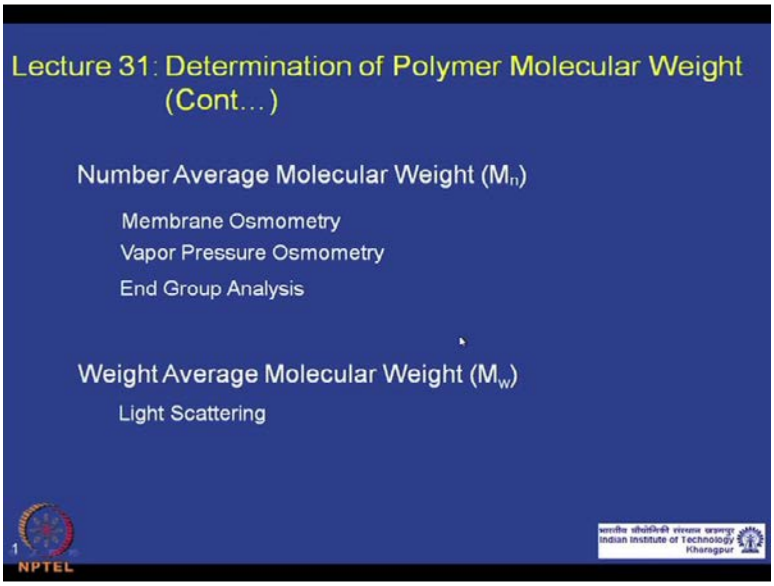
Polymer Chemistry

Prof. Dibakar Dhara
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 31
Determination of Molecular Weight of Polymers (Contd.)

Welcome back to this course on polymer chemistry. In the last lecture we have started our discussion on polymer molecular determination, and we actually discussed how to get the viscosity average molecular weight.

(Refer Slide Time: 00:48)



Lecture 31: Determination of Polymer Molecular Weight (Cont…)

Number Average Molecular Weight (M_n)

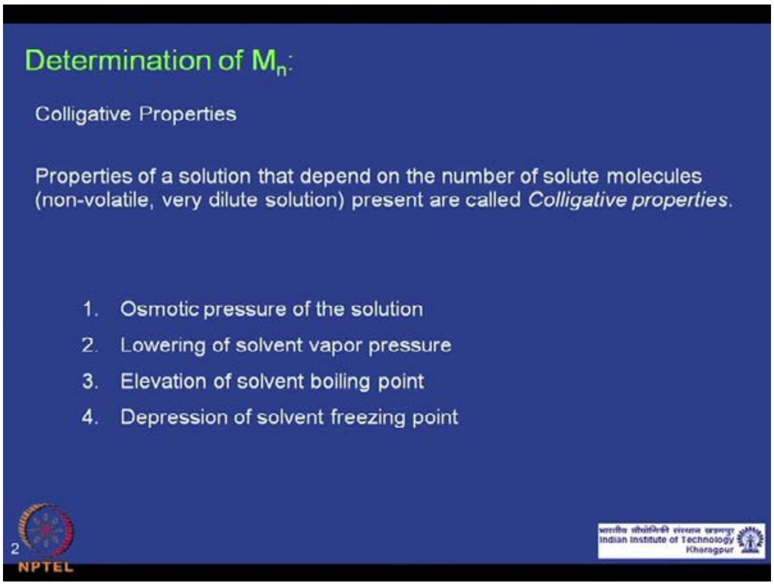
Membrane Osmometry
Vapor Pressure Osmometry
End Group Analysis

Weight Average Molecular Weight (M_w)

Light Scattering

Now, in this lecture we will start discussing about techniques which will enable us to get the number average molecular weight. We will discuss the techniques like membrane osmometry, vapor pressure osmometry, and end group analysis. And then following this discussion on how to get number average molecular weight, we will start discussion on determination of weight average molecular weight by light scattering. This discussion may not end; this lecture we will continue in the following lecture.

(Refer Slide Time: 01:28)



Determination of M_n:

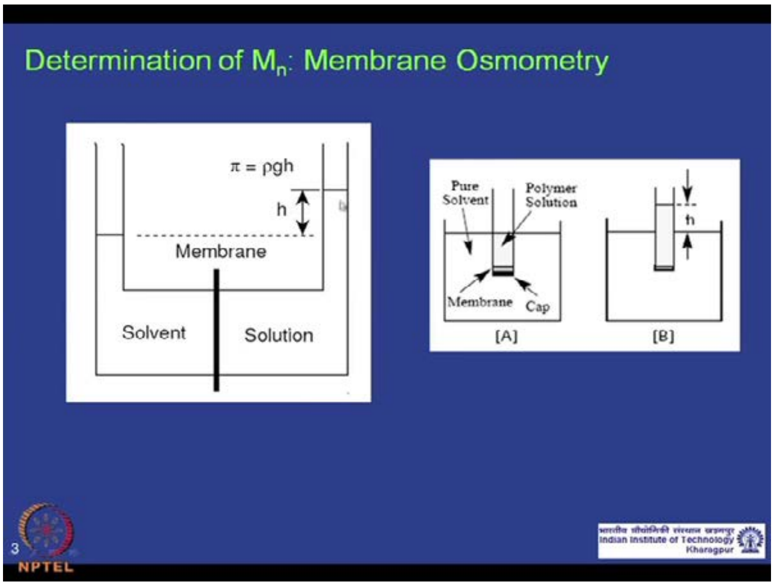
Colligative Properties

Properties of a solution that depend on the number of solute molecules (non-volatile, very dilute solution) present are called *Colligative properties*.

1. Osmotic pressure of the solution
2. Lowering of solvent vapor pressure
3. Elevation of solvent boiling point
4. Depression of solvent freezing point

Let us start with membrane osmometry. You know all of us know about colligative properties you know from our physical chemistry knowledge’s. Colligative properties are those properties of a solution which depends only on the number of solute molecules, provided the solute molecules are nonvolatile and we are doing the measurements at very dilute solutions. These properties are called colligative properties and we know that there are four colligative properties; osmotic pressure of the solution, lowering of solvent vapor pressure, elevation of solvent boiling point, and depression of solvent freezing point. We will discuss the osmotic pressure method in detail following by brief discussion on solvent vapor pressure lowering method and we will just mention about the third and fourth properties.

(Refer Slide Time: 02:46)

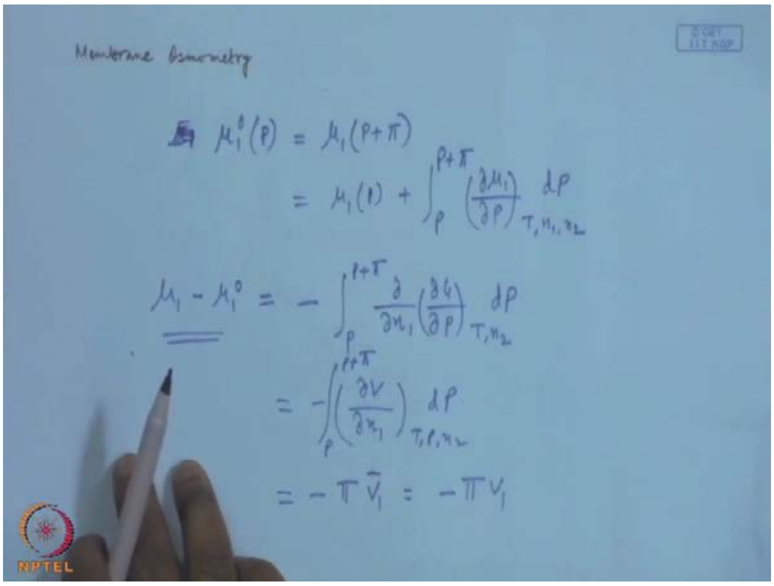


Determination of M_n: Membrane Osmometry

Let us start with membrane osmometry. You know what happened in membrane osmometry? You have a solution in this case polymer solution and the solvent for the solution separated by a membrane which is permeable only to the solvent not the solute. So, solvent can go from solvent side to the solution sides not the solute molecules. Now this case arises; the osmotic pressure difference between the two sides and the solvent because of the chemical potential difference. The chemical potential of solvent molecule in this side is higher than the chemical potential of the solvent in this side which makes solvents to move from solvent side to solution sides and thus increasing the pressure.

If you have a capillary, then there will be rise in the height of the capillary and this will continue till this additional pressure compensate or increases the chemical potential volume of the solvent this side equals to such a extent that it becomes equals to the chemical potential of the solvent in this side. Similarly you can design another equipment where you have a polymer solutions in this capillary and which is separated by a semipermeable membrane which is only permeable to the solvent molecules. And as osmosis, the pressure of the polymer solution side goes up and this excess pressure here; this excess pressure and this residue are called the osmotic pressure. Now as we discussing that this side the solvent chemical potential is higher for a pure solvent than in polymer solution. So, the osmosis happens.

(Refer Slide Time: 05:23)



Membrane Osmometry

$$\mu_1^0(P) = \mu_1(P+\pi)$$

$$= \mu_1(P) + \int_P^{P+\pi} \left(\frac{\partial \mu_1}{\partial P}\right)_{T,n_1,n_2} dP$$

$$\underline{\underline{\mu_1 - \mu_1^0}} = -\int_P^{P+\pi} \frac{\partial}{\partial n_1}\left(\frac{\partial G}{\partial P}\right)_{T,n_2} dP$$

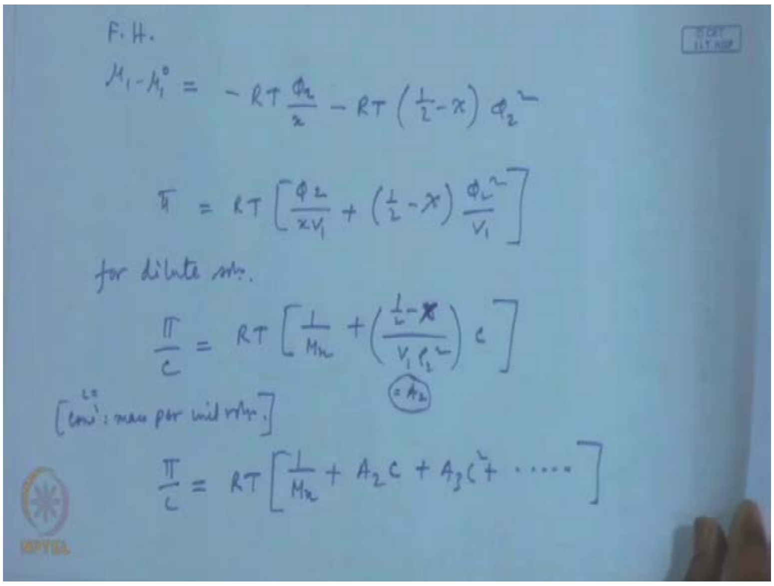
$$= -\int_P^{P+\pi} \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} dP$$

$$= -\pi \bar{V}_1 = -\pi V_1$$

Now so mu if we write 1 for the solvent molecule and this superscript of 0 having for pure solvent at say, original pressure P will be equal to the chemical potential of the solvent where the pressure is increased from P to P plus pi where pi is the osmotic pressure. So, this is the condition from condition for the equilibrium between the solution side and the solvent side and the solution side. So, I can write this and breakdowns this mathematically and just write this one; remember 1 for the solvent and we generally write 2 for the solute molecules. Solute in this case it is the polymer. So, we can rearrange this.

Now pi is very small. So, we can just remove the pressure terms from the bracket and we can write from the definition of mu pi we can write using the help of the partial differential. This is nothing but this is the osmotic pressure which we can detect through our measurement and this is the partial molar volume of the solvent and for a very dilute solution which is our working condition. This partial molar volume can be replaced by just molar volume of the solvent. Now this term we have already determined this term from Flory-Huggins equation in our earlier lecture and this is equivalent to if you can recollect from your knowledge.

(Refer Slide Time: 08:40)



F. H.

$$\mu_1 - \mu_1^0 = -RT\frac{\phi_2}{x} - RT\left(\frac{1}{2} - \chi\right)\phi_2^2$$

$$\pi = RT\left[\frac{\phi_2}{xV_1} + \left(\frac{1}{2} - \chi\right)\frac{\phi_2^2}{V_1}\right]$$

for dilute soln.

$$\frac{\pi}{c} = RT\left[\frac{1}{M_n} + \underbrace{\left(\frac{\frac{1}{2} - \chi}{V_1 \rho_2^2}\right)}_{= A_2} c\right]$$

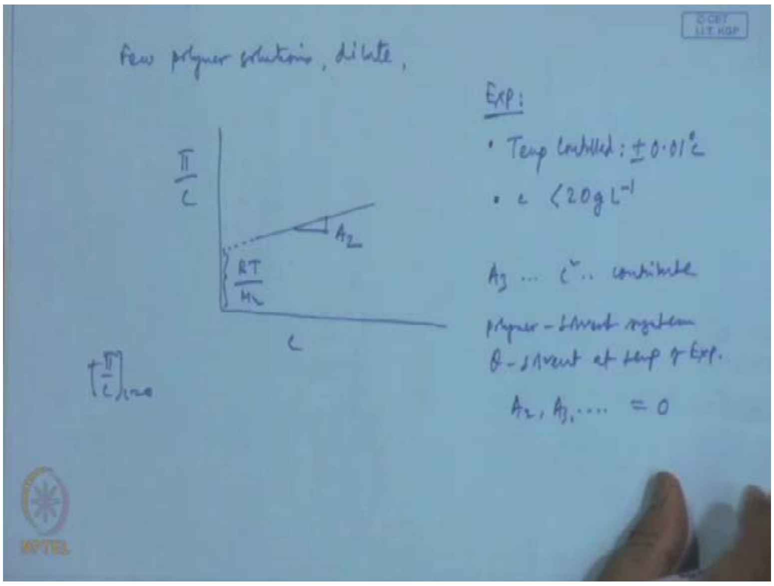
[c = conc^n: mass per unit volm.]

$$\frac{\pi}{c} = RT\left[\frac{1}{M_n} + A_2 c + A_3 c^2 + \cdots\cdots\right]$$

This term mu 1 minus mu 1 0 is minus RT phi 2 x; phi 2 is the volume fraction of the solvent molecules, x is the number of segment of the polymer molecules and so on. So if you compare these two expressions, the one we already wrote in this page and the expressions which we know from Flory-Huggins equation we can write pi is RT. So, for dilute solution it can be mathematically shown that we can write the above expression like this where chi as you know chi is the solvent-solute interaction parameter, rho 2 is the density of the polymer molecule, M n is the number average molecular weight This c is the concentration, concentration in mass per unit volume. So, c is concentration mass per unit volume.

Now as we know that this expression the Flory-Huggins expression, this is from Flory-Huggins theory, Flory-Huggins theory is not applicable for dilute solutions; we can write this expression as instead of this we can write this expression like earlier cases, we can write this as a variant expression. So, instead of like this we can write A 2 c plus A 3 c square like this where A 2 is nothing but this term. So, this term this term is nothing but A 2. So, this is the expression we can utilize to get the number average molecular weight of a polymer from dilute polymer solution.

(Refer Slide Time: 11:54)



Few polymer solutions, dilute,

$\left(\frac{\pi}{c}\right)_{c\to 0}$

Exp:

- Temp controlled: $\pm 0.01^\circ C$
- $c < 20\,g\,L^{-1}$

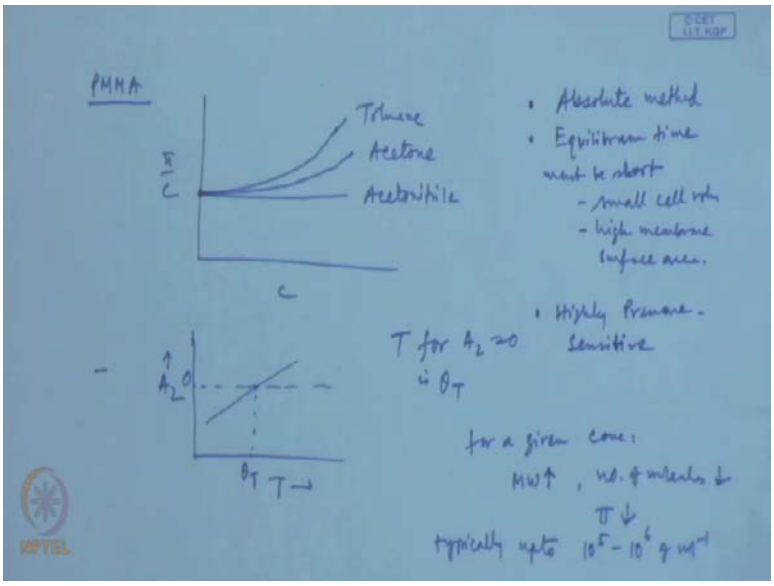
A_3 … c^2 .. contribute

polymer – solvent system
θ-solvent at temp of Exp.
$A_2, A_3, \ldots = 0$

So, what we need to do? We need to make few polymer solutions dilute. So, we can make few dilute polymer solutions having different concentration and then measure pi of each of this solutions and then plot pi c versus c which may be something like this. And then extra plot this value to c equals to 0. So, this intercept is nothing but pi by c at c is equal to 0. This is from this expression this will be RT by M n and the slope will give the value for the second period coefficient from which we can get the value for polymer solvent interaction parameter chi. Now in terms of experiment, what are the things we should remember; one is that temperature control has to be very precise because osmotic pressure is very much dependent on temperature.

So, it has to be very much controlled and we have to keep all this polymer solutions sufficiently dilute. So, that typically we get or we make solutions having concentration having less than 20 gram per liter. Typically we make concentrations 20 gram so that equations are valid. If the solvent becomes good, then the term A 3 in the expression; if the solvent becomes sufficiently good then this term may become significant which means c square terms may also contribute and if A 3 becomes significant then c square terms contribute. And if the polymer solvent system is theta solvent for that particular temperature at temperature of experiment, then A 2, A 3 this will all become 0 which means it will be the osmotic pressure by c will be concentration independent. This is what happened.

(Refer Slide Time: 15:14)



- Absolute method
- Equilibrium time must be short
  - small cell vol.
  - high membrane surface area.
- Highly Pressure-Sensitive

T for $A_2 \to 0$ is θ_T

for a given conc.:
MW ↑, no. of molecules ↓
π ↓
typically upto $10^5 - 10^6$ g mol^{-1}

For example if we have, for polymethyl methacrylate PMMA toluene is very good solvent. So, we start to get contribution from the A 3 term or c squared term. So, the curve deviates from linearity at high concentration. This is what happened for acetone and acetonitrile is a theta solvent for the temperature where this temperature for PMMA which means the pi by c will be independent of the concentration of the solution. So by this way, we can get the number average molecular weight. We can also determine A 2 by plotting or getting or determining A 2 at different temperature; with this expression from the slope we can get A 2.

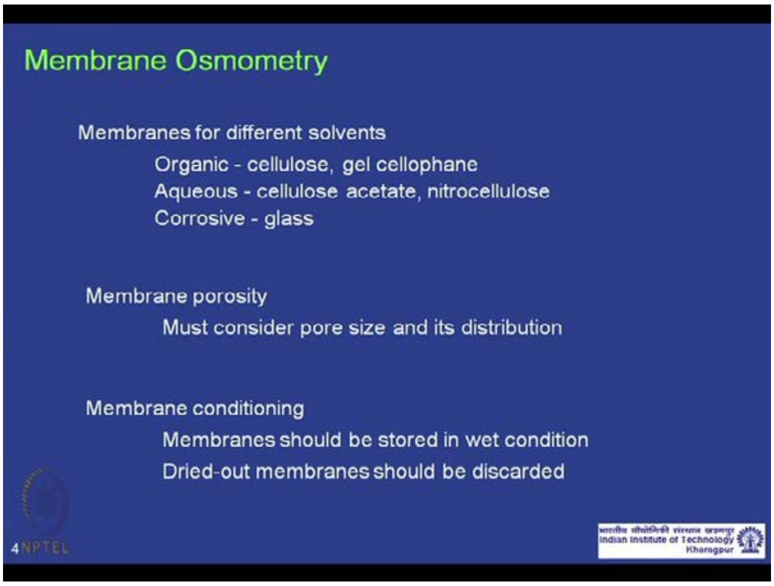
So, from the slope we can A 2 as we can see from this expression and if we measure or if we determine A 2 at different temperature and then plot A 2 versus T and then the temperature for which A 2 is 0; the temperature for which A 2 is 0 that would be the theta temperature. So, this is one way we can determine the theta temperature. What are the considerations we must do as we can see that we do not require any calibration for this method? So, osmotic membrane osmometry is an absolute method. So, you do not need any calibration. So, if you make a new polymer you can get the molecular weight number average molecular weight from first principle. You do not need any calibration.

Now to make the experiment short, this equilibration between the solvent side and solute side must be fast. So, equilibrium equilibration time must be short which can be done either by small cell volume or by high membrane surface area. We also need very highly pressure sensitive equipment because the osmotic value of osmotic pressure is quite low so that we can accurately determine the osmotic pressure. And as we can see that for a given concentration of solution if we increase the molecular weight, the number of molecules goes down. So, for a given concentration if we increase molecular weight, the number of molecules goes down so as osmotic pressure. This method is not very capable of measuring the number average molecular weight for very high molecular weight.

It can determine typically up to 10 to the power 5 to 10 to the power 6 mole per inverse molecular weight. It cannot determine more than that because if we increase weight further, then the osmotic pressure becomes very small. The lower cutoff for this method is determined by the cutoff of the membrane which is used because if the membrane has a higher cutoff, then the polymers chains which have smaller M n that will pass through the membrane to the solvent side and then it will contribute in the osmotic pressure. So, we must be very careful that the samples which we are determining the M n must be the weight of very small molecular weights.

Otherwise those molecular weights will not contribute in the osmotic pressure and hence the determined M n number average molecular weight. So typically, if a polymer sample has quite a few fraction of low molecular weights which are below the cutoff of the membrane, then the M n or the number average molecular weight determined by this method typically becomes little lower estimated. So, these are the criteria’s or these are parameters we must remember while determining molecular weight by this method.

(Refer Slide Time: 21:38)



Membrane Osmometry

Membranes for different solvents

- Organic - cellulose, gel cellophane
- Aqueous - cellulose acetate, nitrocellulose
- Corrosive - glass

Membrane porosity

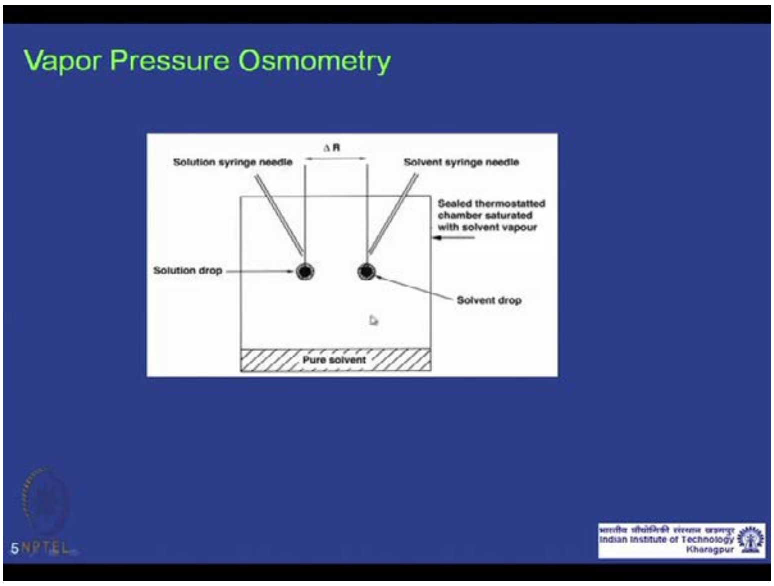
- Must consider pore size and its distribution

Membrane conditioning

- Membranes should be stored in wet condition
- Dried-out membranes should be discarded

Let us move on and try out; some other points which we must just to add some more points in this membrane osmometry that the membranes are different for different solvent. For organic solvents it could be cellulose or gel cellophane; aqueous we can use cellulose acetate, nitrocellulose and if you have a corrosive solution, then we can use glass membranes. Membranes porosity and this situation must be considered because that will determine the lower cutoff and its surface area also continued to the time it requires for equilibration. And typically membranes are supplied in a in a wet conditions in a particular solvent like isopropanol. So, if the solvent you have in your hand is dried-out, then this nature might go bad. So, you should not use that and wet membranes when they are used for the experiment they have to first the solvent has to change gradually so that they are wet. When we may start the experiment they are wet with the solvent which of our interest.

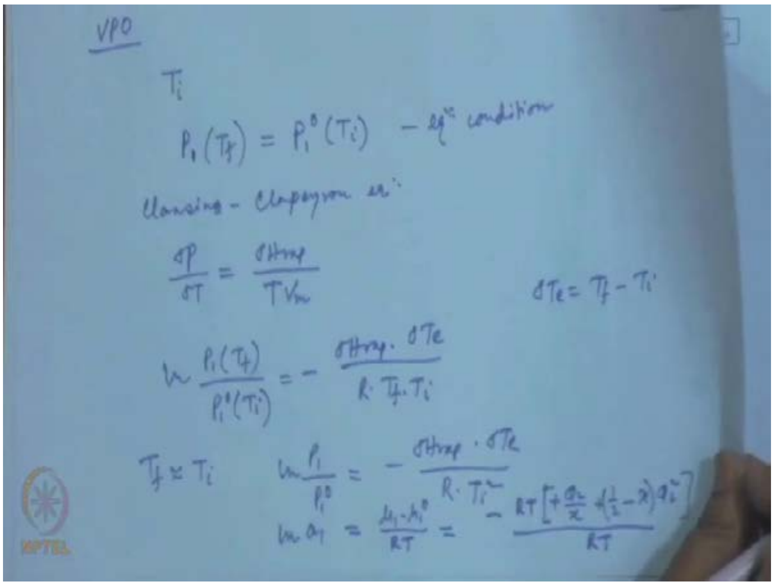
(Refer Slide Time: 22:59)



Vapor Pressure Osmometry

With this let us move on the next technique of determining the number average molecular weight, vapor pressure osmometry. In this method these are the two thermistors which are kept for determining temperature difference as low as 10 to the power minus 4 Kelvin. They are placed in a sealed thermostated chamber which is saturated with the solvent vapor. Now in these conditions, one with a syringe in one thermistor one solvent drop is placed; in another thermistor or solution polymer solution drop is placed. Now a solution in the solvent, chemical potential is lower than in the solvent so the vapor pressure of the solvent in the polymer solution will lower. And as a result the solvent vapor will condense on this thermistor and the heat of condensation will increase the temperature of this thermistor and equilibrium should arise where the vapor pressure of the solvent in this elevated temperature is same as the vapor pressure of the pure solvent in the temperature of the thermostat.

(Refer Slide Time: 24:53)



VPO

T_i

$P_1(T_f) = P_1^0(T_i)$ – eq^n condition

Clausius - Clapeyron eq^n:

$$\frac{\delta P}{\delta T} = \frac{\delta H_{vap}}{T V_m} \qquad \delta T_e = T_f - T_i$$

$$\ln \frac{P_1(T_f)}{P_1^0(T_i)} = - \frac{\delta H_{vap} \cdot \delta T_e}{R \cdot T_f \cdot T_i}$$

$T_f \approx T_i$

$$\ln \frac{P_1}{P_1^0} = - \frac{\delta H_{vap} \cdot \delta T_e}{R \cdot T_i^2}$$

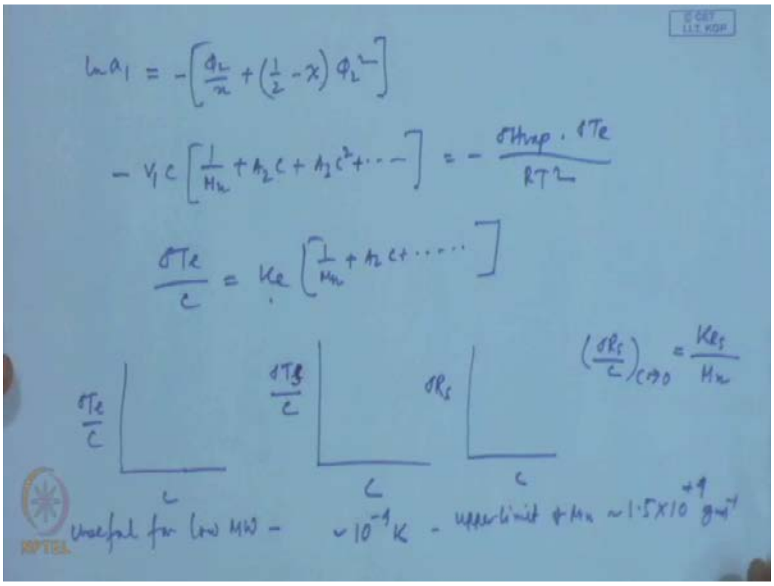
$$\ln a_1 = \frac{\mu_1 - \mu_1^0}{RT} = - \frac{RT\left[+\frac{\phi_2}{x} + \left(\frac{1}{2} - \chi\right)\phi_2^2\right]}{RT}$$

So, basically we started with a VPO vapor pressure osmometry. We started, say, with T initial which is the thermostated the temperature for the thermostated chamber which is filled up with solvent vapor and we add one drop of solution in one thermsitor and one drop of solvent in the other thermistor. So, the vapor pressure will lower and we can write if P 1 is the vapor pressure of the solvent in the final temperature; the elevated temperature because of the condensation of the vapor solvent vapor from vapor phase to the solution phase which will be equal at the initial vapor pressure So, that is the equilibrium condition when the condensation stops.

Remember this is the P 1 is to present the vapor pressure of the solvent in polymer solution if this elevated temperature whereas P 1 0 is the vapor pressure of the pure solvent at the original temperature. Now we can apply Clausius-Clapeyron equation and write del P del T is del H vaporization by T V m; V m is molar volume and if you consider the vapor is the ideal gas, considering the ideal gas vapor we can do few mathematical steps to write. This delta T is the temperature difference from the final to initial. At T e represents at equilibrium. So, while deducing consider that the vapor phase V f as a ideal gas. Now because T f is very close to T I, we can simply write this expression at P 1 by P 1 0 as minus del H vaporization delta T e by R T i square. Now this term is nothing but ln activity of the solvent.

Now from thermodynamics we can write the mu 1 as mu 1 by mu 1 0 by RT; you know this is 40 i. So, we are not writing T i T i. So, these are all T i initial thermostat temperature of the medium. So, if you do not mention T i nor if you just write T then; that means, it is the initial temperature of the thermostated chamber. Now Flory-Huggins equation we can write mu i by mu 0 as earlier case we have seen from the osmotic pressure experiment we can simply write this. So, from there we can write that. So, if you start from this expression we can write RT ln this side the left hand side. So, we can write like this RT.

(Refer Slide Time: 29:52)



$$\ln a_1 = -\left[\frac{\phi_2}{x} + \left(\frac{1}{2} - \chi\right)\phi_2^2\right]$$

$$-V_1 c\left[\frac{1}{M_n} + A_2 c + A_3 c^2 + \cdots\right] = -\frac{\Delta H_{vap} \cdot \Delta T_e}{RT^2}$$

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

$$\left(\frac{\Delta R_s}{c}\right)_{c \to 0} = \frac{K_{es}}{M_n}$$

Useful for low MW – ~10^{-4} K – upper limit of M_n ~$1.5 \times 10^{+4}$ g mol^{-1}

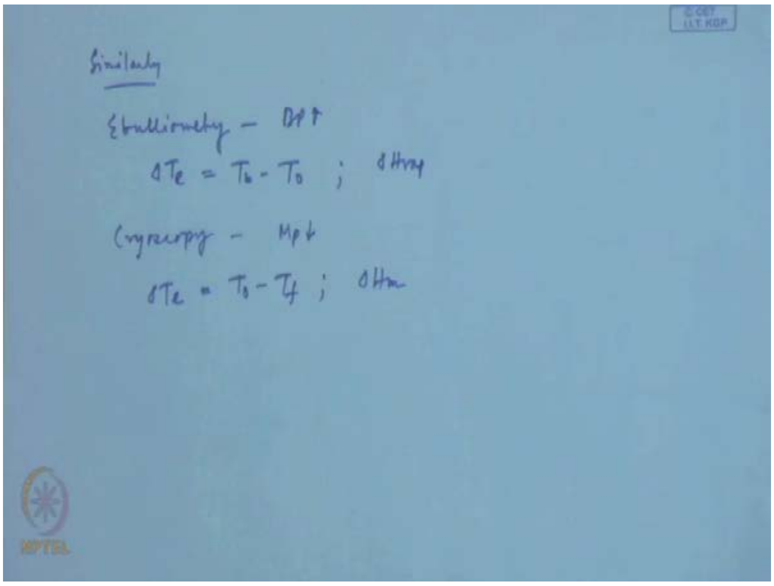
So, if you compare the earlier equation and the osmotic pressure the derivation we did for osmotic pressure, we can simply write this part as minus V 1, see V 1 is the molar volume of the solvent, 1 by M n minus del H vaporization delta T e; so delta T e by C K e 1 by M n. So basically if we can get the delta e, now we can apply the same similar experimental procedure; like osmotic pressure measurement we can make five different or few different dilute solutions of different concentration and measure the delta T e and then plot delta T e by C with concentration to get K e by M n and A 2.

In practice, we actually do not reach to the equilibrium because some of heats of the condensation of the droplets, I should get dissipated on thermistor and the solvent stream. So, what we reach is not a true equilibrium; it is a steady state. So, we need to calibrate the experiment with the known molecular weight polymer solutions to actually determine the number average molecular for the unknown samples.

So, this is not an absolute method; we need calibration. So, actually what we plot is delta s by C versus C; delta T s is the steady state temperature difference as steady state which again is measured by the difference in the resistance between the two thermistors versus C. So finally, delta R s by C at C is equal to 0 will give you the K R s which is this K for the resistance by M n. So, we know this. So, we can get the molecular weight M n for the unknown sample. This is very useful method for low molecular weight samples because if we go for high molecular weight then the increase in the temperature is very low.

So, we do not have the techniques to determine so much, so low temperature difference between thermistors. Typically we can go up to 10 to the power difference of temperature between the two thermistor as low as 10 to the power 4 Kelvin which translate to upper limit of the upper limit of the molecular weight M n, upper limit of M n approximately 10 to the power 4 order gram per mol. This is the upper limit of this. So, if you can get more sophisticated instrument which can detect the temperature difference even lower than this, then you can increase the upper limit of the molecular weight determination in this technique.

(Refer Slide Time: 34:57)



Similarly

Ebulliometry – BP ↑

$\Delta T_e = T_b - T_0$; ΔH_{vap}

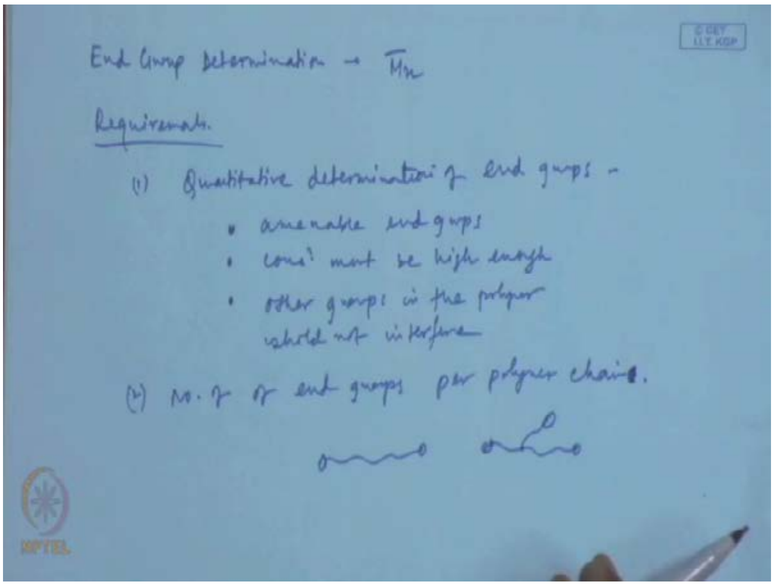
Cryoscopy – Mp ↓

$\Delta T_c = T_0 - T_f$; ΔH_m

Now similar techniques similar methods can be applied to the other two methods like other two colligative properties; for example this similarly the same logic can be applied or same principle can be applied to other two methods like ebulliometry which deals with the elevation of boiling point; boiling point elevation of boiling point where delta T e is T b minus T 0 where T b is the boiling point of the solution and T 0 is the boiling point of the pure solvent. Here we require the value for delta H molar heat of vaporization and with the help of cryoscopy which deals with the depression of freezing point where we can get the same T 0 T f; T 0 is the freezing point of the solvent, T f is the freezing point of the solution where we need the molar enthalpy of freezing or melting.

But these are techniques and not used much; nowadays these techniques are not used much for several reasons though mainly this techniques like osmotic membrane osmometry and vapor pressure osmometry are used and as we have discussed that they are complimentary to each other where membrane osmometry can determine molecular weight, number of molecular weight for little higher range and vapor pressure osmometry can be used for determining molecular rates of low molecular weights of lower range. Let us have brief discussion about the third technique which is end group determination.

(Refer Slide Time: 37:06)



End Group Determination → $\overline{M}_n$

Requirements.

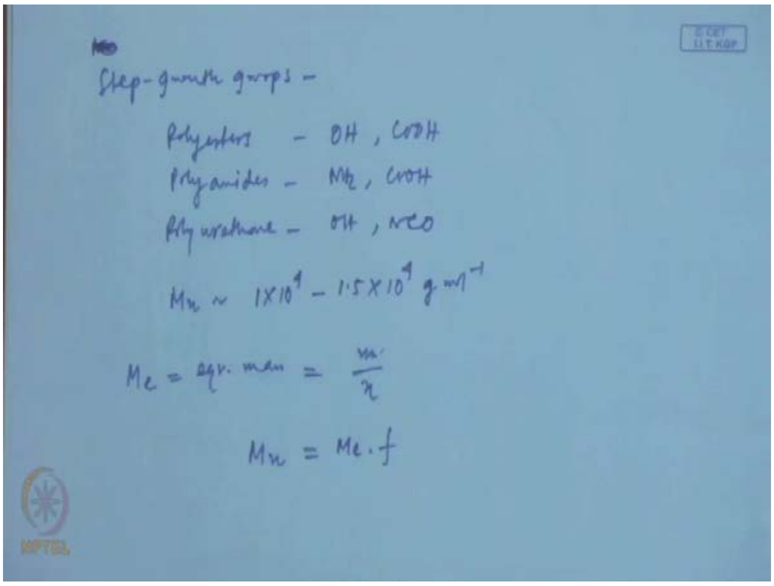
(i) Quantitative determination of end groups –
- amenable end groups
- conc^n must be high enough
- other groups in the polymer should not interfere

(ii) No. of or end groups per polymer chain.

By determining the end group quantitatively, we can also determine the molecular weight; quantitative determination of end group gives M n number average molecular weight. The requirements are that basically we will be able to quantitatively determination of end groups of the polymer. So, polymers must have amenable end groups which can be analyzed by say titrometry or spectophotometrically and concentration must be high enough, so that we can determine the concentration of end group accurately or quantitatively, and the other group presence in the polymer should not interfere in the determination of the end groups of our interest.

Secondly, we must know the number of end groups per polymer chain. So, each polymer chain how many per polymer chain. So, how many chains they have. So, if you have like typically in a linear polymer we have two ends and if they hit the branch and it has three ends, then obviously we must know that this case the sample has two chain ends end groups and this case the sample has three end groups; otherwise the analysis will be erratic with error in the values.

(Refer Slide Time: 39:27)



Step-growth groups –

Polyesters – OH, COOH
Polyamides – NH_2, COOH
Polyurethane – OH, NCO

$M_n \sim 1 \times 10^4 - 1.5 \times 10^4\ g\ mol^{-1}$

M_e = eqv. mass = $\frac{w}{n}$

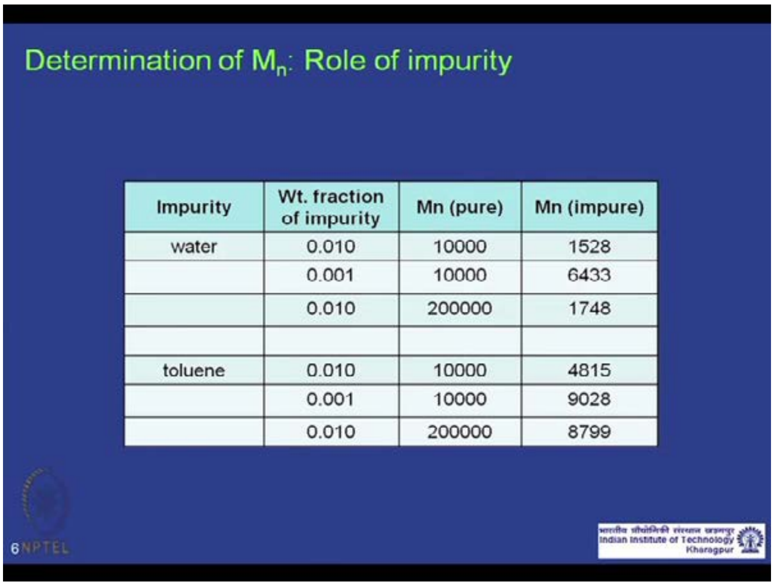
$M_n = M_e \cdot f$

Typically this method is applied to step-growth polymers because we know that step-growth polymers produces end groups functional end groups in the end. For example, polyester; polyester it has O H and COOH group. So, we can determine titrometrically or spectroscopically these group polyamides NH 2, COOH groups or polyurethane. So, these groups can be determined significantly. This is applicable to again to low molecular weights because when the polymer chains becomes very high, the number of end groups the contribution from number of end groups becomes very small. So, detection becomes very difficult.

So, this method typically applies to low molecular weights and typically M n value of around 10 to the power 4 to in the range of 10 to power 4 is the upper limit by which we can determine by these methods. What we measure is basically M e is the equilibrium equivalent mass is M by n which is defined as M by n; M is the mass of the polymers or concentration of the polymers and n is the concentration of the end groups. So, M n would be given by M e multiplied by f where f is the number of end groups per chain. So if we can determine the concentration, we know the concentration of the polymer and what is the concentration of end group which we determined.

We can determine n, the concentration of end groups and then if you know f which is the number of end groups per polymer chain, then we can easily get the number average molecular weight. Now we will give specific examples of determination of end group by spectroscopic method when we discuss the spectroscopy method of polymer characterization in the next or two lectures from now onwards, when we give specific examples of how to determine polymer number average molecular weight by end group determinations spectroscopically.

(Refer Slide Time: 42:41)



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

NPTEL

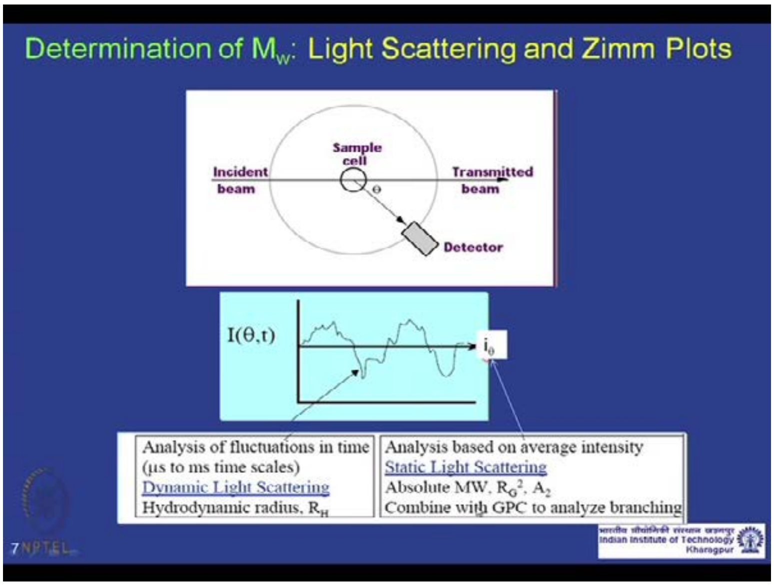
भारतीय प्रौद्योगिकी संस्थान खड़गपुर
Indian Institute of Technology Kharagpur

Before we move on to other methods of determining polymer molecular weight and namely weight average molecular weight, just to emphasize one point that we know the M n is very much sensitive to the low molecular weight species present at the impurities in a polymer sample. For example, if we give a specific example if we have impurities, what were the impurities present in our polymer sample and we analyze that sample.

Actually if the M n for the pure polymer sample is 10000, then if you have 0.01 weight factor of impurity, then the measured M n of the impure would be about 1500. So, basically even 1 percent by weight presence of water impurities is decreasing your determine M n by several factor which means we must be very careful about the impurities; specially the low molecular impurities while determination of number average molecular weight because they have a very detrimental effect in the value we get from the number average molecular weight determination.

Let us move on to the next topic where we determine the weight average molecular rate of the polymers and we will discuss the techniques of light scattering and subsequently gene plot to get the weight average molecular weight and also some other important parameters of polymers like the second variant coefficient and polymer solvent interaction parameters and the radius of gyration.

(Refer Slide Time: 44:42)



Determination of M_w: Light Scattering and Zimm Plots

Analysis of fluctuations in time
(μs to ms time scales)
Dynamic Light Scattering
Hydrodynamic radius, R_H

Analysis based on average intensity
Static Light Scattering
Absolute MW, R_G^2, A_2
Combine with GPC to analyze branching

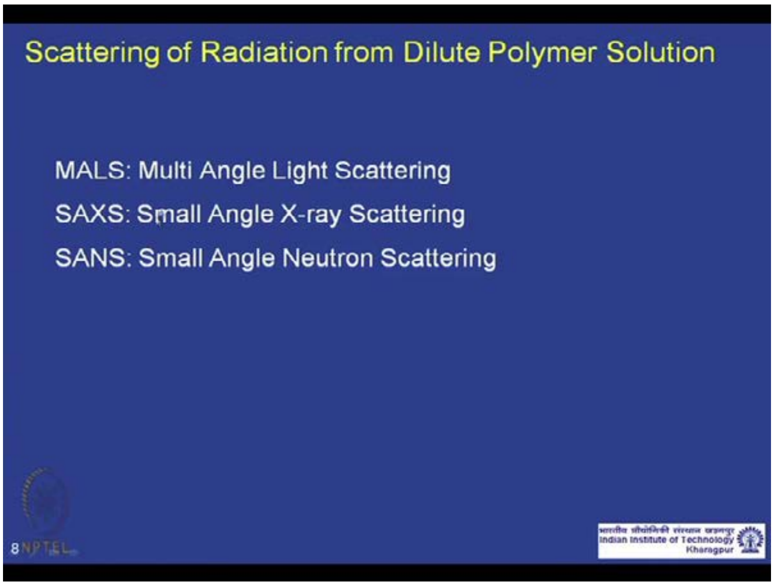
So, what is light scattering? Light scattering as we know when electromagnetic radiation interacts with a molecule or a particle, it induces a dipole in the samples and the magnitude of the dipole will depend on how the charge can be separated. For visible light radiation, it depends on the polarizibilty of the medium polarization of the molecules or the particles which is scattering light or the one which the light is bombarded.

Now once this dipole is formed, it oscillates with the electromagnetic radiation and as we know that oscillating dipole radiates light or electromagnetic radiation. So in this case, this oscillating dipole width emits radiation or electromagnetic radiation at all direction which are the scattered light. And typically this scattered lights have same frequency as the incident light but there are cases where there are shift in the frequency of the scattered light than in comparison to the incident light, but those are called inelastic scattering but for this determination of molecular, we will restrict to only through elastic scattering where the frequency of the scattered light is same as the frequency of the incident light.

So, what is done in the experiments? An incident beam is bombarded on a sample cell which contains these polymer molecules polymer solutions and then the scattered light is detected; the intensity of the scattered light is detected at an angle theta with the incident beam. Now this intensity of the scattered light can be fluctuating with very short time; the time scale is very short like micro seconds to milliseconds. Then you have a fluctuation in the scattering intensity is detected by the detector. Now from this fluctuation of the scatter intensity which we can apply techniques; this is like dynamic light scattering which take advantage of this fluctuation and we can get information about hydrodynamic radius for the polymer molecules

And the time average intensity which we will use in the techniques called static light scattering which will give the information about absolute molecular weight, weight average molecular weight, the radius of gyration and the second semiempirical coefficient which will in turn give the information about polymer solvent interaction parameter. So, basically the light scattering techniques can be used in two ways; in static light scattering where we deal with the time average intensity of the scattered light and second technique can be used where we use the fluctuation of the static intensity in dynamic light scattering which gives the information about the radius of gyration. Let us first talk about the static light scattering, because it gives many information for polymer solution.

(Refer Slide Time: 49:01)

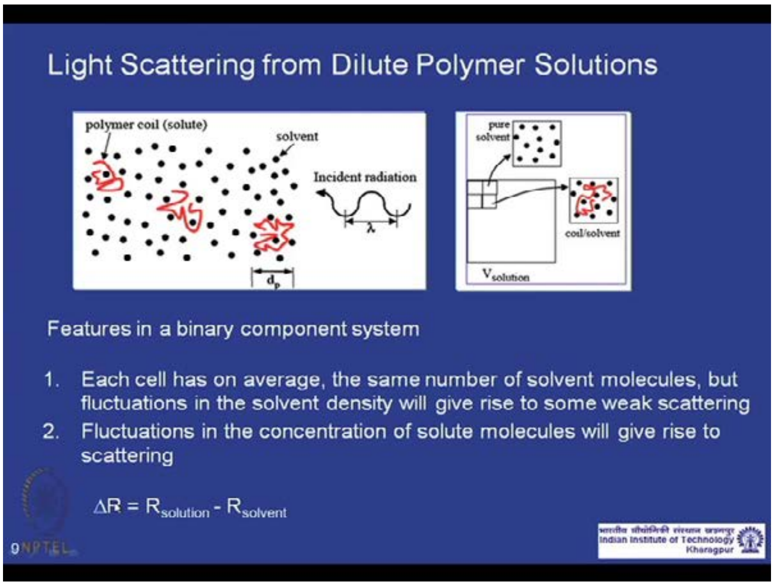


Scattering of Radiation from Dilute Polymer Solution

MALS: Multi Angle Light Scattering
SAXS: Small Angle X-ray Scattering
SANS: Small Angle Neutron Scattering

Now as I just mentioned that this light scattering technique can happen for any electromagnetic radiations like visible light or x-ray or neutrons. So, basically the techniques which are used are utilized to determine or to get information about polymers samples as multi angle light scattering or small angle x-ray scattering or small angle neutron scattering. We will basically restrict our discussion mainly on multi angle light scattering and then we will just briefly mention the difference of small angle x-ray scattering and small angle neutron scattering with light scattering and what are the information you can get from and SAXS and SANS.

(Refer Slide Time: 49:53)



Light Scattering from Dilute Polymer Solutions

Features in a binary component system

1. Each cell has on average, the same number of solvent molecules, but fluctuations in the solvent density will give rise to some weak scattering
2. Fluctuations in the concentration of solute molecules will give rise to scattering

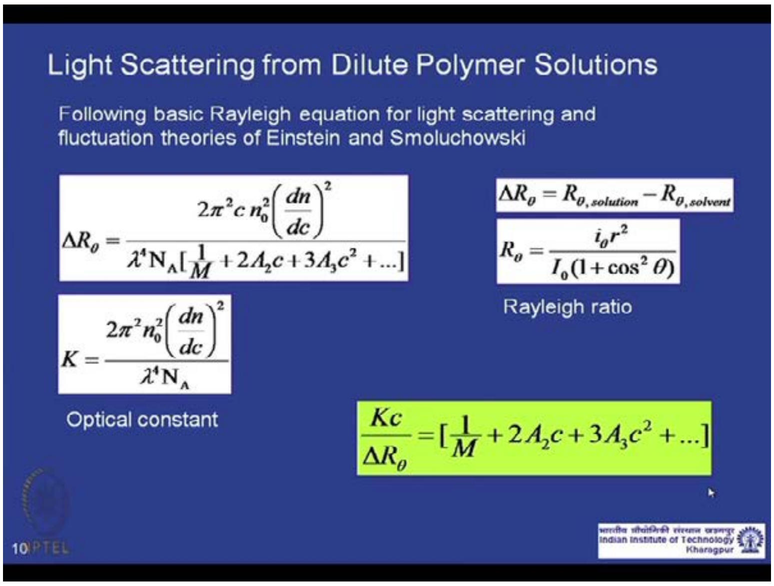
$$\Delta R = R_{solution} - R_{solvent}$$

So, without going much into the theory of light scattering, let us go into the theory directly into the equations for the light scattering from dilute polymer solutions. So, if you consider a polymer solution, where if you consider the polymer solutions, now if you consider its area any area or any particular area from this solution which contain pure solvent another part contain the solute and the solvent. So each cell on an average, these are the assumption we are taking and on basis of which we will formulate this scattering equations. The each cell has on average the same number of solvent molecules but the scattering happens.

So, weak scattering happened because of the minute fluctuation in the solvent density and because of the solute molecule itself, the concentration of solute molecules fluctuate; either because of the translational motion Brownian motion of the solute molecules or if it is a polymer large molecule there will be conformational changes. So because of the effective concentration fluctuation, the light scattering happens from the polymer of the solute molecules.

So, what to do to get the information about the polymer molecules or the solute molecules, we deduct the scattering from the solution from the solvent to get the excess scattering; we will explain the terms R in the next page. So basically in the instrument, we try to detect the scatterings only from the solute molecule in this case the polymer molecule in a dilute solution so that there are not much intermolecular interactions and we deduct the scattering which we detect for or determine from a solute solution from the solvent so that we can get the information of on scattering from only from the solute molecules.

(Refer Slide Time: 52:35)



Light Scattering from Dilute Polymer Solutions

Following basic Rayleigh equation for light scattering and fluctuation theories of Einstein and Smoluchowski

$$\Delta R_\theta = \frac{2\pi^2 c\, n_0^2 \left(\frac{dn}{dc}\right)^2}{\lambda^4 \mathrm{N_A}[\frac{1}{M} + 2A_2 c + 3A_3 c^2 + \ldots]}$$

$$K = \frac{2\pi^2 n_0^2 \left(\frac{dn}{dc}\right)^2}{\lambda^4 \mathrm{N_A}}$$

Optical constant

$$\Delta R_\theta = R_{\theta,\,solution} - R_{\theta,\,solvent}$$

$$R_\theta = \frac{i_\theta r^2}{I_0(1+\cos^2\theta)}$$

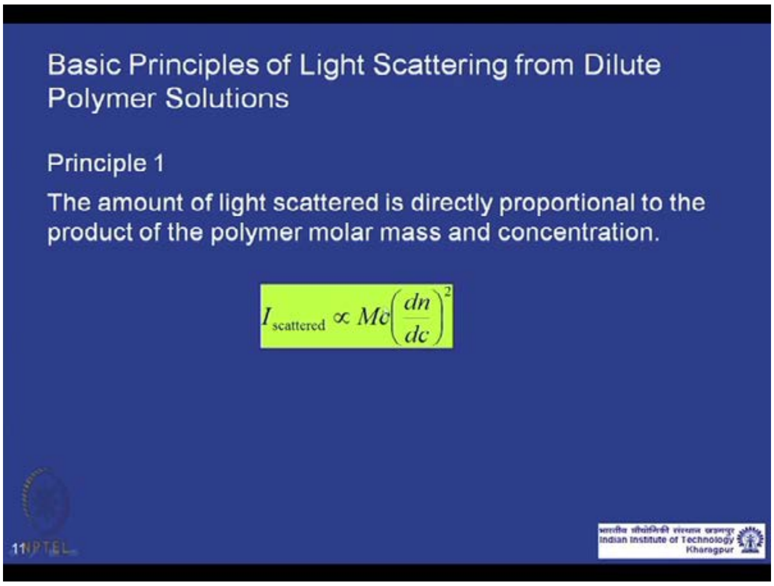
Rayleigh ratio

$$\frac{Kc}{\Delta R_\theta} = [\frac{1}{M} + 2A_2 c + 3A_3 c^2 + \ldots]$$

So, we directly go to the scattering equation which based on the basic Rayleigh equation for light scattering and then also from the fluctuation theory based on Eintsein and Smoluchowski. This is for a small molecule; the solute having a small molecule point scatterer. So, we can get an equation like this where R is delta R theta is as we said that the Rayleigh ratio; this R for Rayleigh ratio basically take cares of the intensity. It is basically the intensity; it is basically the scattering intensity which is normalized with the scattering angle. So, Rayleigh ratio is basically this expression and delta R theta is nothing but Rayleigh ratio for the particular theta for the solution minus Rayleigh ratio for the solvent. We define K in all the terms which we know.

So, for the experiments we know this n 0 or eta 0 is the solvent refractive index, d n by d c is the specific refractive index increment for the solute, lambda is the web length of the incident light, N A is Avogadro number. So, we know all this terms and we define a term called optical constant k as this to make this expression simpler. So finally, we can get an equation like this. So, this expression is valid for point scatterer where no intramolecular interference happen between them no interference happened between the scattered light; the same scattered light originate from the different parts of a scatterer.

(Refer Slide Time: 55:15)



Basic Principles of Light Scattering from Dilute Polymer Solutions

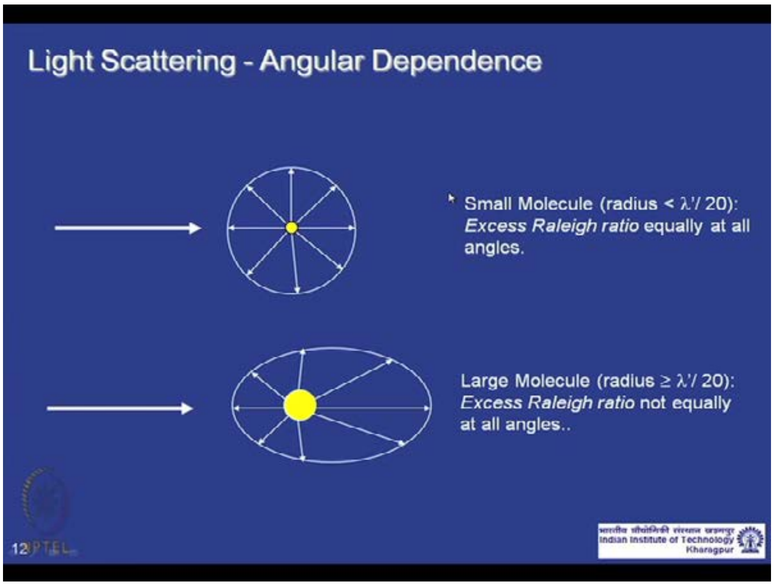
Principle 1

The amount of light scattered is directly proportional to the product of the polymer molar mass and concentration.

$$I_{\text{scattered}} \propto Mc\left(\frac{dn}{dc}\right)^2$$

So, basically we can write or we can say that as a basic principle of light scattering that first principle is that amount of light scattering is directly proportional to the product of polymer molar mass M and concentration and this term which is specific refractive index increment. This expression is valid. This is proportional to the concentration only for dilute solution where the intersolute molecule interaction is absent, basically then we can add the scattering intensity from different molecules without considering any destructive interference between them. Now if we are just talking about this expression at point scatterer where the molecule does not or the scattering from different parts of the molecules do not interfere with each other.

(Refer Slide Time: 56:38)



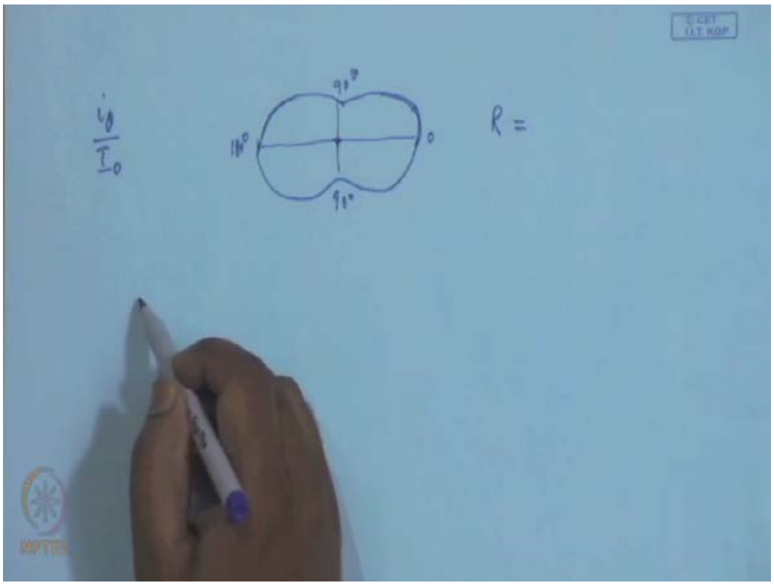
Light Scattering - Angular Dependence

Small Molecule (radius < λ'/ 20): *Excess Raleigh ratio* equally at all angles.

Large Molecule (radius ≥ λ'/ 20): *Excess Raleigh ratio* not equally at all angles..

If we plot the Rayleigh ratio with different angle that will give the same intensity; remember we are talking about Rayleigh ratio which have cos square theta term in the denominator.

(Refer Slide Time: 57:01)



If you only consider the i theta by I 0 then for small molecules your intensity will look like something like this. So, this is 0 angle, and this is 180 angle, this is 90 degree. But if we plot this Rayleigh ratio; so what we will do we will start from. In the next lecture we will discuss the scattering from angular dependence on the light scattering for large molecule or polymer molecules which we have angular dependence; the light scattering will be angular dependence. We will start from there in the next lecture.