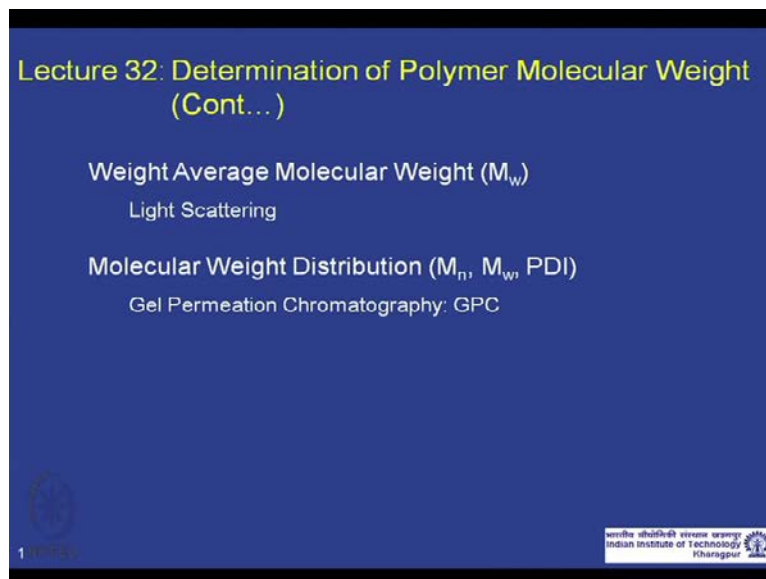


**Polymer Chemistry**  
**Prof. Dibakar Dhara**  
**Department of Chemistry**  
**Indian Institute of Technology, Kharagpur**

**Lecture - 32**  
**Determination of Molecular Weight of Polymers (Contd..)**

(Refer Slide Time: 00:27)



Lecture 32: Determination of Polymer Molecular Weight (Cont...)

Weight Average Molecular Weight ( $M_w$ )  
Light Scattering

Molecular Weight Distribution ( $M_n$ ,  $M_w$ , PDI)  
Gel Permeation Chromatography: GPC

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Welcome back to this course on polymer chemistry. We will continue our discussion on polymer molecular weight determination from our last class. We had started the discussion on light scattering by which we can determine the weight average molecular weight of a polymer sample. And then we will start the discussion on gel permeation chromatography on the later part of this lecture. We will not finish this discussion on gel permeation chromatography in this lecture; we will continue in the next lecture.

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### Light Scattering from Dilute Polymer Solutions

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

$$\Delta R_\theta = \frac{2\pi^2 c n_0^2 \left(\frac{dn}{dc}\right)^2}{\lambda^4 N_A \left[\frac{1}{M} + 2A_2c + 3A_3c^2 + \dots\right]}$$

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



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

Optical constant

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

Rayleigh ratio


$$\frac{Kc}{\Delta R_\theta} = \left[\frac{1}{M} + 2A_2c + 3A_3c^2 + \dots\right]$$

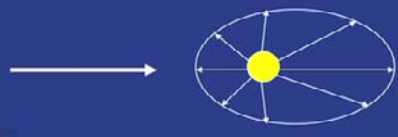
Now, this is where we left in the last lecture. This is the equation based on the basic Rayleigh scattering equation and the fluctuation theories of Einstein and Smoluchowski; and we explained the terms  $Kc$  is the concentration in gram per unit volume;  $\Delta R_\theta$  is the excess Rayleigh ratio, which is the Rayleigh ratio of the polymer molecules or the solute molecules in excess of the solvent molecules. It is the second variant coefficient from which is related to polymer solvent interaction parameter and  $M$  is the molar mass.

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### Light Scattering - Angular Dependence



Small Molecule (radius  $< \lambda/20$ ):  
Excess Rayleigh ratio equally at all angles.

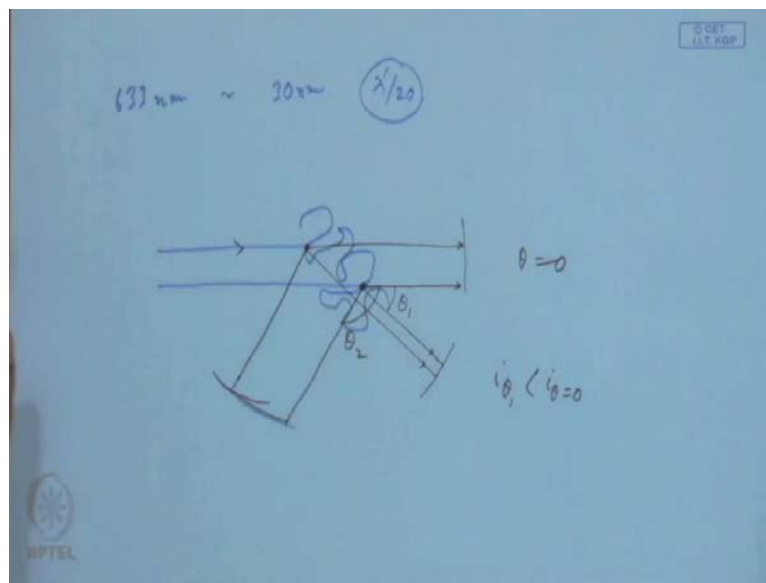


Large Molecule (radius  $\geq \lambda/20$ ):  
Excess Rayleigh ratio not equally at all angles..

Now, this expression becomes not useful or become erratic when the size of the solute molecule grows. If the size goes, this equation is valid for isotropic scatterer which basically have dimension radius less than  $\lambda/20$ ;  $\lambda$  is the wavelength of the incident light in the solvent. So, for those small molecules the excess Rayleigh ratio is does not depend on the  $\theta$  is basically have same value for a different angles and we call this is isotropic scatterer; remember, this we are talking about excess Rayleigh ratio not the scattering intensity. Now, if the size of the solute molecule goes up and becomes sufficiently large so that radius is of the order of  $\lambda/20$ .

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For example, if we talking about laser having 633 nanometer wavelength then it is about say 15 or 30 nanometer; we are talking about  $\lambda/20$ ; or if you take a laser wavelength little lower at the beginning of the visible light then it will be around twenty nanometer. So, it is basically these value depends the cut off value where this angular dependence starts depends upon the wavelength of the incident light which we are using. Now, in this case the excess Rayleigh ratio is angle dependent and it has larger value or the highest value at 0 angle; and as we increase the value of the scattering angle, the value for this excess Rayleigh ratio start decreasing. Why does it happen? This happens, because if the size grows safe if you have a polymer molecule like this and this is in the solution. Now, you have incident radiation coming and it is getting scattered from here, and it is going to the detector at 0 angle. Similarly, there is another part also can scatter light and it is going to the detector. Now, if this is detected at 0 angle there is no phase

lag between two scattered radiations as they travelled the same distance. So, basically there is no destructive interference at theta is equal to 0.

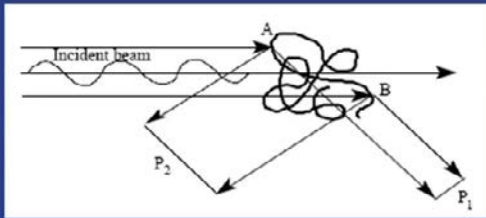
But you have to consider these at an angle other than 0; for example, if I consider this theta then, because these two scattered light have a phase difference they will have a destructive interference between them. Then as a result,  $I_{\theta}$  will be less than  $I_{\theta=0}$ . So, scattering intensity will be lower or excess Rayleigh ratio will be lower in this case then what it was in case of theta equals to 0.

Now, if you consider even higher theta value and you consider a theta like this which is higher than theta two then the phase difference between the two scattered light is even higher. As a result, there will be more destructive interference between the scattered lights from different parts of the polymer molecules; this scattered lights are from different parts of a polymer molecules. So, this diminishing of the excess Rayleigh ratio at a higher angle than 0 is because of the destructive interference between the scattered light from different parts of same molecule or as a result of intra molecular destructive interference; and the higher is the angle, the excess Rayleigh ratio becomes even smaller. So, this shows what we explain in just now.

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Basic Principles of Light Scattering from Dilute Polymer Solutions

Principle 2  
The angular variation of the scattered light is directly related to the size of the molecule.



$I_{\text{scattered}} \propto P(\theta)$

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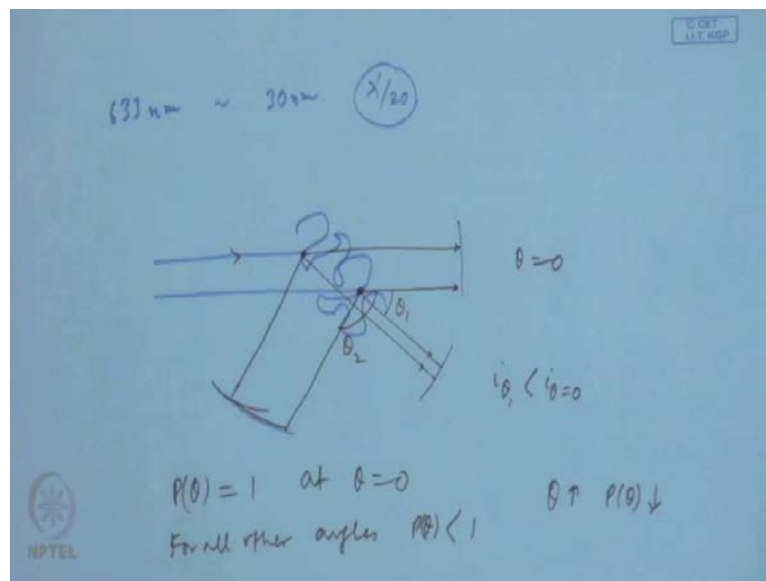
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So, the same what is explained in a minute. So, the angular variation of scattered light is directly related to the size of the molecule; the larger is the size there will be more variation, because there will be more destructive interference because of the scattered

light which is coming from intra molecular different regions; and this starts around as I said  $\lambda/20$ , it starts this destructive.

So, see intensity of the scattered light actually becomes also proportional in addition to it become depend up on the molar mass, concentration and  $d n$  by  $d c$  square, it also depends up on the  $P$  theta which we call the form factor or angular scattering factor.

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And  $P$  theta value is 1 at 0 theta equals to 0, because you do not see any destructive interference and for all other angles  $P$  theta become less than one, and it becomes more and more small as we increase the theta. So, at theta goes up,  $P$  theta goes down in value. So, basically now by studying the angular variation of  $P$  theta we can get information about the size of the polymer molecules.

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Light Scattering from Dilute Polymer Solutions

$$\frac{Kc}{\Delta R_{\theta}} = \frac{1}{P(\theta)} \left[ \frac{1}{M} + 2A_2c + 3A_3c^2 + \dots \right]$$

Following Debye and Guinier, for a monodisperse Gaussian Coil

$$P(\theta) = \left[ \left[ 1 + \frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2} \langle s^2 \rangle \right] \right]^{-1}$$

$$\frac{Kc}{\Delta R_{\theta}} = \left[ \frac{1}{M} + 2A_2c + 3A_3c^2 + \dots \right] \left[ 1 + \frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2} \langle s^2 \rangle \right]^{-1}$$

Valid for dilute solution and low scattering angles

$$\left[ \left[ \frac{4\pi n_0 \sin(\theta/2)}{\lambda} \right]^2 \langle s^2 \rangle \right]^{1/2} < 1$$

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So, now, we modify the original equations for small point scatterer with a term P theta which is an angular scattering factor and as I said this becomes one for theta equals to 0, and becomes less than 1 for any other value for theta. And, Debye and Guinier actually established a relationship or deduced a relationship for equation for P theta for a mono dispersed Gaussian coil which is the case for a polymer coil; P theta can be written like this where again the terms are self-explanatory; s square is the radius of gyration; this z is not there, maybe we can remove this z for time being. So, for mono dispersed Gaussian current this is the equation where s square is the radius of gyration; sometimes, it also written as R g square which is basically radius of gyration.

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So, we can combine these two equations and we get this expression; this covers the original scattering equation by Rayleigh and fluctuation theories of Einstein and Smoluchowski, and this is formed by Debye and Guinier which quantify the  $e$  theta term; angular dependence term. Now, this valid for dilute solution when no intermolecular interference and this also valid for low scattering angles which comes to an equation from like this.

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Light Scattering from Dilute Polymer Solutions

Rayleigh, Debye and Guinier, (RGD) model for a polydisperse Polymer Coil

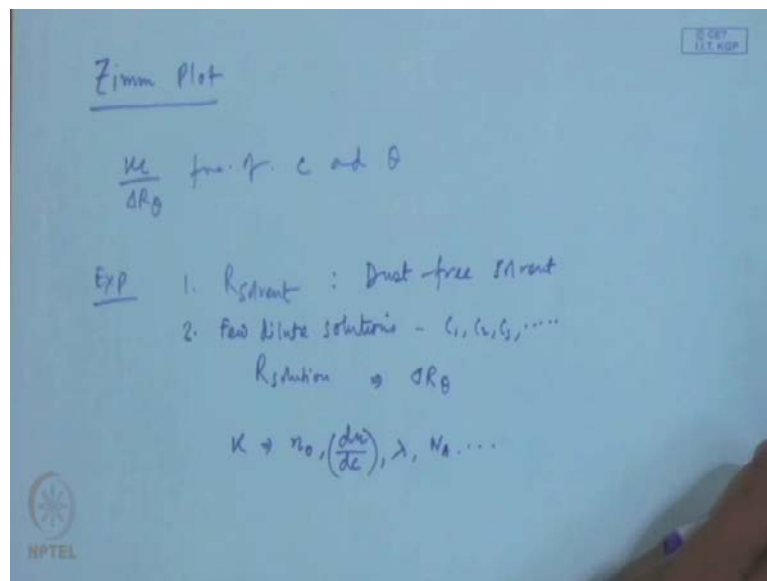
$$\frac{Kc}{\Delta R_{\theta}} = \left[ \frac{1}{Mw} + 2A_2c + 3A_3c^2 + \dots \right] \left[ 1 + \frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2} \langle s^2 \rangle_z \right]$$

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So, finally, we have this expression and if we consider a poly dispersed polymer coil normally we have the polymer chains are not mono dispersed, they are poly dispersed. It can be shown that this  $M$  is  $M_w$  and this  $s$  square is  $s^2$  which is basically  $z$  average is radius of gyration. So, this is the final equation; we called this RGD model in the name of Rayleigh, Debye and Guinier for a poly dispersed polymer coil in dilute solution and this is valid for scattering at low angle. Now, we have this equation.

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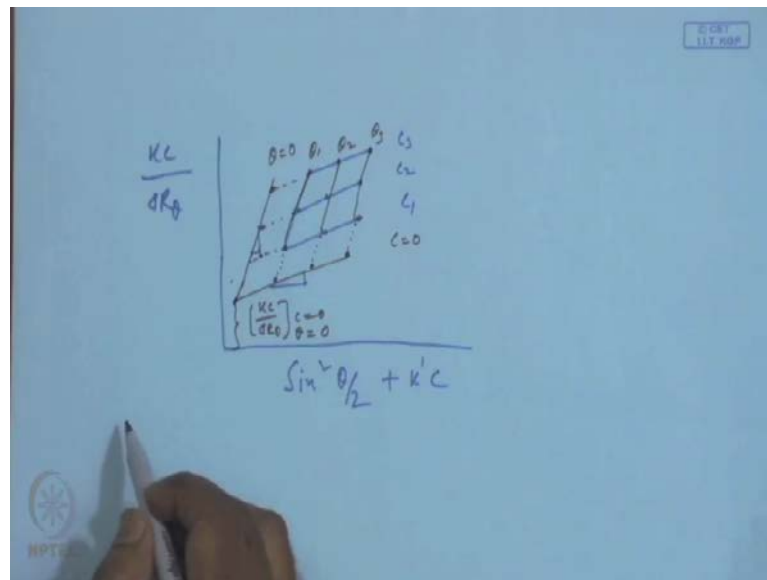
Now, how to get more information with we can deduce from this. I want to plot zimm and see what are the information we can get from this.  $Kc$  by  $R$  theta is a function of both  $c$  and theta. So, now, we can plot this as a combined function of  $c$  and theta. So, for that what we need to do in the experiment, we first need to get the  $R$  solvent for a dust free solvent. First you get the Rayleigh ratio for only the pure solvent which must be completely dust free otherwise, the scattering from the dust molecules and which will give the enormous error in your measurements. Then you make few dilute solutions, polymer solutions of frequent concentrations and say  $c_1$   $c_2$   $c_3$  and so on, and get  $R$  solution for all these concentrations. Now, once we get  $R$  solution, we have the value for  $R$  solvent which will give us the value for  $\Delta R$  and if we measure different angles which will give us the value for  $\Delta R$  theta.

We know the value for optical constant  $K$ , because all the terms remember the refractive index of the solvent molecule we need to get the  $d$  and  $d c$  value for the polymer



molecules; specifically refractive index increment for the molecules; and we know the lambda and so N A, and so on. So, we know the value for K; and we know the concentration term here now delta I R theta. So, we know almost everything; what we need to know to construct a zimm plot? How do you construct a zimm plot?

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We plot  $Kc$  by  $\Delta R_{\theta}$  as we said that this term is a function of both  $\theta$  and concentration, we combine these two with a constant term this is arbitrarily chosen constant. So, that we can free the data points or we can plot the data points well separated with each other. So, we now have the measurements done for all the solutions at different angles. So, we now plot the data for example, to detect for concentration  $c_1$  and plot the points at different angles  $\theta_1$ ,  $\theta_2$  and  $\theta_3$ ; for simplicity we are just maintaining or just taking three data points in practically it should be many more angles. So, that is for the first solution  $\theta_1$ .

Similarly, we can do it for second concentration  $c_2$  and get this value, get  $\Delta R_{\theta}$  excess Rayleigh ratio at different angles; similarly, we get for the third solution. So, here we are already showing for three concentration, but in practically there should be more concentration and we are only showing data for three angles. So, that is your  $\theta_1$ , this is  $\theta_2$  and this is  $\theta_3$ . So, we have three solutions with 3 data for 3 angles; so, 9 data points.

Now, we extrapolate this data. So, for a fixed theta we can extrapolate to  $c \rightarrow 0$ ,  $c$  is equal to zero; similarly, we can extrapolate  $c \rightarrow 0$  and  $\theta \rightarrow 0$ , and also this value to  $\theta$  is equal to 0;  $c \rightarrow 0$  and  $\theta$  is equal to 0 and this two again  $\theta$  is equal to 0. So, this curve now is for  $\theta$  is equal to 0 and this is for  $c$  is equal to 0. So, this two points should match and this is the intercept  $K c \Delta R \theta$  as  $c$  is equal to 0 and  $\theta$  equals to 0.

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The slide is titled "Data analysis - physical picture" and is set against a dark blue background. It contains the following text:

Why extrapolate to:

- Eliminate *intermolecular* scattering effects.  
Ideal experiment: Measure scattering from one molecule.
- Eliminate *intramolecular* scattering effects.  
Ideal experiment: Measure scattering at zero angle.

In the bottom left corner, there is a small logo with the number "7". In the bottom right corner, there is a logo for the Indian Institute of Technology Kharagpur, with the text "Indian Institute of Technology Kharagpur" and a circular emblem.

Now, why we are doing this extrapolation? Why we extrapolate? This expression or scattering equations varied for very dilute solution, we ideally want the scattering intensity from one molecule. So, to avoid or to eliminate any intermolecular scattering effect for that we are extrapolating  $c$  is equal to 0 and we want also eliminate any intermolecular scattering effect. So, we want to extrapolate at 0 angle at 0 angle  $\theta$  will be 1; so, you can eliminate any intermolecular scattering effect and at  $c$  is equal to 0, we can eliminate the intermolecular scattering effect all together.

So, now we have plotted all this data we know this intercept and we can get the slopes for  $c$  is equal to 0 line, and for this  $\theta$  is equal to 0 line. So, if you go back and look at this expression and just plot  $c$  is equal to 0 lines and  $\theta$  equals to 0 line, and see what are the information we can get.

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$$\left(\frac{Kc}{cR_\theta}\right)_{\theta=0} = \frac{1}{M_w} \quad M_w, \langle r^2 \rangle_z, A_2, \chi$$

$$\left(\frac{Kc}{cR_\theta}\right)_{\theta=0} = \frac{1}{M_w} + \frac{16\pi^2 n_0^2 \langle r^2 \rangle_z \sin^2 \theta / 2}{3\lambda^2 M_w}$$
 From slope  $\theta \rightarrow 0 \rightarrow \langle r^2 \rangle_z$ 

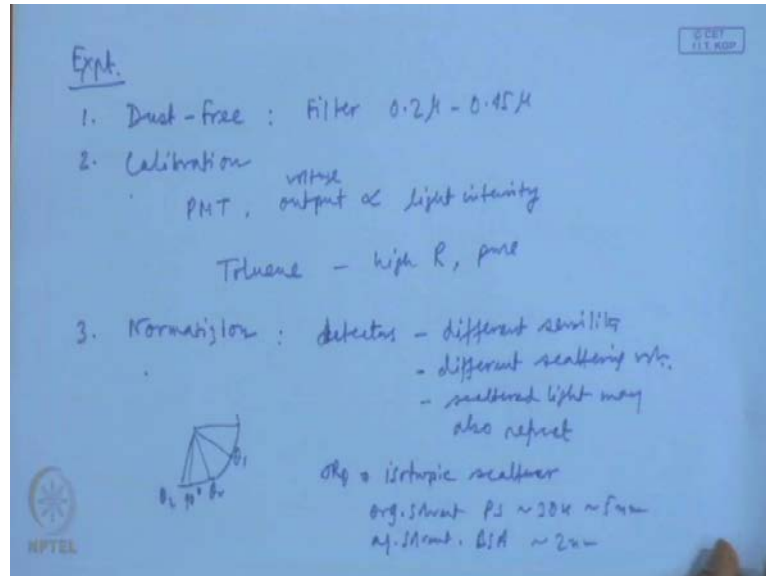
$$\left(\frac{Kc}{cR_\theta}\right)_{\theta=0} = \frac{1}{M_w} + 2A_2c + 3A_3c^2 \dots$$
 slope  $\theta \rightarrow 0$ , and making adjustment for  $K'$  we can get  $A_2 \rightarrow \chi$

So,  $Kc$ , the intercept;  $c$  is equal to 0 and  $\theta$  is equal to 0 should give you one over weight average molecular. So, this two intercept should match this line and this line in the same intercept. So, that is one validation for data point and from the two straight lines one is  $c$  is equal to 0 straight line, another one is  $\theta$  is equals to 0 straight lines. So, slopes for these two straight line will give other information. So, this is the expression for  $\theta$  equals to  $c$  is equals to 0. So, if you put  $c$  is equal to 0 you get this expression and this slope of this line will be given by this is the measure of slope. So, if we know  $M_w$ , we can get slope of  $c$  is equal to 0; we get the value for  $S$  square  $z$ ,  $z$  average radius of gyration.

Similarly, if we write the equation for  $\theta$  equals to 0 line, we get this and if we only dealing with very dilute solution, and if you ignore this higher terms. So, from the slope of  $\theta$  equals to 0 line and making adjustment for  $K'$  we can get  $A_2$  from which we can get the values of polymer solvent interaction parameter. So, what are the things we can get? We can get  $M_w$  from the intercepts or intercepts for  $c$  is equal to 0 and  $\theta$  equal to 0, and we can get  $z$  average radius of gyration which can be converted to weight average radius of gyration, and we can get information of  $A_2$  which will anyway give information about the polymer solvent interaction parameter.

So, this was first practiced by Bruno Zimm. So, this is known as zimm plot; this is very unique way of plotting this three dimension 3 d data into two dimensional using the help of a arbitrarily chosen constant and we can get this information from this zimm plot.

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Now, coming to the experimental points, what are the experimental consideration we must do for this light scattering experiment? One is the solvent and the solute solution all the polymer solution should be absolutely dust free; otherwise, the dust particles will scatter light that will interfere and give error in the your final result.

So, basically we do normally in the lab filter these 0.2 micron to say 0.545 micron filter to get rid of any dust or suspended particle is there. Second, we need to do a calibration the detector is typically a molecular tube; the output of the detector is proportional to the light intensity. So, we need to convert the voltage output to the intensity. So, we need calibration and calibration is typically done. For toluene, it has a very high Rayleigh ratio and we need to purify.

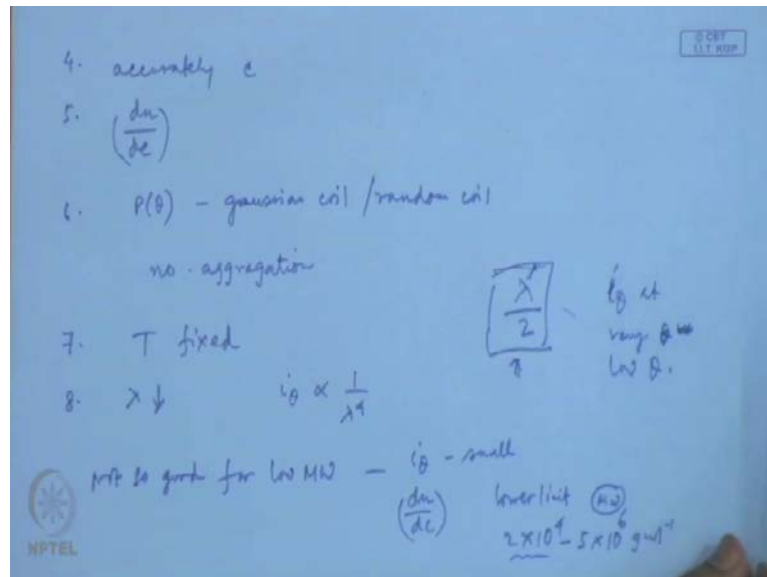
So, toluene has high R value Rayleigh ratio and pure form easily available. So, we use to calibrate the detector with the toluene. So, if we know we can basically get the information about light intensity from the voltage output. Number three, if we are using more than one detector, we have to do normalization of the detectors; we got the detectors may be of different sensitivity; we define sensitivity and they are having

different scattering; if they are placed at different angle then their scattering volume may be different and the scattered light may also refract.

So, for this reason we need to normalize the detector. So, if you have several detector placed at different angles theta one, theta two, theta three and so on, we need to normalize the signal from this detector. So, what we do? We take an isotropic scatterer and because we know isotropic scatterer the  $\Delta R$  theta is the angle independent. So,  $\Delta R$  for isotropic scatterer is angle independent. So, what we do is take an isotropic scatterer; for example, say for organic solvent we can take a polystyrene about thirty K which is typically 5 nanometer; for typically lasers this is less than lambda by 20. So, typically this will act as an isotropic scatterer and signals which we can normalize with a particular signal which is placed at 90 degree for an aqua solvent.

So, for aqua solvent we can use BSA which is aqua solvent typically have 2 nanometer dimension radius is 2 nanometer; so, this is also again an isotropic scatterer. So, we need to do calibration and then we need to do the normalization of the detector signals. Fourth is we must do is accurately EPR solution.

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So, that there is no error in the concentration values, because this is very important to know the concentration values and we need to get the accurate value  $dn$  by  $dc$ , and if this more important because the final expression have given by  $dc$  square term.

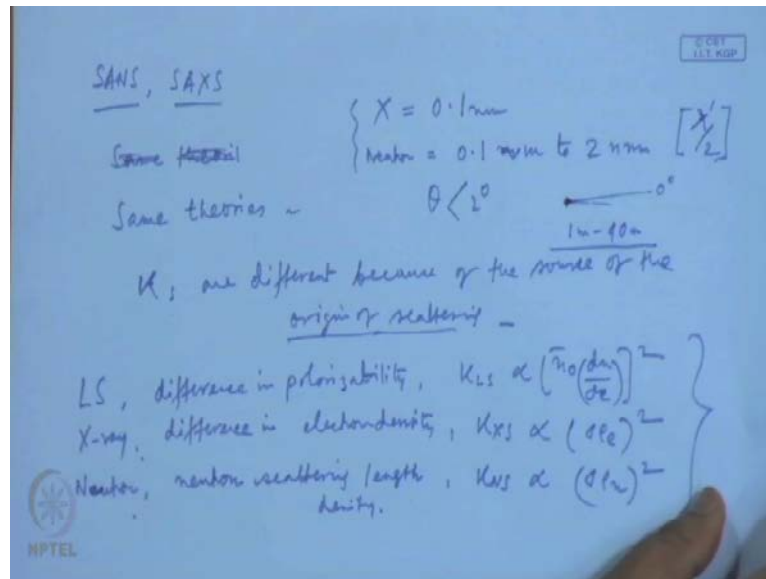
So, if there is error here which gets multiplied more in the final value of determined by  $M_w$ . We also know that the  $P(\theta)$  value or  $P(\theta)$  expression which we just showed it is for Gaussian coil or random coil which typically polymers are in common solvent, but if you anticipate that your polymers are stiff rod like or a very hard sphere like then you need to use the different expression for  $P(\theta)$  and there should not be any aggregate formation even though using a very dilute solution you should make sure that especially this is very important for proteins and the other bio moleculars that no aggregation takes place.  $T$  temperature of the solution must be fixed otherwise, you might get.

If you want to increase the sensitivity you can decrease the  $\lambda$ , because the  $i(\theta)$  is proportional to  $1/\lambda^4$ . So, if you reduce the  $\lambda$  then your sensitivity goes up; the light scattering technique is not good for low molecular weights, because this  $i(\theta)$  value for loads low molecular weights is very small,  $i(\theta)$  is very small; very difficult to detect and also  $dn/dc$  value for molecular is very low.

So, it is very difficult to accurately in the  $dn/dc$  value. So, typically this technique is applied; the lower limit is around the order of  $10^4$  to  $10^5$ ; this is the lower limit and the upper limit is given by  $\lambda^2$ . Now, it is the  $\lambda$  we are using, because what happened if the size of the scatterer or the polymer molecule or the other scatterer is very high and the respective interference between the scattered light from different part of the solute becomes so much that even at a little higher  $\theta$ , this becomes 0; the value of  $P(\theta)$  becomes 0. So,  $i(\theta)$  becomes 0.

So, it is very difficult to get accurate measurements of  $i(\theta)$  for those cases. In that case we need to get  $i(\theta)$  value at very low  $\theta$  to know or to find out accurate information. So, basically upper limit for determination is becomes  $\lambda^2$  where  $\lambda$  is the wavelength of the light in that particular medium. So, this is the conclusion or let us conclude the molecular weight determination by light scattering.

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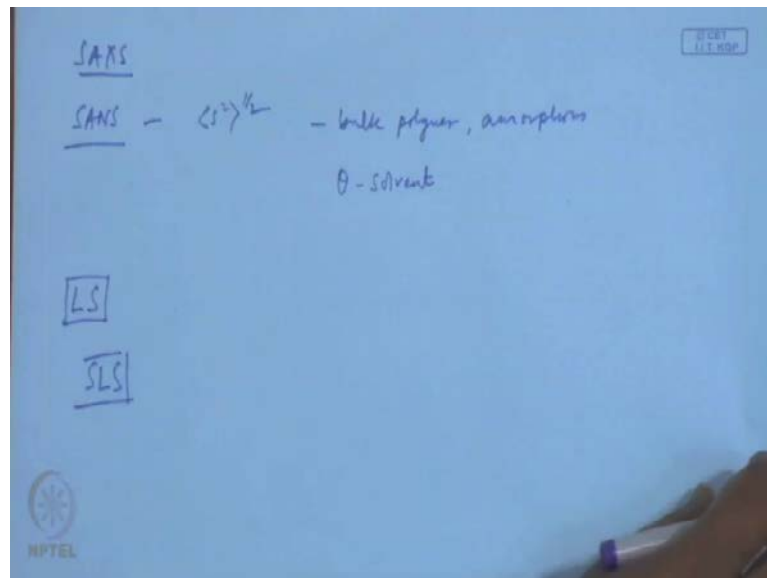
Now, as we said in the beginning, instead of light we can also use the small angle neutron scattering and small angle excess scattering get information about polymer solutions. The same theory applies as in case of light scattering; the expression K is the optical constant is different, because the case is different for different cases; because the source of origin of scattering. For light scattering, for LS, which difference in polarizability of medium which causes the light to scatter. So, K light scattering is proportional to  $dn/dc$  squared; whereas, for x-ray scattering, it is due to difference in the scattering is due to difference in electron density. So, K x scattering is proportional to the difference in the electron density and for neutron this is the scattering is due to neutron scattering length density. So, KNS would be proportional to length density.

So, depending up on which what is the origin for scattering for different electromagnetic radiation whether it is a light scattering or x-ray or neutron scattering; the optical constant will be dependent on the difference in polarizability or electron density and so on. Now, x-ray is very small in compared to a visible light which is having 400 nanometer to 800 nanometer, it is about only 0.1 nanometer whereas, the neutron is about 0.1 nanometer to 2 nanometer. So, remember the upper limit of the measurements where about  $\lambda/2$ . So, that was the upper limit. So, for having any many useful information about this from this x-ray neutron scattering, the scatterer must be very small and what you need to do? You need to place or you need to measurements at

very low theta typically less than 2 degree. Now, if you want to get information or detect the scattering intensity at such low angle then you need to place your scatterer.

If this is 0 degree then if you want to measure a 2 degree then you need to place your scatterer at very large distance having found the scattering particle. So, the path length between the scatterer and the detectors for this techniques is much longer. So, basically you need huge equipments like which equipments where the distance between the scatterer or the sample cell and the detector is about say 1 meter to 40 meter range. So, this is typically that is the difficulty in this technique.

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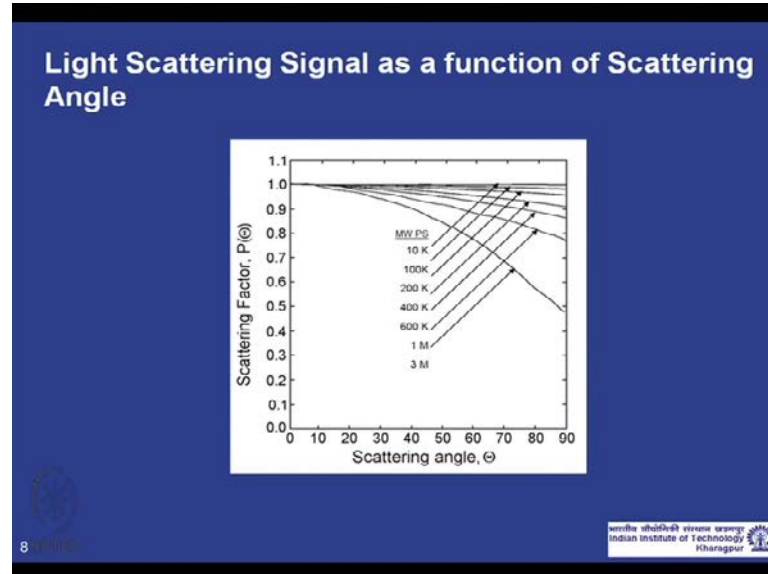


So, very specialized equipment's are made. SAKS is commonly used for measuring sizes of dispersed phases in polymers and also it is suitable for getting polymer morphology; whereas, SANS is basically we got the information about the radius of gyration, it can be used in bulk medium or bulk amorphous polymer. So, with the help of sans it was observed that the radius of gyration in a bulk amorphous polymer is similar as in case of theta solvent; so which was not possible to find out before the invention of this SANS technique; SANS technique help us to get information; both SANS and SAKS get information in solid state or in amorphous bulk state from which will give us the information about the polymer chain the dimension in bulk state; and if you compare the theta solvent, this is the first time after invention of SANS it was found that the dimension of polymer chains are similar in case of theta solvent and in amorphous bulk



solution. We just need to discuss that this techniques are quite good, but this light scattering techniques or the equipments are very costly.

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And one thing if you look at this scattering factor  $P(\theta)$  versus scattering angle; now, if you have some approximate about you know length of the molecular weight of your polymer then you know how this polymer or how the scattering factor  $P(\theta)$  will vary with scattering angle. For example, if you dealing with a 100 K polystyrene molecules which typically we deal in lab, then look that  $P(\theta)$  does not increases much with scattering angle. The scattering angle decreases much with a  $P(\theta)$ ; the scattering factor decreases much with the scattering angle when you have a large molecule where dimension is larger. So, basically the polymers we deal in the lab sometimes we do not require detectors of so many angles may be one detectors at low angles could be sufficient for determination of the molecular weight.

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DLS - QELS, PCS

- Scattering from very small volume at very small time intervals  $\Delta t$ , ns -  $\mu$ s.
- Correlate the scattering intensity fluctuations with time

Fluctuations  $\rightarrow$  Brownian motion / conformational change

$D_z$  - z-average translational diffusion coefficient.

$D_z = \frac{kT}{f_0}$ ;  $f_0 = 6\pi\eta_0 R_h$  (R<sub>h</sub>)

Now, this is what we are discussing the static light scattering technique. Now, in the beginning we said that we can also use the light scattering technique as dynamic light scattering which is also known as quasi elastic light scattering or sometime photo correlation spectroscopy. So, here we detect the scattering from very small volume at very small time intervals; this is what we do;  $\Delta T$  which varies from microseconds to milliseconds and then correlate the scattering intensity fluctuations with time.

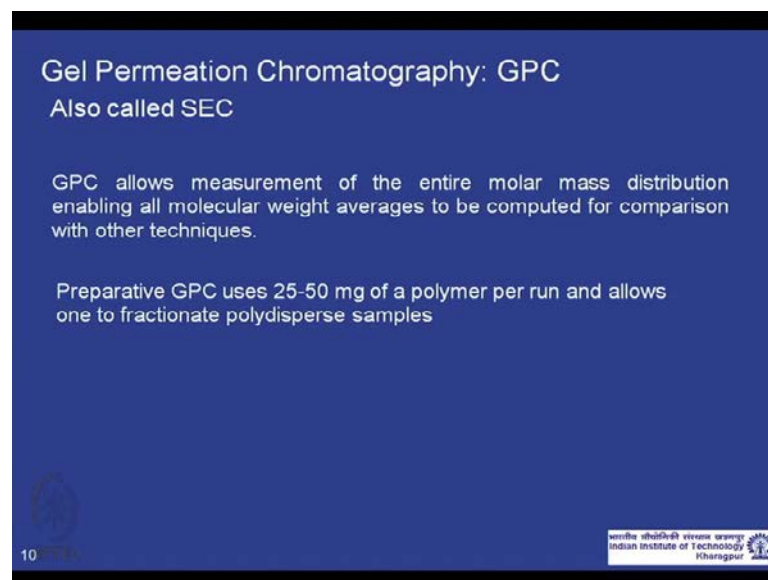
Now, how this scattering intensity fluctuation for say polymer molecule in solutions can be either from this Brownian motion of the polymer molecules which gives translational diffusion and also could be due to the conformational changes of the polymer molecule. If this is the large molecule then conformation changes also may produce or the change the fluctuation in concentration which will give us the fluctuation in the scatter intensity. Now, from this correlation we can get the information about z average diffused translational without going not going too much in the equations, we can just say that this correlation give us the information or the value of z average translation diffusion coefficient.

And this  $D_z$  is equal to this quantity where  $K$  is the Boltzmann constant,  $T$  is the temperature,  $f_0$  is we can get from Stokes equation,  $6\pi\eta_0 R_h$  where  $R_h$  is the hydrodynamic volume; perform this we can get if we know  $\eta_0$  and the temperature, and value of this from this dynamic light scattering correlation. So, the information about

From hydrodynamic radius of the polymer molecules in solution can be obtained. So, now, we discussed the various static light scattering techniques and we use of light scattering technique we can get average molecular weight. We can get also information about the polymer solvent interaction parameter and the radius of gyration, and with the help of dynamic light scattering we can get information about the hydrodynamic radius of the polymer molecules in a solvent for particular temperature.

Now, let us move to the next topic which is gel permeation chromatography, GPC. Till now, we were discussing techniques which either can detect say viscosity average molecular weight or number average molecular weight, or the weight average molecular weight by themselves, but these methods were not enough to get the printed distribution of the polymer sample.

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**Gel Permeation Chromatography: GPC**  
Also called SEC

GPC allows measurement of the entire molar mass distribution enabling all molecular weight averages to be computed for comparison with other techniques.

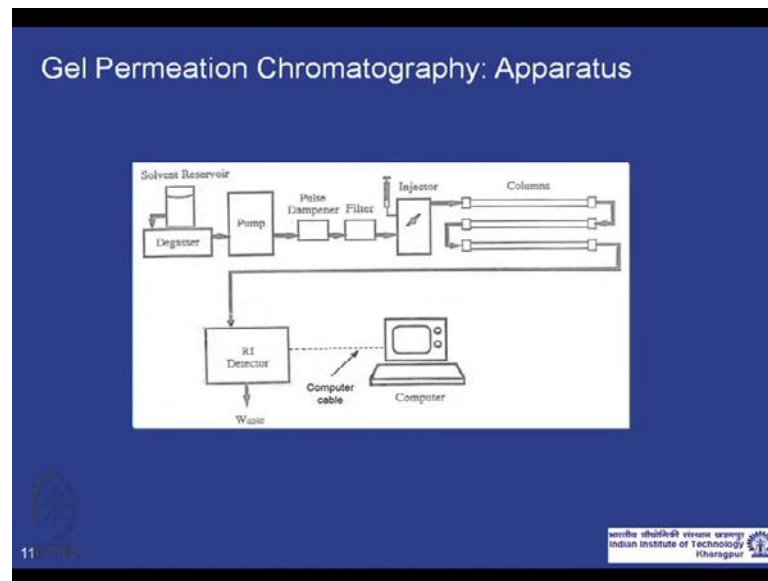
Preparative GPC uses 25-50 mg of a polymer per run and allows one to fractionate polydisperse samples

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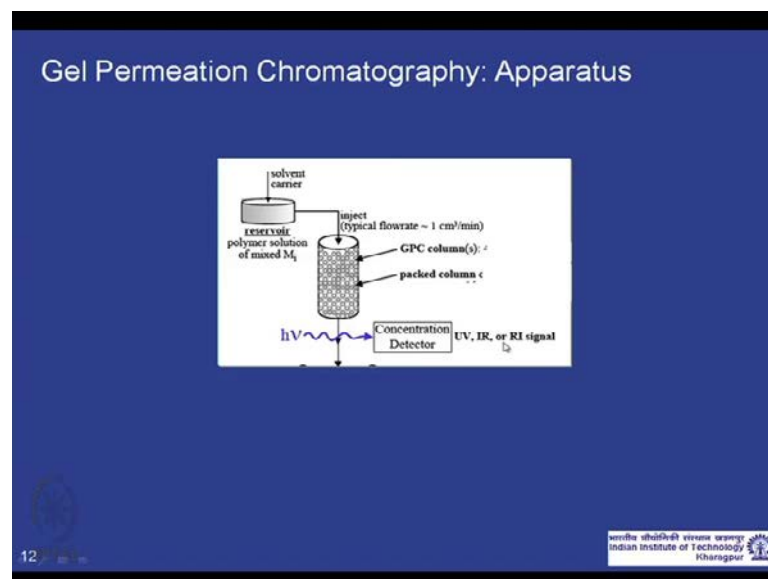
Now, this technique gel permeation chromatography in short GPC allows the measurements of entire molar mass distribution which enables us all the molecular averages to be computed which was not possible with the other techniques and we can use the GPC as the imperative techniques which we can use polymer per run, and then we can fractionate polymers according to their molecular weight. GPC is also called SEC size exclusion chromatography, because we will know now itself that the principle behind the separation of this polymer molecules is based on the exclusion of size.

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Now, this is apparatus of GPC gel permeation chromatography of solvent reservoir which pump the solvent through the columns. Now, to have a steady flow, you might have a pulse dampener which gives the flow at a steady flow rate and you can have a filter which will filter the solvent. So, that no dust particle goes in here you inject sample basically sample goes in the column you can have one or more columns connected in a series, and the polymer sample gets separated according to their size hydrodynamic volume in this columns, and when they come out you have a detector which detect the polymer molecules, and with the help of computer you can analyze this data.

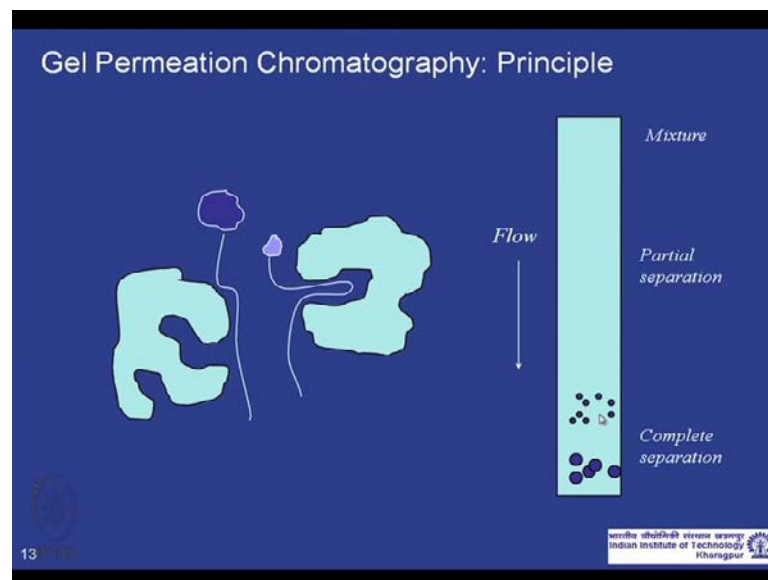
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So, basically in feasible you inject the polymer samples in a column which is consist of highly cross linked gel beads; the beads are typically having diameter of 5 microns to 10 microns and they have definite pore size which can start from say for 10 to the power 100 Armstrong or 50 Armstrong to 10 to the power 5 Armstrong. So, pore size might vary from very low to moderately high and they are packed with having beads of diameter of 5 micron to 10 micron.

These beads are pores with a pore size varies between say 50 Armstrong in to 10 to the power 5 Armstrong. And the polymers gets separated in this column and then you can get detect the polymers using detectors concentration detectors like UV, IR or refractive index detector.

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So, the principle is that you have pores in the column and the polymer molecules which are higher size they do not or cannot go inside this pores. So, they come out fast and the polymers which have lower size they can go inside the pores which makes their path length which are longer compared to a higher sized polymer molecules; and as a results they elute or come out column at a later time.

So, basically if you put a mixture of different size polymer in this case only two size is shown here; may be big and small molecule. Big one cannot go inside the pore so, will come out fast and the smaller one can go inside the pores, and which will take more time

to come out; obviously, polymers chains are also having a distribution. So, it is not that all the pores are having same size, the pores size also have some distribution. So, with the different pore size available and we always know that it is the polymers are not that distinct as this they are also having different size or different molecular weights. So, with flow when this polymer mixture goes through the columns, the larger ones move faster; as a result at the end of the column or end of the path, the larger ones come out earlier and you get the smaller ones come out later.

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Concentration Detectors for GPC

- Refractive Index – Most common
- UV/Vis. - probably second most common
- Evaporative Mass - gaining popularity
- Infrared Spectrometer - probably least common

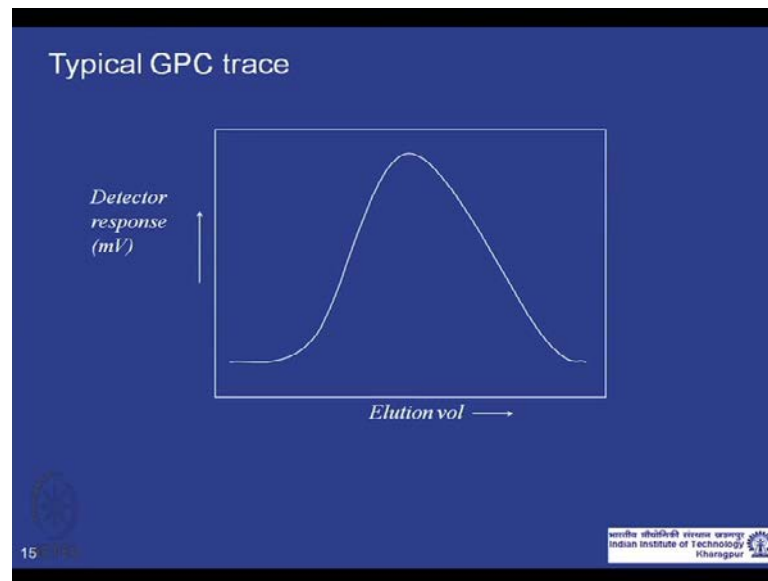
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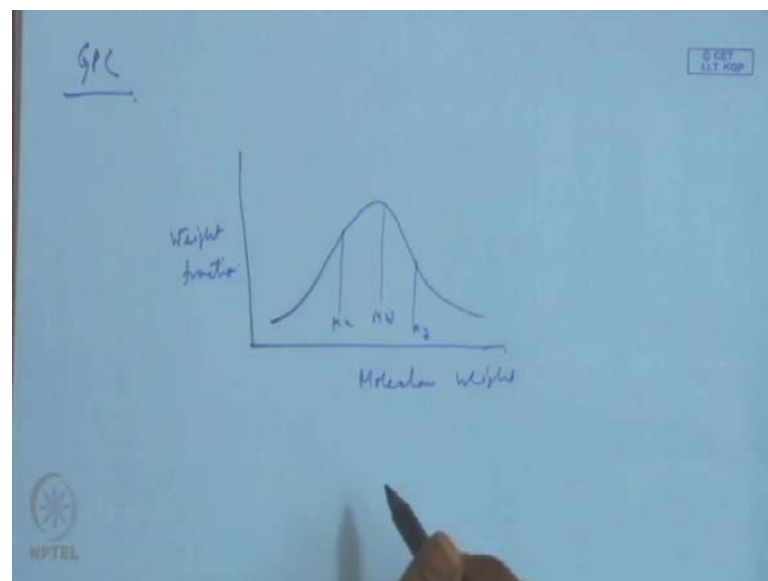
So, when the polymers come out you need to have a detectors which will detect and in most of the cases, because we want to get the concentration of the polymers which are coming out; we usually use concentration detectors in GPC and most common use is refractive index detector; and also in some cases we also UV visible spectrometer which basically is the polymer has some groups which absorb in visible region then we can get the concentration of polymer in that solution by UV visible spectroscopy. Recently, evaporative mass is detector is getting popularity where the polymer solutions are evaporated and the scattering from the polymer globules are measured; and we can also interrogative spectrometer, but it is not very common.

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So, what we get? At the end of GPC experiment, we get a detector response and with the elution volume. So, the higher molecular weight or hydrodynamic size polymers will come out faster with lower elution volume and the lower ones will come out later. So, we get a detector response like this. Now, what you need to convert this raw signal to typically how we represent a polymer distribution? Typically, we present a polymer distribution at weight fraction versus molecular weight.

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So, we need to convert this to this type of expression. So, that we can get a curve like this and we can get  $M_n$ ,  $M_w$  and the other  $M_z$  and so on from this curve. We cannot get the value of  $M_w$ ,  $M_n$  and other average molecular weights from this raw graph. So, what we need to do? We need to convert this detector response to weight fraction of the polymer molecules and we need to convert the elution volume to the polymer molecule weight. So, let us stop here; what we will do in the next lecture is to start from this curve and first we will know how to convert this detector response to weight fraction of the polymers and elution volume to molecular weight, and then discuss about the different aspect of gel permeation chromatography, calibration and other experimental related things. So, let us stop here and we will continue our discussion on gel permeation chromatography GPC or size exclusion chromatography in next lecture.