Introduction to Polymer Science

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Lecture - 28
Membrane Osmometry, End Group Analysis, Dilute Solution Viscometry

Welcome back. In this lecture onwards, I will start a new module, which is on characterization of polymers and specifically about determination of polymer molecular weight.

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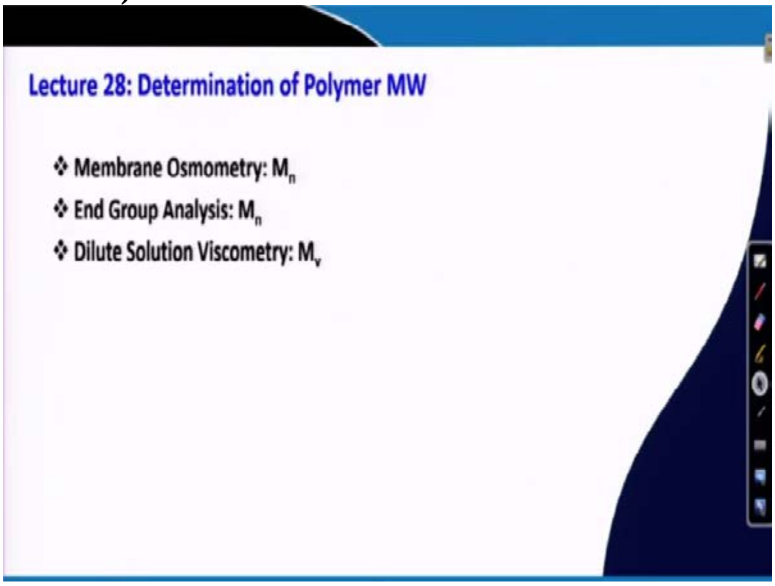

Lecture 28: Determination of Polymer MW

- Membrane Osmometry: M_n
- End Group Analysis: M_n
- Dilute Solution Viscometry: M_v

In this particular lecture, I plan to cover membrane osmometry, end group analysis and dilute solution viscometry.

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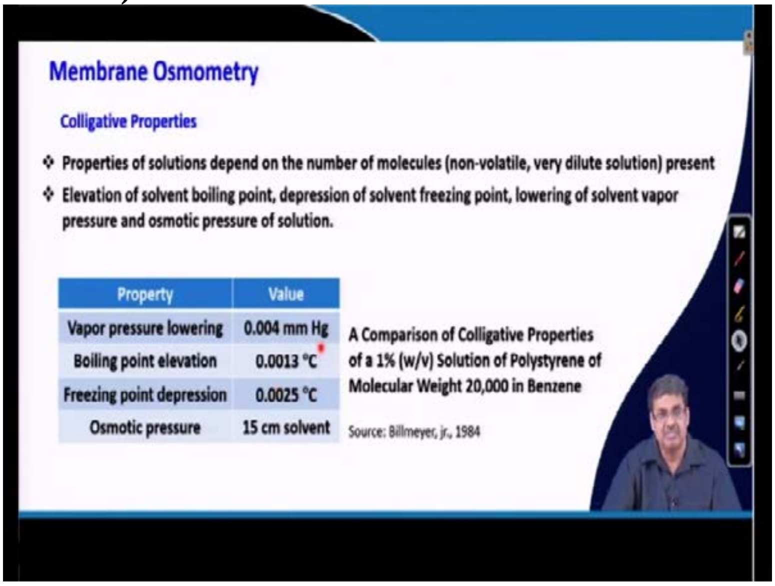

Membrane Osmometry

Colligative Properties

- Properties of solutions depend on the number of molecules (non-volatile, very dilute solution) present
- Elevation of solvent boiling point, depression of solvent freezing point, lowering of solvent vapor pressure and osmotic pressure of solution.

Property	Value
Vapor pressure lowering	0.004 mm Hg
Boiling point elevation	0.0013 °C
Freezing point depression	0.0025 °C
Osmotic pressure	15 cm solvent

A Comparison of Colligative Properties of a 1% (w/v) Solution of Polystyrene of Molecular Weight 20,000 in Benzene

Source: Billmeyer, jr., 1984

Membrane osmometry is based on colligative properties of a solution. From your previous knowledge, you know that colligative properties of a solution depend on the number of solute molecules. When you talk about number of molecules, the molecules should be non-volatile and very dilute solution. So, the magnitude of colligative properties of a solution depends only on the number or moles of solute present in the solution. Four colligative properties are elevation of solvent boiling point, depression of solvent freezing point, lowering of solvent vapor pressure and osmotic pressure of solution. Now, look at the data which is a comparison of colligative properties of 1% solution of polystyrene of molecular weight about 20000 in benzene. Look at the magnitude of the changes in vapor pressure or boiling point, freezing point, osmotic pressure. These are very small in magnitude and so these are very difficult to capture experimentally. There are always some errors involved in these techniques. So, for this course I will mainly talk about osmotic pressure and briefly mention about the other three techniques after osmotic pressure method.

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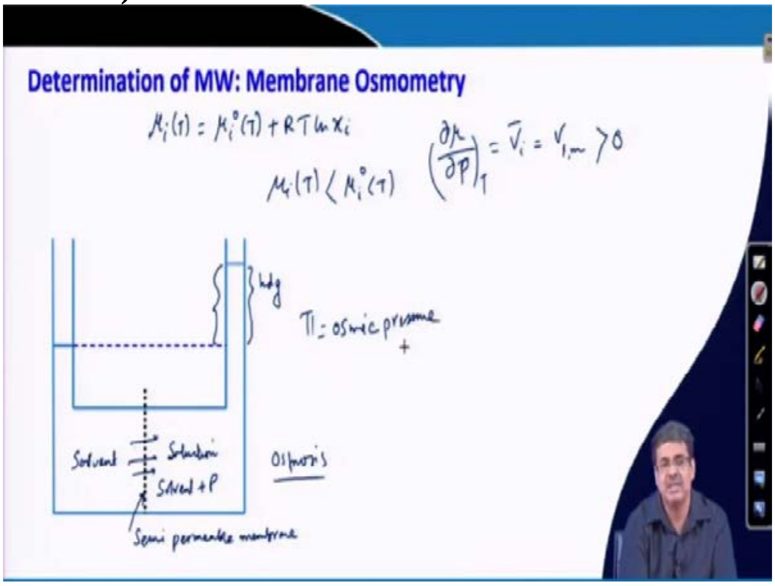

Determination of MW: Membrane Osmometry

$\mu_i(T) = \mu_i^0(T) + RT\ln x_i$

$\mu_i(T) < \mu_i^0(T)$

$\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V}_i = V_{1,m} > 0$

For osmotic pressure measurements, in a chamber we have pure solvent on one side and on the other side we have a solution which contain solvent plus polymer. In this case polymer is the solute and the membrane is semipermeable which means that it is only permeable to the solvent molecules and not the polymer molecules. Now, the chemical potential of a component in a solution at a particular temperature is given by standard chemical potential plus RTlnX_i.

$$\mu_i(T) = \mu_i^0(T) + RTlnX_i$$

Xi is the mole fraction. This is for an ideal solution and for a real solution we write as an activity. We are talking about very dilute solution and so we can consider this as close approximation to ideal solution and so we can consider this equation as valid. Now, for a solution the chemical potential is always less than the chemical potential of the pure solvent because this is a fraction , i.e. $\mu_i(T) < \mu_i^0(T)$. So, chemical potential of solvent in a solution which will be less than the chemical potential of pure solvent at that particular temperature. Now, we know that to maintain or to achieve a chemical equilibrium any component always moves from one phase having higher chemical potential to a phase which is at a lower chemical potential. Hence, the solvent will try to move from pure solvent phase to a solution phase and we call this as osmosis. How long it will continue? Ideally it should continue till all the solvent is over in this side. But in this case as more solvent comes, there is an extra pressure build up which is of the magnitude hdg, where h is the height and d is the density of the solution. So that is the additional height compared to the solvent side, so the pressure at on solution side is more than the solvent side.

$$\left(\frac{d\mu}{dp}\right)_T = \overline{V_i} = V_{i,m} > 0$$

Now, we also know that dμ or chemical potential with respect to pressure at constant temperature is given by partial molar volume. As we are talking about dilute solution here, we can write the molar volume of the solvent $V_{i,m}$ which is a positive quantity always. Hence, the chemical potential will increase with increase in pressure. So, as the pressure increases, it will happen that at one moment the chemical potential of solvent on both the sides will be equal and the equilibrium will be achieved. Now, once the equilibrium is achieved, the corresponding height, the additional pressure is called π or the osmotic pressure. So, osmotic pressure is the additional pressure required to maintain the equilibrium between the solvent phases.

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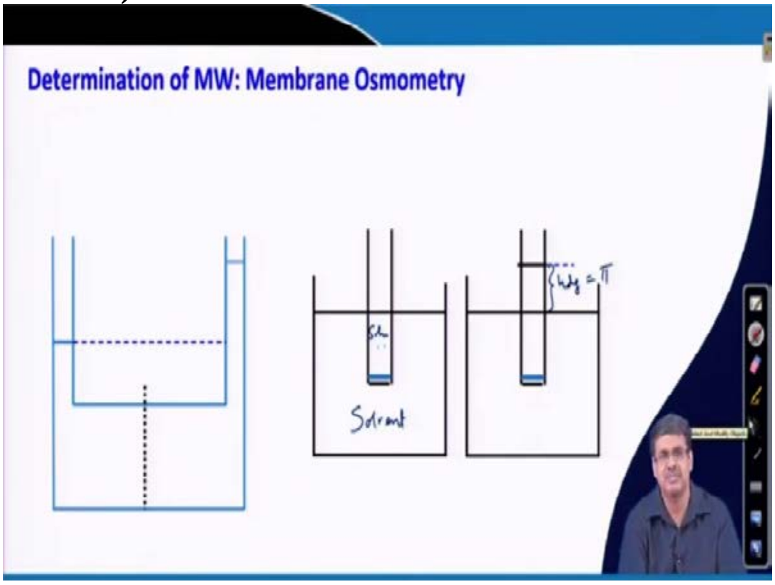

Determination of MW: Membrane Osmometry

Now, we can have other types of setup where we have a solvent in this outside and solution within this separated by semipermeable membrane. So, at equilibrium the height goes up. So, this is, this additional pressure is given by hdg that corresponds to π, called osmotic pressure.

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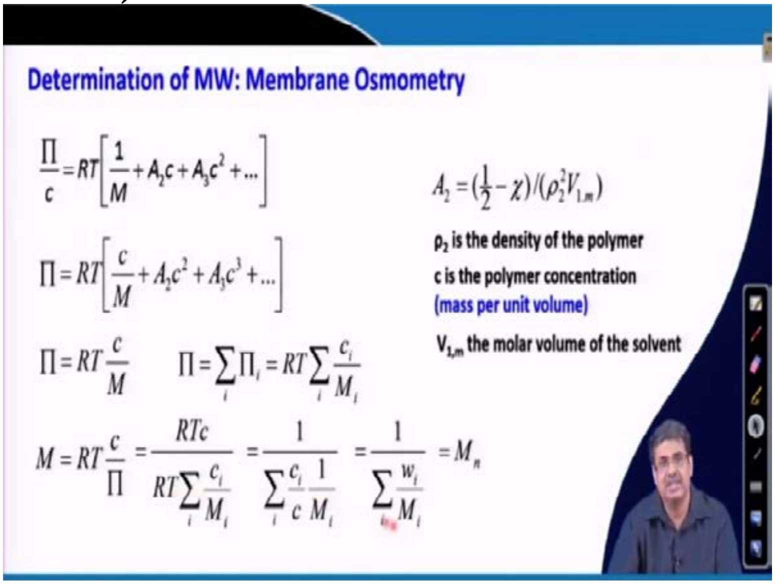

Determination of MW: Membrane Osmometry

$$\frac{\Pi}{c} = RT\left[\frac{1}{M} + A_2c + A_3c^2 + \ldots\right]$$

$$\Pi = RT\left[\frac{c}{M} + A_2c^2 + A_3c^3 + \ldots\right]$$

$$\Pi = RT\frac{c}{M} \qquad \Pi = \sum_i \Pi_i = RT\sum_i \frac{c_i}{M_i}$$

$$M = RT\frac{c}{\Pi} = \frac{RTc}{RT\sum_i \frac{c_i}{M_i}} = \frac{1}{\sum_i \frac{c_i}{c}\frac{1}{M_i}} = \frac{1}{\sum_i \frac{w_i}{M_i}} = M_n$$

$$A_2 = (\tfrac{1}{2} - \chi)/(\rho_2^2 V_{1,m})$$

ρ_2 is the density of the polymer

c is the polymer concentration (mass per unit volume)

$V_{1,m}$ the molar volume of the solvent

Now, we have seen from our earlier lectures that osmotic pressure can be expressed in this way,

$$\frac{\Pi}{c} = RT\left[\frac{1}{M} + A_2c + A_3c^2 + \cdots\right]$$

where M is the molecular weight of the solute, c is the concentration in mass per unit volume. Generally, when we talk about concentration, we generally talk about moles per litre, but as we do not know the molecular weight that we are trying to find out, we will always express this concentration in terms of mass per unit volume. So, it is a mass concentration not mole concentration or number concentration. Please note, this is very important that when you are talking about these polymer solutions and related properties, we are talking about mass per unit volume. A_2 is a second virial coefficient, which is given by this expression

$$A_2 = \left(\frac{1}{2} - \chi\right) \Big/ \rho_2^2 V_{1,m}$$

where ρ_2 is the density of the polymer and $V_{1,m}$ in molar volume of the solvent and χ is the polymer solvent interaction parameter which we discussed earlier.

Now, we can express this by just multiplying c on both sides.

$$\Pi = RT\left[\frac{c}{M} + A_2c^2 + A_3c^3 + \cdots\right]$$

Now, if the solution is very dilute, then we can ignore this second square term and c^3 term onwards from the right hand side. So, we can just write $\Pi = RT\frac{c}{M}$ in case of the dilute solution. Now, if we consider that the osmotic pressure of a solution of a polymer is summation of the osmotic pressure generated by each polymer molecule, we can write the total osmotic pressure is summation of the osmotic pressure generated by individual molecules. Then, we can write

$$\Pi = \sum_i \Pi_i = RT\sum_i \frac{c_i}{M_i}$$

On rearranging, it gives this expression,

$$M = RT\frac{c}{\Pi} = \frac{RTc}{RT\sum_i \frac{c_i}{M_i}} = \frac{1}{\sum_i \frac{c_i}{c}\frac{1}{M_i}} = \frac{1}{\sum_i \frac{w_i}{M_i}} = M_n$$

which is nothing but M_n. So, when you talking about determination of molecular weight by osmotic pressure, we will be determining the number average molecular weight as shown by this derivation.

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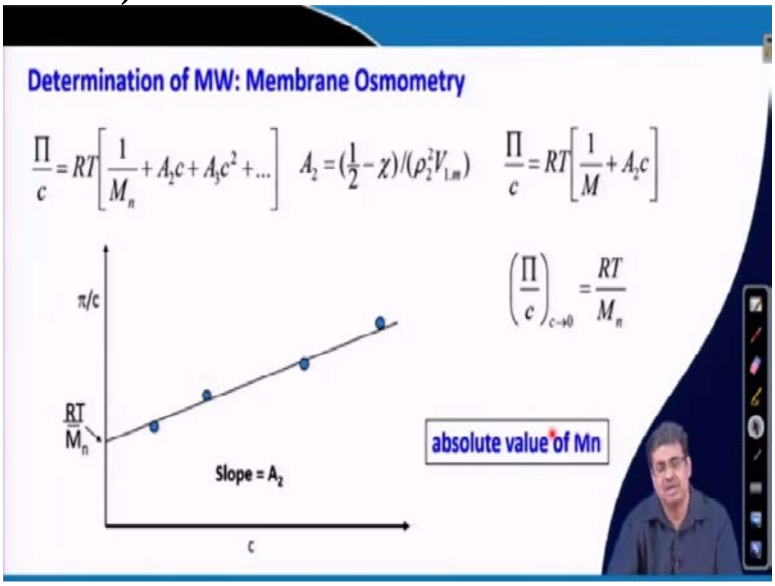

Determination of MW: Membrane Osmometry

$$\frac{\Pi}{c} = RT\left[\frac{1}{M_n} + A_2c + A_3c^2 + \ldots\right] \quad A_2 = \left(\frac{1}{2} - \chi\right)/(\rho_2^2 V_{1,m}) \quad \frac{\Pi}{c} = RT\left[\frac{1}{M} + A_2c\right]$$

$$\left(\frac{\Pi}{c}\right)_{c\to 0} = \frac{RT}{M_n}$$

absolute value of Mn

We can plot this Π / c of several polymer solutions having different concentration and then plot Π / c with respect to c, and then we can get a straight line. If we talk about very dilute solution then we can ignore this second order terms. So, we can just write only the A_2c term and at c = 0 the intercept will give us $\frac{RT}{M_n}$ from which we can get the M_n value.

$$\left(\frac{\Pi}{c}\right)_{c\to 0} = \frac{RT}{M_n}$$

We need to make few solutions of known concentration, concentration means mass per unit volume, and measure osmotic pressure for each of these solutions and then plot Π / c with concentration. From the intercept, we can get number average molecular weight and from the slope, we can get the second virial coefficient from which we can get the polymer solvent interaction parameter as well.

Now, please note that we have not calibrated this osmotic pressures with any known polymer molecular weight, which means this is an absolute method of determining molecular weight. The molecular weight in this case is number average molecular weight which we determine by measurement using of membrane osmometry and is the absolute value of molecular weight.

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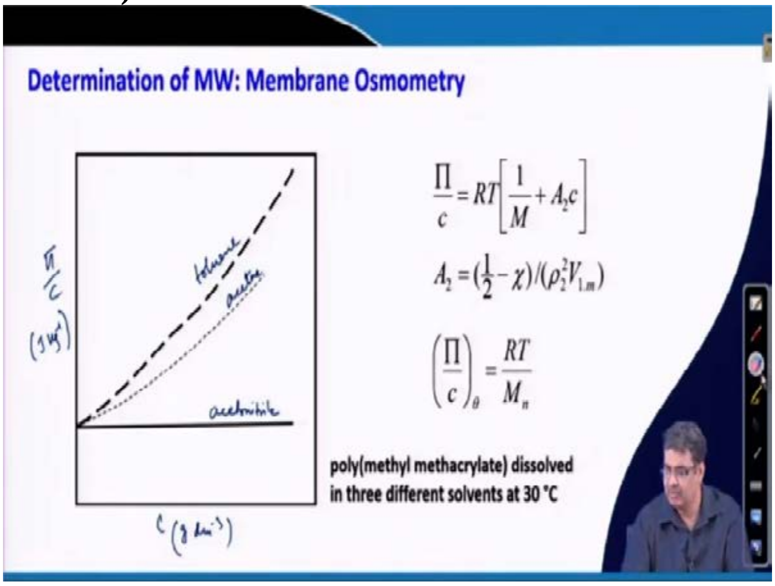

Determination of MW: Membrane Osmometry

$$\frac{\Pi}{c} = RT\left[\frac{1}{M} + A_2 c\right]$$

$$A_2 = \left(\frac{1}{2} - \chi\right)/(\rho_2^2 V_{1,m})$$

$$\left(\frac{\Pi}{c}\right)_\theta = \frac{RT}{M_n}$$

poly(methyl methacrylate) dissolved in three different solvents at 30 °C

Now, when we talk about θ solvent, we know that for θ solvent the value of polymer solvent interaction parameter is 0.5 or half, which means in θ solvent, this A_2 term will be zero. So, we can just determine Π/c at any concentration and we can use that value of Π to get directly M_n value. We do not need any extrapolation in that case, because in this case of θ solvent, values of Π and or Π/c do not depend on the concentration of the solution.

So, this is the example where Π/c is plotted, Π/c unit is joule/kg^{-1} SI unit and concentration is gram/dm^3 that is the unit. So, PMMA dissolved in 3 different solvents this is toluene, this is acetone and this is acetonitrile. This case, you see Π/c value does not depend on the concentration of the polymer solution. Hence, we can use any of this data to find out the molecular weight M_n. If we are not using any θ solvent then from the slope, initial slope we can find out the A_2 value and from the intercept we can determine the M_n value. And as you can see, the more good a solvent, the higher is the deviation from linearity. So, basically, when you have the solvent is good then the additional c^2 term also come in the picture and there is deviation from linearity and the slope is higher when the solvent is good because the χ value becomes less than 0.5 for good solvent and lower the value for χ, we have seen earlier that better is the solvent quality for the polymer, hence the slope also increases.

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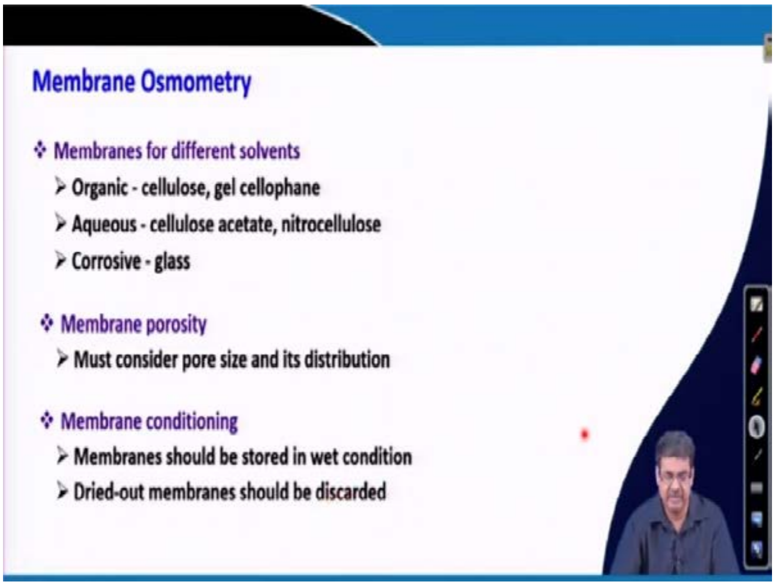

Membrane Osmometry

- Membranes for different solvents
  - Organic - cellulose, gel cellophane
  - Aqueous - cellulose acetate, nitrocellulose
  - Corrosive - glass
- Membrane porosity
  - Must consider pore size and its distribution
- Membrane conditioning
  - Membranes should be stored in wet condition
  - Dried-out membranes should be discarded

Now, we just need to keep this information in mind during membrane osmometry that membranes for different solvents are different. For example, for organic solvents, we have cellulose, cellophane type membrane; for aqueous solvent, we have cellulose acetate membrane, nitrocellulose membrane; for corrosive material, a glass membrane and so on. And, and the membrane should have a proper pore size and its distribution. And should be there in a wet condition and dried out membrane should be discarded because the pore will not be effective in that case.

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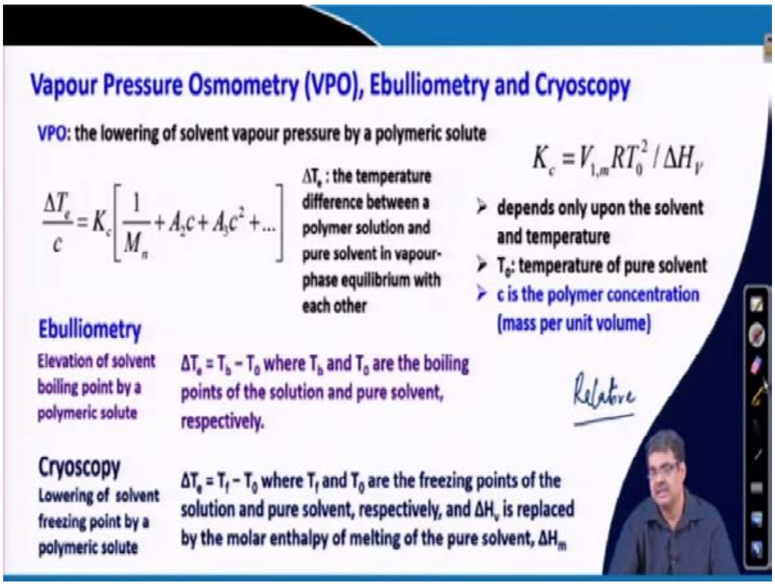

Vapour Pressure Osmometry (VPO), Ebulliometry and Cryoscopy

VPO: the lowering of solvent vapour pressure by a polymeric solute

$$\frac{\Delta T_e}{c} = K_c\left[\frac{1}{M_n} + A_2c + A_3c^2 + \dots\right]$$

ΔT_e : the temperature difference between a polymer solution and pure solvent in vapour-phase equilibrium with each other

$$K_c = V_{1,m}RT_0^2 / \Delta H_V$$

- depends only upon the solvent and temperature
- T_0: temperature of pure solvent
- c is the polymer concentration (mass per unit volume)

Ebulliometry

Elevation of solvent boiling point by a polymeric solute

$\Delta T_e = T_b - T_0$ where T_b and T_0 are the boiling points of the solution and pure solvent, respectively.

Relative

Cryoscopy

Lowering of solvent freezing point by a polymeric solute

$\Delta T_e = T_f - T_0$ where T_f and T_0 are the freezing points of the solution and pure solvent, respectively, and ΔH_v is replaced by the molar enthalpy of melting of the pure solvent, ΔH_m

Next we will talk about briefly the other 3 techniques namely the Vapour pressure osmometry, Ebulliometry and Cryoscopy. As the name suggests, vapour pressure osmometry deals with the lowering of solvent vapour pressure by a polymeric solute. Now, generally in the experiment, we do not measure the vapour pressure difference. What we do? We basically maintain a solvent and a solution chamber and the temperature is varied to keep the vapour pressure in both sides equal and we can express this delta T_e / c like the Π / c as this,

$$\frac{\Delta T_e}{c} = K_c \left[\frac{1}{M_n} + A_2 c + A_2 c^2 + \cdots\right]$$

we have similar expression but the constant term is different. ΔT_e is the temperature difference between the polymeric solution and the pure solvent in the vapour phase equilibrium with each other. So, it is the temperature difference which we need to maintain to have an equilibrium between the solution phase and solvent phase. Now, K_c can we express this way

$$K_c = \frac{V_{1,m} R T_0^2}{\Delta H_v}$$

where ΔH_v is the heat of vaporisation for the solvent and $V_{1,m}$ is the molar volume of the solvent and rest of the thing is explained here. And T_0 is the temperature of the pure solvent; again c is the polymer concentration in mass per unit volume. So, the value of K_c depends only on the solvent and temperature. So, in this case also we can find out M_n by determining or measuring the ΔT_e value for different solutions having different concentration of polymer and then by plotting ΔT / c with c, we can find the M_n from the intercept and A_2 from the slope as we did for osmotic pressure.

Ebulliometry deals with elevation of solvent boiling point by a polymeric solute. In this case, this T is the difference in the boiling point for the solvent and pure solvent, the rest of the meaning remains similar. In case of cryoscopy which deals with lowering of solvent freezing point by a polymer solute. In this case, this temperature difference is the difference in the freezing point of the pure solvent and the solution. In this case, only in place of ΔH_v, we will write ΔH_m which is the molar enthalpy of melting for pure solvent. We are talking about lowering of freezing point. So, you use ΔH_m instead of ΔH_v.

So, we can now use these three techniques as well to find out the value of M_n and A_2. Moreover, these three techniques are actually related techniques because to find out the value of K_c or the other K values, we actually need to use a polymer of known molecular weight. In principle, these should be absolute measurement techniques, but in practical sense, to actually achieve these experiments, we need to have a value of the K_c and other corresponding K terms which can be only obtained by using known molecular weight polymer. Hence, these are relative techniques. So, we can write that, in principle, these should have been absolute techniques but in practically these are relative techniques.

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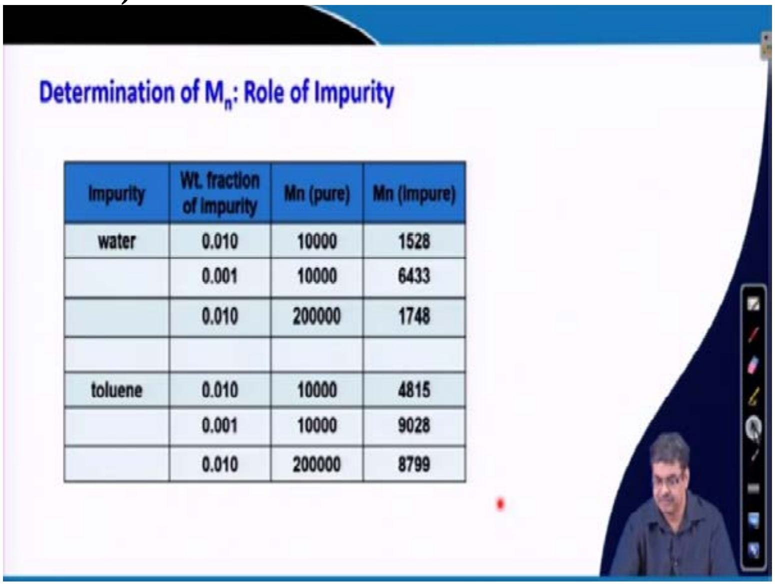

Determination of M_n: Role of Impurity

Impurity	Wt. fraction of impurity	Mn (pure)	Mn (impure)
water	0.010	10000	1528
	0.001	10000	6433
	0.010	200000	1748
toluene	0.010	10000	4815
	0.001	10000	9028
	0.010	200000	8799

We need to be very careful about impurities in this measurement because, in this we are talking about number of molecules present in the solvents, which determine the value of these properties. Hence, even if we have a small impurity that effect the M_n value determined by these techniques a lot. For example, if we have an impurity like water and even for a low weight fraction of 1% the determined Mn will turn out to be 1748 for actual M_n of 2 lakh!! Which means, there is a drastic change in the molecular weight determined by these, any of these techniques, in presence of one weight percent of water as impurity. Similarly, if we had one weight percent toluene, because toluene has higher molecular weight, the number of molecules will be less. Hence, the error is comparatively less compared to the water. So, you need to remember that while using these colligative property measurement techniques, we must be very careful about the impurities present in the solution.

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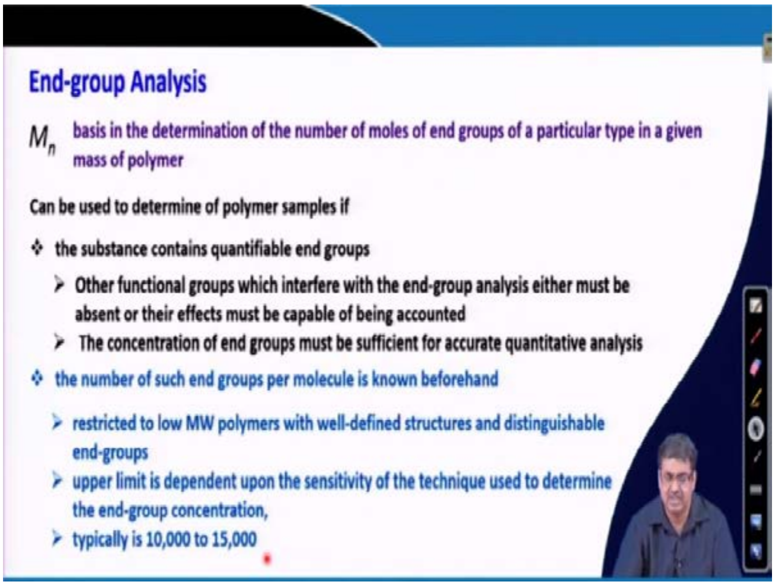

End-group Analysis

M_n basis in the determination of the number of moles of end groups of a particular type in a given mass of polymer

Can be used to determine of polymer samples if

- the substance contains quantifiable end groups
  - Other functional groups which interfere with the end-group analysis either must be absent or their effects must be capable of being accounted
  - The concentration of end groups must be sufficient for accurate quantitative analysis
- the number of such end groups per molecule is known beforehand
  - restricted to low MW polymers with well-defined structures and distinguishable end-groups
  - upper limit is dependent upon the sensitivity of the technique used to determine the end-group concentration,
  - typically is 10,000 to 15,000

Next technique we will talk about end group analysis. Now, this also gives us number average molecular weight and the basis of this measurement is the determination of number of moles of end groups in a given mass of polymer. So, we know how much polymer by weight we have taken in a solution, and if we know what is the number of moles of ends present in this polymer sample then we can get the value of M_n, provided we know that number of ends present in a polymer chain.

This method can be used to determine for the polymer sample if the polymer contain quantifiable end groups. Some cases, if we have end groups, which we cannot determine, or we cannot quantify, there it is not possible. So, we need to have any mechanism or any characterization technique by which we can quantify the number of moles of end groups present. So, that may require that other functional groups which interfere with the end group analysis, must be absent or their effect must be accounted. So, if we have, in addition to the two end groups, another group in the middle in the backbone but not in the end, it will interfere in the end group analysis, then it is very difficult to determine the Mn unless we take care of this interference which is again very difficult to do. Also, the concentration of end groups must be sufficient, so that accurate quantitative measurement is possible and the number of end groups per molecule, per polymer molecule is known before-hand. So, we should know that a linear polymer has two ends, a branch polymer has more than two ends.

This method is also limited to low molecular weight polymers because as we increase the molecular weight the number of ends for a given weight of sample comes down and the measurement or quantification of these ends also become difficult. Hence, this analysis is restricted to low molecular weight polymers with well-defined structure and distinguishable end groups. An upper limit is dependent on the sensitivity of the techniques, which we are using and typically, it is done for polymers having molecular weight less than 10000 to 15000.

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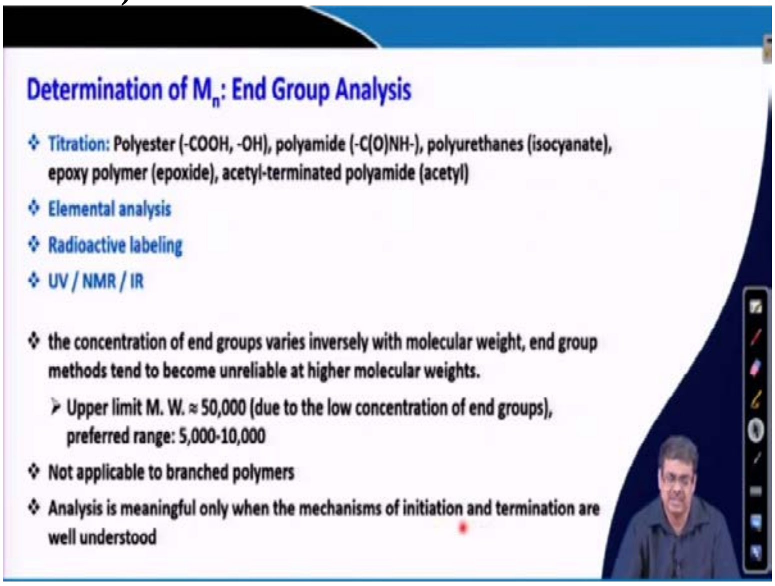

Determination of M_n: End Group Analysis

- Titration: Polyester (-COOH, -OH), polyamide (-C(O)NH-), polyurethanes (isocyanate), epoxy polymer (epoxide), acetyl-terminated polyamide (acetyl)
- Elemental analysis
- Radioactive labeling
- UV / NMR / IR

- the concentration of end groups varies inversely with molecular weight, end group methods tend to become unreliable at higher molecular weights.
  - Upper limit M. W. ≈ 50,000 (due to the low concentration of end groups), preferred range: 5,000-10,000
- Not applicable to branched polymers
- Analysis is meaningful only when the mechanisms of initiation and termination are well understood

Generally, these are the techniques which are used for quantifying the end groups. If we have the acid groups, alcohol groups or basic groups or like, we can use titration technique to quantify the number of moles present in the end groups. Elemental analysis, radioactive labelling or some other spectroscopic techniques that can determine the concentration or number of moles of end groups present in that particular sample may also be used.

The concentration of end groups varies inversely with molecular weight. So, end group methods tend to become unreliable for higher molecular weight as I explained before. So, upper limit is 50,000, but preferred range is 5000 to 10,000. In case of branched polymers, we do not know how many ends are there per polymer molecule; hence, it is very difficult to get the Mn by this method. Therefore, it is not applicable for branched molecules. If we can know how many end groups are present and what are the types of end groups then this method actually helps us to find out the mechanism of initiation and termination reactions for chain polymerization.

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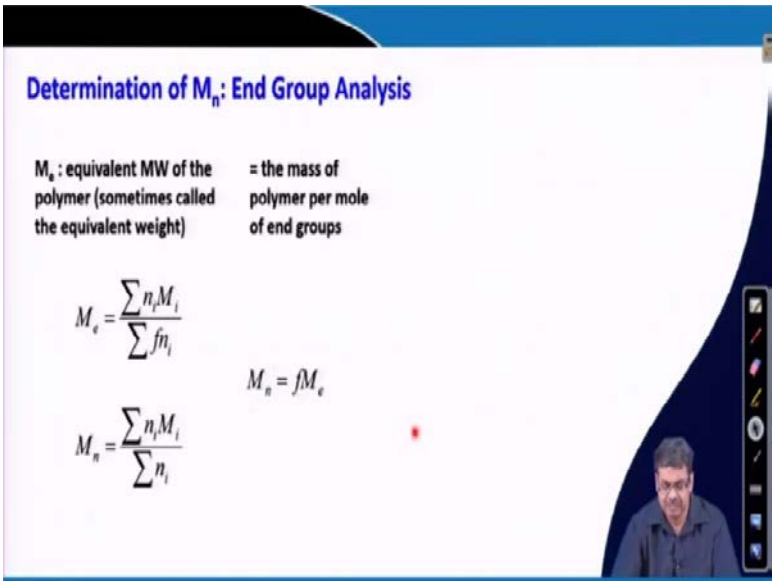

Determination of M_n: End Group Analysis

M_e : equivalent MW of the polymer (sometimes called the equivalent weight)

= the mass of polymer per mole of end groups

$$M_e = \frac{\sum n_i M_i}{\sum f n_i}$$

$$M_n = f M_e$$

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

To find out the molecular weight, we need to find out M_e which is equivalent molecular weight of the polymer, sometimes called equivalent weight, the mass of polymer per mole of end group. This means that Me is given by,

$$M_e = \frac{\sum n_i M_i}{\sum f n_i}$$

So, $\sum n_i M_i$ gives the total weight and $\sum f n_i$ gives us total number of ends; n_i is the number of polymer chains and *f* is the number of moles per polymer chain. So, *f* multiplied by n_i will give us total number of ends. Hence, this is the average mass of polymer per mole of end groups and we know M_n is given by this expression. Hence, M_n would be given by

$$M_n = f M_e$$

We can determine quantitatively by the techniques, which I showed in the last page, and if we know the *f* value, the number of end groups per polymer molecule, and then we can find out M_n.

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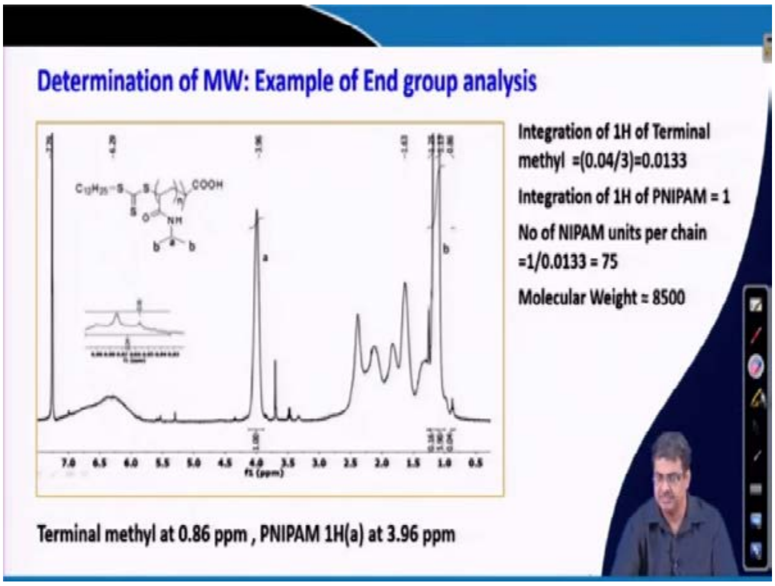

Determination of MW: Example of End group analysis

Integration of 1H of Terminal methyl =(0.04/3)=0.0133

Integration of 1H of PNIPAM = 1

No of NIPAM units per chain =1/0.0133 = 75

Molecular Weight = 8500

Terminal methyl at 0.86 ppm , PNIPAM 1H(a) at 3.96 ppm

I will just give you example of determination of end group analysis by NMR techniques. If you are not aware of NMR technique its fine, you should know that NMR can be used to identify organic compounds chemically or polymeric compounds and in this case proton NMR will be used. Each proton present in different chemical environment will produce different NMR signal and the intensity of the signal will be proportional to the number of such protons present in the molecule.

So, in this particular case, I have poly(N-isopropyl acrylamide) polymer. We need to find out exclusive protons that are present at the end and in the repeating unit. So, in this case, the NCH_3 , this has a long chain $C_{12}H_{25}$. So, at the end it will be CH_3. Now, that peaks come here and it has an intensity of 0.04. The NCH_3 has 3 protons that corresponds to a value of intensity 0.04, whereas each repeating unit has 1 such a proton. This is the proton which is here (refer lecture). So, n number of repeating units will have n such protons. This comes around 3.96. So, this is the signal for these n number of such protons which has intensity of 1. That means, if the number of repeat units is n, I have n such protons. So, this one corresponds to n protons, whereas this 0.04 corresponds to 3 protons which present at the end.

So, I can write that the integration of one proton signal for the terminal methyl, given by this. So, one proton has this intensity for this measurement because 3 terminal protons have intensity of 0.04. So, if we divide 0.04 with 3, this is the value for one single proton. This is the intensity value of 1 proton. Hence, when you have 1 intensity which corresponds to 75 protons. Now, each repeating has 1 proton which means n value is 75. That means, the molecular weight corresponds to approximately.. this in the repeating unit, the molecular weight of the repeating unit in this case is about 113. So, the molecular weight M_n in this case would be 113 multiplied by 75 plus the end group, which comes out approximately 8500. So, basically what we need, exclusive groups; if we can quantify this number of, what is the number of repeating unit if we know what is the ratio of end groups with the repeating unit. Hence, we can find out the molecular weight because we know the molecular weight of that repeating unit of the polymer. We will stop now and in the next lecture, I will talk about determination of molecular weight by dilute solution viscometry.