Principles of Polymer Synthesis
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Lecture - 05
Molecular weight Determination of Polymers (Contd.)

Welcome back to this fifth class of the NPTEL course on Polymer Synthesis Principles. We had been talking about the Molecular Weight Determination of Polymers, number average molecular weight and we talked about viscosity average molecular weight also to some extent. And, something that I want to mention that I did not mention in the previous class about the membrane osmometry; is that this also has a particular limit of the molecular weight just like your vapour pressure osmometry that it can determine.

So, if you have very small molecules polymer molecules, then this method will not work. That is because the membrane can become permeable to the solute molecules. So, the solute molecules can also pass from the solution site to the solvent site which is not desirable. And if you have very high molecular weight also then it will not work because the osmotic pressure that you can measure that will not be measurable anymore; so much of small value that you will get.

So, that way typically if you are looking at membrane osmometry the typical range you will find it changes slightly from here, here to there.

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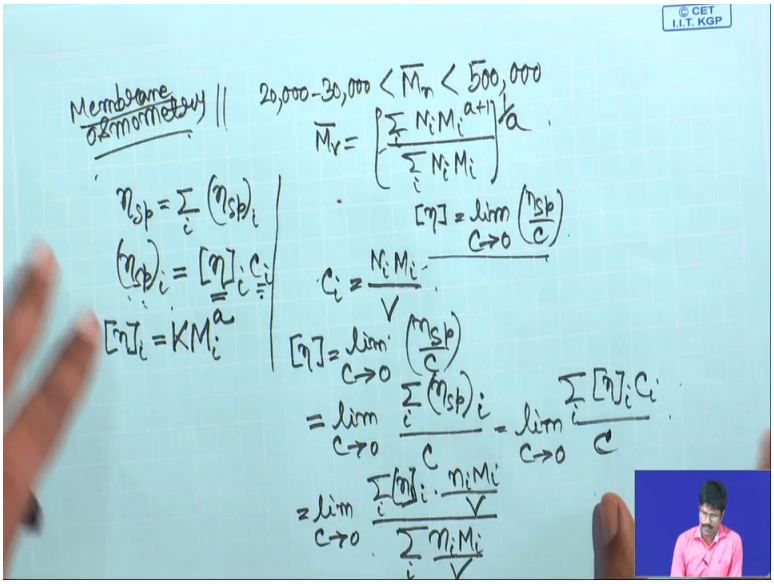

So, 20,000 to 30,000 is the lowest value that you can have and less than 500,000 somewhere in that range.

So, something that I stopped discussing the last class, I was I started talking about the viscosity average molecular weight. So, let us complete the discussion now. So, I gave this particular expression, M v equals to sum over N i M i to the power a plus 1 divided by sum over N i M i to the power 1 divided by a now just want to give you some root derivation of this. So, let us you take dilute polymer solutions and if you are taking dilute polymer solutions your of course, your eta specific. So, certain relations that you should remember when you are trying to derive this thing is that your eta is equal to limit C tends to 0 eta specific divided by c.

Now, eta specific for very dilute solutions of the eta specific of the sample that is the specific viscosity of the sample is equal to the specific viscosity of all the species together, all the different kinds of species. So, this is the i-th species and you sum it over all i's.

Now, this eta specific of the i-th species is nothing but eta i into C i, if you look at this particular relation you have a dilute condition. So, eta specific is equal to C into eta under very dilute condition C tends to 0. So, eta specific viscosity of i-th species is equals to intrinsic viscosity of the i-th species into the concentration of the i-th species. And what about this intrinsic viscosity of the i-th species? You can use the Mark-Houwink equation for this which is K into M to the power a molecular weight of the i-th species average molecular weight of the i-th species. So, these 3 relations are important here.

What is the concentration of the i-th species? This is nothing but number of moles of the i-th species into molecular weight of the i-th species divided by volume. So, that is what you find out that is the expression that you are going to use after.

So now, let us go back to this expression here; your eta specific equals to limit C tends to 0 eta specific divided by C. Now this is nothing but equal to limit C tends to 0. Eta specific is sum over sum of all the eta specifics. So, sum over i eta specific i, i-th species sum over i divided by C. This is equal to limit C tends to 0.

So now use this expression. So, eta specific i equals to eta i into C i. So, sum over i eta i into C i divided by C. And C i is N i M i divided by v just replace that term here. So, that will be equal to limit C tends to 0 sum over i eta i eta I into N i M i divided by v and here at the bottom total concentration if you are looking at the concentration. It will be sum over N i M i divided by v. So, this is the total concentration.

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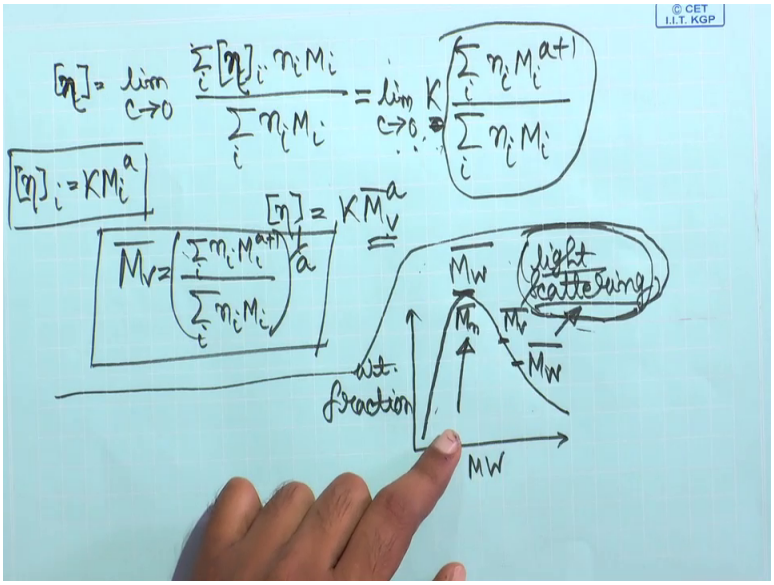

So, what was the expression that we were having? Here eta equal to limit C tends to 0 I am just rewriting that expression again for the sake of continuity. So, this into sum over i sum over i, and then we had eta i into N i M i divided by v that v will go. Because here also at the bottom I have sum over i N i M i divided by v. This is eta, and this is n. You do not mix that up this is eta intrinsic viscosity. So, this is the expression that we have.

Now, your eta i you know that eta i in the previous page, I had written that is equals to K M i to the power a Mark-Houwink equation. So, that you replace here. So, if you replace that here that becomes C tends t 0 K comes out K is constant, and sum over i N i M i to the power a plus 1, divided by sum over i N i M i.

Now, the general expression is eta equals to K into M v to the power a for the Mark-Houwink equation. So, you see eta equals to limit C tends to 0. So, this I am just removing C is very small in concentration. So, let us assume that and remove this C tends to 0. So, that will be K into M v to the power a. So, this M v to the power a is nothing but these value if you see the correlation here. So that means, your M V i am just

putting bar again here just to make sure it is uniform. So, sum over i N i M i to the power a plus 1 divided by sum over i N i M i to the power 1 divided by a. So, we have derived this expression.

So, we have discussed now how to determine the molecular weight through the viscosity method. And we have also discussed a general expression of the molecular weight that you have obtained from the viscosity method. In terms of the number of moles, in terms of the molecular weight of the different species and in terms of the Mark-Houwink constants, so that in general terms concludes our discussion of the viscosity average molecular weight determination.

Now, something that remains is a discussion of the M w. Say, if you are there are different techniques for determination of M w. So, one of them is light scattering experiment. I would not go in to the details of that, but this light scattering experiment you will have more scattering if you have molecules of larger size. So that means, basically you can use this particular technique in order to determine weight average molecular weight. So, as I told you there are different techniques for different molecular weights, and if you are determining through colligative properties the number average molecular weight. So, colligative properties basically will be biased towards low molecular weight fractions, say light scattering will be biased towards high molecular weight factions some of these things are important to keep in mind. So, as I told I will not discuss about the light scattering in detail.

Now, let us see if you are plotting weight fraction on the y axis versus molecular weight on the x axis. The kind of distribution that you typically get is something like this. So, you want to know this full destination M n is somewhere here, the number average molecular weight M w will be somewhere. And M v will be somewhere in between 20 to 30 percent sometimes 10 to 20 percent lower than M w.

Now, the question is if you just determine M n, does that faithfully present the situation of the whole distribution? Typically, the answer is no. And that is because of the reason the methods that you are using to determine M n they will have more biased towards low molecular weight fractions. Now if it is so happens that the total weight of this low molecular weight fractions in the polymer sample is actually low, then you will basically underestimate your total molecular weight if you are just trying the M n value.

So, suppose your 95 percent by weight of polymer fraction which is having large molecular weight. And 5 percent by weight of polymer fraction which is having low molecular weight. If you determine M n that M n will actually biased towards that 5 percent of the sample. But if you are looking at different properties like the strength of the material melt viscosity so on and so forth, that is actually determined by the sample fraction that contributes largest amount of weight to the sample.

Say for example, your 90 by 5 percent of weight fraction of a certain molecular weight. Your 5 percent weight fraction of a certain molecular weight this 95 percent weight fraction that constitutes the bulk of the sample; whatever it is molecular weight maybe it constitutes the bulk of the sample. So, that will determine the property of the sample. So, if you are biased towards the 5 percent then you will miss that property. So, we will give an example a hypothetical example of this situation something that I am illustrating here.

Suppose you have a hypothetical sample which has 95 percent by weight of 95 percent by weight of molecules which have molecular weight 10,000.

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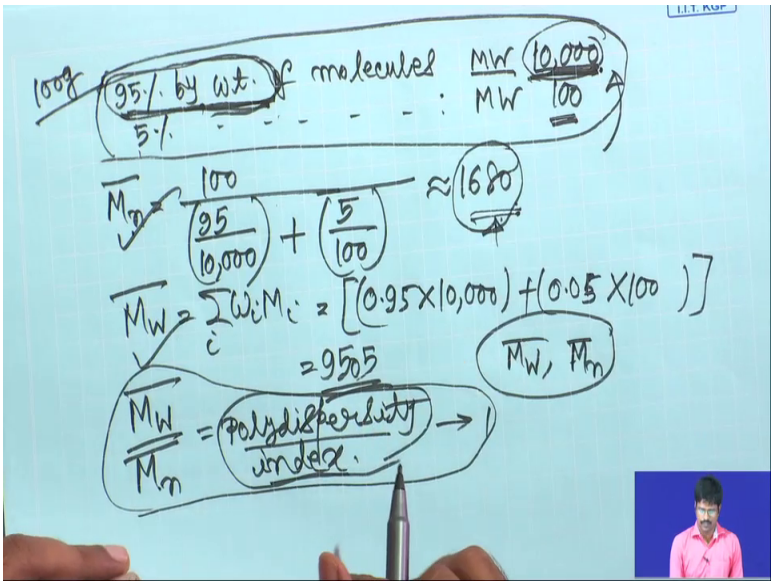

And you have 5 percent by weight of molecules which have molecular weight 100. So, from here what do you think the properties of the sample will be predominantly determined by this 95 percent by weight of molecules; simply because they occupy the most of the weight of the sample. So, you need to use a molecular weight determination that actually is biased towards this 95 percent weight of the sample.

Now so you know this is this much of huge difference 95 percent by weight of molecules say molecular weight 10,000 5 percent only 100. Now if you determine M n number average molecular weight which is equal to the total weight divided by total number of moles; so let us say your sample is 100 gram, if you take 10 grams or whatever it will proportionately change so then total weight is 100 by number of moles total number of moles. So, this is 95 divided by 10,000 this is the number of moles for the species one which occupies 95 percent by weight.

And then this is 5 divided by 100 for the second species because it is 5 percent by weight total weight, we have taken as 100 for the sake of calculation the simplicity of that; so 5 by 100. Now if you do the calculation it comes approximately 1680. So, you see it grossly underestimates the overall molecular weight. 95 percent of weight of the molecules is molecular weight 10,000, but still if you are determining M n it is giving only close to 2,000, much lower value. So, if you go by this you will predict properties based on a lower molecular weight, whereas it is the higher molecular weight sample that actually occupies most of the weight of the sample which will be determining the properties.

So, if you determine M w. So, this is weight fraction sum of the weight fraction, into the corresponding molecular weight. So, that is nothing but weight fraction is 95 divided by 100 for the first sample 0.95 into molecular weight 10,000, plus second sample is 0.05 the weight fraction. So, 5 divided by 100, 0.05 into molecular weight 100. So, that will give you 9505 which is closer to your actual scenario.

So, that is why you should determine both the values of M w and M n, and these ratio of the M w by M n is actually related to the breadth of the molecular weight distribution. And this is called polydispersity index. And later on, we will see when we are talking about controlled polymerization say controlled radical polymerizations. Say, atom transfer radical polymerization so on and so forth. They are actually what we want to have is to have this polydispersity index as low as possible. I mean as low as possible means as close to one as possible. It is the indeed possible that this value will be very close to one this cannot be equal to one that will be close to 1. So, that all the polymer chains are almost of similar length. And in some cases, it will be much away from 1 also. So, this gives you an idea about the breadth of the distribution of the molecular weight for your samples.

So now the question remains of course, you can determine M w you can determine M n separately. How do you know about the distribution that curve with respect to weight fraction how the molecular weight changes? How would you know that? So, one of the processes that I will discuss is; one of the techniques that you can use is GPC which is gel permeation chromatography.

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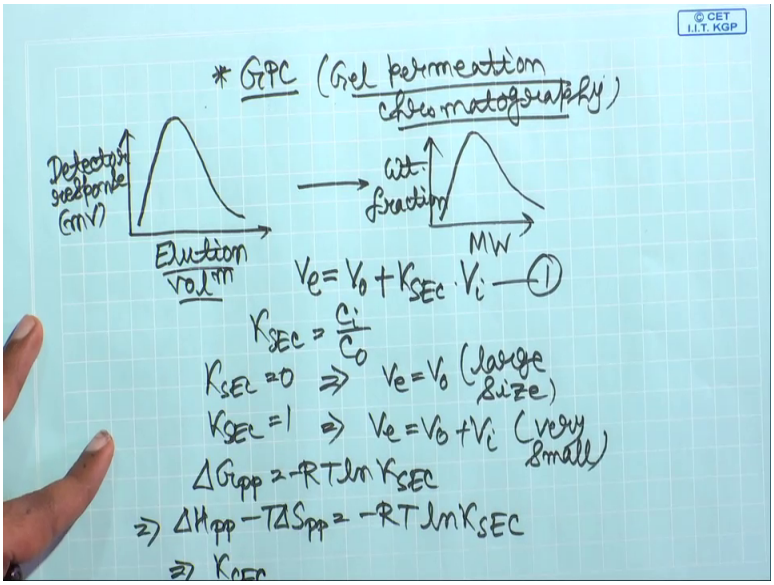

This gives you the distribution of molecular weights, complete distribution of the molecular weight.

So, what is the principle of that? This is basically a size exclusion chromatography. What you can do is that, you have some column you have some materials in this case we can have cross linked polystyrene beads as the column of specific porosity. So, you have the porous solid in the column porous beads in the column. And what you do is that you pass your solution of the polymer for which you want to determine the molecular weight distribution through this column.

Now, this is size explosion chromatography. What will happen is that polymers of different size are present in that sample, because this is not a mono disperse sample this is a poly disperse sample. And you have pores in your stationary phase this is a stationary phase the separate what that you are using the polystyrene material that you are using in the column that is your stationary phase. And the liquid that you are pouring is called elevant. Now this elevant when you are poring, you have polymers of different sizes.

Now size explosion chromatography means this separates the material on the basis of size.

So, if you have a very small molecule that can be go into the pores. And that will take more time to come out with the 11at at the bottom of the column. It need not be at the bottom of the column, it need not be gravity column, if the column might be something like that because you are putting a pressure. And with the pressure you are actually controlling. So, everything is instrument control you are putting a certain pressure, and there is solvate is flowing solution is flowing through that column.

So, if you have a very small molecule it will go into the pores more. So, it is path length will become higher it will take more time to come out, if you have a bigger molecule it will take less time to come out. So, whatever is coming out you can actually use some analytical techniques to determine, what is coming out you can UV you can use refractive index UV if you have a chromo fore you can use in generally refractive index. So, you know that something is coming out and you will get a trace that is the experimental result a trace of the GPC.

So, this is size explosion chromatography; that means, your sample is not interacting with your stationary phase. So, there is no enthalpy change that is associated with it. That will be later important when we are trying to analyse this particular thing. So, there is no interaction, between the stationary phase. And your solute that is in the solution. So, it is separated on the basis of size.

So, what you get is something like this. You have a detector response. So, you have a detector. So, you get some voltage there let us say M v milivolt. And you have elution volume in the x axis. Now elution volume can be equivalent to time at what time the compound is coming. So, instead of elution volume you could use time also here. You have some trace like this. What you want to do is that this is the result. You want to convert this to this kind of graph weight fraction versus molecular weight. That gives you what weight fraction is of what molecular weight similar kind of graph.

So, the raw data you want to convert to this. So, that gives you the molecular weight distribution. Now let us do some analysis. I will write down one equation like this V e equal to V 0 plus K SEC size exclusion chromatography chromatogram into V i.

So, your invent is passing through the through the column, let us say V e is the total volume of the invent that is passing. V 0 is basically the volume of the invent which is outside pore. And V i is the volume that is inside pore. And K SEC is an equilibrium constant. So, it is an equilibrium. So, the species that is present in your solution is in equilibrium between being inside the pore and being outside the pore. So, this K SEC will determine that it will become clearer now. So, what is this K SEC? This is equal to C i divided by C 0. Where C i is the concentration inside the pore, and C 0 is concentration outside the pore. So, if you have a very large size polymer almost nothing will go into the pore because the pores are smaller than this polymer. So, it will just come out. So, if that happens then what is the value of C i the value of C i is 0, for large size polymers.

So, for large size polymers your K SEC will be 0. So, that will mean your V e equals to v naught for large polymers, large size. On the other hand, if you have a very small polymer is concentration inside the pores, and outside the pores will be very similar they are very small. So, the residing time inside and outside is same. So, C i equal to C 0. So, your K SEC will become 1.

So, if that is so, then your V e we will be equal to v naught plus V i for very small polymer. Now this is an equilibrium situation, and you know the delta G equals to minus R T ln K. That expression you can use delta G is the free energy change K is the equilibrium constant; so delta G of pore permeation. So, I am just putting this index this substitute here is minus R T ln K. K is this K SEC delta G of pore permeation. So, this is pore permeation free energy that we are talking about.

Now, here you know delta G equals to delta H minus T delta S delta H minus T delta S from thermodynamics we know that that will be equal to minus R T ln K SEC. Here this delta H is 0, because there is no interaction between the solute in this case the polymer and the stationary phase. So, this delta H the enthalpy change. So, between the polymer and the beads there is no interaction. So, this is 0. So, if this is 0, then this t goes off and what we can have is an expression of K SEC.

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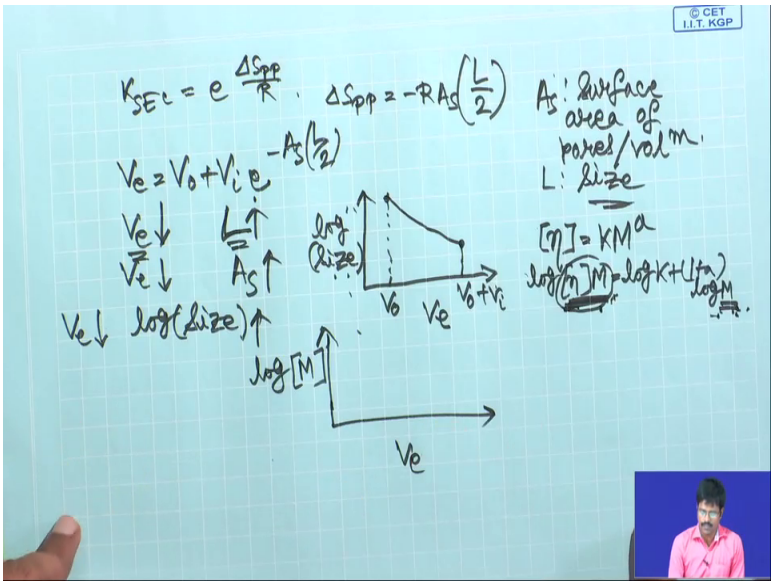

I will write down in the next page. So, what we will can have is an expression of K SEC which is equal to e to the power delta S p p divided by R.

Now, this delta S p p is the entropy change corresponding to this pore permeation. This delta S p p it can be shown, that this is equal to minus R into A s into L by 2. Where A s is the surface area of the pore per unit volume, surface area of the pores per unit volume and L is related to the size of the polymer. So, if you now replace this if you now use this expression in the expression of V e. So, V e equals to v naught plus V i into K SEC.

So, you put that value here. So, that will be V i into K SEC. So, e to the power minus A s into L divided by 2. So, this is the expression that you have ultimately. So, you can see that your V e the elution volume goes down as L goes up here is minus here. Elution volume goes down as a goes up both. Elution volume goes down means that particular compound will come out first earlier, because elution volume is correlated to time. So, at lower elution volume it is coming out means initial phase of the column it will come out. Now V e is going down with increase in l; that means, if polymer size goes up it will come out first it will come out earlier. So, initially I told you this same thing in a physical interpretation sort of way.

And now I am showing you mathematically also this is the same. Also, your V e goes down when A s goes up. A s is the surface area of pores per unit volume. So, if surface area of the pores goes up, how can you increase the surface area of the pores. If the pores

become smaller in size then the surface area of the pores increases. So, if the surface area of the pores increases; that means, the pores becomes smaller in size; that means, the molecules the solute will not be retained they will come out first, come out earlier so that your V e or the individual (Refer Time: 25:28) elution of the volume goes down with increasing surface area of the pores as well as increasing size of the polymers.

So, if you now so, your V e is related to L. So, V e basically is related to log of L because there is a e here, exponential here. So, if you plot this thing ultimately. So, you will have log of size versus V e, because they are related V e goes down with log size. So, L so, you can say V e goes down as log size goes up, as log size goes up.

So, log size versus V e. So, you have this kind of plot. So, in this kind of plot V e goes down as log size goes up. So, this plot will have an endpoint here, and an end point here. So, this point will correspond to V 0, and this point will correspond to V 0 plus v i. So, both sides. So, if you have a very large molecule it will come out here, if you have very small molecule come out on this particular site. So, we have explained it in like this way. Now you know that this value of eta, intrinsic viscosity is equals to K into M to the power a this is your Mark-Houwink equation. So, if you take log of eat and you multiply by M on both sides then it becomes log of K plus 1 plus a into log of M this is the expression.

Now, this side you have eta M and this side you have M. Now it can be shown that hydrodynamic volume of your polymer is basically hydrodynamic volume which is basically related to the size of the polymer; that is proportional to this eta into M.

So, in a way you can put log size here eta into M, you can put log size here and you can put log M is there. So, log size basically is correlated with log M in this kind of fashion. So, instead of log size is you could put log M here, that you have to keep in mind. So, if you put log M on this site, then your log M you can plot versus V e. So, you can plot log M versus V e which actually means that you have log M versus elution volume V e.

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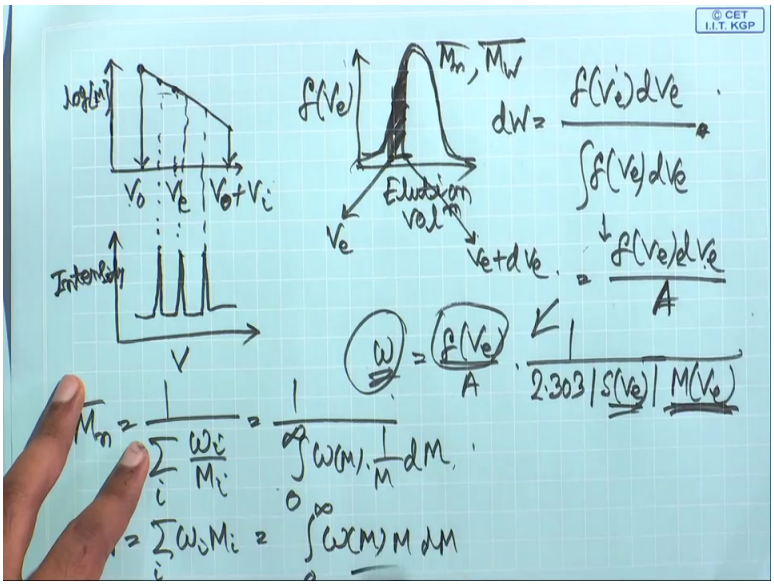

So you can correlate basically, the initial volume with the molecular weight. If you see in the initial diagram on the y axis we wanted to put weight fraction on the x axis we wanted to put molecular weight. So, elution volume has to be related to molecular weight with this relation, you can directly now relate elution volume with molecular weight. So, this is a point where you have total exclusion of the molecule which is V 0, this is a point where you have total permeation of the molecule which is V 0 plus V i.

Now, what you do is you construct a calibration curve. How do you do that? So, you have the detector response on this site intensity. And you plot this intensity with respect to the elution volume. And you use standard materials, standard materials known molecular weight fairly mono disperse molecular weight that we use. And you put in the machine. So, you know at what elution volume or what time it is coming. So, that elution volume you can correlate with molecular weight because you have this linear plot.

So, what you have if you plot intensity versus elution volume. Suppose, you have 3 different mono disperse samples. So, depending on their molecular weight they will come at different times or at different volumes you can use volume or you can use time; that you can use to construct this particular curve of log M versus V. So, if you now have an unknown molecular weight you can basically in this particular curve you can find out that unknown molecular weight with respect to that elution volume because you know

the elution volume. So, in this curve where it comes you know from there you can find the molecular weight of the sample.

So, the final thing that I want to tell before I conclude this particular class is that on the y axis you have detector response. On the x axis you had elution volume that elution volume you have now correlated with molecular weight. On the y axis you have detector response you want to correlate that with weight fraction. And how do you do that? If you plot your detector response say like this, if you are plotting against elution volume. Say you have something like this, you take a very small strip here between volumes V.

So, this is V e and this volume the point here is V e plus d V e. So, what is the weight fraction of polymer that is eluting between these 2 lines? So, in this small strip what is the weight fraction of polymer that is coming out that is nothing but d w equal to f V e into d V e divided by integration total area under the curve. Total area under the curve it is something like that. So, this is ultimately you will have f V e d V e divided by area.

So now you have basically correlated these 2. Actually, you can do an integration after. And so, this a v d V e d V e divided by a. So, if you do an integration and ultimately what you will have is that the weight fraction you will find out weight fraction will be equal to f V e divided by area into 1 by 2.303 into s V e into M V e. So, something like that. So, weight fraction is now correlated with the detector response, and M V e is basically the molecular weight that is obtained at that particular elution volume v equals to V e. So, you can put that and you can construct this weight fraction curve s is basically the slope at that particular point.

So now you can have y axis as the weight fraction, and the x axis as the different molecular weights. And so, the final statement that I want to make is that from these kind of curve how we can find out the values of M n and M w. If you see the value of M n, that is nothing but 1 divided by sum over i W i M i, where W i is the weight fraction. These all these expressions are very similar M n, this expression I did not use before you can actually work out yourself how this expression comes.

So, weight fraction of that particular species which has molecular weight M i; so this is nothing but if you write down in integral form. So, this is 0 to infinity this is w is a function of M 1 by M d M similarly for M w. Now this is the expression that you know sum over i W i M i in integral form 0 to infinity 0 to infinity and this is w M d M.

Now, these integral basically you can find out from this final expression, because you are putting weight fraction versus total the molecular weight on the x axis. So, ultimately then you know the complete distribution of your sample from your gel permeation chromatography. The way I have discussed this is you need standard samples for calibration. And the final concluding statement I could like to give you is that. If you are using say an unknown sample which has which is something related to polystyrene when it is better to use polystyrene mono disperse samples as the reference samples to construct the calibration curve, because the structure the relationship of the size with the hydrodynamic volume is not the same when you change the structure.

f you are using a branched polymer unknown sample to determine the molecular weight. And if you are using a linear polymer known sample of known molecular weight to determine the calibration curve then ultimately your molecular weight determination will not be correct. So, you need to use similar structures of the polymer which you have actually used to construct the calibration curve. So, unknown sample also should be of similar structure.

So, with these we conclude more or less the discussion on the molecular weight, certain techniques we did not discuss certain techniques which I did are very, very important for you I have talked about again in brief and certain analysis I have done.

So, we will stop here today and in the next class; that means, in the lecture 6 we will start talking about the step polymerizations it is mechanisms and it is principles.

Thank you.