

POLYMER CHEMISTRY-SCY1616

Unit-1

INTRODUCTION TO POLYMERS

Monomers, Oligomers, Polymers and their characteristics. Classification of polymers: Natural, synthetic, linear, cross linked and network, Plastics, elastomers, fibers, Homopolymers and Co-polymers. Bonding in polymers: Primary and secondary bond forces in polymers, cohesive energy. Determination of Molecular mass of polymers: Number Average molecular mass (M_n) and weight average molecular mass (M_w) of polymers.

Introduction

1. What are polymers?

Polymers are high molecular weight compounds whose structures are made up of a large number of simple repeating units. The interlinking of many units has given the polymer its name 'Poly' means many, mers means units = polymers. Small molecules are combined to form a big molecule i.e., polymers. It can be formed from one or more chemical compounds.

Eg: Butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$)

butadiene + butadiene + ... \rightarrow polybutadiene (m.w-54)(4000 times)

1.1 DEGREE OF POLYMERISATION:

The number of repeating units in a polymer is known as degree of polymerization.

- If n = low, Mol.Wt = 500 – 5000 Dalton units, it is Oligo polymer.
- If n = High, Mol.Wt = 10,000 – 2,00,000 Dalton units, it is High polymer.

1.2 Monomer:

The repeating units are usually obtained from low molecular weight simple compounds referred to as monomers. The reaction by which monomers are converted into polymers is known as polymerization. The formation of polyethylene from ethylene is an example of polymerization reaction.

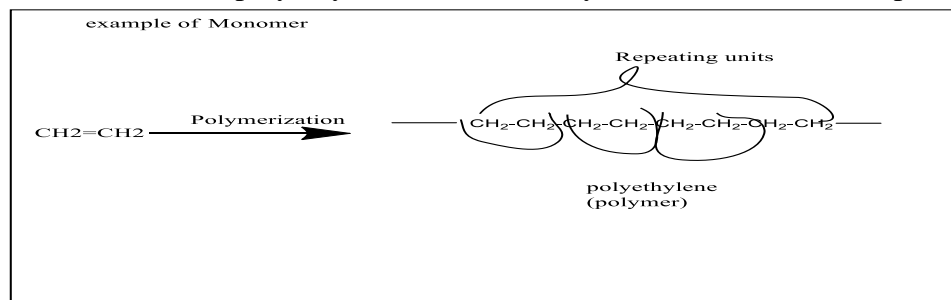


Fig1.2 Example of ethylene monomer

1.2.1 Requirements of monomer

- It should possess at least
 - a) two bonding sites (multiple bonds) or
 - b) reactive functional groups.

1.3 Oligomers: Oligomers are low molecular weight polymers comprising a small number of repeating units. This process of formation is called as oligomerization. Oligomers are significantly dependent on the length of the chain. It is the intermediate of the polymerization reaction.

- Types of oligomers:
 1. Homo oligomers (multiple copies of same subunits)
 2. Hetero oligomers (different protein chains).

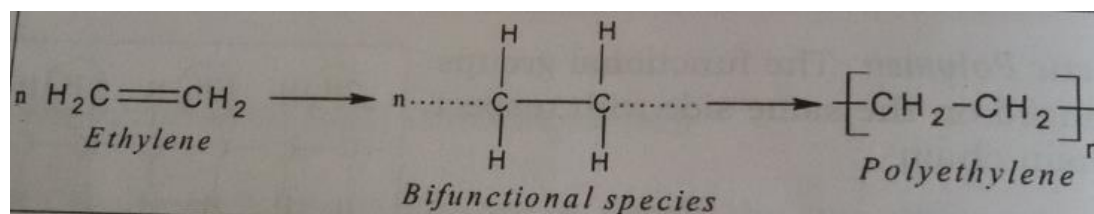
1.4 Characteristics of polymers:

Polymers are having Low density, Economical, Good mould ability, Corrosion resistance, Poor tensile strength, Poor temperature strength, Non-toxic in nature, Low cost.

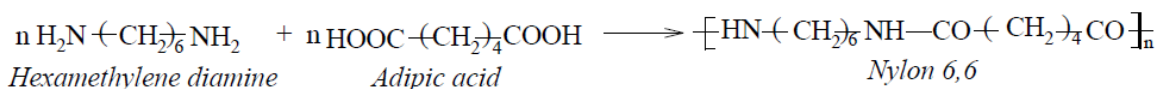
1.5 Types of polymerization

The reaction in which monomers combine to give polymers is known as polymerization. It can be broadly classified into three categories as

- addition polymerization: Monomers having multiple bonds (double or triple bond) undergo addition polymerization. Monomers combine to give polymer through addition reaction without elimination of any smaller molecules. Therefore, the molecular weight of the resulting polymer will be an integral multiple of the molecular weight of monomers. Eg: Ethylene to polyethylene.

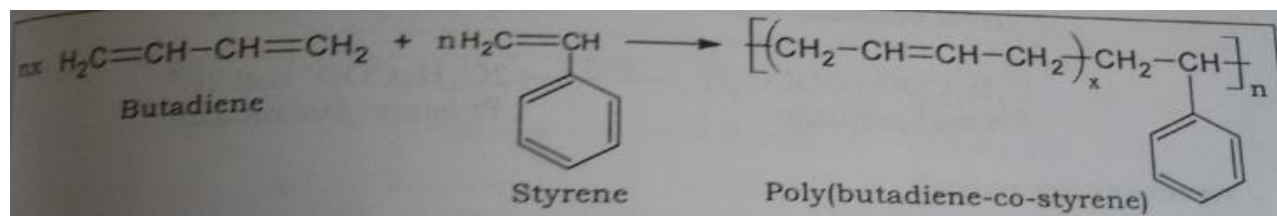


- condensation polymerization: Monomers having same or different types of functional groups undergo condensation polymerization. The polymerization proceeds by step wise reaction between reactive functional groups and small molecules are eliminated. Eg: polymerization reaction of nylon 6,6.



Copolymerization: It is a special kind of polymerization, otherwise known as “Joint polymerization”.

The product is known as ‘Co-polymers’. This is superior to other polymerization because it is used to alter the hardness, strength, rigidity and crystallinity of the monomers.



- The differences between two major polymerization methods are tabulated as follows:

S. No	Addition Polymerization	Condensation Polymerization
1	Eg. PVC	Eg. Nylon 6,6
2	Otherwise known as “Chain growth Polymerization”.	Otherwise known as “Step wise Polymerization”.
3	Monomers are adding together to form polymers.	Monomers are condensed to form polymer.
4	No elimination of other molecules.	Elimination of smaller molecules occur.
5	At least one multiple bond presence is essential condition.	Monomers must have two or more functional groups.
6	Homo polymers are formed.	Hetero polymers are formed.
7	Thermoplastics are formed.	Thermo set plastics are formed.
8	Molecular weight of the polymer is the integral multiple of monomers.	Need not be so.
9	Monomers disappear slow and steadily.	Monomers disappear at the initial stage of the reaction.
10	Longer processing time is needed to increase yield.	Longer time is essential for increasing molecular weight.

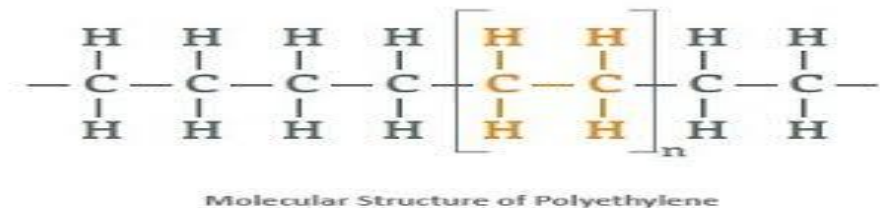
1.2 Classification of polymers:

Based on origin of source:

Natural polymers: Depending on their origin, polymer can be grouped into natural or synthetic. Those isolated from natural materials are called natural polymers. Example: cotton, wool, silk and rubber. It is also non-toxic.

Advantages: Readily and abundantly available, Comparatively inexpensive, Nontoxic products, Biodegradable.

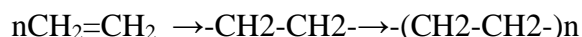
Synthetic polymers: Polymers synthesized from low molecular weight compounds are called synthetic polymers. Example : polyethylene ,nylon, PVC and terylene



Based on the structure:

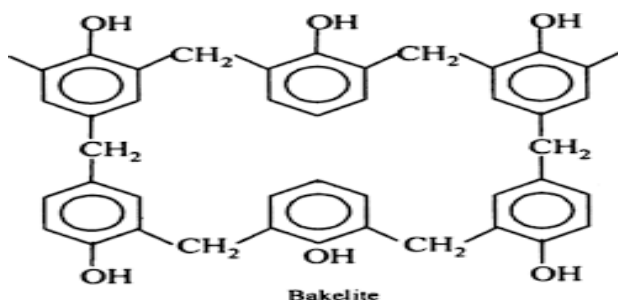
Linear polymer: In these polymers' monomers are linked with each other and form a long straight chain. These polymer chains do not consist any side chains. A linear polymer can be schematically represented by a single line. Example: polyethylene

-A-A-A-A-A-A-A-A-A-A- a polymer made of A atoms.



Cross linked polymer: They have long straight chain with different branched side chains. Molecules are irregularly packed. Example: polyethylene HDPE-High Density polymer LDPE-Low Density polymer

Network polymers: Network polymers have trifunctional monomeric units that are formed by many interconnected polymer chains. They are giant molecules in which movement of individual monomeric unit is prevented by strong cross links. It is having three active covalent bonds. It should be in three-dimensional network. Eg: Bakelite, urea formaldehyde, melamine formaldehyde, etc.



1.3Plastics: The term plastic or plastic material, is given to “organic materials of high molecular weight, which can be moulded into any desired form, when subjected to heat and pressure in the presence of a catalyst”. The term plastics are differentiated from the resin. resins are the basic binding materials which form a major part of the plastics, and which actually has undergone polymerization and condensation reactions, during this preparation.

1.3.1 Thermoplastic polymers:

These polymers are linear, long chain polymers, which can be softened on heating and cooling reversibly. This is called thermoplastics', their hardness is a temporary property, subject to change with rise or fall of temperature. Eg: polythene, polypropylene (PP), polyvinylchloride (PVC), PTFE., etc.

1.3.2 Thermosetting polymers(thermosets): Thermosets are those polymers, which during moulding (by heating) get hardened and once they have solidified i.e. they are permanent polymers. Such polymers during moulding acquire three-dimensional cross-linked structure, with strong covalent bonds.

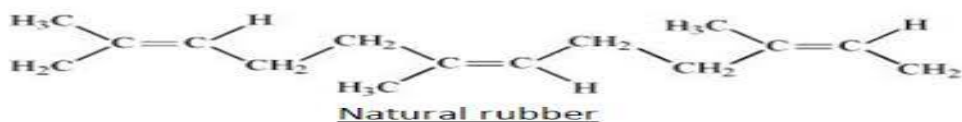
Thus, a thermosetting polymer once moulded cannot be reprocessed.

Eg: polystyrene (terylene), Bakelite, epoxy resin, melamine, urea formaldehyde etc.

Differences between Thermoplastics and thermosetting plastics

S.No	THERMOPLASTICS	THERMOSETTING PLASTIC
1	Eg.PVC , Polyethylene	Polyester, Bakelite
2	Plastics which are melted at high temperature, solidified at low temperature They can be remelted and remoulded into any desired shapes for any number of times.	They cannot be remoulded after their first usage.
3	Scrap can be used again.	Scrap cannot be used again.
4	Formed by addition polymerization	Formed by condensation polymerization
5	The bond strength is low	The bond strength is high
6	Molecular weight is low	Molecular weight is high
7	Soluble in organic solvents.	Insoluble in organic solvents.
8	Prepared by Injection moulding	Prepared by compression moulding.
9	They have linear structure	They have complex 3D structure.

1.4 Elastomers:Elastomer are high polymers, which have elastic properties in excess of 300%.An elastomer(rubber)is any vulcanisable man-made rubber-like polymer. when vulcanized into the rubbery products exhibiting good strength and elongation, polymers used as elastomers. An elastomer molecule is not straight chained eg: polyethene, nylon etc.,but in the case of coil,it can be stretched like a spring.Natural rubber consists of basic material latex, which is a dispersion of isoprene.The isoprene molecules polymerize to form,long –coiled chains of cis –polyisoprene.Structure of natural rubber:



1.4.1Fibres: are those polymers whose chains are held by strong intermolecular forces like hydrogen bonding.They are crystalline in nature and of high tensile strength,due to strong intermolecular forces.

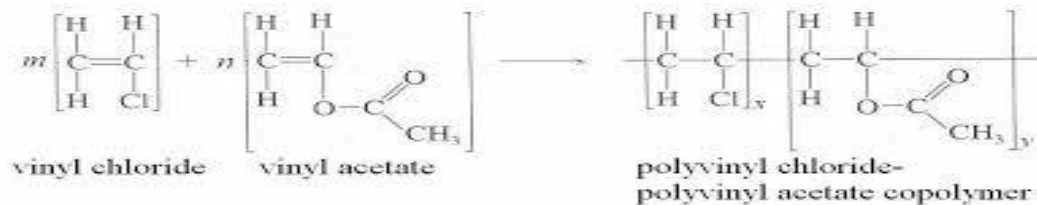
Eg: nylon,polyester

1.5Homopolymers:When all the repeating units in a particular polymer have the same structure,that polymer is called a homopolymer.Eg: vinyl chloride

1.5.1Copolymers:When different repeating units make up the polymer chain ,the polymer is called a copolymer.A-A-B-B-B-A-B-A-A-B—

Types of copolymer:

- Alternating copolymers(A-B-A-B-A-B-)
- Block copolymers (A-A-A-A-B-B-B-B)
- Random copolymers(A-B-B-B-A-A-B-B-)
- Eg:poly[vinyl chloride –vinyl acetate]copolymers



1.5.6 Bonding in polymers: A molecule is connected by covalent bonds. Chemical reactions are required to form or break covalent bonds. Weaker attractions often form between molecules, encouraging them to stick together in groups. The weaker attractions are called secondary bonds or intermolecular forces. These can be overcome by adding heat or dissolving in a liquid. The functional groups on a polymer determine the type and strength of its secondary bonds.

- Types of interactions present in bonding of polymers:

Polar interactions: The valence electrons moving around a molecule may not be symmetrically distributed. The nonmetallic elements closest to the right top corner of the periodic table - nitrogen, oxygen, fluorine and chlorine - tend to shift shared electrons away from carbon and hydrogen. When there is a functional group with one of those elements, it has a slight negative charge and the rest of the molecule (carbon and hydrogen) is slightly positive. The molecule is polarized. Its positive sections are attracted to negative sections of neighboring polymers. eg: PET (Poly (ethylene terephthalate)). It has oxygen-containing functional groups that make it polar. Positive and negative charges can be localized on a covalent molecule since they have no path for conduction of electrons. The carbon atoms in the backbone always follow the octet rule with four covalent bonds, so can't pass extra electrons along the chain. If polymer fibers are rubbed together, they can build up a static electricity charge.

- **Hydrogen bonds:** Molecules with either -N-H or -O-H groups will form strong secondary bonds. Eg: hydrogen bonding in water. This phenomenon is responsible for the relative high boiling point of water, and for the fact that its solid form (ice) is less dense than its liquid form. Polymers with hydrogen-bonding groups will soak up water.

Non-polar interactions: As valence electrons move around the nuclei in a nonpolar polymer, like polyethylene or polyfluoroethylene, they can become temporarily imbalanced. So, one part of a molecule would be negative, another part positive; it is temporarily polar. These occasional imbalances are enough to allow nonpolar molecules to attract each other, but the interaction is much weaker than that observed for polar or hydrogen bonding polymers.

eg: Polyfluoroethylene is nonpolar (not polar) because it is completely covered with fluorine atoms; there is no exposed positive section to interact with a neighboring molecule's negative section.

MOLECULAR WEIGHT OF POLYMERS

The molecular weight of polymers is not unique like small molecules. Since polymeric molecular weights are in the range, it is always given as average molecular weight.

NUMBER AVERAGE MOLECULAR WEIGHT (\bar{M}_n)

It is the ratio of sum of molecular weights of individual molecules to the total number of molecules in the mixture.

It is obtained by measuring the colligative properties.

It is a good index of physical properties such as impact and tensile strength.

Consider a polymer mixture which contains

n_1 molecules are with molecular weight M_1

n_2 molecules with molecular weight M_2 and so on.,

If n_i molecules are with molecular weight M_i then,

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + \dots + n_i M_i}{n_1 + n_2 + \dots + n_i}$$

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

WEIGHT AVERAGE MOLECULAR WEIGHT (\bar{M}_w)

It is the ratio of sum of molecular weights of individual molecules to the total weight of molecules in the mixture. It is obtained by light scattering and ultra-centrifugation techniques.

Consider a polymer mixture which contains

w_1 is the weight of polymer with molecular weight M_1

w_2 is the weight of polymer with molecular weight M_2

and so on.,

Let w_i molecules are with molecular weight M_i , Then,

$$\bar{M}_w = \frac{w_1 M_1 + w_2 M_2 + \dots + w_i M_i}{w_1 + w_2 + \dots + w_i}$$

$$\bar{M}_w = \frac{\sum w_i M_i}{\sum w_i}$$

But, number of moles $n = w / M$

So, $w = nM$

We can replace w_1 by $n_1 M_1$, w_2 by $n_2 M_2$ and w_i by $n_i M_i$

$$\bar{M}_w = \frac{n_1 M_1 M_1 + n_2 M_2 M_2 + \dots + n_i M_i M_i}{n_1 M_1 + n_2 M_2 + \dots + n_i M_i}$$

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

POLYDISPERSITY INDEX (PDI)

The ratio of weight average molecular weight \bar{M}_w to number average molecular weight \bar{M}_n is known as polydispersity index or distribution ratio.

$$\text{Polydispersity index} = \bar{M}_w / \bar{M}_n$$

i. For monodispersed system, $\bar{M}_w = \bar{M}_n$

If a polymer contains molecules of same molecular weight, such system is known as monodispersed system. But it is unreal condition. Such possibility is available only in simple chemical compounds like water, alcohol etc.,

ii. For polydispersed system, $\bar{M}_w > \bar{M}_n$

If a polymer contains molecules of different molecular weight, it is polydispersed system. The deviation of ratio from the unity is taken as a measure of polydispersity of the polymer sample. For all synthetic polymers, PDI is higher than 1.

iii. Higher values of the ratio indicate greater polydispersity. It means all the molecules of the polymers will not have identical molecular weight.

Cohesive energy:

Cohesive energy density Since polymers have negligible vapor pressure, the most convenient method of determining is to use group molar attraction constants. These are constants derived from studies of low-molecular-weight compounds that lead to numerical values for various molecular groupings on the basis of intermolecular forces. Two sets of values (designated G) have been suggested, one by Small, derived from heats of vaporization and the other by Hoy, based on vapor pressure measurements.

Reference:

Textbook of polymer chemistry., Gowrikar, Vishwanathan.,

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UNIT-2

MECHANISM OF POLYMERIZATION

Chain growth polymerization: Cationic polymerization-anionic polymerization –free radical polymerization. Stereo regular polymers: Ziegler Natta polymerization, Step growth polymerization.

Chain growth polymerization

- Chain growth polymerization is characterized by a self –addition of the monomer molecules, very rapidly through a chain reaction. In this polymerization no byproduct is formed. The bifunctionality is provided by the double bonds present in the monomer.i.e. compounds containing reactive double bonds undergo chain growth polymerization. Eg: vinyl,allyl, dienes, olefins. Chain polymerization mainly consists of three major steps, namely,
- Initiation
- Propagation
- termination

followed by the process is, Free radical cationic and anionic polymerization reaction.

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- **1.1Free radical polymerization:**The initiation of the polymer chain is brought about by free radicals produced by the decomposition of compounds called initiators.Chain growth means continuous addition of the monomer units to form polymer chain.
- Initiation:free radicals contains lone pair of electrons.A free radical is highly reactive and can attack any molecule which has a lone pair of electrons this process is calledinitiation. Eg:benzoyl peroxide,azobis isobutyronitrile.
- STEP1: Initiators is thermally unstable compounds and decompose into products called free radicals.
- The initiators can be written as R: R

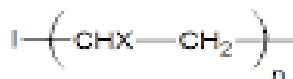
When heat is supplied in this compound, the molecule is split into two symmetrical components.



- STEP2: Propagation:In this propagation step, the radical site at the first monomer unit attacks the double bond of a fresh monomer molecule.This results in the linking up of the second monomer to the first and the transfer of the radical site from the first monomer unit to second, by the unpaired electron transfer process.

- $M1^{\circ} + M \rightarrow M2^{\circ}$
- $M2^{\circ} + M \rightarrow M3^{\circ}$
- $Mn^{\circ} + m \rightarrow Mn+1$
- STEP3: Termination: This process involves coupling of the two lone electrons, this kind of termination is called as termination of coupling.
- There are two types of coupling reactions.

1. disproportionation 2. dead polymer



1.2 Ionic polymerization:

- The ionic mechanism of chain polymerization also involves an attack on the pi electron pair of the monomer. It is a positive or negative ion.
- Two types of ionic polymerization.

1. cationic polymerization

2. anionic polymerization

- 1.2.1 **Cationic polymerization:** The proton pulls the pi electron pair towards it and positive charge of the proton is transferred to the end of the monomer molecules, forming carbonium ion. In this process, a sigma bond is formed between the proton and the monomer unit and the polymer chain growth initiated. The carbonium ion attacks the pi electron of the second monomer molecules and pulls it over. the positive charge is transferred to the second monomer unit.

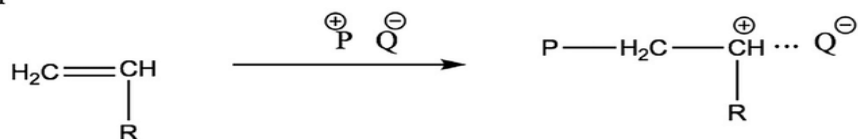
Three steps are involved in this process.

Initiation

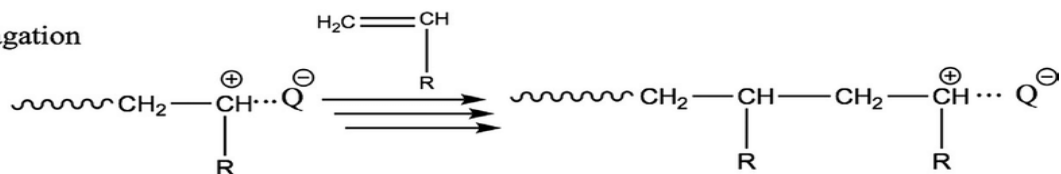
Propagation

termination

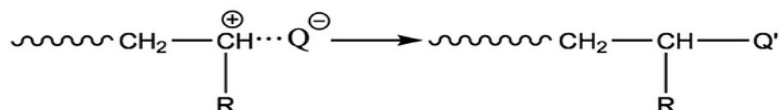
•Initiation



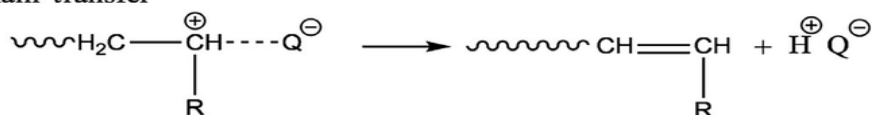
•Propagation



•termination

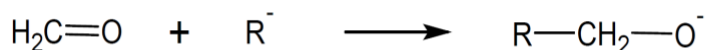


•Chain transfer

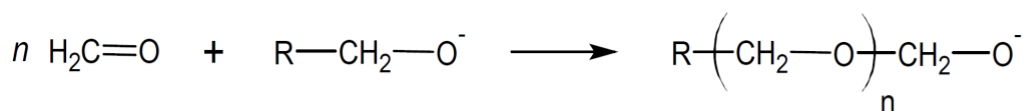


- **1.2.2 Anionic polymerization:** Monomer is done by negatively charged ion, an anion. Such a system has electrons and extra electrons and the resultant negative charge attacks the pi electron pair pushing it, to the end of the molecule. It forms sigma bond with the monomer molecules. Next carbanion is formed and now propagates the chain growth by attacking the second monomer unit followed by termination process.

Initiation



Propagation



Termination

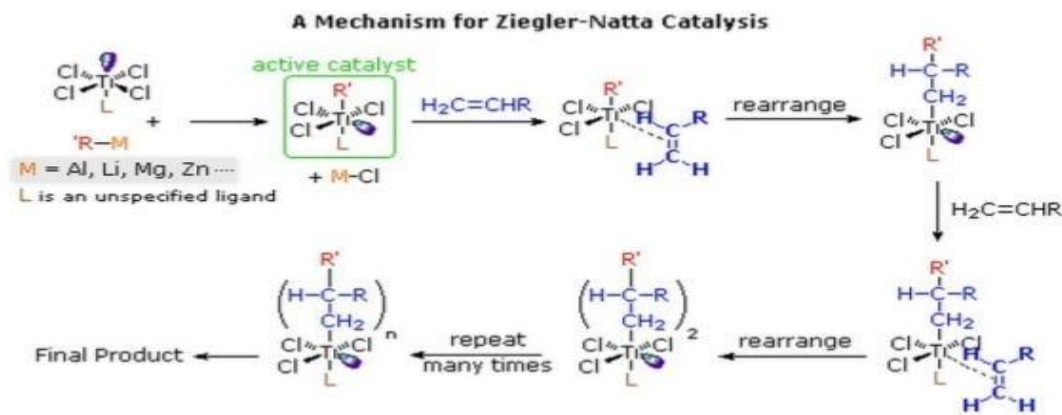


Stereo regular polymers (stereo specific polymers):

- Each monomer segment is in a regular configuration giving a definite structural regularity to the polymer molecules. The structural regularity in a polymer are termed as Optical and geometrical isomerism of the main chain atoms or substituent's in the polymer molecule.

- **1.3.1 Ziegler –Natta polymerization:** Ziegler-Natta process for the polymerization of olefins used as a catalyst formed from TiCl_4 to TiCl_3 and $\text{Al}(\text{C}_2\text{H}_5)$. The rate of polymerization reaction is proportional to the total amount of TiCl_3 . ($\text{Al}(\text{C}_2\text{H}_5)$ reduces to TiCl_4 to TiCl_3 and in the presence of the olefin and is independent of AlEt_3 concentration.
- These are special type of coordination catalyst comprising two components as against single -component organometallic compounds.
- The two components are generally referred to as the catalyst and the co-catalyst. The monomer is complexes with the metal ion of the active center before its insertion into the growing chain. When the catalyst and cocatalyst components are mixed there occurs a chemisorption of aluminum alkyl on the titanium chloride solid surface, resulting in the formation of an electron deficient bridge complex of the structure.
- This complex now active center. The monomer is then attracted towards the Ti-C bond is the active Centre. When it forms a π complex with the π . the bond between R and olefins up producing an electron deficient Ti and a carbanion at R.

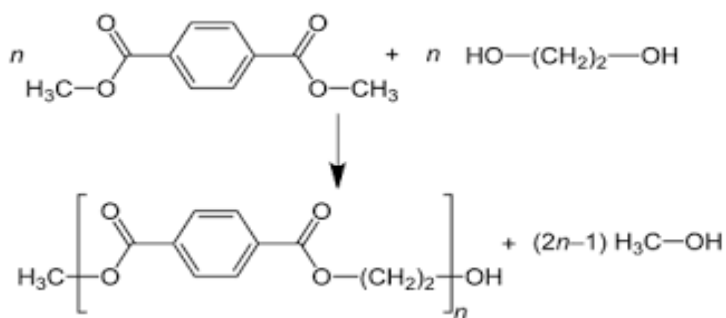
Mechanism Of Ziegler Natta Catalysis



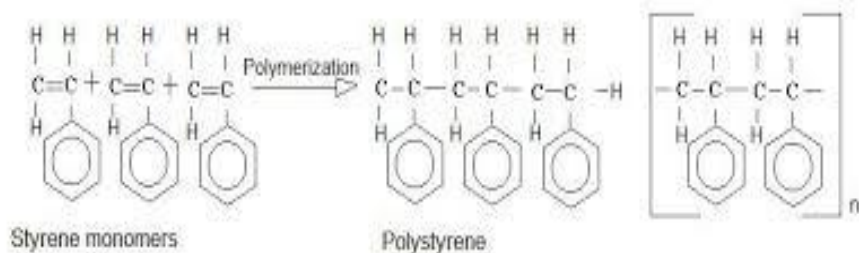
Step growth polymerization:

- The polymer buildup proceeds through a reaction between functional groups of the monomers. Organic functional groups can be made use of this polymerization. Step growth polymerization are mostly accompanied by the elimination of small molecules.
- Polycondensation reaction: This is brought about by monomers containing two or more reactive functional groups condensing with each other. Basic reactions the same as between various functional groups in low molecular weight organic compounds. Foreexample, the reaction between a hydroxyl group and a carboxylic group, giving an ester and a water molecule.
- Step polymerization regarding,
- That monomers should have two functional groups for polymerization to proceed.

- That polymerization proceeds by step wise reaction between functional groups. that only one type of reaction
- The polymer formed still contains both the reactive functional groups at its chain ends and it also active and dead as in chain polymersation.
- Example polycondensation reaction of polyethylene terephthalate.



- Polyaddition reaction: This is brought about by migration of atoms from one another, or to the intermediate product.
- Vinyl monomers as well as monomers pairs with reactive functional groups can undergo polyaddition polymerization.
- Styrene, for example can be polymerized in the presence of perchloric acid by this method.



Reference:

Textbook of polymer chemistry.,Gowarikar.,Viswanathan.,

POLYMER CHEMISTRY-SCY1616

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 of high purity are 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, polyisobutylene and polyacrylonitrile are prepared by this Method.

Solution Polymerization

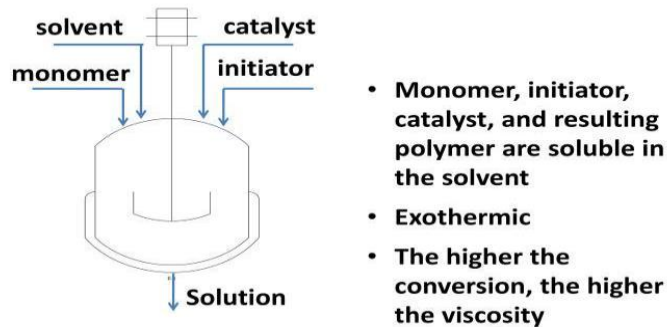


fig2.solution polymerization technique

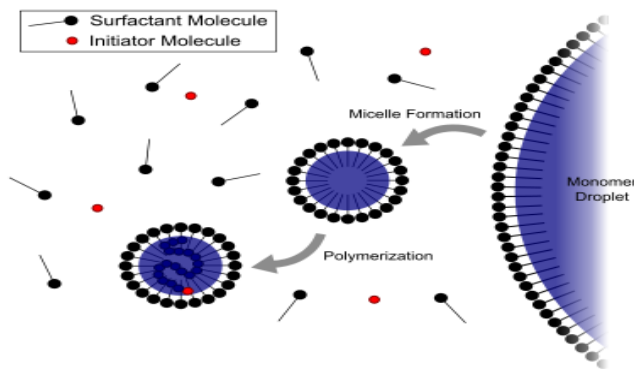
Advantages:

- 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 to 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 continuous 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.

Advantages:

- 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.

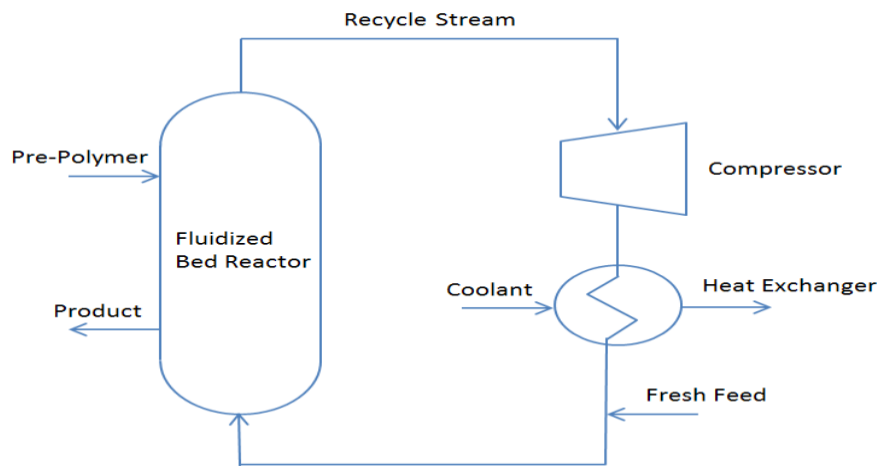


Fig5 Gas phase polymerization

6 Interfacial polymerizations

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

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

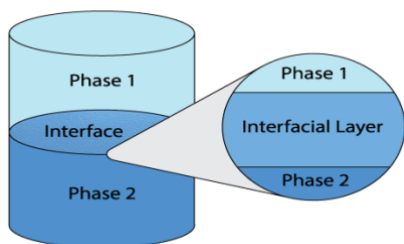
Advantages

- ✓ 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

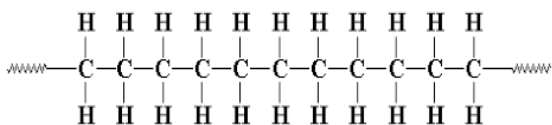
2.random degradation

7.1Thermal degradation

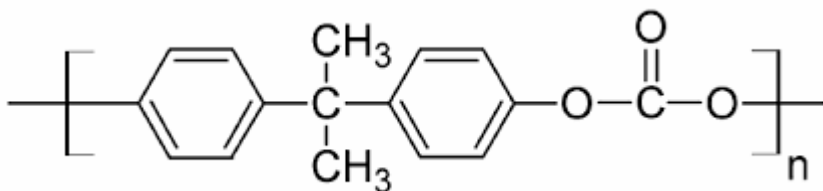
- TD of polymers may follow either unzipping or the random route.
- the unzipping mechanism gives the pure monomer, while random degradation leads to the formation of the host of products, depending on the structure of the polymer.
- since many polymers have a C-C chain as the back bone, their thermal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

Factors affecting C-C bond stability:

- the number of substituents increases 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.



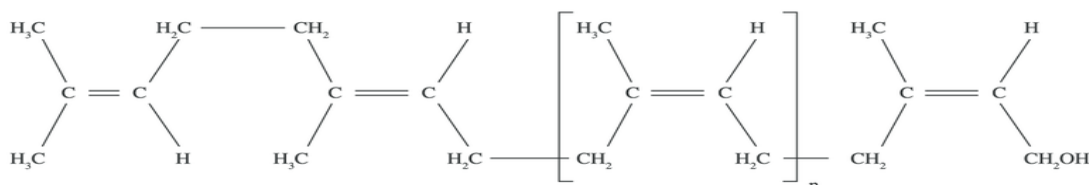
-
- the same H atom is substituted by a phenyl group to give styrene, which will obviously be thermally less stable than ethylene.
- The effect of substitutes groups on the stability of the backbone C-C bond is apparent from a comparison of the bond dissociation energies (in kcal/mole) for C-C in $\text{CH}_3\text{CH}_3=88$, $\text{CH}_3\text{CH}_2\text{CH}_3=85$, 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°C , 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 .



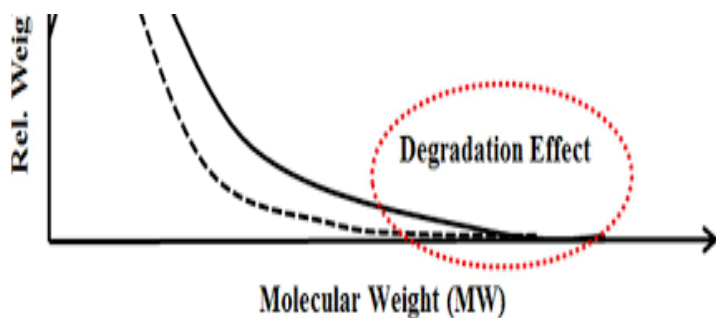
7.2 Mechanical Degradation:

A simple compound which is subjected to 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, undergoes molecular degradation or fragmentation.

Polyisoprene structure:

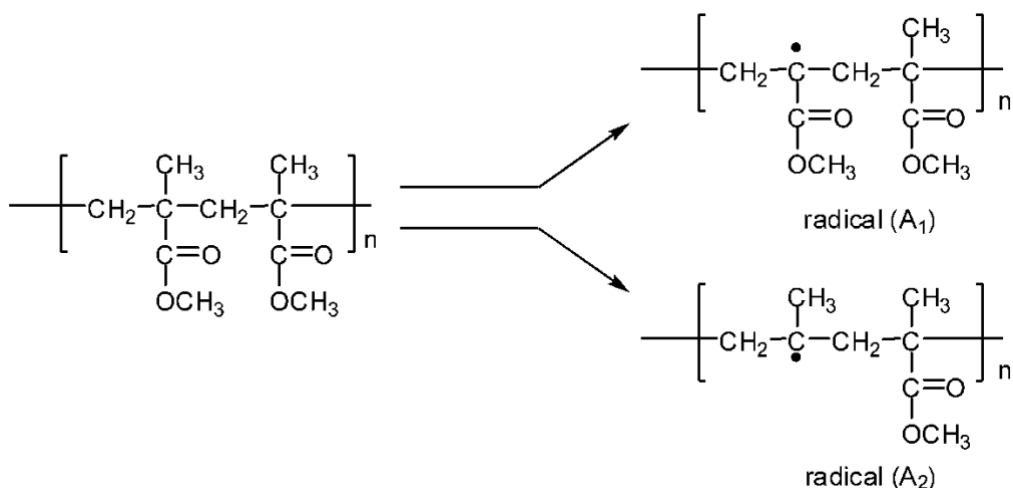


- ✓ In polyisoprene the bonds are the CH₂-CH₂ Links between the isoprene units subjected to mechanical stresses in the form of milling or mastication.
- ✓ For example, when a polymer solution or melts under a high pressure, fragmentation of the polymer molecules can occur.
- ✓ Agitation, grinding or 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.



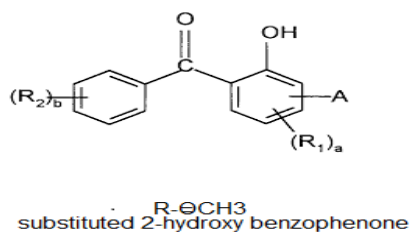
7.3 photo degradation:

- ✚ 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 poly α -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:



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.,

POLYMER CHEMISTRY-SCY1616

UNIT-4

INDUSTRIAL POLYMERS

Preparation of fiber forming polymers, elastomeric material. Thermoplastics: Polyethylene, Polypropylene, polystyrene, Polyacrylonitrile, Poly Vinyl Chloride, Poly tetrafluoro ethylene, nylon and polyester. Thermosetting Plastics: Phenol formaldehyde and epoxide resin. Elastomers: Natural rubber and synthetic rubber - Buna - N, Buna-S and neoprene. Conducting Polymers: Elementary ideas, examples: poly Sulphur nitriles, poly phenylene, poly pyrrole and poly acetylene

Preparation of fiber forming polymers, elastomeric material.

4.Fiber forming polymers

- These are polymeric materials from which man-made fibers are formed.
- Nylon is a typical example of fiber-forming polymers. They exhibit high tensile strength, high rigidity or stiffness and undergo irreversible deformation.
- The molecules in these materials should have a very high DP.
- They should be packed very close to each other in a highly held together by strong interchain cohesion forces which resist deformation and do not allow any relative movement between the chains.
- The material should have a very high Crystallizable.
- This property can be increased by regularity, polar groups in the repeat units and stiffing units such as aromatic and cyclic rings in the chain backbone.

Elastomeric materials:

Elastomeric are popularly known as rubbers. Balloons, shoe soles, tyres, surgeons gloves, garden hoses, are examples of articles made of elastomerics.

Natural rubber is the most classical example made of elastomeric.

These are several synthetic elastomeric include polybutadienes, styrene-butadiene (SBR) and acrylonitrile copolymers, polyisoprene, polychloroprene, ethylene-propylene copolymer, isoprene isobutylene copolymer silicone rubbers.

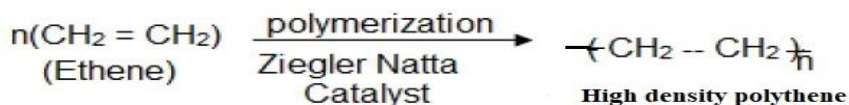
4.1 THERMOPLASTICS

These polymers are linear, long chain polymers, which can be softened on heating and cooling reversibly. This is called thermoplastics', their hardness is a temporary property, subject to change with rise or fall of temperature. Eg: polythene, polypropylene (PP), polyvinyl chloride (PVC), PTFE., etc.

4.1.1POLYETHYLENE

Polyethylene is made by addition or radical polymerization of ethylene (olefin) monomers.

Preparation:



Types of Polyethylene (PE):

Low-density polyethylene (LDPE)
High-density polyethylene (HDPE)

PROPERTIES:

- Higher tensile strength compared to other forms of polyethylene
- Low cost polymer with good processability
- Good low temperature resistance
- Temperature resistance up to 80°C continuously and 95°C for shorter times.
- Low cost polymer with good processability
- High impact strength at low temperature, good weatherability
- Excellent electrical insulating properties
- Very low water absorption
- FDA compliant
- Transparent in thin film form

USES:

It is used in the field of pipe fittings, wire cables, fuel tanks, packaging...

DISADVANTAGES:

- Susceptible to stress cracking
- Lower stiffness than polypropylene
- High mould shrinkage
- Poor UV- and low heat resistance
- High-frequency welding and joining impossible

4.1.2 Polypropylene:

Preparation:



Properties:

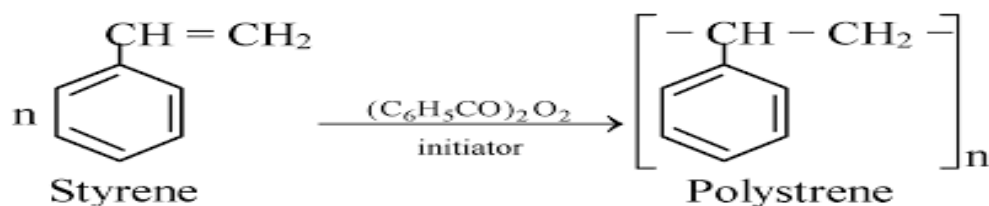
- Resistant to heat distortion
- Excellent electrical properties
- Chemically inert
- Inexpensive and poor resistance capacity

Uses:

It is used in TV cabinets, luggage's, packing films, sterilized bottles.

4.1.3 polystyrene

Preparation:



Properties:

- ✚ Good dimensional stability even at low temperature
- ✚ Good toughness
- ✚ High elongation, high resistance to stress cracking.
- ✚ Lower hardness and rigidity than by alcohols, ketones, ethers etc.

Uses:

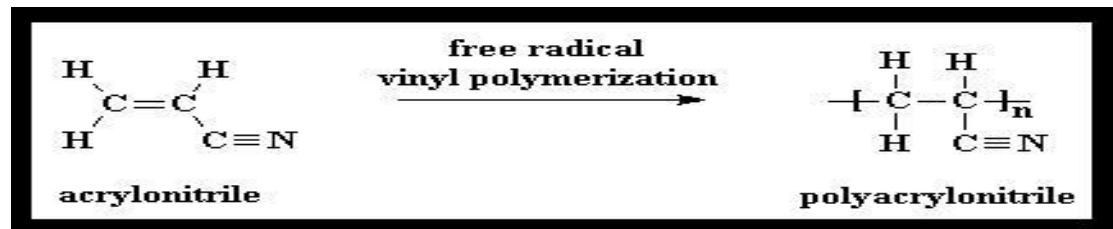
- ✚ Mainly used for the manufacture of motor tyres.
- ✚ Floor tiles, gaskets, foot-wear components
- ✚ Tank linings, insulation for high voltage wire and cables.

4.1.4 polyacrylonitrile

Preparation

It is also called as polyvinyl cyanide. It is produced from acrylonitrile by the radical polymerization technique using peroxide initiators.

Acrylonitrile can be obtained by from acetaldehyde and hydrogen cyanide.



Properties:

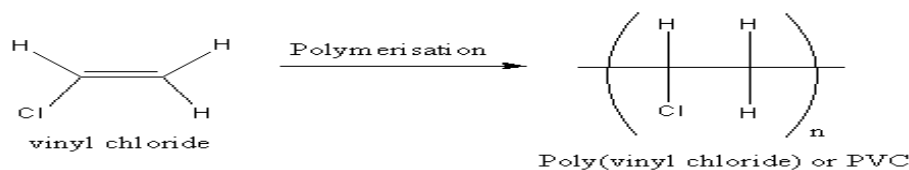
- PAN is soluble in DMF, Dimethyl sulphoxide, adiponitrile,
- Resistance to heat up to around 200°C and exhibits very good mechanical properties.

Uses:

- It is used to produce PAN fibers.
- The copolymer of acrylonitrile with butadiene is a material of great industrial importance.

4.1.5 polyvinyl chloride (PVC)

Preparation: it is obtained by heating a water emulsion of vinyl chloride in presence of a small amount of benzoyl peroxide or hydrogen peroxide in an autoclave under pressure.



Properties:

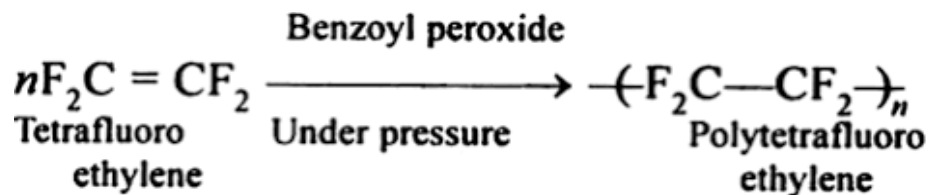
- ✓ PVC is colorless, odorless, non-inflammable chemically inert powder, but soluble in chlorinated hydrocarbons, such as ethyl chloride
- ✓ PVC is most synthetic plastics
- ✓ Greater stiffness and rigidity
- ✓ Uses:
 - Making sheets
 - Tyres, cycle, motorcycle mudguards

- Rain coats, table cloths, curtains, electrical cables

4.1.6, Polytetrafluoroethylene (TEFLON)

Preparation:

It is obtained by polymerization of water-emulsion of tetrafluoroethylene, under pressure in presence of benzoyl peroxide as catalyst.



Properties:

- + High density, waxy touch, very low coefficient of friction,
- + good electrical and mechanical properties.
- + Extreme toughness, high softening point, very viscous, opaque mass.
- +

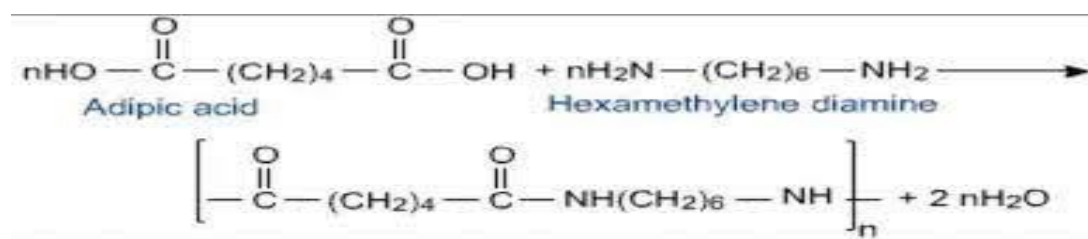
Uses:

- + As insulating material and for making gaskets,
- + packings, pump parts, tank linings, chemical carrying pipes, asbestos fibers and clothes.
- + Non lubricating bearings and non-sticking stop cocks.

4.1.7 NYLON

Preparation:

Nylon 6 6 is obtained by the polymerization of Adipic acid with hexamethylene diamine.



Properties:

- + They are light, horny and high melting
- + They are insoluble in common solvents
- + They have good strength, absorb little moisture and trip dry in nature.
- + Very flexible

Uses:

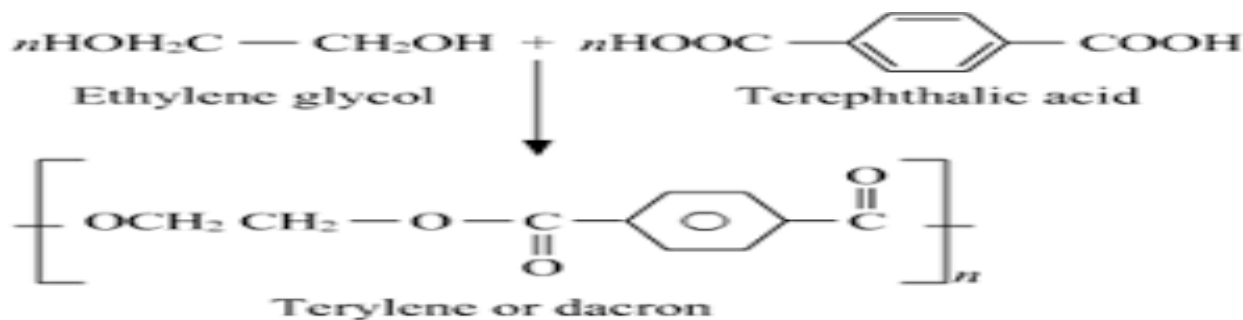
- + It is used for fibers, making socks,

- ✚ ladies' shoes,
- ✚ under garments, dresses, carpets.

4.1. Polyester

Preparation:

Polyester resins are condensation products of dicarboxylic acid with dihydroxy alcohols. For example, terene is formed by condensation of ethylene glycol (a diol) and terephthalic acid (a saturated diacid).



Properties:

- ✚ Polyester is used to good forming material and is converted into commercial fibers.
- ✚ High stretch -resistance
- ✚ High crease and wrinke-resistance
- ✚ High resistant to mineral and organic acids, but is less resistant to alkalis.

Uses:

- ✚ It is mostly used for making synthetic fibers, like terylene, Dacron
- ✚ For blending with wool to provide better crease and wrinkle resistance
- ✚ As glass reinforcing material in safety helmets, aircrafts battery boxes, etc.

4.2 Thermosetting Plastics:

Thermosetting polymers(thermosets):Thermosets are those polymers, which during moulding (by heating) get hardened and once they have solidified i.e., they are permanent polymers. Such polymers during moulding acquire three-dimensional cross-linked structure, with strong covalent bonds.

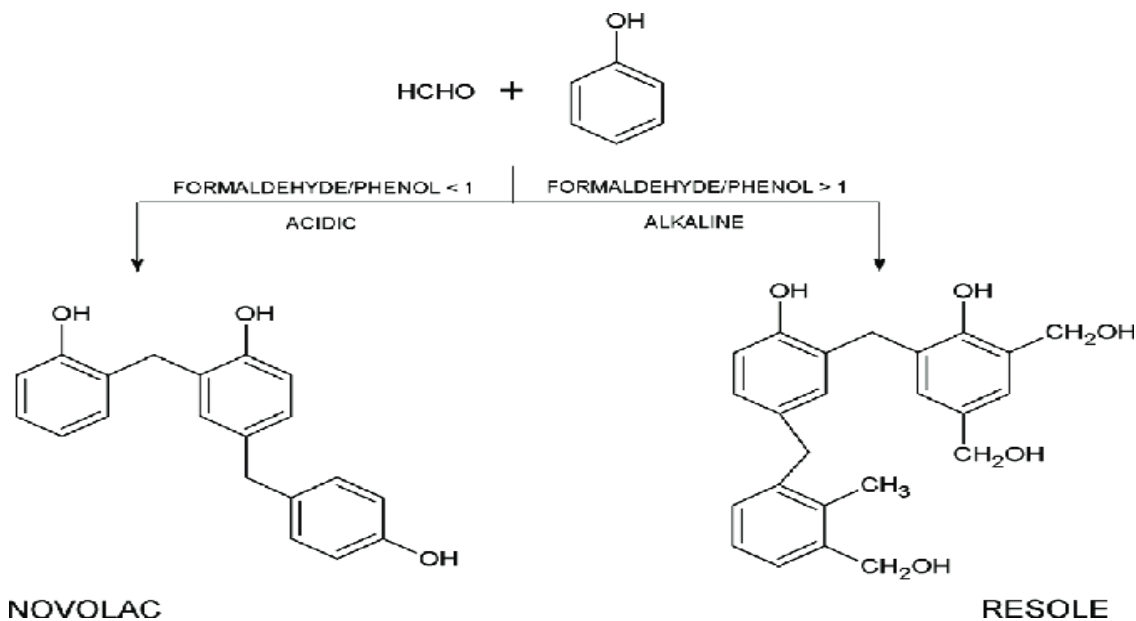
Thus, a thermosetting polymer once moulded cannot be reprocessed.

Eg: polystyrene (terylene), Bakelite, epoxy resin, melamine, urea formaldehyde etc.

4.2.1 Phenol formaldehyde resin

Phenol formaldehyde resins are formed by the condensation between phenol and formaldehyde.

The polycondensation reaction can be catalyzed either by acids and bases.



Uses:

- ✚ The Bakelite resins are usually compounded with fillers such as asbestos powder or sawdust and used for moulding electrical items, telephone instruments.
- ✚ The resols are used for making laminates, paper, fabric or asbestos cloth are impregnated with the resols.
- ✚ Many layers of the impregnated material are pressed together in a hydraulic press and heated to around 500 C.
- ✚ To form a single sheet of a greater thickness.

4.2.2 Epoxide resins:

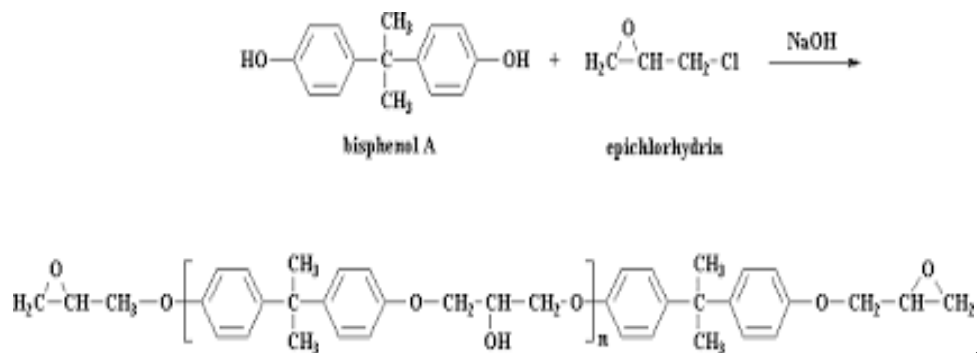
the epoxy polymers are basically polyethers. one type of epoxy polymer is prepared from epichlorohydrin and bisphenol-A.

The reaction is carried out with excess of epichlorohydrin

The epoxy resins obtained through these reactions will be either highly viscous liquids or solids with high melting points.

The epoxy resins can be further cured with substances such as amines, polysulfides and polyamides.

Preparation:



Properties:

- Chemical resistant material
- Good adhesion
- Excellent structural adhesives.

Uses:

- It is used in industrial floorings, foams, potting materials for electrical insulations.,
- One constituent in many of the fiber-reinforced plastics (FRP) is a epoxy polymer.

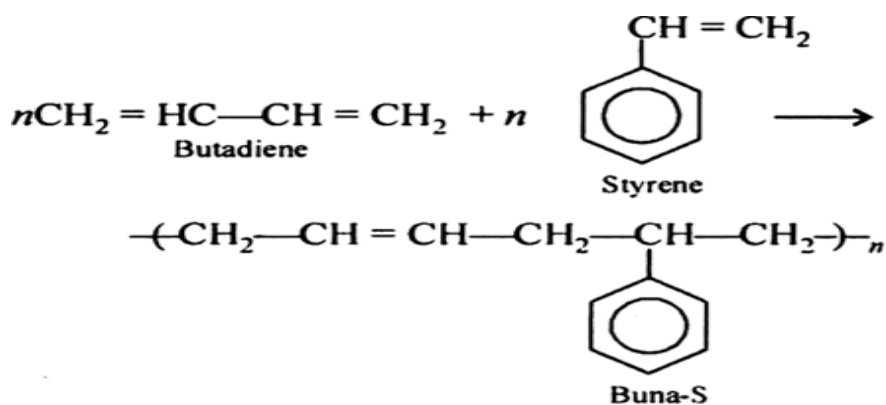
4.3 ELASTOMERS:

- Elastomer are high polymers, which have elastic properties in excess of 300%.
- An elastomer(rubber)is any vulcanisable man-made rubber-like polymer. when vulcanized into the rubbery products exhibiting good strength and elongation, polymers used as elastomers.
- An elastomer molecule is not straight chained Eg: polyethene, nylon etc., but in the case of coil, it can be stretched like a spring.

4.3.1 BUNA-S:

It is probably the most important type of synthetic rubber, which is produced by copolymerization of butadiene and styrene.

Preparation:



Properties:

- It possesses high abrasion-resistance
- High load bearing capacity and resilience. it gets oxidized in presence of ozone present in the atmosphere
- It swells in oils and solvents.
- It can be vulcanized in the same way as natural rubber by Sulphur or Sulphurmonochloride.

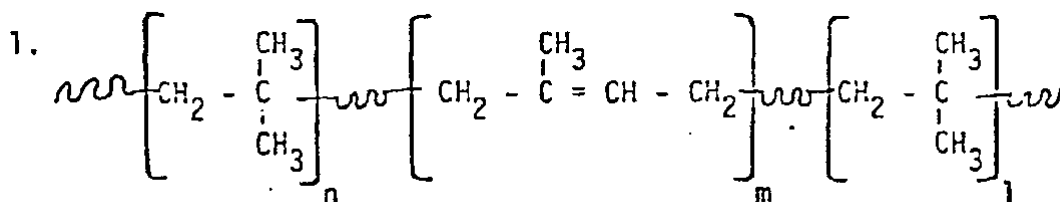
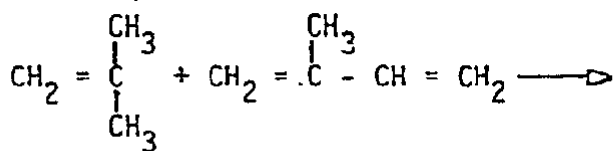
Uses:

- Mainly used in the manufacture of motor tyres.
- Floor tiles, shoe soles, foot wear components, wire and
- cable insulations carpet backing adhesions, tank linings etc....

4.3.2 BUNA-N:

Is made by copolymerization of isobutene with small amounts (usually 1 to 5%) of isoprene.

Preparation:



Properties:

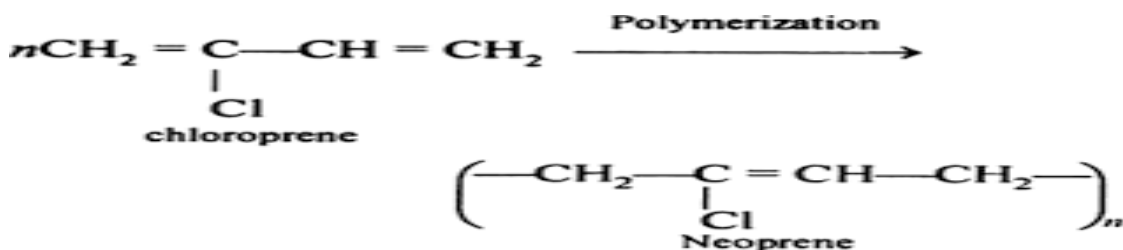
- Low permeability to air and other gases
- Excellent resistant to heat, abrasion, ageing, chemicals, polar solvents
- It is soluble in benzene.
- Good electrical insulating properties.

Uses:

- For making cycle, automobile tubes, automobile parts, hoses,
- conveyor belts for food and other materials,
- tank linings, insulation for high voltage wires and cables.

4.3.3 NEOPRENE:

POLYCHLOROPRENE IS OTHERWISE CALLED AS NEOPRENE.



Chloroprene is manufactured by the addition of hydrogen chloride to vinyl acetylene.

Vinyl acetylene is produced by the dimerization of acetylene.

The polychloroprene is synthesized by the emulsion technique.

It can be readily vulcanized with the help of zinc oxide or magnesium oxide.

Properties:

The vulcanized products are having excellent tensile strength.

Higher oil resistance

Uses:

- Coating to wires and cables
- Shoe soles
- Solid tyres
- Gloves and industrial hoses.

4.4 Conducting polymers:

Polymers which can conduct electricity are called conducting polymers. Ordinary polymers obtained by usual methods are nearly insulators. However, some specific polymers may act as conductors.

Classification: Conducting polymers may be classified as

1. **Intrinsically conducting polymers:** These types of polymers have a solid backbone made up of extensive conjugated system, which is responsible for conductance. They may be of two types: (i) **Conducting polymers having conjugated π -electrons in the backbone:** These polymers essentially contain a conjugated π -electron backbone responsible for electrical charge. Under the influence of electrical field conjugated π -electrons of the polymer get excited, which can then be transported through the solid polymer. Further, overlapping of orbitals of conjugated π -electrons over the entire backbone results in the formation of valence bands as well as conduction bands, which extend over the complete polymer molecule. The presence of conjugated π -electrons in polymers increases its conductivity, e.g., pyrrole.

1. (ii) Doped conducting polymers: The conducting polymers obtained by exposing the polymer to a charged transfer agent in either gas phase or in solution are called doped conducting polymers. Doping is the process by which conductivity of the polymers may be increased by creating negative or positive charge on the polymer backbone by oxidation or reduction. Doping may be of two types: p-Doping and n-Doping
2. Extrinsically conducting polymers: Those conducting polymers which owe their conductivity due to the presence of externally added ingredients in them are called extrinsically conducting polymers. They are of two types: (I) Conductive element filled polymers: In this type, polymer acts as a binder to hold the conducting elements together in solid entity. The minimum concentration of the conductive filler, which is added to let the polymer start conducting is called the percolation threshold. Important characteristics of these polymers are: (a) They possess good bulk conductivity. (b) They are cheaper. (c) They are light in weight. (d) They are mechanically durable and strong. (e) They are easily processable in different forms, shapes and sizes
3. (ii) Blended conducting polymers: These types of polymers are obtained by blending a conventional polymer with a conducting polymer either physically or chemically. Such polymers can be easily processed and possess better physical, chemical and mechanical properties.

Applications of conducting polymers:

Conducting polymers are widely used: 1. In rechargeable batteries. 2. In making analytical sensors for pH, O₂, SO₂, NH₃, glucose, etc. 3. In the preparation of ion exchangers. 4. In controlled release of drugs. 5. In optical filters. 6. In photo voltaic devices. 7. In telecommunication systems. 8. In micro-electronic devices. 9. In bio-medical applications.

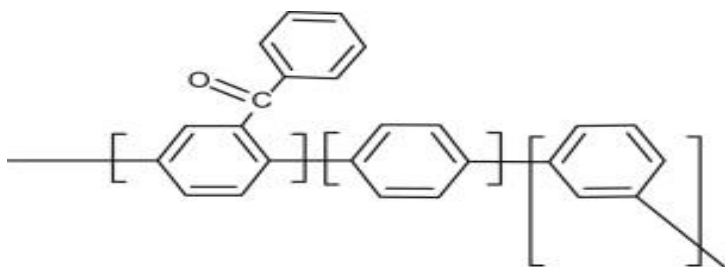
Examples:

Poly phenylene:

This polymer is composed entirely of aromatic rings forming the chain backbone.

The starting material is Para dibromo benzene

This compound when treated with activated copper powder at high temperature, yields Para phenylene as follows.



The polymer can be prepared by the cationic polymerization of benzene with aluminum trichloride and cupric chloride.

This polymer is very brittle and insoluble caused by the presence of aromatic ring chains linked together through p-positions.

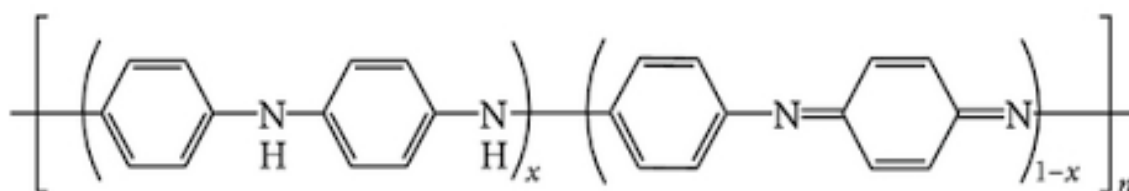
It can derive from the presence of resonance stabilized conjugated double bonds in the aromatic rings.

Polyaniline: it is aromatic conjugated polymer, synthesized by electrochemical oxidation of aniline using ammonium peroxodisulphate or potassium iodate as oxidizing agent.

Polyaniline has a unique structure consisting of an alternating arrangements of benzene rings and nitrogen atoms.

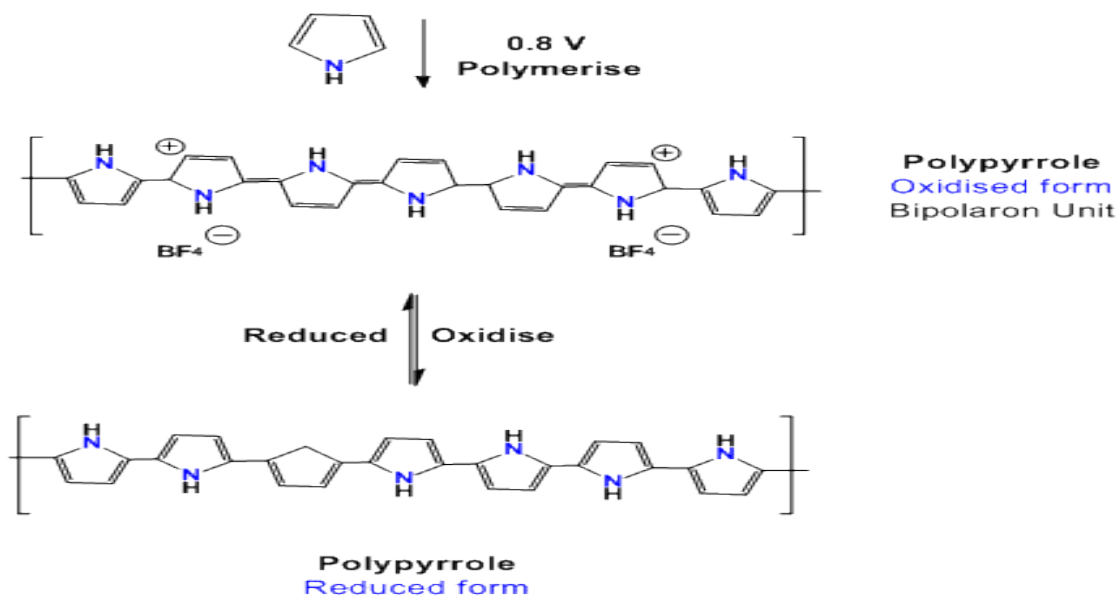
The nitrogen atoms exist either as an amine or imine.

Depending on the relative concentration of nitrogen, polyaniline exists in three different oxidation state.



Polypyrrole:

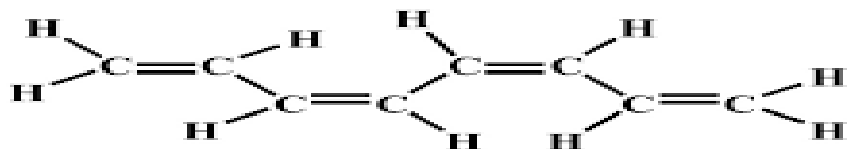
Polypyrrole is a type of organic polymer formed from by polymerization of pyrrole is an insulator but ii is oxidized derivatives are good conductors. The conductivity of the materials depends on the conditions and reagents used in the oxidation, conductivities range from 2 to 100 S/cm.



Polyacetylene (PA)

Polyacetylene is the simplest molecular framework possessing conjugated polymer.

It is also known as aniline black. it is produced from bulk powder, cast films and fibers.



Cis-Polyacetylene



Trans-Polyacetylene

Cis-polyacetylene	$\sigma = 1.7 \times 10^{-9} \text{ S cm}^{-1}$
Trans-polyacetylene	$\sigma = 4.4 \times 10^{-5} \text{ S cm}^{-1}$

POLYMER CHEMISTRY-SCY1616

Unit-5

INTRODUCTION TO POLYMER PROCESSING

Compounding: Polymer Additives: Fillers, Plasticizers, antioxidants, thermal stabilizers, fire retardants and colorants. Processing Techniques: Calendaring, die casting, compression moulding, injection moulding, blow moulding and reinforcing.

COMPOUNDING OF PLASTICS (OR) MOULDING CONSTITUENTS

Compounding is the process by which specific type of additives are added into the resin in order to incorporate certain properties to plastics.

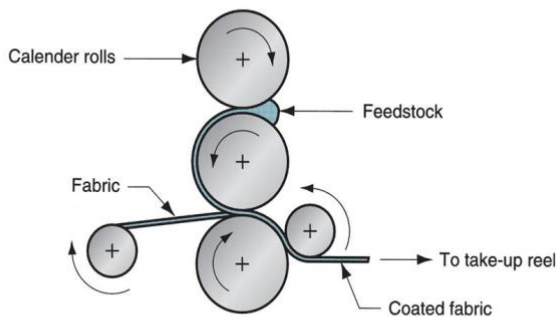
Plastics are compounded to enhance features like:

- Mechanical/Physical and Thermal Properties
- Optical (color/visuals), Functional properties
- Reduced cost
- Polymer additives: foreign substances are called additives are intentionally introduced to enhance or modify many of these properties, related to and controlled by the molecular structure and thus render a polymer more serviceable.
- **Fillers:** filler are most often added to polymers to improve tensile and compressive strengths, abrasion resistance, toughness, dimensional and thermal stability and other properties.
- **Plasticizers:** the flexibility, ductility and toughness of polymers may be improved with the aid of additives called plasticizers. Their presence also produces reduction in hardness and stiffness.
- **Stabilizers:** additives counteract deteriorative processes are called stabilizers (uv light and oxidation)
- **Colorants:** substance that are soluble in the medium (water or oil) is to be colored.
- **Flame retardants:** it is referring to a variety of substances that are added to combustible materials to prevent fires from starting or to slow the spread of fire and provide additional escape time.
- **Antioxidants:** polymers when subjected to oxygen attack, if These exists high concentration of unsaturated c-c bonds, residual polymerization catalyst, it is subjected to highly oxidizing conditions, then it undergo oxidation.

5.2 Processing techniques: the polymeric materials are used in many forms such as rods, tubes, sheets, foams, coatings or adhesives and also as moulded and fabricated articles. The important processes are calendaring, die casting, compression moulding, blowmoulding melt spinning etc....

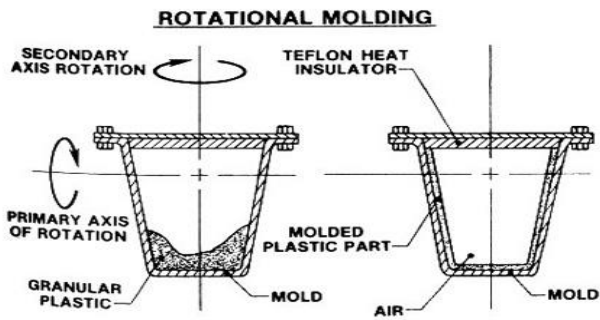
5.2.1 calendaring process:

- A calendar is a device used to process a polymer melt into a sheet or film.
- When the first it was mainly used for processing rubber, but it is commonly used for producing thermoplastic sheets, coatings and films.
- The basic idea of the machine is that squishes a heat softened polymer between two or more rollers to form a continuous sheet. to begin this process the polymer must go through blending and fluxing before it goes through the calendar. it makes it a consistency easier for the calendar to handle. the thickness of the polymer sheet is dependent mainly on the gap between the last two rollers.
- the last set of rollers also dictate the surface finish and texture of the surface.
- Polymer is ready for going through the rollers tends to follow the faster moving roller of the two that it is in contact with and it also sticks more to the other rolls. That's why calendar typically end with a smaller roller at a higher speed to peel the sheet off. it is also the middle roller is kept cooler so that the sheet won't stick to the other rollers nor will it split by sticking to both rollers which can happen



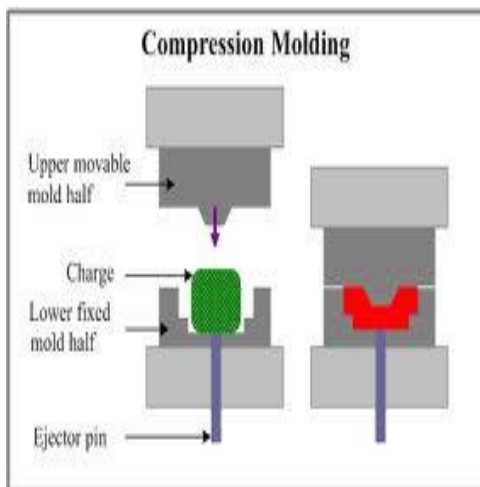
5.2.2 Die casting

- Die casting is a low-cost process.
- Converting a liquid prepolymer to a solid object with a desired shape.
- sheets, tubes, rods with limited length can be produced by the casting process.
- Examples: acrylics, epoxies, polyesters, phenolics and urethanes.
- There are two types of die casting methods
- Rotational casting
- Film casting



5.2.3 Compression moulding

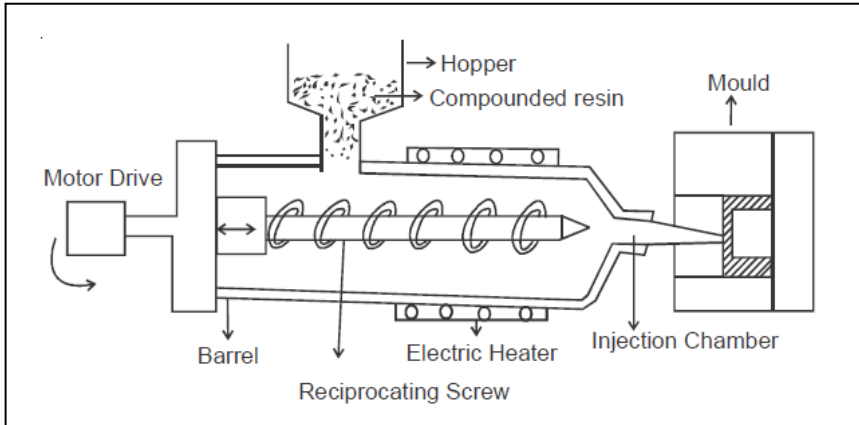
- The compression moulding materials is very widely used to produce articles from thermosetting materials.
- The moulds is made up of two halves.
- Upper and lower halves.
- Lower half usually contains a cavity when mould is closed.
- Upper half is has a projection which fits into the cavity when mould is closed.
- The gap between the projected upper half and the cavity in the lower one gives the shape of the moulded article.
- Moulding pressure and temperature can be high as 200C and 70 kg/cm².



- The compounded material is placed in the cavity of the mould so as to fully fill the cavity.
- As the mould closes down under pressure,
- the material is squeezed or compressed between the two halves and compacted to shape inside the cavity.
- The excess material flows out of the mould as a thin film.
- This film is expelled out of the mould is known as the flash.
- Under the influence of heat, the compacted mass gets cured and hardened to shape.

- The mould can be opened while it is still hot to release the moulded product.

5.2.4 Injection moulding

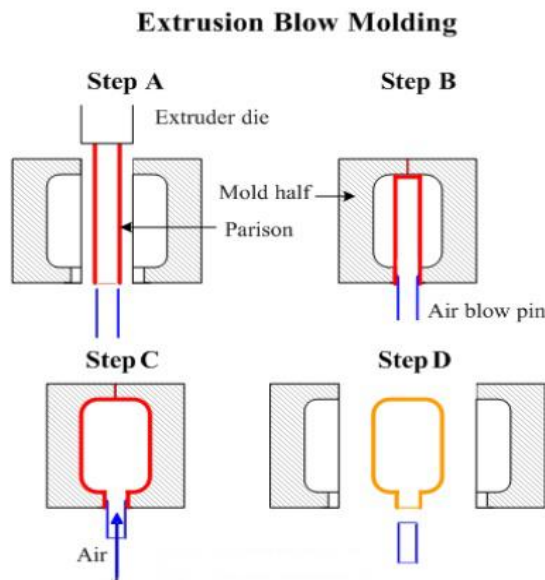


- **Principle:** In Injection molding the molten polymer is injected into a closed and cooled mould under a high pressure where it solidifies to give the product of desired shape.
- **Process:** this technique is used to produce articles from thermoplastic resin. The system consists of two parts namely a cold movable mould and a stationary horizontal cylinder. The compounded material is fed into the horizontal cylinder through the hopper where it gets softened by electrical heating. Then the molten plastic material is injected under a high pressure (1500Kg/cm^2) into a cold movable mould where it solidifies and takes the shape of the mould.
- **Advantages:**
 - Injection moulding is capable of high production rates of 1–50 components/min
 - The wastes can be reclaimed and reused.
- **Disadvantages:**
 - The capital cost is more.
 - Relatively high pressure (1500Kg/cm^2) is required.
- **Applications:** Injection moulding is the most common manufacturing technique for plastic components. It is used for the fabrication of computer parts, automotive and aerospace components.

5.2.5 Blow moulding

- Most of the hollow plastic articles are produced by the blow moulding technique.
- Containers, soft drink bottles and numerous hollow articles are produced by this process.
- Thermoplastic materials such as propylene, polycarbonate, PVC, polystyrene, Under pressure, the parison ultimately assumes the shape of the hollow cavity on the mould.
- The mould is allowed to cool and the rigid thermoplastic article formed is removed by opening the mould.

- The parison needed for blow moulding can be made either by the injection or extrusion process, and the technique can accordingly be called injection or extrusion blow moulding.
- nylon, polypropylene, acrylics, acrylonitrile, and ABS polymer can be blow moulded.
- Blow moulding basically belongs to the glass industry.
- A hot, thermoplastic tube, usually called parison, is properly placed inside a two-piece hollow mould.
- When the two halves of the mould are closed, it pinches and closes one end of the parison and encloses a blowing pin at the other end.
- The parison is now blown by pressurizing from within by blowing compressed air through the blowing pin.
- The hot parison is inflated like a balloon and goes on expanding until it comes in intimate contact with the relatively cold interior surface of the hollow mould.



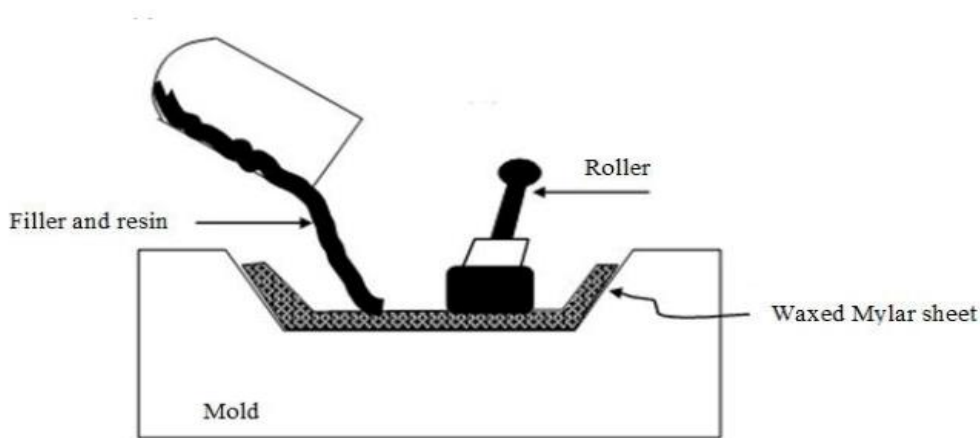
5.2.6 REINFORCING

REINFORCING is plastic matrix with a strength fibre material results in the formation of are called fibre reinforced materials. It having high strength weight ratio and excellent corrosion resistance and are easy to fabricate. Reinforced plastics are produced by suitably bonding a fibre material with a resin matrix and curing the same under pressure and heat. The reinforcement could be in different forms for instance it could be short chopped fibres, continuous filaments or wove fabrics. The common resins fabrics are used in FRPs includes polyesters, epoxy, phenolic, silicone, melamine, vinyl derivatives and polyimides.

There are several methods available for the production of reinforced plastics. Three of the most techniques are

- The hand lay-up technique
- The filament-winding technique
- The spray-up technique

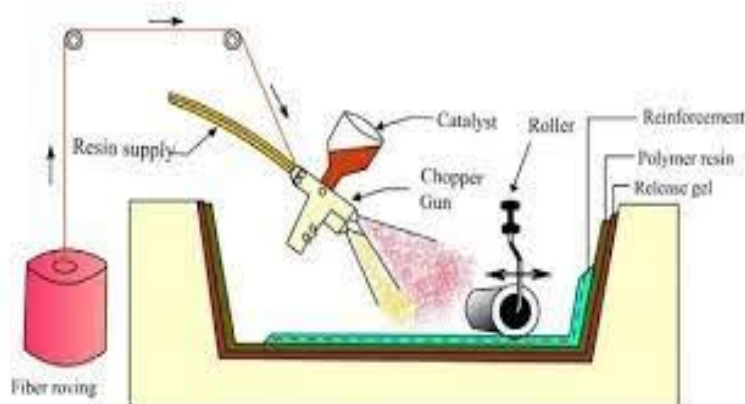
- **Hand Lay-up technique:** The Hand Lay-up Technique This is probably the simplest method for producing reinforced plastic articles. The quality of the end product depends to a large extent on the skill of the operator. The whole process consists of the following steps.
- To begin with, the mold is given a thin coating of a release agent such as polyvinyl alcohol, silicone oil or wax. (This is done to prevent the final fabricated article from sticking to the mold.) The mold is then coated with a resin matrix.
- A precut glass cloth or mat is then laid over the resin layer. Now, another layer of the resin coating is given over the glass cloth.
- Rollers are used to press the glass cloth on the resin uniformly and also to remove the entrapped air bubbles.
- Alternate layers of resin and glass cloth are laid in a similar sequence until the required thickness is built up. The whole set-up is then cured either at the ambient or elevated temperature.
- After the curing is completed, the reinforced plastic material thus formed is removed from the mold and subjected to trimming and finishing. Sheets, auto body parts, boat hulls, ducts and building components are produced by this



Hand Lay-up Technique

- **Filament-winding Technique:** This is a very widely used method for producing reinforced plastic articles such as high-pressure cylinders, storage tanks and rocket motor bodies.
- In this process a continuous length of strand, roving or woven tape of the fiber is passed through a bath of resin and curative.
- As the strand comes out of the bath, the excess resin is squeezed out. The resin-dipped filament or strand is then wound on a mandrel of the required shape and subsequently cured under the influence of heat.
- The winding machine is designed in such a fashion that the fibers can be wound in a predetermined pattern to suit the job.
- The tension of the fiber and the pattern of winding are very important factors as they influence the ultimate tensile property of the finished product.

- **Spray-up Technique:** This technique employs a multiple headed gun.
- A spray of resin, a curative and chopped fibers are discharged simultaneously from Spray gun on the surface of a mold where they get deposited to a uniform thickness.
- The chopped fiber of a suitable length is obtained by continuously feeding roving's to the chopping head of the apparatus.
- Once the required thickness is built up by
- spraying, it is cured under heat. The spray-up technique is a quick method to cover large surface area molds.
- Many present-day reinforced plastic articles such as truck bodies, storage vessels, lorry cabs and boat hulls are produced by the spray-up technique.



- **Other Techniques:** from the techniques described above, there are several other techniques available in the ever-growing reinforced plastic industry, having a specific use.
- For example, a continuous laminating technique is used for producing continuous sheets of reinforced plastic laminates with varying thicknesses.
- In this process, individual layers of woven fabric are fed from individual rolls and impregnated with the resin and curative, and then pressed into a single layer by passing through a set of hot laminating rollers.
- The single layer coming out is cured by applying heat, which results in a laminate of a desired thickness.
- The thickness can be adjusted by selecting the number of layers.
- In yet another technique, known as 'pultrusion', articles such tubing or fishing rods are produced from continuous strands of fiber.
- The process is relatively simple. The continuous strands are pretreated by passing through a resin-curative bath and then pulled through a die of a suitable profile.

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