



CO₂ – Polymeric Materials

Course plan

Introduction:

Types – organic, inorganic, thermoplastics, thermosetting plastics, homo and copolymers, stereoregular polymers.

Degree of polymerisation, average molecular weights.

Polymerisation reactions – chain, condensation – one example each.

Morphology – amorphous and crystalline states.

Properties of polymers:

Thermal properties – glass transition– factors influencing glass transition temperature, determination by DSC.

Mechanical properties – stress-strain analysis, critical radius of curvature for flexible electronics.

Electrical properties:

Insulating properties - dielectric breakdown.

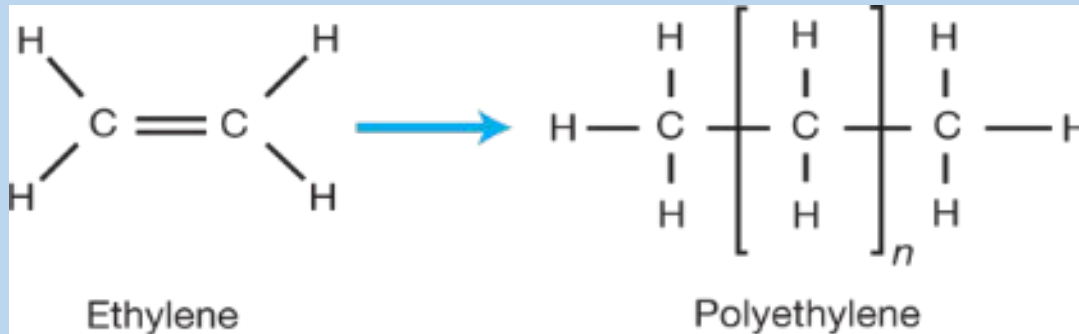
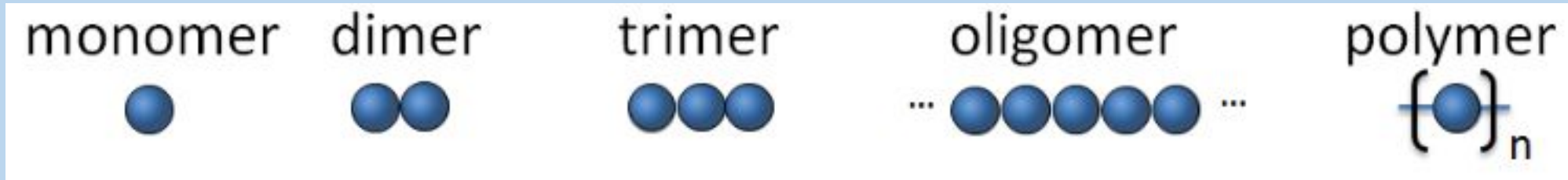
Aging of polymer insulations - discharges in voids, electrical treeing.

Degradation of polymers - thermal and photochemical – significance in polymer electronics.

Additives for polymer electronics – plasticisers, stabilisers, functional additives – metal deactivators, antistatic agents, flame retardants.

Introduction

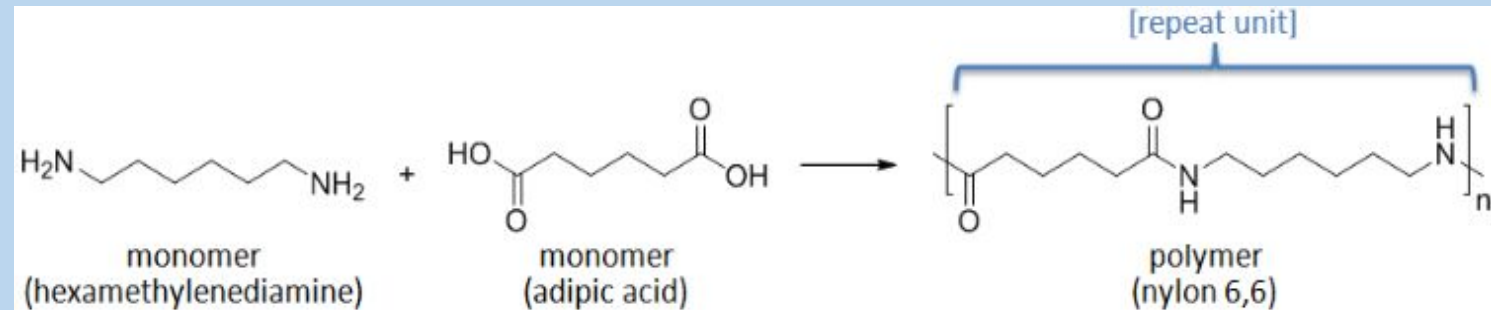
Polymer is a macromolecule of very high molecular weight.



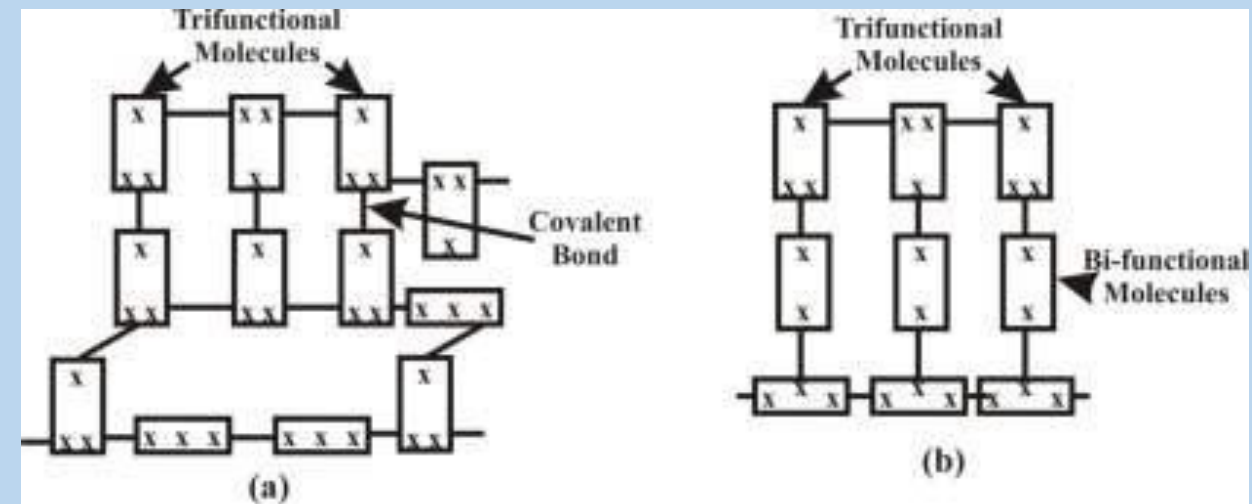
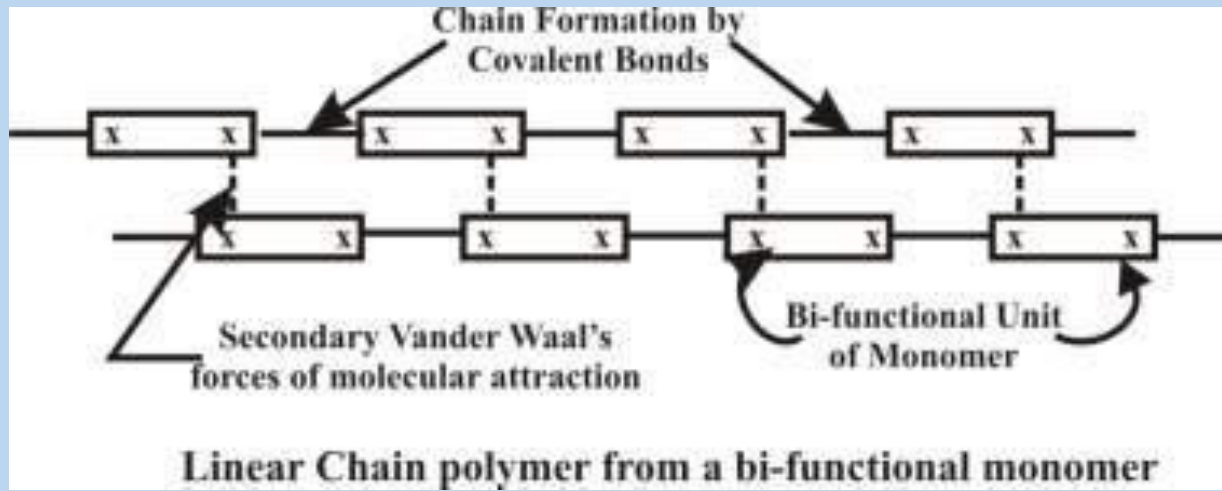
Monomers are the building blocks – Repeating units
Combine with each other to form polymer.
Monomers have two bonding sites:
(=, \equiv , -OH, -COOH, -NH₂)

Polymerization is conversion of monomer into polymer.

Functionality: Total no. of bonding sites or functional groups present in monomer.



Functionality



Formation of three dimensional network polymer

(a) reaction of three functional molecules

(b) reaction between two and three functional molecules

Classification of Polymers

- **Nature of Repeat Units**
 - **Nature of backbone chain**
 - **Structural Characteristics**
 - **Stereochemistry**
 - **Molecular (Functional Group) Classification**
 - **Physical properties**
 - **End Uses**
 - **Polymerisation Process (Chain or Step Growth)**
- All highlight certain aspect or property of the polymer.

Nature of Repeat Units

Homopolymer- A-A-A-A-A-A-A-A-A-A-

(identical repeat units)

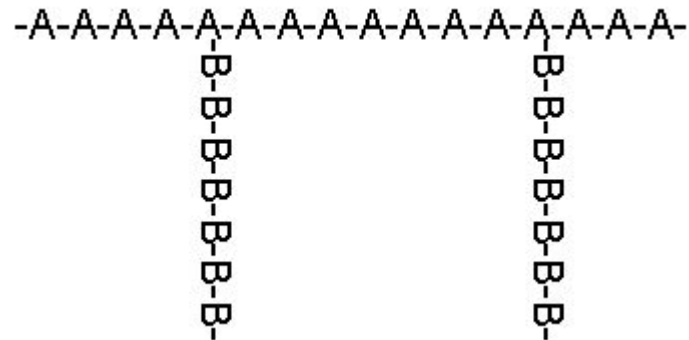
Copolymer - Different repeat units

Alternating Copolymer- A-B-A-B-A-B-A-B-A-B

Block Copolymer - AAAAAAAAA-BBBBBBBBBB

Random Copolymer- AA-B-A-B-B-A-A-A-B-B-A

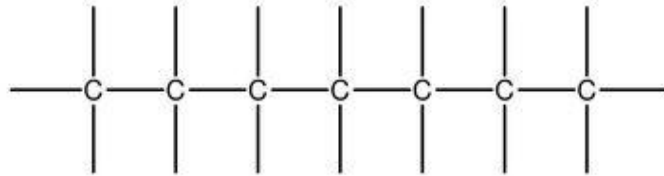
Graft Copolymer-



Nature of Backbone Chain

1) Homochain polymer

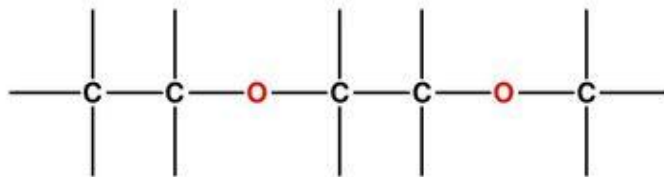
polymer chain (or backbone) consists of a single atom type



e.g., vinyl polymers, polyacetylene, polysulfur, poly(dimethyl silane)

2) Heterochain polymer

contain more than one atom type in the backbone



e.g., polyesters, polyethers, polyamides

Structural characteristics

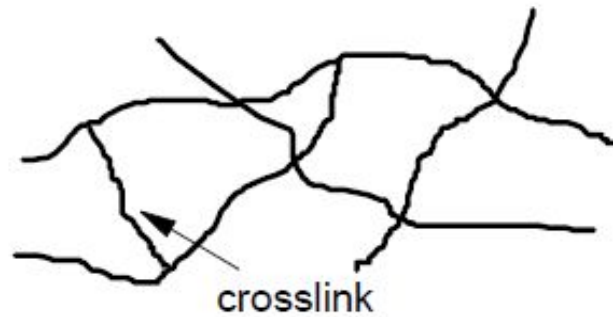
closely related to materials properties



linear (uninterrupted straight chain)

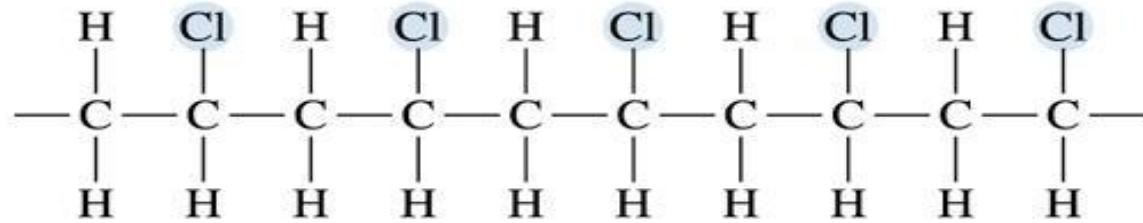


branched (occasional branches off longer chain)

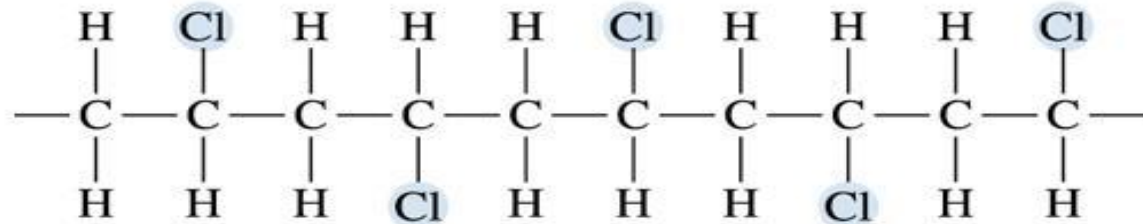


networked (many interconnected linear chains; one giant molecule)

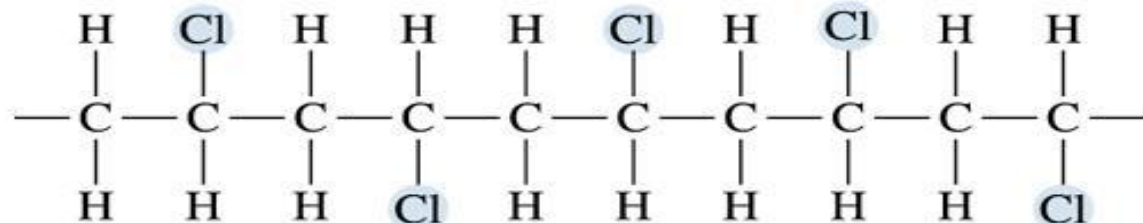
Stereochemistry



(a)



(b)



(c)

Three possible arrangements of nonsymmetrical monomers:

(a) **Isotactic**

side groups in same side

(b) **Syndiotactic**

side groups in alternating side



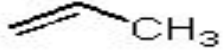
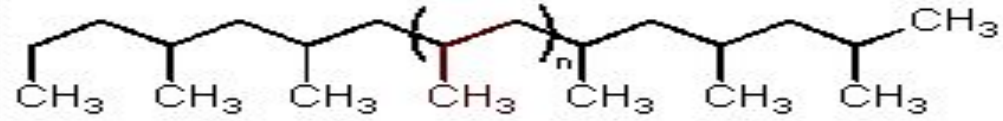

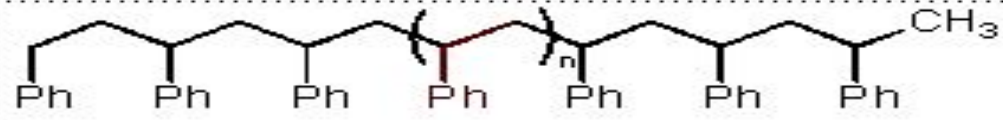

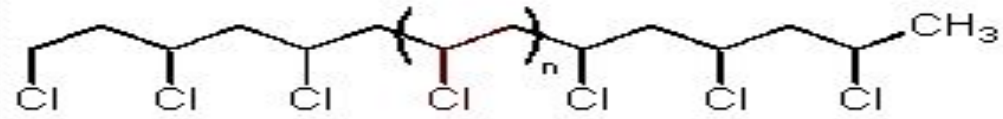
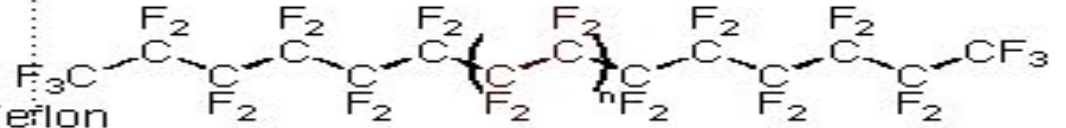
(c) **Atactic**

side groups is random

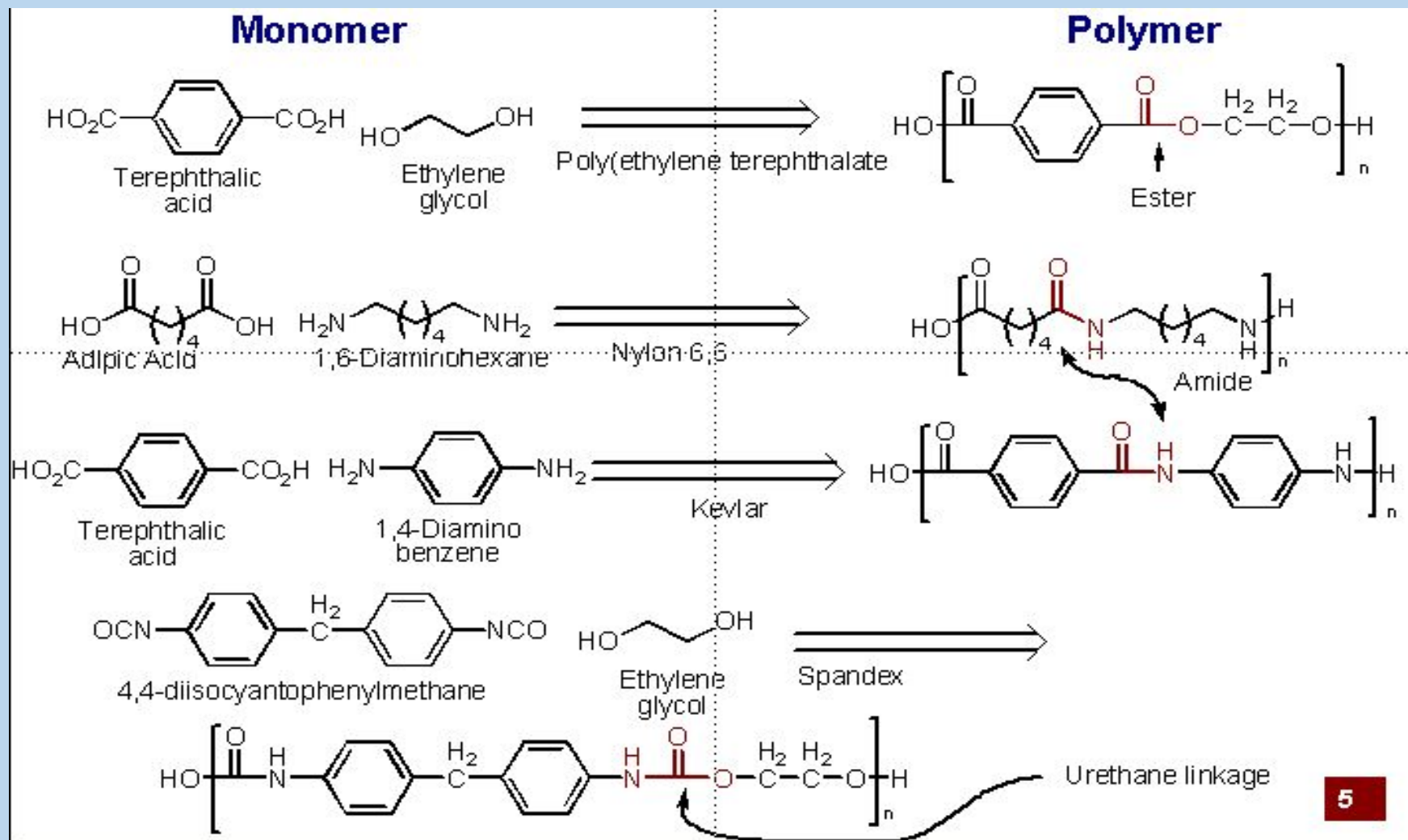
Polymer Families

- Polyolefins: made from olefin (alkene) monomers
- Polyesters, Amides, Urethanes, etc.: monomers linked by ester, amide, urethane or other functional groups
- Natural Polymers: Polysaccharides, DNA, proteins

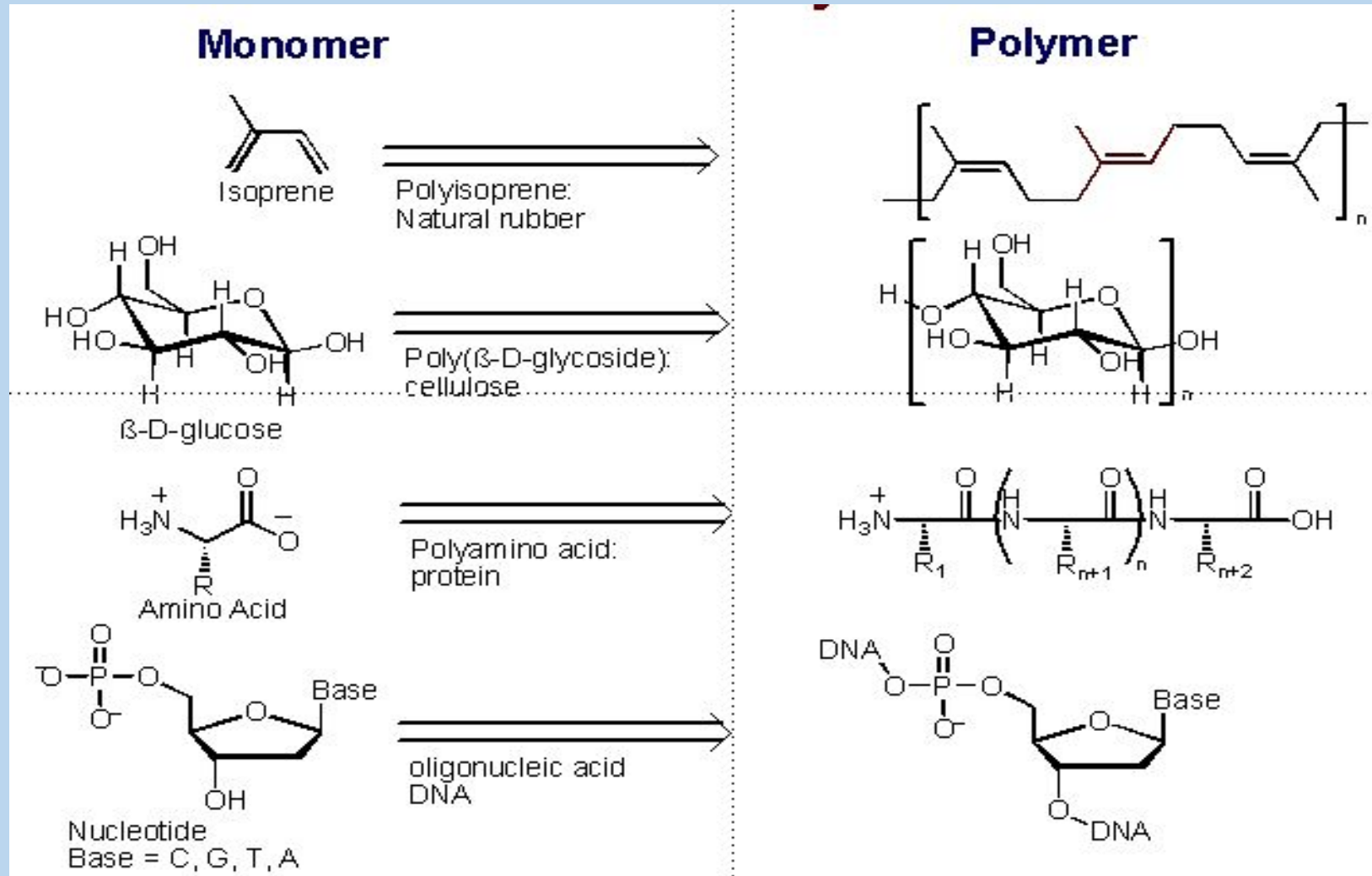
Common Polyolefins

Monomer		Polymer
 Ethylene	$\xrightarrow{\hspace{2cm}}$ Polyethylene	
 Propylene	$\xrightarrow{\hspace{2cm}}$ Polypropylene	
 Styrene	$\xrightarrow{\hspace{2cm}}$ Polystyrene	
 Vinyl Chloride	$\xrightarrow{\hspace{2cm}}$ Poly(vinyl chloride)	
$F_2C=CF_2$ Tetrafluoroethylene	$\xrightarrow{\hspace{2cm}}$ Poly(tetrafluoroethylene): Teflon	

Polyesters, Amides, and Urethanes



Natural Polymers



Physical Property Classifications

Looking at polymers as materials rather than from a chemical point of view, several classifications are widely used.

Temperature

- 1) **Thermoplastics^e** (plastics) — linear, or branched architecture can be melted and reformed on heating.
Soluble in organic solvents
 - a) **Amorphous**—no ordered structure-soften over a relatively wide temperature range (always lower than T_m) known as the glass transition (T_g). Above these temperatures, polymers are liquids
Eg. polystyrene and poly(methyl methacrylate).
 - b) **Semi-crystalline**—composed of microscopic crystallite domains of crystalline structure. Can be ordered.
Semi-crystalline polymers have true melting temperatures (T_m) at which the ordered regions break up and become disordered.
Eg: polyethylene. **Fibers** (nylon, PET polyester)

2) **Thermosets**—(resins)—massively cross-linked

very rigid; degrade on heating. Insoluble in solvents.

Usually synthesised in mold, then shaped by machining (grinding, drilling). E.g
(tires, rubber bands)

3) **Elastomers** (rubbers) — moderately cross-linked can be stretched and rapidly recover their original dimension

4) **Thermoplastic elastomers**: Elastic polymers that can be melted (soles of shoes)

5) **Dendrimers**—multiple branched—multiple consecutive (regular) branches.

Difference Between Thermoplastics and Thermosetting Polymers

Thermoplastics	Thermo-settings
1. They are usually formed by addition polymerization and condensation	1. They are usually formed by condensation polymerization
2. They consist of long chain linear polymers with negligible cross-links	2. They have three dimensional network structure
3. They soften on heating readily, because secondary forces between the individual chain can break easily by heat or pressure or both	3. They cross-link and bonds retain their strength on heating and hence they do not soften on heating.
4. By reheating to a suitable to a suitable temperature, they can be softening, reshaped and thus reused.	4. They retain their shape and structure, even on heating. Hence, they cannot be reshaped and reused.
5. They are, usually, soft, weak and less brittle.	5. They are, usually, hard, strong and more brittle.
6. These can be reclaimed from waste	6. They cannot be reclaimed from waste.
7. They are, usually, soluble in some organic solvents	7. Due to strong bonds and cross-links they are insoluble in almost all organic solvents.
8. Examples: Polyethylene, Polymers etc	8. Phenolic Resin, Epoxy, Polyurethans, Polyesters etc

End Use

Rubbers:- have long range elasticity

low molecular cohesion

tensile strength 300-1000 psi (lbs/sq inch)

Natural rubber, Buna-S-butyl rubber, Silicone rubber

Plastics:- stronger than rubbers

tensile strength 4000-13000 psi (lbs/sq inch)

types -hard and stiff or soft and flexible

Polyethylene, poly vinyl chloride, Teflon

Fibers:- strongest of the three types of polymer

tensile strength 20000-150000 psi (lbs/sq inch)

Jute, Wool, Silk, Nylon-6,6

Resins:- low molecular weight polymers – adhesives

Bakelite, epoxy resin

Polymer Material Properties Depends on

- 1. Degree of Polymerization**
- 2. Molecular Weight of the Polymer**
- 3. Molecular Weight Distribution**
- 4. Glass Transition Temperature**
- 5. Percentage of Crystallinity**
- 6. Structure and Distribution of Chain Branching**

Molecular weight and Degree of polymerisation

Degree of polymerisation

Number of repeating unit in a polymer called as *degree of polymerisation (DP)*. DP provides the indirect method of expressing the molecular weight and the relation is as follows;

$$M = DP \times m$$

Where, M is the molecular weight of polymer, DP is the degree of polymerisation and m is the molecular weight of the monomer

$$DP = M / m$$

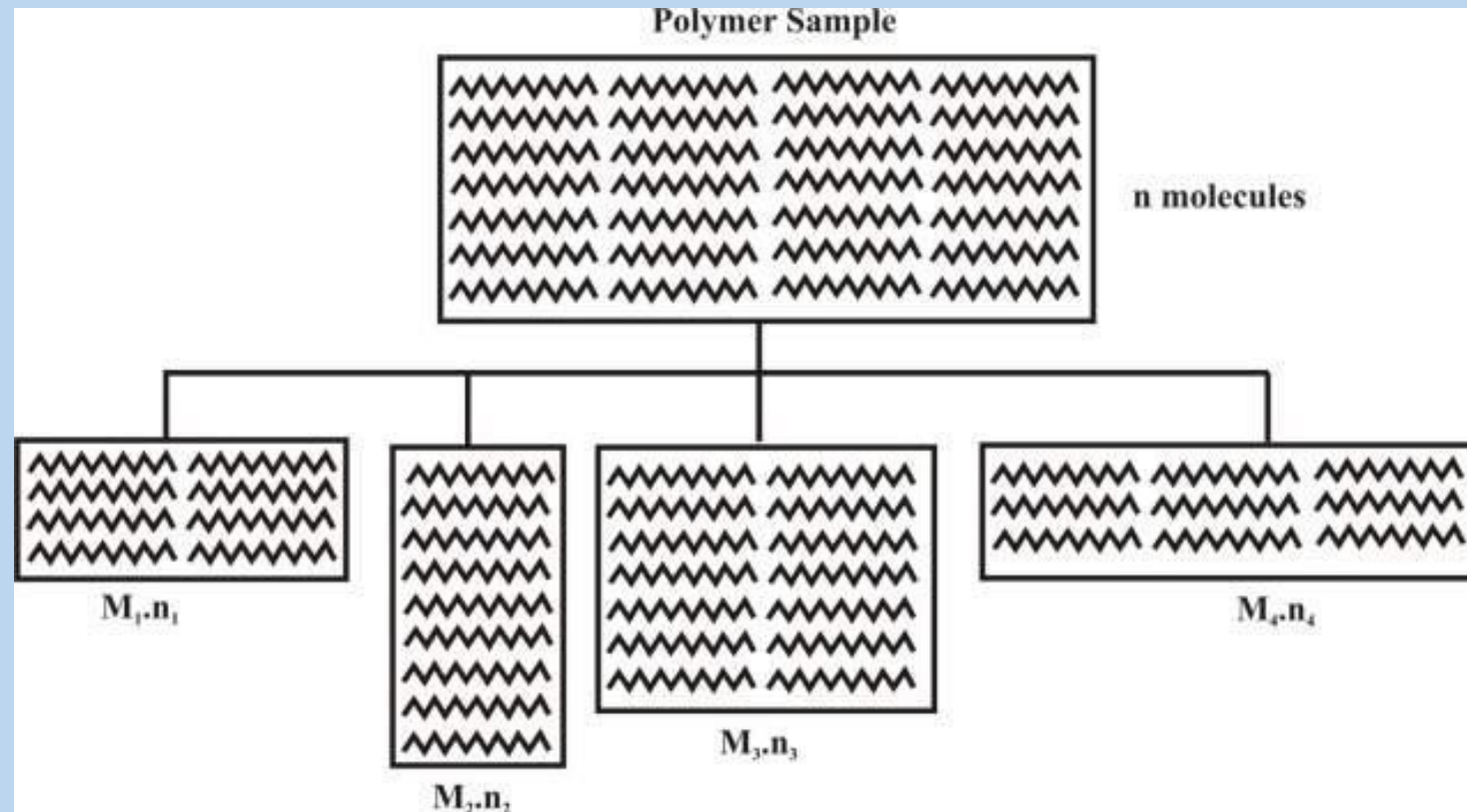
DP can be related to the corresponding molecular weight average by the following two equations;

$$M_n = (DP)_n \cdot m$$

$$M_w = (DP)_w \cdot m$$

Molecular weight of Polymers

Molecular weight of polymer is the sum of atomic weights of the individual atoms that comprise a molecule. It indicates the *average* length of the bulk polymer chains. All polymer molecules of a particular grade do not have the exact same molecular weight. There is a range or distribution of molecular weights.



Number-average molecular weight

$$\overline{M}_n = \frac{\sum_{i=1}^N N_i M_i}{\sum_{i=1}^N N_i}$$

Weight-average molecular weight

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

Viscosity-Average molecular weight

$$\overline{M}_\eta = \left[\frac{\sum_{i=1}^N N_i M_i^{\alpha+1}}{\sum_{i=1}^N N_i M_i} \right]^{1/\alpha} = \left[\frac{\sum_{i=1}^N w_i M_i^\alpha}{\sum_{i=1}^N w_i} \right]^{1/\alpha} = \left[\sum_{i=1}^N w_i M_i^\alpha \right]^{1/\alpha}$$

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

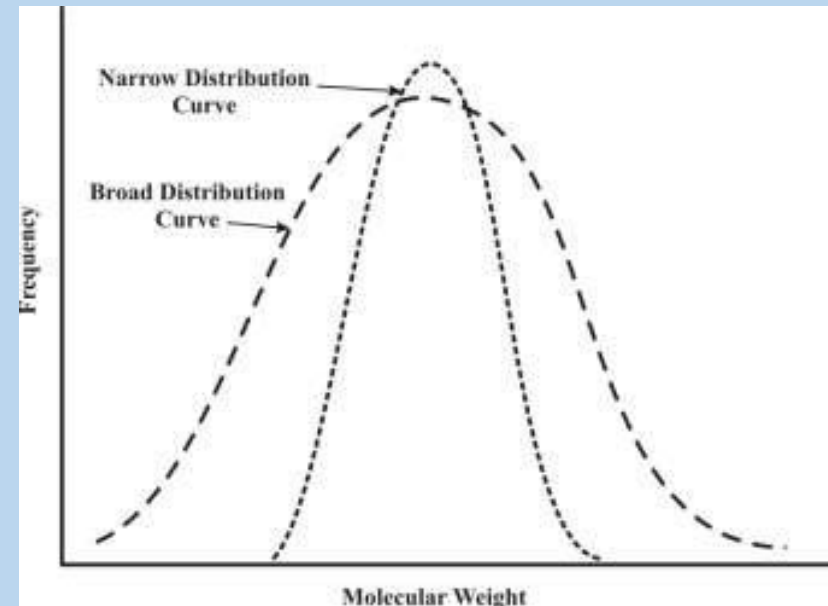
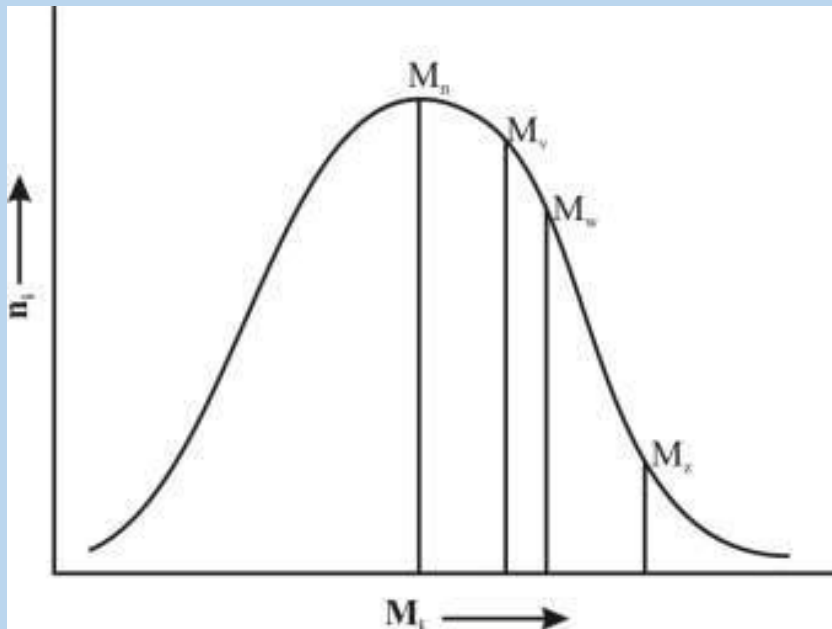
η = Viscosity

Polydispersity Index for Molecular weight of Polymers

- The ratio of M_w/M_n is called as Polydispersity index (PDI) of polymer.
- The narrower the molecular weight range, the closer the values of M_w & M_n and the ratio M_w/M_n may thus be used as an indication of the breadth of molecular weight range in a polymer sample.
- If all the polymer molecules present have the same molecular weight, the system is monodisperse.

$$\text{Polydispersity Index, PDI} = M_w / M_n$$

Molecular Weight Distribution



1. In a polymer, there are 100 molecules of molecular weight 100, 200 molecules of molecular weight 1000 & 300 molecules of molecular weight 10,000. find \bar{M}_n , \bar{M}_w & PDI.

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3}$$

N_i	M_i
100	100
200	1000
300	10000

$$\bar{M}_n = \frac{(100 \times 100) + (200 \times 1000) + (300 \times 10000)}{100 + 200 + 300}$$

$$= \frac{3.21 \times 10^6}{600} = 5.35 \times 10^3$$

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{(100 \times 100)^2 + (200 \times 1000)^2 + (300 \times 10000)^2}{(100 \times 100) + (200 \times 1000) + (300 \times 10000)}$$

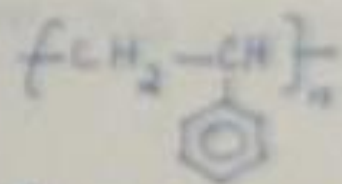
$$= \frac{30201 \times 10^4}{3.21 \times 10^6} = 9.4 \times 10^3$$

$$PDI = \frac{\bar{M}_w}{\bar{M}_n} = \frac{9.4 \times 10^3}{5.35 \times 10^3} = 1.757$$

2. The molecular weight of polystyrene is 10^5 g/mol.
Find its D_p .

$$D_p = \frac{\text{mol. wt. of polymer}}{\text{wt. of repeating unit}}$$

$$= \frac{10^5}{104} = 961.5$$

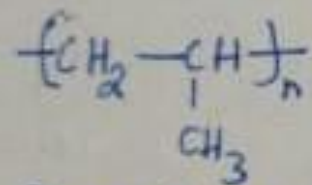


Repeating unit

$$(12 \times 8) + (8 \times 1) = 104$$

3. Find the molecular weight of polypropylene. given its D_p is 10000

Mol. wt. of polymer = $D_p \times$ weight of repeating unit



Repeating unit

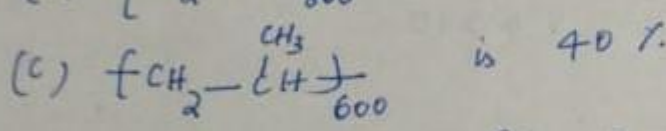
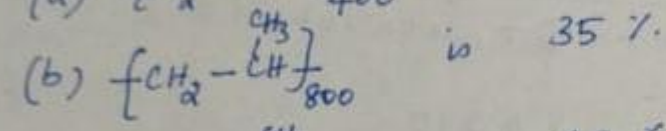
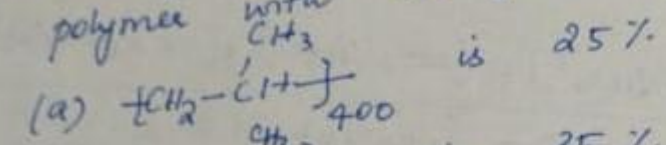
$$(12 \times 3) + (6 \times 1) = 42$$

Mol. wt. of polymer =

$$10000 \times 42$$

$$= 42 \times 10^4 \text{ g/mol.}$$

4. Calculate the ~~no~~ number average & weight average molecular masses of polypropylene polymer with the following composition.



Molecular mass of (a) = $[(12 \times 3) + (6 \times 1)] \times 400 \Rightarrow M_1 = 16800$
 $N_1 = 25$

Molecular mass of (b) = $[(12 \times 3) + (6 \times 1)] \times 800 \Rightarrow M_2 = 33600$
 $N_2 = 35$

Molecular mass of (c) = $[(12 \times 3) + (6 \times 1)] \times 600 \Rightarrow M_3 = 25200$
 $N_3 = 40$

$$\bar{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3}$$

$$= \frac{(25 \times 16800) + (35 \times 33600) + (40 \times 25200)}{25 + 35 + 40} = 26040$$

$$\begin{aligned}
 \overline{M}_w &= \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2}{N_1 M_1 + N_2 M_2 + N_3 M_3} \\
 &= \frac{[15 \times (16800)^2] + [35 \times (33600)^2] + [40 \times (25200)^2]}{260400} \\
 &= 27637 \text{ g/mol}
 \end{aligned}$$

Practical Significance of Molecular weight of Polymers

The influence of molecular weight on the bulk properties of polyolefin's,
an increase in the molecular weight leads to

Increase in:

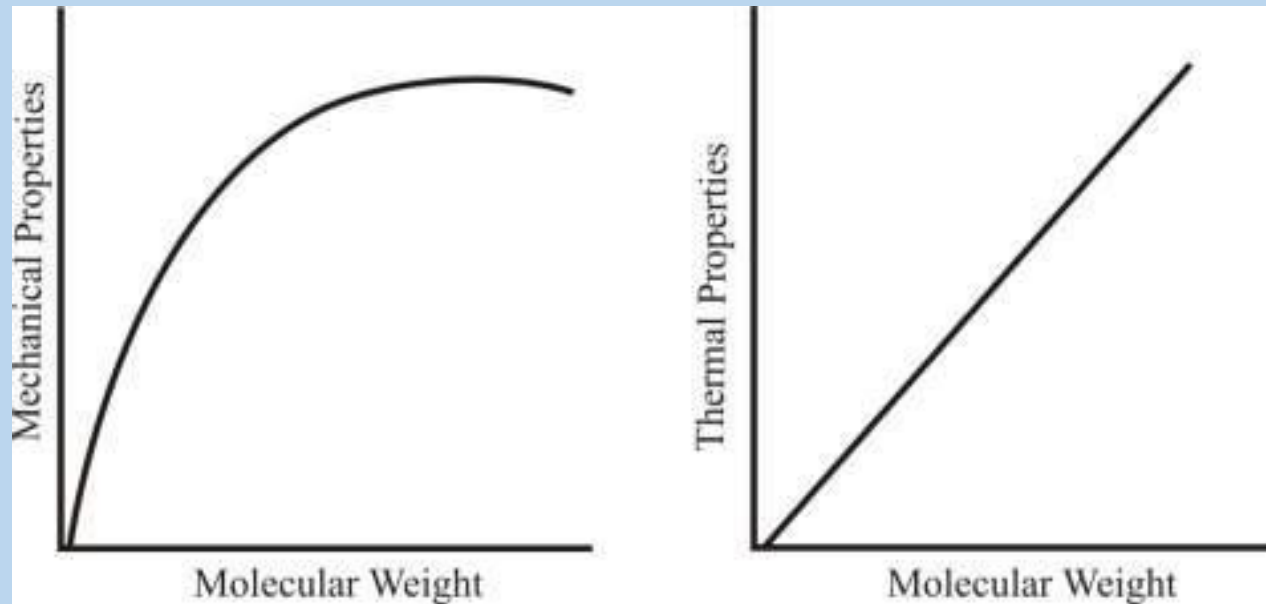
- Melt viscosity
- Impact strength

Lowers in:

- Hardness, Stiffness
- Softening point
- Brittle point

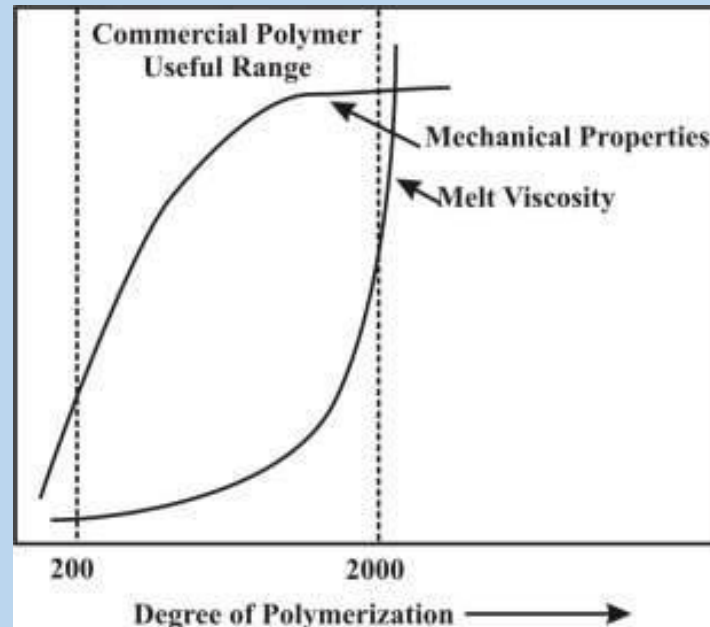
High molecular weight polymer does not crystallize so easily as lower molecular weight material crystallizes due to chain entanglement and that reflect in bulk properties of the high molecular weight polymer.

- A high molecular weight polymer increases the mechanical properties.
- Higher molecular weight implies longer polymer chains and a longer polymer chain implies more entanglement thereby they resist sliding over each other.
- Increasing the molecular weight and the chain length of the polymer increases impact strength.
- Thermal properties can also improved by increasing the molecular weight.

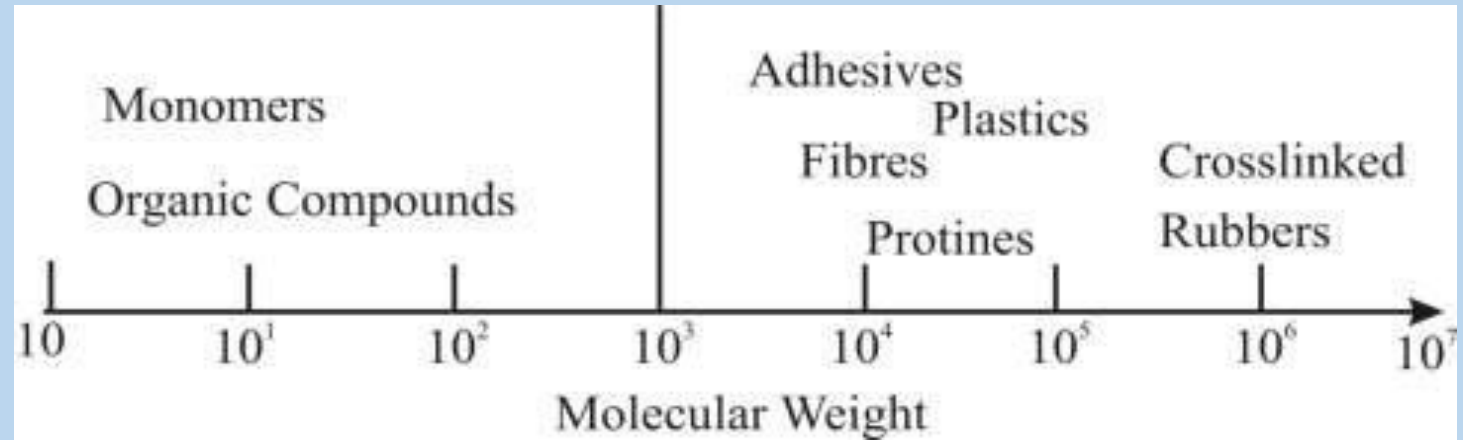


Significance of Degree of Polymerization







- To bring into sharper focus the effect of molecular weight on physical properties, a more generalized form of representation is given in figure, mechanical strength is plotted against 'DP' .
- Threshold value (TV)) for DP – Below which polymer does not possess any strength & exists as powder or liquid resin
- The knee portion of the curve at which polymer attains more or less full strength also varies from one polymer to another.
- The optimum strength of most of polymers is obtained at 600, while they do not exhibit any strength below DP, 30
- The useful range of DP is from 200 to 2000, which corresponds to its molecular weight 20000 to 200000



Molecular weight and Polymers



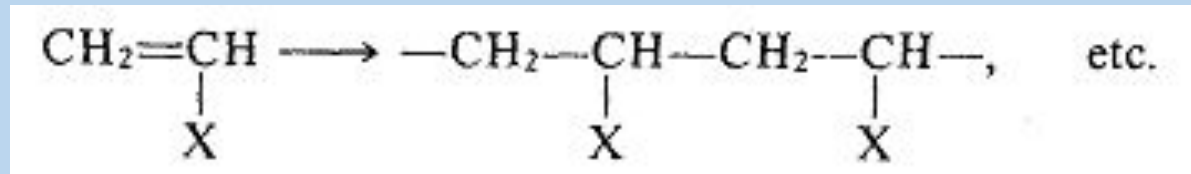
Common Polymers

Monomer	Repeating unit	Polymer name
$\text{CH}_2=\text{CH}_2$	$-\text{CH}_2-\text{CH}_2-$	polyethylene
$\text{CH}_2=\underset{\text{Cl}}{\text{CH}}$	$-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-$	poly(vinyl chloride)
$\text{CH}_2=\text{CH}-\text{CH}_3$	$-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-$	polypropylene
$\text{CH}_2=\underset{\text{C}_6\text{H}_5}{\text{CH}}$ 	$-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}-$ 	polystyrene
$\text{CF}_2=\text{CF}_2$	$-\text{CF}_2-\text{CF}_2-$	poly(tetrafluoroethylene) Teflon [®]
$\text{CH}_2=\underset{\text{C}\equiv\text{N}}{\text{CH}}$	$-\text{CH}_2-\underset{\text{C}\equiv\text{N}}{\text{CH}}-$	poly(acrylonitrile) Orlon [®] , Acrilan [®]
$\text{CH}_2=\underset{\text{COCH}_3}{\text{C}}-\text{CH}_3$ 	$-\text{CH}_2-\underset{\text{COCH}_3}{\overset{\text{CH}_3}{\text{C}}}-$ 	poly(methyl methacrylate) Plexiglas [®] , Lucite [®]
$\text{CH}_2=\underset{\text{OCCH}_3}{\text{CH}}$ 	$-\text{CH}_2-\underset{\text{OCCH}_3}{\text{CH}}-$ 	poly(vinyl acetate)

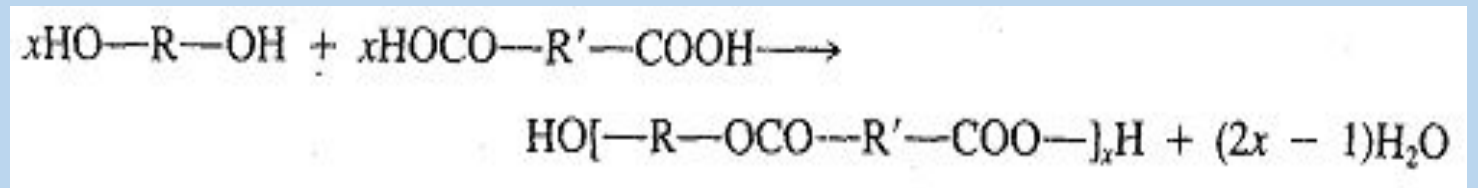
Polymerization

In 1929 W. H. Carothers suggested a classification of polymers into two groups, *addition and condensation polymers* with respect to polymerization

Addition Polymerization



Condensation Polymerization



Difference between Addition and Condensation Polymerization

Addition Polymerization	Condensation Polymerization
Olefinic (or) Vinylic compounds undergo addition polymerization	Monomers with two or more functional groups undergo condensation polymerization
No elimination of by-products	Continuous elimination of by-products
Double-bond provides required bonding sites	Intermolecular condensation reaction
Addition of monomers takes place rapidly	Polymer chain built up is slow and step-wise
Initiators – free radicals are used	Catalysed by acids or alkali
Elemental composition of polymer is same as monomer	Elemental composition of polymer is different from monomer

General Mechanism of Polymerization

Two types of polymerization based on mechanism

1. Chain Polymerization

(i) Free-radical mechanism

(ii) Ionic mechanism

2. Step-growth Polymerization

1. Chain Polymerization

i) Vinyl compounds $-\text{CH}_2=\text{CHX}$

ii) Dienes $-\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

iii) Olefins $-\text{CH}_2=\text{CH}_2$

iv) Allyl compounds $-\text{CH}_2=\text{CH}-\text{CH}_2\text{X}$

(X = -OH, -Cl, -Br, -COOH, -COOCH₃)

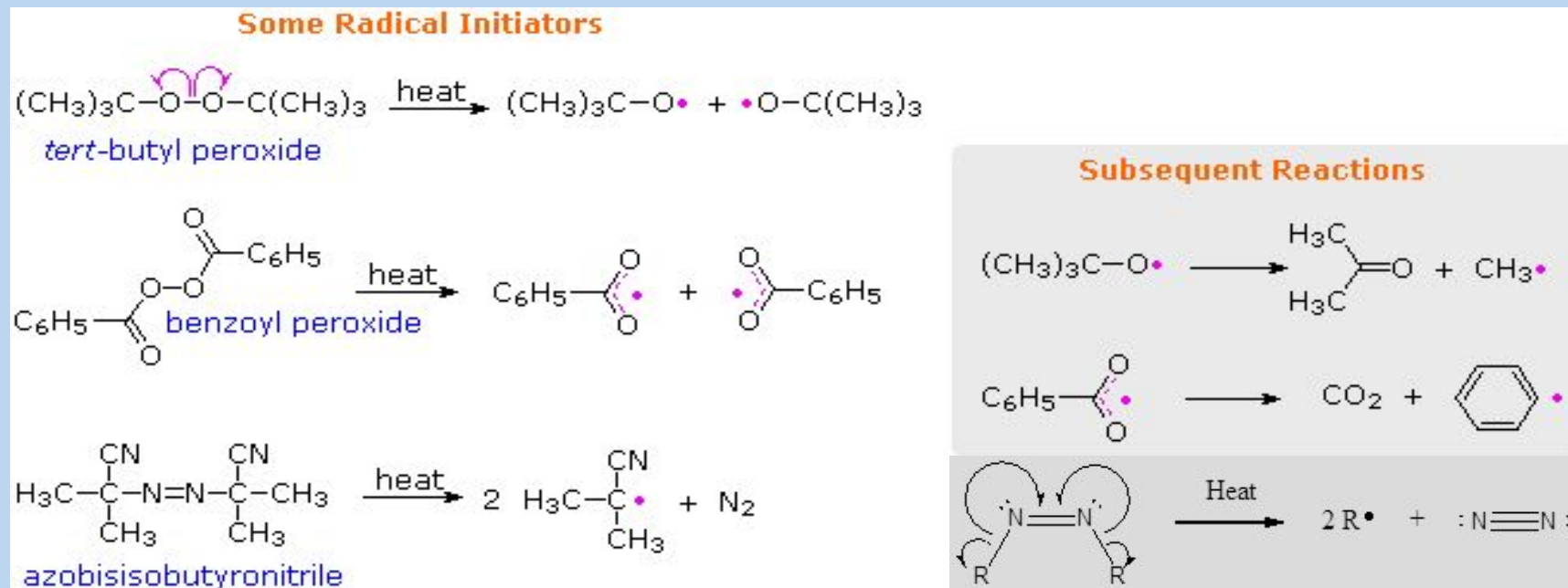
Mechanism of Chain Polymerization

Three major steps:

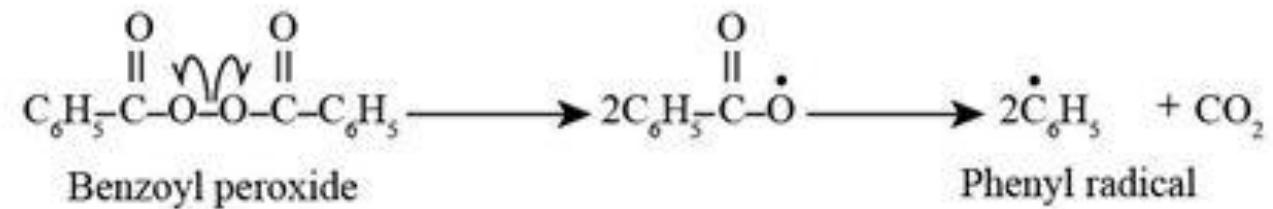
- (i) Initiation
- (ii) Propagation
- (iii) Termination

Free Radical Mechanism

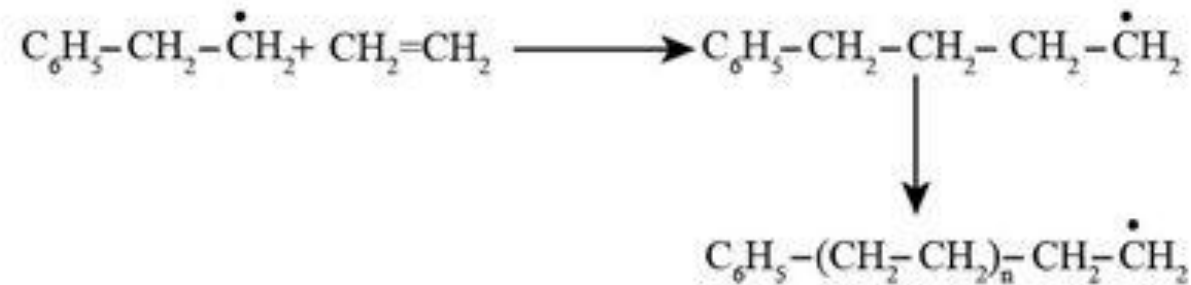
Initiator Compound which is thermally unstable and decompose into products called free-radicals



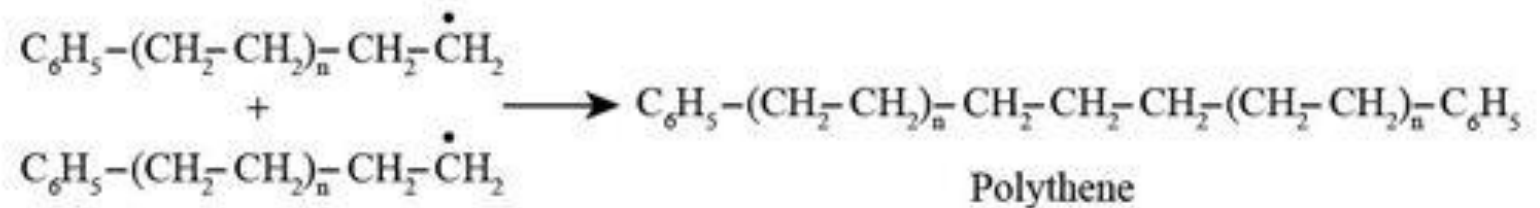
(1) *Chain initiation step*



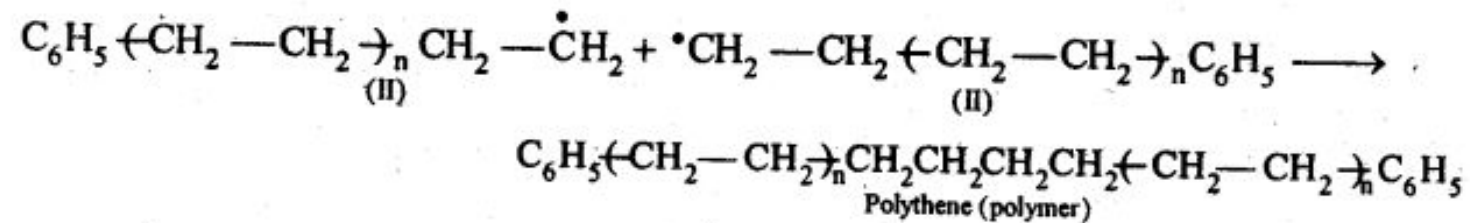
(2) *Chain propagating step*



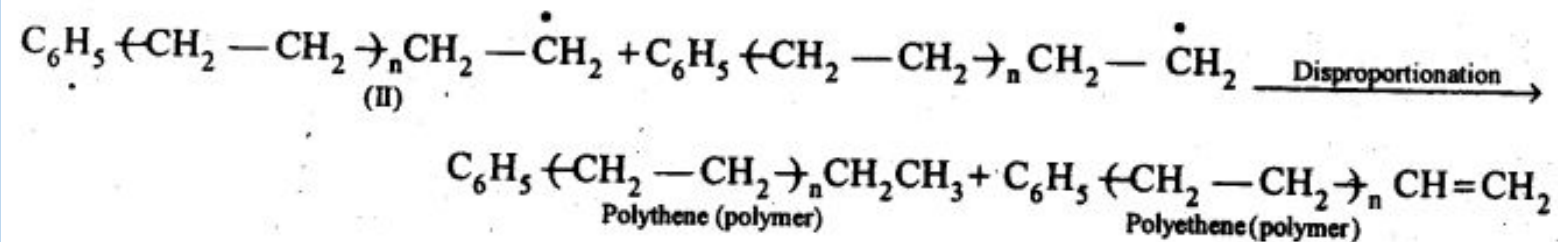
(3) *Chain termination step*



(i) By combination of free radicals (II):



(ii) By disproportionation of free radicals :



- The first step of polymerisation reaction is chain initiation step. In chain initiation step, formation of phenyl free radical takes place which then react with monomer of ethene to form a bigger size free radical.
- The repetition of this sequence occur in chain propagation step and
- In the final termination step, formation of polythene takes place.

Ionic Polymerization

- Cationic Polymerization:

The initiator is an acid (Lewis acids – (AlCl_3 , BF_3), HCl , H_2SO_4 , HNO_3) and the propagating site of reactivity (*) is a carbocation.

Eg. Homopolymerization of isobutylene

- Anionic Polymerization:

The initiator are Alkali metal (Na/K) amides, Alkali metal alkyls (n-butyl lithium) and the propagating site of reactivity (*) is a carbanion.

Eg. Co-polymerization of isobutylene with 2-methylpropene