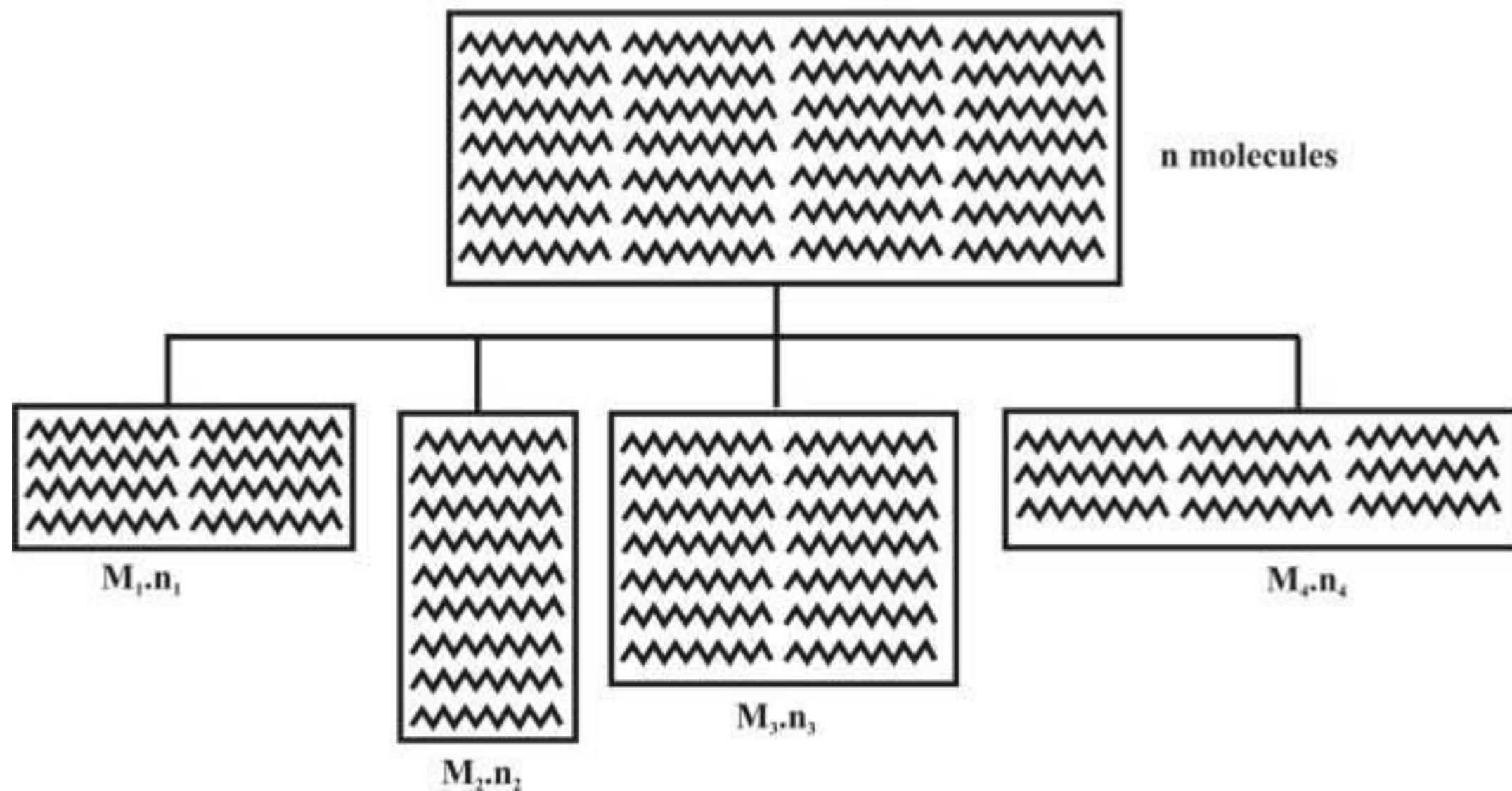# Molecular weight

"Molecular weight of a polymer is defined as sum of the atomic weight of each of the atoms in the molecules, which is present in the polymer"

This distribution of molecular weights is caused by the statistical nature of the polymerization process e.g. methane (CH_4) molecules have the same molecular weight (16), but all polyethylene do not have the same molecular weight because the statistical distribution of molecular weight may be different for the different grade of the polyethylene and the degree of polymerization may also be different.

Polymer Sample

n molecules

$M_1.n_1$

$M_2.n_2$

$M_3.n_3$

$M_4.n_4$

Different molecular weights

Number average molecular weight (Mn): A polymer solution of known concentration is made by dissolving a weight of amount of polymer in its solvent. The colligative properties of this solution are then determined which counts the number of molecules in a given volume or mass. Each Molecule makes an equal contribution to the colligative properties regardless of its weight or mass. Hence this method depends on the number of the molecule present. The molecular weight obtained by colligative property measurement is known as number average molecular weight and denoted by Mn.

$$Mn = \frac{\sum niMi}{\sum ni} = \frac{\sum wi}{\sum wi/Mi}$$

Weight-average molecular weight

$$Mw = \frac{\sum niMi^2}{\sum niMi} = \frac{\sum wiMi}{\sum wi}$$

z-Average molecular weight

$$Mz = \frac{\sum niMi^3}{\sum niMi^2} = \frac{\sum wiMi^2}{\sum wiMi}$$

Where, n = Moles of molecules $(n_1 + n_2 + n_3 + \text{---------} n_i)$

i.e. weight (w) /molecular weight (M)

w = Weight of individual molecules $(w_1 + w_2 + w_3 + \text{--------} w_i)$

M = Molecular weight of each molecules

Number Average Molecular Weight (Mn)

The number average molecular weight is not too difficult to understand. It is just the total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample.

Consider a polymer, which contains four molecular weight polymers in different numbers and weight and these

Polymer entity	Number of unit in each entity, n	Weight of each grams, $M(g)$	Total weight of each entity, $W = nM(g)$
Poly-1	2	10	20
Poly-2	4	20	80
Poly-3	6	100	600
Poly-4	3	250	750
Total	15	-	1450

Number average molecular weight, M_n

Total number of polymer in containing each entity of poly-1, poly-2, poly-3 and poly-4 is = 15

Number of Poly-1 present in the polymer = 2

Number of fraction of poly-1 = 2/15

Similarly, Number of fraction of poly-2 = 4/15, Number of fraction of poly-3 = 6/15, Number of fraction of poly-4 = 3/15

Contribution made by poly-1 towards the average weight of polymer = number of fraction of each polymer x weight of each poly entity

Therefore, each poly contribution is

(2/15) x 10 =1.33g, (4/15) x 20 = 5.33g, (6/15) x 100 =40g, (3/15) x 250 = 50g

Summing up the contribution to get Number Average Molecular Weight=

1.33 + 5.33 + 40 + 50 = 96.66g

Number average molecular weight, M$_n$

Total number of molecules (n) is given by

$$n = n_1 + n_2 + n_3 + n_4 + \ldots\ldots\ldots = \sum n_i$$

Number fraction of each molecule is $= \dfrac{n_i}{\sum n_i}$

Number average weight contribution of each entity is $= \dfrac{n_i M_i}{\sum n_i}$

Number average molecular weight is

$$\frac{n_1 M_1}{\sum n_i} + \frac{n_2 M_2}{\sum n_i} + \frac{n_3 M_3}{\sum n_i} + \frac{n_4 M_4}{\sum n_i} \ldots\ldots = \frac{\sum n_i M_i}{\sum n_i} = M_n$$

Weight average molecular weight; M_w

Total weight of each poly present in the polymer =1450g

Weight of poly-1 present in polymer = 20g

Weight fraction of poly-1 = 20/1450, Weight fraction of poly-2 = 80/1450, Weight fraction of poly-3 = 600/1450, Weight fraction of poly-4 = 750/1450

Contribution made by each poly towards average weight of polymer = weight fraction of poly-1x weight of each unit

For poly-1 (20/1450) x 10 = 0.14g

For poly-2 (80/1450) x 20 = 1.10g

For poly-3 (600/1450) x 100 = 41.38g

For poly-4 (750/1450) x 250 = 129.31g

Summing up the contribution made by each poly to get weight average molecular weight is

0.14 + 1.10 + 41.38 + 129.31 = 171.93g

Weight average molecular weight; M_w

Total number of molecules (n) is given by

$$n = n_1 + n_2 + n_3 + n_4 + \ldots\ldots\ldots = \sum n_i$$

Total weight of the polymer is $= \sum N_i M_i = W$

Weight fraction of each molecule is $= \dfrac{n_1 M_1}{W} = \dfrac{n_1 M_1}{\sum n_1 M_1}$

Weight average weight contribution of each entity is $= \dfrac{n_1 M_1 M_1}{\sum n_i M_i} \dfrac{n_i M_i^2}{\sum n_i M_i}$

Weight average molecular weight is

$$\dfrac{n_1 M_1^2}{\sum n_i M_i} + \dfrac{n_2 M_2^2}{\sum n_i M_i} + \dfrac{n_3 M_3^2}{\sum n_i M_i} + \dfrac{n_4 M_4^2}{\sum n_i M_i} \ldots\ldots = \dfrac{\sum n_i M_i^2}{\sum n_i M_i} = M_w$$

For synthetic polymers Mw is greater than the Mn. If they are equal than they will consider as perfectly homogeneous. (Each molecule has same molecular weight).

Molecular weight and degree of polymerisation

The heavier molecule contributes more to the Mw than the light ones. Mw of polymers is always greater that Mn except for a hypothetical monodisperse polymer. The value of Mw is greatly influenced by the presence of high molecular weight species just as Mn is influenced by species at the low molecular weight species.
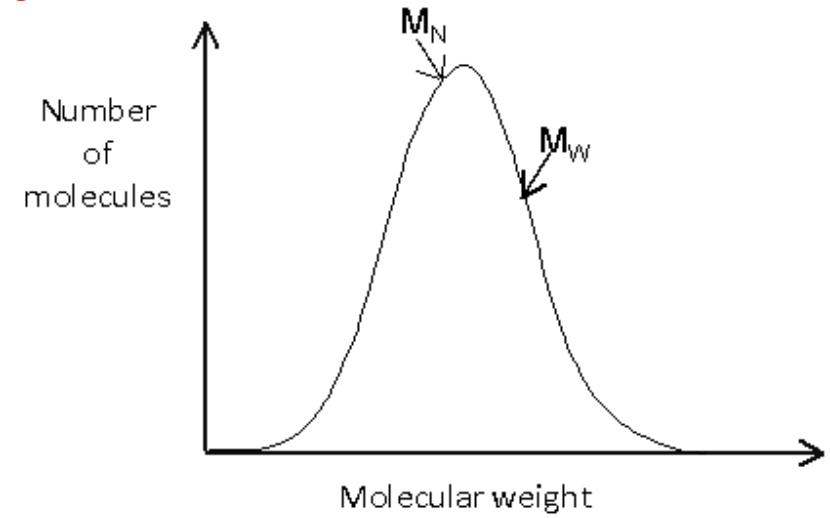
Degree of polymerization (DP) represents the average number of monomer units in the polymer chain and is an alternate way of expressing average chain size of the polymer

Both number average, DPn and weight average, DPw degree of polymerization are defined as

$$DPn = Mn/Mo \quad \& \quad DPw = Mw/Mo$$

Polydispersity index (PDI) or Index of polydispersity, PDI is used as a measure of molecular weight distribution and is defined as PDI=Mw/Mn

In case of monodisperse system(natural polymers and synthetic polymers made by anionic polymerization), PDI= 1 Since, Mn= Mw and for other cases, PDI> 1 or Mw is used as a measure of molecular weight distribution and is defined as Mw>Mn

Molecular weight distribution and its significance

A simple chemical compound contains molecules, each of which has the same molecular weight (a monodisperse system), whereas a polymer contains molecules, each of which can have different molecular weights (polydisperse system). If a polymer sample of molecular weight 40000 Mn, the molecules have molecular weight ranging from 20000- 80000 or 500- 100000 the figure is uncertain. This is the reason why two polymer samples of the same 40000 Mn can display similar properties in some respect but not in the some others To know a polymer property, we must have a knowledge of both the average molecular weight and its dispersion pattern. This dispersity with respect to the lowest to the highest molecular weight homologues is expressed by a simple molecular weight distribution curve by plotting the number fraction (ni) of the molecule having a particular molecular weight(Mi) against the corresponding molecular weight.
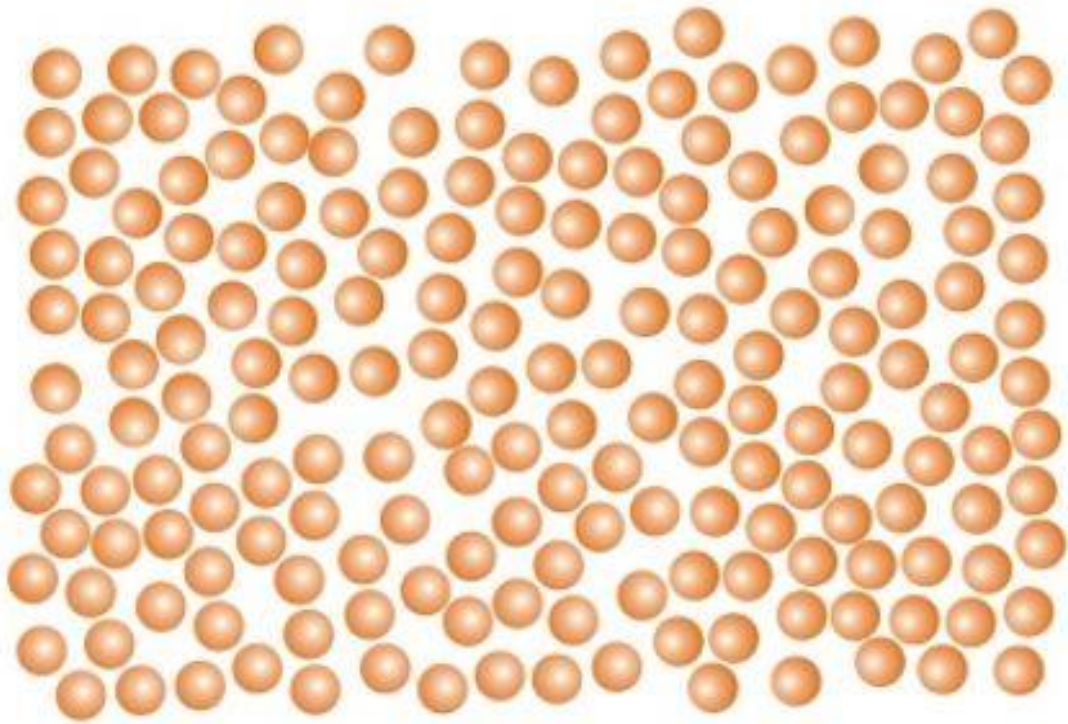
A uniform (monodisperse) collection

A non-uniform (polydisperse) collection

Polydispersity Index for Molecular weight of Polymers

The figure shows molecular weight distribution in two samples having same number average molecular weight but different polydispersities. Sample 1 obviously has narrower dispersion pattern and hence a lower polydispersity than sample 2

Polydispersity is a very important parameter and it gives an idea of lowest and the highest molecular weight species as well as the distribution pattern of the intermediate molecular weight species. Plastics processing are affected by the molecular weight distribution.
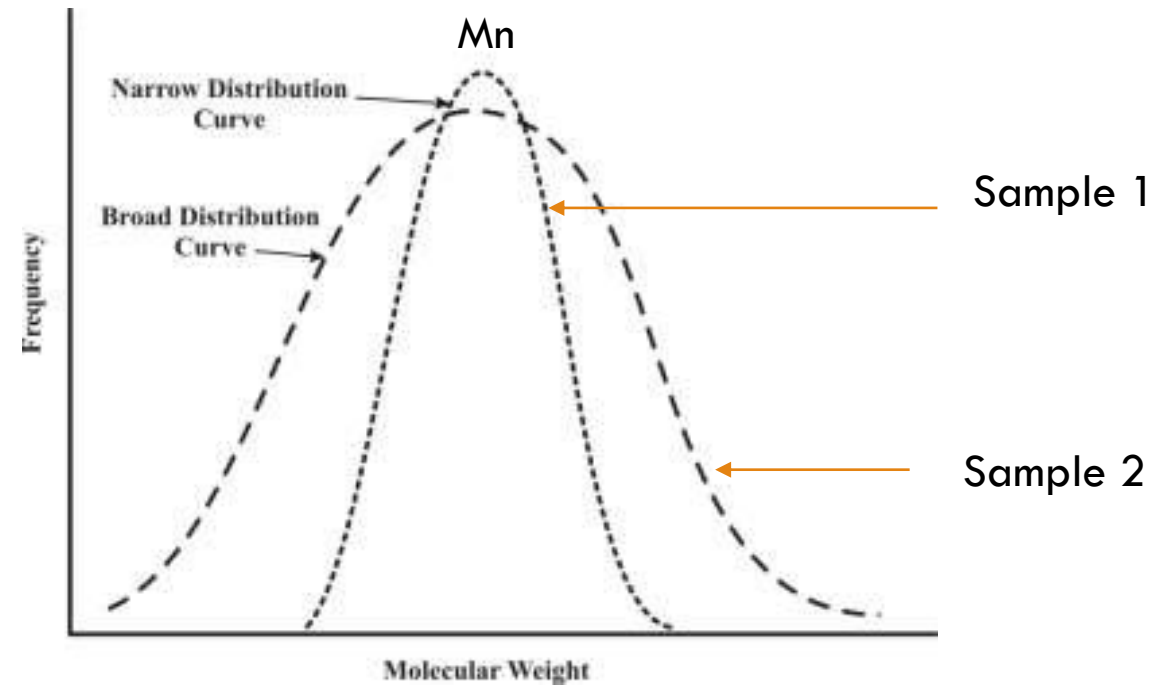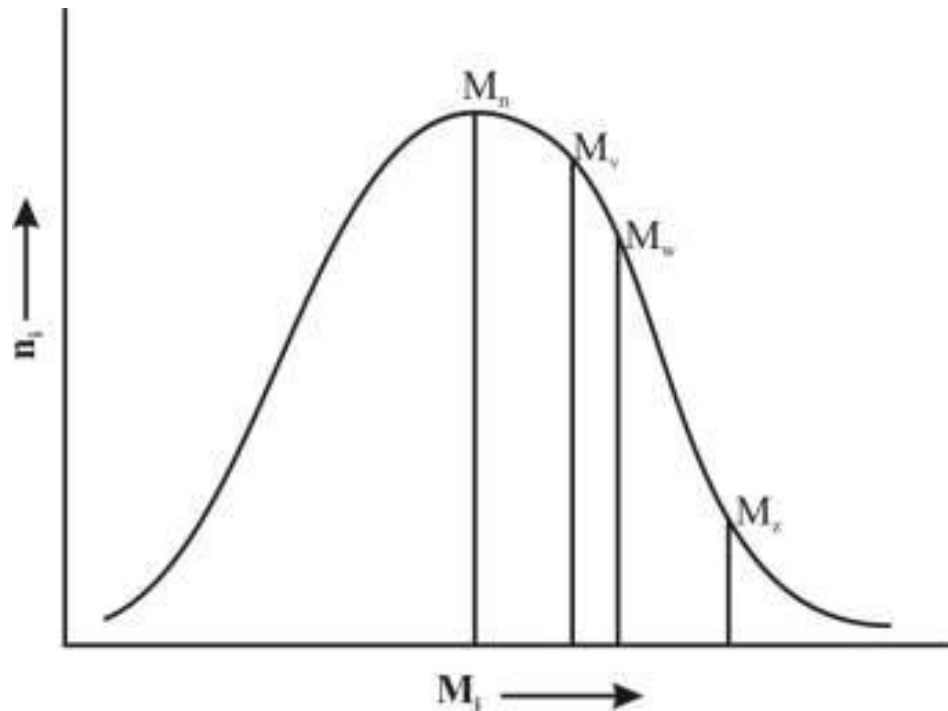
Molecular weight distribution of two hypothetical polymer samples having same number average molecular weight but different polydispersities
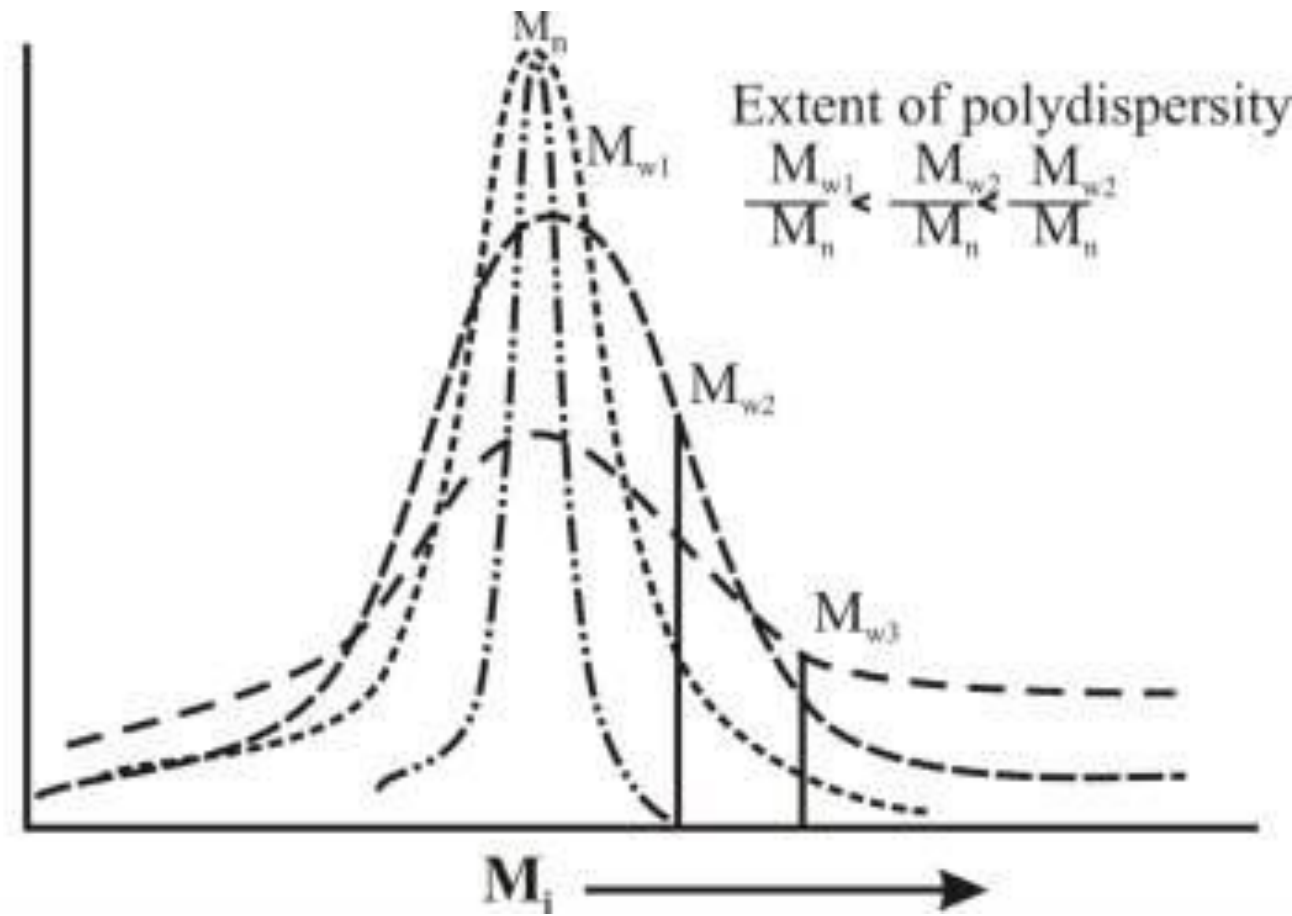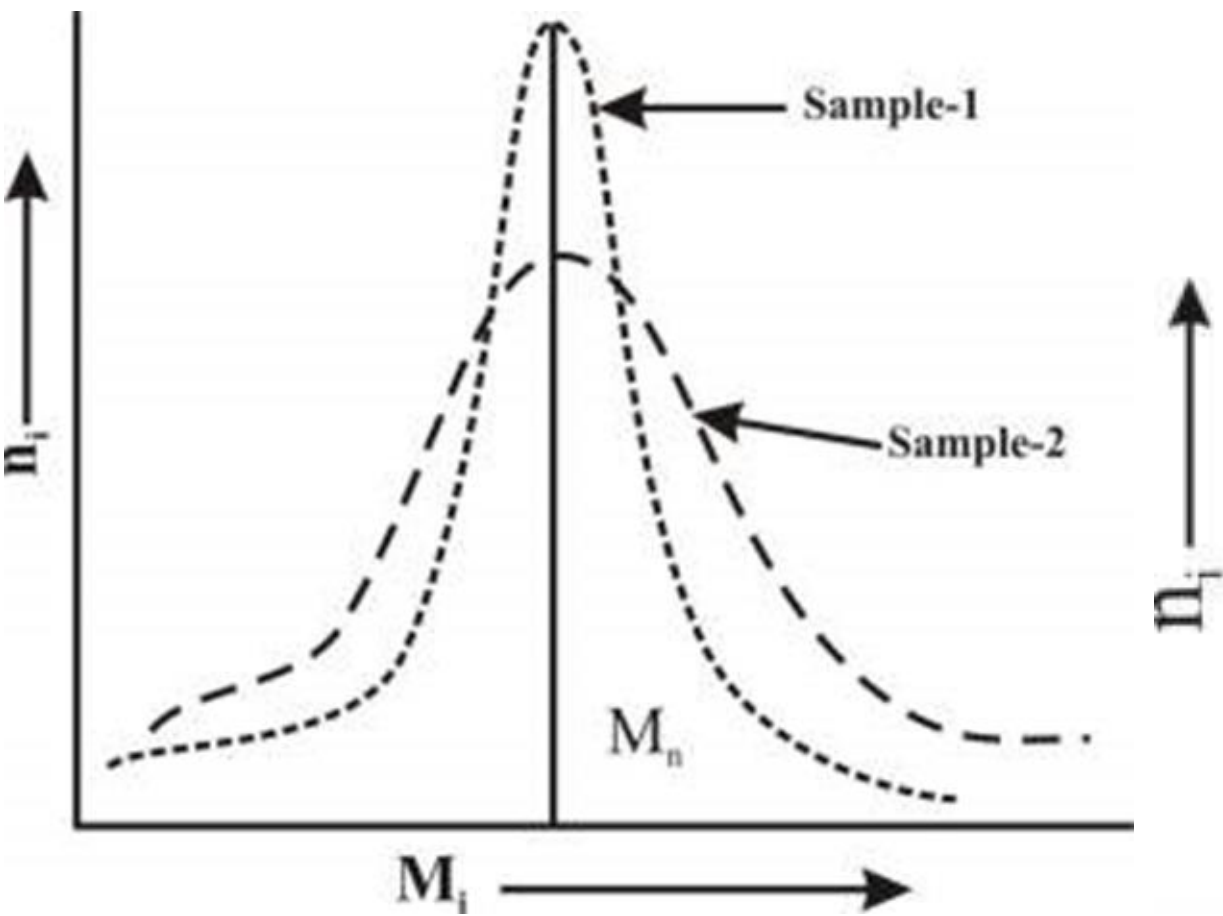
Influence of Molecular weight of Polymers

**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 but decrease in hardness, stiffness, Softening point and Brittle point. **High molecular weight polymer does not crystallize so easily** as lower molecular weight material does due to chain entanglement and that reflects 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 be improved by increasing molecular weight.
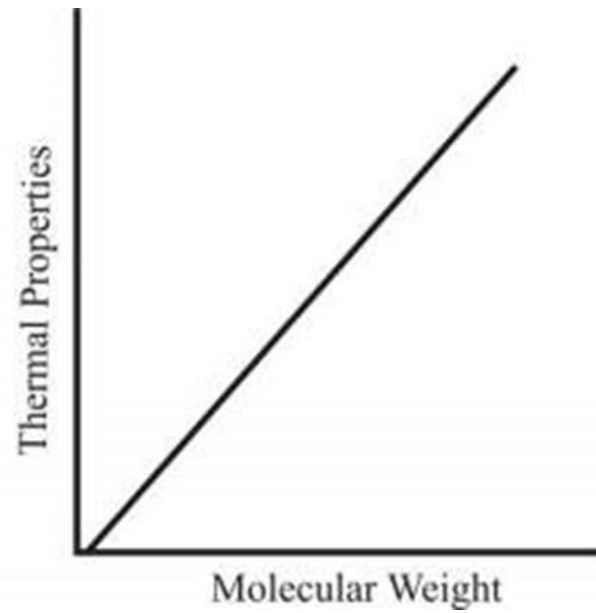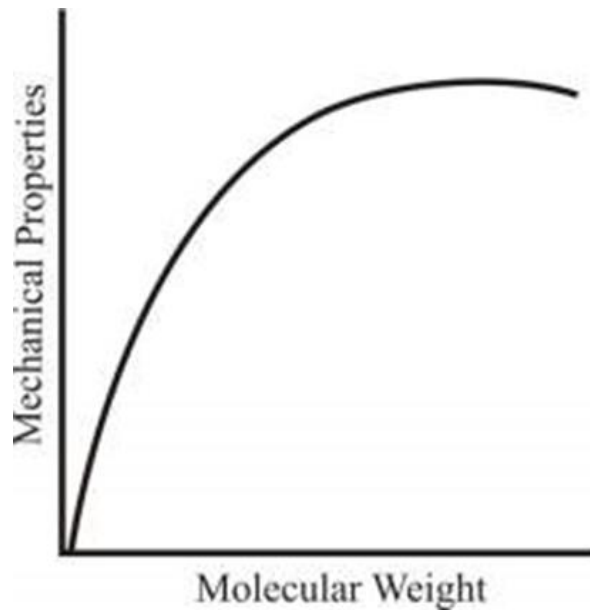
Effect of Molecular Weight on Properties of Polyolefins

Property	With Incease Molecular Weight
Melt Viscosity	↑
Melt Strength	↑
Melt Viscosity	↑
Toughness	↑
Abrasion Resistance	↑
Ultimate Strength	↑
Resistance to Creep	↑

Effect of Molecular Weight Distribution on Properties of Polyolefins

Property	Molecular Weight Distribution Incerasing
Melt Viscosity(High Shear)	↓
Surface Gloss	↓
Toughness	↓
Optical Properties	↓
Melt Strength (Low Shear)	↑

Creep is the tendency of a **polymer** to distort under external loads, especially as the temperature increases. 1 Essentially, the **polymer** chains are uncoiling and begin to slip past each other when a constant stress is applied.

Shearing forces are unaligned forces pushing one part of a body in one specific direction, and another part of the body in the opposite direction

Abrasion is the process of scuffing, scratching, wearing down, marring, or rubbing away. It can be intentionally imposed in a controlled process using an abrasive. **Abrasion** can be an undesirable effect of exposure to normal use or exposure to the elements.

Molecular Weight Determination

Number Average Molecular Weight (M_n)

1. End Group Analysis

2. Colligative properties
   a) Cryoscopy -
      Depression in freezing point
   b) Ebulliometry -
      Elevation in boiling point
   c) Osmometry
      i) Vapour phase Osmometry
      ii) Membrane Osmometry

Viscosity Average Molecular Weight (M_v)

1. Dilute solution viscosity Measurement
   i) Relative Viscosity
   ii) Specific Viscosity
   iii) Reduced Viscosity
   iv) Inherent Viscosity
   v) Intrinsic Viscosity

Weight Average Molecular Weight (M_w)

1. Ultracentrifugation
   a) Sedimentation Velocity Method
   b) Sedimentation Equilibrium Method

2. Light Scattering

3. GPC

Determination of Number Average Molecular Weight

1. End group analysis

- Determination of number average molecular weight (Mn)
- Analysis of functional groups in polymers, particularly of those incorporated at chain ends

- Method of analysis
  - Titrimetric method
  - Spectrophotometric method

- Limitations/disadvantageous
  - This can only be used when a polymer has an end gropup
  - Less sensitive for high molecular weight polymers.
  - Mn < 25,000

End group analysis
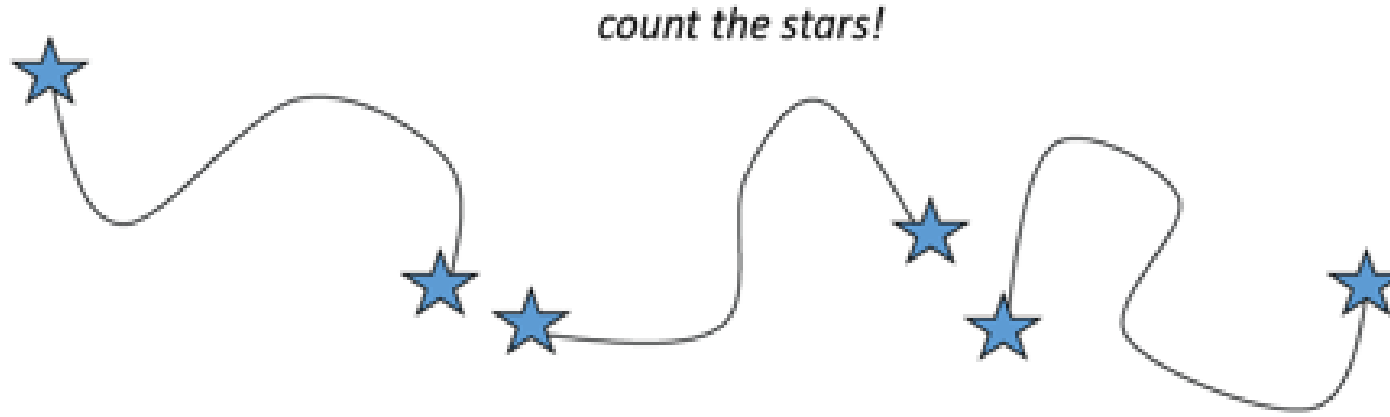
If we know the skeletal structure of a polymer (i.e., how many end groups there are per molecule of polymer) and the end groups are in some way distinguishable from other chemical moieties on the polymer, then end group analysis can be a powerful tool to allow us to "count" the number of molecules in a sample and hence solve for Mn

End group analysis would be like counting the stars on these polymers (6) and knowing there are 2 end groups per molecule – we can use that information to figure out that there are 3 polymer molecules.

End group analysis

The end group analysis is a chemical method used to determine the number average molecular weight of a polymer sample through the analysis of reactive functional groups at one end or both end e.g carboxyl terminate polybutadiene, hydroxyl terminated polybutadiene . Apart from hydroxyl and carboxyl groups, other end groups (aldehyde, amino, ester) can possibly be present in various polymers. For detecting and analyzing quantitatively functional end groups of linear polymers (nylon) the amino end groups of nylon dissolved in m cresol are readily determined by titration with a methanolic perchloric acid solution. Other titratable end groups are the hydroxyl and carboxyl groups in polyesters and the epoxy end groups in epoxy resins . The sensitivity of this method decreases as the molecular weight increases . This method is limited to determination of polymers with a molecular weight of less than about 20,000.

From the knowledge of functional group equivalent and functionality, the molecular weight can be calculated using the following equation

$$Mn = Functionality / Functional group\ equivalent$$

2. Colligative properties

1. Depression in freezing point (cryoscopy) and elevation in boiling point (ebulliometry). As these two properties are Colligative (i.e. depend only on the number of moles of a solute present in a liquid and not on their nature).

2. Colligative properties are those that depend on the number of species present rather than on their kind. From thermodynamic arguments it may be shown that for very dilute ideal solutions

$$\ln \alpha_1 = -X_2$$

Where, α_1 is the activity of the solvent in a dilute ideal solution and X_2 is the mole fraction of solute. From this relationship the solute molecular weight may be calculated if the weight fraction W_2 is known.

$$X_2 = \frac{n_2}{n_1} = \frac{w_2 M_1}{M_2 w_1}$$

Lowering of Vapour Pressure

The partial vapor pressure P_1 of solvent 1 over a solution is lower than the vapor pressure over the pure solvent p_1^0. This is expressed by Raoult's law:

$$p_1 = X_1 p_1^0$$

Where X_1 is the mole fraction of the solvent.

For a binary solution containing a mole fraction X_2 of solute then,

$$X_2 = \frac{p_1^0 - p_1}{p_1^0} = \frac{\Delta p_1}{p_1^0}$$

For a dilute solution,

$$X_2 = \frac{n_2}{n_1} = \frac{w_2 M_1}{M_2 w_1}$$

Combining above two equation,

$$M_2 = w_2 \frac{M_1}{w_1} \frac{p_1^0}{\Delta p_1}$$

Assuming ideal solution behavior, the unknown molecular weight is calculated from

$$M_n = \frac{w_2 M_s V_s}{V_2 w_n}$$

Ebulliometry

Ebulliometry is another technique for determining the depression of the solvent activity by the solute. In this case the elevation of the boiling point is determined. The boiling-point elevation ΔT_b is measured with sensitive thermocouples or matched thermostats in a Wheatstone bridge. The molecular weight <u>M</u>" is calculated from

$$M_n = \frac{K_b c}{\Delta T_b}$$

Where c is the concentration of solute in g/1000g of solvent and

$$K_b = \frac{RT_b^2 M}{1000\Delta H_v}$$

is the molal ebullioscopic constant. *M* is the molecular weight of the solvent and T_b its boiling point; ΔH_v is the molar latent heat of vaporization of the solvent.

Cryoscopy

The freezing point of a solution is depressed below that of the pure solvent by an amount proportional to the mole fraction of solute. The value for Mn is obtained from

$$M_n = \frac{K_f c}{\Delta T}$$

Where c is the concentration of solute in g/1000 mL of solvent and

$$K_f = \frac{RT_m^2 M}{1000 \Delta H_{fus}}$$

is the molal cryoscopy .constant; M is the molecular weight of the solvent and Tm its melting point; ΔH_{fus} is the molar latent heat of fusion of the solvent.

Osmometry: Membrane osmometry is absolute technique to determine M_n. The solvent is separated from the polymer solution with semipermeable membrane that is strongly held between the two chambers. One chamber is sealed by a valve with a transducer attached to a thin stainless steel diaphragm which permits the measurement of pressure in the chamber continuously. Membrane osmometry is useful to determine M_n about 20,000-30,000 g/mol and less than 500,000 g/mol. When M_n of polymer sample more than 500,000 g/mol, the osmotic pressure of polymer solution becomes very small to measure absolute number average of molecular weight. In this technique, there are problems with membrane leakage and symmetry. The advantages of this technique is that it doesn't require calibration and it gives an absolute value of M_n for polymer samples.

Since osmotic pressure is dependent on colligative properties, i.e., the number of particles present, the measurement of this pressure (osmometry) may be applied to the determination of the osmotic pressure of solvents vs. polymer solutions.
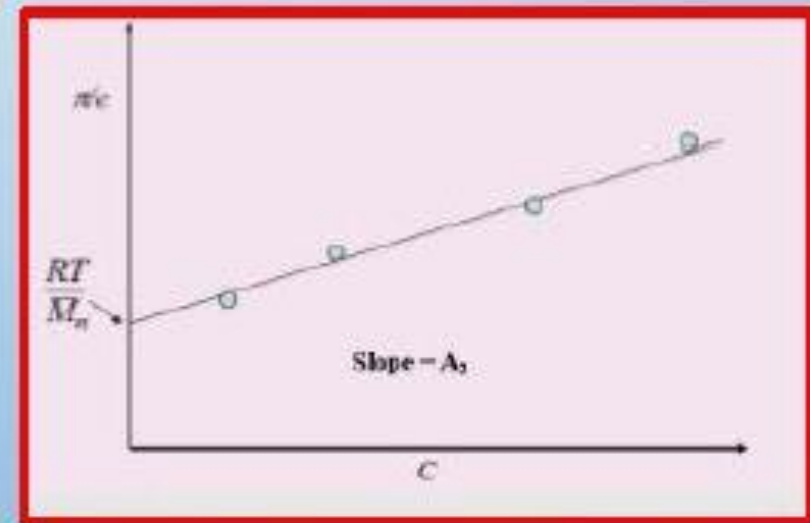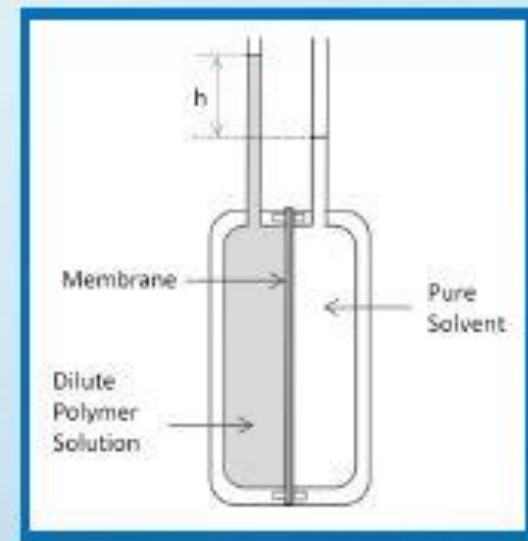
$$\pi = \frac{RT}{M_n} C + BC^2$$

Osmotic pressure

The difference in height (h) of the liquids in the columns may be converted to osmotic pressure (π) by multiplying the gravity (g) and the density of the solution (p), i.e., $\pi = hpg$.
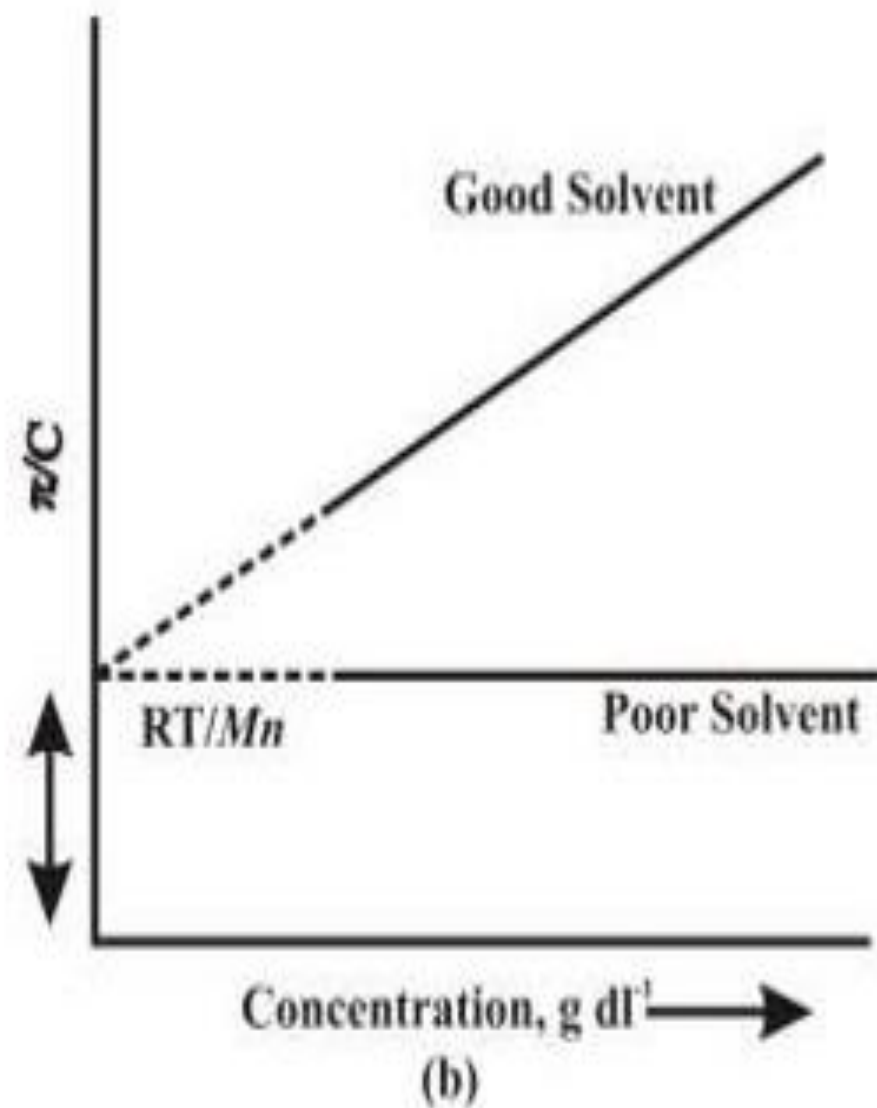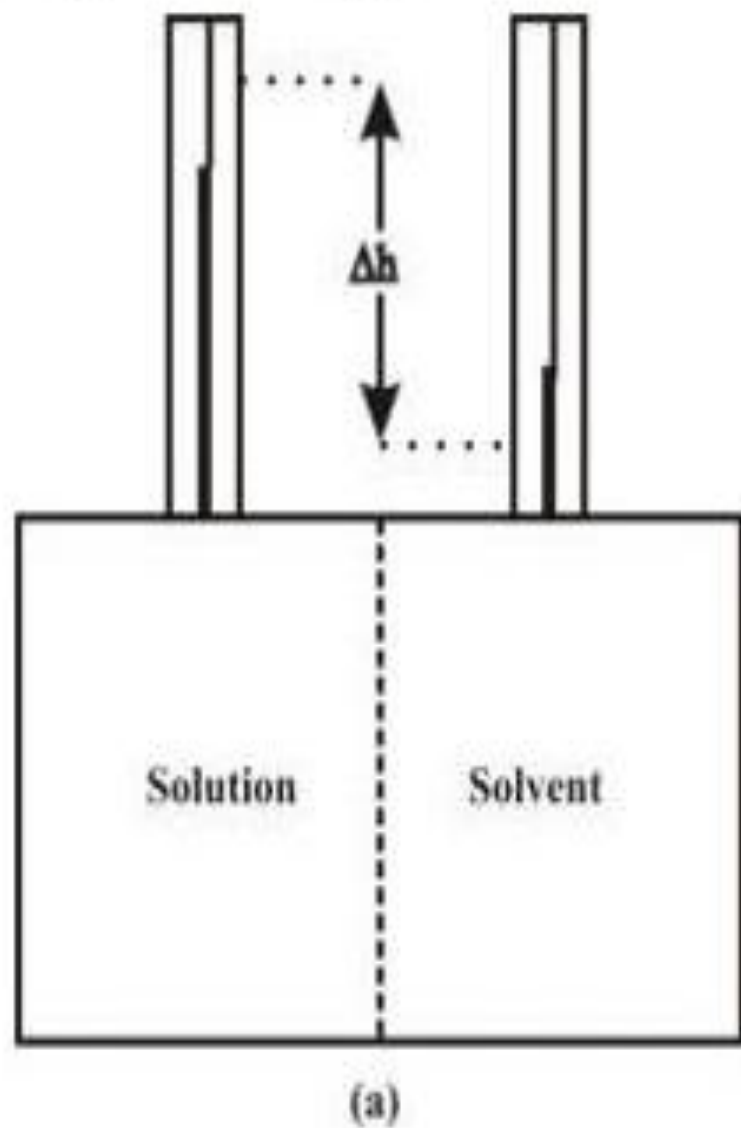

In an automatic membrane osmometer, the unrestricted capillary rise in a dilute solution is measured in accordance with the modified van't Hoff equation:

$$\pi = \frac{RT}{M_n} C + BC^2$$

The reciprocal of the number average molecular weight (M_n) is the intercept when data for π/RTC vs. C are extrapolated to zero concentration.
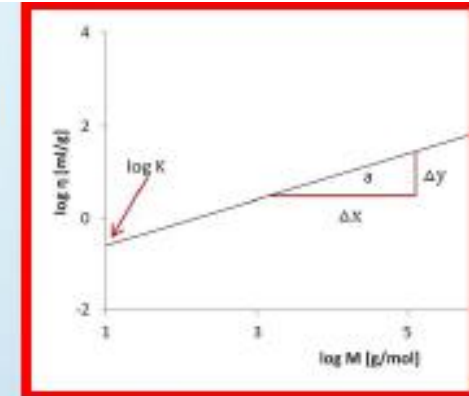
Working Principle

(a)

(b)

Determination of Viscosity Average Molecular Weight

Viscometry: A plot of log [η] against log M gives a straight line. From the graph, the value of K and a can be determined from their ordinate intercept and slope of the line.

$$[\eta] = KM^a$$
$$\log\ [\eta] = \log K + a\ \log M$$

Now, let us see how the intrinsic viscosity can be measures. Assume that a liquid is flowing through a capillary tube. The time required for the liquid of volume V to pass through the capillary of radius r and length l is related to its absolute viscosity by the Poiseuille Equation-

$$\eta = \frac{3.14\ Pr^4 t}{8\ V\ l} \implies t = \frac{8Vl\eta}{3.14Pr^4}$$

Where P is the pressure head under which the liquid flow takes place.

If η and η_o are the absolute viscosities of a solution and the pure solvent respectively and t and to are their corresponding time flow, then $\implies$ $$\eta_r = \frac{t}{t_o} = \frac{\eta}{\eta_o}$$

η/ η_o is known as the relative viscosity, η_r or η_{rel}

Determination of Weight Average Molecular Weight

Light scattering

Light Scattering Method: Light scattering methods to determination of weight average molecular weight, Mw. When polarizable particles are placed in the oscillating electric field of a beam of light, the light scattering occurs. Light scattering method depends on the light, when the light is passing through polymer solution, it is measure by loses energy because of absorption, conversion to heat and scattering. The intensity of scattered light relies on the concentration, size and polarizability that is proportionality constant which depends on the molecular weight..
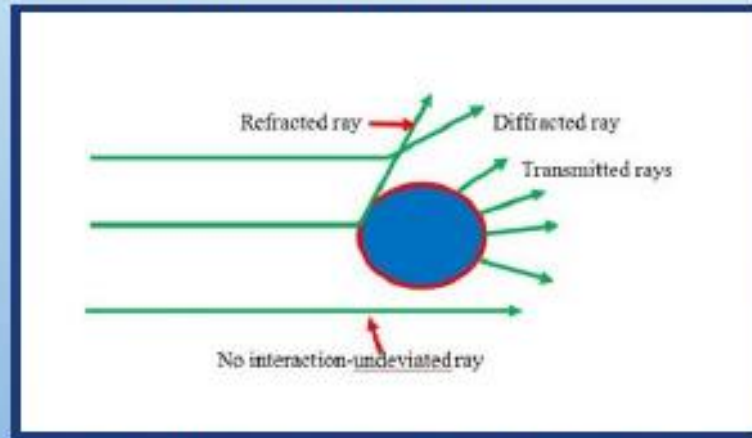

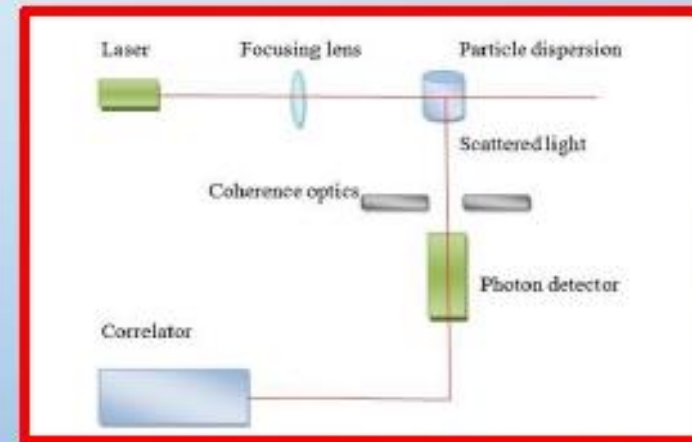Figure: Modes of scattering of light in solution.

Figure: Schematic representation of light scattering.

For light scattering measurements, the total amount of the scattered light is deduced from the decrease in intensity of the incident beam, I0, as it passes through a polymer sample. This can be described in terms of Beer's law for the absorption of light.

In other words it can be described as follows

When a beam of light is passed through a colloidal solution, it is scattered. This is well-known Tyndall effect, which results from the scattering of a part of the beam of light by the colloidal particles in all directions. Since polymer solutions can be considered as colloidal (lyophilic) solutions and as the intensity of light scattered depends on the size of colloidal particles (or polymer molecules)
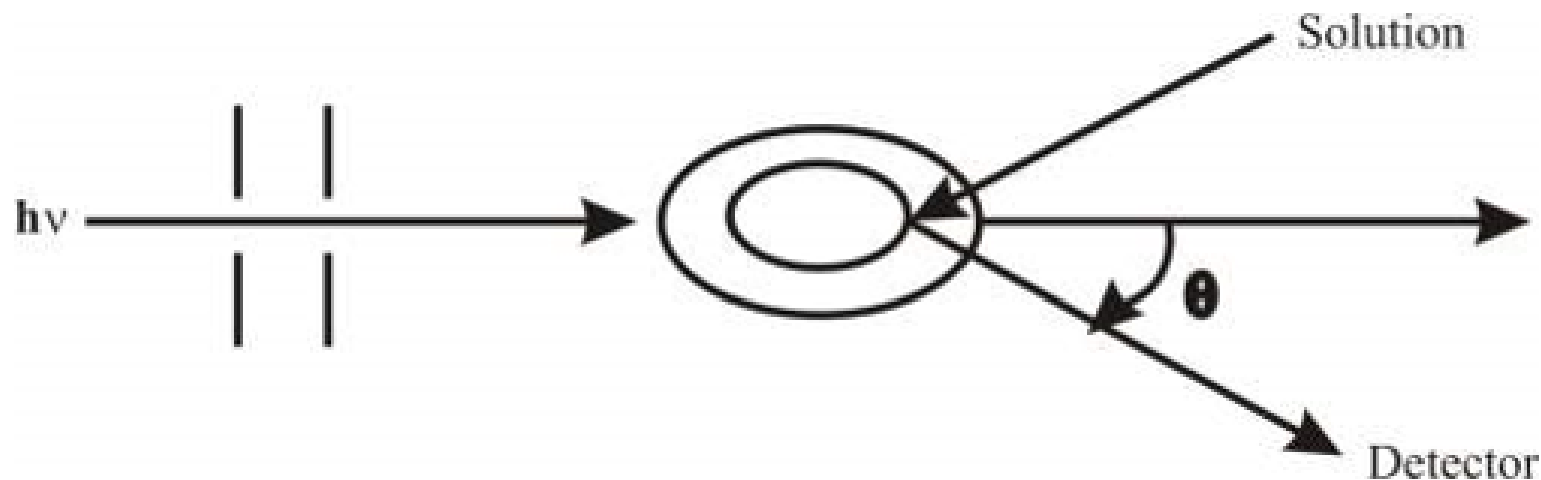
$$KC / R_{90} = HC / \tau = 1/ M_w + 2BC$$

$$\left[\frac{KC}{R_\theta} \right]_{\theta \to 0} = \frac{1}{Mw} + 2BC$$

$$\left[\frac{KC}{R_\theta} \right]_{\theta \to 0} = \frac{1}{Mw}$$

Where **B** is the second virial coefficient, C is the concentration of the solution, and R_{90} is the Rayleigh ratio at 90° observation angle. This ratio in a generalized case is represented as $R\theta$ i.e. the Rayleigh ratio is determined at an observation angle of 90°, $R\theta = R90'$

Ultra centrifuge

Gel Permeation Chromatography
or
Size Exclution Chromatography

The basic principle underlying the separation of different' fractions of a polydispersed sample is based on the size of individual polymer molecules that explore the pore system of the column material.

Large molecules are excluded from small pores and diffuse into a restricted part of the pore system within the beads whereas smaller ones enter into the pores of the bead.

Thus large molecules would reside for lesser time and would be released prior to those of smaller ones.
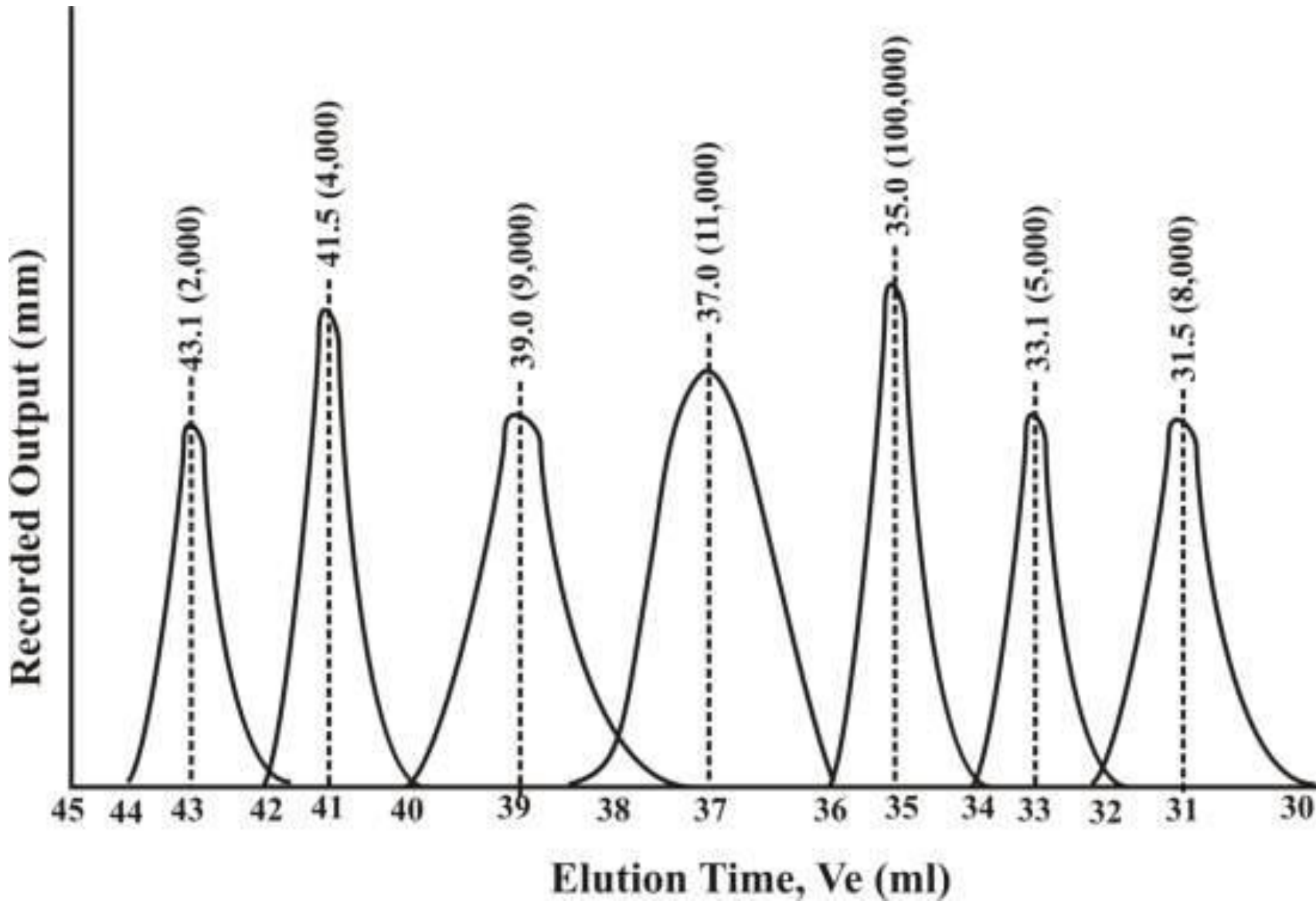
Hypothetical GPC Curve indicating elution volumes corresponding to different molecular weights

Different molecular weight determination methods: A comparison

Method	Type of average	Mol. wt. range
Ebbuliometry or Cryoscopy	M_n	< 10,000
Vapour pressure osmometry*	M_n	< 25,000
Memberane osmometry	M_n	1500-100,000
Dilute solution viscosity**	M_v	15,000-1000.000
Light scattering	M_w	2000-10,000,00
Ultracentrifuge	M_w	2000-10,000,00
Gel permeation chromatography*	M_v, M_z' MWD	2000-10,000,00
	M_w, M_z, MWD	up to 50,00,000

*Relative methods and need calibration from standard polymers samples

**Indirect method and needs values of *k* and *a* for particular polymer - solvent system