COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
UNIVERSITY GRANTS COMMISSION

CHEMICAL SCIENCES CODE:01

2.13. Polymer chemistry

At a Glance

Degree polymerization, number average molecular weight, weight average molecular weight.

Key Statements

Basic Key statements: Polymers (2.13.1), Degree of polymerization (2.13.2), Number average molecular weight (2.13.8), Weight average molecular weight (2.13.9), Intrinsic viscosity molecular weight relation (2.13.10),

Standard Key statements: High polymers and oligomers (2.13.3), Probability density curve for molar masses (2.13.6), Various type of polymers (2.13.11/12)

Advance Key statements: Addition polymerization (2.13.4), Condensation polymerization (2.13.5), PDI (2.13.7), The average number of monomers per polymer molecule (2.13.14)

2.13. Polymer chemistry

2.13.1. **Polymers:** These are long chain high molecular weight compounds. They are obtained by the combination of a large number of simple molecules. the simple molecules taking part in the formation of polymers are called monomers and the process is called polymerization.

$$nCH_2{=}CH_2 \rightarrow [-CH_2 - CH_2-]_n$$

2.13.2. **Degree of polymerization:** The number of repeat units in the polymer chain is called degree of polymerization.

The molecular mass of the polymer = $n \times M_M$

Where, n = degree of polymerization

M_M= molecular mass of the monomeric unit.

2.13.3. **High polymers and oligomers:** The polymers which have high degree of polymerization are called high polymers and which have low degree of polymerization are called oligomers.

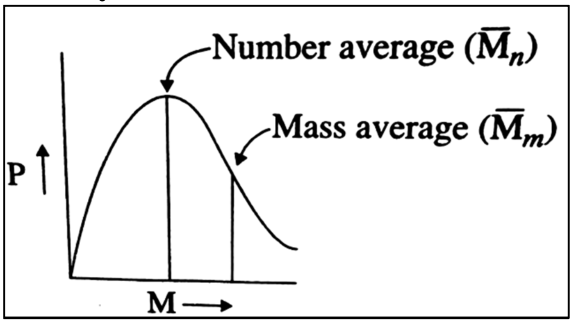
2.13.4. **Addition polymerization:**

- Monomers are linked together without of any by product molecule.
- Monomers contain a double bond but do not contain any functional group or contain them as lateral substituent.
- The molecular mass of the polymer is an integral multiple of that of the monomer.
- It proceeds through radical or carbonium ion chain mechanism.

2.13.5. **Condensation polymerization:**

- Monomers are linked together with the elimination of by product molecules usually water.
- Monomers contain the active functional groups which react together with the elimination of some molecules usually water.
- The molecular mass of the polymer is not integral multiple of that of the monomer.
- It proceeds by stepwise intermolecular condensation of functional groups.

2.13.6. **Probability density curve for molar masses:**



2.13.7. **Polydispersity index:** Polydispersity index (PDI) is the ratio of mass average molar mass to number average molar mass ($\bar{M}_m/\ \bar{M}_n$).
The mass average molar mass is always larger than the number average molar mass. When the sample is monodisperse $\bar{M}_M = \bar{M}_N$.

2.13.8. **Number-average molecular weight:** When the total molecular weight of all the molecules of a sample is divided by the total number of molecules, the result obtained is called the number average molecular weight. Osmotic pressure method gives number average molecular weight.

$$\bar{M}_n = \sum_{i=1}^{n}\left(\frac{N_i M_i}{N_i}\right)$$

Where, N_i = i^{th} number of molecule
M_i = molecular weight of the i^{th} molecule.

2.13.9. **Weight average molecular weight:** When the total molecular weight of the group of molecules having particular molecular weights are multiplied with their respective molecular weight, the products are added and the sum is divided by the total weight of the all molecules, the result obtained is called weight average molecular weight. Viscosity method, light scattering method and sedimentation method gives weight average molecular weight.

$$\bar{M}_w = \sum_{i=1}^{n}\left(\frac{N_i M_i^2}{N_i}\right)$$

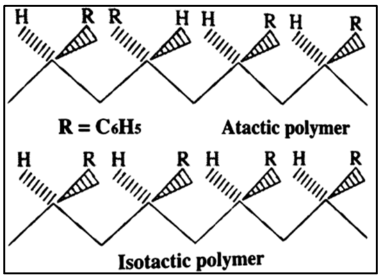
2.13.10. **Intrinsic viscosity molecular weight relation:**

$[\eta] = KM^a$

Where, a is constant. It lies between 0.5 to 1.

When a = 1 the viscosity average becomes equal to the mass average molecular mass.

2.13.11. **Isotacticpolymer:** If all the asymmetric carbon atoms have the same configuration with respect to each other the polymer is isotactic.



Atactic polymer: In the atactic polymer a random arrangement of group is observed as in the case of free radical polymerization.

Syndiotactic polymer: When the configuration alternate it is Syndiotactic.

isotactic and syndiotactic polymers are usually obtained with Ziegler-Natta catalyst.

2.13.12. **Stereoregular polymers:** Isotactic and syndiotactic polymers are collectively referred as stereoregular polymers. They are always arranged in a head to tail arrangement.

2.13.13. **Kinetic chain length:** The Kinetic chain length 'v' is a measure of the efficiency off the chain propagation mechanism. It is defined as the ratio of the number of monomer units consume per active centre produced in the initiation step:

v = number of monomer units consumed/number of active centers produced

the Kinetic chain is therefore equal to the ratio of the propagation and initiation rates:

v = propagation rates/initiation rates

2.13.14. **The average number of monomers per polymer molecule is**

$$\langle n \rangle = \frac{[A]_0}{[A]} = \frac{1}{1 - P}$$

2.13.15. **The degree of polymerization is**

$$\langle n \rangle = 1 + kt[A]_0$$

NET JUNE 2016

Q. The condensation of a hydroxy acid produces a polyster with the probability of linkage at both ends being p. The mole fraction of k-mer chain formation is

(a) p^k (b) $p(1-p)^{k-1}$ (c) $p^{k-1}(1-p)$ (d) p^{k-1}

Ans. In FLorySchulz distribution

$$p_k = Mo(1-P)^2 p^{k-1}$$

Therefore, mole fraction of polymer with a chain length k is

$$y_k = \frac{p_k}{M} = \frac{Mo(1-P)^2 p^{k-1}}{Mo(1-P)} = (1-P)p^{k-1}$$

Correct option is (c).

NET DEC 2016

Q. Mark-Houwink equation ([η]=KM^a) is used for the determination of

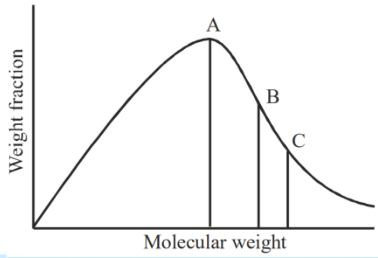
(a) number-average molar mass (b) weight-average molar mass

(c) viscosity-average molar mass (d) z-average molar mass

Ans. In the equation ([η]=KM^a), [η] represents intrinsic viscosity.

Correct option is (c).

Q. Distribution of molar masses in a typical polymer sample is shown below



The A, B and C represent

(a) $\bar{M}_W$, $\bar{M}_V$ and $\bar{M}_n$, respectively (b) $\bar{M}_n$, $\bar{M}_V$ and $\bar{M}_W$, respectively

(c) $\bar{M}_V$, $\bar{M}_W$ and $\bar{M}_n$, respectively (d) $\bar{M}_n$, $\bar{M}_W$ and $\bar{M}_V$, respectively

Ans. Correct order is $\bar{M}_n<\bar{M}_V<\bar{M}_W$.

Correct option (b).

NET JUNE 2017

Q. For a monodisperse polymer, the number-average molar mass ($\bar{M}_n$) and weight-average molar mass ($\bar{M}_W$) are related according to

(a) $\bar{M}_W < \bar{M}_n$ (b) $\bar{M}_W = \bar{M}_n$ (c) $\bar{M}_W > \bar{M}_n$ (d) $\bar{M}_W < \log \bar{M}_n$

Ans. PDI = $\frac{\bar{M}_W}{\bar{M}_n} = 1$; **Correct option is (b).**

NET DEC 2017

Q. The number–average molar mass ($\bar{M}_n$) for a monodisperse polymer is related to the weight-average molar mass ($\bar{M}_W$) by the relation

(a) $\bar{M}_n = \frac{\bar{M}_W}{3}$ (b) $\bar{M}_n = \frac{\bar{M}_W}{4}$ (c) $\bar{M}_n = 2\bar{M}_W$ (d) $\bar{M}_n = \bar{M}_W$

Ans. PDI = $\frac{\bar{M}_W}{\bar{M}_n} = 1$

Correct option is (d).

Q. A polymer has the following molar mass distribution

Number of molecules	Molar mass (g.mol^{-1})
50	5000
75	6000

The calculated number average molar mass $\bar{M}_n$ of the polymer is

(a) 5200 (b) 5600 (c) 5800 (d) 6000

Ans. $\bar{M}_n = \frac{N_1M_1+N_2M_2}{N_1+N_2} = \frac{(50\times5000)+(75\times6000)}{(50+75)} = 5600$

Correct option is (b).

NET JUNE 2018

Q. A 5 g/L polymer solution is prepared with a polymer whose molar mass is 25 kg. The osmotic pressure (in atm) of this solution at 25°C is (consider RT ≅ 2500 $Jmol^{-1}$)

(a) 0.002 (b) 0.05 (c) 0.005 (d) 0.008

Ans. $\pi = \frac{CRT}{M} = \frac{5\times10^{-3}0.084}{25} = 0.005$atm. **Correct option is (c).**