Unit-3

TECHNIQUES OF POLYMERIZATION AND POLYMER DEGRADATION

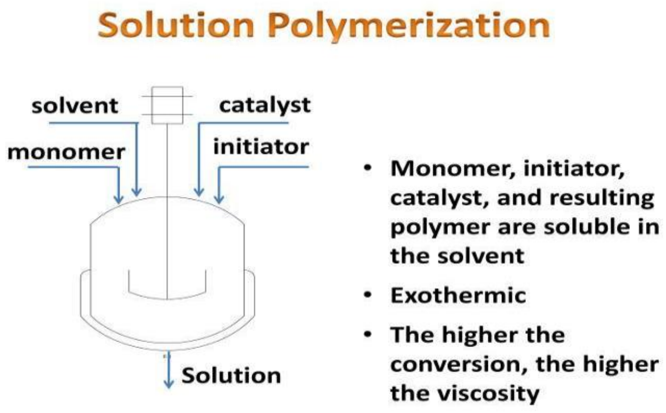
Bulk, Solution, Emulsion, Suspension, interfacial and gas phase polymerization.Types of Polymer Degradation, Thermal degradation, mechanical degradation,photodegradation, Photo stabilizers.

3.1**BULK POLYMERIZATION**

- It is the simplest method of polymerization.The monomer is taken in a flask as a liquid form and the initiator, chain transfer agents are dissolved in it.The flask is placed in a thermostat under constant agitation and heated.Monomer(liquid)+initiator (mixed with monomer) +chain transfer agent=polymer.The reaction is slow but becomes fast as the temperature rises. after a known period of time,the whole content is poured into a methanol(non-solvent) and the polymer is precipitated out.
- Example,POLYSTYRENE.
- **ADVANTAGES:**
- It is quite simple and requires simple equipment’s.
- Polymers are high purity obtained.
- As a monomer is solvent, excess monomer can be removed by evaporation.
- It is having high optical clarity.
- **Disadvantages:**
- During polymerization, viscosity of the medium increases. hence mixing and control of heat is difficult.
- Highly exothermic.
- **Applications:**
- The polymers obtained by this method are used in casting formulations.
- Low molecular weight polymers are obtained.
- It is used as adhesives, plasticizers and lubricant additives.

Solution polymerization

In solution polymerization, the monomer, initiator and the chain transfer agents are taken in a flask and dissolved in an inert solvent.The whole mixture is kept under constant agitation.After required time, the polymer produced is precipitated by pouring it in a suitable non-solvent.Monomer (dissolved in inert solvent) +initiator (DIS)+chain transfer agent (in solution) =polymer.The solvent helps to control heat and reduces viscosity built up. Eg: polyacrylic acid, polyisobytylene and polyacrylonitrile are prepared by this Method.



Solution Polymerization

- Monomer, initiator, catalyst, and resulting polymer are soluble in the solvent
- Exothermic
- The higher the conversion, the higher the viscosity

fig2.solution polymerization technique

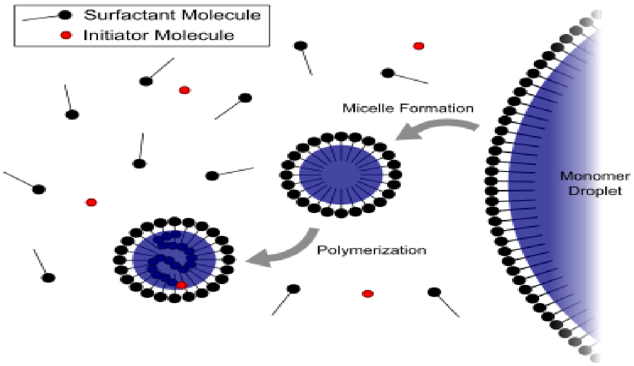
Advantages:

- Heat control is easy
- Viscosity built up is negligible.
- The mixture can be agitated easily.
- **Disadvantages:**
- The removal of last traces of solvent is difficult.
- This polymerization requires solvent recovery and recycling.
- It is difficult to get very high molecular weight polymer.
- The polymer formed must be isolated from the solution either by evaporation of the solvent or by precipitation in a non-solvent.
- **Applications:**
- Adhesives and coatings.

1. Emulsion polymerization

- Emulsion polymerization is used for water insoluble monomer and water-soluble initiator like potassium persulphate.The monomer is dispersed in a large amount of water and then emulsified by the addition of a soap.Then initiator is added. the whole content is taken in a flask and heated t a constant temperature with vigorous agitation in a thermostat with nitrogen atmosphere.After 4 to 6 hours, the pure polymer can be isolated from the emulsion by addition of deemulsifier like 3% solution of Aluminum tri sulphate.

Monomer+initiator+surfactant=polymer (emulsion in water).fig3.emulsion polymerization technique



Advantages:

- The rate of polymerization is high.
- Heat can be easily controlled and hence viscosity built it up.
- High molecular weight polymer can be obtained.
- **Disadvantages:**
- Polymer needs purification.
- It is very difficult to remove entrapped emulsifier and deemulsifier.
- It requires rapid agitation.
- **Applications:**
- It is used to water-based paints, adhesives, plastics.
- Manufacturing of butadiene and chloroprene.

4 Suspension polymerizations:

- Suspension polymerization is used only for water insoluble monomers. this polymerization reaction is carried out in heterogeneous system.At the end of polymerization, polymer is separated out as spherical beads or pearls. this method is also called pearl polymerization.The water insoluble monomer is suspended in water as tiny droplet and an initiator is dissolved in it by continueous agitation.The suspension is prevented from coagulation by using suspending agents like PVA, gelatin, methyl cellulose. Each droplet of the monomer contains dissolved initiator. the whole content is taken in a flask and heated at constant temperature with vigorous agitation in a thermostat with nitrogen atmosphere.After the end of 8 hours, pearl like polymers are obtained, which is filtered and washed by water.

Monomer (suspension in water) +initiator (dissolved in monomer) +suspending agent=polymer

Eg: polystyrene, polystyrene-divinyl benzene.

<u>Advantages:</u>

- Since water is used as a solvent, this method is more economical
- Products obtained is highly free.
- Isolation of products is very easy.
- Efficient heat control.

- Viscosity buildup of polymer is negligible.
- Disadvantages:
- This method is applicable only for water insoluble monomers.
- Control of particle size is difficult.
- Applications:
- Polystyrene beads are used as ion exchangers.
- This technique is used in heterogeneous system.

5 Gas phase polymerizations

- Vapour phase polymerization, also called gas phase or gas fluidized bed polymerization, is a widely used polymerization technique for gaseous monomers such as ethylene (LDPE, HDPE), tetrafluoroethylene (PTFE), and vinyl chloride (PVC). Many other common thermoplastic polymers can be made by this method. This includes high volume resins such as propylene (PP), methyl methacrylate (PMMA), methyl acrylate (PMA), vinyl acetate (PVA), ethylene vinyl acetate (PEVA) and many other polymers that are stable in the gaseous phase. On an industrial scale, however, vapour phase polymerization is mainly used to produce HDPE, LDPE, and PEVA.
- The method has the advantage that it does not require any diluent and that no residual catalyst remains in the resin granulate or powder which is continuously removed from the reactor.
- A simplified flow diagram of the process is shown in the figure5 below. A highly purified (olefinic) monomer gas is continuously fed into a fluidized bed reactor and combined with a dry-powder catalyst.
- Polymerization occurs at the interface between the fluidized catalyst and the polymer particles which are swollen with monomer during polymerization.
- The growing polymer particles sink downwards and are continuously removed at the bottom of the reactor and separated from residual monomer and pre-polymer which is fed back into the reactor.
- The monomer (mixed with gaseous diluent) is also continuously fed into the reactor and passes upward in the reactor through a series of vertical fluidized bed reaction zones. At the top of the reactor gas is removed, compressed and cooled and fed back into the reactor to control the temperature.

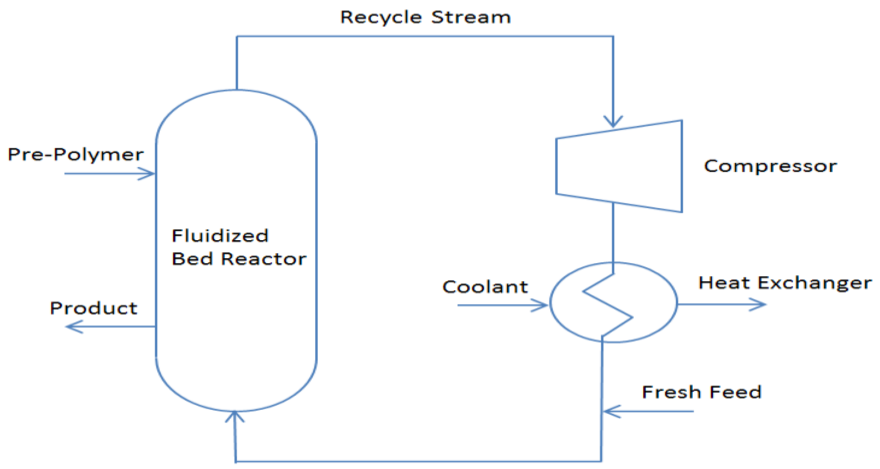


Fig5 Gas phase polymerization

6 Interfacial polymerizations

A variation in solution polymerization is called as interfacialpolymerization.in this method, one monomer of a condensation pair is dissolved in a ligand, and other member of the pair is another liquid.

The liquids are insoluble in one another. The polymers are not soluble in any forms at the interface between them. Also, one of the phases generally also contains an agent reacts with the molecule of condensation to drive the reaction of completion.

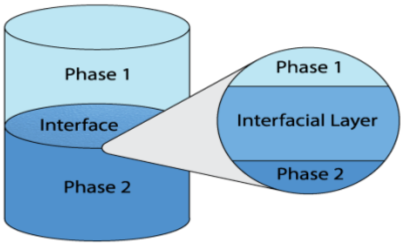
Advantages

- ✓ Reaction proceeds very rapidly at room temperature and atmospheric pressure.
- ✓ In contrast to the long time, at high temperature and pressure associated with polycondensation reaction.
- ✓ Separation of polymers from the interface is easier even during reaction

Disadvantages

Separation of solvents and unreacted monomers may come too high.

Fig 6 interfacial polymerization



7Types of polymer degradation

Degradation:

Deterioration in properties is due to the phenomenon called polymer degradation, which is characterized by an uncontrolled change in the molecular weight or constitution of the polymer.

Types:

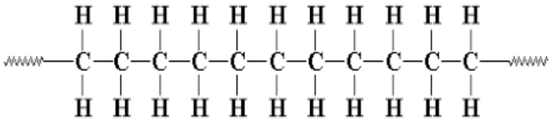
1.chain end degradation

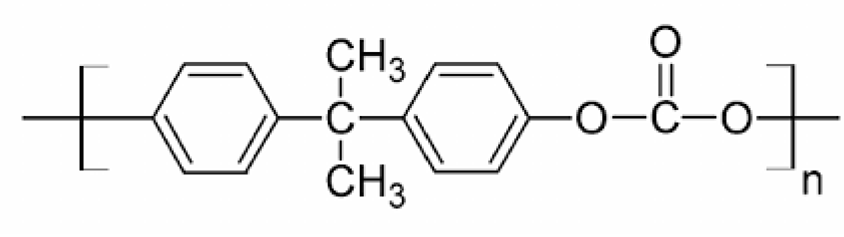
2.random degradation

7.1Thermal degradation

- TD of polymers may follow either unzipping or the random route.
- the unzipping mechanism gives the pure monomer, while random degradation leads to the formation of the host of products, depending on the structure of the polymer.
- since many polymers have a C-C chain as the back bone, their thermal stability is dependent on the stability of the C-C bond.

Factors affecting C-C bond stability:

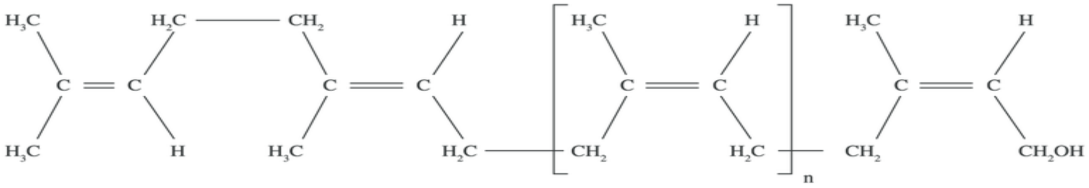
- the number of substituentsincreases and the stability of the polymer backbone bond decreases
- the result is that while the polyethylene is thermally stable, polypropylene is less stable and polyisobutylene is least stable.
- 
- the same H atom is substituted by a phenyl group to give styrene, which will obviously be thermally less stable than ethylene.
- The effect of substitutes groups on the stability of the backbone C-C bond is apparent from a comparison of the bond dissociation energies (in kcal/mole) for C-C in CH_3-CH_3=88, CH_3CH_2-CH_3=85,80 and 70 etc.
- All substituents do not always reduce the thermal stability of the polymeric system. Teflon has all hydrogen atoms of ethylene substituted by fluorine, but is one of the most stable polymers. Teflon temperature is high 400^0C, without undergoing degradation.
- It is highly useful for industrial and domestic applications.
- In Teflon fluorine is the electronegative atom and it has higher dissociation energy (108kcal/mole) C-F bonds. Fluorine is protecting the C-C bond in Teflon from an external attack.
- A substance like polyphenylene, where the chain backbone is formed entirely of aromatic groups ,is thermally more stable .



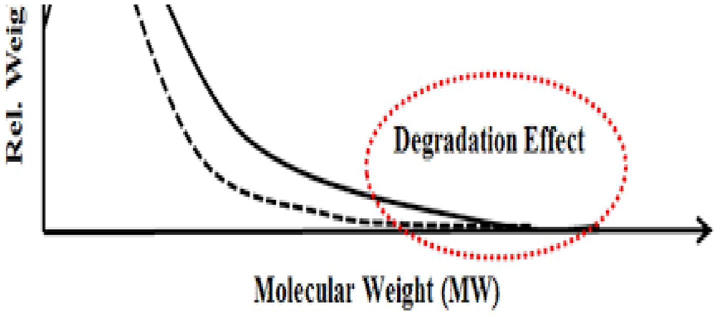
7.2 Mechanical Degradation:

A simple compound which is it subjecting into mechanical stresses arising from high speed stirring or milling. But a polymer such as polystyrene, dissolved in a solvent, when subjected to vigorous stirring or beating, under goes molecular degradation or fragmentation

Polyisoprene structure:

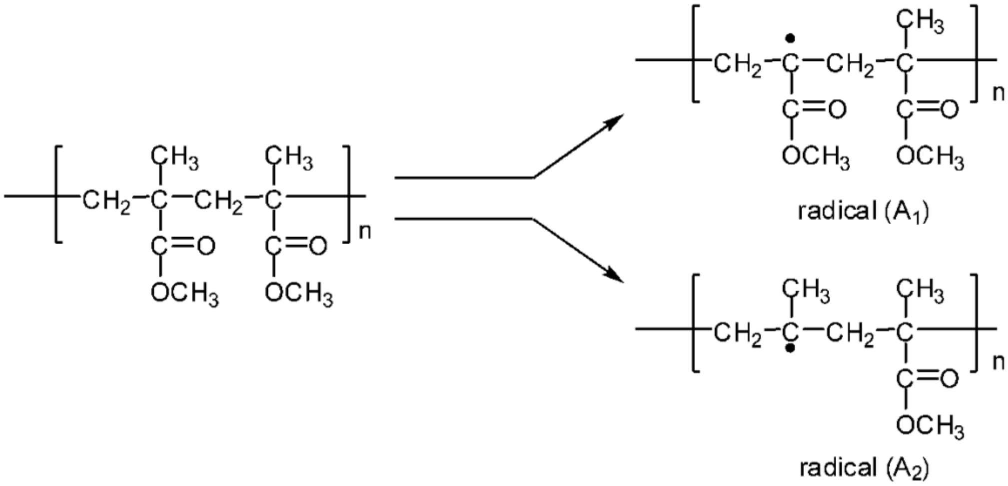


- ✓ In polyisoprene the bonds are the CH2-CH2 Links between the isoprene units subjected to mechanical stresses in the form of milling or mastication.
- ✓ For example, when a polymer solution or melts under a high pressure, fragmentation of the polymer molecules can occur.
- ✓ Agitation. grinding or extrusion are other well-known methods for effecting the mechanical degradation of the polymer.
- ✓ The polymer to a very powerful force that breaks the molecule.
- ✓ The bigger molecules are found to be affected much more than the smaller ones during mechanical degradation.
- ✓ This means that the larger the initial molecular weight, the greater the MW drop due to mechanical degradation.



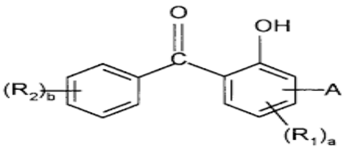
7.3 photo degradation:

- The yellowing and the embrittlement on storage, of some of the transparent plastics or colored rubber articles are also due to their interaction with uv light.
- Example of photodegradation by uv light radiation of polymethylmethacrylate (PMMA). this polymer in a molten state gives irradiation with uv rays an almost quantitative yield of monomer.
- It is generally believed that free radicals are initially found formed during photodegradation.
- Free radicals are depending on the physical state of the materials.
- The molten polymer does not give any quantitative yield of the monomer, the solid polymer does not give any significant quantity of the monomer.
- Small quantities of methylformate formed during the photodegradation of the solid., PMMA.
- A similar type of photodegradation is observed in the case of polyα-methyl styrene also.
- Fig7.3 Photo degradation



7.5 photo stabilizers:

- ✓ Photo stabilizers protects polymers from the deteriorating effects of light
- ✓ Phenyl salicylate, known as salol, is one of the stabilizers.
- ✓ Stabilizers such as 2,4-hydroxy benzophenone (Uvinul400),2-hydroxy,4-hydroxy ,4-methoxy benzophenone and 2-hydroxy ,4-hydroxy benzophenone (DOBP) are used in the plastic industry.
- ✓ The function of photo stabilizer is to absorb UV radiation and dissipate the energy thus absorbed to the environment.
- ✓ The submitted energy is transmitted back as heat or radiations of a longer wavelength.
- ✓ The stabilizer acts aa filter and does not allow the radiation energy to attack the polymer molecules.
- ✓ Stabilizers usually are molecules with aromatic rings having hydroxy groups and ketonic groups.
- ✓ Example:



R-ΘCH3
substituted 2-hydroxy benzophenone

Hydroxyl and ketonic groups are in the ortho position which encourages the formation of the hydrogen bond. Other example is 2-(hydroxy phenol) benzophenone.Photostabilizers are normally used to protect polymeric products of bright colors.

Reference:

Textbook of polymer chemistry.,Gowarikar.,viswanathan.,