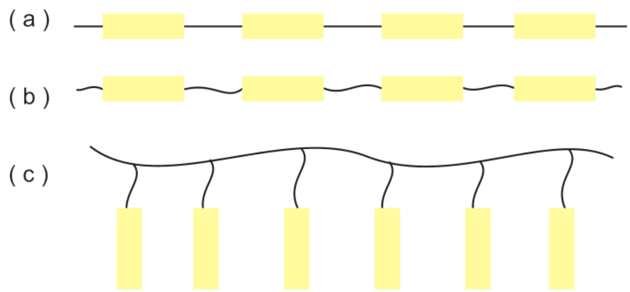
Sami Crystalline polymer are a combination of crystalline polymer and amorphous polymer.



Example- Poly propylene(PP), Poly ethylene(PE), Poly ethylene terepthelate(PET) etc.

Liquid Crystalline Polymer:-

Liquid Crystalline Polymer are a unique class of soft materials that combine liquid crystal and polymer characteristics.



Mechanical Properties of Polymer

Stress:-

Stress can be defined as a load per unit area of minimum original cross section of the test specimen at any moment.

$$\boldsymbol{Stress = \frac{Force}{Area}}$$

Strain:-

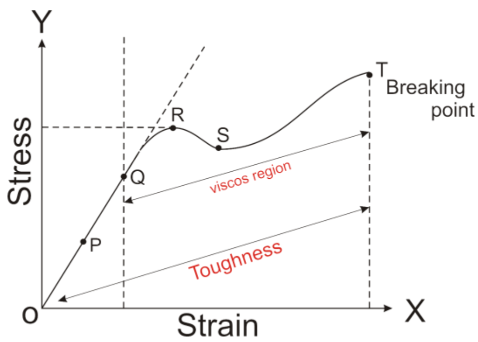
This is a ratio of elongation to the gauge length of the test specimen, the change in length per unit of original length on application of tensile load.

$$\boldsymbol{E = \frac{L_0 - L_1}{L_0} = \frac{\Delta L}{L_0}}$$

$L_1 = Final\ lenght.$
$L_0 = Initial\ lenght.$
$\Delta L = Change\ in\ length.$

Yield Point:-

The point on the stress strain curve at which an increase in strain occurs without an increase in stress.



Stress-Strain behavior:-

Any force applied on a strain creates a stress and strain in it.
Stress is measured by the force per unit area of a plane.
The tensile strain is expressed as elongation per unit length.

Polymer toughness:-

Polymer toughness, the ability of a polymer to exhibit plastic deformation and resistance to an impact load without failure, is a very desirable property of a material or product.

Fracture of Polymer:-

- The fracture strength of polymeric materiel are low relative to those of metals and ceramics.
- The mode of fracture in thermoset polymer is brittle.
- In a simple term during the fracture process crack from at resion where is a locale stress consentration.
- Thermoplastic polymer more ductile and brittle.

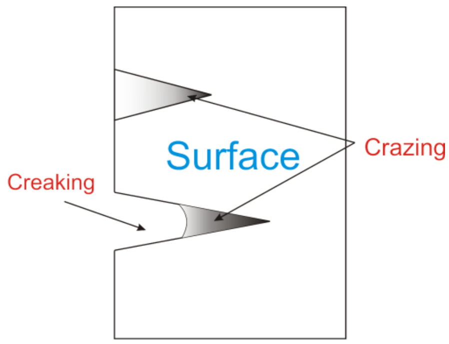
Example- at 4^0C PMMA (Poly methyl metha acrylate.] is brittle there at 60^0C it extremely ductile.

Cracking and Crazing

Cracking:-

The external damage of polymer is called cracking.

Cracking is easily defined by the observer visually and physical touch.



Crazing:-

The internal damage of polymer without a change of the surface texture is called crazing.

Crazes can be seen because light reflects off the surface of the gaps.

Thermal and Electrical property of Polymer

Thermal property polymer:-

When a polymer is hot, it's molecules have a lot of kinetic energy and move around very fast.

Electrical property of polymer:-

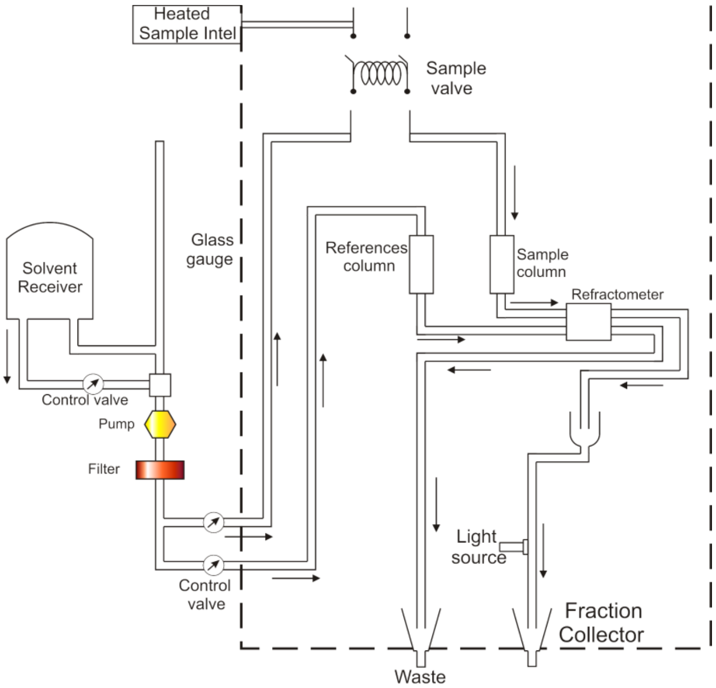
1. Polymer are usually electrical insulator.
2. The key electrical properties are-

Dielectric strength, Constant.

Unit -IV Polymer Characterization

Gel Permeation Chromatography(GPC):-

A gel permeation chromatograph(GPC) is used to separate the components of a sample by size.



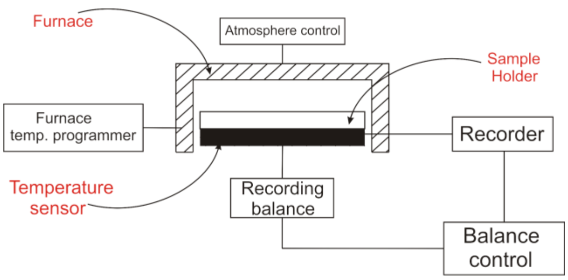
- This method is extrrimly effeceant it require 0.5 to 2 hours per sample and only a few melligram of sample.
- Chromatography column are packed with spiral or irregular shap.

Advantages:-

1. Shorts analysis time.
2. Well defined separation.
3. Narrow bands and good sensitivity.
4. There is no sample loss.
5. The flow rate can be set.

Thermo Gravimetric Analysis (TGA):-

"Thermo gravimetric analysis" of polymer is conducted to measure weight changes as a function of temperature and time.



Sample Holder:-

Shape size and material of the sample holder (crucible) made of Quartz, Platinum, ceramics, stain less steel.

Recording balance:-

Accuracy, sensitivity and capacity similar to analytical balancer

- Automatic weight adjustment.
- Rapid response to weight changes.

Furnace and furnace temp. controller:-

- Choise of the furnace heating element.
- Depends upon the temperature range being studied.

Temperature Sensor:-

Common method for measurement of temperature use of a thermocouple.

- For temp. upto1100^{0}C – Chromel or alumel thermocouple
- For temp. upto1750^{0}C – Thermocouples alloys of platinum or rhadium are used
- For higher temp. – Tungeston thermocouple

Application of TGA:-

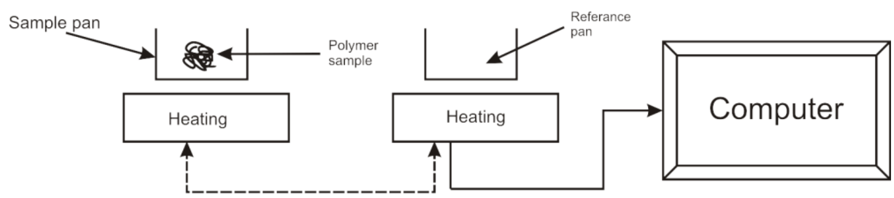
- It is an especially useful technique for the study of polymeric materials. Including thermoplastic and thermosetting.
- TGA is used to study of the kinetics of the reaction rate constant.

Differential scanning Calorimatry (DSC):-

DSC is a technique used to investigate the response of polymer to heating

OR

DSC is a thermal analysis apparatus measuring how physical properties of a sample change, along with temperature against time.



Equipment:-

1. **Furnace:-** To provide uniform controlled heating (cooling) of a specimen.
2. **Temperature Sensor :-** To provide an indication of the specimen temperature up to ±10 mk (0.01^{0}C)
3. **Differential Sensor :-** To detect heat flow difference between the specimen and reference pan equipment to 1 MW.
4. **Containers:-** (pan) that are inert to specimen and reference material.

Test Specimen :-

The test sample may be in the form of a powder, liquid or crystal of representative of material.

Dynamic Mechanical Analysis:-

Dynamic mechanical analysis is a thermal analysis technique used to measure changes in the viscoelastic response of a material as a function of temperature, time or deformation frequency by subjecting it to a small oscillating force.

Significance:-

- DMA determines elastic modulus, loss modulus, and damping coefficient as a function of temperature, frequency or time.
- DMA is also particularly useful for qualitatively characterizing the glass transition temperature and other sub Tg transition of polymer and composite materials.
- DMA also measures
  - The degree of phase separation in multicomponent systems,
  - Filler type, amount, pretreatment, and dispersion
  - Effects of certain processing treatment.