Principles of Polymer Synthesis

Prof. Rajat K Das
Material Science Centre
Indian Institute of Technology, Kharagpur

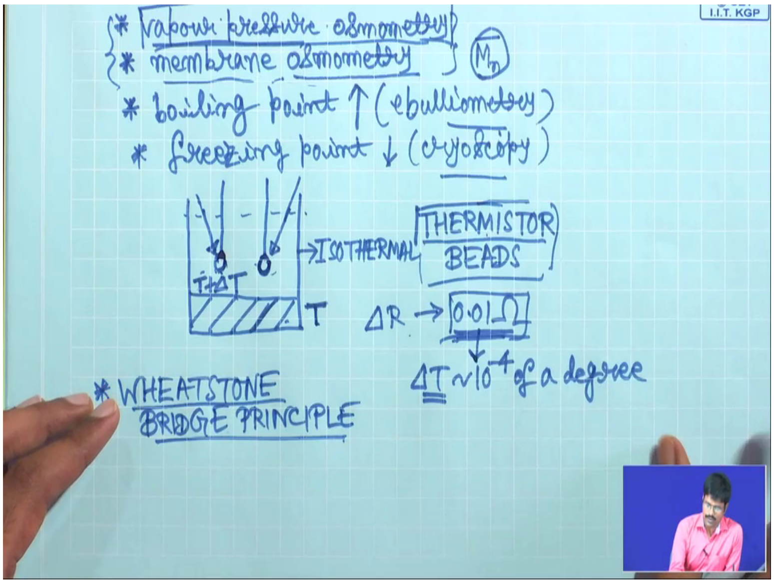
Lecture - 03
Molecular Weight Determination of Polymers (Contd.)

Welcome back to this 3rd class of the Principles of Polymer Synthesis course. We have been talking about this molecular weight from the previous class and the topic of the previous class as well as this class and it is going to continue until we finish this topic is a Molecular Weight Determination of Polymers that we are continuing.

So, we talked about this number average molecular weight, weight average molecular weight we also mentioned in passing something called viscosity average molecular weight. So, we started talking about this colligative properties for M n which is the number average molecular weight determination and we told that this depend on the depends on the number of particles that are present in that particular solution.

So, what are the different colligative properties that we can use, in order to determine this number average molecular weight? So, I am going to give you a list of that.

(Refer Slide Time: 01:17)



- * vapour pressure osmometry
- * membrane osmometry

$\overline{M_n}$

- * boiling point ↑ (ebulliometry)
- * freezing point ↓ (cryoscopy)

ISOTHERMAL THERMISTOR BEADS

$\Delta R \rightarrow \boxed{0.01\,\Omega}$

$\Delta T \sim 10^{-4}$ of a degree

* WHEATSTONE BRIDGE PRINCIPLE

So, we can have experiments that major changes in vapour pressure, vapour pressure osmometry we can have membrane osmometry.

Actually these are the 2 techniques that I am going to discuss in respect of determining this M n and so what are the colligative properties there are different ways actually to determine this value of M n. Say you can look at boiling point elevation, which is called ebulliometry or freezing point depression lowering of the freezing point cryoscopy or you can have a look at the vapour pressure change or you could have something called membrane osmometry. We will talk about that in detail in a little while, but something let us talk about this thing the vapour pressure osmometry to start with.

Now, what happens when you have a solution of a polymer, say you have a dilute solution of a polymer at a particular temperature. So, if you just have the solvent it has a particular vapour pressure, because some molecules of the solvent is they are going from the solvent phase to the vapour phase liquid phase to the vapour phase some molecules are coming back. So, there is a vapour pressure if it is in equilibrium at a particular temperature with it is vapour. So, it has a particular vapour pressure, now if we dissolve a solute in this case a polymer into that solvent what happens is that there is a colliding of vapour pressure of that solvent in that solution we have heard about something called Raoult's law like if you have an ideal solution.

So, the vapour pressure of a particular component is basically equal to it is say if you have 2 liquid mixture suppose. So, the vapour pressure of any component here is basically equal to it is vapour pressure in it is pure state multiplied by it is mole fraction. So, it is depressed to that extent or decreased to that extent. So, this vapour pressure method this basically deals with how we can find out how much vapour pressure is depressed when we have dissolved the polymer into that particular solvent. Now this depression we do not directly measure what we measure is basically the temperature change of the particular solution.

So, I am going to give you a schematic, schematic diagram of that and try to analyse a little bit about how we find the final expression. I could write down the final expression and tell you that this is how it is determined, but then you do not get the whole of the thing the holistic picture of the thing. So, you need to get into the basics and try to understand as much as possible without avoiding maybe some of the complicated stuff with avoiding I would say avoiding some of the complicated stuff I will try to make it as simple as possible.

So, vapour pressure osmometry. So, the kind of setup that you have looks something like this. So, you have a chamber in which you have a solvent I am going to explain this to you here see you have 2 thermistor beads that are fixed at a certain position above the solvent. So, thermistor beads I will explain what the beads are and then you have syringe here, somewhere here you have a syringe which can put a drop of solvent or solution you have a syringe here and the whole setup is basically temperature control. So, this is isothermal. So, thermistor here basically you have 2 terms 1 is thermal and 1 is resistor.

So, thermistors are nothing but registers, which change the resistance when you change the temperature and they have high temperature coefficient of resistance. So, high temperature coefficient of resistance means the higher the temperature coefficient of resistance the higher is the response to a change in temperature. So, if you have a very small change in temperature you will have a measurable change in the resistance. So, you know with this where we are going we are trying to see how the resistance changes and from there we will correlate to the change in temperature that can be correlated to the molecular weight of your polymer average molecular weight of your polymer.

So, this thermistor this typically are made of polymers or ceramics they are not made of metals they might have positive temperature coefficient or negative temperature coefficient whatever. So, the idea here is that this solvent is basically in equilibrium with it is vapour inside. So, these are 2 thermister bead which are lowered at a particular position and both of them have same temperature coefficient of resistance carefully, you know controlled where you have made the materials. And now the solvent is at a temperature T it is in equilibrium with it is vapour.

So, what you do is that you put a small drop of the solvent that is here by the edge of a syringe on this bead and you put a small drop of a solution of the polymer the molecular weight the average molecular weight of each you want to measure in that particular solvent that solution you put a small drop here on this.

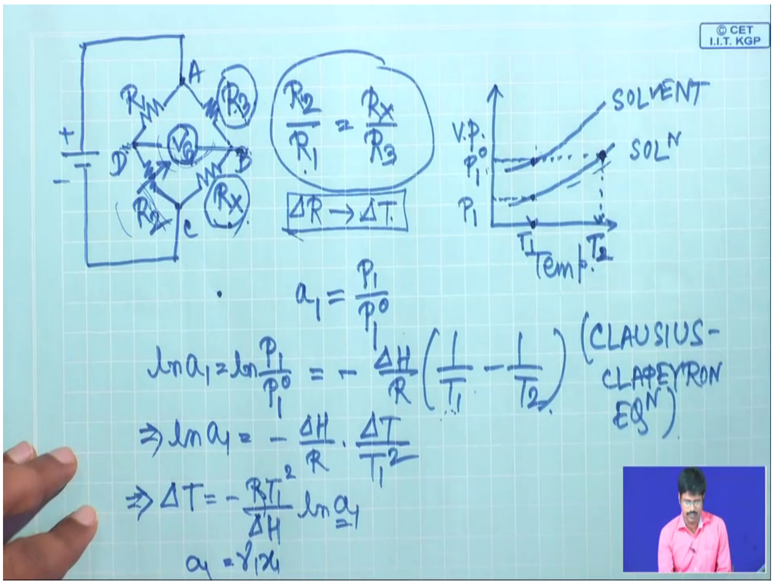
Now, you know the solvent vapour is in equilibrium with the liquid phase and if you say this solvent here the solvent layer is in equilibrium with it is vapour phase. So, then no net condensation or evaporation of the solvent occurs from the drop or from the vapour into the drop condensation of the vapour to the drop or evaporation of the solvent from the drop, but here what is happening is that you have a solute in the form of a polymer in that solvent.

So, the vapour pressure of the solvent is lowered and that is related to the mole fraction of the solvent. So, this lowering of vapour pressure what does that mean. So, vapour pressure of the solvent is lower because of the presence of the polymer. So, what will happen is that in order to equilibrate the situation will dictate that some of the solvent vapour condenses on to this drop and when the solvent vapour is condensing on the drop trying to reach an equilibrium of course, when the solvent vapour is condensing on the drop, you know there is something called latent heat of vaporization, when a liquid is there you are vaporising the liquid it takes up some heat the same way when the vapour is condensed it will basically release that heat.

So, that latent heat of vaporisation, it will release some heat and in the same process it will heat up this solution drop. So, if this temperature is T for the solvent it is in equilibrium with it is vapour at temperature T. So, what is happening is that this drop will have an increase in temperature. So, let us say the temperature becomes T plus delta T. So, you are going to measure this temperature change and this thermister beads are quite sensitive in a way, that say a resistance change of say 0.01 ohm can be measured very easily and this can correspond to a delta T of 10 to the power minus 4 of a degree. So, this much of small change in temperature can be correlated with change in resistance which is of course, measurable.

So, the question then is how do we measure this resistance change, simply what we use is Wheatstone bridge principle without going into too much of details this Wheatstone bridge principle is something like this.

(Refer Slide Time: 11:03)



So, you have 4 resistors that are connected in this fashion. So, this is say R 1 and this is R 2 this is R 3 and this is R x R x means you have to determine this resistance. So, this R x and this R 2 is a variable resistance you can change this resistance and this is connected like this to a source and here you are putting a galvanometer V G. So, you are putting a galvanometer here. So, these are the points A B C and D.

Now, here you are putting your reference thermistor bead; that means, the bead on which the solvent drop is there and on this side here you are putting your sample thermistor bead; that means, the thermistor bead on which you have put a solution. Now under certain condition what will happen is that there will be no current between the points B and D that can be measured actually by this instrument here. So, you change this variable resistance in such a way. So, that ultimately there is no current between these 2 under that condition this particular relationship is valid R 2 by R 1 equals to R x by R 3, since you know R 1 R 2 and R 3 you can easily determine R x.

So, what will happen is that after the experiment is over there is a change in temperature of that sample bead that the thermistor bead on which the solution is there and so the resistance has changed. So, there is some current here. So, what you do is that you change this variable resistance you know what is this resistance this 1 you change these 2 also you know, because this is reference bead you change until there is no current and then you apply this ratio. So, you know the final resistance you know the original distance of R x what it was before the temperature change. So, from there you can find the delta R that you can actually correlate with delta T I am going to talk about that and this delta T actually is related to your molecular weight of the polymer.

Now, let us going to the details of this particular thing I told you that the vapour pressure of a particular solvent decreases. So, this is vapour pressure on the y axis and x axis is temperature vapour pressure of solvent decreases when you have a solute present. So, let us plot the variation of vapour pressure of the solvent with temperature that will be something like this.

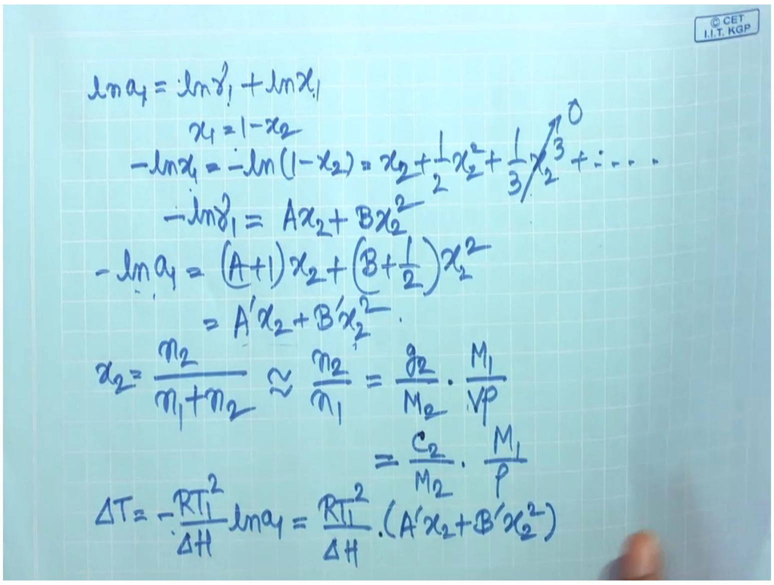
So, it is solvent and variation of the vapour pressure of the solution with temperature this is solution. Now let us say you have a temperature T 1 here, at that temperature T 1 0 is the vapour pressure of the solvent that is the pure solvent. However, at that temperature if you have a solution the vapour pressure decreases it is somewhere here now and that vapour pressure is P 1, but you know that that temperature the solution vapour pressure is lower than the pure solvent vapour pressure, but we increase the solution temperature if we increase the solution temperature a time will come a temperature will come sorry a temperature, will come at which the vapour pressure of the solution will be equal to the vapour pressure of the solvent at the original temperature I mean this is from the graph you can see.

So, now let us analyse this particular graph. So, at this particular temperature T 1 the activity of the solvent is a 1 let us say the activity is equal to activity coefficient into concentration. So, activity of the solvent is P 1 divided by P 1. So, if you take l n of that l n a 1 is equal to l n P 1 divided by P 1 0 that will be equal to minus delta H by R into 1 by T 1 minus 1 by T 2. So, this is how the vapour pressure of a solution changes with temperature this relationship is basically Clausius, Clapeyron, Equation.

Now, this T 1 and T 2 basically T 1 is the original temperature the equilibration temperature of the solvent, which was actually termed as T before and T 2 is the final temperature of your sample bead. That means, where you put a solution the latent heat of vaporization is deposited when the solvent condensed on that solution. So, the temperature has increased. So, that is T 2 you know how we are correlating the things. So, l n a 1 then is equal to minus delta h by R into delta T divided by T 1 square. T 1 square because it was T 1 into T 2, but T 2 is very close to T 1 they almost similar there is a very small temperature change that happens.

So, your delta T becomes equal to minus R T 1 square divided by delta H into l n a 1. Now this is an important equation, what is this a 1 this a 1 is basically gamma 1 into x 1 a 1 is equal to gamma 1 into x 1, because gamma 1 is your activity coefficient x 1 is your mole fraction or concentration whichever way you want to say it.

(Refer Slide Time: 17:27)



© CET I.I.T. KGP

$$\ln a_1 = \ln \gamma_1 + \ln x_1$$

$$x_1 = 1 - x_2$$

$$-\ln x_1 = -\ln(1-x_2) = x_2 + \frac{1}{2}x_2^2 + \cancel{\frac{1}{3}x_2^3}^{\,0} + \ldots$$

$$-\ln \gamma_1 = A x_2 + B x_2^2$$

$$-\ln a_1 = (A+1)x_2 + \left(B+\frac{1}{2}\right)x_2^2$$

$$= A' x_2 + B' x_2^2.$$

$$x_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1} = \frac{g_2}{M_2} \cdot \frac{M_1}{V\rho}$$

$$= \frac{c_2}{M_2} \cdot \frac{M_1}{\rho}$$

$$\Delta T = -\frac{RT_1^2}{\Delta H} \ln a_1 = \frac{RT_1^2}{\Delta H} \cdot (A' x_2 + B' x_2^2)$$

So, your l n a 1 l n a 1 is, basically equal to l n gamma 1 plus l n x 1 just take l n on both sides. Now x 1 is basically the mole fraction of the solvent in the solution. So, x 1 is equal to 1 minus x 2 remember x 2 is very small it is a very dilute solution for all these experiments you are using a very dilute solution; so minus l n of x 1. So, this mathematical treatment is nothing but to try and simplify the things later on to correlate delta T with delta R and molecular weight.

So, minus l n x 1 is nothing but minus l n 1 minus x 2 now it can be shown that that minus l n 1 minus x 2 can be written as this kind of power series in x 2 x 2 plus half x 2 square plus 1 third x 2 cube so on and so forth, when x 2 is very small it can be shown. I am just ignoring the higher terms all these terms are 0 because let us say x 2 is very small here. So, only these 2 terms we will consider and let us also assume. So, this l n a 1 in terms of gamma and x 1 we are trying to express. Now l n x 1 is this let us say this l n gamma l n gamma that you are putting here l n gamma gamma 1 the relationship of l n gamma 1 with x 2; that means, the activity coefficient of solvent 1 with the mole fraction of solute also follows these kind of expression let us assume. So, that will be A some kind of constant we do not know the form of that constant. So, I am writing A x 2 plus B by 2 or actually 2 also is included. So, B some constant into x 2 square I am trying to simplify the methods. So, both of them have the have very similar forms here.

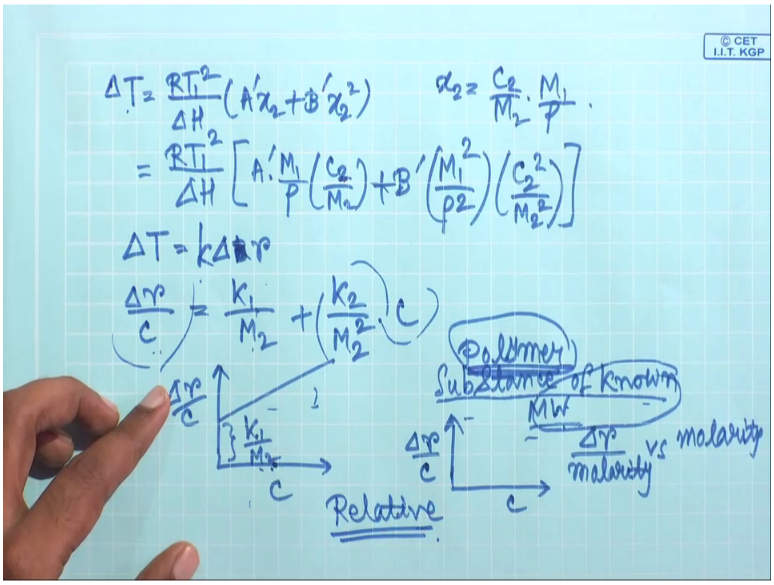
Now, if we assume this then your l n a 1 what does it become, actually there is a minus term here we will come to that after because delta T in the expression there is a minus term. So, this minus l n A 1 is nothing but A plus 1 into x 2 plus b plus half into x 2 square, this is another constant. So, you can say prime x. So, B plus half is another constant B prime x 2 square. Now what is x 2 x 2 is the mole fraction of solute. So, number of moles of solute n 2, divided by number of moles of solvent plus number of solute which is approximately equal to n 2 divided by n 1.

Because n 2 is very small number of moles of solute is very small. So, this becomes n 2 divided by n 1. Now n 2 number of moles of so any if you are expressing number of moles in terms of weight that is equal to the weight, divided by molecular weight. So, number of moles of solute which is actually solute is being designated by subscript 2 and the solvent is being designated by subscript 1. So, this n 2 is basically equal to the weight of the solute divided by molecular weight of the solute. So, you see the molecular weight comes into the picture into n 1 that is the number of moles of solvent is basically equal to the weight of the solvent, which is nothing but volume into density divided by molecular weight of the solvent.

So, this is equal to so this is the weight of the solute divided by volume of the solution or in this case the solvent. So, this this ratio is basically the concentration of the solute. So, that is C 2 divided by M 2 into M 1 divided by row. So, this is what we have come to now let us go back to our original expression of delta T. So, this delta T was equal to minus R T 1 square divided by delta H into l n a 1 this is the expression that we had. So, this l n a 1 is basically it is nothing but. So, this minus l n 1 a 1 is this expression.

So, minus l n a 1 if you replace that R T 1 square divided by delta h into minus l n a 1 that is your A prime x 2 plus B prime x 2 square. So, this is the expression now x 2 value you already know you are going to put that value here. So, if you put that value there. So, let us right down this thing here again. So, you have delta T equal to R T 1 square divided by delta H, into a prime x 2 plus B prime x 2 square.

(Refer Slide Time: 22:18)



$$\Delta T = \frac{RT_1^2}{\Delta H}(A' x_2 + B' x_2^2) \qquad x_2 = \frac{C_2}{M_2}\cdot\frac{M_1}{\rho}$$

$$= \frac{RT_1^2}{\Delta H}\left[A'\frac{M_1}{\rho}\left(\frac{C_2}{M_2}\right) + B'\left(\frac{M_1^2}{\rho^2}\right)\left(\frac{C_2^2}{M_2^2}\right)\right]$$

$$\Delta T = k\Delta r$$

$$\frac{\Delta r}{C} = \frac{K_1}{M_2} + \left(\frac{K_2}{M_2^2}\right)C$$

Now this particular expression you are now replacing the x 2 R T 1 square by delta H. So, that will be a prime into you know the value of x 2 was C 2 divided by M 2 into M 1 divided by rho see just put those values here. So, this will be M 1 divided by rho into C 2 divided by M 2 plus B prime into x 2 square, which is M 1 square by rho square into C 2 square divided by M 2 square.

Now, you know that change in temperature is proportionate to some proportionality constant to the change in resistance, now if you correlate so this resistance let us say we will put small R because this small R and this capital R you may be confused. So, let us put small R for the resistance change. So, if you take these 2 equations into account then your this this C 2 that will come on this side. So, this delta delta T equals to k into delta R. So, that k that constant will come on this side and your concentration will come on this side.

So, ultimately you will have an expression like this delta R divided by C this is the concentration equals to some constant, because these will go into the constant and this M 2 will be still there C 2 has come down here. So, this will be K 1 divided by M 2 plus K 1 divided by M 2 plus another constant k 2 divided by M 2 square into C, I am just putting C, I am just vomiting the C 2 I mean you can put C 2 here also just for the sake of you know simplifying the maters. So, this is the concentration of the solute in this case polymer and M 2 is the molecular weight K 1 2 determine.

So, what will happen is that if you are plotting delta divided by C against C then you will have a straight line. So, you have a straight line here and this intercept. So, this is the it of the form M x y equals to M x plus C. So, this intercept is K 1 divided by M 2 and the slope will be equal to this, now what you have to do here you do not know the value of K 1. So, how can you determine the value of M 2? So, what you should do here is you use a substance of known molecular weight to construct a calibration a curve. So, what you do you take a substance of known molecular weight and what you do is change the concentration of that substance in the solvent and plot delta delta R divided by C verses delta R you know, from the Wheatstone bride principle you can find out delta R. So, you plot that as a function of C and if you are plotting that so basically you are plotting delta R divided by say molarity verses molarity.

So, if you plot that from that plot the intercept you know the M 2 value you know M 2 is the molecular weight, you know the molecular weight of the substance known molecular weight it may be an average molecular weight of course, but you know that so from there you can find the value of the unknown constants. So, if you have now an unknown sample you can actually determine the molecular weight of that unknown sample by this method. So, you know that you just cannot put an unknown polymer and found the and find the molecular weight of that polymer, unless you have already used a reference in this case a reference substance of a polymer in this case a polymer a polymer of known molecular weight. Of course, you are using the same polymer with the same structure and you have synthesized in a controlled fashion of known molecular weight or you have determined this value of M by some other method and you are putting that value of M here number average molecular weight.

So, this is basically a relative method it is a relative method of determination of molecular weight and this vapour pressure osmometry this particular method is typically it has a limitation that beyond a certain molecular weight 10,000 to 15,000 if the molecular weight is higher than that it cannot determine. That is because if you go to very high molecular weight what happens is that the amount of compound if you dissolve in that solvent the polymer if you dissolve in that solvent. The concentration becomes that much lower. So, the delta T value will become even smaller. So, beyond this particular molecular weight let us say 10,000 to 15,000 molecular weight what will happen is that you cannot determine this value of delta T, because the delta T and correspondingly the delta R will be. So, small you cannot measure.

So, there is a limitation to all these methods. So, I hope you appreciate that ultimately when you are plotting this delta R divided by C verses C, why you are plotting that and what is the correlation this analysis that we have done it should make concepts little bit clearer that overall what is the experimental setup and overall what is the principle that correlates this vapour pressure change with molecular weight. And as you can see actually you are not measuring vapour pressure change you are measuring the change in the resistance and the change in the resistance is easily measurable through Wheatstone bridge principle and if you have worked out all the things you just plot the thing with a known molecular weight and find out the constant and later on you can find out the molecular weight through this vapour pressure osmometry technique.

So, we will conclude our class here. So, in the next class what we will do is we will talk about membrane osmometry and then we will briefly talk about the correlation of different molecular weights question is of course, we will say how do you determine the value of M average molecular weight average molecular weight, there are different techniques like this only. So, which 1 should we determine when we are characterizing a polymer sample we have made our polymer sample how do you characterize we determine the molecular weight.

So, if we determine the molecular weight the number average molecular weight is that complete or if we determine the weight average molecular weight is that a complete description. It turns out that typically if you just determine the number average molecular weight it is not a complete description it can give you a misleading information about the average molecular weight of the sample. So, you should typically determine at least M W or if possible M W and M n both and then check the ratio this ratio is the polydispersity index this gives the breadth of the distribution, actually this is related to the breadth by distribution of the polymer molecular weight and that gives you a fair bit of understanding about the properties of the polymer how the properties might evolve, because that depends on the average molecular weight basically that depends on these distribution of molecular weight.

So, till then thank you, and see you in the next class.