Science and Technology of Polymers

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Lecture - 12

Structure and Properties of Polymers (contd.)

Good morning, today we will continue the structure and properties relationship of polymer materials. In the last class, I told you that there is a relation of properties with the molecular weight, with the increase in molecular weight the properties, different properties increase up to certain molecular weight, at beyond weight it levels up. That means beyond certain high molecular weight, the property increments and not very pronounced. So, this indicates that while you are synthesizing or manufacturing the polymer, you can stop at some point where one can get adequate level of properties.

Now, since there is a dependence of properties on the molecular weight, now you must know the molecular weight or you must estimate the molecular weight or you must determine the molecular weight of polymers. You know since the polymer samples are mixture of molecules of different sizes of different molecular weights, so we must calculate the molecular weight with the help of averaging techniques. Now, there are basis like number count basis, rid bases, viscosity bases like this. That means through end group analysis, we can count the number of molecules of different size present in the sample of polymer or by measuring the viscosity we can calculate the molecular weight of polymers.

Today, we will see those expressions for averages averaging of molecular weight in various ways. Say number of average molecular weight, what is number average molecular weight? You know this relation, that if you divide a mass of a material by its total number of moles present, if you divide some quantity of material by its number of moles, then you can get the molecular weight, a simple concept.

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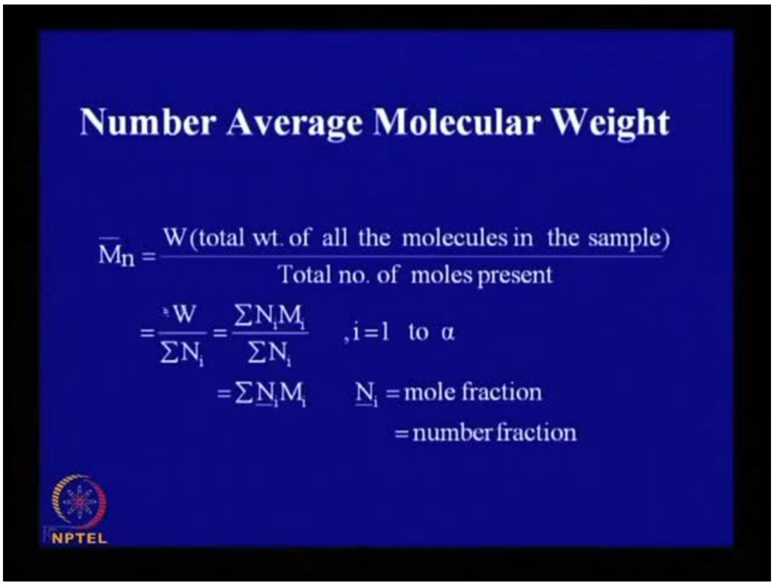

Number Average Molecular Weight

$$\overline{M}_n = \frac{W\text{(total wt. of all the molecules in the sample)}}{\text{Total no. of moles present}}$$

$$= \frac{W}{\sum N_i} = \frac{\sum N_i M_i}{\sum N_i} \quad , i = 1 \text{ to } \alpha$$

$$= \sum \underline{N}_i M_i \qquad \underline{N}_i = \text{mole fraction}$$

$$= \text{number fraction}$$

From that concept here you see, the number average molecular weight can be calculated using this relation. Now, since it is based on counting of number of molecules of any species, say if you consider i th species. In ith species there are N number of molecules having M molecular weights. Then sum of, that means each species will can be considered as one fraction, one part. So, sum of this total, sum of this total mass is the weight of the polymer.

We have taken for measurement of or determination of molecular weight. In the denominator see, sum of N sum of N sum of N means the total number of moles present in the mass. So, this relation gives you number of average molecular weight. Here is the parameter, it is the mole fraction or number fraction. This is very simple thing, if you little analyze this equation you will understand.

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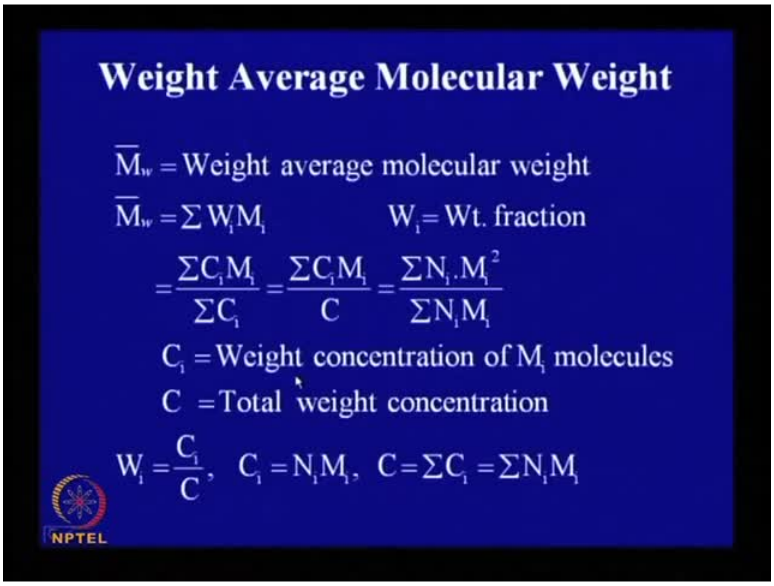

Weight Average Molecular Weight

$\overline{M}_w$ = Weight average molecular weight

$\overline{M}_w = \Sigma W_i M_i$ $\quad$ W_i = Wt. fraction

$$= \frac{\Sigma C_i M_i}{\Sigma C_i} = \frac{\Sigma C_i M_i}{C} = \frac{\Sigma N_i . M_i^2}{\Sigma N_i M_i}$$

C_i = Weight concentration of M_i molecules

C = Total weight concentration

$W_i = \frac{C_i}{C}$, $C_i = N_i M_i$, $C = \Sigma C_i = \Sigma N_i M_i$

Weight average molecular weight, by measuring the weight of the individual molecule or individual fractions. In the last class I told you how you can fractionate a polymer a polymer sample? By dissolving the polymer in a solution, a solvent you will get the polymer solution. Then by solvent programming, you can isolate several fractions several fractions having molecules of different sizes or different molecular weights. From there you can calculate this weight average molecular weight. It is the sum of weight fraction of i th species multiplied by molecular weight of that particular species. If it is expressed in terms of concentration, then you can have this kind of relations introducing the concentration terms of i th species.

Then if those are converted to number of moles or molecules, whatever it may be, then the expression for weight average molecular weight becomes sum of the product of Ni and Mi square divided by the total concentration C, which is equal to sum of product of sum of the product of molecules with their mass of the each species present in the sample. This is not very difficult thing and here is how these are defined. These parameters are defined, they are explained over here. Another parameter comes Z average molecular weight.

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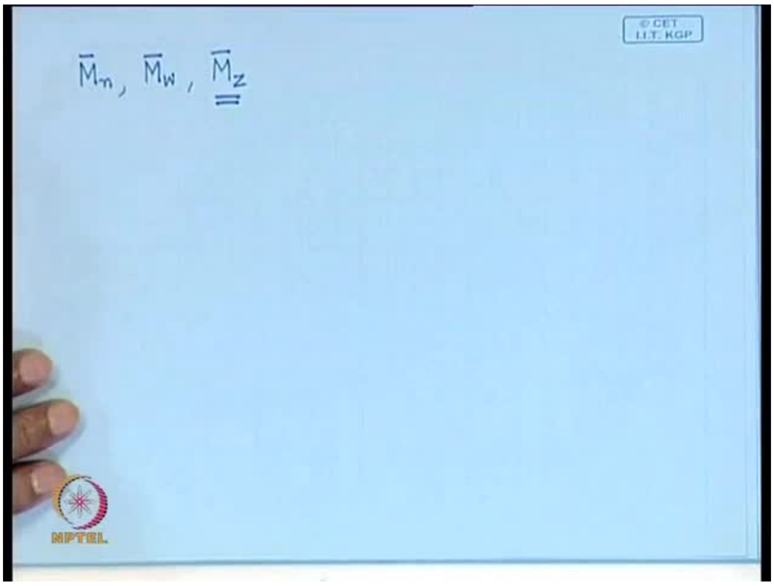

$\overline{M}_n$, $\overline{M}_w$, $\underline{\underline{\overline{M}_z}}$

So, what we have seen? We have seen that we can get number average molecular weight, weight average molecular weight and z average molecular weight. Actually in this Z average molecular weight more weightage is given on this product Ni Mi square because it indicates that the higher molecular weight molecules are weighted even more heavily in this case, than in the case of weight average molecular weight.

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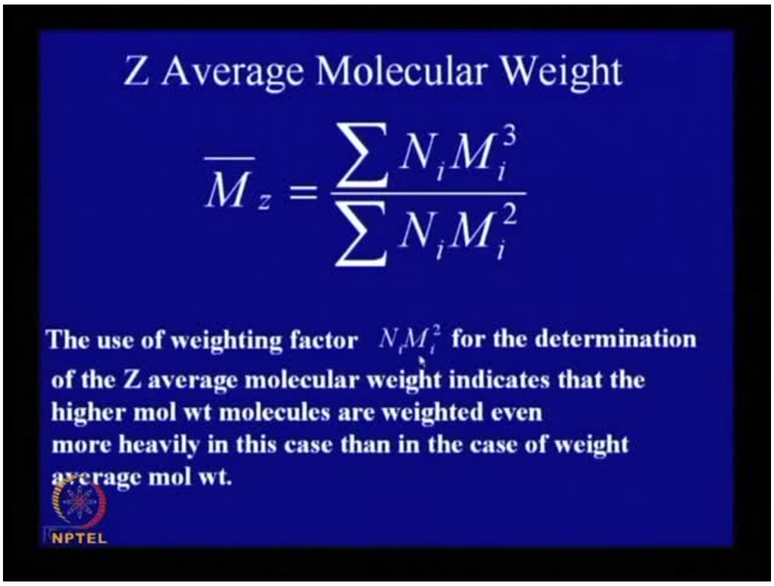

Z Average Molecular Weight

$$\overline{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

The use of weighting factor $N_i M_i^2$ for the determination of the Z average molecular weight indicates that the higher mol wt molecules are weighted even more heavily in this case than in the case of weight average mol wt.

So, this is another averaging technique weight average technique, but if you deal with MN bar or MW bar, then there is one more averaging technique. I will come later MV bar viscosity of molecular weight.

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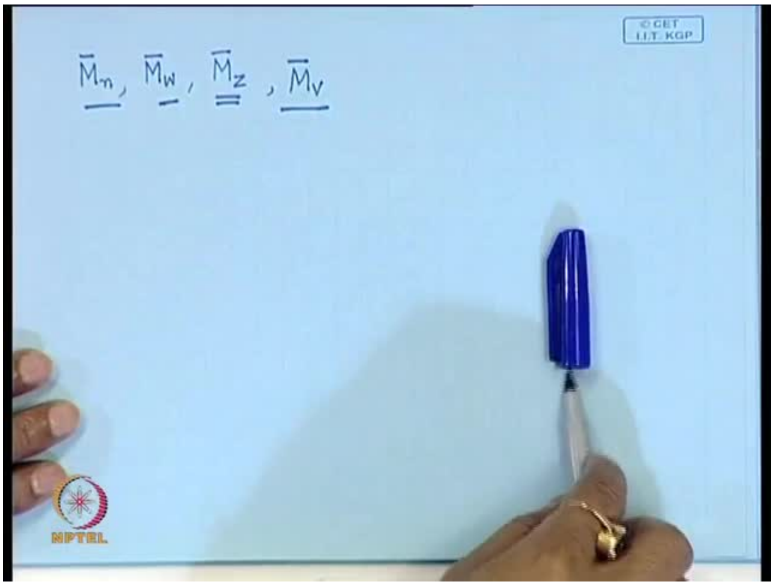

So, with the help of these average average molecular weights, we can draw a molecular weight distribution curve. From the molecular weight distribution curve we can see we can see or we can understand the nature of the, understand the polymer material. We can have some indication about its processability, about its fabrication behavior, about its properties. so we can have certain indication.

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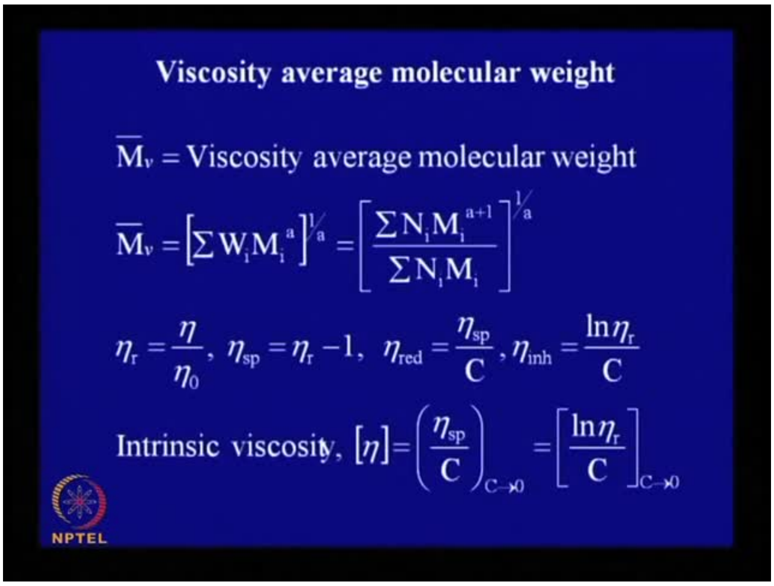

Viscosity average molecular weight

$\overline{M}_v$ = Viscosity average molecular weight

$$\overline{M}_v = \left[\sum W_i M_i^{a}\right]^{1/a} = \left[\frac{\sum N_i M_i^{a+1}}{\sum N_i M_i}\right]^{1/a}$$

$$\eta_r = \frac{\eta}{\eta_0},\ \eta_{sp} = \eta_r - 1,\ \eta_{red} = \frac{\eta_{sp}}{C},\ \eta_{inh} = \frac{\ln \eta_r}{C}$$

Intrinsic viscosity, $[\eta] = \left(\frac{\eta_{sp}}{C}\right)_{C \to 0} = \left[\frac{\ln \eta_r}{C}\right]_{C \to 0}$

Now, look at the viscosity average molecular weight. Here again this viscosity average molecular weight is calculated with the help of weight fraction and weight fraction of one species multiplied by the molecular weight of that particular species to the power a some exponent a is there. a a small a and whole to the power sum of this parameter product raise to the power 1 by a. Again if you split W i into N i and M i so it is a plus 1. In the screen probably you cannot see properly, it is a plus 1 divided by sum of product of N i and M i raise to the power 1 by a.

So, this is the expression for weight average molecular weight. You need to practice of calculating molecular weights. In the book you can get some data, say weight fraction data and corresponding to that weight fraction you can have molecular weights. Datas, data weight fraction data are provided with their molecular weights in the book. With the help of those data you can calculate this weight average molecular weight, viscosity average molecular weight and number average molecular weight even Z average molecular weight.

So, there are certain problems in the exercises given, so you calculate solve those problems. So, you will understand how to determine the molecular weight? Then calculate the average molecular weights of a polymer sample. Now, the most important thing comes is viscosity. Since, it is viscosity average molecular weight, how this viscosity average molecular data are obtained? That means how this data can be generated from the polymer sample you have?

You have a polymer sample, then if you are asked to measure the viscosity average molecular weight, how to do? So, you have to take a viscometer, you have in your lab previous lab classes you have measured the viscosity of the solvent viscosity of a solution you have seen. That can be obtained by measuring the flow times through a narrow capillary, that means you have to take a capillary viscometer. Could you name a capillary viscometer? No, that is not a viscometer Ostwald viscometer.

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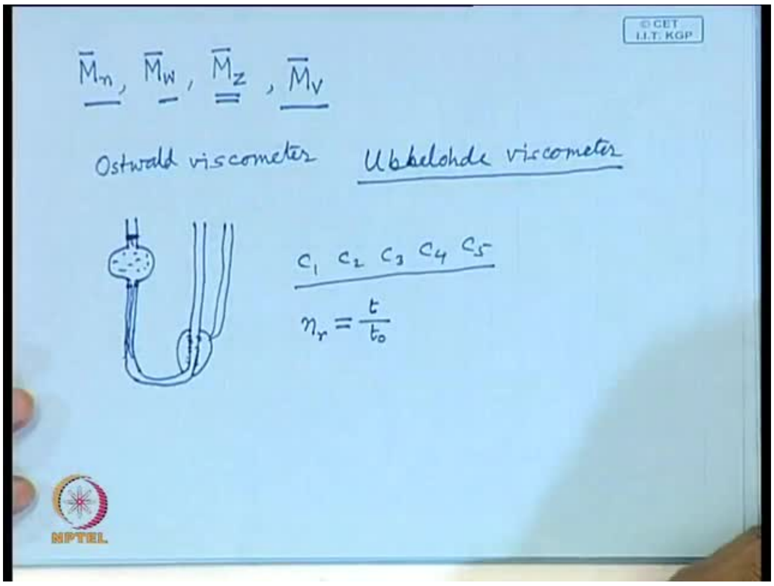

$\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, $\bar{M}_v$

Ostwald viscometer Ubbelohde viscometer

c_1 c_2 c_3 c_4 c_5

$\eta_r = \frac{t}{t_0}$

How it looks? It has a a simple Ostwald viscometer here, is a mark and inside there is a narrow capillary. You fill this ball with the solution up to this mark by sucking with the help of a sucker, it can have one ball over here. It can have a ball over here, there is no problem. You can have a ball, so that you can have a more volume of liquid, more volume of solvent or more volume of solution. You can take over here, so this is one Ostwald viscometer. So, when this liquid actually is passes through this capillary by the action of gravity, you can measure the flow time.

You take a stop watch, you suck the liquid to this limb reach beyond this level, then you start counting time when the meniscus starts coming down from this level, till it crosses this another mark over here. So, that is the flow time for this solvent or liquid that is passing through this capillary. So, with the help of that flow time, you can calculate the viscosity, but for polymer another viscometer is used that is known as Ubbelohde viscometer, Ubbelohde viscometer. Now, in this viscometer there is a provision for dilution within this ball, which is having another limb over here.

So, you can see this diagram of Ubbelohde viscometer given in text books. You can see Ubbelohde viscometer, there if you want to measure the viscosity of solution of varying concentration, if you start with one higher concentration, then you can introduce calculated quantity of solvent. So, that you can go for higher dilution and you can have other concentrations or dilute concentrations from the first one. So, in this way you can have concentrations C 1, C 2, C 3, C 4, C 5 in grams per deciliter.

So, taking only one concentrated solution, you can have so many measurements of flow time, for so many different concentration. Then the question arise is, where is the necessity? Why should we go for that? Every time I can drain out this solution then fill with fresh solution, then what you have to do? While you are draining out this thing then some quantity will remain adhered at the inner wall of the operates. So, you have to rinse it again you have to dry it, again you have to fill with next concentration. So, that is a combustion process.

In order to avoid that, if you start with one concentration just add calculated quantity of solvent for the next concentration. Record it and then record the flow time, from this way you will get the different flow times. So, you can get this relative viscosity from the ratio of the two flow times, flow time for the solution and flow time for the pure solvent. Eta 0 is equal to t by t 0 or eta by eta 0. That is the relative viscosity, it is shown over here. Then specific base viscosity is the eta relative minus 1 and reduced viscosity is eta specific by C. C is expressed in grams per deciliter, then eta inherent ln eta relative by C.

So, if you get this flow time for this solution as well as the solvent, so this relative flow time will help you to get different viscosity terms; specific viscosity, reduced viscosity, inherent viscosity. Inherent viscosity can give some idea about the molecular weight of the polymer, not exactly the exact value of molecular weight, but it can help you to know about the molecular size some rough idea approximate idea. Then, there is another viscosity term which is written here intrinsic viscosity. What is intrinsic viscosity? Now, here you have to have some certain concept, you have to gather this intrinsic viscosity.

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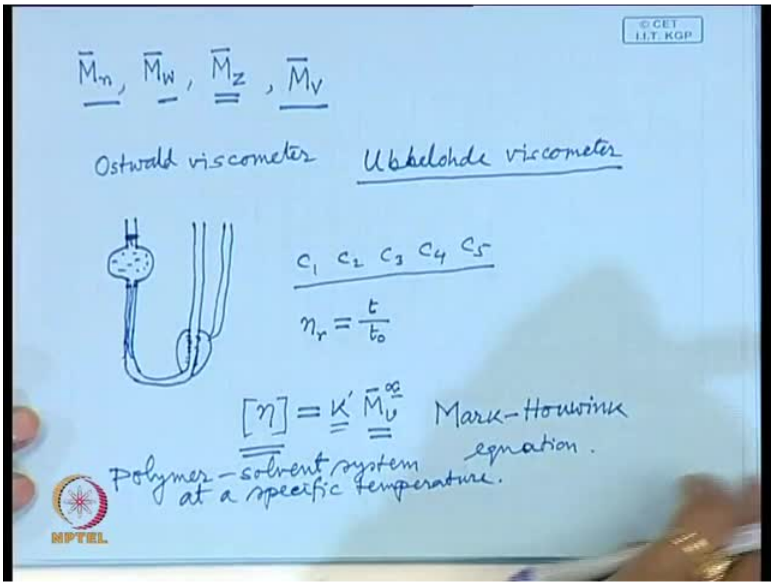
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$\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, $\bar{M}_v$

Ostwald viscometer   Ubbelohde viscometer

$c_1 \quad c_2 \quad c_3 \quad c_4 \quad c_5$

$\eta_r = \frac{t}{t_0}$

$[\eta] = K' \bar{M}_v^{\alpha}$ Mark-Houwink equation.

Polymer-solvent system at a specific temperature.

Intrinsic viscosity is a viscosity term which is related to eta in the square bracket is equal to some constant say k or k prime into MV bar, that viscosity average molecular weight rise to the power alpha or A. That means this intrinsic viscosity is related to molecular weight because there is an obvious question, sir after measuring this flow times then how can you get this viscosity average molecular weight data? How can we get?

So, that is related to this thing, it is actually known as this equation is known as Mark-Houwink equation. It is a famous equation Mark-Houwink equation, which relates viscosity average molecular weight with the intrinsic viscosity. What are these? These are actually constant parameters dependent on a particular polymer solvent system for a specific polymer solvent system at a specific temperature. Hope you will not forget this relation, intrinsic viscosity is related to viscosity average molecular weight and two parameters, two constants parameters are there k prime and alpha or k and alpha. These parameters are known as polymer solvent interaction parameters.

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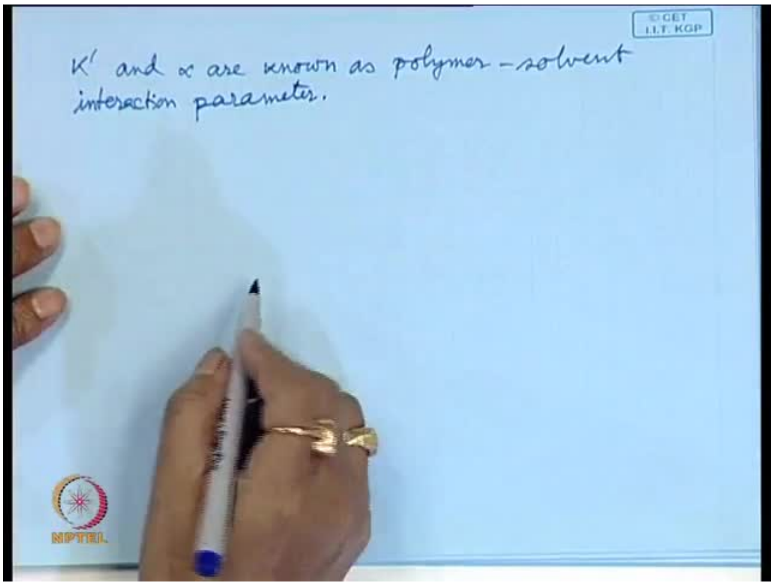

K′ and α are known as polymer-solvent interaction parameter.

What are this polymer solvent interaction parameters? I was telling you in the last class, that when you put a solute in a solvent, that solute can enter into solution can make a solution only when there is a interaction between the solvent. Solute that interaction depends on the cohesive energy density cohesive energy density of both the components. If the cohesive energy density of both the components are close to each other, then only they can form a solution, that is related to miscibility of a solute with a solvent. Now, here you can extend your concept of alloy metal, alloy in metal alloy.

What we, do we just put a foreign substance in a base metal, if that foreign substance becomes soluble in the base metal. Then we get an alloy, so there is some concentration limit for the alloying element in a base metal. If it is a solution, solid solution then we call it an alloy, am I right? Alloy is the solid solution of foreign substance in a metallic alloy. Similarly, you can get polymer alloy, a solid solution. You can dissolve one polymer in another, if two components of the polymer are highly miscible or one soluble in the other, then we can say it is a miscible polymer blend or polymer alloy.

On the contrary you can see that some polymer can be miscible to a limited concentration and sometimes one component made even dispersed in the base polymer. The stages of these two components can distinctly viewed under electron microscope, that we cannot call a miscible blend. Although it is a blend physical blend, so this physical blend alloy and solution, solid solution or liquid solution all these are formed based on the cohesive energy density of each of the components. What is cohesive energy density? Again that is related to the bonding force that means the residual force fields which is available surrounding a molecule.

That force field actually enter into inter molecular interaction in terms of cohesive energy density. If these two your cohesive energy density of the two components is very close, then only they can form a solution here. When a polymer is put in a solvent, what happens? This solvent molecules being smaller that can penetrate inside the balk of the solid polymer samples molecules. That means if the cohesive energy density of these two close to each other, then the salvation energy of the solvent will be sufficient enough to break inter molecular forces between the molecules solid solute or solid polymers, you understand?

So, here this terminology comes inter polymer solvent interaction parameter. These are all polymer solvent interaction parameter and this polymer solvent interaction parameter for one system of polymer. Their solvent differs from other system of polymer and their solvent, am I clear? This is very simple thing. So, looking at the cohesive energy density, we can calculate the solubility capability, solution capability solution capability of a solvent for a polymer. We can calculate that, we will see that thing later with the help of solubility parameter and molecular weight of the repeatively of the polymer as well as the density of the polymer.

With this parameters one can calculate the solubility parameter of a solvent as well as the solubility parameter of a polymer. Again these solubility of parameters gives a measure of cohesive energy density. So, I think it is clear to you, that when a polymer is put in a solvent, if the salvation energy of the solvent is higher, then the inter molecular force of the polymer molecules. Then only the solution can happen and there are terminal considerations also. Pre energy of mixing of solvent and polymer should be negative, then only one can get solution. So, here k prime and alpha polymer solvent interaction parameter, if those values are known for a system, then from this relation that is this eta entity is equal to k prime and MV bar to the power alpha.

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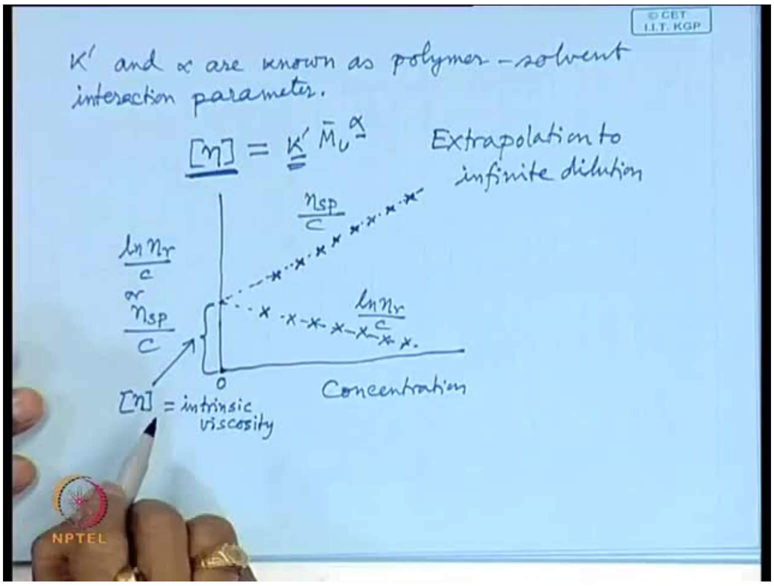

K′ and α are known as polymer – solvent interaction parameter.

$[\eta] = K' \bar{M}_v^{\alpha}$

This is an experimental, experimental determinable parameter, you are getting from its flow times and these are available from data book at a particular temperature. Because the viscosity is measured at a constant temperature, flow time is measured at a constant temperature, by immersing the viscometer in a thermostatic bath, all right? So, at that particular temperature you have to find out the values of k prime and alpha, then only you can get this eta r.

From eta r you can get this parameters, it has specific, eta reduced and eta inherent. Now, what is intrinsic viscosity? These are null these are not intrinsic viscosity how to obtain intrinsic viscosity. So, you have to make a plot of either ln eta related by C or eta specific by C. This you can calculate from the flow times against concentration. This is 0 concentration and you have to measure the viscosity of different fractions or different concentrations. So, what you can get? You can get say eta specific by C. Suppose, for different concentration you are getting eta specific by C values, then you extra pole it to this axis y axis.

If you plot ln eta relative by C, it can show you relation like this. So, this is eta specific by C and this is ln eta relative by C. Extra piloting to y axis, that means at 0 concentration which is known as extrapolation to infinite dilution, infinite dilution extrapolation to infinite dilution. Now, this value actually is known as eta intrinsic or intrinsic viscosity, you understand? Intrinsic viscosity, why this is necessary?

Extrapolation to infinite dilution you have to have a concept again. Now, you have you have…

Student: (( ))

Yes you are right, to attain an ideal situation. Ideal situation means again you have dissolved certain quantity of a polymer in solvent. Now, there will be interaction between polymer and solvent as well as polymer and polymer. If the concentration is more that is for higher concentration, there will be more interaction between polymer and polymer molecules because this polymers actually the configuration of polymer in solution looks like this.

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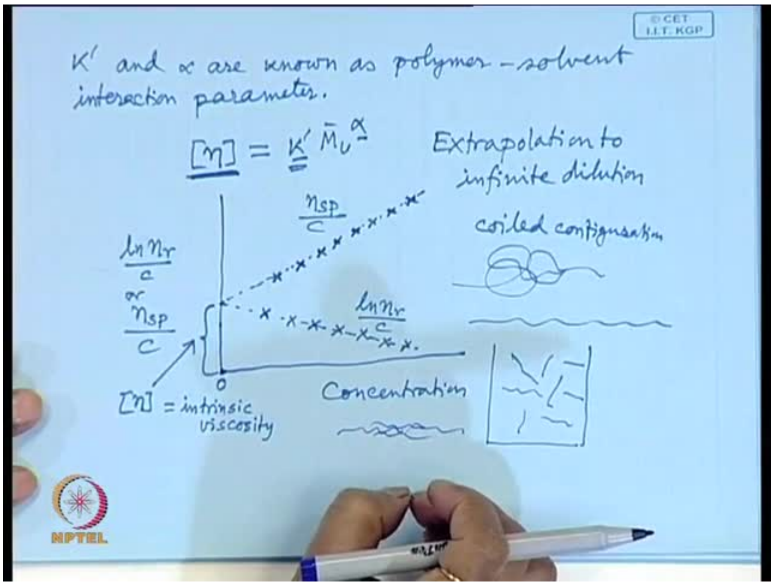

K′ and α are known as polymer - solvent interaction parameter.

$$[\eta] = K' \bar{M}_v^{\alpha}$$

Extrapolation to infinite dilution

It remains in folded and curved configuration, it is not for that linear molecule remains like this in this configuration. That means coil configuration, this is actually called coiled configuration. In a dilute solution, it is expected or that is the ideal situation, ideal case where if you assume that the polymer solvent interaction parameter cohesive energy density of the polymer and the solvent are almost same. If you assume in that case, in that case, the polymer can assume its extended chain configuration in a solution.

So, the contact between one polymer molecule with the another polymer molecule will be minimized in infinite dilution hypothetical situation. In that hypothetical situation condition of concentration, we can expect that in a polymer solution, you can have isolated molecules not even touching each other. Why it is necessary? Now, when this polymers are flowing in solution, state through capillary. Through capillary if one molecule remains attached or close to another polymer molecule, then the resistance offered against the flow is fully more. Now, here you get one more concept. If you have given two samples of a polymer having same molecular weight same, say 5,00,000 each per gram, but one is linear and another is branched. Two samples, sample one and two both are having same molecular weight and this sample one contains linear molecules and sample two contains branched molecules.

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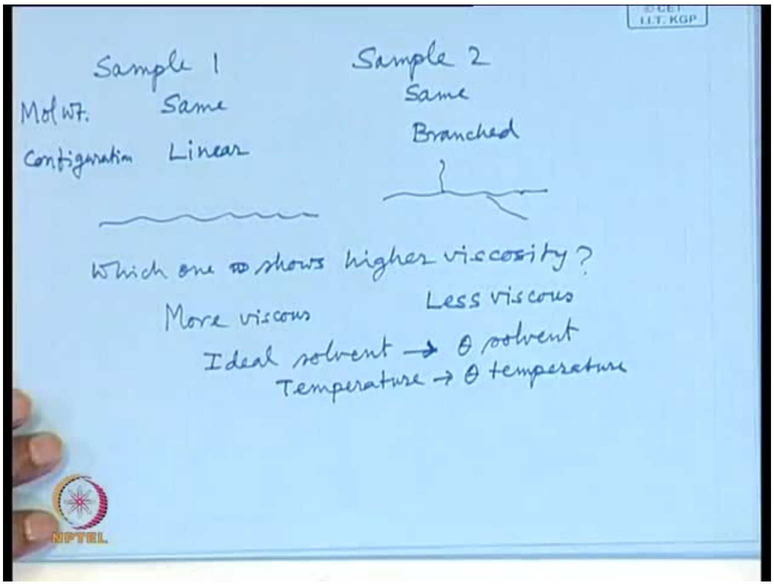

	Sample 1	Sample 2
Mol wt.	Same	Same
Configuration	Linear	Branched

Which one ~~to~~ shows higher viscosity?

More viscous

Less viscous

Ideal solvent → θ solvent

Temperature → θ temperature

Again if I show you in this way, so this is the length of the polymer molecule. Now, this length can be, can be shown this way. So, overall length and overall mass of the polymer is same. This is branched and this is linear, you tell me when you measure the viscosity of the sample one and sample two, taking same concentration same concentration of these two samples, how the viscosity of two will be same?

Student: (( ))

You are telling viscosity of sample one will be more, what you are telling density you have taken the same concentration that means the quantity of polymer is same in both the cases. Only difference is that one is linear and another one is branched.

Student: (( ))

You are telling it is more viscous and it is less viscous.

Student: (( ))

So, you have divided into two groups one group is telling the linear will be more viscous. The other group is telling sample two will be more viscous, then what is the correct answer? Who can say?

Student: (( ))

Which way? If I agree with you that linear molecule linear configuration offers more resistance,

Higher surface (( ))

Higher surface, surface is same. It is not the question of surface.

Student: (( ))

No, you just forget about the entanglement. It is the ideal situation, an ideal situation where I said that the cohesive energy density or solubility parameter of of polymer and the solvent are very close. I mean to say the solvent is ideal, known as another parameter theta solvent and the temperature at which it is measured viscosity is measured is known as theta temperature. That means it is a hypothetical situation or ideal situation, where the solvent polymer interaction is minimum. I have not got the answer to this question that, which one will be more viscous?

Probably I have to say because you are just opposing the answers, so I have to solve the problem. This sample one will be more viscous. The reason is when in case of ideal solution, very dilute solution this molecule is gyrate or rotate during movement through the capillary, all right? It is not that true that this molecules always will penetrate the capillary through one end, it is not that kind of good boy, it will take its own course that you have to think on radius of gyration. So, this system will provide higher radius of gyration than this one. Suppose, if you are sitting in a chair. Now, you are sitting in a chair in attention position.

So, if you are just told to sit in this fashion for more than 2 hours, you will become impatient. You need to stretch your legs and hands, twist your body, twist your head also because of the free energy requirement, isn’t it? From free energy point of view, you need to stretch your hands, legs, you like to stand all. Now, you think of the volume you require now while you are sitting in the attention position. Now, if you stretch your hands, legs, you stretch your hands, legs this way, this way and if you stand then, so the space requirement will be more. So, that is the radius of gyration in case of branched that an remain squeezed so the radius of gyration of this system will be less.

So, this will be of less viscous, then this linear configuration for all these reasons actually there was necessity of extrapolation to infinite dilution here. That means in order to eliminate all sorts of interaction problems, interaction polymer polymer interaction problems and coiling problems, we can expect that in dilute solution, in theta solvent at theta temperature this molecule will give extended chain configuration. Then only we can get the proper flow time proper viscosity because bases on this flow time data and viscosity data, we are going to calculate the molecular weight, mind it.

So, if it remains in coiled configuration like this, coiled configuration, then can we get the accurate data. Know it will give you misleading data or misleading result of molecular size, that is why when we like to measure the molecular weight by viscosity measurement, we have to go for this higher dilution or extrapolation to 0 concentration infinite dilutions. Because you cannot, because at this regions, at this region the flow times will be same for solvent and the solution are very close. You cannot distinguish where as you have to start with.

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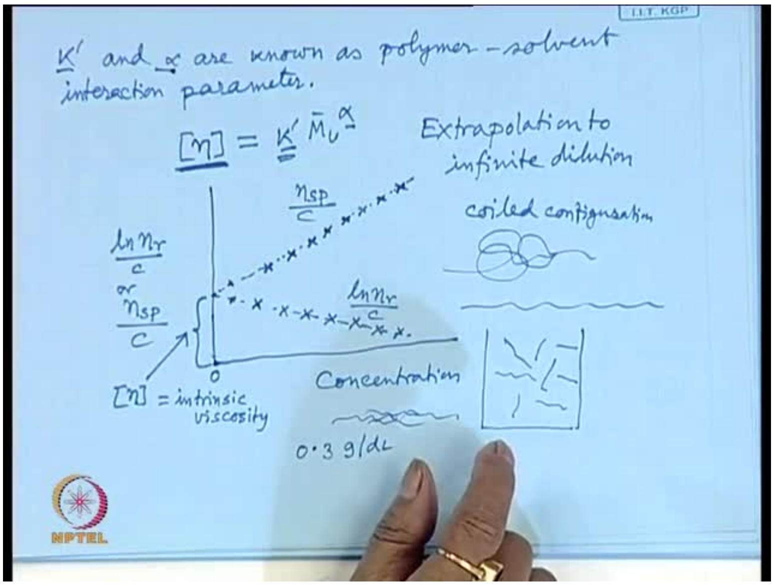

K′ and α are known as polymer – solvent interaction parameter.

$[\eta] = K' \bar{M}_v^{\alpha}$

Extrapolation to infinite dilution

coiled configuration

Say you have to start with probably point 0. say 3 grams per deciliter and onwards 0.3, 0.5, 1, 2, 3, 4 grams per deciliter like this, then only you can get this type of curve. During your lab class you take one polymer sample dissolve in a suitable solvent. Say for example, say polymethyl methacrylate, dissolve in chloroform or benzene measure the flow times and then calculate these viscosity parameters.

Then after plotting you get this intrinsic viscosity and then from data book, you get the values of this k prime and alpha polymer solvent interaction parameters. At that temperature at which you have measured the flow times and you can calculate the molecular weight. So, it is shown the intrinsic viscosity. Intrinsic viscosity either you can go through specific viscosity at C tends to 0 means infinite dilution or ln eta relative by C up to infinite dilution.

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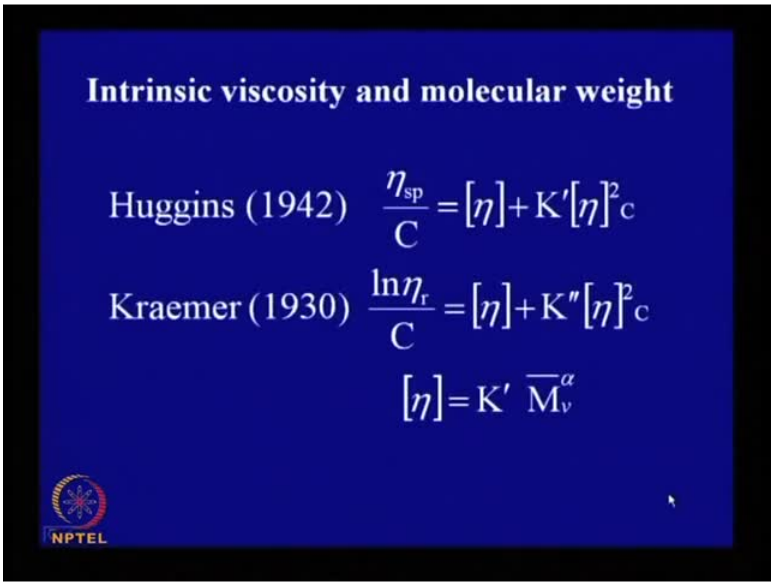

Intrinsic viscosity and molecular weight

Huggins (1942) $\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 c$

Kraemer (1930) $\frac{\ln \eta_r}{C} = [\eta] + K''[\eta]^2 c$

$$[\eta] = K' \,\overline{M}_v^{\alpha}$$

Now, there are two equations which relates this specific viscosity and inherent viscosity inherent viscosity. This is actually, this is actually inherent viscosity. This is specific viscosity reduced viscosity and inherent viscosity and this is related to intrinsic viscosity by this relation. This is Huggins equation, this is Kraemers equation and these are constants and the difference between the these two constants are 0.5.

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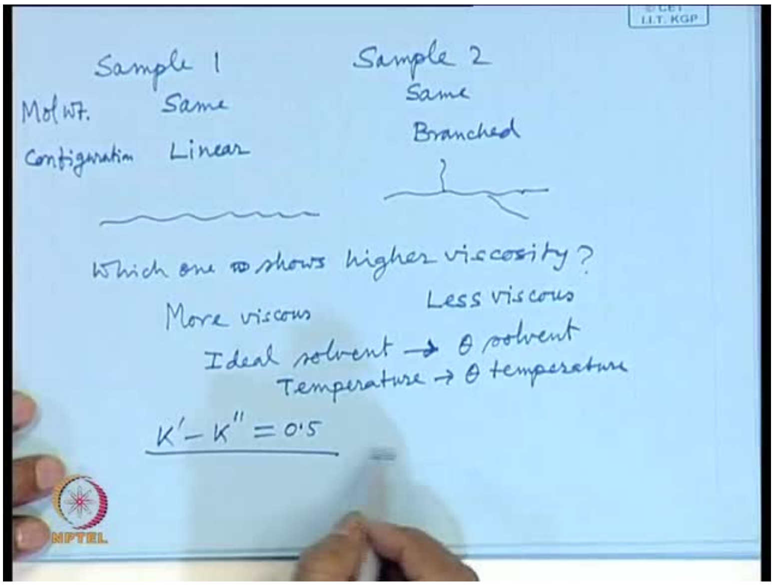

	Sample 1	Sample 2
Mol wt.	Same	Same
Configuration	Linear	Branched

Which one ~~to~~ shows higher viscosity?

More viscous Less viscous

Ideal solvent → θ solvent

Temperature → θ temperature

$K' - K'' = 0.5$

K prime and K double prime is equal to 0.5. Now, one question can arise, sir if we are unable to measure the flow times of a polymer solution of varying concentration, but if we measure a flow time of the solution of single concentration, is it possible to get this intrinsic viscosity value? Then can we calculate the molecular weight is a question. You have seen in the previous case that, I told you that you have to measure the concentration your flow times for different concentration, but if not have that access, if you have only one flow time data, can we get it?

Then how can we get this eta intrinsic, this value? Eta intrinsic? Without extrapolation to infinite dilution we cannot calculate this eta intrinsic, intrinsic viscosity. Can anybody think of? Suppose, if you know these two equations, know these two equations Huggins equation and Kraemers equation. With the help of these equations from a single point flow time measurement or flow time measurement of a single concentration solution of a polymer, is it possible to get this eta intrinsic value? How?

Student: (( ))

Yes, very good. Yes, it is possible by simple algebraic sum, by simple algebraic sum you can get it because you have told that the difference between these two is 0.5, so you can substitute one of these two constants. Then by some simple algebraic sum because concentration C value is known, ln eta relative value is known, eta sp value is known and then you calculate this eta intrinsic. Once you get it, then from this relation you can calculate the viscosity average molecular weight. So, this is the way how to calculate the viscosity average molecular weight?

This is the easiest way to get some molecular weight value of a polymer provided provided you get this K prime and alpha value from the data book. Because this K prime and alpha value have been evaluated or obtained from some absolute measure of viscosity by some other technique using samples of known molecular weight. Now, in that case you have MV bar values. Then you measure the intrinsic viscosity of that polymer sample. From there you can calculate K prime and alpha. So, this way this K prime and alpha values has been evaluated from one polymer solvent system. This way you can have say polyethylene benzene, you can have polyester DMF system or you can have poly (( )) tetrahydrofuran.

That means if you put into tetrahydrofuran, it will dissolve or if you can take polystyrene and tetrahydrofuran or benzene. So, these values for these polymer solvent system at one different temperature systems, those are available in data book. So, those data are computed calculated by measuring the your obsolete molecular weight of those polymer by some other techniques and taking that polymer sample of known molecular weight by viscosity measurements. These data has been evaluated that is K prime and alpha.

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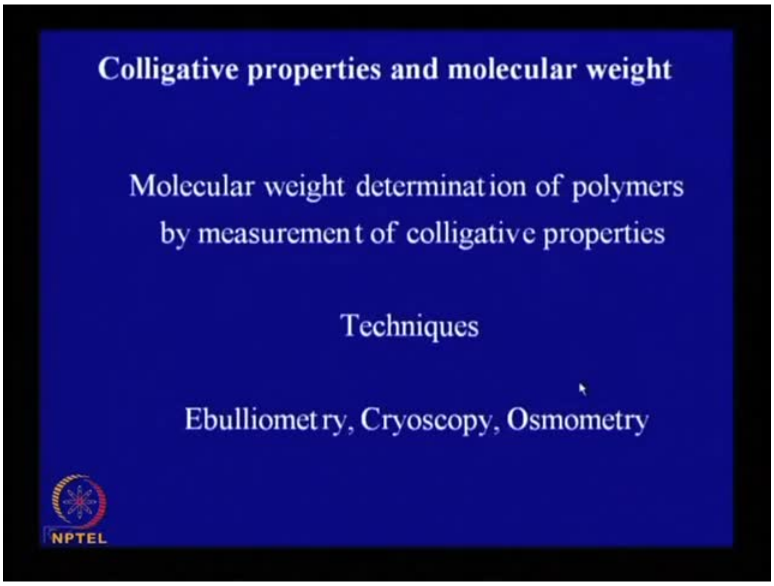

Colligative properties and molecular weight

Molecular weight determination of polymers by measurement of colligative properties

Techniques

Ebulliometry, Cryoscopy, Osmometry

Now, this slide shows colligative properties and molecular weight molecular weight determination of polymers by measurement of colligitive properties. What are those? Techniques are ebulliometry, cryoscopy and osmometry. Elevation of boiling point, depletion of freezing point and the osmotic pressure. So, with the help of these techniques one can get the molecular weight of polymers.

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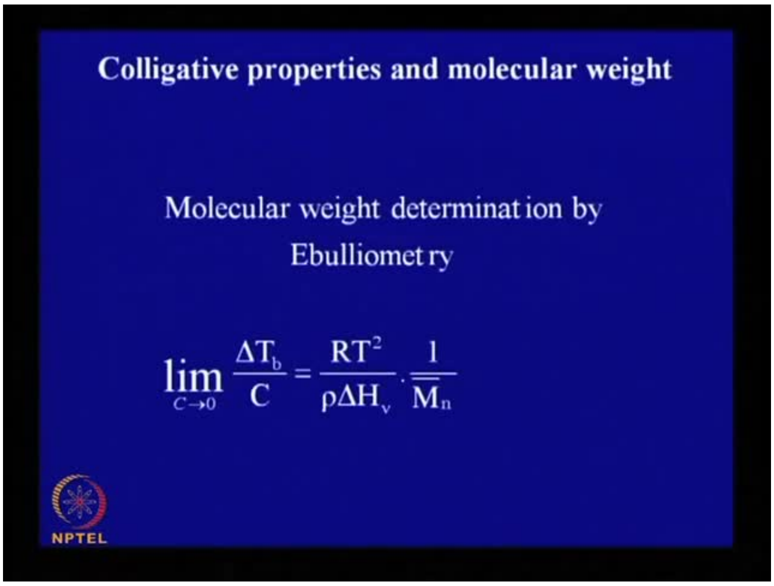

Colligative properties and molecular weight

Molecular weight determination by
Ebulliometry

$$\lim_{C\to 0}\frac{\Delta T_b}{C} = \frac{RT^2}{\rho\Delta H_v}\cdot\frac{1}{\overline{M}_n}$$

So, what is ebulliometry? You know, this is the temperature elevation enthalpy averisation. So, from this values and this is the concentration and this is the number average molecular weight. So, these techniques ebulliometry cryoscopy and osmometry provide you number average molecular weight samples some time. If you have a vapor pressure osmometer, vapor pressure osmometer with the help of vapor pressure osmometer one can calculate, one can determine number of average molecular weight of a polymer sample.

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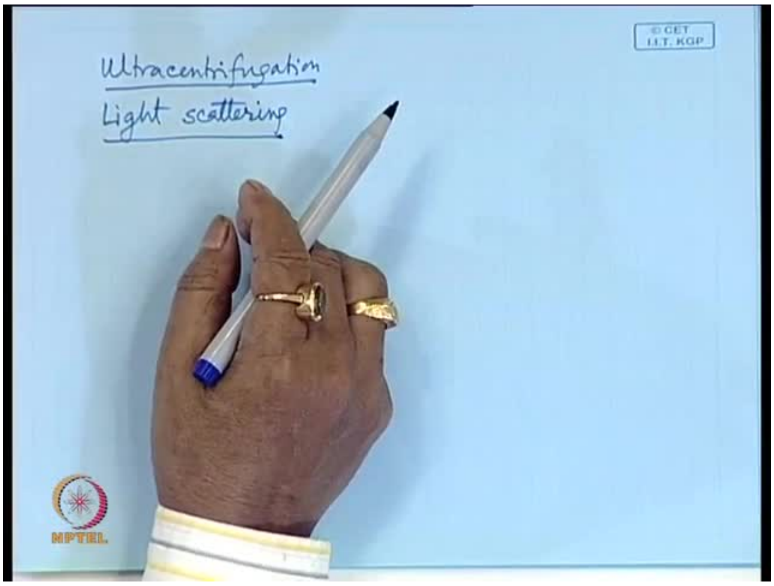

Ultracentrifugation

Light scattering

Other than this there are techniques like ultracentrifugation. This ultracentrifugation gives you weight average molecular weight because you have the experience of centrifuging a dispersion or a suspension or even a solution, you know due to ultracentrifugal force. So, you can separate a suspension or separate a solid from an immolation by ultracentrifugation by that technique. One can calculate the molecular weight or light scattering techniques, one can calculate, one can determine the molecular weight.

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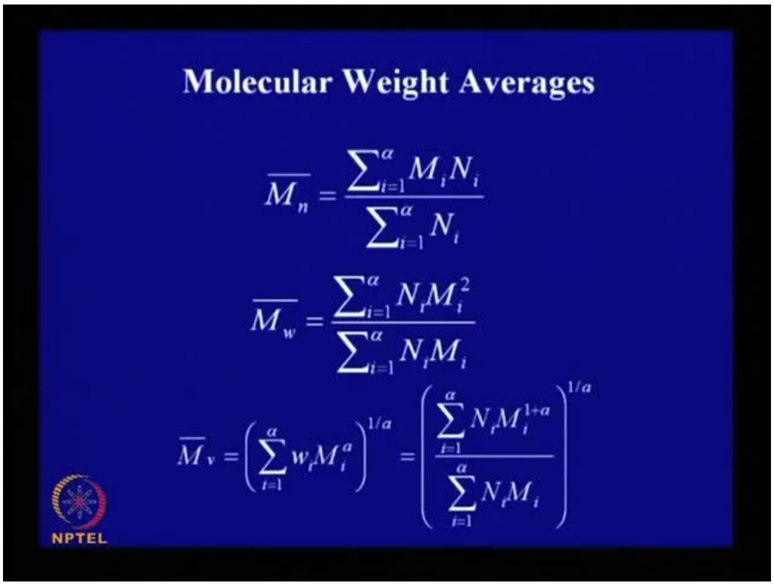

Molecular Weight Averages

$$\overline{M_n} = \frac{\sum_{i=1}^{\alpha} M_i N_i}{\sum_{i=1}^{\alpha} N_i}$$

$$\overline{M_w} = \frac{\sum_{i=1}^{\alpha} N_i M_i^2}{\sum_{i=1}^{\alpha} N_i M_i}$$

$$\overline{M}_v = \left(\sum_{i=1}^{a} w_i M_i^a\right)^{1/a} = \left(\frac{\sum_{i=1}^{a} N_i M_i^{1+a}}{\sum_{i=1}^{a} N_i M_i}\right)^{1/a}$$

So, look at the summery of this molecular weight, average number, average molecular weight, weight average molecular weight, viscosity average molecular weight.

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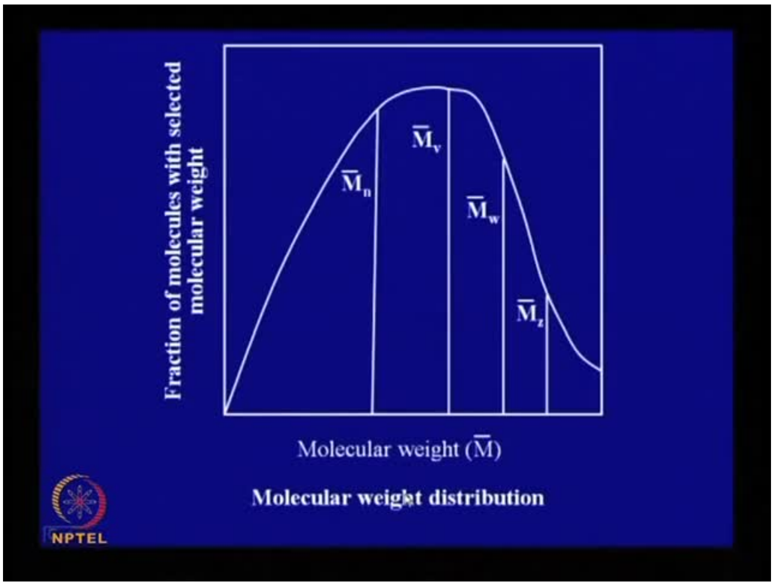

Molecular weight distribution

Then you draw the distribution curve. This is a distribution curve for different fractions of polymer solution having different molecular weight. So, where does this number average can be located or the viscosity average or weight average can be located or the Z average can be located? This shows that Z average molecular weight is higher than weight average molecular weight than viscosity average molecular weight, than number average molecular weight. So, the number count gives you the determination molecular weight of a polymer sample having low molecular weight, species for low molecular weight polymers for high molecular weight sample. If you want to measure the molecular weight by number average technique, then the result will be wrong misleading

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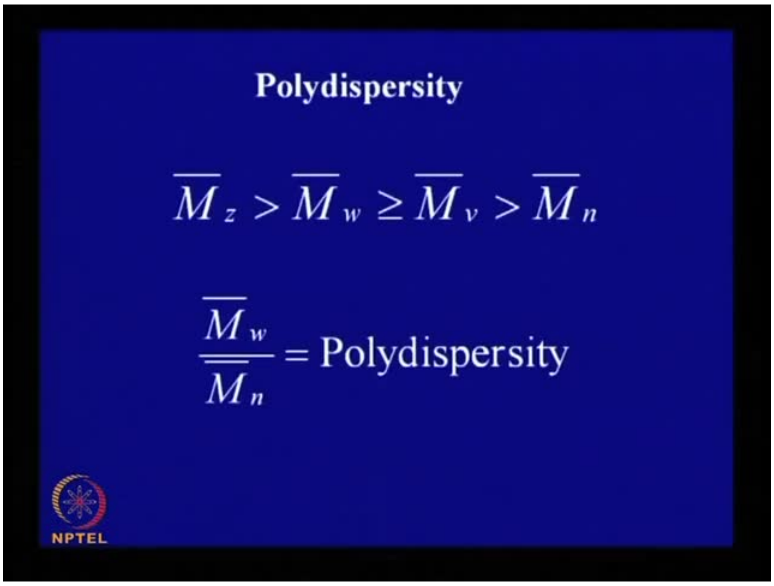

Polydispersity

$$\overline{M}_z > \overline{M}_w \geq \overline{M}_v > \overline{M}_n$$

$$\frac{\overline{M}_w}{\overline{M}_n} = \text{Polydispersity}$$

So, the relation is you see look at this thing M z bar is greater than Mw bar greater than or equal to M v bar greater than to M n bar. M n bar is the lowest and the ratio of these two parameters M w bar over M n bar or M z bar over M n bar is known as polydispersity.

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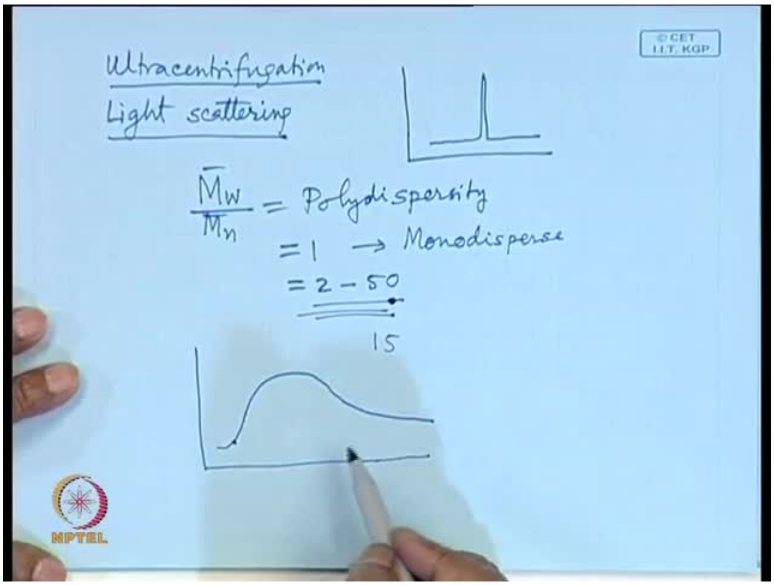

Ultracentrifugation

Light scattering

$\frac{\overline{M}_w}{\overline{M}_n}$ = Polydispersity

= 1 → Monodisperse

= 2 – 50

15

If this is equal to 1, this is known as monodisperse. In that case the distribution curve look like this. Disperse monodisperse, the polydispersity can be 2 to 50. Suppose, it is more than 1 it can range from 2 to 50. Higher the polydispersity, then you can have inferior properties of the polymer inferior property, higher the polydispersity. Suppose, if a polymer sample of say polydispersity 15, means it indicates the broadness of the distribution like this. That means this is a mixture of molecules of very low molecular weight with medium molecular weight with higher molecular weight. So, this polydispersity value is an indication of processibility of a polymer either by solution or by melt technique.

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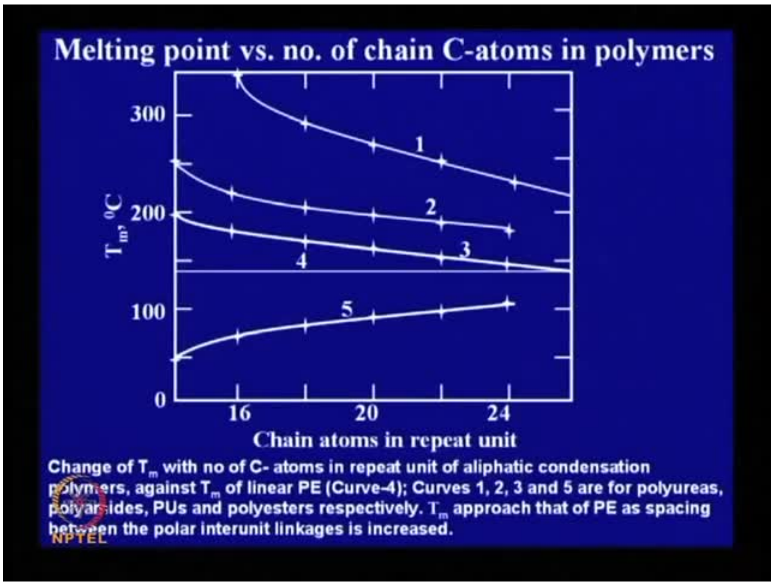

Melting point vs. no. of chain C-atoms in polymers

Change of T_m with no of C- atoms in repeat unit of aliphatic condensation polymers, against T_m of linear PE (Curve-4); Curves 1, 2, 3 and 5 are for polyureas, polyamides, PUs and polyesters respectively. T_m approach that of PE as spacing between the polar interunit linkages is increased.

Now, during processing what is the situation we face, when you place some polymer in a machine for compounding, compounding? I mean a polymer product, I told you a polymer product is a mixture of pure or original polymer with functional additives. So, this this is a polymer product it contains say colorants, it contains lubricants, contains stabilizer, it contains curing agent, all these things. Now, polymer is a high viscosity material and these additives are either liquid or solids. So, you have to mix this liquid or solid additives in the form of particles for the solid additives or particular additives.

You have to disperse this properly into the matrix of the polymer. So, that is done by working the polymer by sharing force in a machine at elevated temperature, then only one can get proper fluidity or viscosity of a polymer. So, that it can show a show an adequate melt viscosity property flow behavior or rheological property. So, that it can be transferred to a mold and then it can fill the mold. So, that you can get one particular shape, there it needs a lubricant or some plasticizer say PVC. I told you PVC, we can have rigid PVC or flexible PVC, rigid PVC, you have seen medicine files where this capsules tablets are packed in some transparent with the help of some transparent plastic sheets.

These are rigid PVC sheets. Whereas this same PVC when it is mixer with some extra plasticizer like dibutyl phthalate, it becomes flexible leather like. So, plasticizer PVC is known as artificial leather plasticizer PVC is known as artificial leather, whereas rigid PVC does not contain any plasticizer. So, there is a difference between pure polymer sample and a mixture of polymer sample and a plasticizer of a low molecular weight. Now, here why I have told this thing? Now, if in a polymer sample, you can see there are certain fractions of low molecular weight species; that low molecular weight species will act as plasticizer. You understand? So, that adds to the processing behavior of the polymer.

Thank you.