



CHEM3020: POLYMER CHEMISTRY

Unit-4: Determination of molecular weight of polymers

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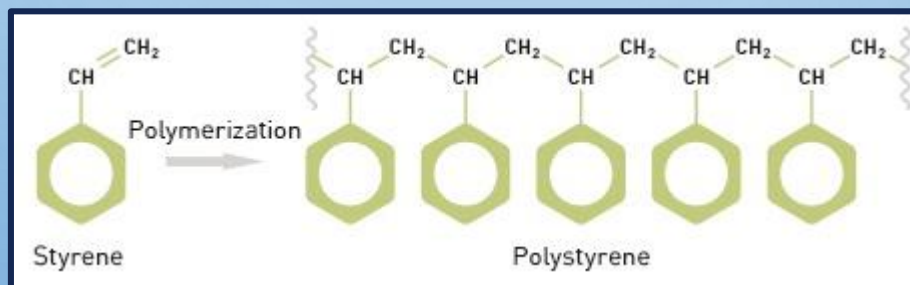
Molecular weight of polymers

Molecular weight of polymers: If we think about the molecular weight of any organic molecule, we can calculate the same from their molecular formulae. But what's about the molecular weight of a polymer? As we know that during the polymerization process, the growth of the chain is random in nature and the product contains a mixture of chain of different length. As in a polymer, there is a spread or distribution of different polymer molecules of different chain length, hence the molecular weight of the polymer is given as an average molecular weight. Different methods of determination of molecular weight provide different average molecular weight.

The methods of determining molecular weight of polymers are of two types:

1. **Primary or absolute methods:** This method is capable of determining the molecular weight from the principles of colligative properties and light scattering methods.
2. **Secondary or relative methods:** In this methods, requires calibration with the sample of known molar mass.

MW of styrene:
104.15 g/mol



MW of polystyrene??
chain length??



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Molecular weight of polymers

Molecular weight of polymers: Regarding the molecular weight of a polymer, we will discuss three types of molecular weight-Number average Molecular weight (M_n), Weight average molecular weight (M_w) and viscosity average molecular weight (M_v).

Number average molecular weight (M_n): 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 M_n .

Thus M_n is determined by Osmometry (Osmotic pressure measurement), Ebullimetry (elevation of boiling point measurement), Cryoscopy (Freezing point depression measurement) and end group analysis.

If a sample contains N_i molecules of molecular weight M_i , the number average molecular weight is given by

$$M_n = \frac{\sum M_i N_i}{\sum N_i}$$



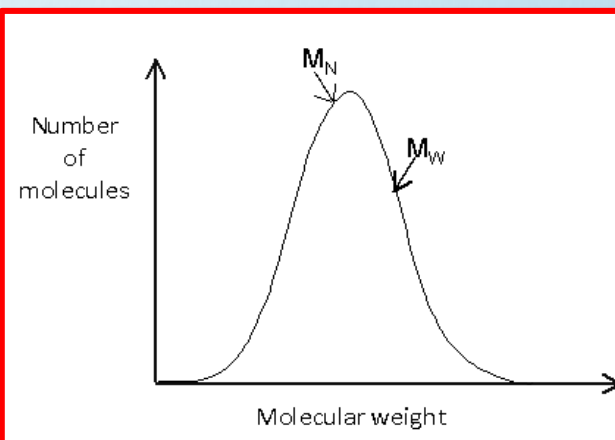
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Molecular weight of polymers

Weight average molecular weight of polymers: The weight average molecular weight is given by

$$M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$$

The heavier molecule contributes more to the M_w than the light ones. M_w of polymers is always greater than M_n except for a hypothetical monodisperse polymer. The value of M_w is greatly influenced by the presence of high molecular weight species; just as M_n is influenced by species at the low molecular weight species.



Viscosity average molecular weight (M_v): The viscosity average molecular weight is obtained from the measurement of viscosity and is given by-

$$M_v = \left[\frac{\sum w_i M_i^a}{\sum w_i} \right]^{1/a} = \left[\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right]^{1/a}$$



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Molecular weight of polymers

$$M_v = \left[\frac{\sum_i w_i M_i^\alpha}{\sum_i w_i} \right]^{1/\alpha} = \left[\frac{\sum_i N_i M_i^{1+\alpha}}{\sum_i N_i M_i} \right]^{1/\alpha}$$

Where N_i is the number of molecules of molecular weight M_i , α is the exponent in the Mark-Howkin-Sakurada equation, $[\eta] = KM^\alpha$ where η is the intrinsic viscosity., When $\alpha = 1$ then $M_v = M_n$; Generally the value of α is $0.5 < \alpha < 0.9$ hence $M_v < M_w$. The value of α varies with polymer, solvent and temperature systems.

Degree of polymerization (DP): 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 (DP_n) and weight average (DP_w) degree of polymerization are defined as-

$$DP_n = \frac{M_n}{M_o}$$

$$DP_w = \frac{M_w}{M_o}$$

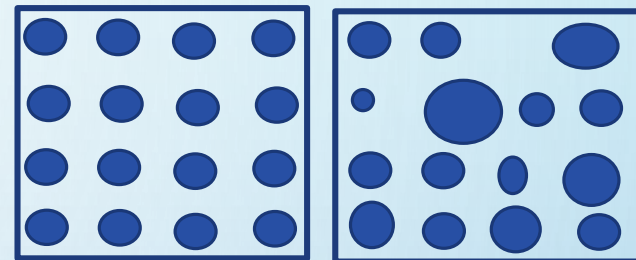
Polydispersity index(PDI): Index of polydispersity or PDI is used as a measure of molecular weight distribution and is defined as-

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

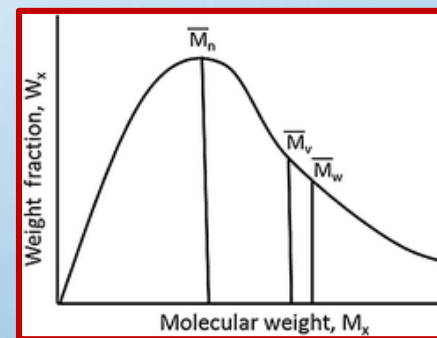
In case of monodisperse system(natural polymers and synthetic polymers made by anionic polymerization), $PDI = 1$, Since, $M_n = M_w$; and for other cases, $PDI > 1$ or M_w is used as a measure of molecular weight distribution and is defined as- $M_w > M_n$.

**Molecular weight of polymers**

Molecular weight distribution and its significance: It may be recalled that a simple chemical compounds contains molecules, each of which has the same molecular weight (a monodispersed system), whereas a polymer contains molecules, each of which can have different molecular weights(polydisperse system).



Polydisperse nature of the polymer is the basis of the concept of average molecular weight. If a polymer sample of molecular weight 40000 $\bar{M}_n$, 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 $\bar{M}_n$ can display similar properties in some respect but not in the some others.



To know a polymer property, we must have a knowledge of the 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. Such a curve for a polymer sample is computed by plotting the number fraction (n_i) of the molecule having a particular molecular weight(M_i) against the corresponding molecular weight.



Molecular weight of polymers

Figure in this slide 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 gives an idea of the lowest and highest molecular weight species as well as the distribution pattern of the intermediate molecular species.

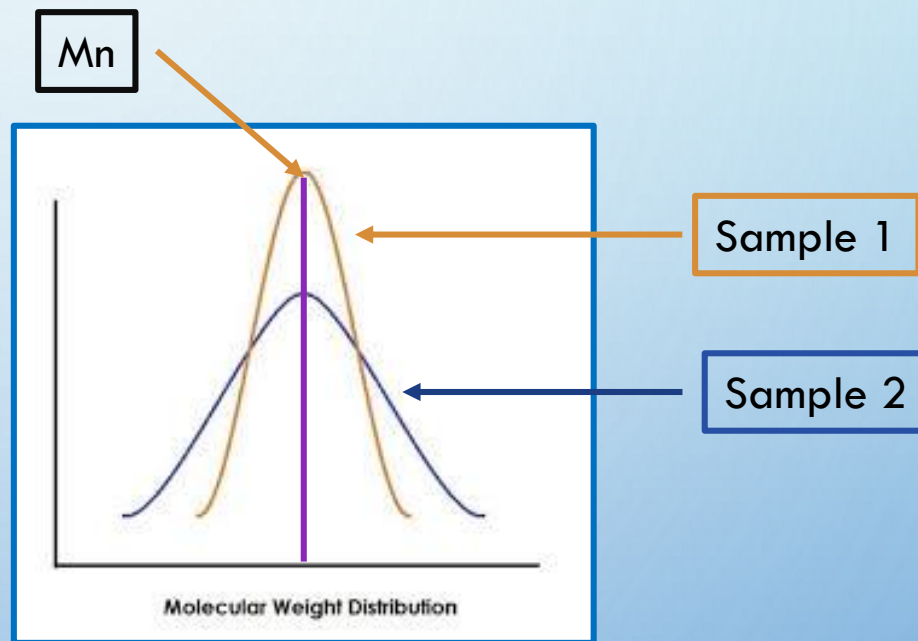


Figure: Molecular weight distribution of two hypothetical polymer samples having same number average molecular weight but different polydispersities.



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Determination of Molecular weight of polymers

Methods: End group analysis, viscometry, light scattering and osmotic pressure

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 terminated 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 polymer (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 the 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-

$$M_n = \frac{\text{Functionality}}{\text{Functional group equivalent}}$$



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Determination of Molecular weight of polymers

Methods: End group analysis, viscometry, light scattering and osmotic pressure

End Group Analysis: Example: The carboxyl value of carboxyl terminated polybutadiene (CTPB) can be determined by dissolving a known amount of the polymer in a mixture of toluene and ethanol (1:3) and titrating against alcoholic KOH using phenolphthalein indicator.

Let, the volume of KOH consumed = V ml; Normality of KOH = N ; and Weight of the sample taken = w g

$$\text{Carboxyl value} = \frac{V \times N \times 56.1}{w}$$

$$\text{Carboxyl equivalent/100g} = \frac{V N (56.1) \times 100}{w (1000) \times 56.1}$$

In a particular measurement, if 0.8734 g of the sample has consumed 5.1 ml of 0.1242 (N) alcoholic KOH solution then

$$\text{Carboxyl equivalent/100g} = \frac{5.1 \times 0.1242}{10 \times 0.8734} = 0.0725$$

Assuming functionality of 2,

$$\text{Number average Molecular weight; } M_n = \frac{2 \times 100}{0.0725} = 2760$$

The chemical analysis method is limited to the insolubility of the polymer in the solvent.



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Determination of Molecular weight of polymers

Methods: viscometry, light scattering and osmotic pressure

Viscometry: The molecular weight obtained by this technique is the viscosity average molecular weight, M_v . The viscosity of a polymer solution is considerable high as compared to that of pure solvent. The increase in viscosity by the macromolecules in a solution is a direct function of the hydrodynamic volume and hence the molecular weight of the macromolecules.

The relationship between viscosity of a polymer solution and molecular weight is given by Mark-Houwink equation-

$$[\eta] = KM^a$$

Where $[\eta]$ is the intrinsic viscosity, M - molecular weight and a and K are constant for a particular polymer/solvent/temperature system. Values of K and a are available for many known polymers.

For a polymer type of known K and a values what is required is the determination of the intrinsic viscosity using the above equation.

For unknown polymer systems, the K and a values are generated by fractionating the polymer sample into several fractions and for each fraction the molecular weight is determined by Osmometry or light scattering method and corresponding intrinsic viscosity is measured.



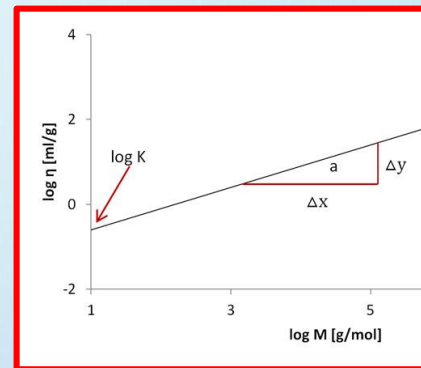
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Determination of Molecular weight of polymers

Viscometry: A plot of $\log [\eta]$ 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 measured. 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-

$$\eta = \frac{3.14 Pr^4 t}{8 V l} \rightarrow t = \frac{8 V l \eta}{3.14 P r^4}$$

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 t_o are their corresponding time flow, then $\rightarrow$

$$\eta_r = \frac{t}{t_o} = \frac{\eta}{\eta_o}$$

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



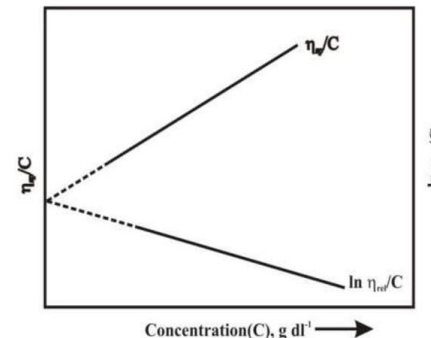
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Determination of Molecular weight of polymers

Commonly used terms in viscometry:

Relative viscosity	Viscosity ratio	η/η_0	$\eta_{rel} = \eta_r$
Specific viscosity	—	$(\eta/\eta_0) - 1$ or $(\eta - \eta_0)/\eta_0$	η_{sp}
Reduced viscosity	Viscosity number	η_{sp}/c	η_{red} or η_{sp}/c
Inherent viscosity	Logarithmic viscosity number	$\ln(\eta_r)/c$	η_{inh} or $\ln(\eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	$\lim(\eta_{sp}/c)_{c \rightarrow 0}$ or $\lim(\ln \eta_r/c)_{c \rightarrow 0}$	$[\eta]$ or LVN

Intrinsic viscosity is also known as Staudinger index or limiting viscosity index (dimension is reciprocal of concentration). For calculating the intrinsic viscosity of a polymer sample in solution, we need not know the absolute viscosities of solvent and solution, but only the flow time of constant volume of solvent and the solution through a particular tube. This principle is used in the viscometric technique of molecular weight determination. The term $[\eta]$ has related to the two viscosity functions through the following two equations by Huggins and Kraemer equations.



Huggins Equation

$$\eta_{sp}/C = [\eta] + \kappa' [\eta]^2 C$$

Kraemer Equation

$$(\ln \eta_{rel})/C = [\eta] + \kappa'' [\eta]^2 C$$

κ'' & κ' are constants for a given polymer solvent/ temperature system



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Determination of Molecular weight of polymers

Problem: Calculate the relative viscosity, specific viscosity, and reduced viscosity of a 0.5% (made by dissolving 0.25 g of polymer in 50 mL of solvent) solution where the time for solvent flow between the two appropriate marks was 60 s and the time of flow for the solution was 80 s.

Solution: Using the relation of time of flow with relative viscosity,

$$\eta_r = \frac{t}{t_o} = \frac{\eta}{\eta_o}$$

$$\text{Relative viscosity } \eta_r = 80 \text{ s} / 60 \text{ s} = 1.3$$

The specific viscosity η_{sp} is determined by using the relation,

$$\eta_{sp} = \frac{\eta}{\eta_o} - 1$$

$$\text{Specific viscosity, } \eta_{sp} = 1.3 - 1 = 0.3$$

The reduced viscosity is η_{red} is given by the relation-

$$\eta_{red} = \frac{\eta_{sp}}{c}$$

The most widely employed concentrations in viscosity determinations are g/mL (g/cc) and g/dL or %. The units g/cc are recommended by IUPAC, while the units of % or g/dL are the most commonly used units.

The reduced viscosity, η_{red} is-

$$\frac{\eta_{sp}}{c} = \frac{0.3}{0.5} = 0.06\%^{-1} \text{ or } 0.6 \frac{\text{dL}}{\text{g}}$$



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Determination of Molecular weight of polymers

Problem: Determine the molecular weight of a polystyrene sample which has an a value of 0.60, a K value of 1.6×10^4 dL/g, and a limiting viscosity number or intrinsic viscosity of 0.04 dL/g.

Solution: The molecular weight can be found by the relationship:

$$\begin{aligned}[\eta] &= K\bar{M}^a \\ \log [\eta] &= a \log M + \log K \\ \log M &= [\log [\eta] - \log K]/a = [\log (0.04) - \log (1.6 \times 10^4)]/0.60 \simeq -4 \\ \therefore M &= 1 \times 10^4\end{aligned}$$

Hence, the molecular weight of the polymer is 1×10^4

Problem: If the value of K and a in the Mark-Houwink equation are $1 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ and 0.5, respectively, what is the average molecular weight of a polymer whose solution has an intrinsic viscosity of 150 cc/g? (Try to solve the problem and send it to me)



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Determination of Molecular weight of polymers

Osmotic pressure Method:

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.

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



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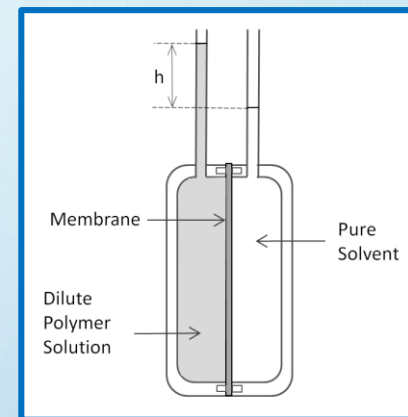
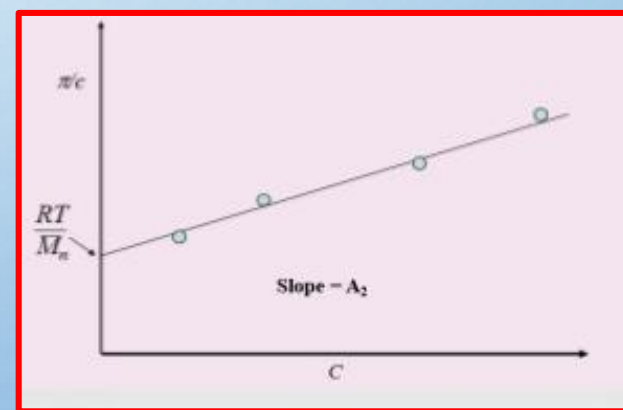
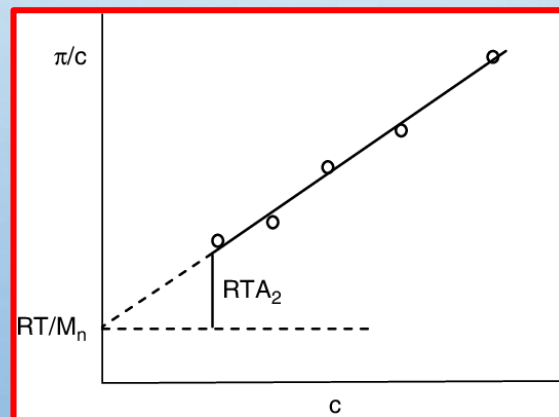
Determination of Molecular weight of polymers

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 (ρ), i.e., $\pi = h\rho g$.

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.



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Determination of Molecular weight of polymers

Light Scattering Method: Light scattering methods to determination of weight average molecular weight, M_w . 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..

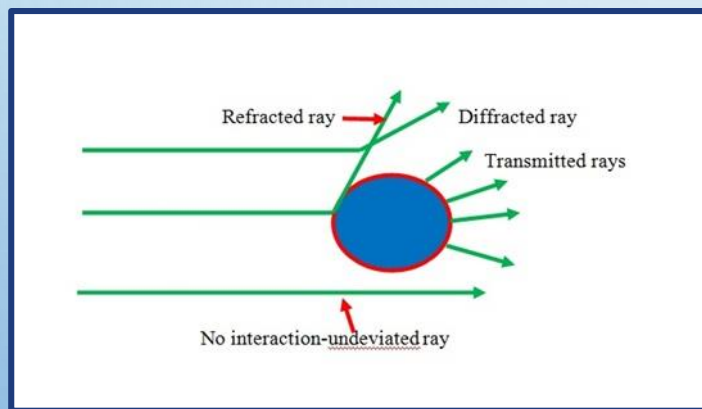


Figure: Modes of scattering of light in solution.

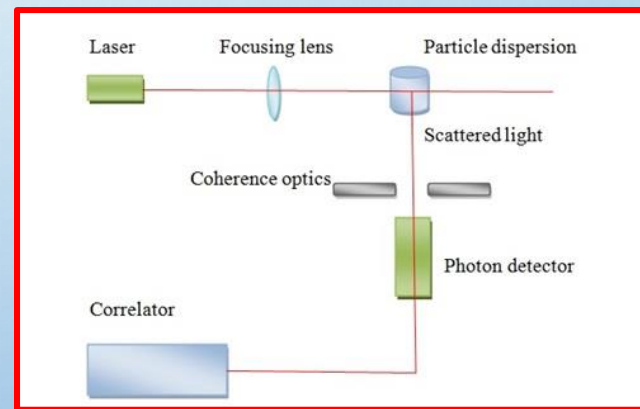


Figure: Schematic representation of light scattering.

For light scattering measurements, the total amount of the scattered light is deduced from the decrease in intensity of the incident beam, I_0 , as it passes through a polymer sample. This can be described in terms of Beer's law for the absorption of light.

**Determination of Molecular weight of polymers**

The Beer's law for the absorption of light as follows:

$$\frac{I}{I_0} = e^{-\tau l}$$

where τ is the measure of the decrease of the incident beam intensity per unit length l of a given solution and is called the turbidity.

The intensity of scattered light or turbidity (τ) is proportional to the square of the difference between the index of refraction (n) of the polymer solution and of the solvent n_0 , to the molecular weight of the polymer (M), and to the inverse fourth power of the wavelength of light used (λ). Thus,

$$\frac{Hc}{\tau} = \frac{1}{M_w P_\theta} (1 + 2Bc + Cc^2 + \dots)$$

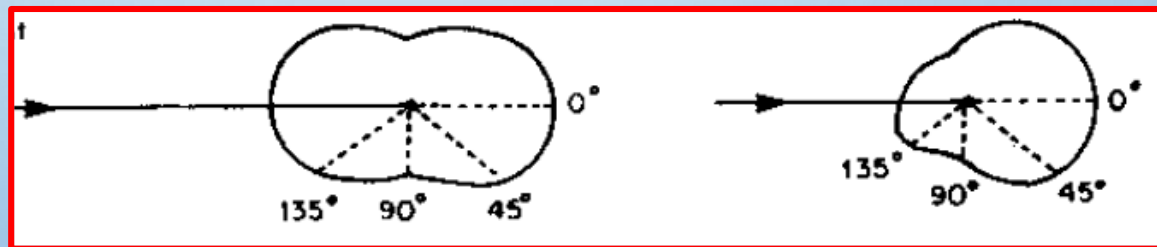
where the expression for the constant H is

$$H = \frac{32\pi^2}{3} \frac{n_0^2 (dn/dc)^2}{\lambda^4 N} \text{ and } \tau = K' n^2 \left(\frac{i_{90}}{i_0} \right)$$

where n_0 index of refraction of the solvent, n index of refraction of the solution, c concentration, the virial constants B , C , etc., are related to the interaction of the solvent, P is the particle scattering factor, and N is Avogadro's number. The expression dn/dc is the specific refractive increment and is determined by taking the slope of the refractive index readings as a function of polymer concentration.

**Determination of Molecular weight of polymers**

In the determination of the weight-average molecular weight of polymer molecules in dust-free solutions, one measures the intensity of scattered light from a mercury arc lamp or laser at different concentrations and at different angles (θ), typically 0, 90, 45, and 135. The incident light sends out a scattering envelope that has four equivalent quadrants. The ratio of scattering at 45° compared with that for 135° is called the dissymmetry factor or dissymmetry ratio Z . The reduced dissymmetry factor Z_0 is the intercept of the plot of Z as a function of concentration extrapolated to zero concentration

Scattering particle**Scattering particle****Incident Light**

Light-scattering envelopes. Distance from the scattering particle to the boundaries of the envelope represents the magnitude of scattered light as a function of angle.

**Determination of Molecular weight of polymers**

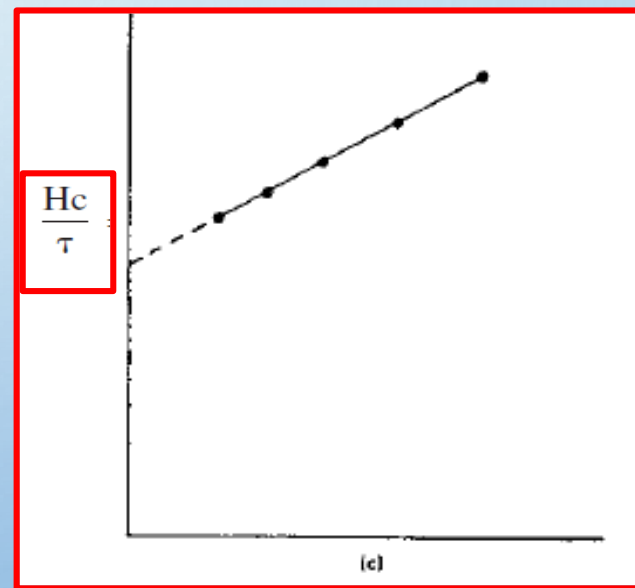
Several expressions are generally used in describing the relationship between values measured by light scattering photometry and molecular weight

$$Kc/R = 1/M_w (1 + 2Bc + Cc^2 + \dots)$$

At low concentrations of polymer in solution, the above equation reduces to an equation of a straight line ($y = b + mx$):

$$\frac{Hc}{\tau} = \frac{1}{M_w} + \frac{2Bc}{M_w}$$

When the ratio of the concentration c to the turbidity (related to the intensity of scattering at 0 and 90) multiplied by the constant H is plotted against concentration, the intercept of the extrapolated curve, is the reciprocal of M_w and the slope contains the virial constant B , as shown in Figure



Typical plot used to determine M_w^{-1} from light scattering data



References and suggestions for further reading:

1. Textbook of Polymer Science by Fred W. Billmeyer, Wiley
2. Polymer Chemistry by Charles E Carraher, Jr., Marcel Dekker, Inc.
3. Principle of Polymerization by George Odian, Wiley

The background is a light blue gradient. It is decorated with numerous water droplets of various sizes. Some droplets are large and prominent, while others are small and scattered. The droplets have a realistic 3D appearance with highlights and shadows, giving them a sense of depth and volume. They are distributed across the entire frame, with a higher concentration in the upper and lower portions.

THANK YOU