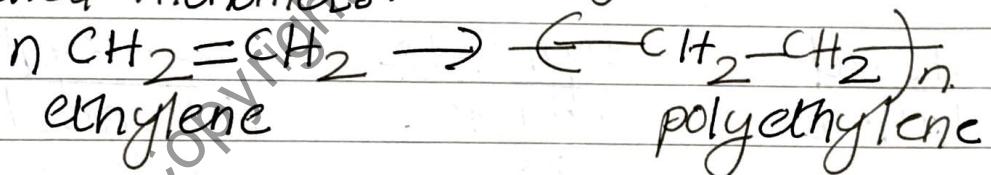


Polymers

When life started on Earth four basic elements C, H, O, N combined to form compounds like CH_4 , NH_3 , CO_2 , O_2 which further combined to form the polymer i.e protein. This was the basic unit which further ultimately resulted in bigger form of life i.e we human being. As man's life progressed he came across other polymers like wood, cellulose, starch etc. Today his wanton need have exceeded so much that he has synthesised many polymers to meet this needs.

Polymer: The word polymer is derived from two Greek words poly (many) mers (part or units). A polymer is a large molecule which is formed by repeated linking of small molecules called monomers.

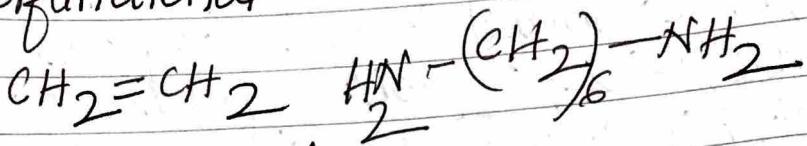


Degree of polymerisation: The number of repeating units in the chain so formed called degree of polymerisation

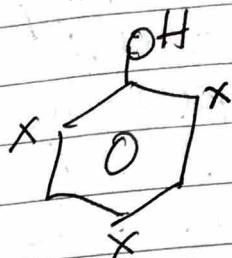
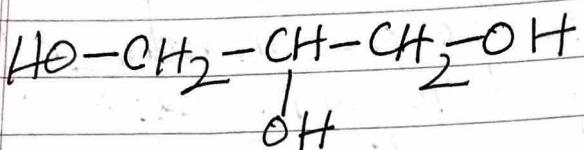
High polymers: have very high degree of polymerisation (> 100 monomers) hence they have high degree

Functionality: For a substance to act as monomer it must at least have two reactive sites or bonding sites. The number of bonding sites in a monomer, is referred to as its functionality.

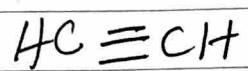
Bifunctional



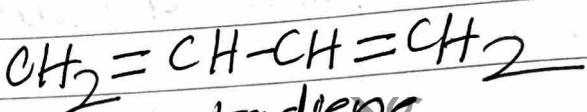
Terfunctional



Tetrafunctional



Acetylene



Butadiene

Classification

① On basis of Origin

Natural

cellulose

Rubber

Proteins

Synthetic

polyester

silicones

Nylon

Semisynthetic

vulcanised rubber

cellulose nitrate

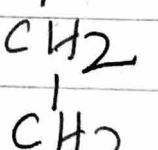
② Homopolymers and co-polymers

Homopolymer - Monomer same

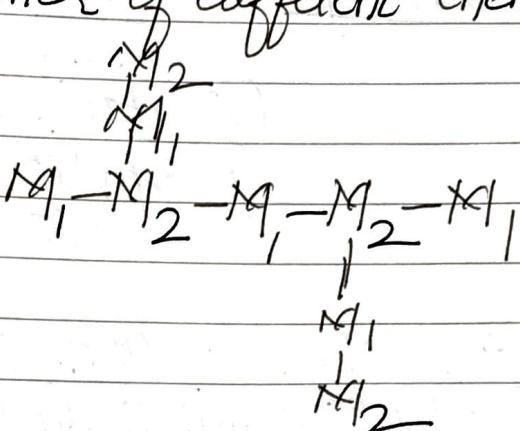
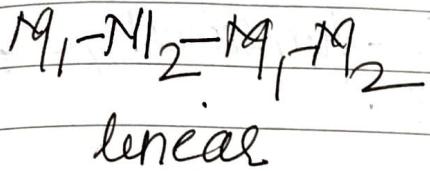


Homopolymer  linear $(\text{CH}_2-\text{CH}_2)_n$

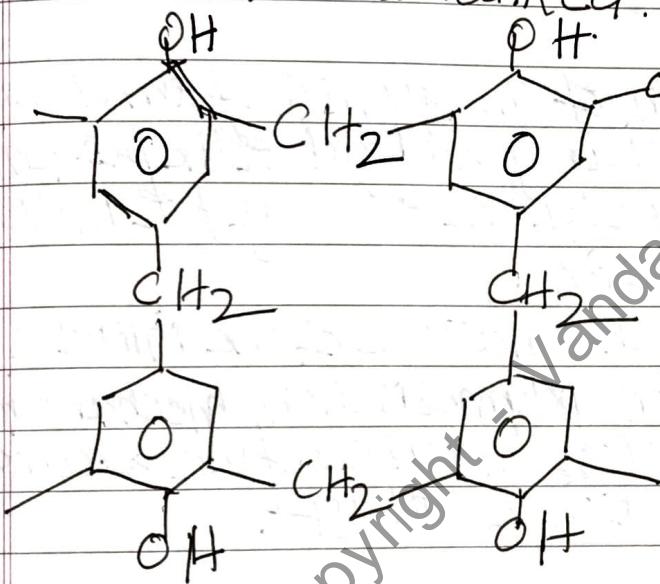
Blended. $\text{CH}_2-\underset{\text{CH}_2}{\underset{|}{\text{CH}}}-\text{CH}_2$



co-polymers - Monomer of different chemical structure



Crossed linked.



Both homopolymer

and co-polymers
form crosslinked
polymers.

3. Organic and Inorganic polymers

A polymer whose backbone chain is essentially made of carbon atoms is termed as organic polymer.

eg - polyethylene, Ureaformaldehyde
Inorganic polymers no carbon atom in their backbone chain eg - polysilane, silicones.

4. Thermoplastic and Thermosetting plastics

Depending on its ultimate form and use, a polymer can be classified as plastic, elastomer, fibre, a liquid resin.

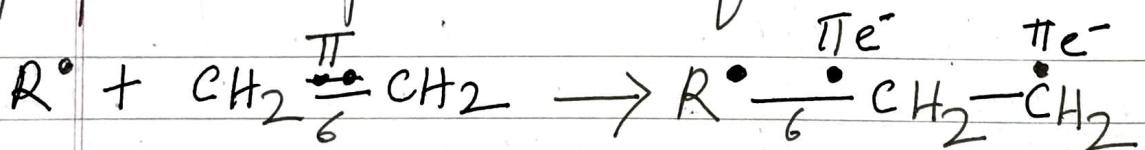
- 6- Tacticity
- (1) Isotactic - functional group on the same side
 - (2) atatic - functional group random
 - (3) Syndiotactic - functional group alternate.

Addition Polymerisation : is a reaction that yields a product which is an exact multiple of original molecule.

Initiation - Application of energy in the form of heat, light, pressure, ionising radical or the presence of catalyst is usually necessary for initiating the chain polymerisation.

Depending upon the nature of the initiator used the different addition polymerisation mechanisms are possible. The initiator may be a free radical ion or co-ordination catalyst.

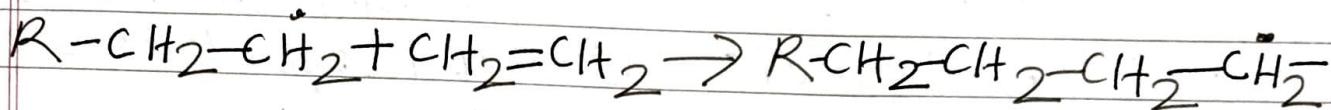
Initiators (free radical) - A free radical is a highly reactive species and can attack any molecule, either has a lone electron or is prepared to part with one of its electron.



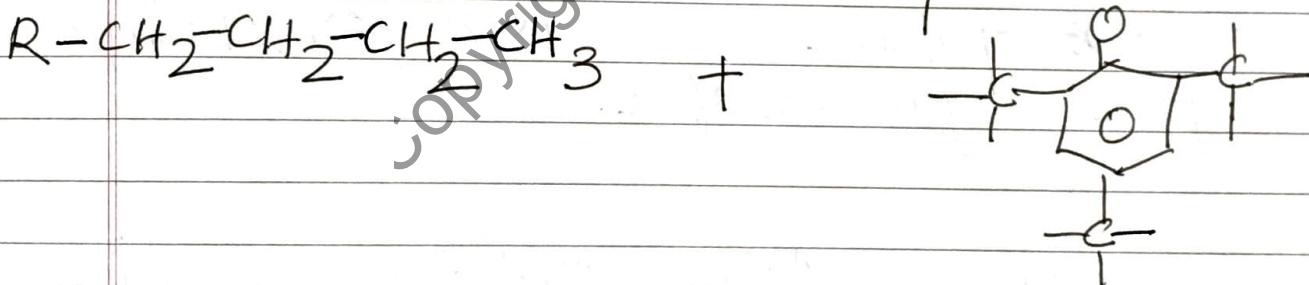
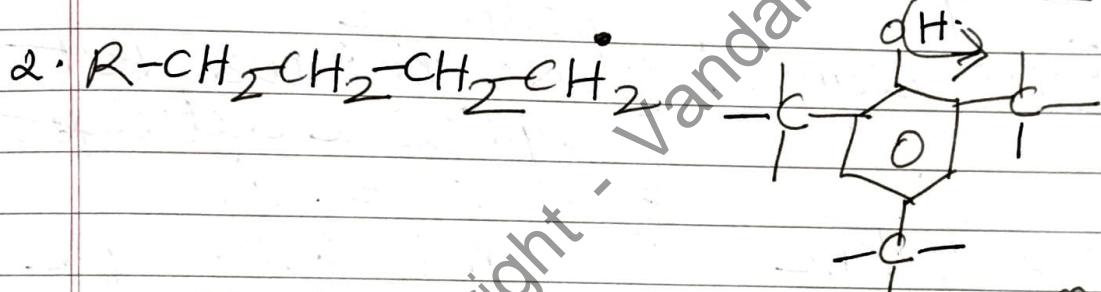
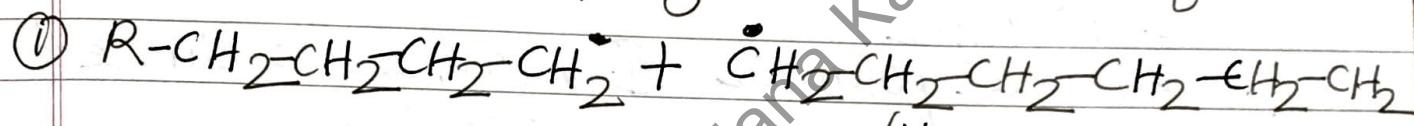
The π bond in carbon atom has two π electrons. The free radical takes one electron from it and forms a σ bond with carbon. This leaves one π electron on 'C' atom, the free radical radical site is now shifted from the initiator to the monomer unit.

This process of electron pair coming down from its π energy level to σ level is associated with release in energy (exothermic.)

2. Propagation: In propagation the radical site at the first monomer unit attack the double bond of fresh monomer molecule.



3. Termination ① coupling ② chain transfer.



Condensation or Step polymerisation: a reaction occurring between two simple polar group containing monomers monomers ($-OH$, $-NH_2$, $-COOH$, $-CHO$ etc) with the formation of polymer and elimination of small molecules like water, HCl etc.

Important group taking part in condensation polymerisation are amino, amido, aldehyde, carboxyl, hydroxyl etc. A monomer must

contain two or more functional groups.

Difference between Addition polymerisation
and condensation polymerisation

Addition

1. unsaturated monomers

2. NO by product

3. Quick formation of polymers

4. linear polymers

5. Initiators required

6. exothermic

7. eg polyethylene
polypropylene
polymethylmethacrylate.

Condensation

① Two molecular species having functional group

② By product always formed.

③ slow (Stepwise)

④ mostly crosslinked polymer

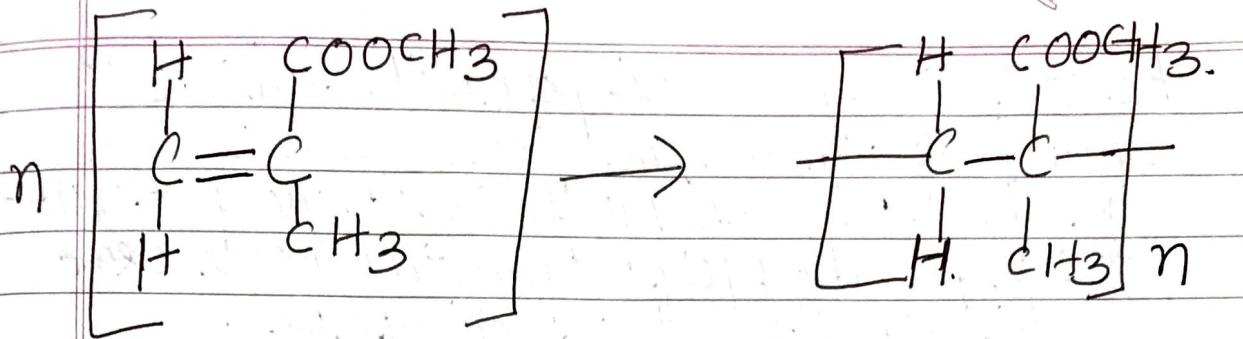
⑤ NO initiators, but requires a catalyst

⑥ endothermic

⑦ phenol formaldehyde
urea formaldehyde

Poly(methyl methacrylate) (PMMA) or lucite or Plexiglass.

Preparation : It is obtained by polymerisation of methyl methacrylate (ester of methyl acrylic acid $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$) in presence of acetyl peroxide or hydrogen peroxide. It is an acrylic polymer.



methyl methacrylate
MMA

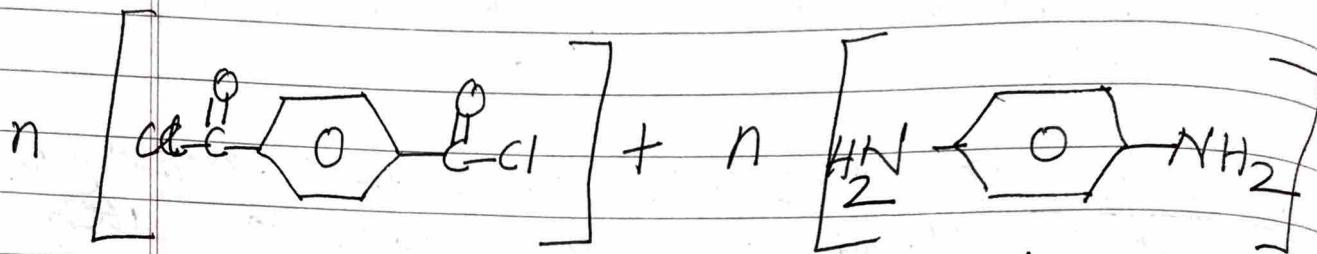
polymethylmethacrylate

- Properties
 - ① lighter than glass (density - half of glass)
 - ② shatter proof
 - ③ softer and easier to scratch than glass
 - ④ Transmits more light than glass (92% of visible light)
 - ⑤ Does not filter UV light (may be coated with UV film.)
 - ⑥ More transparent than glass, so window can be made thicker

- Uses
 - ① safety glass - windows for aquariums, underwater restaurants.
 - ② Used as bone cement
 - ③ used in pacemakers
 - ④ dentures
 - ⑤ Artificial eye lenses used for cataract surgery
 - ⑥ Acrylic paints
 - ⑦ Black light tattoo ink (97.5% PMA, 2.5% fluorescent dye)

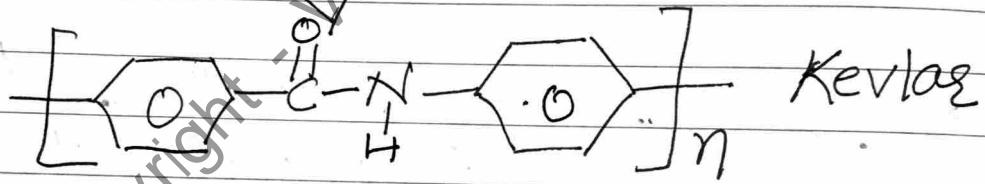
The link received USFDA approval in 1995 for use in animals, plants and fish for the purpose of tracking migration growth patterns, breeding habits etc.

Kevlar is an aromatic polyamide similar to nylons, but with benzene rings rather than aliphatic chains linked to the amide group CONH- . It is prepared by polycondensation between ~~one~~ aromatic dichloride and aromatic diamines.



Jerephthalic acid dichloride

p-amino aniline
(1,4-diamino benzene)

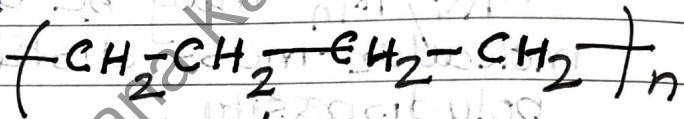
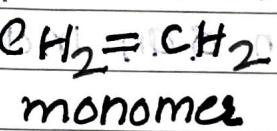


Properties: ① low thermal shrinkage ② lightweight
 ③ flexible ④ comfortable ⑤ low electrical conductivity
 ⑥ high toughness ⑦ high cut resistance ⑧ high chemical resistance
 ⑨ flame resistance

Uses: ① Reinforced in car tyres ② used to make ropes ③ reinforced in aircraft wings and bullet proof vests ④ sports equipment ⑤ automotive parts ⑥ fire resistant materials

Molecular weight

- Repetitive units make up a polymer
- These repetitive units were originally the monomer molecules.
- When polymer chains form their lengths and thus their weight differ.
- It is important to be able to characterize the polymer structure.
- Determining the weight-average molecular weight or the number-average molecular weight is a part of any polymer characterization.



(One molecule)

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

Polymers are mixture of molecule of different molecular masses.

Num-average molecular weight: is defined as total mass (weight) of all the molecules in the polymer sample divided by the total number of molecules present.

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

N_i is the number of molecules of mass M_i ;

① A polymer has following molar mass distribution

$$n_1 = 50 \quad m_1 = 5000$$

$$n_2 = 75 \quad m_2 = 6000$$

$$\bar{M}_n = \frac{\sum N_i M_i}{N_i} = \frac{50 \times 5000 + 75 \times 6000}{50 + 75}$$

$$= 5600 \text{ gm. } \cancel{\text{per mole}}$$

② Consider a polymer, which contains four molecular weight polymers in different number

$$n_1 = 2$$

$$m_1 = 10$$

$$n_2 = 4$$

$$m_2 = 20$$

$$n_3 = 6$$

$$m_3 = 100$$

$$n_4 = 3$$

$$m_4 = 250$$

$$\bar{M}_n = \frac{\sum N_i M_i}{N_i} = \frac{2 \times 10 + 4 \times 20 + 6 \times 100 + 3 \times 250}{2 + 4 + 6 + 3}$$

$$= \frac{1450}{15} = 96.67 \text{ g}$$

weight average molecular

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

$$n_1 = 50 \quad m_1 = 5000$$

$$n_2 = 75 \quad m_2 = 6000$$

$$\textcircled{1} \quad M_w = \frac{50(5000)^2 + 75(6000)^2}{50 \times 5000 + 75 \times 6000}$$

$$5642 \text{ gm.}$$

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

$$\begin{array}{ll} n_1 = 2 & m_1 = 10 \\ n_2 = 4 & m_2 = 20 \\ n_3 = 6 & m_3 = 100 \\ n_4 = 3 & m_4 = 250 \end{array}$$

$$\begin{aligned} \bar{M}_w &= \frac{(2 \times 10^2) + (4 \times 20^2) + (6 \times 100^2) + (3 \times 250^2)}{(2 \times 10) + (4 \times 20) + (6 \times 100) + (3 \times 250)} \\ &= \frac{249300}{1450} = 17139 \text{ gm.} \end{aligned}$$

Assignment - 6

If polymer sample has population as.

$$\begin{array}{ll} n_1 = 10 & m_1 = 5000 \\ n_2 = 20 & m_2 = 7500 \\ n_3 = 25 & m_3 = 10,000 \\ n_4 = 25 & m_4 = 15,000 \\ n_5 = 25 & m_5 = 20,000 \\ n_6 = 05 & m_6 = 25,000 \end{array}$$

$$\text{Ans. } \bar{M}_n = 13,000 \quad \bar{M}_w = 15,480$$

Molecular weight and Molecular weight distribution determines the properties of polymers

High molecular weight - Increases how far the material can stretch, becomes impact resistant, chemical resistant more, viscosity increases,
 Low molecular weight - less stronger, easy to flow, more crystalline.

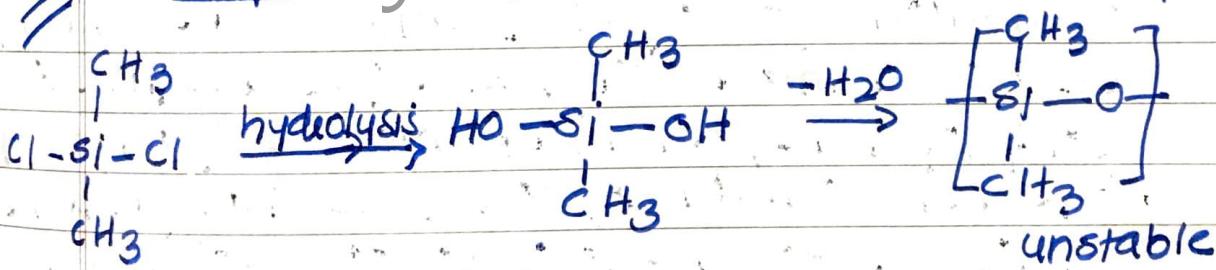
Viscoelasticity

We live with an idea that materials are either solid, liquid or gas. Yet there are many materials that can not be so easily classified. These materials can behave as a fluid but also as an elastic solid. We call these materials viscoelastic materials because, at the same time they have both fluid (viscous) properties and elastic properties.

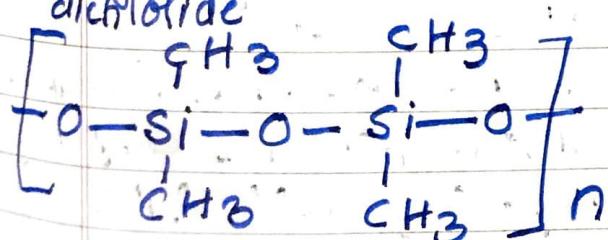
According to chemists and physicists, a fluid is any substance that has fixed shape and yields easily to external pressure.

Viscosity is the key property of fluids.

1. In Newtonian fluids viscosity varies with temperature (eg - Water, Honey, molasses, molten glass)
2. In Non Newtonian fluids viscosity varies with temperature and on the force applied on it (corn starch solution, silly putty)
silly putty behaves like viscous fluid at high temperature, elastic solid at low temperature.



Dimethyl silicon dichloride

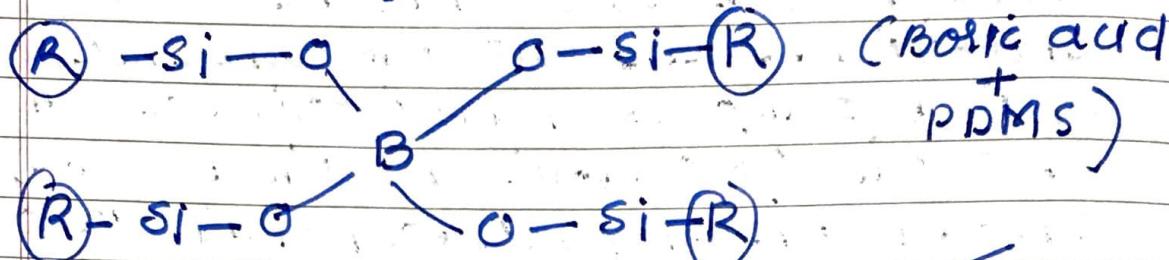


Polydimethyl siloxane

The polydimethylsiloxanes in silly putty end in $\text{Si}-\text{OH}$ groups. The basic acid reversibly reacts with these to form short lived crosslinks between polymer chains. Shear deformation gives these crosslinks time to break and reform, allowing viscous flow.

but rapid forceful deformation does not, so elastic behaviour is instead seen.

((R- rest of the PDM's polymer chain).



Glass transition temperature, (T_g)

is the point below which an amorphous solid (such as glass, polymers, rubbers) goes from being ductile to brittle. For most materials, this temperature is so high or so low that it is not easily observed.

The T_g of window glass is 564 degrees and that of rubber is -72 degrees.

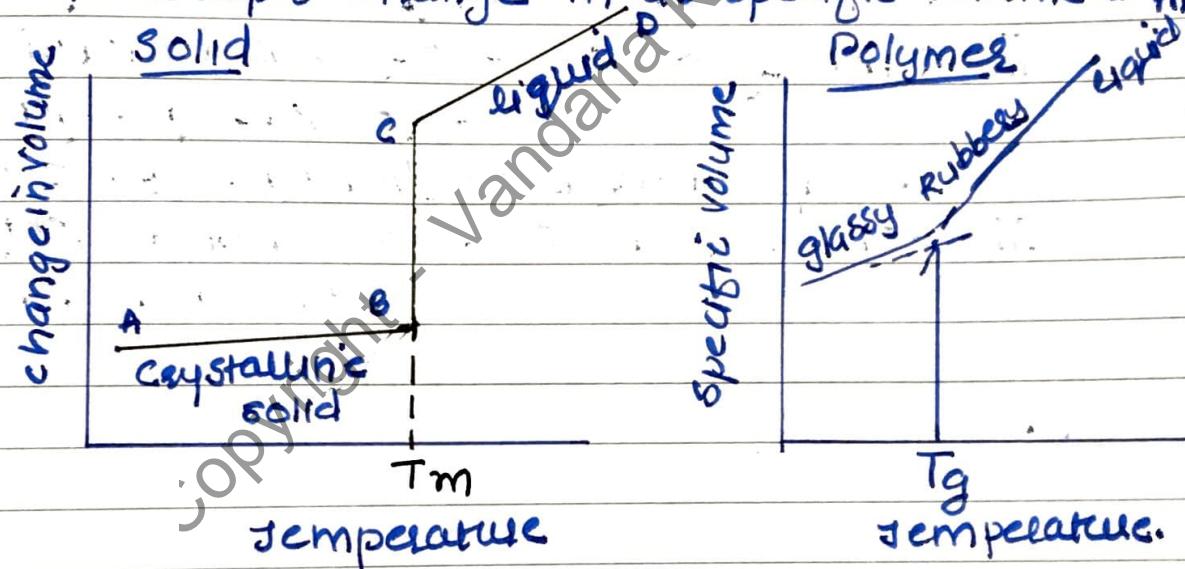
But many plastics exhibit their transition at everyday temperatures and can be frozen into brittleness. One example is polypropylene, an inexpensive material often used in containers, toys, recycling bins has a T_g of between -20 °C to 0 °C, so it can easily lose its molecular mobility and become shatter prone on a winter day.

This happens because there is temperature boundary for all amorphous polymers and many semi-crystalline polymers. Only above which the substance remains soft, flexible and rubbery and below which it is hard.

brittle and glassy. The temperature below which it is hard and above which it is soft is called glass transition temperature.

The hard brittle state is known as the glassy state. The soft flexible state as rubbery or viscoelastic state. On further heating the polymer (if it is linear) becomes highly viscous liquid and starts flowing, this is termed as viscofluid state.

If we take a crystalline solid and measure its volume change with temperature, we will see an abrupt change in its specific volume at T_m .



Let us take three polymer samples of same chemical structure, but different crystallinity

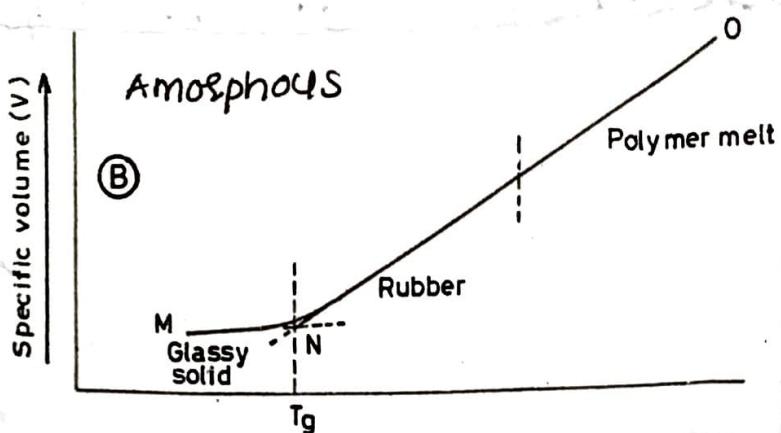
- ① Amorphous polymer
- ② Semi crystalline polymer
- ③ semi crystalline polymers

15

Segmental mobility - some part of polymer molecule moves.

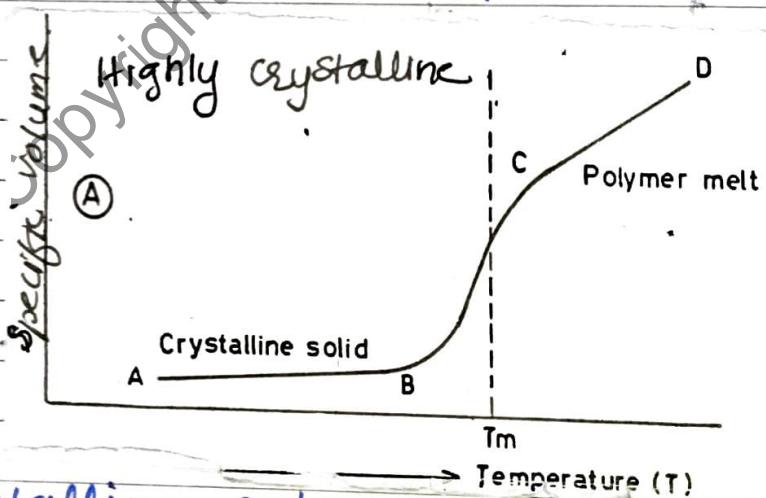
Molecular mobility - entire molecule moves.

①

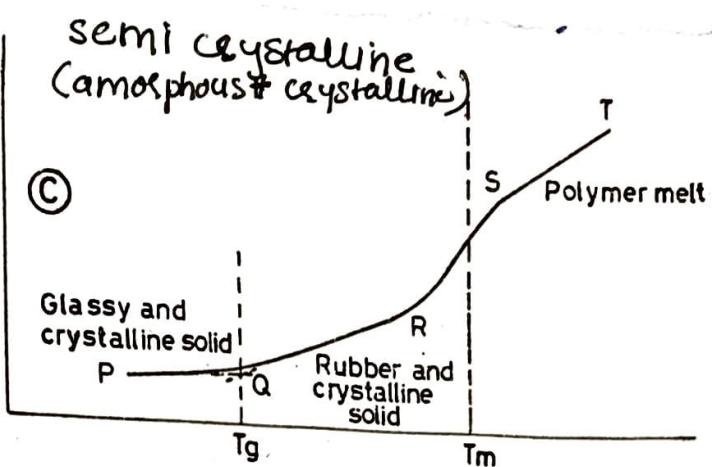


- i Low temp - glassy state - No segmental mobility
No molecular mobility
on heating further
- ii Rubbery state - segmental mobility
No molecular mobility
Temperature is further increase it flows.
- iii Polymer melt - segmental mobility
molecular mobility

Q.



Crystalline polymer segmental mobility and molecular mobility sets in almost abruptly the polymer passes from a solid state to a liquid state. T_m



semi crystalline polymers (partially crystalline and partially amorphous) hence posses both T_g and T_m .

factors influencing T_g

- ① Molecular weight increase $T_g \uparrow$
- ② Cross linking increase $T_g \uparrow$
- ③ Presence of bulky group $T_g \uparrow$
- ④ Addition of plasticizer $T_g \downarrow$

significance T_m and T_g are important parameters relative to application of polymers. They define the lower and upper temperature limits for various applications. They also influence the fabrication and processing procedures for polymers.

Advance Polymers Materials.

Conducting Polymers Most polymeric materials are poor conductors of electricity because of the non-availability of large number of free electrons in the conduction process.

Polymeric materials have been synthesized which possess electrical conductivities as par with metallic conductors such polymers are called conducting polymers.

Types of conducting polymers.

1. Intrinsically conducting polymers or conjugated π electrons conducting polymers
It is a polymer whose backbone of associated groups consist of delocalised electron pair or residual charge (conjugated π electrons) which is responsible for electrical charge. In an electric field, conjugated π electrons get excited, and thereby can be transported through the solid polymeric material.
eg. polyacetylene, polyaniline, poly-p-phenylene

Types of conducting Polymers

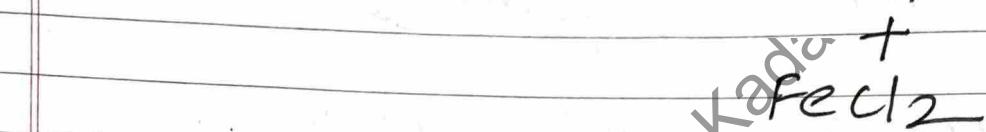
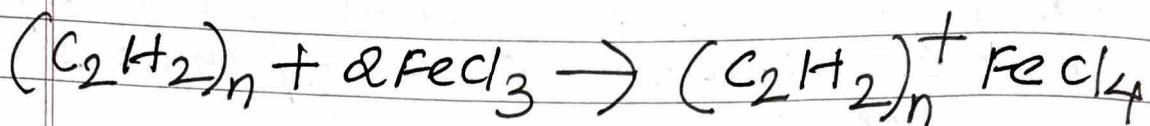
- + Intrinsically conducting polymer of
2. Doped conducting polymer is obtained by exposing a polymer to a charge transfer agent in either gas phase or in solution.

Intrinsically conducting polymer possess low conductivity, but they possess low ionisation potential and high electron affinity. so they can be

easily oxidised or reduced. The technique is called doping.

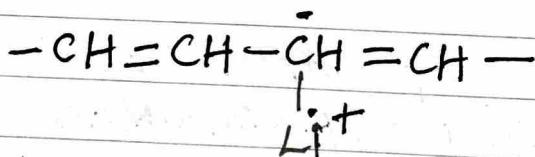
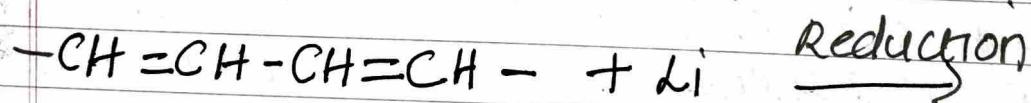
P-doping involves treating an intrinsic conducting polymer with Lewis acid, thereby oxidation process takes place and positive charge on the polymer backbone are created.

e.g. P-dopant I_2, Br_2, AsF_5, PF_6 etc



N-doping: involves treating an intrinsically conducting polymer with a Lewis base, thereby reduction process takes place and negative charge on the polymer backbone are created.

e.g. N-dopant - Li, Na, Ca



Extrinsically conducting polymers: are those polymers whose conductivity is due to the presence of externally added ingredient in them.

i. conductive element filled polymers: is a

resin or polymer filled with conducting element such as carbon black, metallic fillers, metal oxide etc. In this polymer acts like a binder holding the conductive element together in the solid entity.

(1) Blended conducting polymers - is product obtained by blending a conventional polymer with conducting polymer.

Applications:

- (1) In rechargeable light weight batteries based on perchlorate doped polyacetylene-lithium system. These are 10 times lighter than conventional lead storage batteries. (Another example Polypprole-lithium)
- (2) In optically display devices based on polythiophene. When the structure is electrically biased, the optical density of the film changes i.e its colour changes. Such electrochromic system produced coloured display with faster switching time and better viewing than conventional LED.
- (3) In wiring in aircrafts and aerospace components
- (4) In telecommunication System
- (5) antistatic coating for clothing
- (6) In molecular wires and molecular switch.
- (7) In photo voltaic devices.
- (8) Solar cells - low cost, flexible, but poor efficiency
- (9) Printed circuit Boards: used in electrical and electronic instruments. They contain copper coated epoxy resin which are expensive. But polymer sheets covered with conducting polymers are inexpensive and better adhesive properties.
- (10) Artificial intelligent materials = (Smart materials). The interesting aspect of these materials is that they can remember configuration and can confirm when exactly same stimulus is given. Used in generating passcodes where high security is required.

Plastics or resins are of two types.

Thermoplastic

Thermosetting resins

Thermoplastic Thermo softening plastics are those which don't undergo any chemical change during moulding but which can be softened on heating and harden on cooling reversibly. Thus they soften on heating and on cooling regain their original rigidity and hardness.

The hardness of such plastic is temporary property, subjected to rise and fall of temperature.

The molecular weight or chemical structure are not changed during heating. (only secondary bonds between the individual molecular chain are broken on heating)

They are weak and soft as compared to thermosetting plastics

They have low molecular weight as compared to thermosetting plastics

They are soluble in organic solvent because of weak intermolecular forces between the molecules.

Examples. Polyethylene, polypropylene PMMA

Thermosetting: These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and become infusible. These cannot be reused.

They are formed by condensation polymerisation. The chemical structure of these plastics is somewhat three dimensional.

They have high molecular weight.

when these material are moulded crosslinking is formed between the long chain leading to the formation of mesh like structure (These are strong covalent bond) Hence it is hard, tough brittle and non swelling.

The strength of these bonds are retain even on heating and hence they cannot be softened or remoulded or reclaimed once they are cured.

Example - urea formaldehyde, phenol formaldehyde

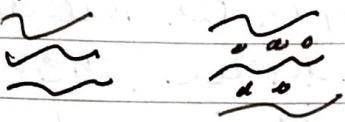
Compounding of plastics - The high polymer material is usually mixed with 4 to 10 ingredients which imparts some useful function during moulding to the finished product. This is known as compounding

1. Resin : They are the basic binding material which holds the other constituents together. They may be thermosoftening or thermosetting resin. Depending on the type of resin the moulding operation is decided. Thermosetting are usually provided as linear polymers, they undergo crosslinking only at the time of curing.

2. Plasticizers - It is added to increase the plasticity and flexibility. Plasticizers when added occupy the spaces in between the molecules there by decreasing the intermolecular attraction imparting free movement to the molecules. Increasing flexibility and plasticity.

eg - Vegetable oils, Camphor, tricresyl phosphate (added only to thermosoftening plastics)

Q. why plasticisers are added during moulding



3. Fillers are added to reduce cost give opacity, better hardness, increase tensile strength. Some time fillers impart special property.

Ba salts - plastics impervious to X-rays

Carborundum - hardness.

quartz, mica

Asbestos - provide heat, corrosion resistance

Other fillers - wood flour, clay, talc, husk carbon black etc.

Added upto 50% of the total moulding material.

4. Lubricant - waxes, oils, soaps etc. glossy finish and plastic material do not stick to the mould.

5. Catalyst or accelerators : are added in cases of thermosetting plastics. So that the cross linking of the polymer takes place during moulding.

6. Stabilizers - During the process of moulding certain polymer decompose and decolorise at the moulding temperature. Therefore stabilizers are added to give thermal stability.

opaque moulding : Salts of lead, white lead red lead.

Transperant moulding - stearates of lead, cadmium and barium.

7. Colouring materials: To make the final product more appealing.
eg - organic dye, inorganic pigments.

Q. Explain any three moulding constituent of plastics

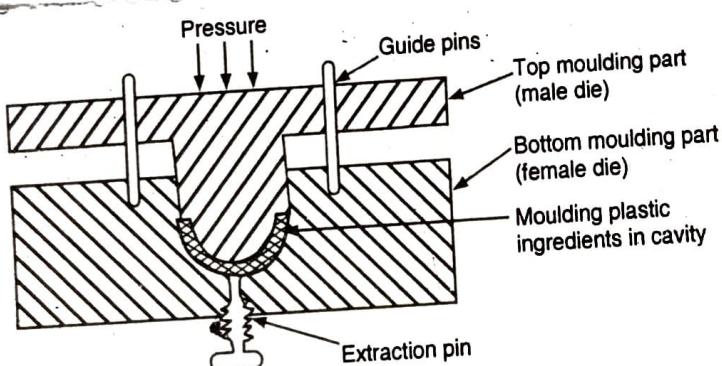
Q. what are plastics? write their main constituents. write the functions and examples of each constituent.

Fabrication of polymers

Fabrication or moulding is defined as giving desired shape to the plastic. Depending on the type of plastic we have different fabrication method.

- ① compression moulding
- ② transfer moulding
- ③ Extrusion moulding
- ④ Injection moulding

Compression Moulding:



This method is applied to both thermoplastic and thermosetting resins. But most widely used for thermosetting plastics.

In this method, the raw materials of right composition (charge) is placed in the mould and the mould is carefully closed under low pressure. Then high pressure of order of 100 to 500 kg/cm² and temperature 100°C - 180°C are applied to complete the curing process. (If used for thermosoftening, the mould should be cooled and opened.)

Examples - 3 pin mains plugs, Handles of electric iron, toilet seats, electrical switches, sockets screws on bottle tops.

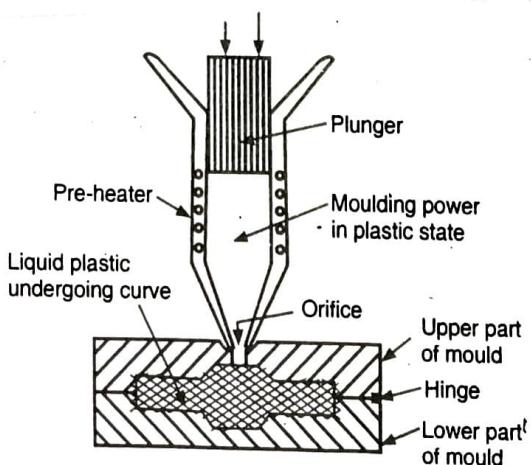
Advantages ① applied to both thermoplastic as well as thermosetting materials.

② Machinery is simple ③ can fabricate simple designs

Disadvantages - ① pressure applied is not very high hence only simple articles can be manufactured.

② Hard and strong fillers can not be used ③ Fabricated articles may not be completely flawless.

Transfer Moulding :

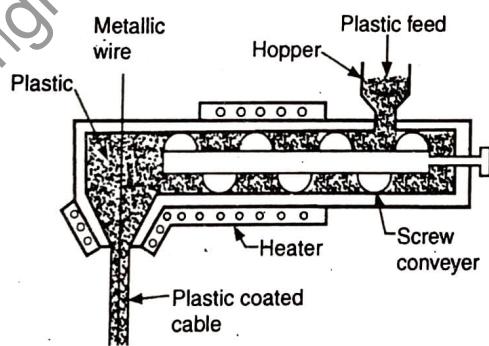


It is a modification of compression moulding. It is used for making parts of thermosetting materials and used for more complicated shapes and delicate design. The moulding composition is first plasticized by applying minimum heat and pressure in a chamber outside the mould, and then it is injected into the mould, where curing takes place under the influence of heat and pressure.

Advantages

- ① delicate articles could be made
- ② intricate shapes ③ free from flow marks.
- ④ NO BLISTERS ⑤ finishing costs is less.
- ⑥ Mould cost is less.

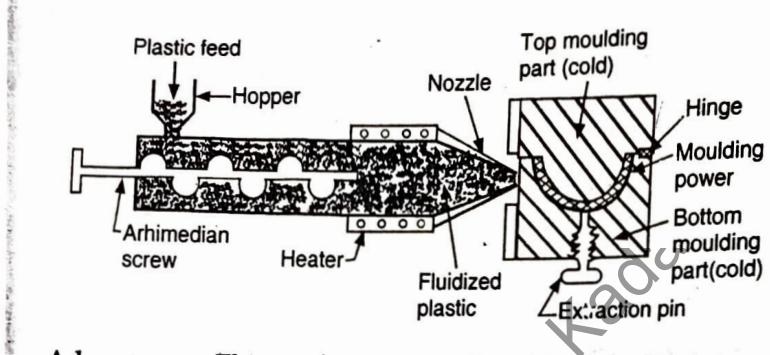
Extrusion moulding



It is used mainly for continuous moulding of thermoplastic material into articles uniform cross section like tubes, rods, filaments, insulated electric cables. The thermoplastic ingredients are heated to plastic condition and then pushed by means of a screw conveyor into a die having the required outer shape of the article to be manufactured. Here the plastic mass get cooled,

due to atmospheric exposure or artificially by air jets. A long conveyor carries away the cooled product.

Injection Moulding



This method is generally used for thermoplastics. The moulding composition is heated in a suitable chamber from where it is injected at a controlled rate into the tightly locked cold mould by means of screw arrangement. In this cold mould the curing takes place to give the final product. The temp $90^{\circ}\text{C} - 260^{\circ}\text{C}$

Advantages

- ① High speed production
- ② low moulding part cost
- ③ low finishing cost
- ④ very low loss of material

This method is used to shape articles like buckets, mug, bottles etc.

A polymer has the following molar mass distribution of molecules.

$$n_1 = 50$$

$$n_2 = 75$$

Molar mass (g mol⁻¹)

$$m_1 = 5000$$

$$m_2 = 6000$$

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{50 \times 5000 + 75 \times 6000}{50 + 75} = 5600 \text{ gm} \cdot \text{mol}^{-1}$$

$$\overline{M}_w = \frac{\sum N_i \overline{M}_i^2}{\sum N_i M_i} = \frac{50 \times (5000)^2 + 75 \times (6000)^2}{50 \times 5000 + 75 \times 6000} = 5642 \text{ gm} \cdot \text{mol}^{-1}$$

$$P.D = \frac{\overline{M}_w}{\overline{M}_n} = \frac{5642}{5600} = 1.0075$$