Principles of Polymer Synthesis
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Lecture - 04
Molecular Weight Determination of Polymers (Contd.)

Welcome back to this course of Principles of Polymer Synthesis. Today is lecture number 4 and we will continue discussing about the Molecular Weight Determination of Polymers.

Just to recap what we discussed in the previous classes, we talked about number average molecular weight, we talked about weight average molecular weight viscosity average molecular weight in the passing did not talk about it much, we give expressions of that we worked out a little problem to clear out the idea of the expression how you can use that, in a scenario where you have mixed different polymer samples. And then we straight away went into different experimental techniques discussion of different experimental techniques that are used to determine the molecular weight in this case we are talking about number average molecular weight so different colligative properties.

And in the last class we discussed in detail about the vapour pressure osmometry process and if you recollect that, we determine the change in resistance, when we have dissolved the polymer into the solvent in the Wheatstone bridge principle. So, basically what happens is that the temperature changes ever. So, slightly for the solution if you are comparing with the pure solvent, that is because the solvent from the vapour phase deposits it is latent heat of vaporization on the solution drop. And basically condensation to the solution drop this temperature change, we do not measure we measure the change in resistance and we correlate to temperature change. And this temperature change is basically correlated with the molecular weight this case a number average molecular, weight we have to keep in mind that when you are determining this colligative properties basically you are using very dilute solutions of the sample.

So, in today's class we will start with discussing another technique called membrane osmometry that can be used to determine the number average molecular weight. Now membrane osmometry has 2 terms 1 is membrane and 1 is osmometry. So, basically you are using a membrane for some purpose and osmometry here it relates to the phenomenon of osmosis. So, what is osmosis suppose you have a solution you have a solute, which you have dissolved in some solvent and you have a pure solvent. So, if you separate them by some kind of membrane which is semi permeable, semi permeable means it is selectively permeable to something in this case it is permeable to the solvent, but not solute.

So, the solute molecules cannot permeate through that membrane only solvent molecule can permeate. So, you separate 1 solution in which you have the solvent plus solute with a solvent. If you do that what will happen is that the solvent molecules will pass to the membrane, because a membrane allows the solvent molecules to pass through from the solvent site to, the solution site, until the chemical potential of the solvent in both the compartments becomes equal.

So, chemical potential is a term it is like you know it is kind of it a similar to potential energy. So, it has some potential to do work. So, it will do that work and basically if you have a solution your chemical potential of the solvent in solution is lower in order to equalise that chemical potential the solvent has to flow from the solvent site to the solution site and then the chemical potential will be equalised.

So, what will happen in the solution site the level of the solution will increase? So, these particular process is called osmosis, osmosis is of course, you might have heard about osmosis it is a very important process it is a very important phenomenon observed in many biological processes I would not go in to the details of those. So, just I was discussing the principle of osmosis now what is osmotic pressure then osmotic pressure basically you have. So, your solution site the layer of the solution has gone up in order for the solution site the layer to remain the same as before we have to apply some pressure. So, you have to do some work against the solvent flowing now this work is basically related to the osmotic pressure.

So, membrane osmometry basically it is a way to find out you know the you have an experimental design a set up in which you find out how much pressure you have to use. So, as to counteract this movement of solvent from the solvent site to the solution site, so basically you are trying to determine the osmotic pressure and that osmotic pressure is related to the molecular weight of your solute and as I can say again it is a dilute solution that you are using, these are colligative properties that you are measuring this does not dependent on the identity of the solute molecules it depends on the number of the particles of the solute molecules that are present in the solution that is the idea here.

So, the colligative properties for example, if you are looking at boiling point elevation if you are looking at freezing point depression or vapour pressure depression, whether you are using a large molecular weight sample or you are using a small molecular weight sample, ultimately it will depend on the number of particles that are present in this system. So, we would not elaborate on that further, we will now come to this membrane osmometry process and we will describe experimental setup we will describe little bit later. Now I am trying to give you a little bit theoretical understanding of this whole process and the yes.

So, once I give you the theoretical understanding in passing we will mention about the experimental setup to some extent and correlate the 2. So, we will start with this Membrane osmometry.

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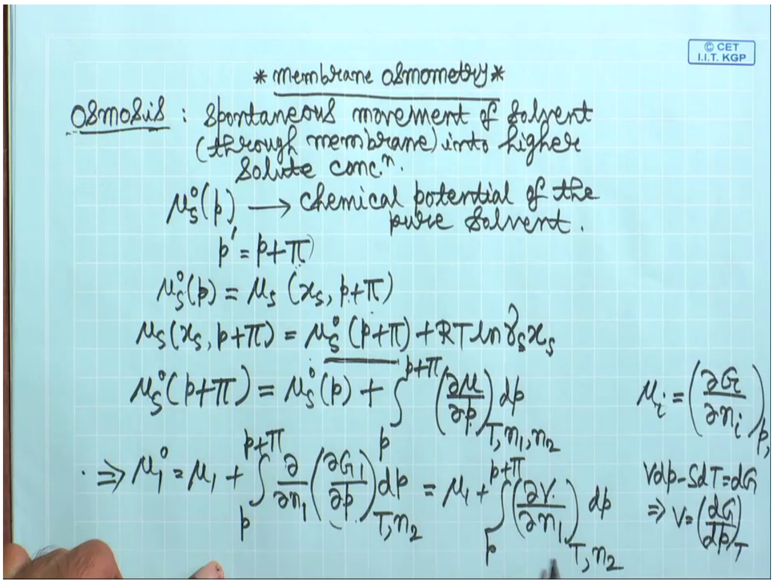

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* Membrane osmometry *

Osmosis : Spontaneous movement of solvent (through membrane) into higher solute conc.^{n}.

$\mu_s^0(p) \longrightarrow$ chemical potential of the pure solvent.

$$p' = p + \pi$$

$$\mu_s^0(p) = \mu_s(x_s, p+\pi)$$

$$\mu_s(x_s, p+\pi) = \underline{\mu_s^0(p+\pi)} + RT\ln \gamma_s x_s$$

$$\overline{\mu_s^0(p+\pi)} = \mu_s^0(p) + \int_p^{p+\pi} \left(\frac{\partial \mu}{\partial p}\right)_{T, n_1, n_2} dp$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,}$$

$$\Rightarrow \mu_1^0 = \mu_1 + \int_p^{p+\pi} \frac{\partial}{\partial n_1}\left(\frac{\partial G_1}{\partial p}\right)_{T, n_2} dp = \mu_1 + \int_p^{p+\pi} \left(\frac{\partial V}{\partial n_1}\right)_{T, n_2} dp$$

$$Vdp - SdT = dG$$

$$\Rightarrow V = \left(\frac{dG}{dp}\right)_T$$

So, you know then osmosis I talked about that. So, this is spontaneous spontaneous movement of solvent through membrane into higher solute concentration. So, you can basically have solutions also on both sites on 1 site you will have concentration lower on 1 site may be concentration is higher. So, from the lower concentration site the solvent will flow to the higher concentration site so on and so forth.

Now, of course, the osmotic pressure it will depend on the molar concentration of the solute. So, let us say mu 0 p p is the pressure is the chemical potential of the pure solvent. Now as I told you have to apply a pressure on the solution site let us say p plus pi. So, this pi you have to apply this pressure pi in order to equalise in order to maintain the equality of the level on the solution site say level of the liquid on the solution site and the solvent site.

So, let us say on the solution site then the pressure is p prime which is equal to p plus pi pi is the osmotic pressure. Of course, now under equilibrium condition I am just putting this mu S s as the subscript which is your solvent. So, under equilibrium condition this mu S 0 0 means this tells you this is a pure pure solvent mu S 0 p p is equal to mu s. So, I am just putting here in the bracket some terms to designate, which side it is x S p plus pi. So, this is on the solution site x S is the mole fraction of the solvent in the solution because this is not 1 and p plus pi is the pressure that site is pressure is higher. So, under that condition equilibrium may be reached. So, that the chemical potential of the solvent in pure state is equal to the chemical potential of the solvent in the solution site whatever be the value of this mu S we will look at that after.

Now, general expression of a chemical potential term is x s. So, actually this term we want to have an expression here just to simply the matters further. So, this is on. So, mu is basically is the chemical potential of the solvent in solution in the bracket we are trying to designate, what are the main properties say it has x S is the mole fraction of the solvent in solution p plus pi is the pressure on that site. So, mu typically is equal to mu 0 under that condition plus R T l n activity.

So, this is from physical chemistry this equation is there chemical potential is equal to chemical potential in standard state this pure state and of course, here also you have to see the pressure is p plus pi because you are expressing the chemical potential on this site that plus R T l n activity; activity is equal to activity coefficient which is gamma S into mole fraction of the solvent. Now this mu S 0 p plus pi this particular term what is that value this is basically the chemical potential of the pure solvent when the pressure is p plus pi this is chemical potential of the pure solvent when the pressure is p.

So, now let us have the expression of this mu S 0 p plus pi how the chemical potential the pure solvent at pressure p plus pi is related to the chemical potential of the pure solvent at pressure p that relationship is something like this. So, chemical potential of the pure solvent at pressure p plus pi equal to chemical potential of the pure solvent at pressure p plus, if we do some work in order to increase the pressure from p to p plus pi and that work is equal to del mu del p a change in the pressure, but the temperature and the number of moles are constant number of moles of solute and solvent they are constant into d p. So, it will do some work then only they become equal. So, the chemical potential of the pure solvent in at higher pressure is equal to chemical potential of the pure solvent at a lower pressure plus some work you have to do that is designated by this in order to go from p to p plus pi.

Now, you know this value of mu mu is a chemical potential mu of the i-th component in a mixture for example, that will be equal to the change in free energy with respect to the change in the amount of the number of moles of that particular species in that mixture when the other things are constant for example, p p is not constant here, but I am telling in general p T in j other number of moles say j-th species or whatever. So, this is general expression. So, that expression we are going to bring in here. So, mu is del G del n. So, if you are writing this expression so mu S 0 p plus pi.

So, let us say I am just simplifying this as mu 1. So, mu 1 0 equals to mu 1 plus integral p to p plus pi p plus pi del mu del p. so that mu G will G is related to mu in this condition this way. So, you can actually write it like this del n 1 in this case the species is 1 let us say this is the solvent species. So, del G 1 del p. So, del. So, mu is del G del n and this del is still there. So, that T and n 2 are constant into d p. So, that will be equal to mu 1 plus p to p plus pi del v del n 1 d p T n 2.

Now**,** how this relationship is coming from thermodynamics we know that there is a relation v d p minus S d T equals to d g. So, from here your v is d G d p at constant t. So, the d G d p your expressing that as v. So, that becomes del v del n 1 T and n 2 now this particular expression I am going to write it down again this particular expression.

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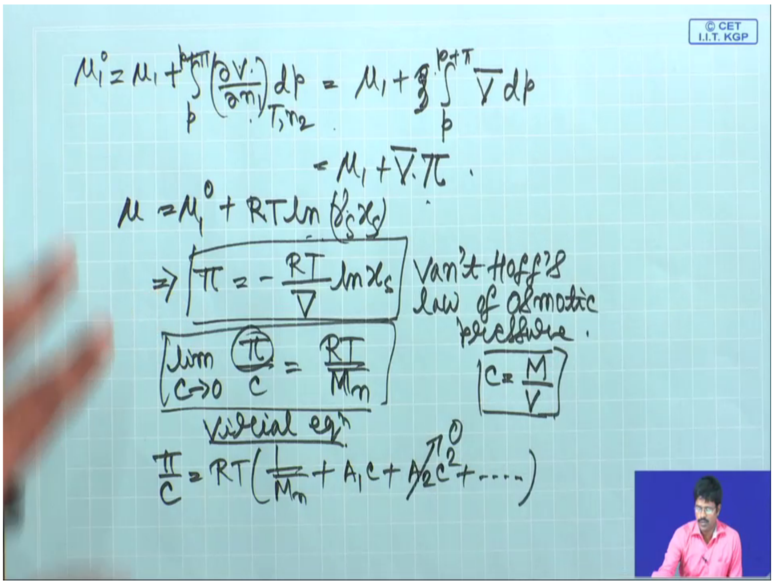

$$\mu_1^0 = \mu_1 + \int_p^{p+\pi} \left(\frac{\partial V}{\partial n_1}\right)_{T,n_2} dp = \mu_1 + \int_p^{p+\pi} \bar{V}\, dp$$

$$= \mu_1 + \bar{V}.\pi$$

$$\mu = \mu_1^0 + RT \ln(\gamma_s x_s)$$

$$\Rightarrow \boxed{\pi = -\frac{RT}{\bar{V}} \ln x_s}$$ Van't Hoff's law of osmotic pressure.

$$\boxed{\lim_{C \to 0} \frac{\pi}{C} = \frac{RT}{M_n}}$$ $$\boxed{C = \frac{M}{V}}$$

virial eq^n

$$\frac{\pi}{C} = RT\left(\frac{1}{M_n} + A_1 C + \overset{0}{\cancel{A_2}} C^2 + \ldots.\right)$$

So, mu 1 0 mu 1 0 is equal to mu 1 0 is equal to mu 1 plus p to p plus pi p to p plus pi del V del n 1 T n 2 constant d p, now this particular relation is nothing, but mu 1 plus integral. So, mu 1 plus integral p 2 p plus pi into v bar d p v bar is nothing, but molar volume so volume per mole. So, this is molar volume. So, in case of an incompressible material liquid this is constant with pressure. So, this can come out from the integration and this becomes equal to mu 1 plus v bar into pi so mu 1 into v bar plus pi.

So, you know this relation mu equals to mu 1 0 plus R T l n x mu equals to mu 1 0 plus R T l n x. So, R T l n x is nothing, but gamma S x S that x is basically you know I am just interesting the terms here if you are this is R T l n activity, activity is equals to gamma S into x S x is the mole fraction I have talked about that before.

So, if you correlate these 2 then your pi becomes equal to minus R T by v bar into l n gamma S into x S now this gamma term very dilute solution gamma S is close to 1 activity coefficient. So, this becomes l n x s. So, basically this is nothing, but Vant Hoff's law of osmotic pressure Vant Hoff's law of osmotic pressure and in the limit where c tends to 0 from here you can show that your pi by C becomes equal to R T by M n, because this volume this volume term you know your concentration is equal to M by v. So, concentration is equals to weight by volume.

So, this equals to R T by M n this is how it comes. So, you know that your pi osmotic pressure is related to your number average molecular weight. And this particular equation we do not use as such like this we expressed in terms of a virial equation and that will be something like this in a power series we express it like this 1 R T into 1 by M n M n bar you can put M n bar that is how we are doing and then some constant into concentration plus some constant into concentration square so on and so forth. Now here since your concentration is very small some of these terms will tend to 0. So, only these 2 terms you take.

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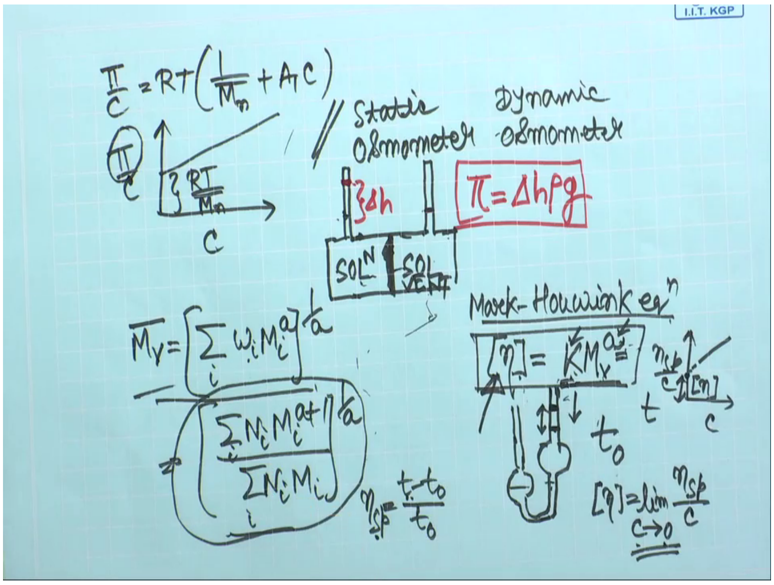

And what you do is. So, pi by C equals to R T into 1 by M n plus A 1 C let us say you have this expression. So, you plot this pi by C as a function of concentration and then what you will obtain is. So, it is a straight line as a function of concentration and it is intercept will be R T by M n.

So, this pressure if you can measure and you take different concentrations of the polymer and then you plot this thing pi b y C verses c and then you can find out R T by M n and as you can see it is an absolute method, because you do not need to create a curve a calibration curve for example, with a polymer of non-molecular weight. So, you can directly put the polymer of unknown molecular weight and you can determine the value of M n here. Now the question remains how to determine this value of pi. So, basically this osmotic pressure you have something called a static osmometer and you have what you call as a dynamic osmometer these are different instrument in order to measure osmotic pressure you can use static osmometre and dynamic osmometer. So, you have. So, I am just drawing a schematic.

So, you have basically chambers like this see you have a semi permeable membrane here say, you have a solution say you have a solvent or solution here and you have the solvent here and you have some capillary here both sides. So, initially both of them have the same height. Now when you put up semi permeable membrane what will happen the solvent will flow on this side and this height will change. So, let us say this height changes to here. So, this difference of the height this difference of the height is equal to your osmotic pressure that will be equal to delta h delta h is this difference of the height.

So, this difference of the height is basically correlated to the osmotic pressure. So, that osmotic pressure is equal to difference in height into the density of the liquid into g. So, from here you can find out the osmotic pressure. So, what you typically do in dynamic osmometer although we would not discuss it too much is that you measure the solvent flow from the solvent site to the. So, the to the solution site and how do you measure that you have some air bubble there the movement of air bubble will give you an idea of the solvent flow from the solvent to the solution site.

And then you have basically another solvent reservoir that is attached elephant with this solvent vessel this part. So, that solvent reservoir you can lower that solvent reservoir or you can raise that solvent reservoir and that way you can adjust the pressure on the solvent site and this lowering or raising of the solvent reservoir that is related to the osmotic pressure that is how you can determine in a dynamic osmometre the osmotic pressure. So, as you can see if you compare with the vapour pressure measurement vapour pressure experiment and this osmotic this membrane osmometry, so you can see that this is an absolute method you do not need a reference molecular weight compound to start with in contrast to your vapour pressure method where you have to actually have a reference in order to know the value of constants. So, that is a relative method and this is a absolute method.

So, now we have discussed 2 methods for M n determination 1 is relative 1 is absolute we still have some time remaining in this class. So, what we will do now is to tell you about another viscosity method viscosity average molecular weight, another molecular weight we will tell you about other than the weight average and number average molecular weight there is another 1 viscosity average molecular weight we talked about it before, but we did not tell what it is in detail so that we will talk about right now.

So, this is M v viscosity average molecular weight is basically this w i into M i to the power a to the power 1 by a, now you might know that there is something called mark Houwink equation. Now this Mark-Houwink equation correlates your intrinsic viscosity with the molecular weight in this case, I am turning it as the viscosity average molecular weight by these 2 constants these are Mark-Houwink constants which are specific for a specific polymer solute polymer as a solute specific polymer solvent system this K and a values are specific or constant.

So, from there you know the intrinsic viscosity expression from the Mark-Houwink equation and that a is this a. So, this w I w is the weight fraction you know that when we had say the weight average molecular weight the expression was summation w i into M i where w i is the weight fraction of the species for which the molecular weight is M i. So, i x species and here it is to the power a and whole to the power 1 divided by a.

Now, and this particular thing is nothing, but equal to sum over i N i you can work it out yourself a plus 1 divided by sum over i N I M i i mean here I am putting M N as capital or you can put n as small is such the symbolism nothing else to the power 1 by a. And so in the next class what I am going to do is that, I am going to talk about how we derive this particular expression, but before we go to that this class in conclusion first I will talk about the determination of this intrinsic viscosity and how you correlate with the molecular weight.

So, this particular expression and this particular expression you can actually use both of these expressions to determine the molecular weight. So, what we do is that we have Ostwald viscometer and we have very dilute solution of your polymer in the solvent very dilute solution you take and you make different concentrations of the polymer in that particular solvent.

So, in the Ostwald viscometer again this is not to scale you have something like this. So, you have something like this and in there you have 2 lines. So, what you do is that you take a liquid here and you pull the liquid up beyond this line and allow the liquid to come down after and the time it takes to pass between these 2 lines you record it either by visual inspection or by some other means you record that particular time. So, what you do is that for the solvent you record this time which is nothing, but T 0 and for the liquid that is your solvent plus solute in this case it is a dilute polymer solution this mixture for that you record this particular time. So, that will be say T.

Now, you can define specific viscosity here also specific viscosity is equals to t minus t 0 by t 0 and the specific viscosity is related to the intrinsic viscosity by this particular equation your intrinsic viscosity is equal to eta specific divided by the concentration at the limit where C tends to 0. So, if you can determine this specific this intrinsic viscosity that and if you know the value of K and a I am assuming you know the value of K and a we might talk about how to determine it later. So, if you know those values then you can determine a molecular weight average molecular weight which is viscosity average molecular weight.

So, how do you do that? So, you prepare polymer solutions of different concentrations and you determine this value of t, suppose you prepare 4 concentrations then you can find 4 different times corresponding to the time it takes for the solution to come from this point to this point. So, the limit t 1 t 2 t 3 t 4 and that t 1 t 2 3 t 4 correspondingly you can find the value of eta specific and then what you do is you plot this eta specific divided by C as a function of concentration, it will be something like this a straight line and then you extrapolate that to 0 concentration. So, that in the limit of C tends to 0 this value here will be basically your intrinsic viscosity. So, from there you can directly find out the average molecular weight provided you know the value of K and a.

So, what we will do is that we will stop here today and tomorrow we will start with how we can determine this particular expression, how you can have N be correlated with this because we are actually finding similar expressions for M w and M n. So, an expression of this shot might be useful for M v.

So, thank you for your attention for this class; what we will do in the next class is after we discuss about the average molecular weight determination from viscosity method we will talk about average molecular weight, weight average molecular weight determination by different means.

Thank you.