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1. Learning Outcomes

After studying this module, you shall be able to

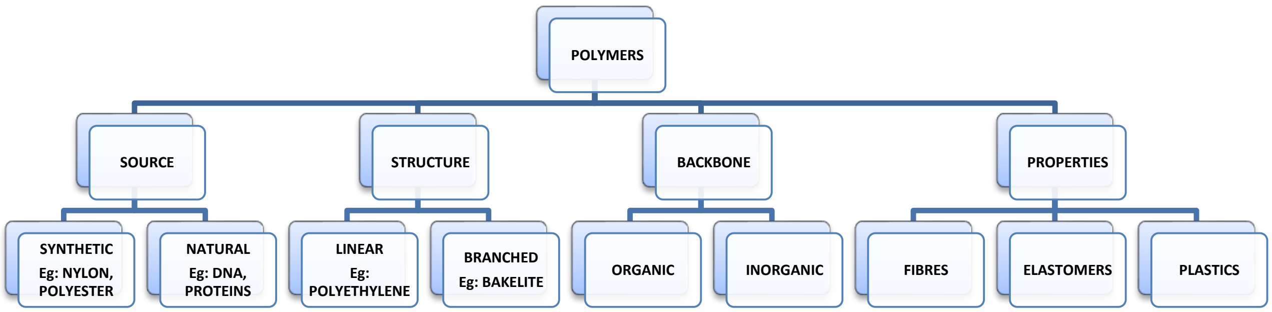
- Know about the distribution of molar masses of polymers
- Learn about different formulas for calculating average molar masses of polymers.
- Compare number average molar mass and weight average molar mass

2. Introduction

Polymers or macromolecules are the long chain high molecular weight compounds, formed by the combination of a large number of simple molecules. The simple molecules taking part in the formation of polymers are called “monomers” and this process of polymer formation is called polymerization. The product formed is known as a - dimer, trimer or tetramer, depending upon the number of molecules combining - two, three or four respectively. If large number of molecules combines together, then the product is known as a polymer.
Example: polythene polymer is obtained by combining n number of molecules of ethylene.
The number of repeating units in the polymer chain is called degree of polymerization. The product of degree of polymerization (n) and the molecular mass of the monomeric unit M_m is equal to the molecular mass of the polymer. Mathematically,

Molecular mass of the polymer = $n \times M_m$

CLASSIFICATION OF POLYMERS



Polymers are replacing metals. The reason behind this approach is freedom of design and the elimination of many secondary operations. Moreover, metals are prone to corrosion while the polymers are not. Some of the key benefits of replacing metals with polymers include:

- Weight reduction (up to 80%): They are light weight as they are composed of carbon, hydrogen, oxygen, nitrogen, etc. as the basic atoms.
- Faster installation: easy to process
- Greater workability
- Five times higher mechanical properties.
- Example: Polyaniline, polythiophene, polypyrrole.

Polymer molecular weight is essential as it helps in determination of many of its physical and mechanical properties such as strength, viscosity etc. For low molecular weight polymers, their mechanical strength may be too low to be used. When the polymer has high molecular weight, the strength increases saturating to infinite molecular weight.
The Molar mass of polymers increases on condensation or addition reaction. Since, at different stages polymerizing chains are broken, resultant macromolecules do not have the same molar mass i.e. macromolecules do not have unique molecular weight. In linear polymers, different polymeric chains have different degrees of polymerization and hence, different molar masses. Therefore same polymer may have different molecular weight depending upon the method by which it has been produced. Hence, distribution or average of molecular weights is used. In this module we will be considering different ways of calculating molecular weight of polymers.

3. Molar mass distribution

There are different ways of expressing molar mass of polymers. Some commonly used averages are as follows:

- Number average molar mass
- Mass average molar mass
- Viscosity average molar mass
- Z - average molar mass

3.1 Number average molar mass

Consider a polymer sample which has:
N_1 no of chains of monomers having the molar mass as M_1.
N_2 no of chains of dimers having molar mass M_2.
Similarly, there are in general N_i chains of i-mers with the molar mass M_i.

Number average molar mass is obtained by carrying out the summation over the fraction of molecules multiplied by their corresponding molar mass, i.e. mathematically it can be seen as:

$$\overline{M_n} = \sum_i f_i M_i \qquad ..(1)$$

Where

- $\overline{M_n}$= number average molar mass
- The number fraction (f_i) is given by

$$f_i = \frac{N_i}{N_{total}} \qquad ..(2)$$

Where
N_i=number of molecules having molar mass Mi
N_{total}= total number of molecules present in the polymer sample
Also,

$$N_{total} = \sum_i N_i \qquad ..(3)$$

Substituting eq (2) in (1), we get,

$$\overline{M_n} = \sum_i \left(\frac{N_i}{N_{total}}\right) M_i = \frac{\sum_i N_i M_i}{N_{total}} \qquad \text{...(4)}$$

Substituting eq (3) in (4), M_n becomes

$$\overline{M_n} = \frac{\sum_i N_i M_i}{\sum_i N_i} \qquad \text{...(5)}$$

The expression for number average molar mass in terms of no. of moles and number fraction can be derived in the following manner.

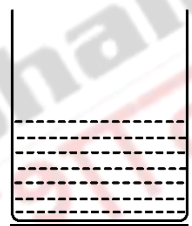


Fig1: Polymer sample containing N_i chains of i- mers

Consider a sample of polymer,
N_1 molecules have molecular weight M_1 each.
N_2 molecules have molecular weight M_2 each.
N_3 molecules have molecular weight M_3 each.
And so on.

Then we have;
Total molecular weight of all the N_1 molecules = N_1M_1
Total molecular weight of all the N_2 molecules = N_2M_2
Total molecular weight of all the N_3 molecules = N_3M_3
Therefore, total molecular weight of all the molecules,
$= N_1M_1 + N_2M_2 + N_3M_3 + \ldots$
$= \sum N_i M_i$
Total number of all the molecules
$= N_1 + N_2 + N_3 + \ldots$
$= \sum N_i$
Therefore, from the definition of number average molar mass we have;

$$\overline{M_n} = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \dots}{N_1 + N_2 + N_3 + \cdots} \quad \dots(6)$$

Divide equation (5) by N;

$$\overline{M_n} = \frac{\sum_i \frac{N_i}{N} M_i}{\frac{\sum N_i}{N}} \quad \dots(7)$$

Where, N is the total number of chain of all types in the sample:

$N = N_1 + N_2 + N_3 + \dots\dots + N_i$

$$\overline{M_n} = \frac{\sum_i \frac{N_i}{N} M_i}{\frac{N}{N}}$$

$$\overline{M_n} = \sum_i \chi_{ni} M_i \quad (8)$$

where χ_{ni} = number fraction

Dividing eq (5) with N_A

$$\overline{M_n} = \frac{\sum_i \frac{N_i}{N_A} M_i}{\sum_i \frac{N_i}{N_A}} = \frac{\sum_i n_i M_i}{\sum_i n_i} \quad \dots(9)$$

where n= number of moles

In certain experiments, it is easier to measure the weight of polymer instead of number of molecules of polymer. Therefore, it is useful to derive alternative form of M_n in terms of weight fraction of polymers mole fraction of polymers.

In most experimental measurements, the thermodynamic calculations are based on the number of molecules present in the system, and hence, depend on the number-average molar mass. For example, the colligative properties which include osmotic pressure, freezing point depression, elevation in boiling point, relative lowering of vapor pressure. Colligative properties depend only on the number of molecules present and not on the shape, size or mass of the molecules. Therefore the number average molar mass is the most relevant average molar mass. Colligative properties are used for polymers because they are non- volatile.

NOTE:

- M_n values are independent of molecular size.
- M_n values are determined by Rault's techniques that are dependent on "Colligative Properties"
  (a) Ebulliometry (Boiling Point Elevation)
  (b) Cryometry (Freezing point depression)
  (c) Osmometry
- Mn can also be determined by viscometry, gel permeation chromatography, end group determination or proton NMR.

3.2 Weight average molar mass

Weight average molar mass is the different way of describing molar mass of a polymer. There are certain properties which not only depend on the number of molecules but also on size and weight of each polymer molecule. Such properties include sedimentation, light scattering, diffusion, etc. Since the properties are dependent on the size of the molecule, so larger the molecule greater will be its contribution in calculation of M_w as compared to the smaller molecule.

When the total molecular weight of group of molecules having particular molecular weights are multiplied with their respective molecular weights, the products are added and the sum is divided by the total weight of all the molecules, the result obtained is called weight average molecular weight. Mathematically weight average molar mass can be represented as:

$$\overline{M_w} = \sum_i \frac{w_i M_i}{w_i} \qquad ..(10)$$

Dividing eq (10) by w;

Where w= $w_1 + w_2 + w_3 + \ldots + w_i = \sum_i w_i$

Therefore,

$$\overline{M_w} = \frac{\sum_i \frac{w_i}{w} M_i}{\sum_i \frac{w_i}{w}} \qquad \ldots(11)$$

$$\overline{M_w} = \sum_i \chi_{wi} M_i \qquad \ldots(12)$$

where χ_{wi} = weight fraction

$$= \frac{w_i}{w}$$

Since w_i can be written as;

$= \frac{N_i}{N_A} M_i$

In terms of number of moles, weight average molar mass can be written as:

$$\overline{M_w} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \qquad \ldots(13)$$

Where n is the number of moles.

In terms of number of molecules, weight average molar mass can be written as:

$$\overline{M_w} = \frac{\sum_i \frac{N_i M_i^2}{N_A}}{\sum_i \frac{N_i M_i}{N_A}}$$

$$\overline{M_w} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \qquad \ldots(14)$$

As $w_i = N_i(M_i/N_A)$, using this we get:

$$\overline{M_w} = \frac{\sum_i [N_i (M_i/N_A)] M_i}{\sum_i N_i (M_i/N_A)} = \frac{\sum_i N_i M_i{}^2}{\sum_i N_i M_i} \qquad ..(15)$$

In terms of fraction of molecules i.e. f_i , mass average molar mass is written as,

$$\overline{M_w} = \frac{\sum_i f_i M_i{}^2}{\sum_i f_i M_i} \qquad ..(16)$$

The M_w can be determined by various techniques like X-ray scattering, sedimentation velocity, static light scattering and small angle neutron scattering.

3.3 Z- Average molar mass

Z- Average molar mass is the third power of the molar mass and is defined by the formula;

$$\overline{M_z} = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} \qquad ..(17)$$

Where
N_i = number of molecules
M_i= respective molar mass of the molecules
Since in this average weighing factor is $N_iM_i^2$, i.e. dependent of weight, therefore heavier the molecule greater will be its contribution in calculating M_z.

3.4 Viscosity average molar mass

The viscosity average molar mass is defined as

$$\overline{M_v} = \left(\frac{\sum_i N_i M_i^{a+1}}{\sum_i N_i M_i}\right)^{1/a} \qquad ..(18)$$

Where:
'a' is the constant and is dependent on the polymer /solvent pair used in viscosity experiments. It lies in the range of 0.5 < α < 1.0. The constant '**a**' is known as the Mark-Houwink exponent.
The viscosity average molar mass is not absolute value but a relative mass based on prior calibration with known molar mass for the same polymer solvent temperature conditions.

The overall order of the above mentioned average molar mass for any molecular weight distribution is:

$$\overline{M_n} < \overline{M_v} < \overline{M_m} < \overline{M_z}$$

4. Polydispersity Index

The most important property of a polymer is its heterogeneous character. A polymer sample will contain chains of different lengths, two polymeric samples made from the same monomer cannot be identical, so the molar mass of the polymer can't be exactly defined and it varies from sample to sample. This property of a polymer of possessing different chain lengths in a sample is termed as polydispersity.
Monodisperse substances have only one value of molar mass. Eg: water, alcohol.
System which has range of molecular weights, such systems are termed as polydispersed.

Polydispersity index is the measure of the distribution of molecular masses of different polymeric chains in a given sample and any system having a range of molecular weights, is said to be polydispersed. In other words, PDI is used as a measure of the broadness of molecular weight distribution of a polymer.
PDI is the ratio of mass average molar mass and number average molar mass i.e.

$$PDI = \frac{M_w}{M_n}$$

Where
M_w is the mass average molar mass and is more sensitive to molecules having higher molecular mass,
M_n is the number average molar mass and it is more sensitive to molecules having low molecular mass.

Conditions when number average molar mass is equal to mass average molar mass (M_n= M_w):-

$$\overline{M_n} = \frac{N_1M_1+N_2M_2+\cdots}{N_1+N_2+..}$$

$$\overline{M_w} = \frac{N_1M_1^2+N_2M_2^2+..}{N_1M_1+N_2M_2+..}$$

If $\overline{M_n}$ = $\overline{M_w}$ then,

$$\frac{N_1M_1+N_2M_2+\cdots}{N_1+N_2+..} = \frac{N_1M_1^2+N_2M_2^2+..}{N_1M_1+N_2M_2+..}$$

The two sides, L.H.S. will be equal to R.H.S. only if:

$M_1 = M_2 = \dots = M$

i.e. all molecules should have the same molecular weight. In such case average has no significance.

- For a monodisperse sample: (where all the chain lengths are equal)

$\overline{M_n} = \overline{M_w}$

$$\overline{M_n} = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{N \times M}{N} = M$$

$$\overline{M_w} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{N \times M^2}{N \times M} = M$$

Therefore for a monodisperse sample (e.g. water)

$\overline{M_n} = \overline{M_w} = M$ (molar mass)

Thus, $PDI = \frac{\overline{M_n}}{\overline{M_w}} = \frac{M}{M} = 1$

- For a polydisperse sample:

$\overline{M_w} > \overline{M_n}$

$$\frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} > \frac{\sum_i N_i M_i}{\sum_i N_i}$$

Let i = 1,2 only

$$\frac{N_1 M_1^2 + N_2 M_2^2}{N_1 M_1 + N_2 M_2} > \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2}$$

$$\frac{N_1 M_1^2 + N_2 M_2^2}{N_1 M_1 + N_2 M_2} - \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2} > 0$$

$$\frac{(N_1 + N_2)(N_1 M_1^2 + N_2 M_2^2) - (N_1 M_1 + N_2 M_2)^2}{(N_1 + N_2)(N_1 M_1 + N_2 M_2)} > 0$$

$$N_1^2 M_1^2 + N_1 N_2 M_1^2 + N_1 N_2 M_2^2 + N_2^2 M_2^2 - N_1^2 M_1^2 - N_2^2 M_2^2 - 2N_1 N_2 M_1 M_2 > 0$$

$N_1N_2M_1^2 + N_2N_1M_2^2 - 2N_1N_2M_1M_2 > 0$

$N_1N_2\big((M_1^2 + M_2^2) - 2M_1M_2\big) > 0$

$N_1N_2(M_1 - M_2)^2 > 0$

Since N_1 and N_2 are always positive and $(M_1 - M_2)^2$ is also positive as it is a square term. Therefore
$\overline{M_w} > \overline{M_n}$

Moreover, for a polydisperse sample

$$\frac{\overline{M_w}}{\overline{M_n}} > 1$$

PDI has the value equal to or greater than 1. It cannot have value less than 1 because M_w can never become less than M_n. However, as the polymer chains approach uniform chain length, PDI approaches to unity. That is when the distribution of molecular weight in polymer sample becomes narrow, under these circumstances M_w becomes equal to M_n. Larger the PDI, broader will be the molecular weight distribution or variation.

5. Comparison of M_n and M_w

Number average molar mass (M_n)	Weight average molar mass (M_w)
1) The number average molar mass i.e. M_n is just the arithmetic mean of all molar masses	1) The weight average molar mass i.e. M_w is the sum of the fractional masses that each molecule contributes to the average according to the ratio of its mass to that of whole sample.
2) In number average molar mass, each molecule counts equally to it.	2) In weight average, molecules contribute according to their respective masses.
3) Colligative methods give the number average molecular weight.	3) Sedimentation techniques , light scattering techniques and ultracentrifugation techniques gives the weight average molar mass
4) The number average is more sensitive to changes in the weight fractions of low – molecular weight species , and relatively insensitive to similar changes of high molecular weight species	4) The weight average is very sensitive to changes in the weight fractions of high – molecular weight species. (as in case of light scattering techniques , larger molecule contributes more as they scatter more light effectively)

5.1 Molecular weight distribution

The most important feature distinguishing polymers from low- molecular weight species is the existence of a distribution of chain lengths and therefore degrees of polymerization and molecular weights in all known polymers. This distribution can be illustrated by plotting the weight of polymer of a given molecular weight against molecular weight.

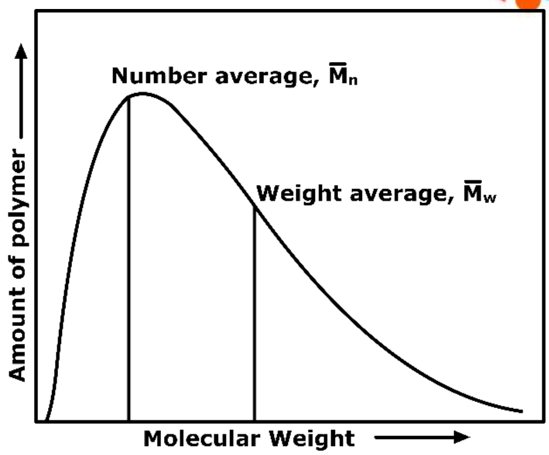


Fig2: Distribution of molecular weights in a typical polymer

When the molecular weight distribution of polymer sample is narrow, the value of M_n approaches to the value of M_m , that is narrower the molecular weight range, closer will be the values of M_m and M_n. Moreover , heavier molecules contribute more to M_w than the lighter ones , M_w is greater than M_n , except for a hypothetical mono lisperse polymer. The value of M_w is greatly influenced by the presence of high molecular – weight , just as M_n is influenced by species at the low end of the molecular – weight distribution curve. Thus, the ratio of M_w/ M_n gives the indication of breadth of the molecular weight range in polymer sample and this parameter is most often quoted for describing this feature.

6. Understanding the concept of number average and mass average molar masses - numerically

Example 1:
A sample of polymer consists of two components present in equal masses , one having M_1 = 30Kg/mol and the other having M_2=12Kg/mol . Calculate the mass average and number average molar masses.

Solution:
Given: Molecular weights of the two polymers
M_1 = 30Kg/mol
M_2=12Kg/mol

Therefore we can calculate mass average $(\overline{M_w})$ and number average $(\overline{M_n})$ molar masses using the formulas:

$$\overline{M_w} = \frac{W_1 M_1 + W_2 M_2}{W_1 + W_2} \qquad \text{(i)}$$

$$\overline{M_n} = \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2} \qquad \text{(ii)}$$

We are also given that the sample contains equal masses of the two components i.e

$\Rightarrow W_1 = W_2$

Therefore,

$$\overline{M_w} = \frac{M_1 + M_2}{2} \qquad \text{(from Equation (i))}$$

$$\overline{M_w} = \frac{30\ Kg/mol + 12Kg/mol}{2}$$

Hence, $\overline{M_w} = 21\ Kg/mol$

Now we have to calculate $\overline{M_n}$:

$$W = n \times M$$

Where :
n = no of moles

M = molecular mass

$$W = \frac{N}{N_A} M$$

$$N = (\frac{W}{M}) N_A \qquad \text{(iii)}$$

Using equation (iii) in (ii)

$$\overline{M_n} = \frac{\left(\frac{w_1}{M_1}\right) N_A M_1 + \left(\frac{w_2}{M_2}\right) N_A M_2}{\left(\frac{w_1}{M_1}\right) N_A + \left(\frac{w_2}{M_2}\right) N_A}$$

Again we have,

$\Rightarrow W_1 = W_2$

Therefore,

$$\overline{M_n} = \frac{1+1}{\frac{1}{M_1} + \frac{1}{M_2}}$$

$$\overline{M_n} = \frac{2M_1M_2}{M_1 + M_2}$$

$$\overline{M_n} = \frac{2 \times 30 \times 12}{30 + 12}$$

Thus ,

$$\overline{M_n} = 17.14\ Kg/Mol$$

From the two results we also get to know that $\overline{M_w} > \overline{M_n}$

Example 2:

A polydisperse sample of polystyrene is prepared by mixing three monodisperse samples in the following proportions:

1g	10,000 molecular weight
2g	50,000 molecular weight
2g	100, 000 molecular weight

Using this information, calculate the number average molecular weight, weight average molecular weight and polydispersity index of the mixture.

Solution:

We can calculate mass average ($\overline{M_w}$) and number average ($\overline{M_n}$) molar masses using the formulas:

$$\overline{M_w} = \frac{W_1M_1 + W_2M_2}{W_1 + W_2} \qquad \text{(i)}$$

$$\overline{M_n} = \frac{N_1M_1 + N_2M_2}{N_1 + N_2} \qquad \text{(ii)}$$

Therefore we obtain:

$$\bar{M}_n = \frac{\sum_{i=1}^{3} N_i M_i}{\sum_{i=1}^{3} N_i} = \frac{\sum_{i=1}^{3} W_i}{\sum_{i=1}^{3} \left(W_i / M_i\right)} = \frac{1+2+2}{\frac{1}{10,000} + \frac{2}{50,000} + \frac{2}{100,000}} = 31,250$$

$$\bar{M}_W = \frac{\sum_{i=1}^{3} N_i M_i^2}{\sum_{i=1}^{3} N_i M_i} = \frac{\sum_{i=1}^{3} W_i M_i}{\sum_{i=1}^{3} W_i} = \frac{10,000+2(50,000)+2(100,000)}{5} = 62,000$$

$$PDI = \frac{\bar{M}_W}{\bar{M}_n} = \frac{62,000}{31,250} = 1.98$$

7. Summary

- Polymers are the mixture of molecules that have different molecular sizes and weights. Therefore there is a need to find their molecular mass averages.
- There is dependence of type of averages obtained through experiments on chemical and physical properties of the molecules involved.

Hence, number average molar mass can be calculated by measuring colligative properties. Likewise, mass average molar mass can be calculated by light scattering measurements.

- Various molecular mass averages lies at different point of molecular mass distribution of polymer. If the polymer has identical molecules, then all its molecular mass averages would be identical.
- Weight average molar mass is always greater than the number average molar mass.
- The width of molar mass distribution of polymer is determined by calculating polydispersity index M_w/M_n. if the value of polydispersity index is close to 1, narrower will be the polymer's molecular mass distribution.