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

Lecture - 30
Frictional Properties of Solutions (Contd.) and Determination of Molecular Weight

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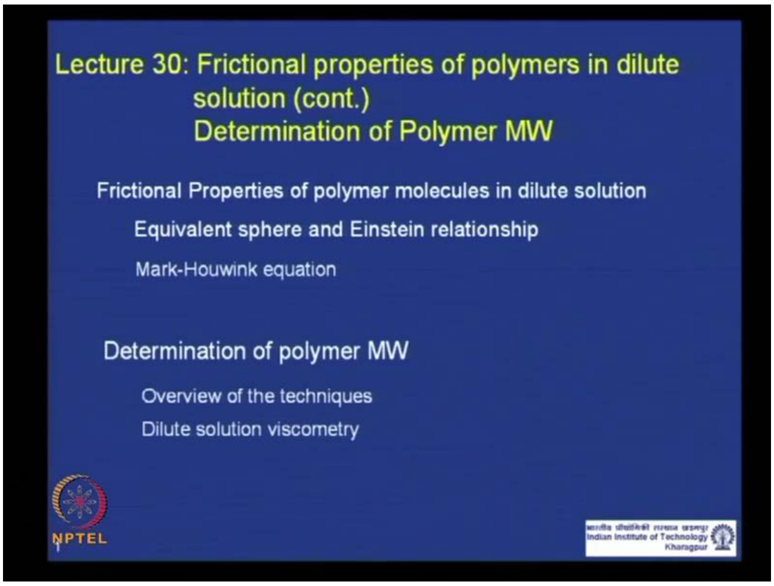

Lecture 30: Frictional properties of polymers in dilute solution (cont.)
Determination of Polymer MW

Frictional Properties of polymer molecules in dilute solution
- Equivalent sphere and Einstein relationship
- Mark-Houwink equation

Determination of polymer MW
- Overview of the techniques
- Dilute solution viscometry

So, welcome back to this course on polymer chemistry, and in this lecture today we are continuing our discussion which is left over from last lecture on frictional properties of polymer in dilute solution. And then we will begin the important discussion on polymer characterization which is basically how to determine polymer molecular weight. We plan to give just an overview of the techniques which can be used for a polymer determination of polymer molecular weight today. And if time permits we will continue and discuss the method of dilute solution viscometry by which we can determine viscosity average molecular weight.

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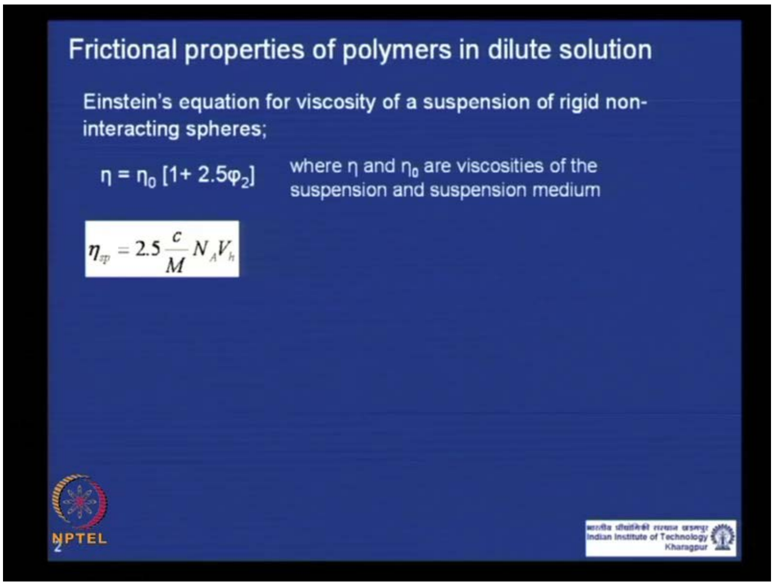

Frictional properties of polymers in dilute solution

Einstein's equation for viscosity of a suspension of rigid non-interacting spheres;

$\eta = \eta_0 [1 + 2.5\varphi_2]$ where η and η_0 are viscosities of the suspension and suspension medium

$$\boxed{\eta_{sp} = 2.5 \frac{c}{M} N_A V_h}$$

Now let us continue the discussion we are having in last lecture. Now as we understand in last lecture that most of the chain most of the polymer chains are flexible, and when they are dissolved in solution and they are moved in solution, they actually carry the solvent molecules which are attached to the polymer coil; they move along with the polymer coil. So, you can imagine a equivalent sphere width which contains a polymer chain and the solvent molecules as impermeable hard sphere, and for that hard sphere we know that Einstein's equation of viscosity is given by this expression where eta and eta 0 is the viscosities for the suspension and suspension medium which is basically a polymer solution and the solvating medium or the solvent. Now, it can be easily shown to have this expression; let me show that.

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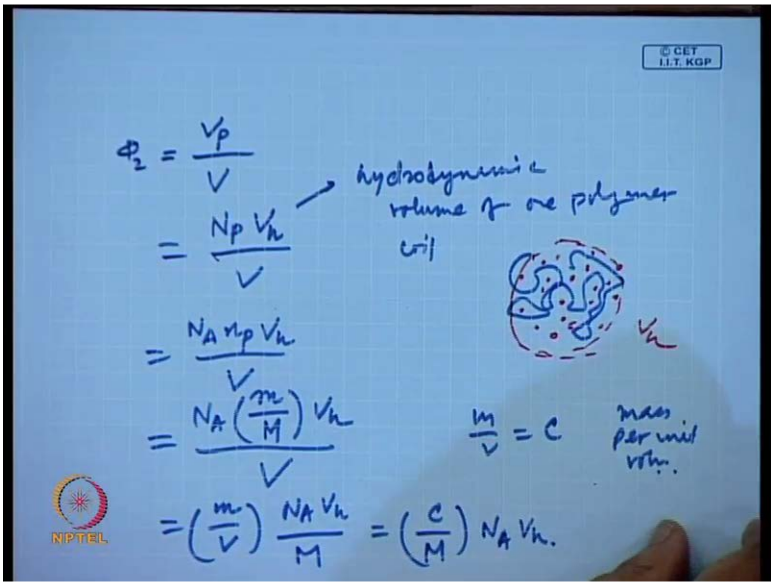

$$\Phi_2 = \frac{V_p}{V}$$

$$= \frac{N_p V_h}{V}$$

hydrodynamic volume of one polymer coil

V_h

$$= \frac{N_A n_p V_h}{V}$$

$$= \frac{N_A \left(\frac{m}{M}\right) V_h}{V}$$

$\frac{m}{V} = c$ mass per unit vol.

$$= \left(\frac{m}{V}\right) \frac{N_A V_h}{M} = \left(\frac{c}{M}\right) N_A V_h.$$

Phi 2 is the volume fraction which is given by volume of polymer divided by total volume; this is total volume. Volume of polymer is given by number of polymer molecules V h; V h is the volume of one polymer, hydrodynamic volume of one polymer coil. It is basically the sphere which I showed in last one; the polymer chain plus the solvent molecules which moves along with the polymer coil and you can imagine an equivalent sphere. So, the V h is the volume of that sphere divide by total volume is the number of particle which is Avogadro number multiplied by moles of polymer V h by total volume N A. The number of polymer and the moles of polymers can be expressed by mass of the polymer divided by the molecular rate of the polymer V h by total volume. This gives m by V N A V h by M; m by V is the concentration, c concentration in mass per unit volume. So, we can write this as c by M N a V h.

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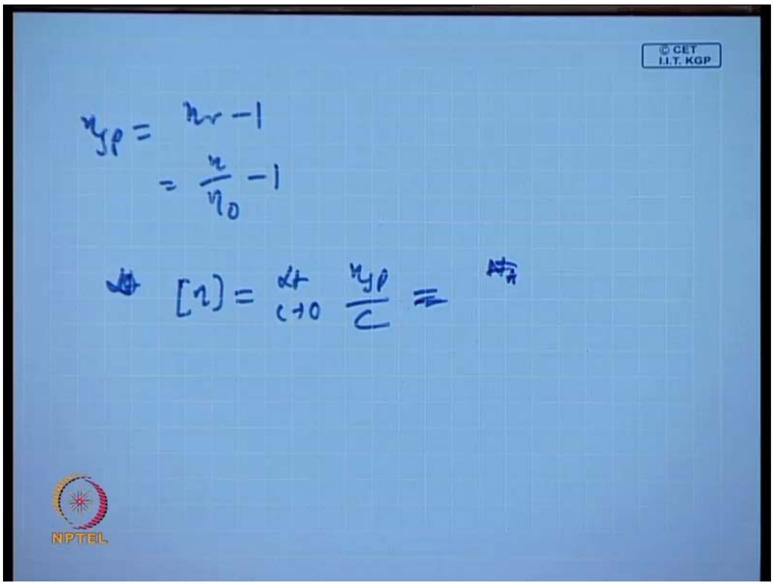

$$\eta_{sp} = \eta_r - 1$$
$$= \frac{\eta}{\eta_0} - 1$$
$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} =$$

And eta s p you know if you recollect; eta s p is eta r minus 1, eta by eta 0 minus 1. So, you can directly write this expression from this. Now I can rearrange it; because increasing viscosity is given by limits c tends to 0 eta s p by c which is basically given by N A eta s p by c which is you can write from here, you divide by c and you get this expression.

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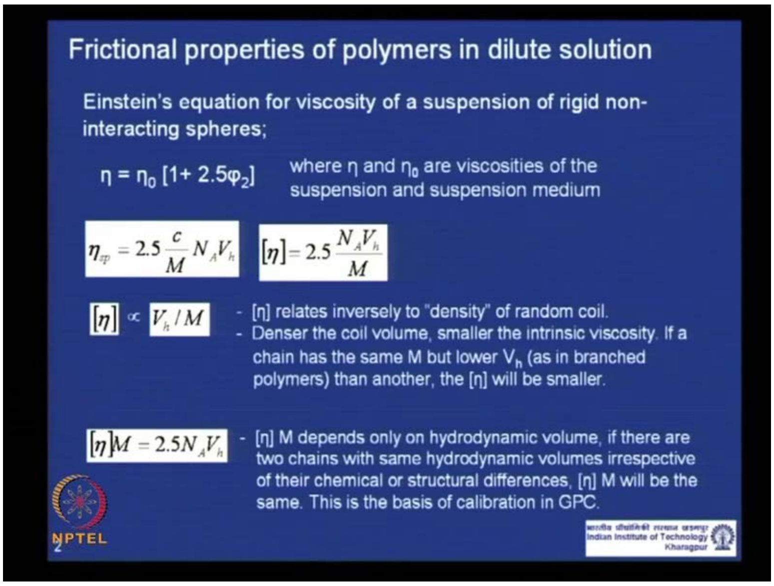

Frictional properties of polymers in dilute solution

Einstein's equation for viscosity of a suspension of rigid non-interacting spheres;

$\eta = \eta_0 [1 + 2.5\varphi_2]$ where η and η_0 are viscosities of the suspension and suspension medium

$\eta_{sp} = 2.5 \frac{c}{M} N_A V_h$ $[\eta] = 2.5 \frac{N_A V_h}{M}$

$[\eta] \propto V_h / M$

- [η] relates inversely to "density" of random coil.
- Denser the coil volume, smaller the intrinsic viscosity. If a chain has the same M but lower V_h (as in branched polymers) than another, the [η] will be smaller.

$[\eta] M = 2.5 N_A V_h$

- [η] M depends only on hydrodynamic volume, if there are two chains with same hydrodynamic volumes irrespective of their chemical or structural differences, [η] M will be the same. This is the basis of calibration in GPC.

Now what does it mean? It means that intrinsic viscosity is proportional to V h by M; V h by m is volume by mass of the polymer coil. This is the volume of a polymer coil one polymer coil and this is the molecular weight; that means mass of one polymer coil; that means intrinsic viscosity relates inversely to the density; it is inverse to the density of the random coil. So denser the coil volume, the smaller the intrinsic viscosity as we have been discussing earlier that if the coil becomes more denser, then smaller is the size and smaller is the intrinsic viscosity for the same molecular weight. If the chain has same molecular weight but lower V h lower size for more compact coil which we can imagine for a applicable or which we will get for a branched polymer. As we discussed for branched polymer if you compare between linear and a branched polymer from same molecular weight, the branch will have more compact volume. So, it may have much lower hydrodynamic volume per coil. So, in that case intrinsic viscosity will be smaller.

Now another information this expression gives is that the term intrinsic viscosity multiplied by the molecular weight is given by this which only depend up on the volume of the polymer coil in the solution. So, intrinsic viscosity does not depend only on the volume; it depends on inverse of the density. But if you have intrinsic viscosity multiplied by the molecular weight, the intrinsic viscosity only this term the intrinsic viscosity multiplied M depends only on the hydrodynamic volume. So, if there are two hydrodynamic chains having same hydrodynamic volume irrespective of the chemical and structural difference, the product of intrinsic viscosity and the molecule would be the same. If the two polymer coils have same hydrodynamic volume, irrespective of their chemical and structural difference, the product of intrinsic viscosity and molecular weight will be same.

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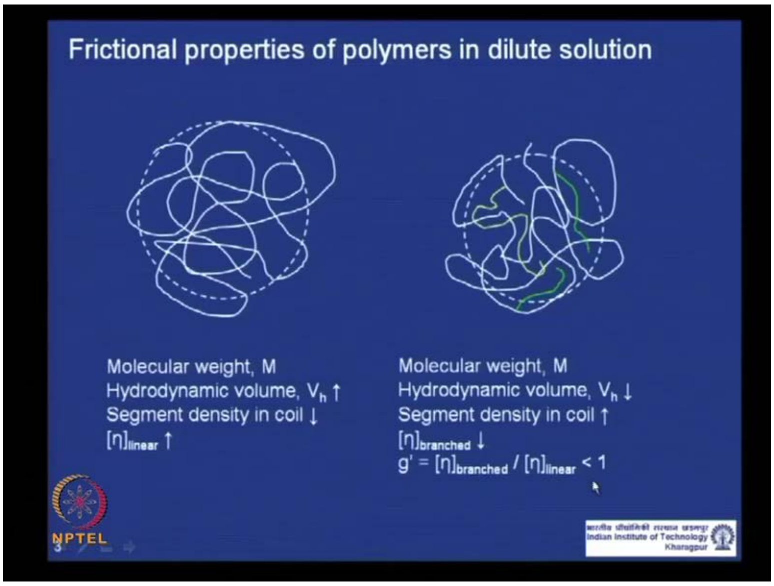

Frictional properties of polymers in dilute solution

Molecular weight, M
Hydrodynamic volume, V_h ↑
Segment density in coil ↓
$[\eta]_{linear}$ ↑

Molecular weight, M
Hydrodynamic volume, V_h ↓
Segment density in coil ↑
$[\eta]_{branched}$ ↓
$g' = [\eta]_{branched} / [\eta]_{linear} < 1$

Now just the same information which we discussed we can compare between a branched chain and a linear chain. These are the yellow ones of the branched of this linear polymer; imagine this two have same molecular weight. If this two have same molecular weight obviously if you have branches then it will have more compact structure. So, hydrodynamic volume will be lower in this case. So, molecular weight is M; in this case molecular weight also M. So, hydrodynamic volume is higher in this case; hydrodynamic volume is higher in this case. Segment density of the coil is lower; segment density is higher. So, intrinsic viscosity of this will be higher than the intrinsic viscosity of the branched polymer chain have the same molecular and if you divide branch by the linear, the value of the branch intrinsic viscosity of linear one you can get the extent of branching in this polymer coil.

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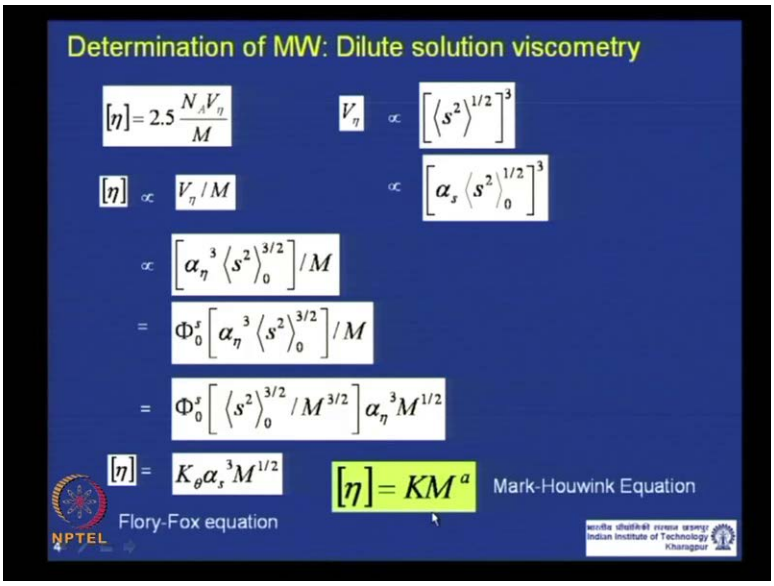

Determination of MW: Dilute solution viscometry

$$[\eta] = 2.5\frac{N_A V_\eta}{M} \qquad V_\eta \propto \left[\left\langle s^2\right\rangle^{1/2}\right]^3$$

$$[\eta] \propto V_\eta / M \qquad \propto \left[\alpha_s \left\langle s^2\right\rangle_0^{1/2}\right]^3$$

$$\propto \left[\alpha_\eta{}^3 \left\langle s^2\right\rangle_0^{3/2}\right]/M$$

$$= \Phi_0^s\left[\alpha_\eta{}^3 \left\langle s^2\right\rangle_0^{3/2}\right]/M$$

$$= \Phi_0^s\left[\left\langle s^2\right\rangle_0^{3/2} / M^{3/2}\right]\alpha_\eta{}^3 M^{1/2}$$

$$[\eta] = K_\theta \alpha_s{}^3 M^{1/2}$$

Flory-Fox equation

$$[\eta] = KM^a$$

Mark-Houwink Equation

Now we will further treat this expression and see whether we can arrive at an expression which can help us in determining the molecular weight by dilute solution viscometry. We have not started discussion on molecular weight determination. So, this title is probably inappropriate at this moment. So, you can just ignore this title for this moment and just concentrate on the mathematical part of this expression. We have got this earlier. So, this was written V h; now we are writing you can consider this as V h. So, I am writing this. Now V h is the volume of the particle. This is the volume of this particle. Now remember while discussing the radius of gyration, we discussed that radius of gyration is almost like the radius of that sphere. So, this radius of gyration would be related proportional to the actual radius of this hydrodynamic polymer coil.

So, the volume V h would be proportional to the R g cube; volume given by four-third pi r square, r is this r. Now this r we said it is proportional to the radius of gyration. If you can recollect our discussion in the definition of radius of gyration, these are very close. So, we can write that V h is proportional; this proportionality sign is missing here. V h is proportional to the radius of gyration to the power 3 and radius of gyration can be written as the expansion factor and radiation gyration for the unpart of chain. So, we can write that intrinsic viscosity is proportional to; the proportionality sign is also missing here is V h which is proportional to this term divide by M.

Now, we can remove this proportionality by applying or introducing a constant; this is a constant. So, we can write intrinsic viscosity is equals to this term. So, remember this should be h because we have mentioned h in the last lecture. So these are all h, V h expansion factor h. So, this is the expansion factor because of the polymer solvent interaction. This is expansion happened due to because the polymer coil is in solvent. We can rearrange this expression and write like this which is just a mathematical rearrangement; you can write this.

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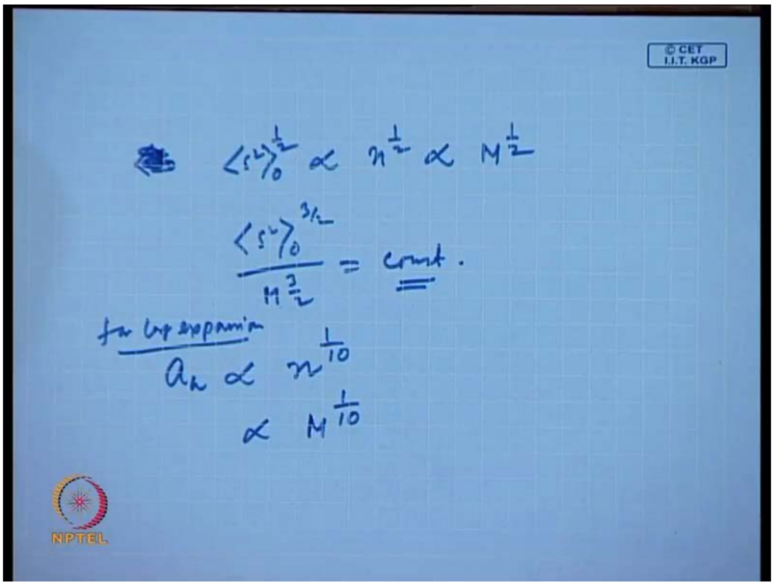

$$\langle s^2\rangle_0^{\frac{1}{2}} \propto n^{\frac{1}{2}} \propto M^{\frac{1}{2}}$$

$$\frac{\langle s^2\rangle_0^{3/2}}{M^{\frac{3}{2}}} = \text{const.}$$

for large expansion

$$a_h \propto n^{\frac{1}{10}}$$

$$\propto M^{\frac{1}{10}}$$

Now if we recollect, this was proportional to n to the power half which is proportional to molecular into half which means three by two divide by m 3 by 2 would be some constant term because this two are proportional. So, what we are doing here; this is a constant as I just discussed, this is also constant and we are clubbing these two in another constant and you have the expansion factor and molecular weight to the power half. These expressions are Flory-Fox equation and remember as we said this expansion factor is for large expansion, it was proportional to n to the power one-tenth. Remember we just discussed in last lecture which just means this is not exactly, but this is approximately proportional. So, it is approximately proportional to n into the power 10.

So, you can now write; you can express this is in terms of molecular weight and then couple those two and write k is M to power A. So, this expression we got from the theoretical calculation which we just carried out but it was before this theoretical expression was arrived by Flory Fox, Mark and Houwink has actually arrived to this expression semiempirically by experimentally. So, this expression is known as Mark-Houwink equation. This equation later we will use for determining molecular weight by dilute solution viscometry So, please remember this expression where k is constant and a is also constant. We will learn more about k and a, and we will discuss the solution determination of molecular in solution viscometry or you can now complete that discussion.

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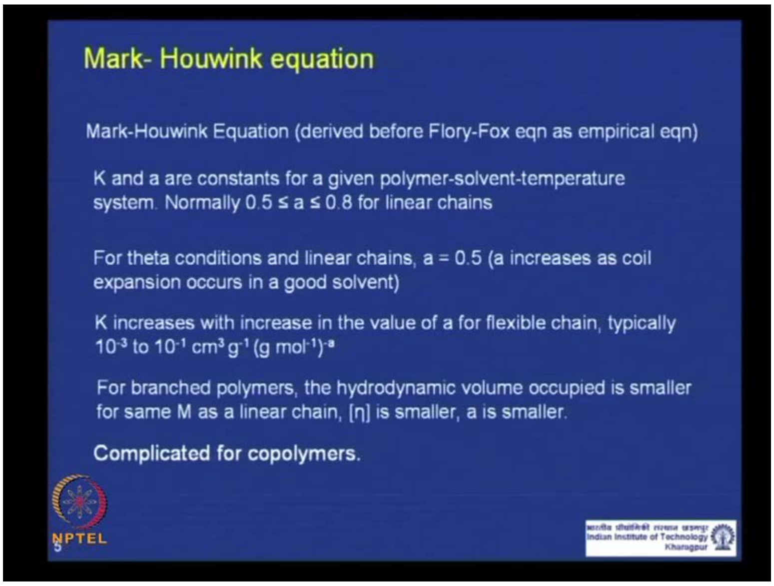

Mark- Houwink equation

Mark-Houwink Equation (derived before Flory-Fox eqn as empirical eqn)

K and a are constants for a given polymer-solvent-temperature system. Normally $0.5 \leq a \leq 0.8$ for linear chains

For theta conditions and linear chains, $a = 0.5$ (a increases as coil expansion occurs in a good solvent)

K increases with increase in the value of a for flexible chain, typically 10^{-3} to 10^{-1} $cm^3 g^{-1} (g\ mol^{-1})^{-a}$

For branched polymers, the hydrodynamic volume occupied is smaller for same M as a linear chain, $[\eta]$ is smaller, a is smaller.

Complicated for copolymers.

So, as I said that Mark-Houwink equation derived before Flory-Fox equation as a empirical equation. Now k and a are constant as we just discussed while deriving the expression and t s; that is same that is constant for a given polymer solvent temperature system. So if you change any of these three polymer solvent and temperature, then k and a value will be changed. So, this is only constant if you have same polymer and solvent temperature because if you change either of them V h, the coil dimension will change and your gyration radius of the expansion factor will also change. So, these values also will change. Normally a lies 0.5 to 0.8 for linear chains and if your very stiff chains like rod-like, then it a can move up to 1. But for linear flexible chains, it will be between 0.5 to 0.8 and for theta condition what we have seen earlier for theta condition, what is the value of a s or expansion factor for theta condition efficient? It was for one.

S, if this is one, then for theta conditions a value would be 0.5. So, it is same as if there was no expansion of the coil due to the presence of the solvent. Now a increases as the coil expansion occurs in good solvent; in good solvent the coil expands. So, the value of expansion factor becomes more than one. So, a value becomes more than 0.5. Now k increases with the value of a for flexibility; typically you have seen it has been seen that k also increases with the increase in the value of a and it is typically around this range. a is more informative in polymer; you will find that a is more probably more important than between these two constant. Now for branched polymer, obviously, even if even you consider theta condition and put a branched polymer, then the expansion factor will be lower than the one if you compare with a linear polymer.

So, you are a value could be lower 0.5. For linear polymer it can never go down below 0.5 but if you have branched polymer it is more compact. So, the expansion factor will be; if you compare the expansion factor of unperturbed linear polymer chain it may go down below that below one. So, the intrinsic viscosity would be smaller as a becomes smaller. Now, this expression becomes little more complicated when you have copolymers, you are characterizing copolymers. As I said we will use this expression Mark-Houwink expression when we try to determine the molecular weight; we will discuss the determination of molecular weight of polymer chain by viscosity method. Now let us start our very important discussion how to determine the molecular weight and at the beginning what I would like to do I will just give an overview of the techniques which are available and used to determine the molecular weight.

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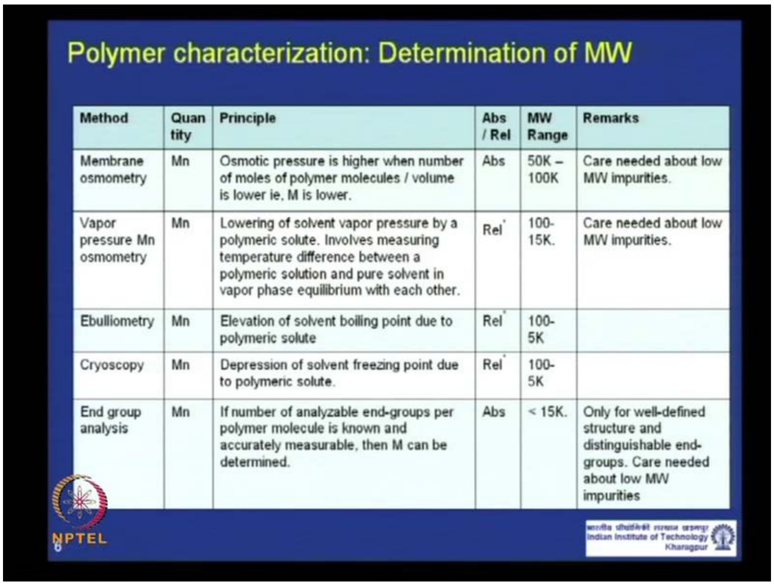

Polymer characterization: Determination of MW

Method	Quantity	Principle	Abs / Rel	MW Range	Remarks
Membrane osmometry	Mn	Osmotic pressure is higher when number of moles of polymer molecules / volume is lower ie, M is lower.	Abs	50K – 100K	Care needed about low MW impurities.
Vapor pressure Mn osmometry	Mn	Lowering of solvent vapor pressure by a polymeric solute. Involves measuring temperature difference between a polymeric solution and pure solvent in vapor phase equilibrium with each other.	Rel*	100-15K.	Care needed about low MW impurities.
Ebulliometry	Mn	Elevation of solvent boiling point due to polymeric solute	Rel*	100-5K	
Cryoscopy	Mn	Depression of solvent freezing point due to polymeric solute.	Rel*	100-5K	
End group analysis	Mn	If number of analyzable end-groups per polymer molecule is known and accurately measurable, then M can be determined.	Abs	< 15K.	Only for well-defined structure and distinguishable end-groups. Care needed about low MW impurities

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These are the different techniques and what I have done is I have just listed the principles and some of these techniques are absolute techniques; that means we do not require any calibration by the polymers of no molecular weight. Actually you can divide these techniques into two types; one is absolute molecular weight determination where we do not require any calibration curve of priority by known polymer molecular weights. And there are relative methods where you actually require a calibration curve by known polymer molecular weight where the molecule and the molecular have been determined by these absolute techniques. We will discuss the principle and the other things the process while we discuss this techniques individually. So, time being we are not spending much time on these techniques.

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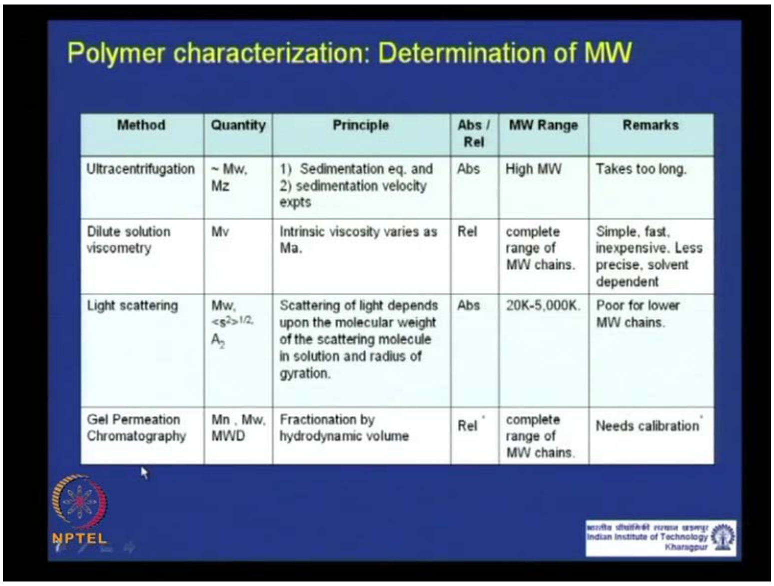

Polymer characterization: Determination of MW

Method	Quantity	Principle	Abs / Rel	MW Range	Remarks
Ultracentrifugation	~ Mw, Mz	1) Sedimentation eq. and 2) sedimentation velocity expts	Abs	High MW	Takes too long.
Dilute solution viscometry	Mv	Intrinsic viscosity varies as Ma.	Rel	complete range of MW chains.	Simple, fast, inexpensive. Less precise, solvent dependent
Light scattering	Mw, $<s^2>^{1/2}$, A_2	Scattering of light depends upon the molecular weight of the scattering molecule in solution and radius of gyration.	Abs	20K-5,000K.	Poor for lower MW chains.
Gel Permeation Chromatography	Mn , Mw, MWD	Fractionation by hydrodynamic volume	Rel	complete range of MW chains.	Needs calibration

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What we will do, again this is the continuation of the list we have and we will spend significant of time on the techniques which are used very frequently in the labs like Gel Permeation Chromatography, light scattering technique, dilute solution viscometry and end group analysis and membrane osmomtery. These first four techniques are based on colligative property, so the principles are similar. So, if you discuss or understand one of them, the rest will be clear to you and all this gives because colligative property is based on the number of average molecular weight. So, this all gives number of molecular weight. Instead of spending more time on this table, which we will discuss in more detail when we discuss the individual techniques, let us move to the actual techniques.

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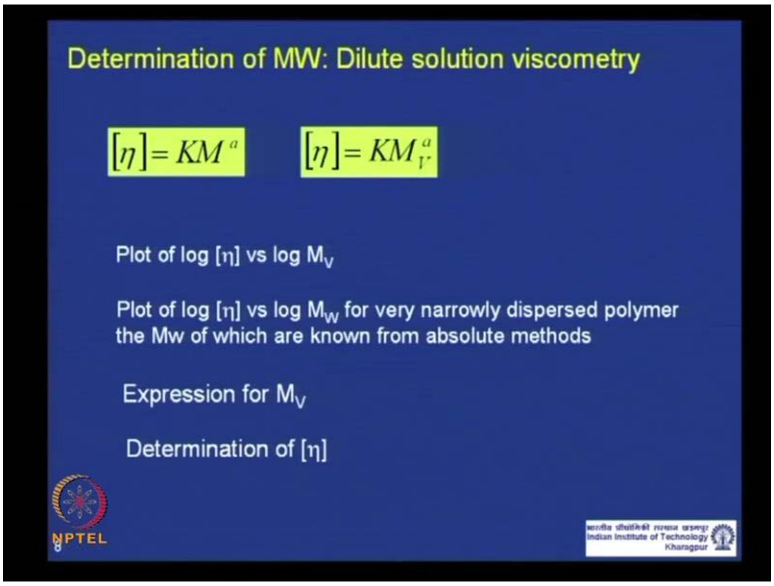

Determination of MW: Dilute solution viscometry

$[\eta] = KM^a$ $[\eta] = KM_V^a$

Plot of log [η] vs log M_V

Plot of log [η] vs log M_W for very narrowly dispersed polymer the Mw of which are known from absolute methods

Expression for M_V

Determination of [η]

Because we were having the discussion on Mark-Houwink equation, let us start the method or the techniques which uses dilute solution viscometry. Now we have seen that this is the expression for dilute polymers, the intrinsic viscosity of polymers in dilute polymer solution and what I can find out.

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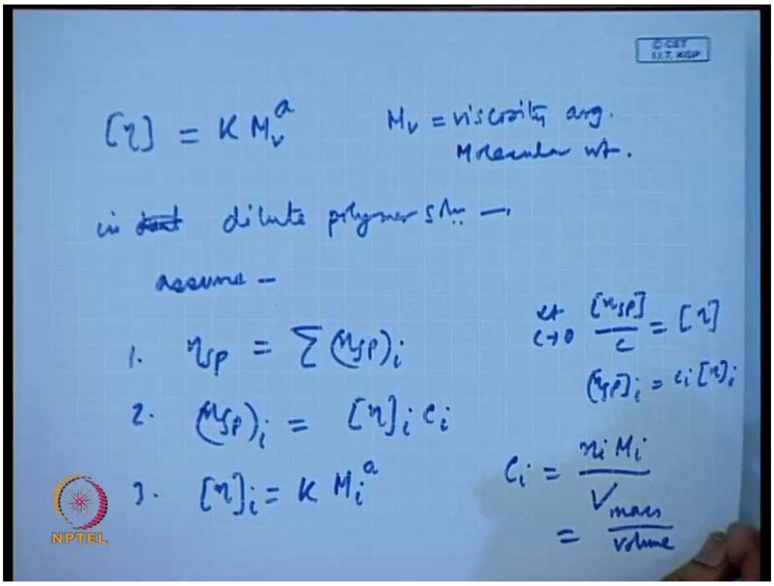

$[\eta] = K M_v^a$ M_v = viscosity avg. Molecular wt.

in ~~dust~~ dilute polymer sln —

assume —

1. $\eta_{sp} = \sum (\eta_{sp})_i$

2. $(\eta_{sp})_i = [\eta]_i c_i$

3. $[\eta]_i = K M_i^a$

$\lim_{c \to 0} \frac{[\eta_{sp}]}{c} = [\eta]$

$(\eta_{sp})_i = c_i [\eta]_i$

$c_i = \frac{n_i M_i}{V}$ $= \frac{\text{mass}}{\text{volume}}$

This intrinsic viscosity is k by M. Now as the technique suggest this is using the dilute solution of viscometry. So, the molecular weight given is M v where M v is viscosity average molecular weight. We will just in a minute we deduce what the expression for viscosity average molecular weight. In dilute polymer solution, we can assume the following reasonably well. You know this assumption is reasonably okay to do is one; the eta specific viscosity is given by the summation of the specific viscosity of the individual chains. Now as you know that radial polymer mixtures, there are numerous polymer chains having different molecular weight. So in intrinsic, these are the assumptions we are making that specific viscosity can be obtained by summing up the specific viscosity of the individual polymer chain.

Second, a specific viscosity of the individual chains can be obtained by this expression. Because we know that limit c tends to 0 eta sp by c is your intrinsic viscosity. So if the solution is very dilute, then we can write eta s p i is c i eta i. Third is the intrinsic viscosity of i chain is given by k M i a; that means what we are assuming that k and a values are independent of the molecule. So, eta s p i is the intrinsic viscosity of n i moles of molecules having molecular weight M i present at a concentration of c i per unit volume. So, c i can be written as n i is the number of molecule; M i is the molecular weight of that molecule. So, this gives you total mass of i molecule divided by volume mass. So, this gives your concentration in terms of mass by volume. So, we have these three assumptions and which is reasonably fair if we deal with dilute polymer solution.

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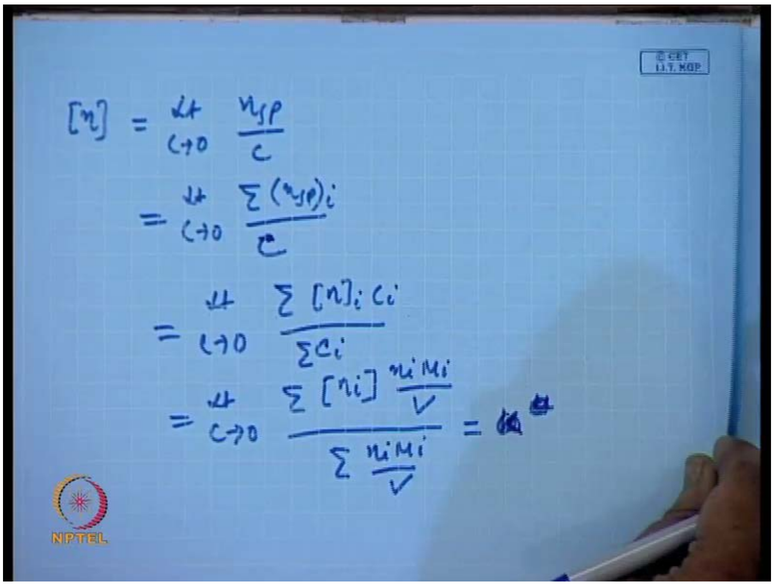

$$[\eta] = \underset{c\to 0}{lt} \frac{\eta_{sp}}{c}$$

$$= \underset{c\to 0}{lt} \frac{\Sigma (\eta_{sp})_i}{c}$$

$$= \underset{c\to 0}{lt} \frac{\Sigma [\eta]_i c_i}{\Sigma c_i}$$

$$= \underset{c\to 0}{lt} \frac{\Sigma [\eta_i] \frac{n_i M_i}{V}}{\Sigma \frac{n_i M_i}{V}} =$$

So now, we can find out the expression for the intrinsic viscosity for the polymer sample which is the mixture of all the polymer chain which is given by limit c tends to 0 eta specific by c; eta specific is given by summation of i c. We can continue to write this is as summation of eta i c i by c. We can write the value for c i n i M i by V and c is basically summation of c i. So, we can write n i M i by V. So I can write, let me write in a separate page.

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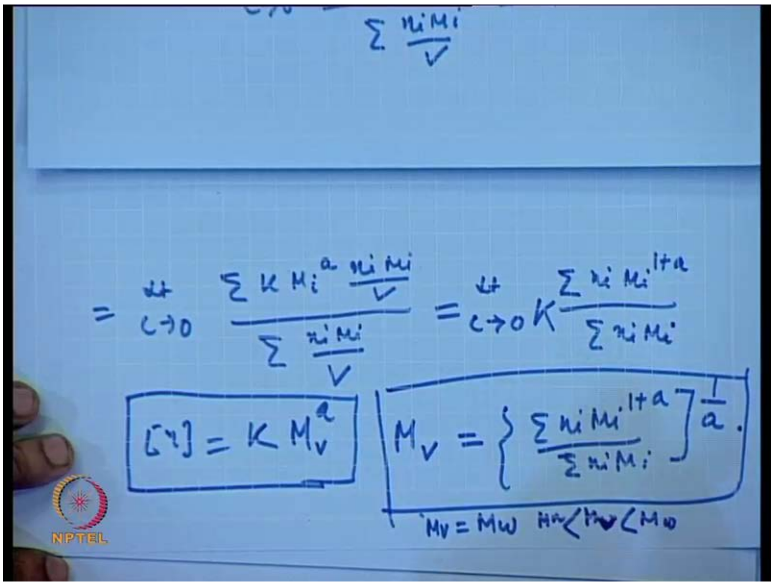

$$\sum \frac{n_i M_i}{V}$$

$$= \lim_{c \to 0} \frac{\sum K M_i^{a} \frac{n_i M_i}{V}}{\sum \frac{n_i M_i}{V}} = \lim_{c \to 0} K \frac{\sum n_i M_i^{1+a}}{\sum n_i M_i}$$

$$\boxed{[\eta] = K M_v^{a}}$$

$$\boxed{M_v = \left\{ \frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right]^{\frac{1}{a}}.}$$

$M_v = M_w$ $M_n < M_v < M_w$

n i is given by, if I can take out k outside this summation. Now we can write; so you get this expression. This is for ultimately the expression for we started from this intrinsic viscosity and we did this all the steps and finally reached here. Now intrinsic viscosity; if you compare this two expressions then we can write this m V is. So, you get this expression. So, in the expression of this m V we just found out that it is having the expression of this. If a is one which we just we discussed it is for highly elongated rod like molecule, then m V would be same as M w. If a one then it will be n i M i square by n i M i. So, it will be equals to M w as a value lies between 0.5 to 0.8; M w will be M v, M v would be more than M n and less than M w. Let me write in a fresh paper.

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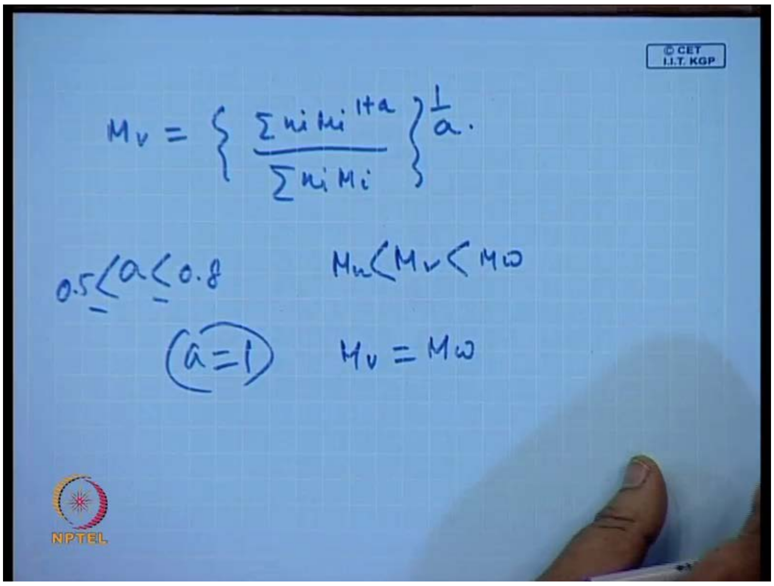

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$$M_v = \left\{ \frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right\}^{\frac{1}{a}}.$$

$0.5 \leq a \leq 0.8$ $M_n < M_v < M_w$

$\boxed{a = 1}$ $M_v = M_w$

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M v is given by as a is between 0.5 to 0.8 M v would lie M n and M w and it will be much more closer towards M w if a is higher; if the coil expand, it will be more expansion more closer to M w and for highly stiff rods where a is 1, M v becomes equals to M w.

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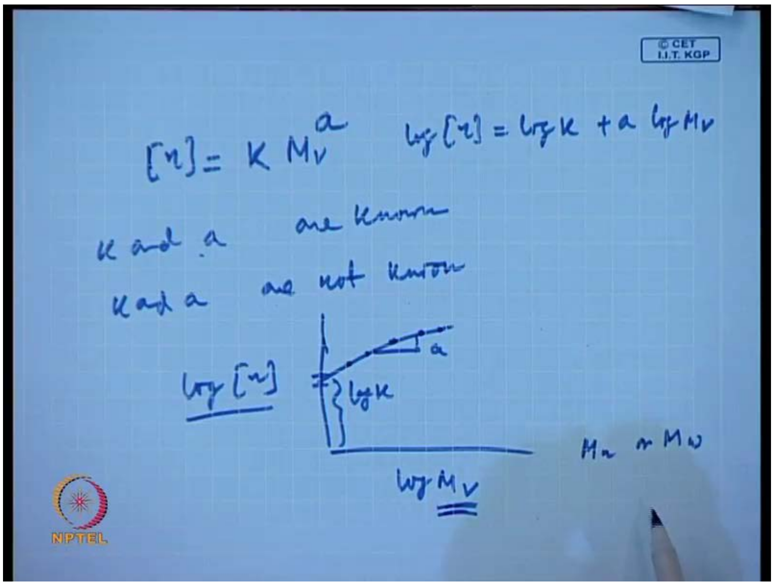

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$[\eta] = K M_v^a$ $\log[\eta] = \log K + a \log M_v$

K and a are known

K and a are not known

M_n or M_w

NPTEL

So now, we know k is intrinsic viscosity is M v by a. Now we just got the expression for M v which is given here which is the expression for M v. So, from here if you plot. So, how to get the value for M v? If you know k and a; if k and a are known, obviously you can find experimentally the value of intrinsic viscosity and then if you know k and a value, then you will be able to find the value for M v. What happened if k and a are not known? Then you can find, you take log eta plot with log M v; you get log eta is log k plus a log M v. So, if you plot log of intrinsic viscosity with log of viscosity average molecular weight, the intercept will give you log k and the slope will give you a.

So, what you need to find out; if you know for experiment or if you from literature in the book, you are fine, you can get and determine experimentally the value for intrinsic viscosity and you can utilize this expression to get the viscosity average molecular weight. But if you do not know; somebody has done it before means for unknown sample, the unknown sample this k and a are not listed. For unknown sample, then how do you determine the viscosity average molecular weight? Then what you need to do; you need to plot log of intrinsic viscosity with many known molecular weight and then you do you do a experimental take five to ten samples and make dilute solutions from that determine the intrinsic viscosity and plot this to get log k and a.

Now the question is here? You need to plot log M v; that is what you need to determine. If you are plotting here log m v, now you are again targeting M v for the unknown molecules. So, then you do not know the M v. This is a calibration curve which you are getting by doing experiments of intrinsic viscosity measurement of many polymer molecular of known molecular weight. Now known molecular weight can be either M n or M w which you already determined by the absolute techniques. We will come back and say it again.

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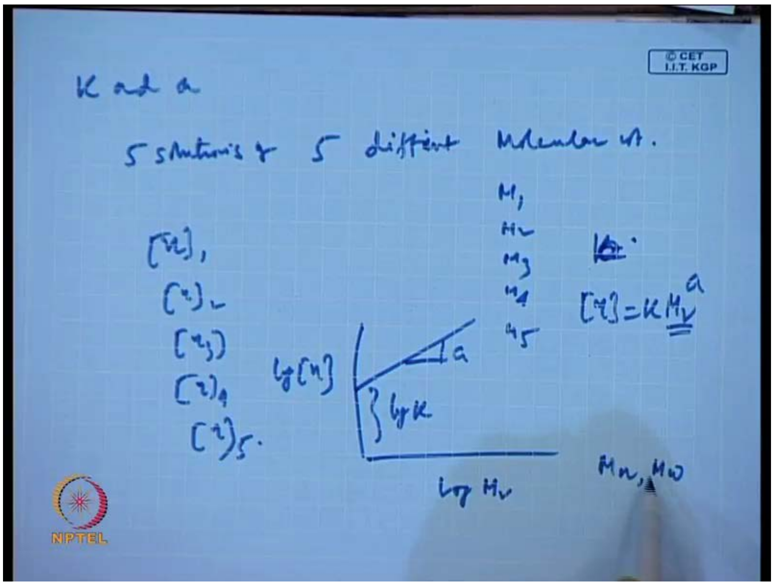

If k and a are not known, what you need to do? You make, say, 5 solutions or 5 different molecular weight; M 1, M 2, M 3, M 4, M5 and then measure the intrinsic viscosity for these eta 1, eta 2, eta 3, eta 4, eta 5 and then plot log of eta versus log of M and get log of k. Now actually this is supposed to M v, the expression gives you k is eta is k M v to the power a. So, ideally you should have M v value for all these samples which you do not have because that is what you are determining. So, what samples you will use for calibration where M v is much closer to any of the known molecular weight, say, M n and M w. Now if you have very narrow dispersed polymer, then you can consider M w or M n is same as M v. If you have very narrow dispersed polymer then M w are very close to M v. So, you can take those M w’s and use here and do the calibration curve.

So if your k and a are not known, you need to have five different molecular weight of that solution where the molecular weights are known by other absolute techniques and the samples should be such that they are very narrowly dispersed. So, that M n and M w can be equated to the M v. So, that is the reason it is a relative method; it is not a absolute method. You cannot determine M v for a unknown polymer by as such; you need to have a calibration curve and for doing calibration curve, you need to have 5, 6, 7, 8 known molecular weight narrow dispersed same polymer whose molecular weight you need to get it from the other absolute techniques like osmotic pressure or light scattering techniques. Then you can determine the viscosity average molecule rate of the unknown sample which k and a is not known in the literature.

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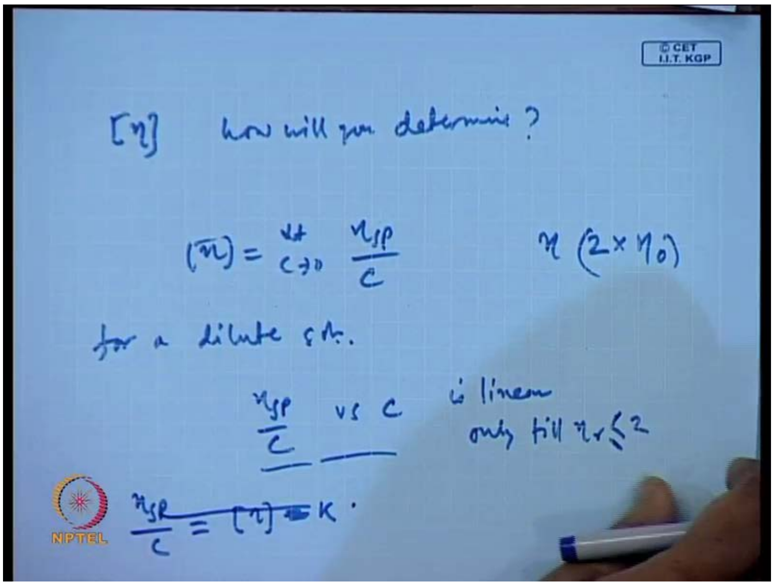

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[η] how will you determine?

$(\eta) = \lim_{c \to 0} \frac{\eta_{sp}}{c}$ η $(2 \times \eta_0)$

for a dilute soln.

$\frac{\eta_{sp}}{c}$ vs c is linear only till $\eta_r \leq 2$

$\frac{\eta_{sp}}{c} = [\eta] \cancel{=} K$ ·

NPTEL

So, for all this case we need; we said that will determine the intrinsic viscosity. Now how will you determine? For a given polymer sample in a solvent for a particular temperature how will you determine, how will you determine eta intrinsic viscosity? Eta is given by limit c tends to 0 eta s p by c. Now if for a dilute solution, the plot of eta s p versus c is linear only till your eta r is less than equals to 2. So, if your eta value of the solution is twice 2x the eta 0 maximum, then you can find out that eta s p is linearly related with the concentration term. So, we can write the eta s p is linearly related to c concentration only till eta r is less than 2.

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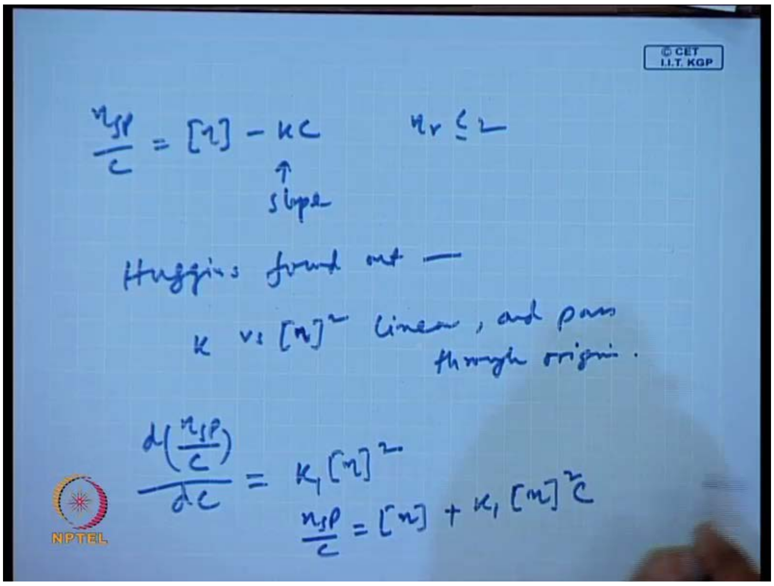

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$\frac{\eta_{sp}}{c} = [\eta] - \underset{\substack{\uparrow \\ \text{slope}}}{k}c$ $\eta_r \leq 2$

Huggins found out —

k vs $[\eta]^2$ linear, and pass through origin.

$\frac{d\left(\frac{\eta_{sp}}{c}\right)}{dc} = k_1 [\eta]^2$

$\frac{\eta_{sp}}{c} = [\eta] + k_1 [\eta]^2 c$

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So eta s p by c can be written as, this is the slope of that linear relationship between eta s p by c with c and that is only applicable till eta r is less than 2. Now this k the slope depends on the molecular rate of polymer; it is not equal for all the lengths of polymer. So, we need to find out something else where that constant can be applied to any of the molecular rate of the polymer chains. So, Huggins found out that k versus eta square is linear and pass through origin; k is the slope. So, we can write d eta s p by c by d c; this is the slope k that is proportional linear. So, I can put another constant k 1 and eta square because there is no constant term because this passes through the origin. Now you can integrate this; you integrate this, you get c is equal to eta 1. Now because Huggins has established this relationship, sometimes this k 1 is written as k H.

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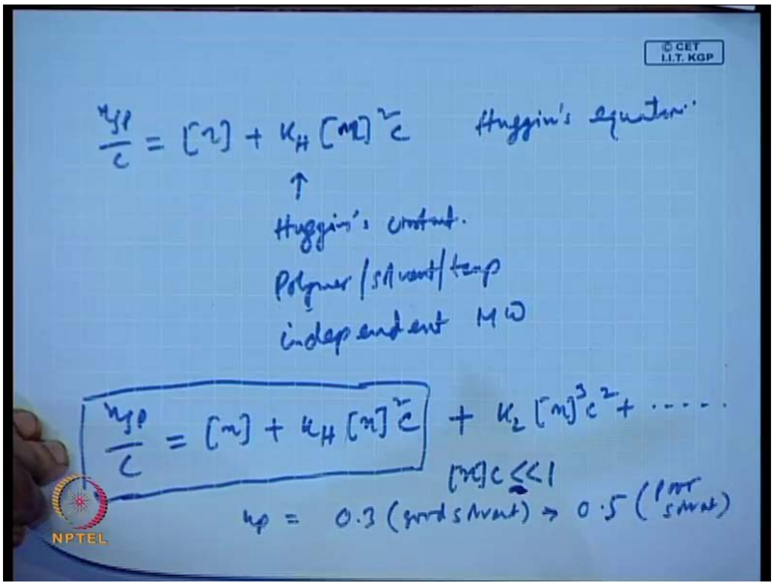

$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c$ Huggin's equation

↑

Huggin's constant.

Polymer/solvent/temp

independent MW

$$\boxed{\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c} + k_2 [\eta]^3 c^2 + \cdots$$

$[\eta] c \ll 1$

k_H = 0.3 (good solvent) → 0.5 (poor solvent)

So, eta s p by c is written as plus k h eta square c. This is Huggins constant; this is Huggins equations. Now this is constant for a particular polymer solvent temperature system. You change any of this change. You change any of these three; polymer solvent or temperature, it will vary; the value of k H will vary. It is of course independent of M w of the polymer. So, now you can use this for the mixture of the polymer or interpolymer distribution so that it can be useful, because it is independent of molecular weight. Now if the concentration is little higher, we talked about this is only applicable for eta r is less than equals to two if the concentration is higher, then this expression can be expressed like the real expression where plus other constant and so on if eta c is less than much less than one, you can ignore this terms higher term c square onwards terms, then you land up getting the Huggins expression again.

So only in case of dilute solution, you can consider only up to; these higher terms you can neglect. k H have value between 0.3 for good solvent to 0.5 for poor solvent. Now in this case from this Huggins expression or Huggins equation, you only need the value of k H. If this is known if k H is known, then obviously you can determine intrinsic viscosity by plotting eta s p by c versus c till the c is very dilute; you know c should not be very high. So the solution remains very dilute, then you can keep the expression for eta from the intercept and if you know k H, then you can get the expression; you can get the value of molecular weight directly. If you know k H, you also will know intrinsic viscosity, then you will know from the expression you can get that molecular weight.

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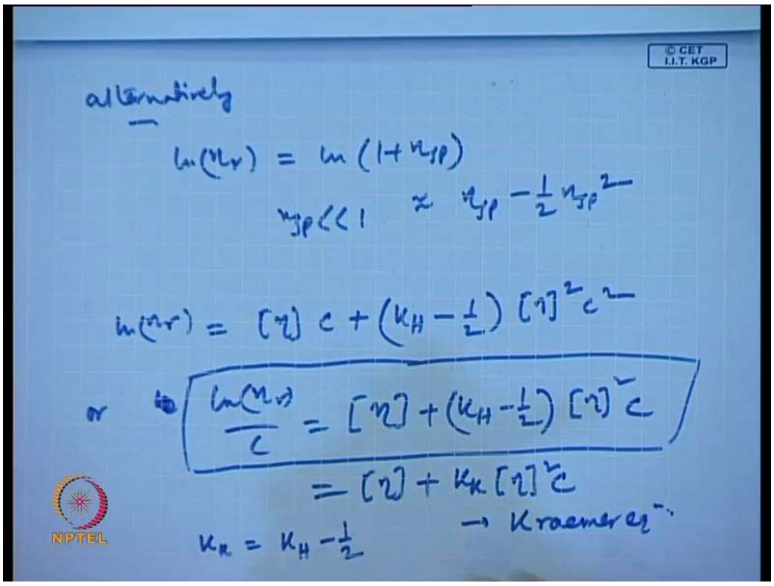

alternatively

$$\ln(\eta_r) = \ln(1+\eta_{sp})$$

$$\eta_{sp} << 1 \quad \approx \eta_{sp} - \frac{1}{2}\eta_{sp}^2$$

$$\ln(\eta_r) = [\eta]c + \left(k_H - \frac{1}{2}\right)[\eta]^2 c^2$$

$$\text{or} \quad \boxed{\frac{\ln(\eta_r)}{c} = [\eta] + \left(k_H - \frac{1}{2}\right)[\eta]^2 c}$$

$$= [\eta] + k_K [\eta]^2 c$$

$$k_K = k_H - \frac{1}{2} \qquad \rightarrow \text{Kraemer eq}^n$$

Now alternatively we can use the inherent viscosity which can be expressed and specific viscosity is much lower than 1. This expression can be written eta s p minus half eta square. So, this Huggins equation can now be written as directly eta r is equals to c plus. So, this gives the similar expression like the Huggins expression but this in terms of the inherent viscosity and this expression this constant is named at the person who has given this; this is Kramer’s equation where K k is k H minus half. So, it will be a negative quantity. So, now we have two expressions Huggins equation and Kramer’s equation.

So, you can plot eta s p or this term inherent viscosity with respect to c and then from slope and the intercept, you can get the value of intrinsic viscosity.

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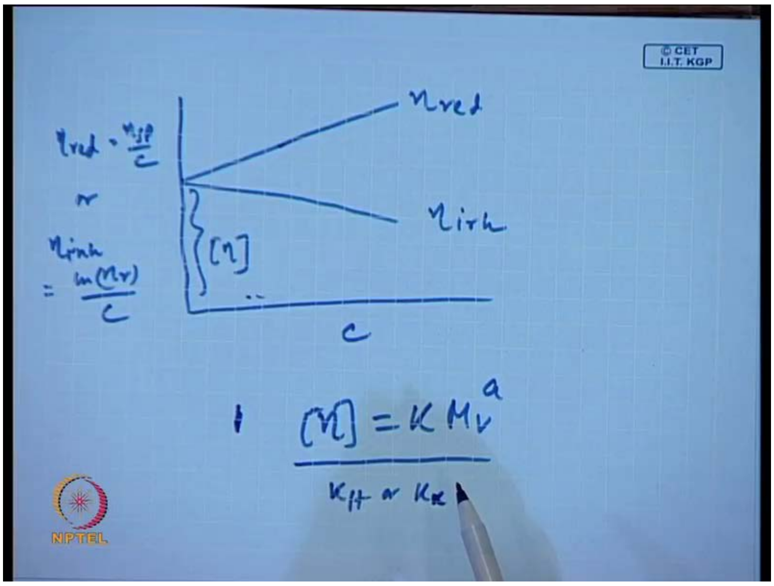

So, I can plot either eta reduced which is nothing but eta s p by c or we can plot eta inherent which is ln into r by c and we will get. In case of Kramer that constant is negative we just saw. In case of Kramer this is negative, so the slope will be negative. And in case of Huggins this is positive; the slope will be positive. So, this will be eta reduced plot for eta reduced and the other one will be plot eta inherent. So, from this you can get the value of the intrinsic viscosity. So in summary if we know this Mark-Houwink equation where M v expression we just have seen. Now using either this Huggins equation or Kramer equation, you can plot either the reduced viscosity or the inherent viscosity with the concentration term to get experimentally the intrinsic viscosity.

So, this is in your hand. You can make solutions of different concentration and you can measure viscosity of the solvent and viscosity of the solution and from viscosity of the solution and solvent you get relative viscosity and from there you get specific viscosity and from there you get reduced viscosity and inherent viscosity. So, these are all in your hand. You can get a viscometer and typically the viscosity is measured by passing using this different viscometer where the solvent and the solution is passed through the capillary where the time is proportional to the viscosity. So, basically if you measure the time of reflux time of the solution and the solvent from the receiver, you can get the relative viscosity and from there you can get the reduced viscosity and inherent viscosity.

So basically you plot, you make different solution with different concentration and plot; with this you get the intrinsic viscosity. So once you know this, if you know k and a, you can use this expression to find out M v. As you have seen if you know the k H or K k the Huggins constant or the Kramer constant k H or K k, then only from one concentration itself you can get the value of intrinsic viscosity the molecular weight. And if you do not know this k or a the k H or K k, then the process is to determine some or few or very narrowly dispersed same polymer and get the absolute molecular weight from any other techniques, and because it is suppose has to be very narrow dispersed polymer, you can take any of the M n or M w as equals to M v.

And you find out the intrinsic viscosity for this given polymer and then by plotting log intrinsic viscosity versus log molecular weight, you can get k and a value; from that you can get this M v. So with this, we conclude the discussion on determination of molecular weight by viscosity method. Remember whatever we are doing in this determination there are few precautions you have to take; you have to make the solution to determine the intrinsic viscosity such that the concentrations of the solutions is very low. It must be in dilute solution, a very dilute solution region and also you need to remember that relative number in this method, you cannot get a measurement for an unknown polymer as such. It is not absolute method; it is a relative method. So, what we will do in the next lecture we will start discussing about the other methods of determining molecular weight namely M n and M w and other polymer solvent interaction parameters.