

POLYMERS

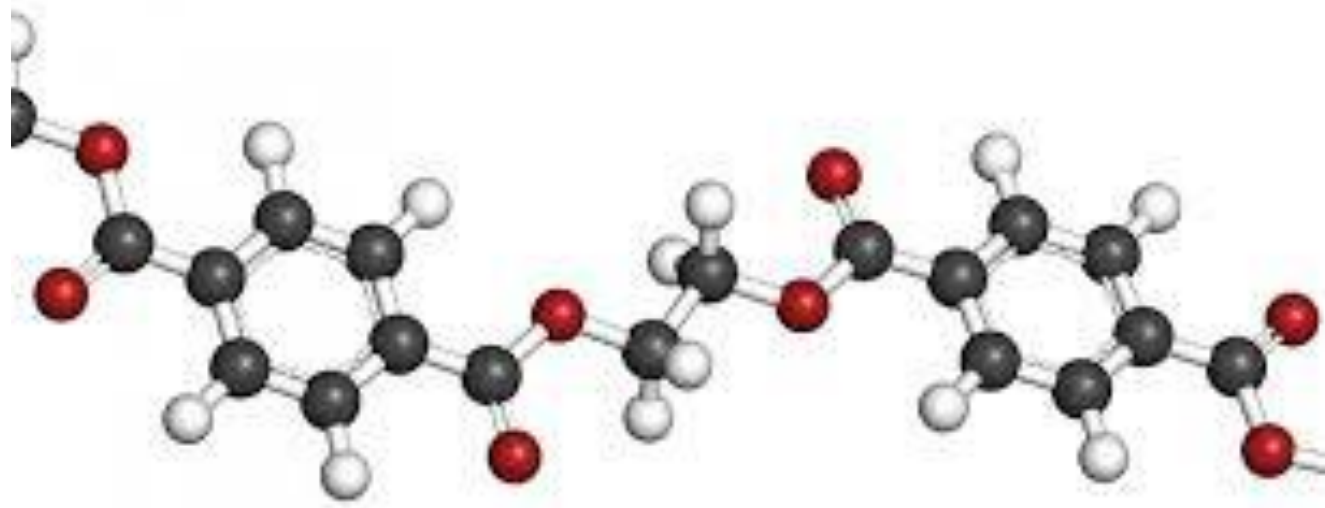
FE SEM –I

Engineering Chemistry-I

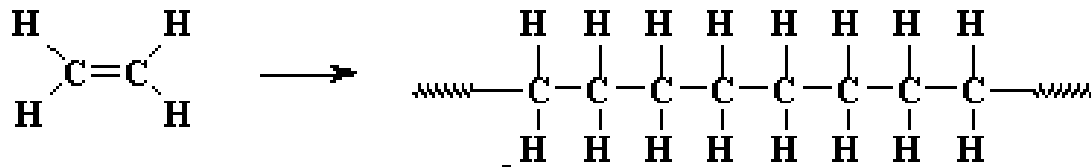
POLYMERS

- **Polymers are macromolecules formed by linking together of a large number of small molecules called monomers. The polymers are giant molecules with high molecular masses. For example, the monomer ethylene gets linked with many other ethylene molecules to form polyethylene, or large number of vinyl chloride molecules combines to form polyvinyl chloride.**
- **The single repeating unit is called as monomer, and the resultant high molecular weight compound is called as polymer.**

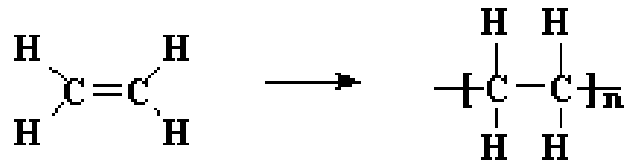
POLYMERS



POLYMERS



This can get tedious to draw, so we often use shorthand like this.



(Note: A line drawn between two atoms represents a pair of electrons shared by those atoms, which constitutes a chemical bond. Two lines represent two pairs of shared electrons, a double bond.)

And when we're feeling really lazy we just draw it like this:



POLYMERS

- On the basis of this physical property, the polymers with high degree of polymerization are known as **high polymers** while those having comparatively low degree of polymerization are known as **oligopolymers**. The molecular weights of polymers are generally in the range of 5000 to 200,000. Hence, these are also known as **macromolecules**.
- The total number (n) of single monomer units combined together to form a polymer is known as **degree of polymerization (DP)**. DP affect physical properties of polymers.

CLASSIFICATION

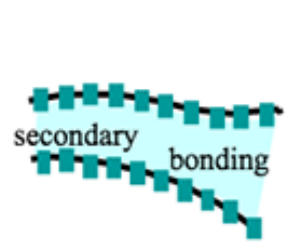
- **i) Based on source:**
 - **a) Natural: e.g starch, cellulose, protein**
 - **b) Semi synthetic: Nitro cellulose**
 - **c) Synthetic: Polythene, polyvinyl chloride**

CLASSIFICATION

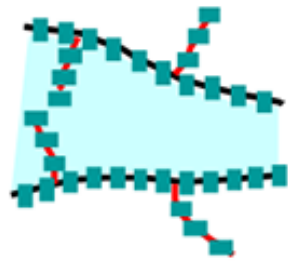
- **ii) The nature of monomer**
- **(a) Homo-polymers: A polymer containing identical monomers.**
 - **A-A-A-A**
 -
- **(b) Co-polymers are the compounds formed by two different small molecules. For example in polystyrene butadiene. One molecule of butadiene combines with one molecule of styrene. The product obtained acts as a monomer to get the polymer.**
 - **A-B-A-B-A-A-B**

- iii) **On the basis of arrangement of monomeric units** in polymer, these are named as linear, branched or cross — linked (three dimensional structures),
- Some examples of linear high polymers are rubber,
- polyethylene, cellulose, polyvinyl acetate
- Polyethylene may also have branched chains.
- The vulcanised rubber is the best known example of cross-linked polymers in which -S-S- cross links are joined irregularly. Due to cross linking polymer structure becomes three dimensional cross linked or network polymer. This makes the polymer very hard and rigid.

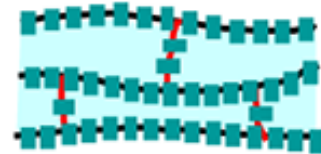
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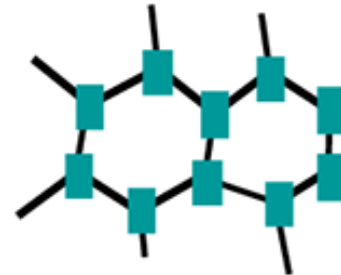
Linear



Branched

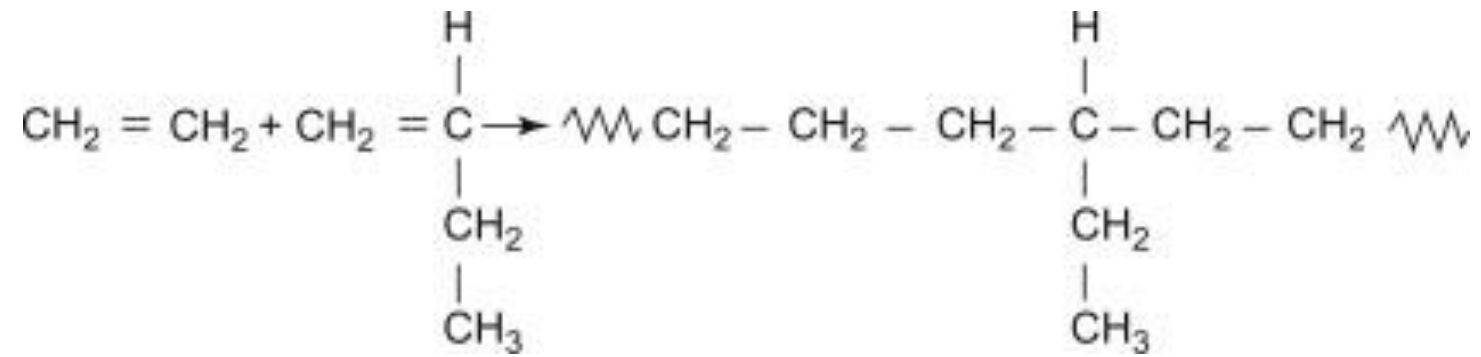


Cross-Linked



Network

Branched polymer



CLASSIFICATION

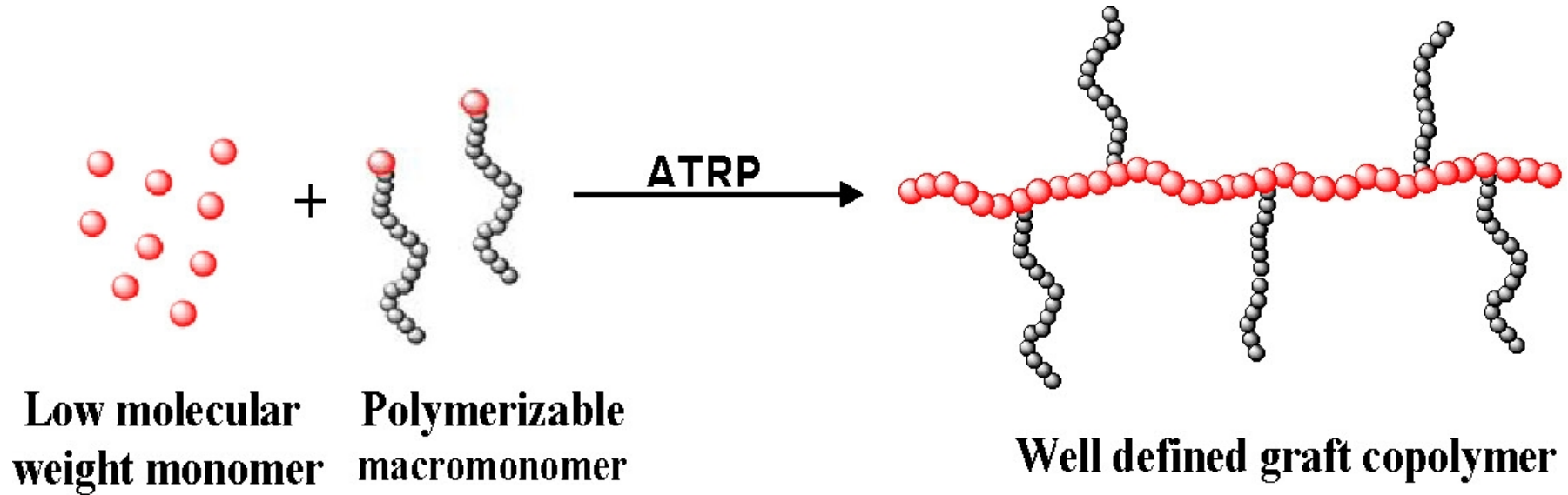
- **iv) Based on atoms-** If the main chain of the polymer is of same atoms, it is known as homo-chain polymers while if is of different atoms it is known as hetero polymer.
- e.g. -C-C-C-C-C- Homochain polymer
- -C-O-C-O-C-O- Heterochain polymer

- **v) Co-polymer** is named as regular or irregular on the basis of arrangement.
- e.g. -A-B-A-B-A-B-A-B-A- Regular
- -A-B-B-A-B-A-A-B-B- Irregular
-
- —A.—B—A—B—A—B-A Linear co-polymer
-
- Branched chain homopolymer
-

CLASSIFICATION

- **If co-polymer chain possesses relatively long sequence of like monomers, it is called as block co-polymer where as if co-polymer possesses branched structures in which the monomer segments are not in same sequence on branch and backbone, it is known as graft co-polymers.**
- **vi) Based on effect of heat polymers are of two types**
- **Thermoplastics and Thermosetting**

CLASSIFICATION



CLASSIFICATION



1a) -AB-Diblock linear copolymer



1c) -ABC-triblock linear copolymer



1d) Random block copolymer



1e) Alternating block copolymer



1b) -AB-Diblock Y-shaped copolymer

CLASSIFICATION

- **vii) Polymers are also classified on the basis of **configuration** of macromolecule known as Tacticity of polymers in following ways**
- **a) Isotactic polymers**
- **In isotactic, the head to tail configuration in macromolecule with respect to functional groups is iso, i.e. all the functional groups lie on the same side of the chain.**

CLASSIFICATION

- **b) Atactic polymers**
- **In atactic, the head to tail configuration is random i.e. the functional groups are arranged randomly.e.g polypropylene**

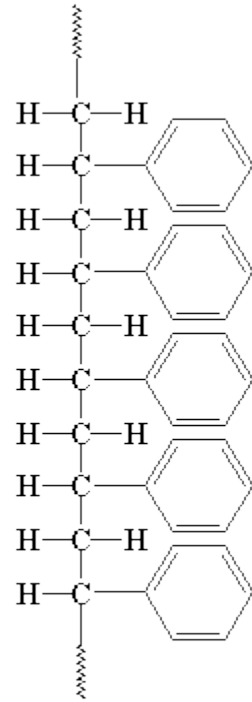
- **c) Syndiotactic polymers**
- **Arrangement of side group in alternating fashion is called syndiotactic polymer. e.g gutta percha**

CLASSIFICATION

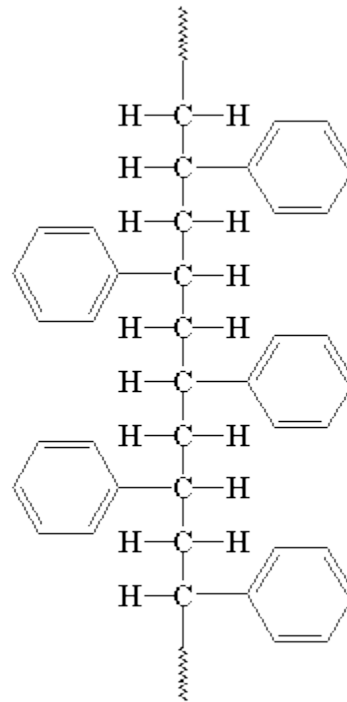
- **b) Atactic polymers**
- **In atactic, the head to tail configuration is random i.e. the functional groups are arranged randomly.e.g polypropylene**

- **c) Syndiotactic polymers**
- **Arrangement of side group in alternating fashion is called syndiotactic polymer. e.g gutta percha**

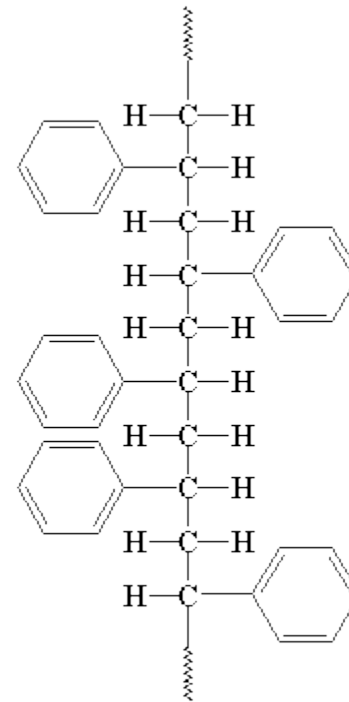
CLASSIFICATION



Isotactic



Syndiotactic



Atactic

CLASSIFICATION

- **Vii-These are examples of homo-organic polymers.** Other examples of organic polymers are polysaccharides, proteins, DNA, viii) On the basis of chemical composition, the polymers are also called either organic or inorganic polymer. Generally in organic polymers, carbon with or without N, S, O, forms the skeleton while in inorganic, other elements form the skeleton.
- e.g Polyethylene., [- - - - H₂ C - CH₂ -----)
- e.g. Polysilanes
- RNA etc. Man made organic polymers include PVC, PP, PVA, PF, UF, polyesters, polyamides, polyurethanes, synthetic rubbers etc.

CLASSIFICATION

- **Inorganic polymers** are those in which atoms other than carbon form the skeleton of polymer. Polysiloxanes or polytioxane⁰ are the examples of polymers where side chain may be of organic nature. They are also known as elemento-organic or hetero-organic polymers. Polysilanes are purely inorganic in nature. Other examples of this class are MgO polymer or hydrogen borons.

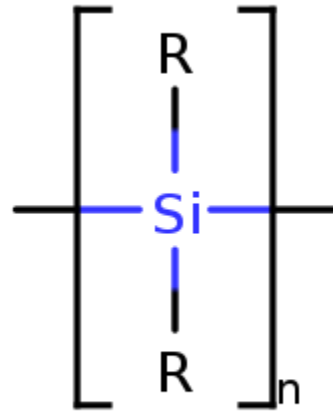
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CLASSIFICATION



POLYMERIZATION

- **The reaction of monomers to form a polymer is known as polymerization. The polymers are formed mainly by**
- **i) Addition polymerization (Chain polymerization).
; ii) Condensation polymerization (Step polymerization).**
- **iii) Copolymerization**

POLYMERIZATION

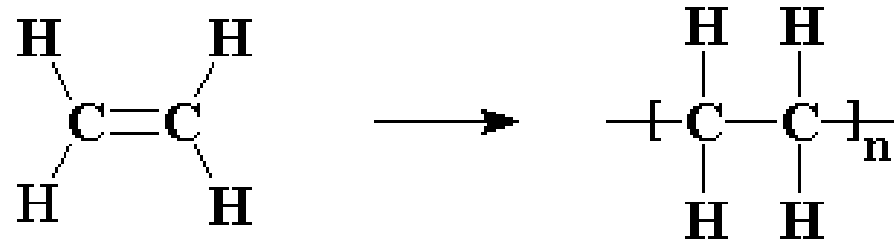
- 1) **Addition or Chain Polymerization-**

- **The word chain indicates elongation of carbon skeleton to form a polymer. Generally such a polymerization involves the (C = C) link in monomer. The double bond breaks and as a result two single bonds on either side of each carbon are formed and thereby elongation of carbon chain continues. The product of this type of polymerization is exact multiple of monomer number, having no by-product or loss of any molecule.**

Thus,

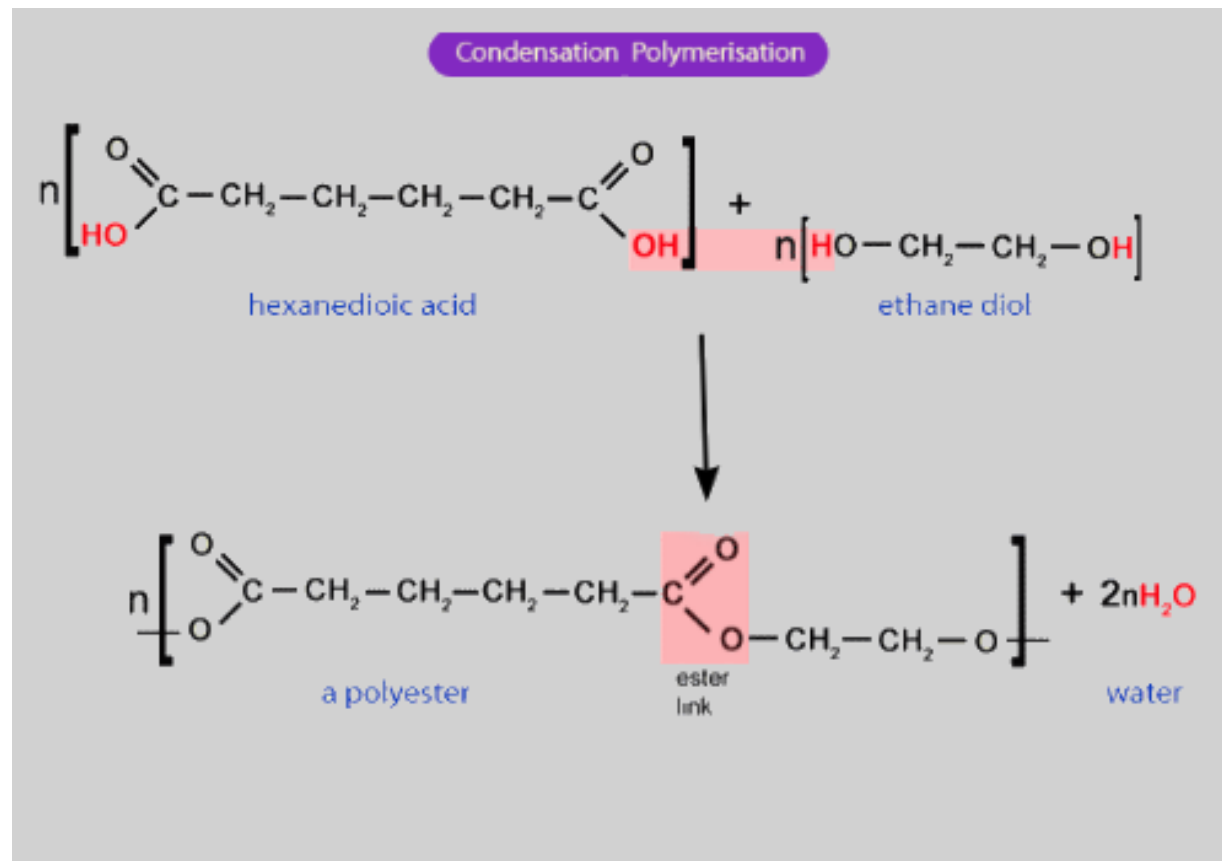
- a. Addition polymerization is undergone by monomers having C = C linkage, e.g.
 - ethylene, vinyl chloride, propylene, butadiene, styrene etc.
- b. The rate of reaction is very high.
- c. The polymerization reaction involves three steps such as
 - a) Initiation.
 - b) Propagation or branching and
 - c) Termination.

POLYMERIZATION



Ethylene has two carbon atoms and four hydrogen atoms, and the polyethylene repeat structure has two carbon atoms and four hydrogen atoms. None gained, none lost.

POLYMERIZATION



POLYMERIZATION

- **ii) Condensation Step Polymerization-**
- **The monomers having certain functional groups such as -OH, -COOH, -NH₂ etc. show the tendency to undergo polymerizations by the elimination of one molecule of a simple by-product such as H₂O, HCl, salt or alcohol etc. Unlike addition / chain polymerizations, polymer loses simple molecules at every combination, as a result does not have exact multiple number of monomer units.**

POLYMERIZATION

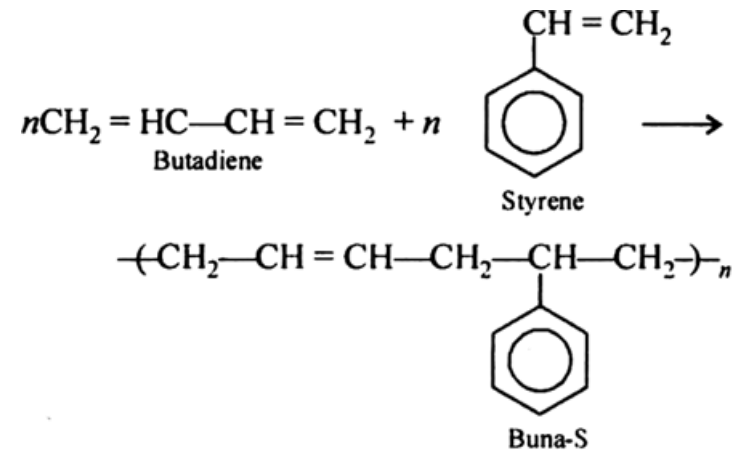
Thus,

- **a. Condensation polymerization is undergone by the monomers which possess functional groups.**
 - **b. Generally monomers are like acids, amines, alcohols, phenols, carbonyl compounds etc.**
 - **c. This type of polymerization occurs stepwise, hence the rate of polymerization is comparatively slow, it depends on kind of catalyst the temperature and the time of reaction**
-
- **Ex: Nylon 66 Phenol formaldehyde**

POLYMERIZATION

- **iii) copolymerization:**
- **It is a joint polymerization of two or more monomers. High molecular weight compounds obtained by copolymerization are called copolymers. For example butadiene and styrene copolymerizes to give GRS-rubber or Buna-S**
- **Ex:Buna S**

POLYMERIZATION



PLASTICS

- **Polymers are called as plastics since they can be moulded to desired shape by application of heat and pressure.**
- **Classification of Plastics**
- **On the basis of setting manner in final stage of manufacture, the plastic materials are plastic articles which are classified in two classes viz. thermo setting and thermo plastic.**

PLASTICS

- **a)Thermo Setting Plastics:** These are the polymers which on heating change irreversibly into hard and rigid materials. This melt of polymer when set into a mould to form an article, is almost a permanent set. On reheating the article does not soften again. They are hence known as thermo hardening plastics or permanent setting resins and during moulding acquire three dimensional cross linked structure with strong covalent bonds. On reheating, these bonds retain their strength and hence such a plastic does not soften on reheating.

PLASTICS

- **Thermo setting plastics can not be reclaimed from waste due to their irreversibility. They are hard, strong and brittle than thermo plastics. The method by which these are formed is called as condensation polymerization. They are insoluble in almost all organic solvents, due to their cross linked three dimensional structure. Phenol formaldehyde / bakelite, amino plastics and alkyl plastics, epoxy plastics, silicon plastics etc are the best known examples of thermosets.**

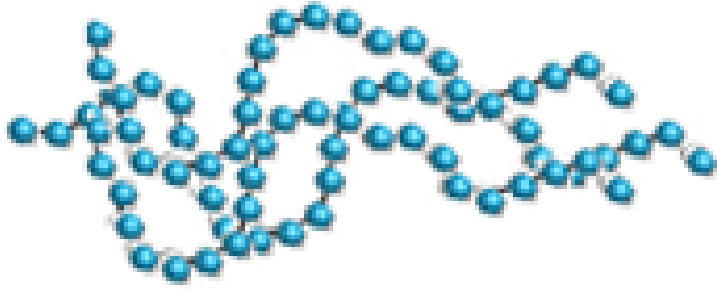
PLASTICS

- (b) **Thermo Plastics:** These show reversible change on heating i.e they soften on heating but regain their original properties on cooling. They gain or lose hardness with rise or fall in temperature. Their chemical nature does not get affected even on repeated heating and cooling, i.e the changes are more of physical nature. If these resins are softened, they retain their softness at that temperature. These resins can be reclaimed from waste, and they are soft, weak , less brittle as compared to former type of plastics resins. The method usually used to manufacture is addition polymerisation. They are generally long linear polymer with occasional or no cross linkingng. They are soluble in specific organic solvents, nples of this class of resins are cellulose nitrate, polyacrylates, ethyl cellulose , polyvinyl resins, or polystyrene resins, polyamides (nylons), 'rc'.yethers, polypropylene, polyethylene etc.

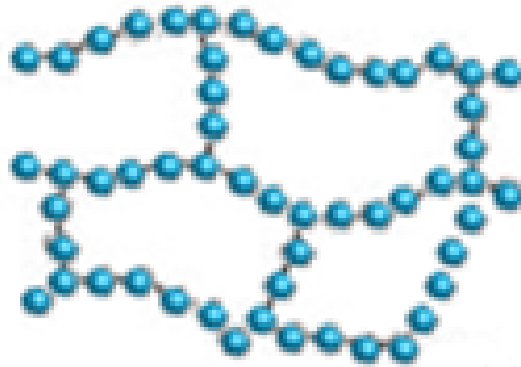
PLASTICS

Thermosetting Plastics	Thermosetting or Thermohardening Plastics
These are long chain linear polymers with negligible branching formed by addition polymerization	These are formed by condensation polymerization
These have linear and branched structure	These have three-dimensional network structure with number of cross links
They have low molecular weight as compared to thermosetting type plastics	They have high molecular weight as compared to thermosetting plastics
They are usually soft, weak and less brittle	They are usually hard, strong and more brittle
They are usually soluble in some organic solvents	Due to strong bonds and cross links, they are insoluble in all organic solvents.
They get softened on reheating readily because secondary forces between the individual chain can break easily by heat or pressure.	The crosslinks and bonds retain their strength on heating and hence, they do not soften on heating.
By reheating to a suitable temperature they can be softened, reshaped and thus reused	They retain their shape and structure even on heating. Hence, they cannot be reshaped and reused.

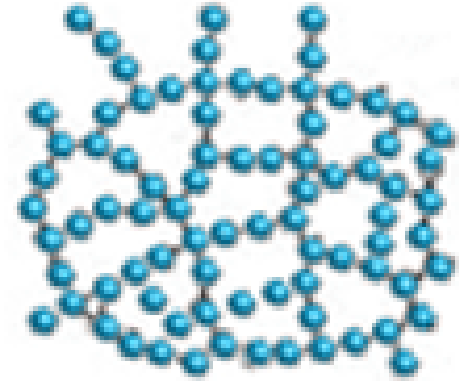
PLASTICS



Thermoplastic

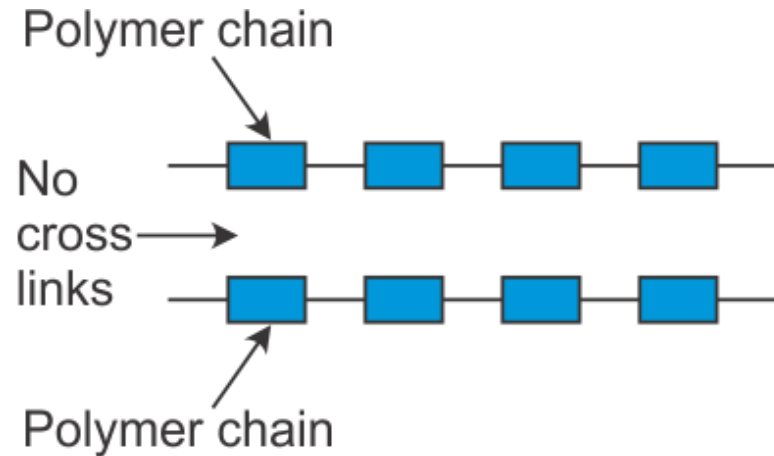


Elastomer

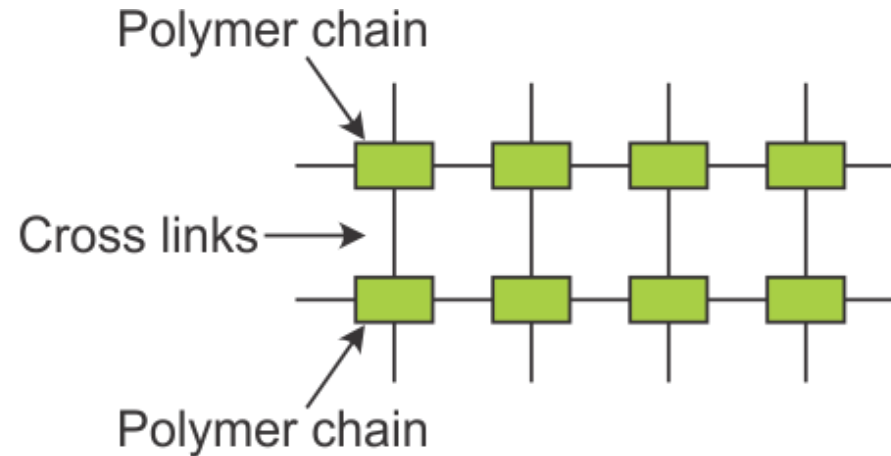


Thermoset

PLASTICS



(a) Polymer chains in thermoplastics (like polythene) are linear, having no cross-links



(b) Polymer chains in thermosetting plastics (like bakelite) have cross-links

COMPOUNDING OF PLASTICS

- **Plastics are manufactured synthetically using raw materials mostly from natural gas and petroleum, or from coal mines, forests, farms and paper and textile mills.**
- **In addition to the raw materials chosen the plastics are generally compounded with some other substances so as to impart certain specific properties to the product. Usually such moulding compositions are prepared from two or more of the following material groups.**
- **Binders or resins.**
- **Fillers or extenders.**
- **Pigments or dyes or colouring agents.**
- **Catalysts or accelerators.**
- **Plasticizers.**
- **Lubricants.**
- **Stabilizers.**

COMPOUNDING OF PLASTICS

- **1) Binders** hold the other constituents together during manufacture. Usually natural or synthetic resins or cellulosic derivatives are used as binders, which are high molecular weight substances. Binders influence the properties of plastics. The type of the treatment during moulding operation also depends upon binders. If binder used has comparatively low molecular weight, then plastic article gets moulded easily and vice versa.

COMPOUNDING OF PLASTICS

- 2) **Fillers or Extenders** impart better tensile strength hardness of plastic material, finish workability opacity etc. They reduce shrinkage and brittleness. They also reduce cost of the plastic per unit weight. The fillers may be of organic or inorganic origin. The fillers which are added only to improve the mechanical strength of the plastic are called as reinforcing fillers.

Example

- Carborundum (silicon carbide), Quartz/ mica improve hardness of plastic material whereas, barium salts help to make the plastic impervious to x-rays. The heat and corrosion resistance can be improved by adding asbestos.
- Other examples are Wood flour, cotton pulp, paper pulp, carbon black, graphite, powdered rubber,

COMPOUNDING OF PLASTICS

- **3) Pigments / dyes / Colouring matter** imparts desired colour to plastic. Organic dyestuffs and inorganic pigments are used for this purpose in small proportion.
- **4) Catalyst or accelerators** are used to increase the rate of polymerisation of fusible resin binder to form cross linked infusible form during moulding operations. Generally thermosetting plastics involve use of catalyst normally an acidic or basic catalyst depending upon the type of thermosets. The catalyst is added in small quantities. Commonly used catalysts are hydrogen peroxide, benzoyl peroxide, metallic oxides etc.

COMPOUNDING OF PLASTICS

- **Plasticizers** help to increase the plasticity of the plastics. The adequate quantity of plasticizer also helps to soften the plastic at comparatively lower temperature. The functions of plasticizers are to Enhance flexibility or plasticity. decrease brittleness. reduce the viscosity of resins so that they can be moulded even at high temperature and pressure. lower softening temperature. lower moulding or remoulding temperature. Plasticizers are not used in thermosets, they are added in thermo softening
- They reduce intermolecular attraction and thereby increases tendency of sliding or moving. Thus the plastics which are plasticized possess high percentage of flexibility. The commonly used plasticizers resins only.
- Plasticizers occupy the position with uniform distribution between the polymer molecules. This type of dispersal of plasticizers reduces the forces are lubricants, camphor, alkyl phosphates, vegetable oils, fatty acids and some phosphates (tricresyl phosphate, triphenyl phosphate). They are added to the extent of 8-10 % of the total bulk of plastic.

COMPOUNDING OF PLASTICS

- **Lubricants** help during moulding operations, especially during low or room temperature moulding. The use of lubricants imparts flawlessness, and glossy finish to the plastic products. This is because the lubricants tend to get dispersed towards outer surface of the finished product, hence during moulding, they form a layer between the article and mould. This layer prevents the plastic material from sticking to the surface of the mould, and thereby facilitating the moulding operations. Commonly used lubricants are soaps, or esters of fatty acids such as oleic and stearic acids or waxes

COMPOUNDING OF PLASTICS

- **Stabilizers** help to improve thermal stability of the plastic. These are required especially in the processing stage for plastics, which have tendency to decompose or change their colours at moulding temperatures. a) opaque moulding compounds like salts of lead e.g. white lead, lead chromate. b) transparent moulding compounds like stearates of lead , cadmium and barium.

FABRICATION OR MOULDING OF PLASTICS

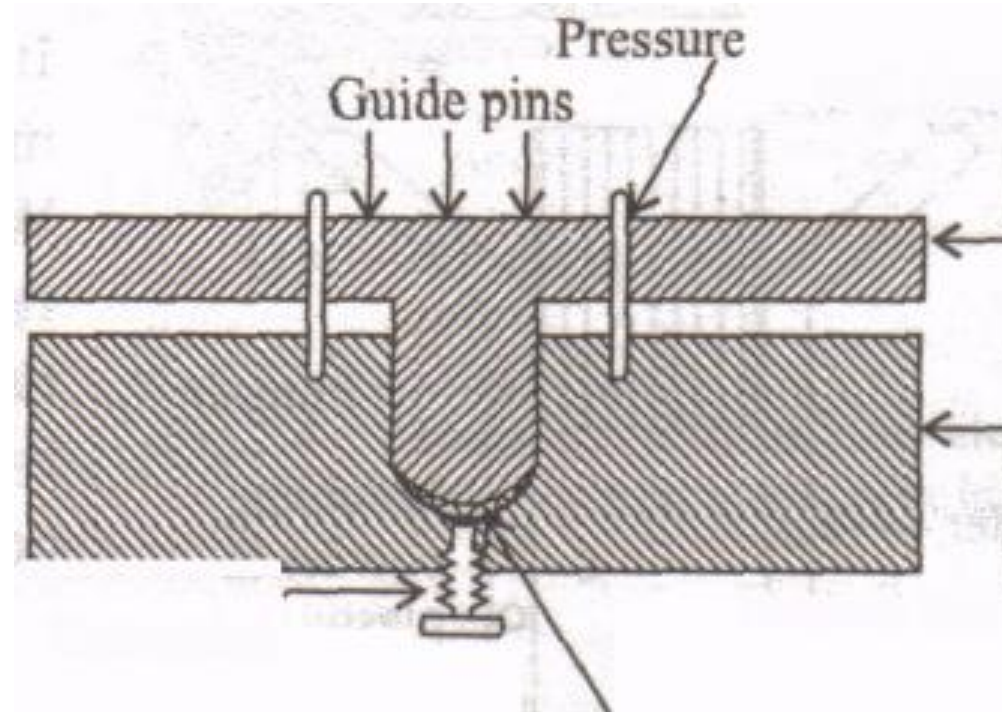
- **The fabrication is the process in which the prepared resins in the form of granules or powder are converted into desired shape by using various machines or moulds. There are many ways by which the compound materials are transformed into familiar finished articles. The basic principle involved in this is partially melting (softening) resinous mass by the application of heat. These softened resins are further compressed in dies, moulds with the help of high pressure to get the desired shape.**

FABRICATION OR MOULDING OF PLASTICS

- **In this case of thermosetting plastics moulded hot 'plastic is ultimately solidified through further [polymerisation, called curing or setting stage while it still in the mould. In the case of thermosoftening plastic, the moulded plastic material is further cooled chilled for solidification of article, thermosoftening plastic material, injection, extrusion, blow moulding, vacuum forming are usually used. For thermosetting compression moulding, transfer moulding are generally employed.**

COMPRESSION MOULDING

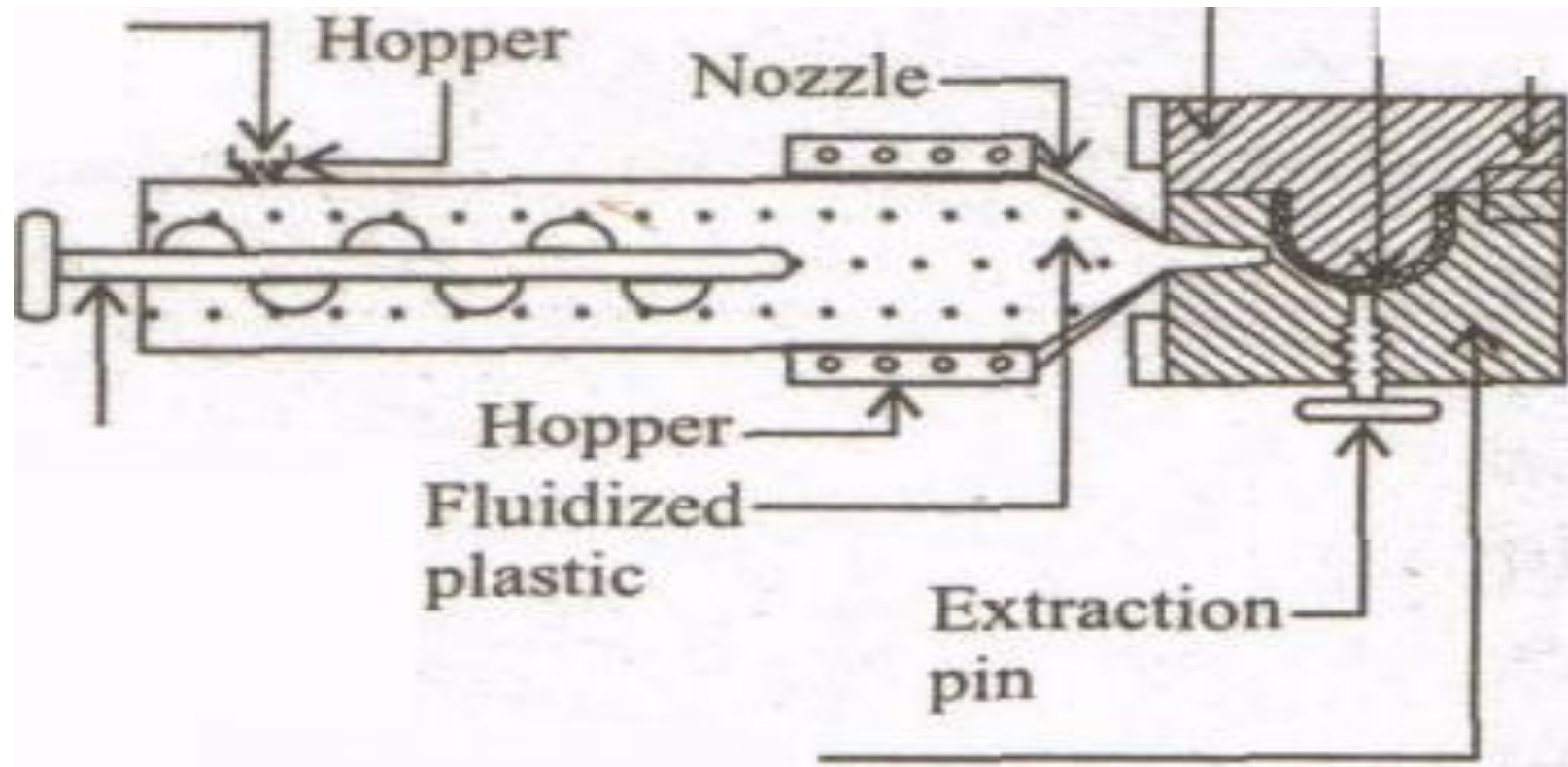
Top moulding part (male die)



COMPRESSION MOULDING

- This process consists of pressing the molten resinous material into the shape by the use of moulds, heat and pressure.
- Predetermined quantity of resin powder or pellets is preheated to about 120 °C before the cavity is filled with it. After charging the two parts of mould are carefully brought together under low pressure. It is then pressed by hydraulic pressure. Pressures of about
- 10,000 p.s.i are used. This pressure and heat make the resin to melt and flow, thereby filling the cavities between the two parts of the mould. Than the mould is kept for the specified time Than curing is done either by heating for thermoseetts or cooling in case of thermosofts

INJECTION MOULDING



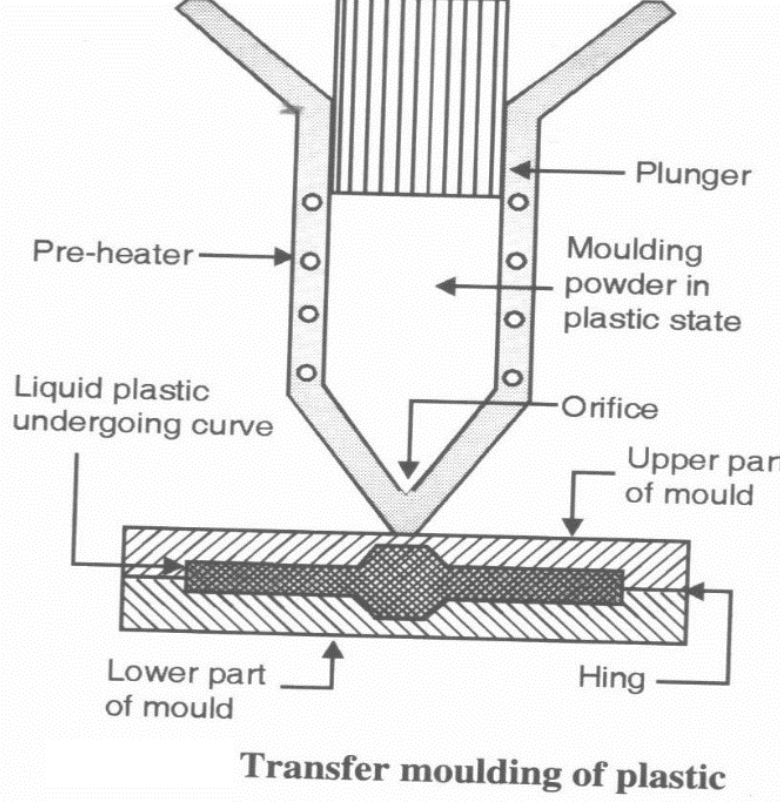
INJECTION MOULDING

- **It is one of the most widely used processes for thermoplastic raw materials into products. It is fundamentally simple and easy to operate and capable of producing a very wide range of industrial and domestic articles**
- **In this process a predetermined quantity of granular or powdered resin is fed into a cylinder from where it is injected at a controlled rate through a nozzle into the tightly locked mould means of a screw arrangement or by piston plunger shown in the Fig.. Pressure upto 1758 kg/cm² used for injections. The mould is kept cold so that the hot plastic cures and become rigid**

INJECTION MOULDING

- **This method is the most widely used for moulding thermoplastics because of high speed production mould cost, very low loss of material and finishing cost. However, there are limitation design of articles to be moulded because many number of cavities cannot be filled simultaneously.**

TRANSFER MOULDING



TRANSFER MOULDING

- **It is a method which uses the principle of injection molding and is used for thermosetting material when relatively intricate designs are required of fabricated products. This transfer moulding is a combination of injection and compression molding, In this molding powdered resins are placed in heated chamber, maintained at a minimum temperature due to which the powdered resins just begins to become plastic. This plastic material is then injected through orifice into the mould by plunger, working at high pressure. Due to which high friction develops at the orifice, the temperature of the material at the of ejection from the orifice rises to such an extent that moulding powder becomes almost liquid, consequently it flows quickly into the mould, it is heated upto the curing temperature. The moulded article is then ejected**

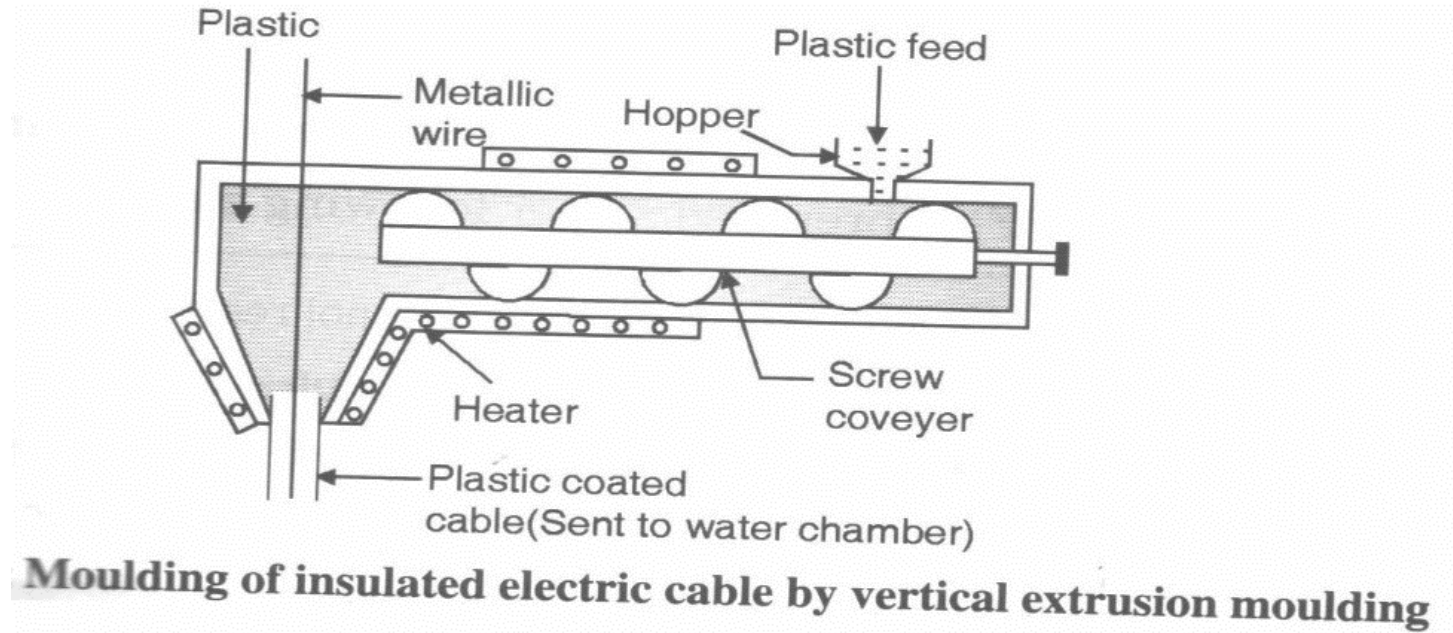
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TRANSFER MOULDING

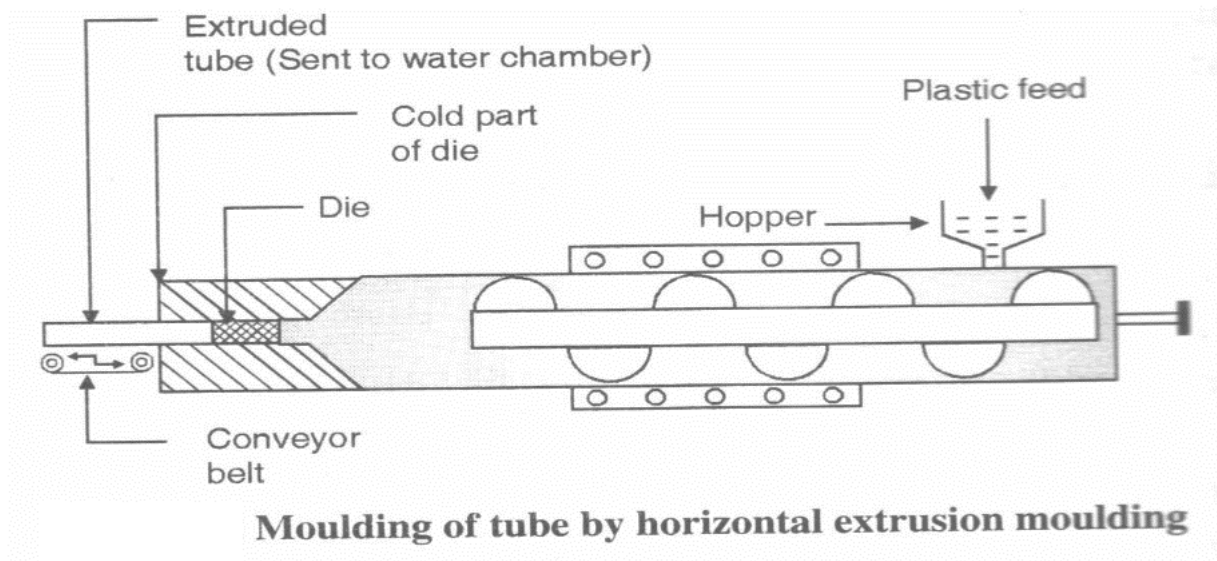
Advantages;

- **1. Intricate shapes not attainable by compression moulding can readily be produced.**
- **2. Article produced is free from flow mark.**
- **3. Even thick pieces cure almost completely and uniformly.**
- **4. Finishing cost of fabricated article is almost entirely eliminated.**
- **5. Blistering is almost eliminated, since air and excluded gases are expelled in the plasticizing chamber itself.**
- **6. Mould cost is less, since it involves very low abrasive action.**
- **7. Fine wires and glass fibres can be inserted into the mould.**

EXTRUSION MOULDING



EXTRUSION MOULDING

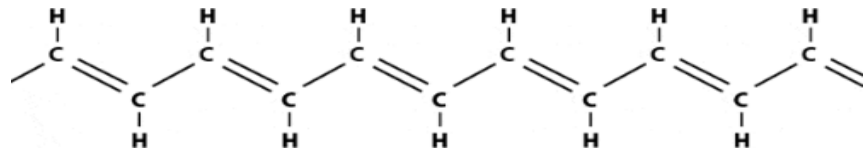


EXTRUSION MOULDING

- It is mainly used for continuous manufacturing articles with uniform cross sectional area of thermoplastic resins. For example tubes, rods, strips, insulated cable materials. In this method dry moulding powder is first fed through hopper into the heated chamber which has a revolving screw. the screw is rotated the molten material is forward through the small orifice of the die to continuous uniform shaped articles. When it leaves the orifice, it is allowed to pass through water for solidification of plastic material.

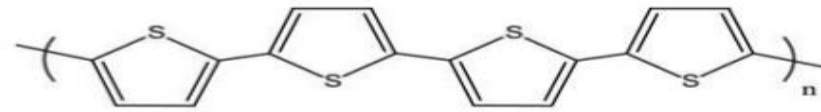
CONDUCTING POLYMERS

- Polymeric materials having conductivities on par with metallic conductors are called as conducting polymers. Polymers having conjugated double bond are conducting in nature due to presence of delocalized pi electrons. Conductivities as high as $1.5 \times 10^7 \text{ ohm}^{-1} \text{ m}^{-1}$.

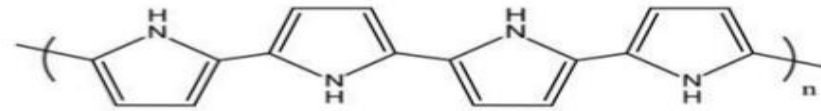


CONDUCTING POLYMERS

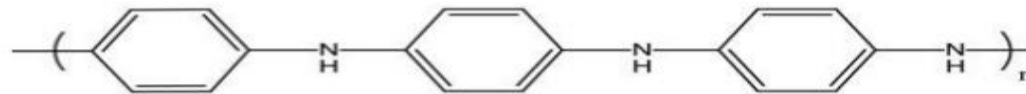
few Common Conducting Polymers



polythiophene

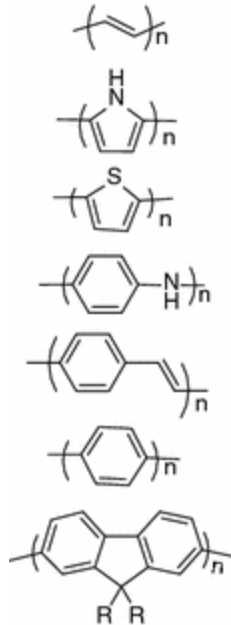


polypyrrole



polyaniline

CONDUCTING POLYMERS



Polyacetylene (PA)

Polypyrrole (PPy)

Polythiophene (PTh)

Polyaniline (PAn)

Poly(p-phenylene vinylene)

Poly(p-phenylene)(PPP)

Polyfluorene (PF)

CONDUCTING POLYMERS

- Conducting polymers are of four types: **1) Intrinsically conducting 2) Doped conducting 3) Extrinsicly conducting 4) Co-ordination conducting polymers**
- **Intrinsically conducting polymers (ICP) or conjugated π -electrons conducting polymer** is a polymer whose backbones or associated groups consist of delocalized electron-pair or residual charge. Such polymers essentially contain conjugated π -electrons backbone which is responsible for electrical charge. In an electric field, conjugated π -electrons of the polymer get excited, thereby can be transported through the solid polymeric material. Overlapping (of conjugated π -electrons) over the entire backbone results in the formation of valence bands as well as conduction bands which extends over the entire polymer molecule. Presence of conjugated π -electron in a polymer increases its conductivity to a larger extent.

CONDUCTING POLYMERS

- Important commercially produced conducting polymers :
- **Polyacetylene polymers .e.g. poly-p-phenylene, polyquinoline, polyphenylene-co-vinylene, poly-m-phenylene sulphide ,etc.**
- **ii) With condensed aromatic rings ,e.g ployaniline, polyanthrylene, polyphenanthrylene,etc.**
- **iii) With aromatic heteroaromatic and conjugated aliphatic units, e.g. polypyrrole, polythiophene, polyazomethine, polybutadienylene ,etc.**

CONDUCTING POLYMERS

- **2) Doped conducting polymers** are obtained by exposing a polymer to a charge transfer agent in gas/solution phase. Conductivity of intrinsically conducting polymers can be increased by creating either positive or negative charge on the polymer backbone by oxidation or reduction.
- A) **p-doping**-In this an intrinsically conducting polymer is treated with lewis acid where oxidation takes place. Common lewis acids are I₂, Br₂ etc
- $2(\text{C}_2\text{H}_2)_n + 3\text{I}_2 \rightarrow 2(\text{C}_2\text{H}_2)_n^+ + 3\text{I}_3^-$

CONDUCTING POLYMERS

- B) **n-doping**--In this an intrinsically conducting polymer is treated with lewis base where oxidation takes place. Common lewis acid are Li,Na etc.
- $-\text{CH}=\text{CH}-\text{CH}=\text{CH}+\text{B} \longrightarrow -\text{CH}=\text{CH}-\overset{\ominus}{\text{C}}\text{H}=\text{CH}$
B+

CONDUCTING POLYMERS

- 3) Extrinsicly conducting polymers are the polymers whose conductivity is due to presence of externally added ingredients. They are of two types;
- A) Conductive element filled polymers - Polymer act as a binder to hold the conducting elements eg carbon black, metal oxide.
- B) Blended conducting polymers - A conventional polymer is blended with conducting polymers.

CONDUCTING POLYMERS

- 4) **Co-ordination conducting polymers**-It is a charge transfer complex containing polymer obtained by combining a metal atom with poly dentate ligand.

Applications of Conducting Polymers

- 1. In rechargeable light weight batteries based on perchlorate doped polyacetylene Li system. These are 10 times stronger than conventional lead storage batteries
- 2. In wiring in aircrafts and aerospace component.
- 3. In transistors and diodes.
- 4. In electromagnetic screening materials
- 5. In photovoltaic devices.
- 6. In molecular wires and switches

Glass Transition Temperature:

- The temperature at which the polymer experiences the transition from rubbery to rigid states is termed the glass transition temperature (T_g). These sequences of events occurs in the reverse order, when a rigid glass at a temperature below T_g is heated.
- Glass transition temperatures : Glass transition temperature is important parameters relative to applications of polymers. It define respectively, the upper and lower temperature limits for numerous applications, especially for semi crystalline polymers. Moreover, they also influence the fabrication and processing procedures for polymers and polymer-matrix composites.

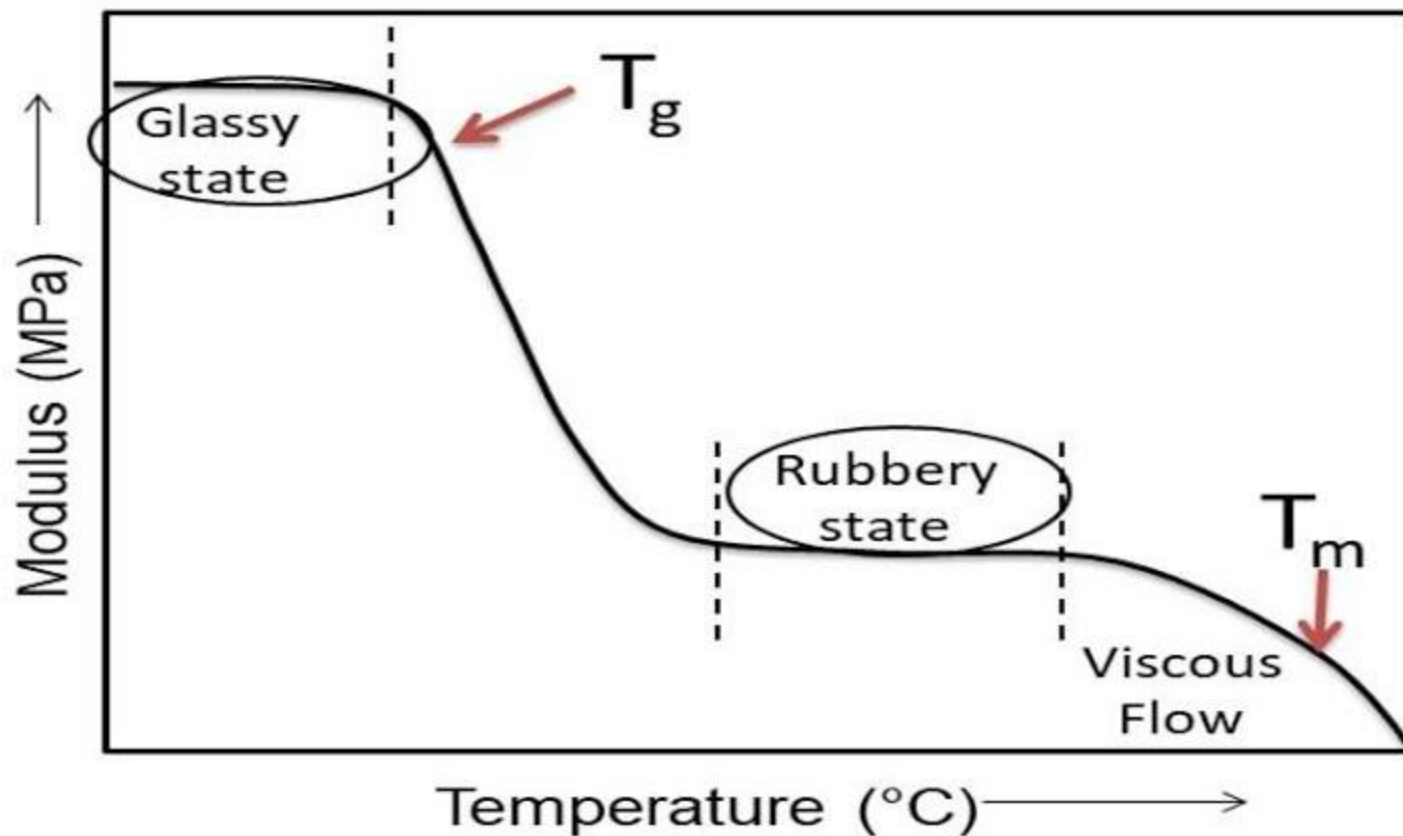
Glass Transition Temperature (T_g)

The temperature at which the polymers undergo the transition from glassy to rubbery state

Below T_g : Polymers are hard and brittle like glass, due to lack of mobility

Above T_g : Polymers are soft and flexible like rubber due to some mobility

Above T_g : Physical and mechanical properties of polymer change



Cooperative segmental mobility: mobility of tens to a few hundreds of repeat units of a polymer

Factors influencing glass transition temperature:

- Upon heating through the glass transition temperature, the amorphous solid polymers transform from a rigid mass to a rubbery state and the molecules which are virtually frozen in position below T_g begin to experience rotational and translational motions above T_g .
- 1. The presence of bulky side groups (this may be confirmed from Table 1, the respective values for polypropylene and polystyrene are -18°C and 100°C).
- 2. Polar side atoms or groups of atoms {this may be confirmed by comparing T_g values for polyvinyl chloride and polypropylene (87°C versus -18°C) }.
- 3. Double –chain bonds and aromatic chain groups which tend to stiffen the molecular backbone
- 4. Increasing the molecular weight also tends to raise the glass transition temperature

Factors influencing glass transition temperature:

- 5. A small amount of branching will tend to lower T_g ; on the other hand a high density of branches reduces chain mobility and elevates the glass transition temperature .
- 6. As crystallinity increases T_g also increases.
- 7. As cross linking increases T_g also increases
- 8 Effective Plasticizers – Addition of plasticizer decreases T_g of the polymer .

Viscoelasticity of Polymers:

- An amorphous polymers behave like glass at lower temperature ,a rubbery solid at intermediate temperature and a viscous liquid at higher temperature .For intermediate temperature the state is rubbery solid .That exhibits the combined properties of two extremes of solid and liquid ,the condition is called as viscoelasticity .This material exhibits both viscous and elastic characteristics .
- Viscous material like honey resist strain linearly with time when stress is applied .Elastic materials strain instantaneously when stretched and quickly return to their original state once the stress is removed.

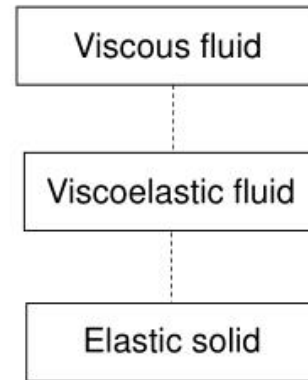
Viscoelasticity of Polymers:

Introduction to Viscoelasticity

All viscous liquids deform continuously under the influence of an applied stress – They exhibit viscous behavior.

Solids deform under an applied stress, but soon reach a position of equilibrium, in which further deformation ceases. If the stress is removed they recover their original shape – They exhibit elastic behavior.

Viscoelastic fluids can exhibit both viscosity and elasticity, depending on the conditions.



Polymers display VISCOELASTIC properties

Viscoelasticity of Polymers:

- Polymer show a behavior in between elastic solids and flowy liquids. These properties depend on temperature and time duration .As elastic solids restore shape after removal of external forces ,while in case of viscous liquids there is no definite shape hence when external forces are applied it flows out irreversibly Viscoelastic materials have elements of both these properties .Viscoelasticity is molecular rearrangement. Under stress polymer chains change position (creep) and polymer remain in solid state .

Viscoelasticity of Polymers

Viscoelastic Behavior

Viscoelasticity is observed in materials that exhibit both a linear elastic response and a time-dependent viscous response simultaneously under applied load

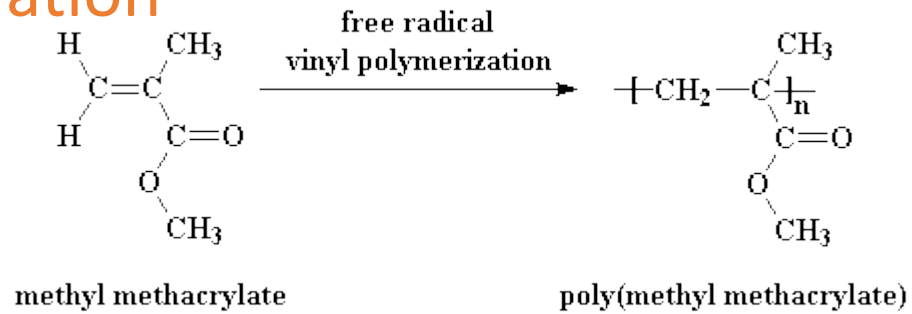
This effect is most commonly seen in polymers at temperatures between T_g and T_m .

Polyurethane foams and gels have a T_g of $\sim 20^\circ\text{C}$, allowing them to deform easily at room temperature.



Poly methyl meth acrylate(PMMA)

- Preparation



Poly methyl meth acrylate(PMMA)

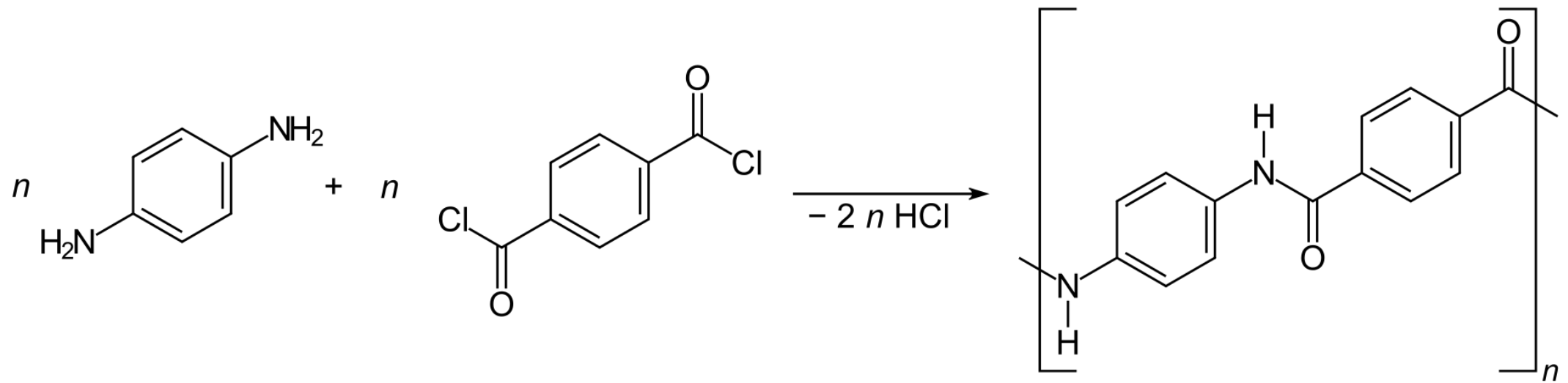
- Properties-

- 1. It is transparent and having good optical properties.
- 2. Softening temperature is 130-140°C.
- 3. It has low scratch resistance.

- Uses-

- 1. It is used for making lenses, artificial eyes and optical parts of instruments.
- 2. It is used for making window glasses.
- 3. It is used for making scientific models.

Kevlar



Kevlar

- Properties-
- 1. Exceptionally strong, 5 times stronger than steel and 10 times stronger than aluminium.
- 2. It is highly stable and flexible.
- 3. It is stable at -196°C
- 4. It degrades by UV radiation.

Kevlar

- Uses-
- 1.It is used in aerospace and aircraft industries.
- 2.It is used for making car parts such as tyres and brakes.
- 3.It is used for preparation of ropes,cables.protective cloths,helmets etc.

Molecular weight of polymers

- It is very important phenomena, since physical properties of macro molecules depends on M.W. Higher the M.W. , tougher the polymer. The M.W and its distribution decides the viscous and elastic behavior of molten molecule.
- Methods of M.W. Determination-
- (1) Number -average M.W.
- (2) Weight average M.W.

Number average M.W.

Number-average molecular weight

- The number average molecular weight is not too difficult to understand.
- It is just the total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample

$$M_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum w_i / M_i}$$

Where,

n = Moles of molecules ($n_1 + n_2 + n_3 + \dots + n_i$) i.e. weight (w)/molecular weight (M)

w = Weight of individual molecules ($w_1 + w_2 + w_3 + \dots + w_i$)

M = Molecular weight of each molecules

Weight average M.W.

$$\overline{M}_w = \frac{\sum_{i=1}^N N_i M_i^2}{\sum_{i=1}^N N_i M_i} = \frac{\sum_{i=1}^N w_i M_i}{\sum_{i=1}^N w_i} = \sum_{i=1}^N w_i M_i$$

Polydispersity Index

- It is the ratio of weight average M.W and number average M.W.
ie M_w/M_n
- If value of polydispersity index is 1, polymer is identified as monodispersed, where consisting molecules have identical mass. If value is 2, polymer is identified as polydispersed, where consisting molecules have different mass.