School of Chemistry and Biochemistry, TIET, Patiala Applied Chemistry (UCB008)

Solutions to the Tutorial Sheet (Chemistry of Polymers)

1. **What is polymerization and degree of polymerization? How polymers are classified?**

   Ans: The chemical reaction in which high molecular mass molecules are formed from monomers is known as ***polymerization*** **or** the fundamental process by which low molecular weight compounds are converted into high molecular weight compounds.

   The ***degree of polymerization*** (DP) refers to the number of repeat units in the chain, and gives a measure of molecular weight.

   Polymers can be classified as;

   A. Classification on the basis of source:

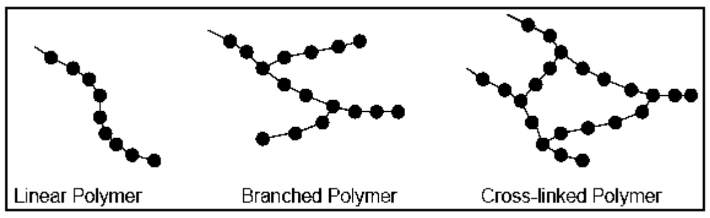
   i. **Natural polymers** – Polymers which are found in nature in plants and animals e.g. Starch, cellulose, proteins, natural rubber etc.

   ii. **Synthetic polymers**- These are man-made polymers like polyethylene, polypropylene, polyvinylchloride, nylon etc.

   B. Classification on the basis of structure:

   i. **Linear polymers** – Monomeric units in these polymers are joined in form of long straight chains e.g. nylons, polyester etc. They have high M.P, density and tensile strength due to close packing of chains.

   ii. **Branched polymers** - have a chain structure that consists of one main chain of molecules with smaller molecular chains branching from it.



   iii. **Cross linked Polymers**- In cross-linked polymers, adjacent linear chains of polymer are joined one to another at various positions by covalent bonds e.g. Vulcanized natural rubber, where sulfur joins the chains of natural rubber, Bakelite etc. Due to cross links, they are hard and rigid.

Other Ways to Classify Polymers

Classification Based on Polymerization

i. **Addition Polymerization:** Example, polyethylene, Teflon, Polyvinyl chloride (PVC)
ii. **Condensation Polymerization:** Example, Nylon -6, 6, perylene, polyesters.

Classification Based on Monomers

i. **Homomer:** In this type, a single type of monomer unit is present. For example, Polyethene
ii. **Heteropolymer or co-polymer:** It consists of different type of monomer units. For example, nylon -6, 6

Classification Based on Molecular Forces

i. **Elastomers:** These are rubber-like solids weak interaction forces are present. For example, Rubber.
ii. **Fibres:** Strong, tough, high tensile strength and strong forces of interaction are present. For example, nylon -6, 6.
iii. **Thermoplastics:** These have intermediate forces of attraction. For example, polyvinyl chloride.
iv. **Thermosetting polymers:** These polymers greatly improve the material's mechanical properties. It provides enhanced chemical and heat resistance. For example, phenolics, epoxies, and silicones.

2. Differentiate the following with examples:

i. Addition and condensation polymerisation

Addition polymerisation	Condensation polymerisation
1. The method involves the repeated addition of monomers to produce long chains without elimination of any by-products	1. The method involves series of condensation reactions, generally involving two monomers with the elimination small molecules like H_2O, NH_3 or HCl
2. Monomers must have a double or triple bond	2. Monomers must have two similar or different functional groups
3. The molecular weight of the resultant polymers is a multiple of monomer's molecular weight	3. The molecular weight of the resultant polymer is not a multiple of monomer's molecular weight
4. Lewis acids or bases, radical initiators are catalysts in addition polymerization	4. No such catalysts are required
5. High molecular mass polymers are formed at once	5. Polymer molecular mass rises steadily throughout the reaction
6. Example-polyethylene, Teflon, Polyvinyl chloride (PVC)	6. Example-Nylon -6, 6, perylene, polyesters.

ii. Homopolymer and copolymer

Homopolymer	Copolymer

1. Homopolymers are produced by using a single type of monomer or single species of repeating units	1. Copolymers are formed by polymerisation of mixture of two or more monomers/two or more types of repeating units.
2. Homopolymers are formed through addition polymerisation	2. Copolymers are formed through condensation polymerisation
3. They often have a simple structure	3. They usually have complex structure
4. Example-polyethylene, Teflon, Polyvinyl chloride (PVC)	4. Example-polyethylene-vinyl acetate (PEVA), nitrile rubber, and acrylonitrile butadiene styrene (ABS)

iii. Thermoplastic and thermosetting polymer

Thermoplastic polymer	Thermosetting polymer
1. They soften on heating readily and once moulded they can be resoftened and reused	1. They do not soften on heating, hence once moulded, they set permanently
2. They are softer and less strong; the polymeric chains are held together by weak vander Waals forces	2. They are strong and hard, there are cross linkages and covalent bond formation between the adjacent polymeric chains
3. They are generally formed by addition polymerisation reaction	3. These are formed by condensation polymerisation reaction
4. As they soften again and again, they can be recycled, reused and reclaimed from waste.	4. They cannot be recycled, reused or reclaimed from waste.
6. Example-polyethylene, Teflon, Polyvinyl chloride (PVC)	6. Example-Bakelite, melamine formaldehyde.

3. **Why polymers are expressed in terms of average molecular weights? For a polymeric sample, discuss the number average and weight average type of molecular mass.**

Ans: In the process of polymerisation, the chain termination is a random process, all the polymeric chains formed are of different lengths, hence it becomes difficult to express the molecular weight of the polymer. Therefore, the molecular weight can be expressed as average of the molecular weights contributed by individual molecules in the sample. In other words, polymers are mixtures of molecules of different molecular masses (polydisperse and heterogeneous).

The molecular weight of a polymer is expressed in two ways:

i. **Number average molecular weight M_n. -** If N_1, N_2, N_3, … are the numbers of molecules with molecular masses M_1, M_2, M_3, …, respectively, then the number average molecular weight is:

$$\overline{Mn} = \frac{[N_1M_1 + N_2M_2 + N_3M_3 + \text{-----}]}{N_1 + N_2 + N_3 + \text{----}} = \Sigma N_iM_i / \Sigma N_i$$

Where N_1, N_2, N_3 -number of molecules, M_1, M_2, M_3 – Mol. wts

Total mass of the polymer sample / Total number of molecules present in the sample

ii. **Weight average molecular weight Mw** - If m_1, m_2, m_3 ,... are the weights of species with molecular masses M_1 , M_2 , M_3 , …, respectively, then the weight average molecular weight is:

$$\overline{Mw} = \frac{m_1M_1 + m_2M_3 + m_3M_3 + \text{---------}}{m_1 + m_2 + m_3 + \text{-----------}}$$

$$\overline{Mw} = \frac{\sum m_i M_i}{\sum m_i}$$

But

$m_i = n_i M_i$

Hence,

$$\overline{Mw} = \frac{[N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \text{-----}]}{N_1M_1 + N_2M_2 + N_3M_3 + \text{--}} = \Sigma N_iM_i^2 / \Sigma N_iM_i$$

where n_i = number of molecules of mass M_i

4. **Weight average molecular weight is higher than number average molecular weight in polymers. Explain. What is polydispersity index?**

Ans: Compared to Mn, Mw takes into account the molecular weight of a chain in determining contributions to the molecular weight average. The more massive the chain, the more the chain contributes to Mw. “Mn” the number average molecular weight, is evaluated from the mole fraction distribution of different sized molecules in a sample while Mw, the weight average molecular weight, is calculated from the weight fraction distribution of different sized molecules. Since larger molecules in a sample weigh more than smaller molecules, the weight average (Mw) has higher values, and is always greater than Mn. Moreover, the weight average is proportional to the square of the molecular weight.

Polydispersity Index (**PDI**): The polydispersity index or heterogeneity index is a measure of the distribution of molecular mass in a given polymer sample. **The PDI calculated is the weight average molecular weight divided by the number average molecular weight**. It indicates the distribution of individual molecular masses in a batch of polymers. The PDI has a value equal to or greater than 1, but as the polymer chains approach uniform chain length or as the weight dispersion of molecules in a sample narrows, Mw approaches Mn, and in the unlikely case that all the polymer molecules have identical weights (a pure mono-disperse sample), the ratio Mw/ Mn (i.e PDI) becomes unity.

5. In a polymer sample, 30% molecules have a molecular mass 20000, 40% have molecular mass 30000 and rest have 60000. Calculate mass average and number average molecular masses.

Ans:

$$\overline{Mn} = \frac{[N_1M_1 + N_2M_2 + N_3M_3 + \text{-----}]}{N_1 + N_2 + N_3 + \text{----}} = \Sigma N_iM_i / \Sigma N_i$$

$$= \frac{(30 \times 20{,}000) + (40 \times 30{,}000) + (30 \times 60{,}000)}{30 + 40 + 30}$$

$= 36000$

$$\overline{Mw} = \frac{[N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \text{-----}]}{N_1M_1 + N_2M_2 + N_3M_3 + \text{--}} = \Sigma N_iM_i^2 / \Sigma N_iM_i$$

$$= \frac{30(20{,}000)^2 + 30(20{,}000)^2 + 30(20{,}000)^2}{(30 \times 20{,}000) + (40 \times 30{,}000) + (30 \times 60{,}000)}$$

$= 43333$

6. In a polymer there are 150 molecules of molecular weight 100, 200 molecules of molecular weight 1000 and 300 molecules of molecular weight 10000. Find the number and weight average molecular mass of the polymer and PDI.

Ans:

$$\overline{Mn} = \frac{[N_1M_1 + N_2M_2 + N_3M_3 + \text{-----}]}{N_1 + N_2 + N_3 + \text{----}} = \Sigma N_iM_i / \Sigma N_i$$

$$= \frac{(150 \times 100) + (200 \times 1000) + (300 \times 10000)}{150 + 200 + 300}$$

$= \mathbf{4946.15}$

$$\overline{Mw} = \frac{[N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \text{-----}]}{N_1M_1 + N_2M_2 + N_3M_3 + \text{--}} = \Sigma N_iM_i^2 / \Sigma N_iM_i$$

$$= \frac{150(100)^2 + 200(1000)^2 + 300(10{,}000)^2}{(150 \times 100) + (200 \times 1000) + (300 \times 10{,}000)}$$

$= \mathbf{9393.93}$

PDI =

$$\frac{\overline{Mw}}{\overline{Mn}}$$

$$= \frac{9393.93}{4946.15}$$

$= 1.89$

7. **Calculate the degree of polymerization of vinyl chloride if the number average weight of polymer is 1.31×10^5 g/mol.**

   Ans: $M\bar{n}$ = D.P (molar mass of monomer)

   1.31×10^5 g/mol = D.P (62.5 g/mol), hence D.P = 2096

8. **When 52 g of styrene was polymerized, average degree of polymerization was found to be 1.5×10^5. Calculate the number of styrene molecules in the original sample and number of molecules of polystyrene produced.**

   Ans: (i) No. of molecules of styrene in 52g = 52 × (6.023×10^{23}/ 104.15) = 12.07×10^{23} molecules

   (ii) No. of molecules of polystyrene formed

$$= \frac{\text{No. of styrene molecules}}{\text{Degree of polymerisation}}$$

$$= \frac{12.07 \times 10^{23}}{1.5 \times 10^5}$$

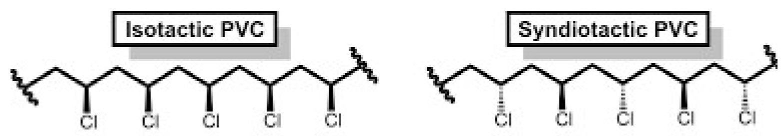
$= 8.04 \times 10^{18}$ molecules

9. **What is tacticity? Draw and differentiate syndiotactic and isotactic forms of polyvinyl chloride.**

   Ans: Tacticity is defined as the way pendant groups (side groups/functional groups) are arranged along the backbone chain of polymer. This refers to different atomic configurations for the same composition. Based on the orientation of the side groups polymers can be classified as isotactic, syndiotactic or atactic polymers:

   Isotactic polymers: When the orientation of the side groups on alternate asymmetric carbon atoms is the same, the polymer is termed as a syndiotactic polymer.

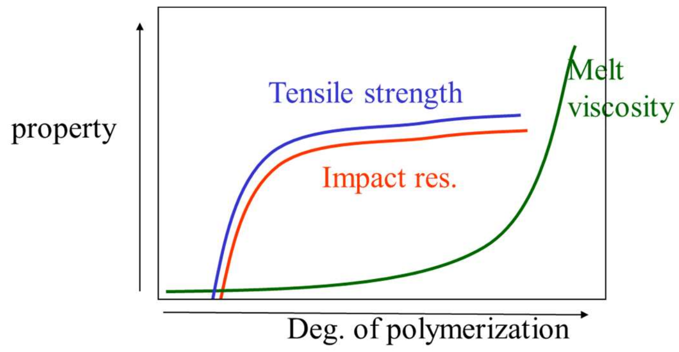
   Syndiotactic polymers: When the orientation of the side groups on alternate asymmetric carbon atoms is the same, the polymer is termed as a syndiotactic polymer.



10. What is threshold molecular weight? How tensile strength, impact resistance and melt viscosity are related to the degree of polymerization? Discuss.

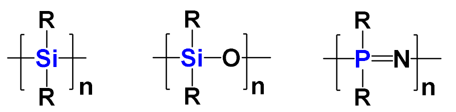
Ans: Threshold molecular weight is the minimum molecular weight that a polymer must attain to develop the properties needed for a particular application. Therefore, polymerization process should be controlled after certain stage depending upon the application. The degree of polymerization has a dramatic effect on the mechanical properties of a polymer.

- Tensile strength and impact resistance increase with increase in degree of polymerization upto a point after which slow increase is there. At lower molecular weight, the polymer chains are loosely bonded by weak van der Waals forces and the chains can move easily, responsible for low strength, although crystallinity is present. In case of large molecular weight polymer, the chains become large and hence are entangled, giving strength to the polymer.
- Melt flow viscosity initially increases slowly then rapidly after the polymer has attained a certain degree of polymerization, a high molecular weight increases the viscosity of the material making it harder to process the material using conventional methods. The longer the chains, the harder it is to get them to flow because they are more tangled.



11. What are inorganic polymers? How are their properties different from organic polymers?

Ans: The polymers in which backbone of the carbon (as in organic polymers) is replaced by silicon, phosphorous or any other inorganic atom are called **Inorganic Polymers**.



In contrast to organic polymers, inorganic polymers exhibit following properties:

- Nonflammability
- Low temperature flexibility
- Electrical conductivity

12. What are biodegradable polymers? Give two examples each of natural and synthetic biodegradable polymers

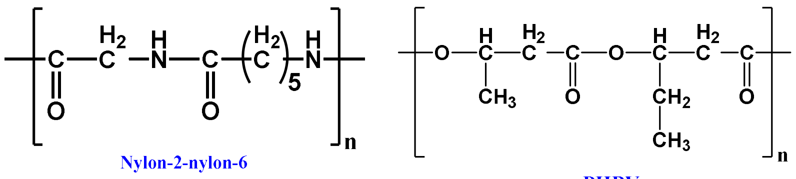
Ans: The polymers that can be degraded into small segments after their intended purpose by bacterial decomposition process to result in natural byproducts such as gases (CO_2, N_2), water, biomass and inorganic salts are called "Biodegradable polymers".

i. Natural - Starch, Cellulose, Proteins, DNA, Polyhydroxyalkanoates (PHA)

ii. Synthetic - Nylon-2-nylon-6, PHBV, Polylactic acid

13. Which functional groups are generally present in the biodegradable polymers? With the help of suitable examples, explain how the synthetic polymers are also being degraded by biocatalysts (enzymes)?

Ans: Biodegradable polymers tend to consist of ester, amide or ether functional groups. Synthetic polymers can be biodegraded only if they possess same chemical linkage as that present in natural polymers.



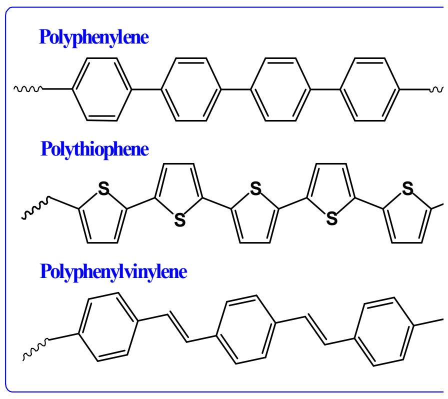
Nylon-2-nylon-6

PHBV
Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

Nylon-2-nylon-6 has a peptide linkage that can be hydrolysed by same enzymes that degrade a protein in nature while **PHBV** has an ester linkage that can be hydrolysed by living organisms and the products of hydrolysis are further metabolized by soil microbes.

14. What are conducting polymers? Give examples. Write their applications

Ans: Some polymers, under certain conditions, have electrical conductivities comparable to that of metallic conductors due to delocalized **π electrons.** Such polymers are called **conducting polymers.** Examples of conducting polymers are given as below:



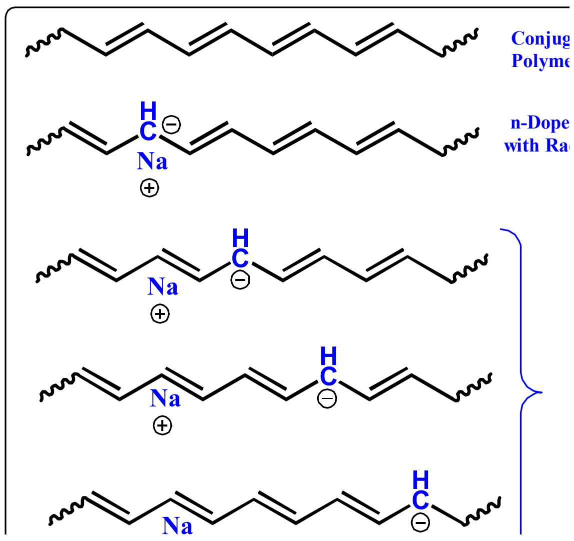
Applications of conducting polymers

- **Replacement of Metal Conductor:** Conducting polymers have replaced conventional metallic conductors due to their light weight and comparable conductivities in electronic devices.
- **Chemical Sensors:** Conducting polymers, such as polypyrrole, polyaniline, polythiophene and their derivatives, have application as gas sensors.
- **Printed Circuit Boards (PCBs):** Conducting Polymer coated polymer sheets for PCBs are inexpensive and have better adhesive properties compared to metallic conductors coated with epoxy resins.
- **Rechargeable Batteries:** The capability of repeated oxidation and reduction of CPs make them eligible for rechargeable batteries as compared to conventional Ni-Cd Cells.
- Numerous other applications such as **Light Emitting Diodes (LEDs)**, in **Display Device**

15. Why doping is required in conducting polymers? Explain the mechanism of conduction in n-doped polymers

Ans: The conductivity in conducting polymers is due to presence of conjugated system in the backbone or delocalized π electrons but conjugated bonds do not render polymeric materials to be highly conductive. Therefore, to enhance their conductivity a dopant needs to be added that either generates a free electron or a hole, as in case of semiconductors.

Mechanism of Conduction in n-Doped Polym



n-Doping: An electron-rich species (Lewis bases) like napthyl radical anion is added in the conjugated system to induce reduction and thus generate a radical anion. Thus, a radical anion or an electron is generated that when moves through the doped conjugated system causes electrical conduction.