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Engineering Chemistry-**II** (BS-104)

Polymers

Dr. Shruti Khanna Ahuja

Assistant Professor

USAR, GGSIPU

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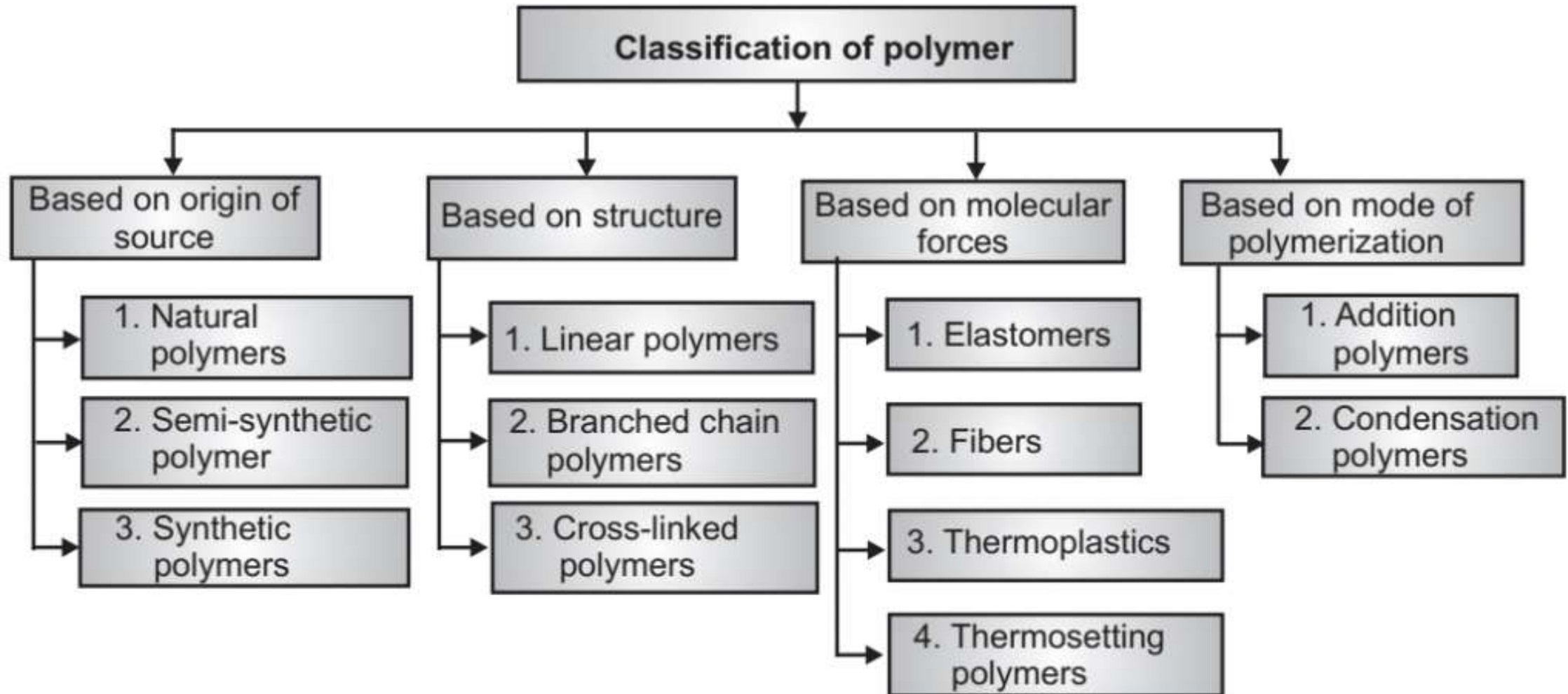Delhi - 110092

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- **Polymers** is a larger molecule or a macromolecule with very high molecular masses (10^3 - 10^7 microns), each molecule of which consists of a very large number of simple repeating structural units joined together through covalent bonds.

- The simple and reactive molecules from which the repeating structural units are derived are called **monomers**.

- The process by which monomers are converted into polymers is called **polymerization**.

- Their consequently large molecular mass, relative to small monomers, produces unique physical properties such as toughness and viscoelasticity

Monomers

Polymerization

Polymer

n CH_2=CH $\longrightarrow$ [CH_2—CH]$_n$

styrene (monomer)　　　polystyrene (polymer)
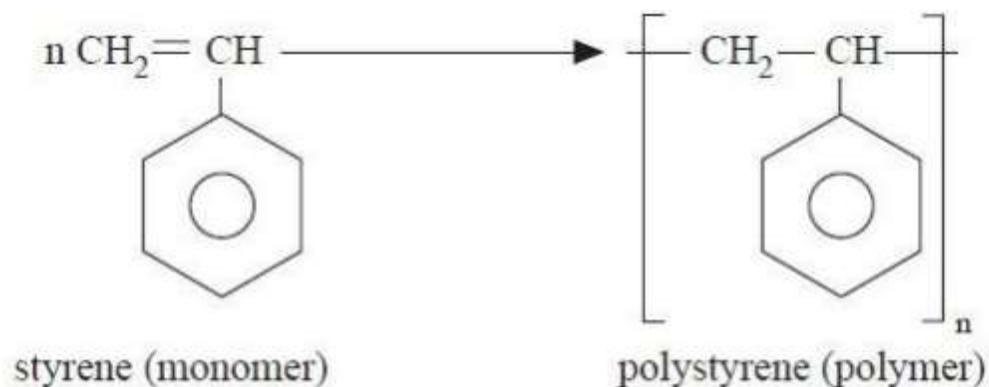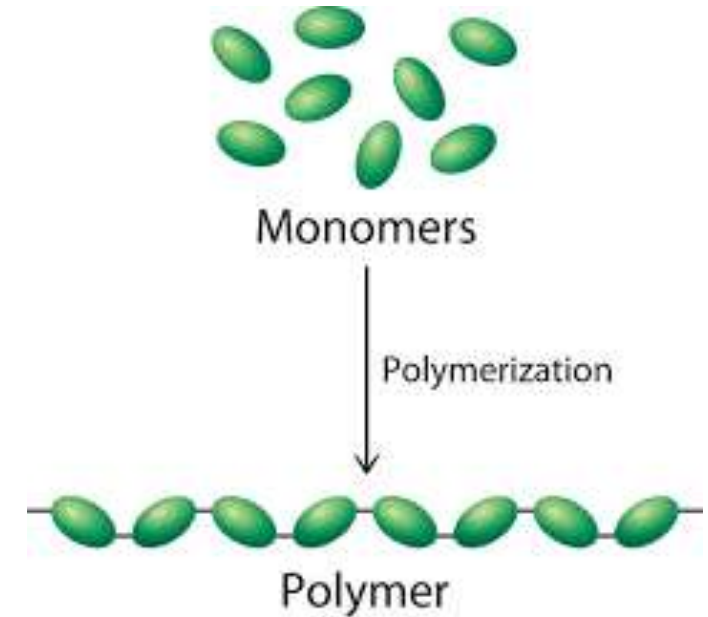
The styrene molecule contains a double bond and is the monomeric unit. The resulting structure, enclosed in square brackets, is the polymer polystyrene (2). The unit in square brackets is called the repeating unit.

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Classification of polymer

Based on origin of source
1. Natural polymers
2. Semi-synthetic polymer
3. Synthetic polymers

Based on structure
1. Linear polymers
2. Branched chain polymers
3. Cross-linked polymers

Based on molecular forces
1. Elastomers
2. Fibers
3. Thermoplastics
4. Thermosetting polymers

Based on mode of polymerization
1. Addition polymers
2. Condensation polymers

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- **Based on origin of source:** Polymers are broadly divided into the following three classes:

(i). **Natural polymers:** They occur naturally and are found in plants and animals. Enzymes, nucleic acids, proteins, carbohydrates are polymers of natural origin. Their structures, are normally very complex. Starch, cellulose, and natural rubber, on the other hand, are examples of polymers of plant origin (natural) but have relatively simpler structures than those of enzymes or proteins.

(ii). **Semi-synthetic polymers:** They are derived from naturally occurring polymers and undergo further chemical modification. For example, cellulose nitrate, cellulose acetate.

(iii). **Synthetic polymers:** These are man-made polymers, which are extensively used in daily life as well as in industry. These include fibers (nylon, polyester), plastics (polythene, polypropylene), rubbers (neoprene, polystyrene), etc.

Examples of Natural and Synthetic Polymers

Natural polymers are made by living organisms.

Synthetic polymers are made by chemical reactions in a lab.

DNA | Rubber | Nylon | Polyester

Cellulose | Wool | Teflon | Epoxy

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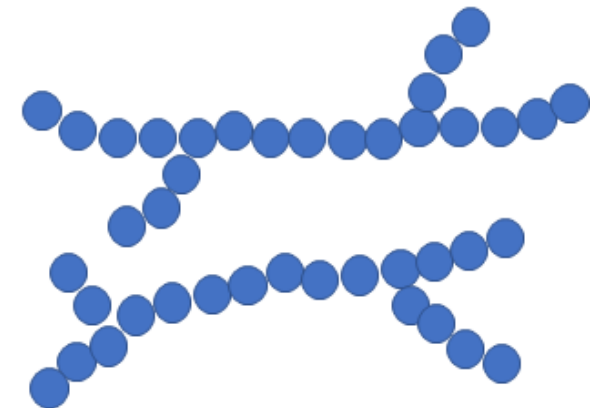USAR
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- **Based on structure of the monomer chain:**

(i). **Linear polymers:** Polymers in which monomer units are connected end-to-end along the while length of the chain. The polymeric chains are stacked over one another, held together by van der Waals and H-bonding interactions. These type of polymers are often quite flexible and have high melting points, high densities and high tensile strength. E.g. polyvinyl chloride (PVC), high density polythene.
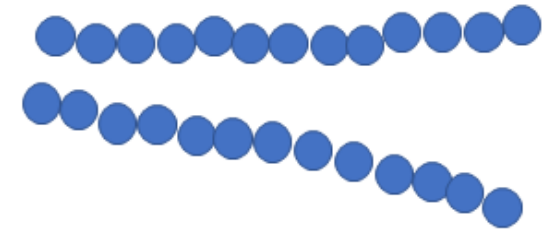
Linear Polymers

(ii). **Branched chain polymers:** In these, the monomer units not only combine to produce the linear main chain but also forms branches of different lengths. These polymer molecules because of branches do no pack well and have therefore lower melting points, densities and tensile strength. E.g. low density polythene.

Branched Polymers

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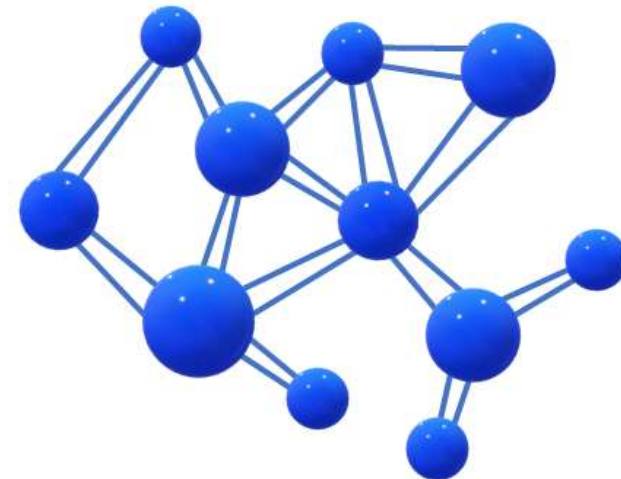UNIVERSITY SCHOOL OF AUTOMATION AND ROBOTICS

(iii). **Cross-linked polymers:** They are composed of bifunctional monomers. They have a stronger covalent bond in comparison to other linear polymers and are hard, rigid and brittle. Bakelite and melamine are examples.
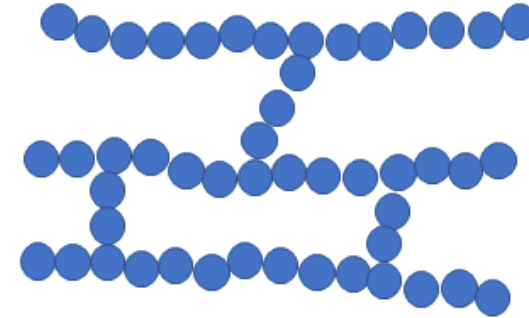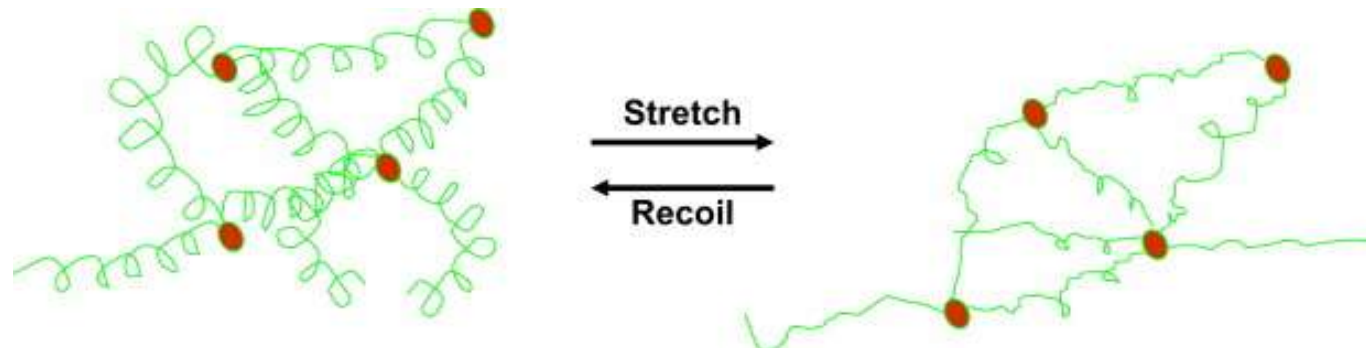

Crosslinked Polymers

(iv) **Network polymers:** They are trifunctional and have three points on the monomer that can react leading to three-dimensional network structure. They are highly cross-linked. In other words, a cross-linked polymer that includes numerous interconnections between the chains. E.g. phenol-formaldehyde resins, epoxy.

Networked Polymers

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- **Based on molecular forces:** The application of polymers in the relevant are depends largely on its mechanical properties such as tensile strength, elasticity, toughness etc., which in turn depend on the intermolecular forces of attraction such as van der Waals forces, hydrogen bonds and dipole-dipole interactions between the adjacent polymeric chains. Greater the length of the polymeric chain, stronger are the intermolecular forces.

- Depending upon the magnitude of these intermolecular forces, polymers have been divided into four categories:

(i). **Elastomers:** Polymers with weakest intermolecular forces of attraction.

- They are amorphous polymers and have high degree of elasticity i.e., they have ability to stretch out over 10 times their normal length and return to their original position when the force is withdrawn.

- Whereas weak van der Waals forces of attraction permit the polymer chains to be stretched, the cross links enable the polymer to come back to the original position.

- They consist of randomly coiled molecular chains of irregular shape having a few cross links. E.g. **natural rubber**, vulcanized rubber, Buna-S etc.

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(ii). **Fibers:** Polymers with **strongest** intermolecular forces of attraction, which are due to H-bonding or dipole-dipole interactions.

- They have high modulus, high tensile strength and least elasticity.
- The molecules of these polymers are long, thin and thread-like and hence can be easily packed.
- This close packing results in their high melting points and low solubility.
- E.g. nylon (polyamides with H-bonding), polyesters and polyacrylonitrile (dipole-dipole interactions between the polar carbonyl groups and between carbonyl and cyano groups, respectively)
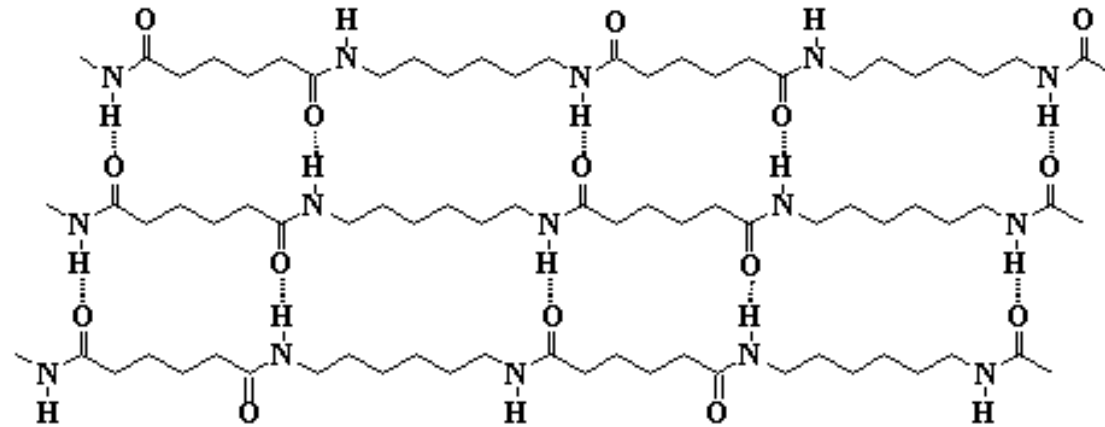
In nylon 6,6, the carbonyl oxygens and amide hydrogens can hydrogen bond with each other. This allows the chains to line up in an orderly fashion to form fibers.

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(iii). **Thermoplastics:** Polymers in which the intermolecular forces of attraction are in between those of elastomers and fibers.

- They are linear or slightly branched chain polymers which are hard at room temperature, become soft and viscous on heating and again rigid on cooling. They have little or no cross-links.

- As a result, these plastics can be easily moulded.

- E.g. polythene, polypropylene, polystyrene, PVS, nylon 6, nylon 6,6.

- **Plasticizers:** Those plastics which do not soften very much on heating can be made soft and readily working by addition of organic compounds known as plasticizers. E.g. dialkyl phthalates
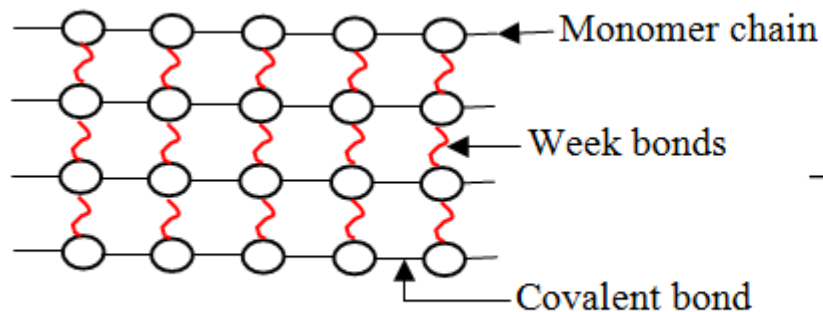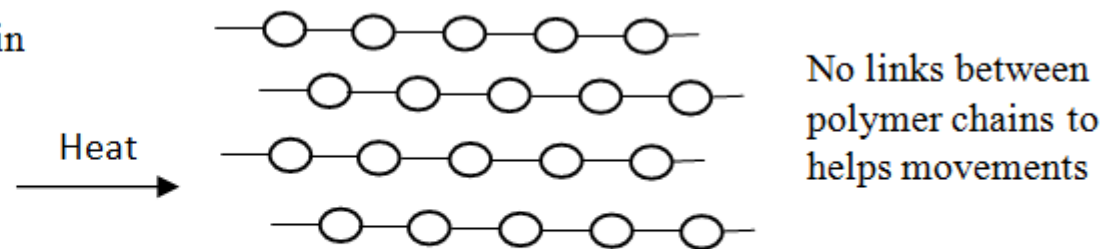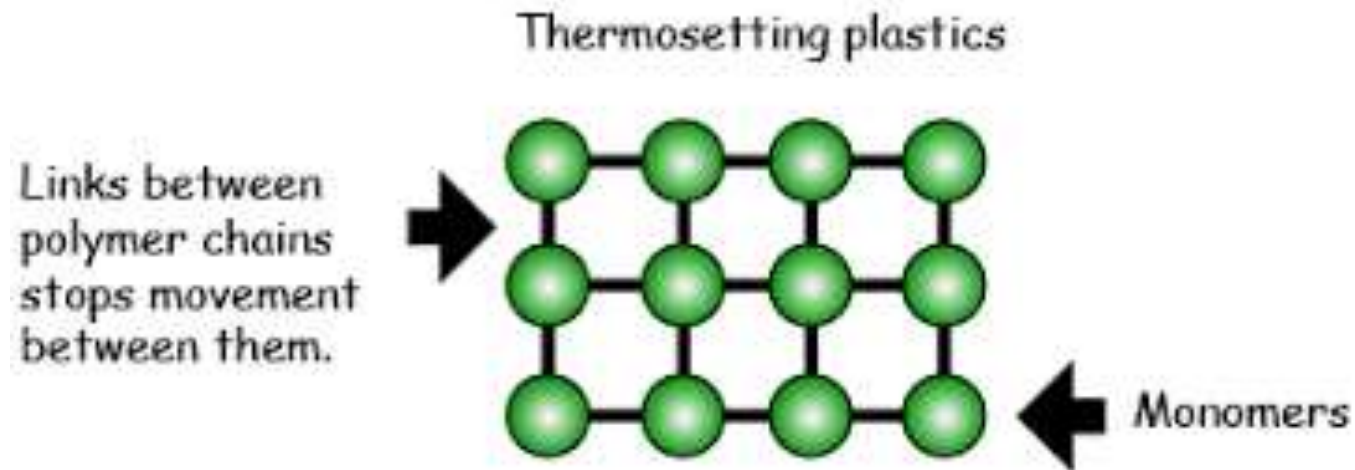

Figure 1. Thermoplastic polymer   Figure 2. Thermoplastic softened state

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(iv). **Thermosetting polymers:** These are semi-fluid substances with low molecular masses which when heated in a mould undergo a permanent change in chemical composition to give a hard and infusible mass.

- This hardening on heating is due to extensive cross-linking between different polymer chains to give a 3D-network solid.
- E.g. phenol-formaldehyde (Bakelite), urea-formaldehyde, melamine-formaldehyde.
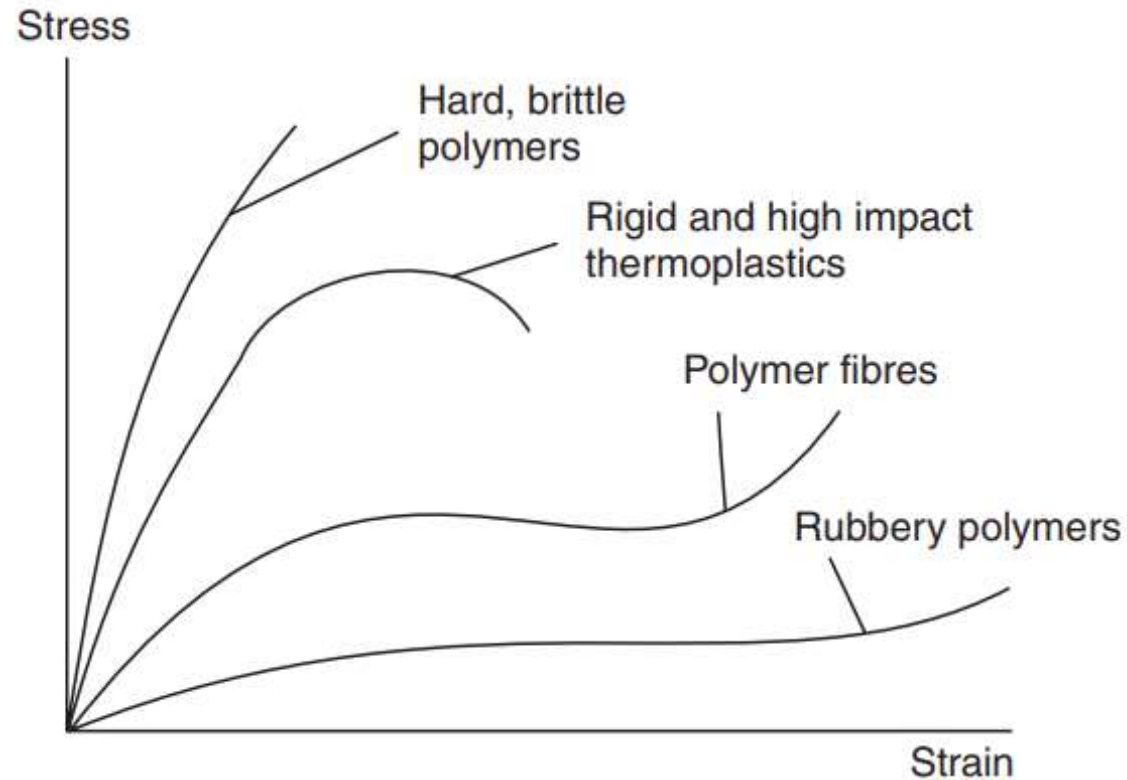
Thermosetting plastics

Links between polymer chains stops movement between them.

Monomers

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Thermoplastic	Thermosetting plastic
A) Maximum thermoplastic polymer are formed by addition polymerization in few cases condensation polymerization.	A) Thermosetting plastic polymer are formed by only condensation polymerization.
B) The molecular forces are normally weak.	B) The molecular forces are tremendously strong.
C) Polymer backbone chains are connected together by Van der Wall's or dipole-dipole attraction or H-bonding.	C) Polymer backbone chains are connected together by strong covalent bond.
D) These polymers are normally soft and flexible.	D) These polymers are normally hard and brittle.
E) These polymers are normally linear or branch	E) These polymers are normally cross linked polymer
F) On application of heat these polymers become soft and again become hard on cooling.	F) On application of heat the these polymers become more hard due to farther cross linking.
G) On continuous heating these polymer get melt.	G) On continuous heating these polymers get burnt.
H) These polymers are recyclable.	H) These polymers are not recyclable.
I) These polymers soluble in many organic solvent.	I) These polymers insoluble in organic solvent.
J) Example of these hese polymers are PF resin(Bakelite), MF resin, UF resin Epoxy rein, Polyester resin etc.	J) Example of these hese polymers are PVC,PE, PP

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- **Mechanical properties of polymers:**

Stress

Hard, brittle polymers

Rigid and high impact thermoplastics

Polymer fibres

Rubbery polymers

Strain

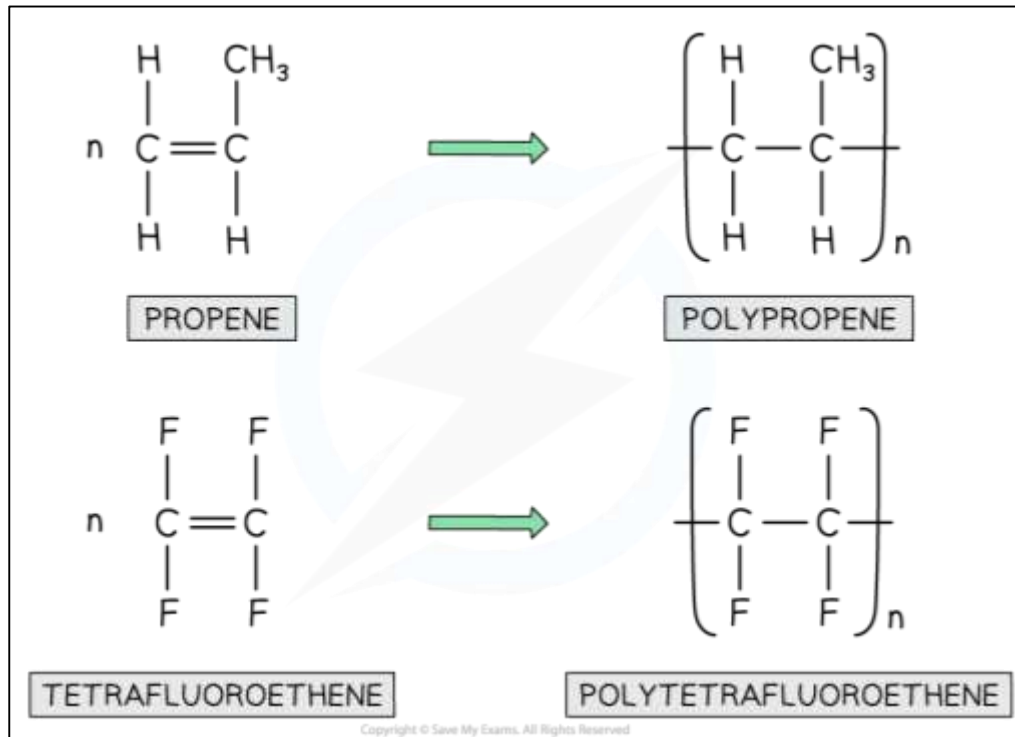Four types of stress-strain curves illustrating how polymers of different types behave (the lines end where the sample breaks).

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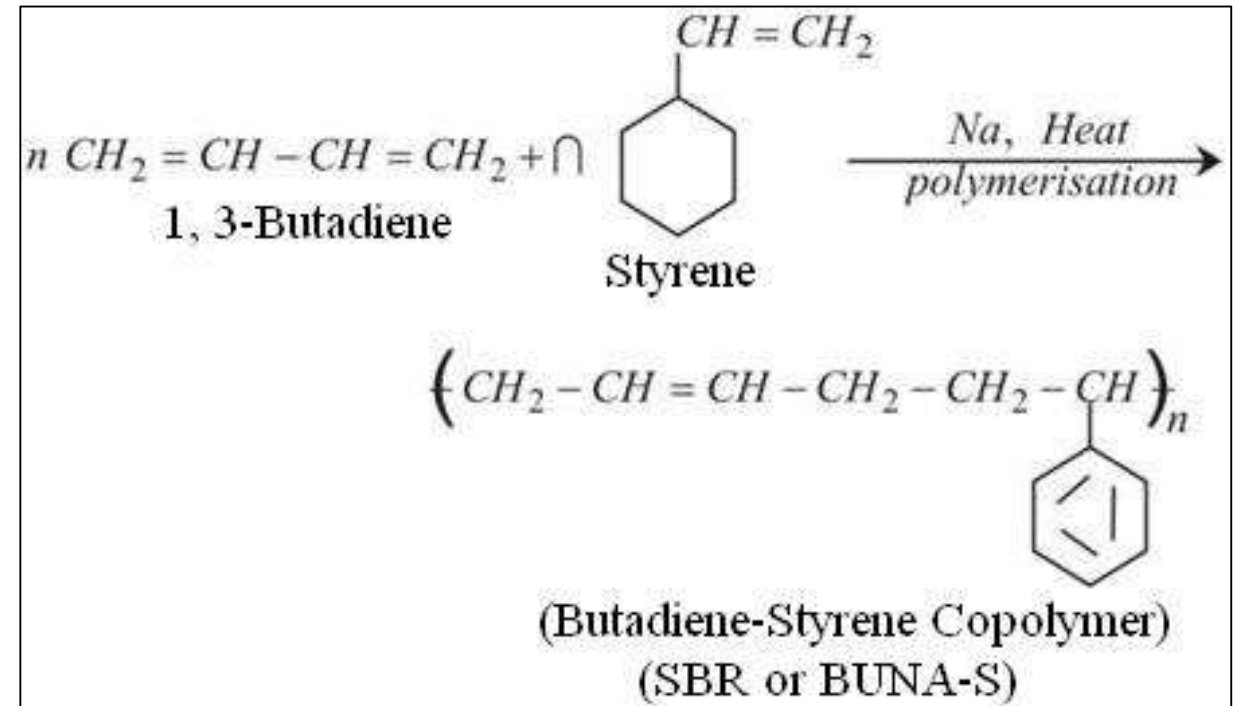USAR
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- **Based on mode of polymerization:**

(i). **Addition or chain growth polymers:** They are formed by repeated addition of a large number of same or different monomers possessing **double and triple bonds**.

- They can be either addition homopolymers or addition copolymers.
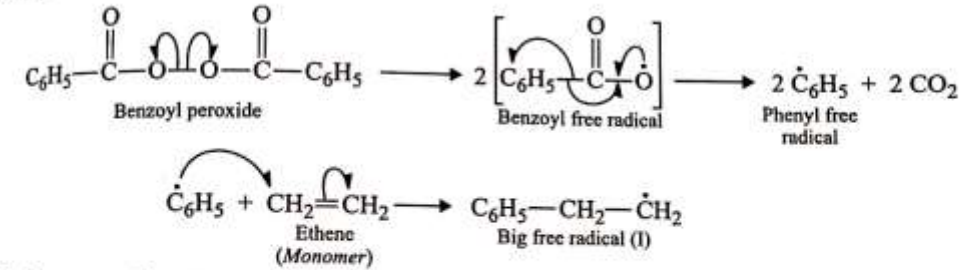

Addition homopolymers

Addition copolymers

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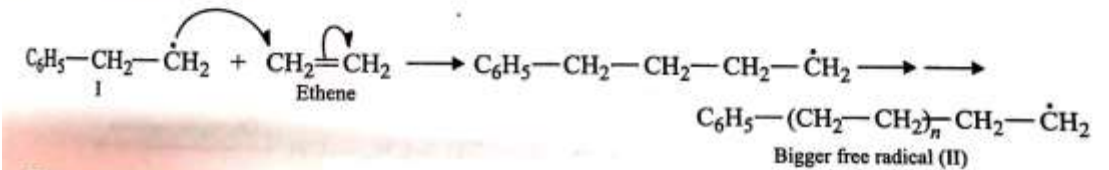USAR
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- Addition polymerization involves successive addition of monomer units to the growing chain carrying a reactive intermediate such as a free radical, a carbocation or a carbanion

- It is also known as chain growth polymerization as it takes place in stages leading to increase in chain length and each stage produces a reactive intermediate for use in next stage of growth of the chain.

- The manufacture of polyethylene employs a free-radical initiator that donates its unpaired electron to the monomer, making the latter highly reactive and able to form a bond with another monomer at this site.

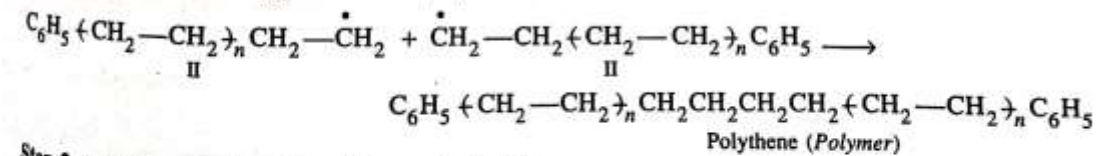- Common radical initiators are benzoyl peroxide, t-butyl peroxide, dioxygen
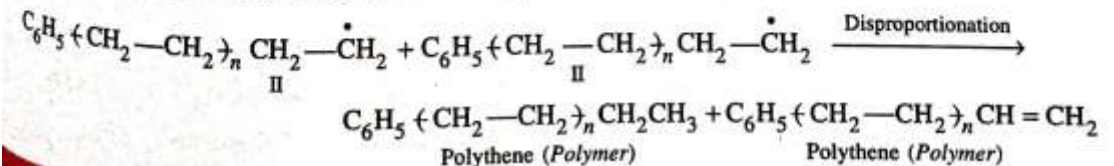
Free radical addition polymerization

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- **Common examples of addition polymers:**

Monomer	Polymer	Polymer Name [Trade Name(s)]	Some Uses
$CH_2=CH_2$	$\sim CH_2CH_2CH_2CH_2CH_2CH_2\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
$CH_2=CHCH_3$		polypropylene	carpeting, bottles, luggage, exercise clothing
		polystyrene	"take-out trays", foam "packaging peanuts", CD cases, foam-walled drink cups, and other thin-walled and moldable parts.
$CH_2=CHCl$	$\sim CH_2CHCH_2CHCH_2CH\sim$ (Cl, Cl, Cl)	polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$CF_2=CF_2$	$\sim CF_2CF_2CF_2CF_2CF_2CF_2\sim$	polytetrafluoroethylene (Teflon)	Non-stick coating for cooking utensils, chemically-resistant specialty plastic parts, Gore-Tex

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- **Synthesis of some important addition polymers:**

1. **Polythene or polyethylene:** Prepared by **free radical or high-temperature polymerization of ethane**.

a. **Low Density Polyethylene (LDPE):** It is prepared by heating ethylene monomer at 250°C under high pressure (1000 - 4000 atm) in presence of oxygen or hydrogen peroxide (free radical generator). In this process huge branched chains are formed through out every long back bone chain. The presence of branches repel each other and the long chains are not well fitted to each other having some gap produce low density (0.91 to 0.925 gm/cc) and low melting point (384 K) polymer.

(low density poly ethene)
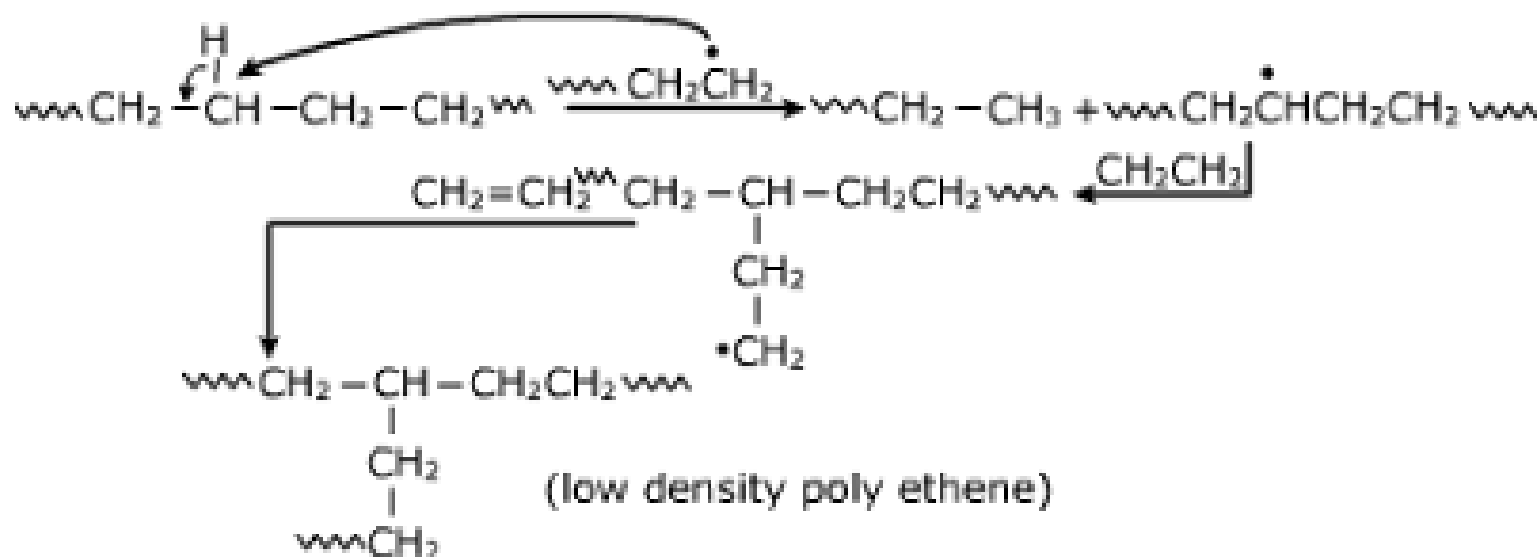
- **Uses:**

a) As LDPE is a good insulator they normally used for the preparation of electrical wires and cables.

b) Pouch pack, squeeze bottles, delivery pipes are prepared from LDPE.

c) Toys, refill for ball pen and ball pen also prepared from LDPE.

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b. **High Density Polyethylene (HDPE):** polymerization of ethylene monomer at low pressure (5 - 7 atm) and temperature (60−700C) in presence of **Zieglar Natta catalyst** like triethyl aluminum and titanium tetrachloride. In this process of polymerization as there is absence of branch through out the long chain back bone, the chains are well fitted to each other which makes the polymer a high density (0.95 to 0.97 gm/cc) polymer.

- **Characteristics** of high density polythene:

i. High density polyethylene have high density (0.95 to 0.97 gm/cc).

ii. It is less branched.

iii. Highly crystalline polymer having crystallinity 80-90 percent.

iv. Chemically inert, nonpolar and having dielectric property zero.

v. Highly tough but flexible.

vi. Melting point 130 − 1350C.

- **Uses** of high density polythene:

i. As HDPE is a good insulator they normally used for the preparation of high performance electrical cables.

ii. Bucket, cup, toys.

iii. Due to inertness it is used for the storage of H_2SO_4, pipes for LPG gas and water reservoir also.
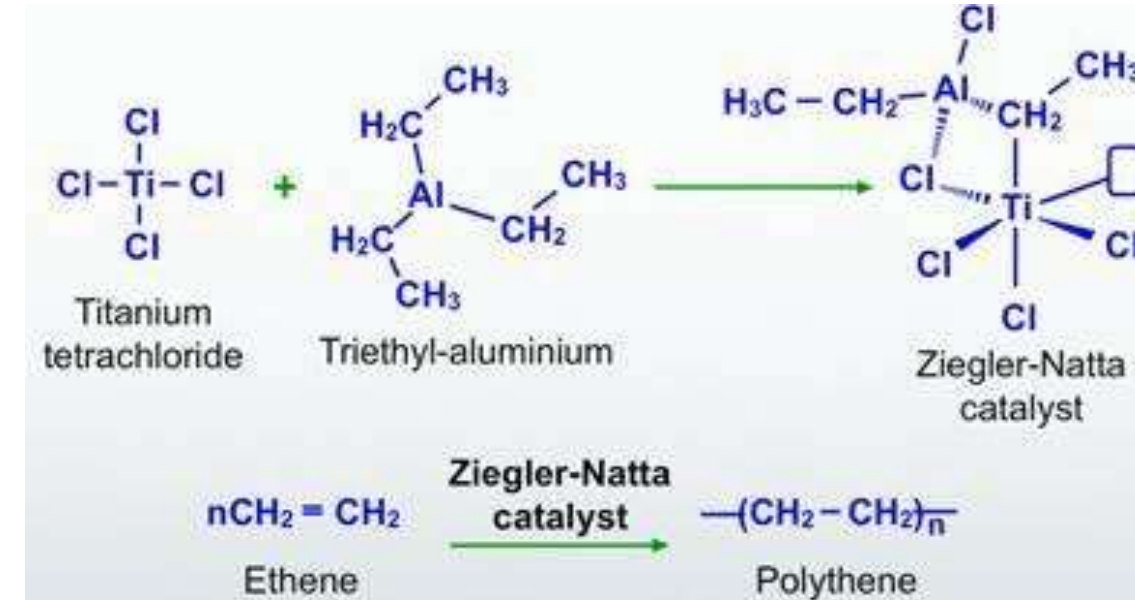
2. Polytetrafluoroethene (PTFE) or Teflon:

- Catalyst used: peroxides or ammonium persulfate at high pressure.
- **Characteristics:**

i. Chemically inert and resistant to attack by corrosive reagents

ii. High thermal stability

- **Uses**:

i. Used for making non-sick utensils

ii. Used for making gaskets, pump-packings, valves, seals, etc.

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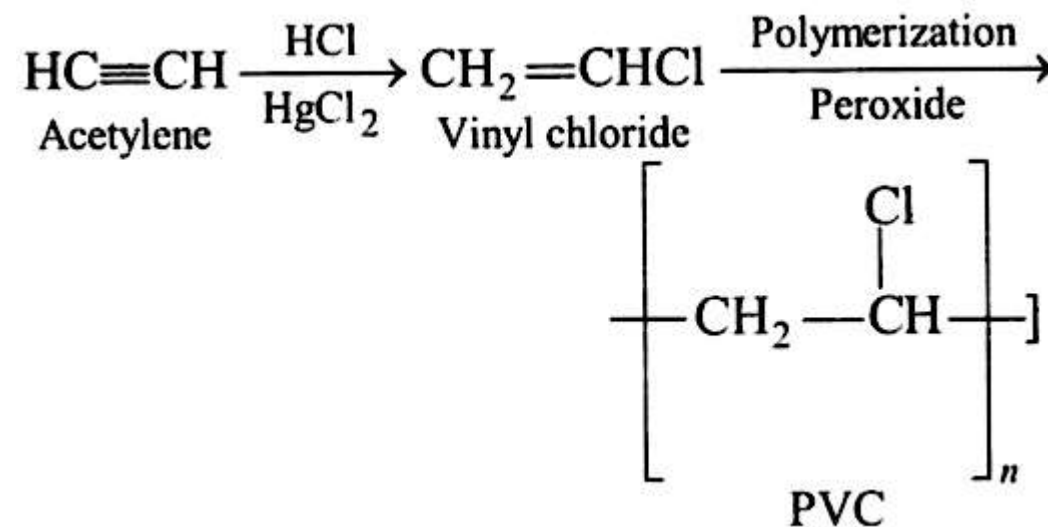**GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY**
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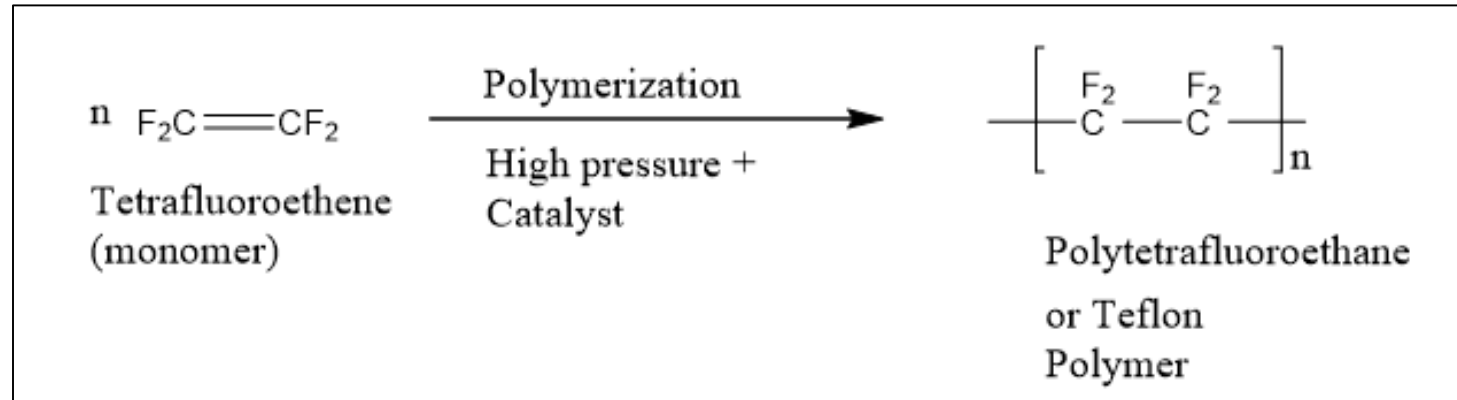
3. Polyvinyl chloride (PVC):

- **Characteristics:**

i.   Colorless, odorless, non-inflammable, chemically-inert powder

ii. High rigidity but brittle

iii. Resistant to water, light, O_2, inorganic acids and alkalis, oil, but soluble in hot chlorinated hydrocarbons.

- **Uses**:

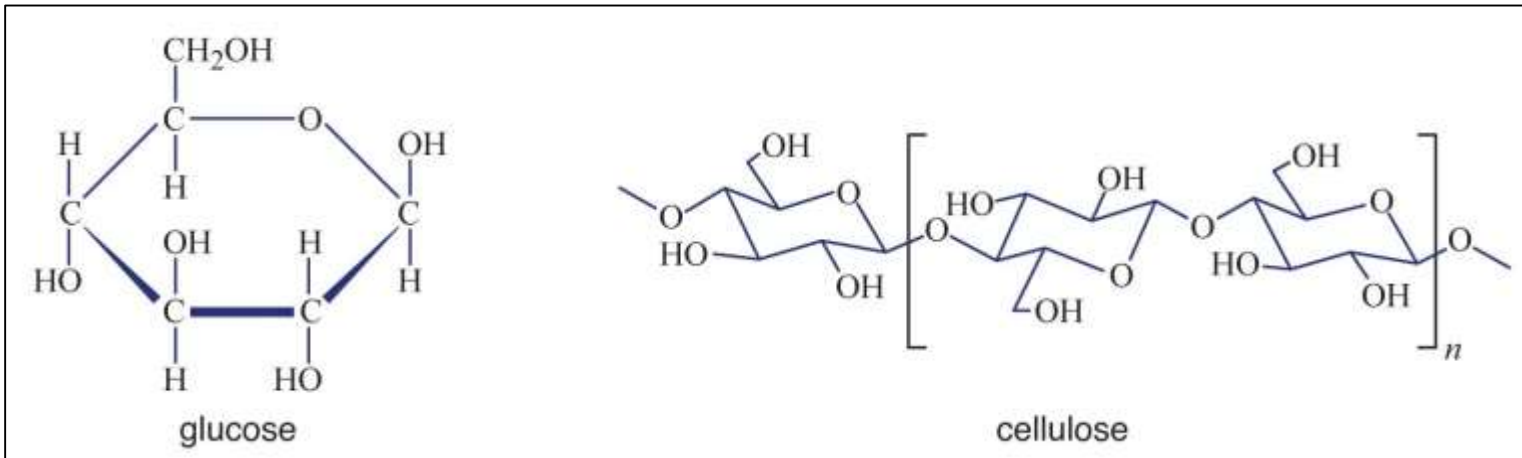i.   Used for making cables, water hoses, pipes of petroleum industry, refrigerator components

ii. Used for making toys, raincoats, tyres, cycles etc.

$$HC\equiv CH \xrightarrow[\text{HgCl}_2]{\text{HCl}} CH_2=CHCl \xrightarrow[\text{Peroxide}]{\text{Polymerization}}$$

Acetylene   Vinyl chloride

$$\left[-CH_2-\overset{\displaystyle Cl}{\underset{\displaystyle |}{CH}}-\right]_n$$

PVC

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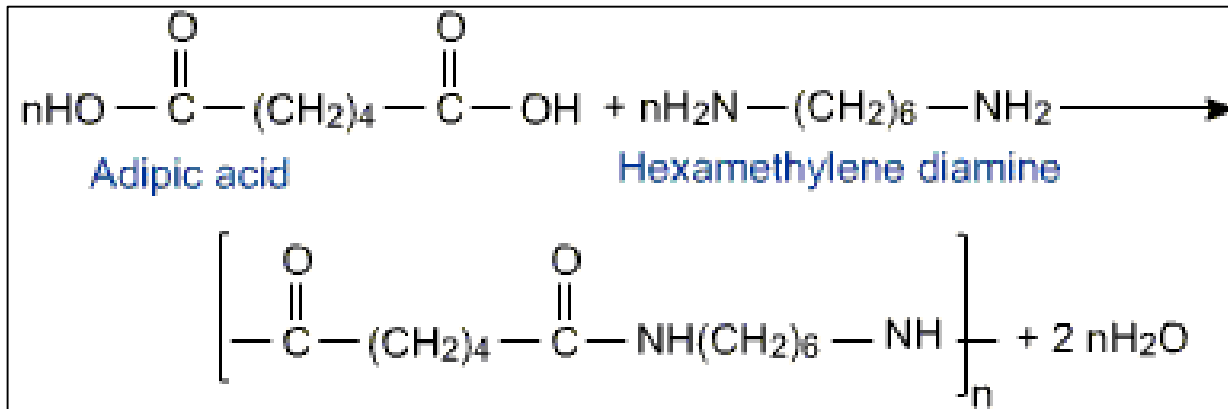USAR
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(ii). **Condensation or step growth polymers:** They are formed by repeated condensation reaction between two bifunctional and trifunctional monomer units usually with elimination of small molecules like water, alcohol, ammonia, CO_2, HCl etc.

- They can be either condensation homopolymers or addition copolymers.
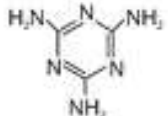
Condensation homopolymers

glucose   cellulose

Condensation copolymers

$$nHO-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-OH + nH_2N-(CH_2)_6-NH_2 \longrightarrow$$

Adipic acid   Hexamethylene diamine

$$\left[-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-NH(CH_2)_6-NH\right]_n + 2\,nH_2O$$

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• **Common examples of condensation polymers:**

POLYMER	MONOMER	STRUCTURE	USES
1. Nylon 6, 6	a) Adipic acid HOOC-(CH₂)₄-COOH b) Hexamethylene diamine NH₂-(CH₂)₆-NH₂		For making fabrics, for clothing, sports wear, combs, bristles of brushes.
2. Nylon 6	Caprolactum 		Mainly used for making cords for types, ropes and fabrics.
3. Polyester	a) Ethyleneglycol CH₂OH | CH₂OH b) Terephthalic acid HOOC-⟨O⟩-COOH		Crease resistant fibres, safety helmets.
4. Phenol - formaldehyde Resin (Bakelite)	a) Phenol b) Formaldehyde HCHO		Manufacture of switches, plugs, cooker handles, Iron handles and parts.
5. Melamine-Melamine - formaldehyde Polymer	a) Melamine b) Formaldehyde CH₂O or HCHO		In the manufacture of unbreakable tableware, trays clocks, knobs, litensil handles etc.

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- **Synthesis of some important condensation polymers:**

1. **Polyamides:** Polymers with amide linkages. E.g., nylon 6,6 and nylon 6

a. **Nylon-6,6:**

Nylon 6, 6

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b. Nylon 6:

cyclohexane → oxidation → (cyclohexanone) → NH$_2$OH, –H$_2$O → cyclohexanone oxime → H$_2$SO$_4$, Beckmann rearrangement → caprolactum → H$_2$O/Δ → Amino cabroic acid → Δ, –H$_2$O → Nylon-6

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2. Polyesters: Polymers with ester linkages. E.g., terylene or Dacron

a. **Terylene:**
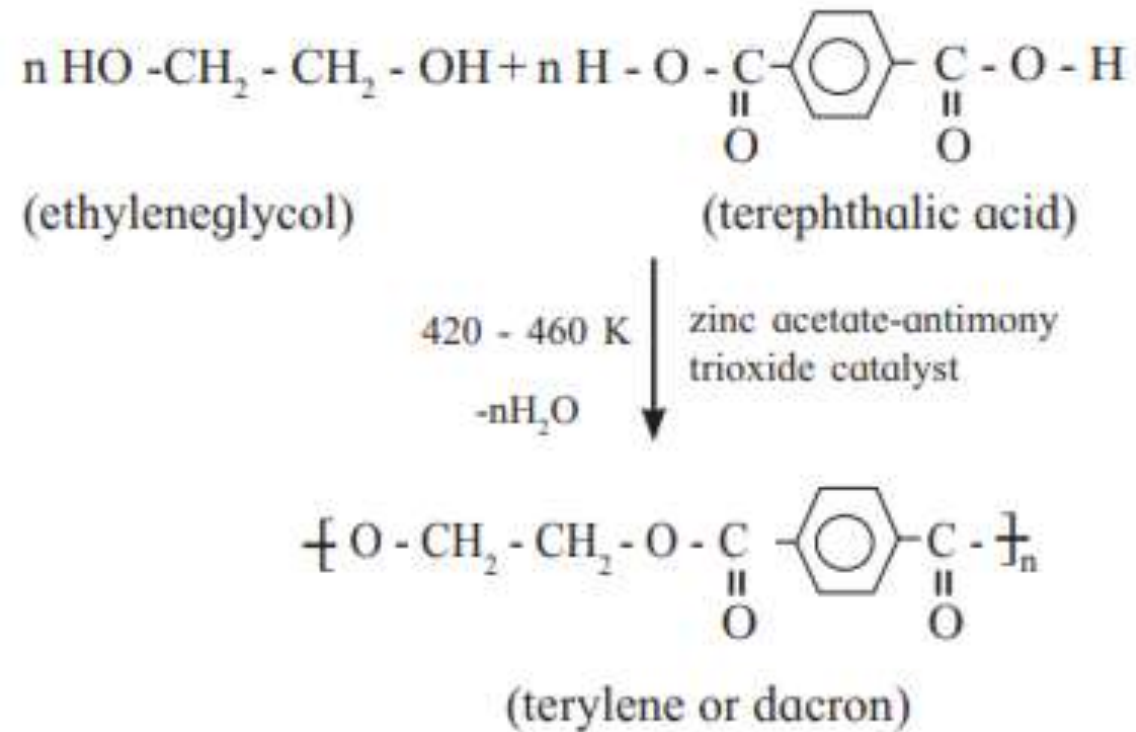
(terylene or dacron)

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3. Phenol-formaldehyde polymers: E.g., bakelite

a. Bakelite:

Properties of bakelite:

a) It is high thermal and electrical resistance.

b) It is hard rigid and scratch proof.

c) It is resistant to many inorganic and base.

Use of bakelite:

a) Novoloc is used for the preparation of laminates.

b) Resol is used for preparation of comb, P.O. Box, marine grade, shutter grade, Boilling water proof ply board, block board, flush door etc.

c) Resol is used for preparation of electrical board, switch etc.

Novolac

Bakelite

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4. Melamine-formaldehyde polymers: E.g. Melmac

Melamine-formaldehyde polymer

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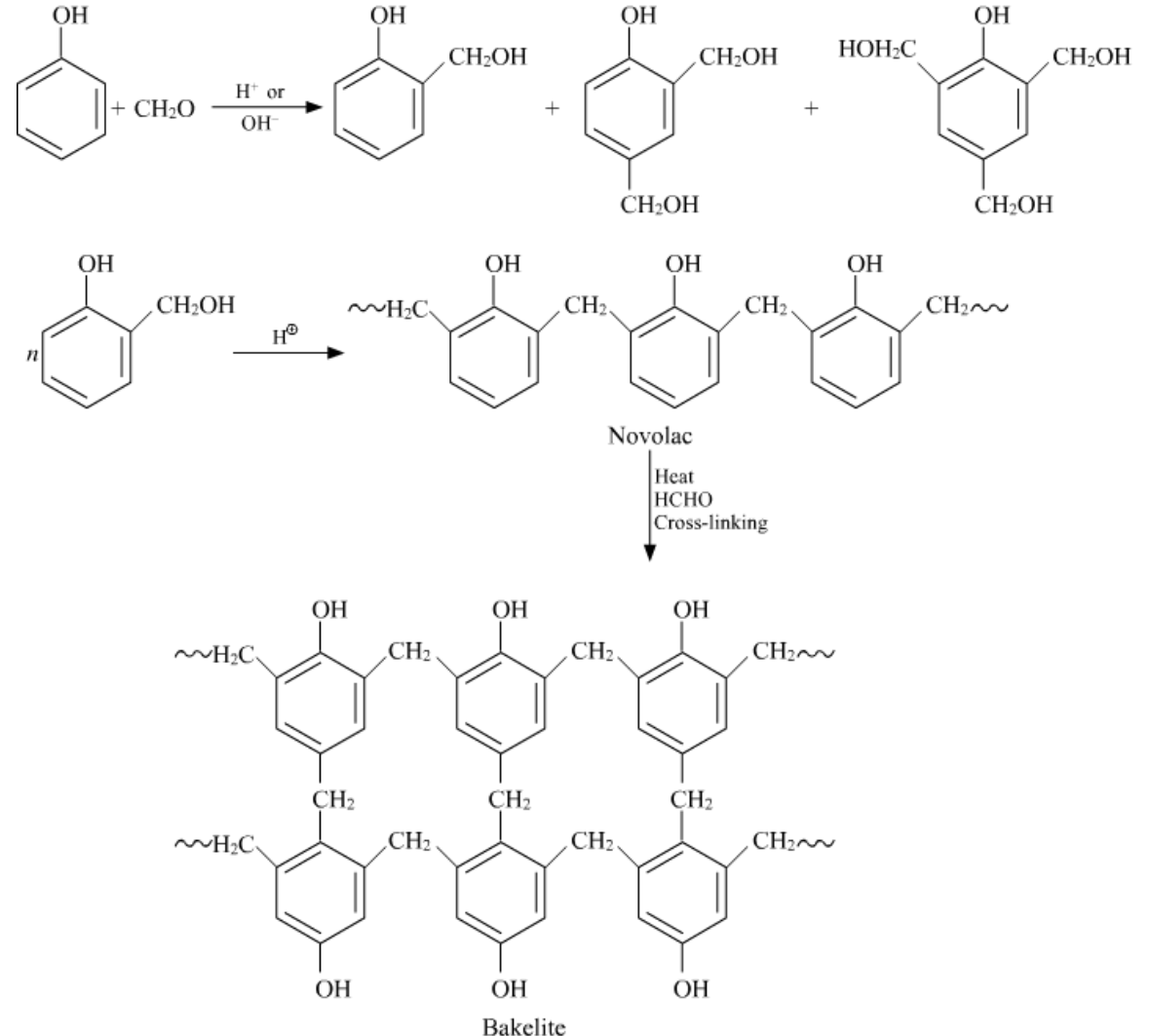
3. Phenol-formaldehyde polymers: E.g., bakelite

a. Bakelite:

Properties of bakelite:

a) It is high thermal and electrical resistance.

b) It is hard rigid and scratch proof.
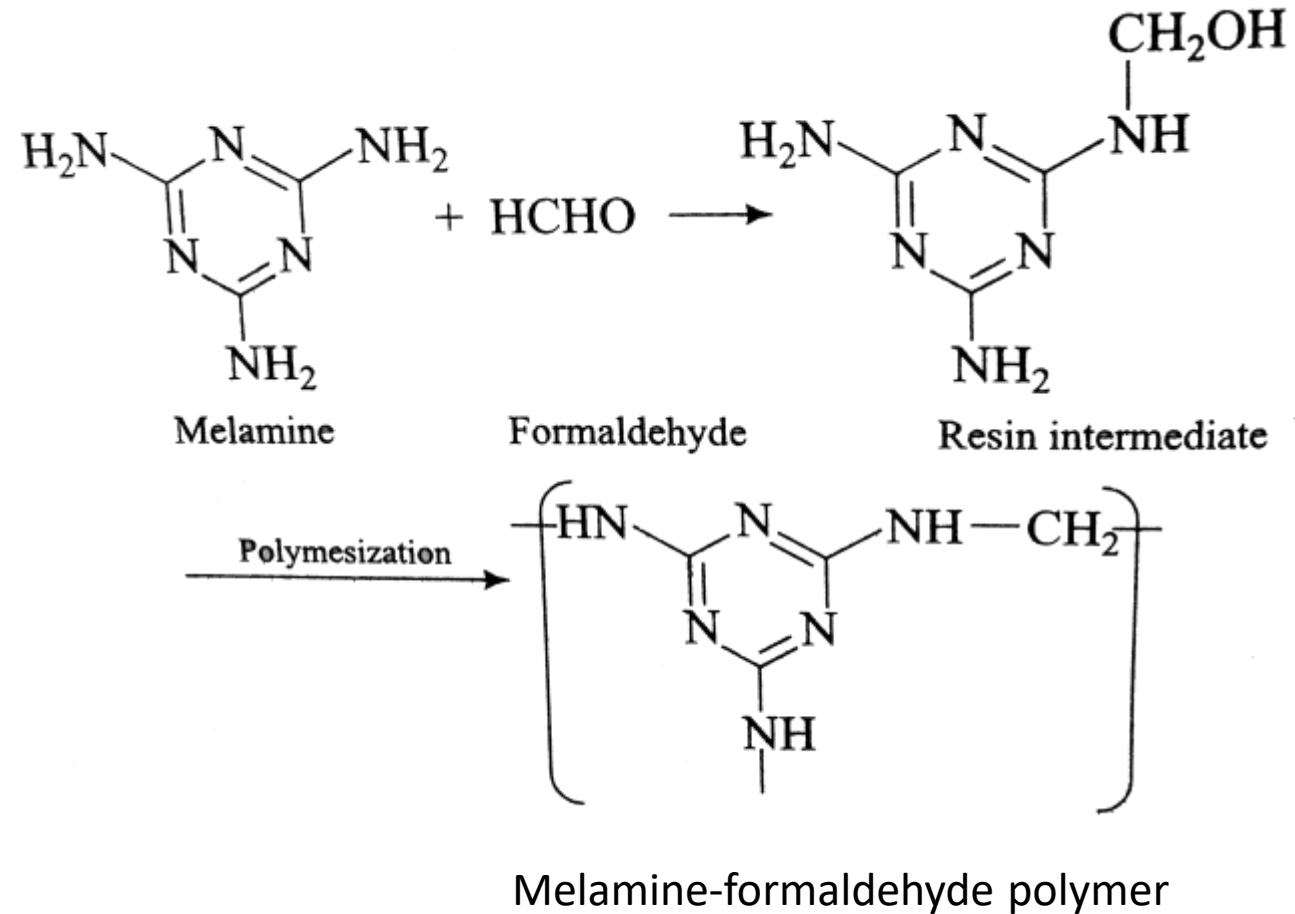
c) It is resistant to many inorganic and base.

Use of bakelite:

a) Novoloc is used for the preparation of laminates.

b) Resol is used for preparation of comb, P.O. Box, marine grade, shutter grade, Boilling water proof ply board, block board, flush door etc.

c) Resol is used for preparation of electrical board, switch etc.

Novolac

Bakelite

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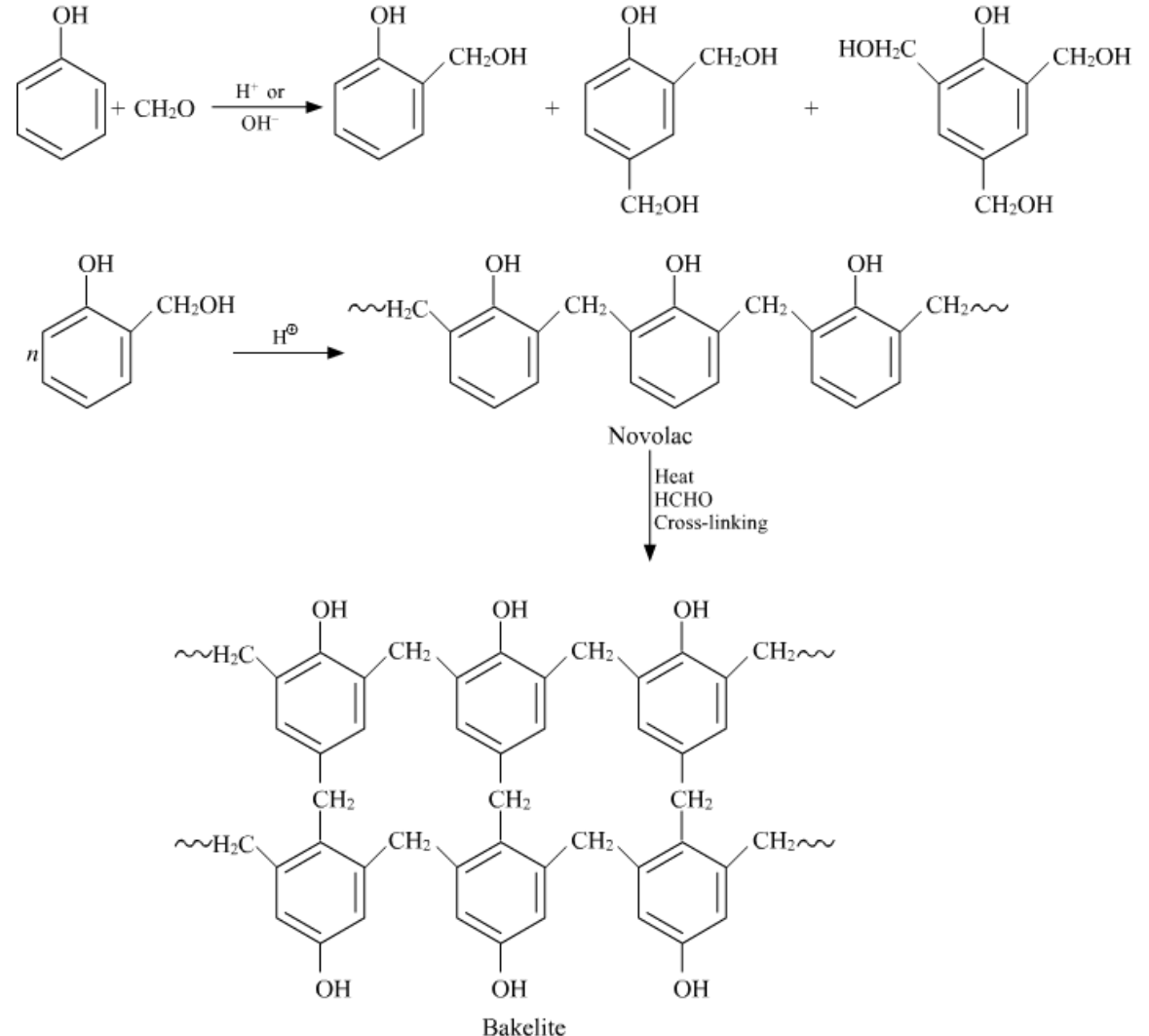
- **Molecular weight of a polymer:**

- The properties of polymers depend largely upon their molecular size and structure.

- Since the polymers are made up of monomeric units with different molecular mass in different chain length, the polymer as a whole has an average molecular mass.

i.   **Number average molecular mass ($\overline{M}_n$):** It is the simple arithmetic mean and is defined as the total mass (w) of all the molecules of a polymer divided by the total number of molecules present. In other words, it gives the average of the molecular masses of the individual macromolecules. It is the **mole fraction of molecules** in a polymer sample.

- If N_1, N_2, N_3…. are the number of macromolecular with molecular masses. M_1, M_2, M_3….. , respectively then the number average molecular masses of the polymer is given by:

$$\overline{M}_n = \frac{w}{\Sigma N} = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

where N_i is the number of molecules of mass M_i. $\overline{M}_n$ can be determined by measuring the colligative properties like lowering of vapor pressure, depression of freezing point etc.

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- **Molecular weight of a polymer:**

ii. **Weight average molecular mass ($\overline{M}_w$):** It is the **weight fraction of molecules** in a polymer sample. It is another way of determining the molecular mass of a polymer. It gives the average of the molecular masses of the individual macromolecules in the polymer sample.

- If w_i is the weight fraction of molecules having mass M_i, then the weight average molecular masses of the polymer is given by:

$$\overline{M}_w = \frac{\Sigma w_i M_i}{\Sigma w_i} = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

- We can determine this parameter using static light scattering, small angle neutron scattering, X-ray scattering, and sedimentation velocity.

- The weight-average molecular weight is larger than or equal to the number-average molecular weight.

- The ratio of the weight-average and number-average molecular weights, **$\overline{M}w/ \overline{M}n$** is a measure of the **polydispersity** of a polymer mixture - how widely distributed the range of molecular weights are in the mixture. A ratio that is around 1.0 indicates that the range of molecular weights in the mixture is narrow; a high ratio indicates that the range is wide. With rare exceptions, all synthetic polymers are polydisperse.

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- **Molecular weight of a polymer:**

iii. **Viscosity average molecular mass ($\overline{M}_v$):** The molecular weight of the polymer is measured by using viscometer and the molecular weight obtained by this technique is called viscosity average molecular weight. The molecular weight of the polymer solution is very high so the viscosity of polymer solution is very high compared to that of pure solvent.

From the Mark-Houwink equation the relationship among the molecular weight and viscosity are given below:

$$[\eta] = KM^{\alpha}$$

Where $[\eta]$ is the intrinsic viscosity, M is the Molecular weight, K and α are constants for a particular polymer solvent system.
If we know the K and α values for a given polymer solution the intrinsic viscosity and molecular weight can be calculate using the above equation.

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- **Degree of Polymerization (DP):**

- It is usually defined as the number of recurring monomeric units in a macromolecule or polymer or oligomer molecule.

- The chain length in a polymer generally varies from 100 to 200 or sometimes even 1000, hence we use the term average degree of polymerization ($\overline{DP}$).

- The degree of polymerization has a dramatic effect on the mechanical properties of a polymer. As chain length increases, mechanical properties such as ductility, tensile strength, and hardness rise sharply and eventually level off.

- For a homopolymer, there is only one type of monomeric unit and the number-average degree of polymerization is given by

$$DP_n \equiv X_n = M_n / M_o$$

where, M_n is the number-average molecular weight and M_o is the molecular weight of the monomer unit.

- **Ex:** calculate the degree of polymerization of a sample of polyethylene [(CH_2-CH_2)n], which has a molecular weight of 150,000 g/mol.

- The molecular weight of a repeating unit, M_o = (12 x 2 + 1 x 4) g/ mol = 28 g/mol

$$DP = M/M_o = 150{,}000 \text{ g/mol} / 28 \text{ g/mol}$$

$$= 5.35 \times 10^3$$

=> The particular molecule contains 5.35×10^3 of repeat units.