Simple concepts related to single macromolecule
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Lecture - 27
Frictional Properties of Polymer Molecules in Dilute Solution, Determination of Polymer MW

Welcome back, in this lecture I will discuss frictional properties of polymer molecules in dilute solution and give you an overview of polymer molecular weight determination techniques.

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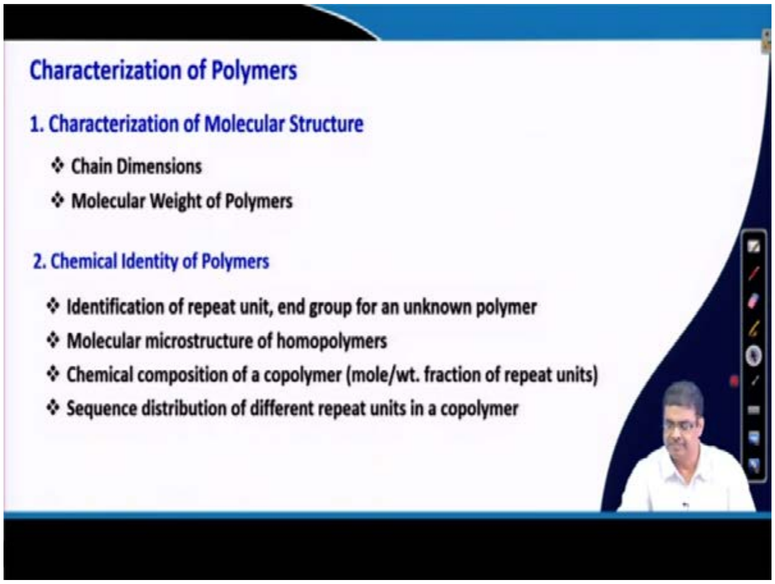

Characterization of Polymers

1. Characterization of Molecular Structure
   - Chain Dimensions
   - Molecular Weight of Polymers
2. Chemical Identity of Polymers
   - Identification of repeat unit, end group for an unknown polymer
   - Molecular microstructure of homopolymers
   - Chemical composition of a copolymer (mole/wt. fraction of repeat units)
   - Sequence distribution of different repeat units in a copolymer

We have started discussing characterization techniques of polymers. And in the last lecture we have discussed about chain dimension. Frictional properties of polymers also related to chain dimensions. If the polymer chains become larger in size, then the viscosity of the polymer solution will be higher which means the dimension of polymer chains had very close relationship with the frictional properties with of the polymer solution. Let us discuss frictional properties of polymer in this lecture.

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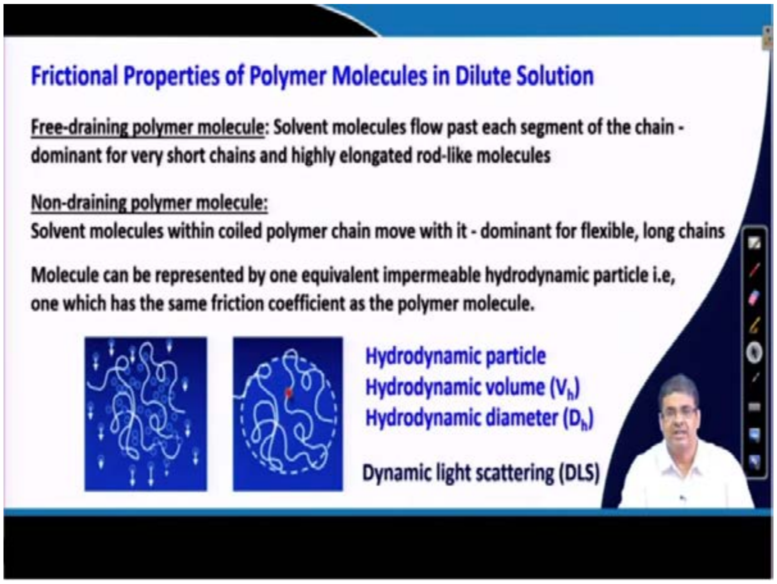

Frictional Properties of Polymer Molecules in Dilute Solution

Free-draining polymer molecule: Solvent molecules flow past each segment of the chain - dominant for very short chains and highly elongated rod-like molecules

Non-draining polymer molecule:
Solvent molecules within coiled polymer chain move with it - dominant for flexible, long chains

Molecule can be represented by one equivalent impermeable hydrodynamic particle i.e, one which has the same friction coefficient as the polymer molecule.

Hydrodynamic particle
Hydrodynamic volume (V_h)
Hydrodynamic diameter (D_h)

Dynamic light scattering (DLS)

We will consider dilute solutions because most of the polymer characterization techniques are done in dilute solution. We are not interested in concentrated solutions at this moment. We are learning the friction properties that will help us to understand the techniques, which are used to determine polymer molecular weight.

There are two types of polymer molecules can be possible in solution. One is freely draining polymer molecule, in this case, solvent molecules flow past each segment of the chain. So, solvents do not intermingle with the polymer coil. In fact, we do not have any polymer coil in this particular case. If I have a rod like polymer structure or a short polymer structure then it basically flows through the solvent without interacting too much with the solvent molecules. Solvent molecules flow past each other each segment of the chain and this behavior dominates for the very short chain and highly elongated rod like molecules. Now, these polymer molecules are not very frequently encountered. Most of our regular synthetic polymers are not freely draining type of molecules. So, we will not discuss this topic in detail. Most of our synthetic polymers are non-draining polymers molecules in solution that means solvent molecules within the coiled polymer structure move along with the polymer molecule and this behavior dominates for flexible long chain polymer molecules, which are generally encountered polymers in our most of the applications. Now, in this case of non-draining polymer molecules, the molecule or the polymer molecule can be represented by one equivalent impermeable hydrodynamic particle, the one which has same frictional coefficient as the polymer molecule.

Let me explain this little more. Consider that white one is the polymer coil. Now, just like any other molecule, this will have Brownian motion and so, it will undergo translational motion through the solvent molecules. Now, when it moves it will move along with these small solvent molecules which as shown here. So, when this polymer coil actually travels across the solvent, it moves along with these solvent molecules that are present in the coil. Now, we can represent this as an impermeable hydrodynamic particle like this spherical particle that has the same frictional coefficient as this polymer molecule. So, in this case, we are considering an equivalent rigid or impermeable hydrodynamic particle which has same friction coefficient as a real coiled polymer chain which moves along with the solvent molecules. Now, for this hydrodynamic particle, we have corresponding volume which we call hydrodynamic volume, which is represented V_h. And we have corresponding hydrodynamic radius and hydrodynamic diameter. So, when you talk about hydrodynamic size, then we can talk about either hydrodynamic radius, diameter or volume, and dynamic light scattering technique is actually used to determine the size hydrodynamic size of a polymer particle or polymer molecule in solution.

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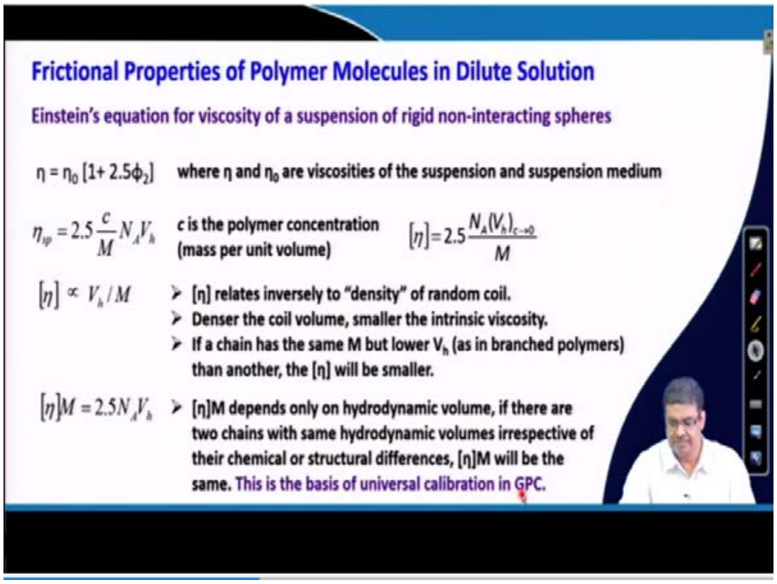

Frictional Properties of Polymer Molecules in Dilute Solution

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

$\eta = \eta_0 [1 + 2.5\phi_2]$ where η and η_0 are viscosities of the suspension and suspension medium

$\eta_{sp} = 2.5 \frac{c}{M} N_A V_h$ c is the polymer concentration (mass per unit volume) $[\eta] = 2.5 \frac{N_A (V_h)_{c \to 0}}{M}$

$[\eta] \propto V_h / M$

- [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 universal calibration in GPC.

Now, we will talk about Einstein equation for viscosity of a suspended rigid non-interacting sphere as we described in last slide. We talked about an impermeable hydrodynamic particle effectively, which does not interact with the solvent molecules. The frictional coefficient of which is same as the polymer chain along with the solvent molecule. So, Einstein equation is given by

$$\eta = \eta_0[1 + 2.5\phi_2]$$

where η is the coefficient of viscosity of the solution, η_0 is the coefficient of viscosity of the solvent and ϕ_2 is the volume fraction of the solute which is polymer in this case.

In this case, the suspending medium is a solvent. In this case, we know specific viscosity η_{sp} is given by $\eta/\eta_0 - 1$. We know this expression of that specific viscosity as η/η_0 then we can rearrange $\eta = \eta_0[1 + 2.5\phi_2]$ as $\eta_{sp} = 2.5\frac{c}{M}N_A V_h$, where c is the polymer concentration in terms of mass per unit volume, M is the molar mass, N_A is Avogadro number and V_h is, as described in the last slide, hydrodynamic volume, which is the volume of rigid non interacting sphere.

Now, we know intrinsic viscosity, which is given by η_{sp} / c at limit c tends to 0. So, if we rearrange $\eta_{sp} = 2.5\frac{c}{M}N_A V_h$ expression, we bring c in this denominator. Then we can write intrinsic viscosity as $[\eta] = 2.5\frac{N_A(V_h)_{c\to 0}}{M}$ where we write V_h hydrodynamic volume when concentration is tending to 0. So, we can write this because we are talking about very dilute solution, then we will not write this subscript c tend to 0 now onwards we write simply hydrodynamic volume. So, the intrinsic viscosity is proportional to the ratio of hydrodynamic volume divided by the molar mass.

$$[\eta] = 2.5\frac{N_A(V_h)_{c\to 0}}{M}$$

So, intrinsic viscosity is inversely related to the density of the random coil, because $\frac{V_h}{M}$ effectively is one over density of the random coil, as the density increases the intrinsic viscosity goes down and vice versa. $[\eta] \propto \frac{V_h}{M}$ .So, denser the coil volume, smaller is intrinsic viscosity for a chain which has same molecular weight, but lower hydrodynamic volume. In case we have a branched chain, then for a given molecular weight we can have a lower hydrodynamic volume. Then the intrinsic viscosity will be smaller. We can rearrange this expression take this M to left hand side and we can get this expression $[\eta]M = 2.5N_A V_h$. Now, this shows that the multiplication of intrinsic viscosity and molecular weight or molar mass is proportional to the hydrodynamic volume. So, this term intrinsic viscosity multiplied by the molar mass depends only on the hydrodynamic volume. So, if there are two chains of same hydrodynamic volume, irrespective of their chemical or structural differences (they could be branched, they can be linear or they could be of different chemical nature), then the product of molar mass and intrinsic viscosity also would be same. And this is the basis for a universal calibration of GPC which we will talk in a later lecture.

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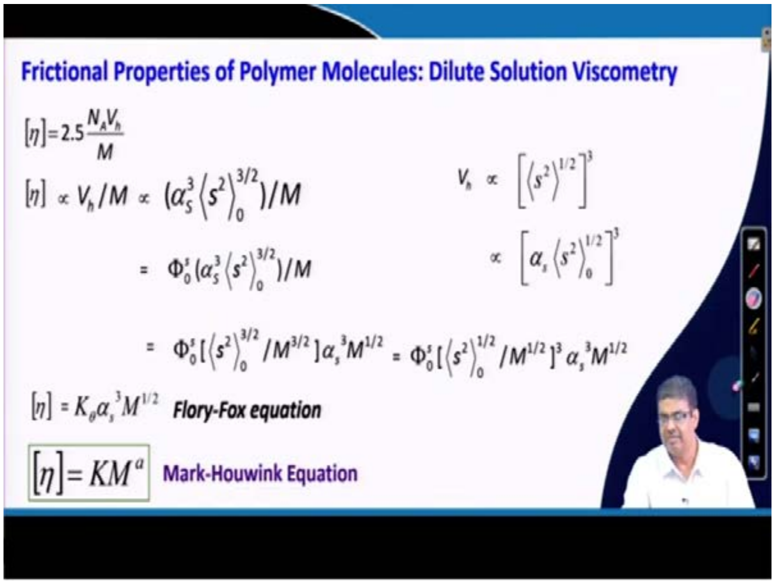

Frictional Properties of Polymer Molecules: Dilute Solution Viscometry

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

$$[\eta] \propto V_h/M \propto (\alpha_S^3 \langle s^2 \rangle_0^{3/2})/M \qquad V_h \propto \left[\langle s^2 \rangle^{1/2}\right]^3$$

$$= \Phi_0^s (\alpha_S^3 \langle s^2 \rangle_0^{3/2})/M \qquad \propto \left[\alpha_s \langle s^2 \rangle_0^{1/2}\right]^3$$

$$= \Phi_0^s [\langle s^2 \rangle_0^{3/2} / M^{3/2}] \alpha_s^3 M^{1/2} = \Phi_0^s [\langle s^2 \rangle_0^{1/2} / M^{1/2}]^3 \alpha_s^3 M^{1/2}$$

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

$\boxed{[\eta]=KM^a}$ Mark-Houwink Equation

We have seen this expression before, so, we can say that intrinsic viscosity is proportional to V_h / M. Now, hydrodynamic volume can be expressed as the radius of gyration, it is like the radius of that hydrodynamic particle. So, the volume would be $\frac{4}{3}\pi r^3$, so, $\langle s^2 \rangle_0^{1/2}$ is kind of radius so, the hydrodynamic volume is proportional to the radius of gyration to the power 3. Now, we know this radius of gyration can be expressed as the unperturbed size and the expansion factor. So, we can write, in place of V_h we can write this term

$$[\eta] \propto V_h/_M \propto \left(a_S^3 \langle s^2 \rangle_0^{3/2}\right)/_M$$

So, instead of proportionality if we write equal, the equal sign, then we have a constant. Φ_0^s is the constant and we have this same expression.

$$= \Phi_0^s \left(a_S^3 \langle s^2 \rangle_0^{3/2}\right)/_M$$

Now, we can rearrange this little bit, as shown here

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

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

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

$$[\eta] = K M^a$$

Now, we have seen in the last class that $\langle s^2 \rangle_0^{1/2}$ is proportional to the root mean square end to end distance which is proportional to $n^{1/2}$ (n is the number of bonds), which is proportional to the molecular weight to the power half, which means, if we divide $\langle s^2 \rangle_0^{1/2}$ with $M^{1/2}$ then $\langle s^2 \rangle_0^{1/2}/M^{1/2}$ would be a constant term. So, this means, the term inside this bracket is constant. So, we can put the two constants together make a new constant K. So, this is the constant which accommodates these terms and I explained why this is a constant. This expression is called Flory Fox equation, a_s the expansion factor for radius of gyration. Now for θ solvent, below which we get poor solvent and the chain dimension is minimum in θ solvent. So, for θ solvent, we know what θ solvent we have this value of a_s as 1 as we have seen before. Now, for dilute solution, when the solvent quality is good a_s actually proportional to $M^{1/10}$, which means, a_s^3 is proportional to $M^{3/10}$ which means, when we talk about these 2 terms, these 2 terms will be proportional to $M^{0.8}$. now, this happens for solvent which is good solvent for the Polymer. So, for a poor solvent or θ solvent we have $M^{0.5}$ and in good solvent we have $M^{0.8}$. So, if we write, instead of this two constants, together if you now take these together and write θ is equal to some other constant into the power *a*, then *a* would be varying from 0.5 for a θ solvent to 0.8 for an expanded coil in a good solvent. Now, it can go beyond 0.8 when the polymers become elongated in rod like shape, but which is not very frequently observed in our case. So, the value of *a* would be between 0.5 and 0.8. 0.5 is for the θ solvent and 0.8 is for the good solvent when the polymer coil is expanded, and this expression we call Mark-Houwink equation. So, we can write as I explained this expression, this K is another constant, M is the molecular weight, raised to the power *a*, and K and *a* are constant for a particular polymer-solvent-temperature system which means, if any of these three quantity changes, either temperature changes or solvent changes or polymer changes. The value of *a* and K would also change and we call this as Mark-Houwink equation. And later we will see that this molecular weight is actually M_v which is viscosity average molecular weight and this will be utilized to determine the molecular weight viscosity average molecular weight in the coming class or coming lecture.

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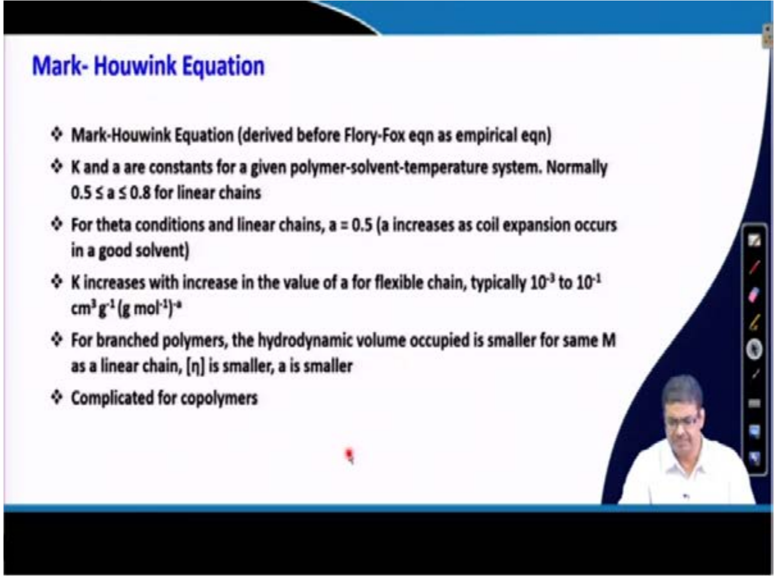

Mark- Houwink Equation

- 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, [η] is smaller, a is smaller
- Complicated for copolymers

Mark-Houwink equation, which actually was derived later experimentally, was derived theoretically as we explained from Flory-Fox equation as the empirical equation and K and *a* are constant for a given polymer-solvent-temperature system as I described just now, and the value of *a* is normally between 0.5 to 0.8 for linear chain. For elongated chain this can go beyond 0.8 but which is not very frequently observed for polymer chain. For θ condition, and linear chain *a* is 0.5 as I described a few minutes back and K increases with increase in the value of *a* for flexible chain and typically, this is the value for K. For branched polymer molecule, the hydrodynamic volume occupies smaller volume for same molecular weight. Hence, the intrinsic viscosity becomes smaller which means *a* becomes smaller.

So, *a* kind of represents the expansion of the polymer coil. If you have a θ solvent then it is not expanded, so, value is 0.5; if we have good solvent then the polymer expands, the value of *a* increases to 0.8 and so on. For same molecular weight if we have a branched structure, obviously, hydrodynamic size will be lower which means *a* value should be lower. The value of K and *a* for copolymers are very difficult to obtain, they are complicated.

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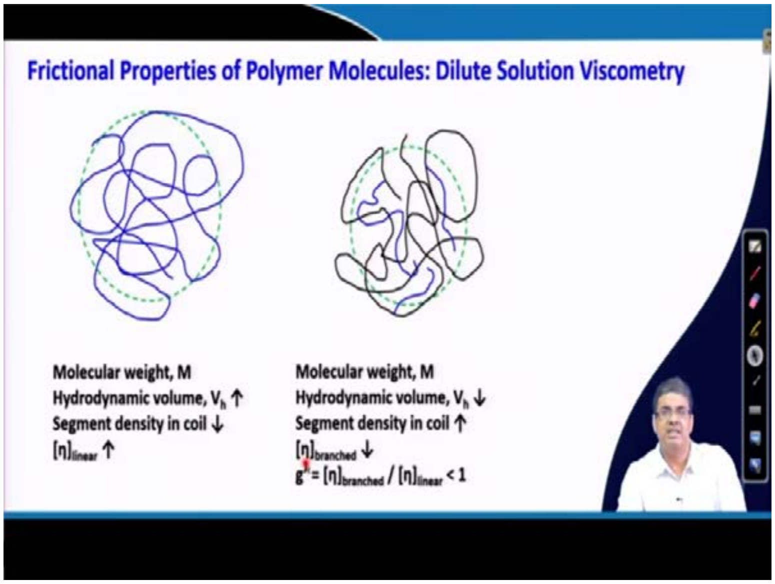

Frictional Properties of Polymer Molecules: Dilute Solution Viscometry

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

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

So, as we discuss before, if we compare two chains - one is linear without any branch and other is linear with branches which is shown in different color, both are having same molecular weight. Then we can compare between these two that they have same molecular weight, but hydrodynamic volume for the linear will be higher, for the other will be lower because the presence of branches and density of the coil for the second will be higher, it will more dense coil. Intrinsic viscosity of this branched polymer will be lower compared to the linear without branch. g′ is generally used to express the branching or extent of branching, which is the ratio of the intrinsic viscosity of the branched structure and linear structure having same molecular weight, and higher is the branching g′ becomes lower and lower compared to 1, if there is no branch then it will be equals to 1. So, this g' is the value which generally used to describe a quantify the extent of branching in a polymer chain.

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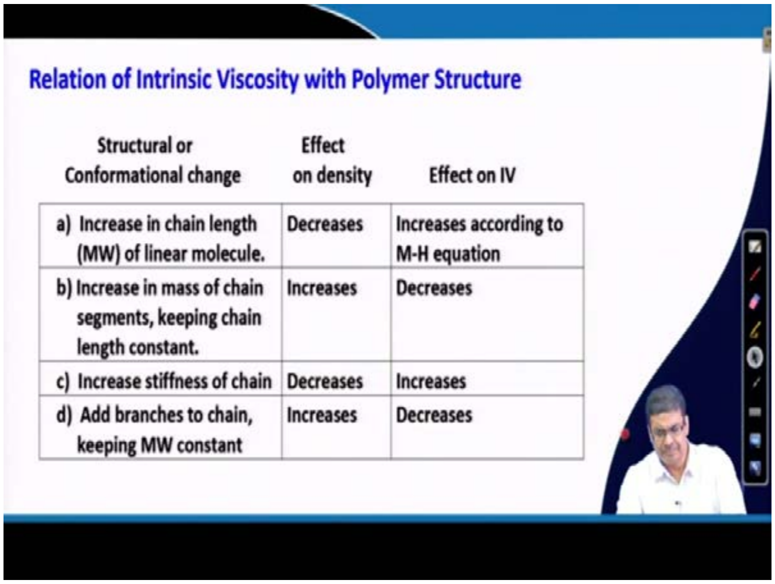

Relation of Intrinsic Viscosity with Polymer Structure

Structural or Conformational change	Effect on density	Effect on IV
a) Increase in chain length (MW) of linear molecule.	Decreases	Increases according to M-H equation
b) Increase in mass of chain segments, keeping chain length constant.	Increases	Decreases
c) Increase stiffness of chain	Decreases	Increases
d) Add branches to chain, keeping MW constant	Increases	Decreases

So, just to repeat what we understood that with increase in chain length for linear molecule density decreases, intrinsic viscosity goes up. If we increase the mass of a chain, the density increases keeping the length same, the density increases & intrinsic viscosity decreases; if we increase the stiffness of the chain, the chain becomes more elongated. Hence, the intrinsic viscosity increases as density goes down. And as we discussed earlier, if we add branches keeping molecular weight same the density increases and intrinsic viscosity decreases.

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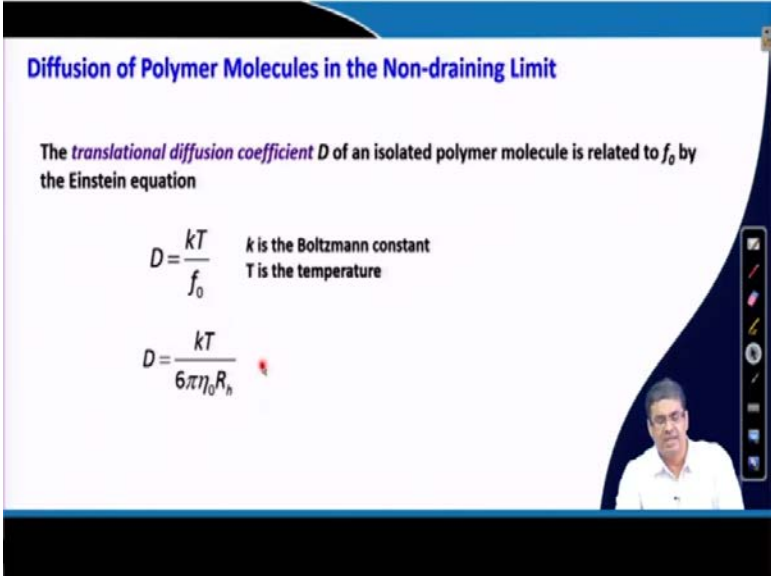

Diffusion of Polymer Molecules in the Non-draining Limit

The *translational diffusion coefficient* D of an isolated polymer molecule is related to f_0 by the Einstein equation

$$D = \frac{kT}{f_0}$$

k is the Boltzmann constant
T is the temperature

$$D = \frac{kT}{6\pi\eta_0 R_h}$$

We talked about this hydrodynamic particle of a polymer chain now, the translational diffusion coefficient of this isolated polymer chain is related to frictional coefficient by Einstein equation like this,

$$D = \frac{kT}{f_0}$$

$$D = \frac{kT}{6\pi\eta_0 R_h}$$

where this D is the diffusion coefficient, translational diffusion coefficient, k is the Boltzmann constant, T is the temperature, and f_0 is the frictional coefficient. This frictional coefficient is linked to the hydrodynamic radius by Stokes equation. So, if we find out the diffusion coefficient, we can use $D = \frac{kT}{6\pi\eta_0 R_h}$ to find out the size of the hydrodynamic particle, which is done by using dynamic light scattering, which I will discuss in a coming lecture.

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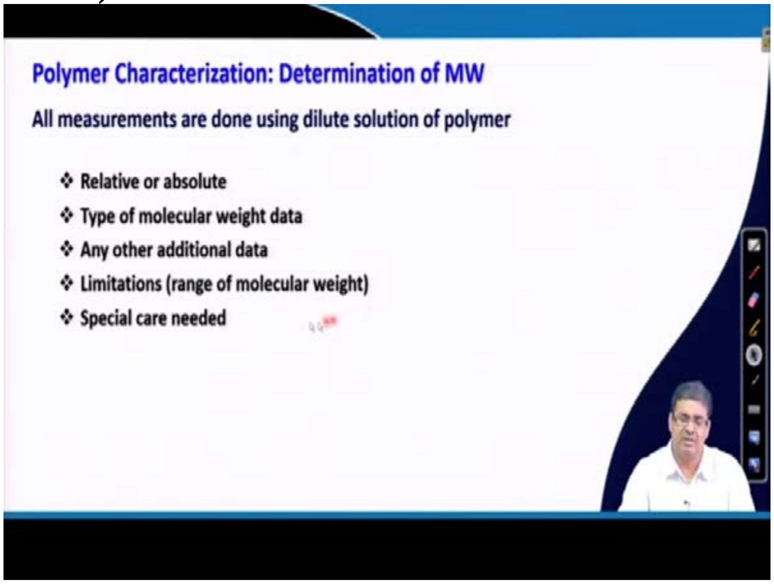

Polymer Characterization: Determination of MW

All measurements are done using dilute solution of polymer

- Relative or absolute
- Type of molecular weight data
- Any other additional data
- Limitations (range of molecular weight)
- Special care needed

Now, let us move to the molecular weight determination techniques for polymers. I mentioned earlier, that most of, almost all molecular weight determinations are done using dilute polymer solution, and that is why we were discussing understanding the polymer behavior in dilute solution. So, while we use different techniques, we must remember or understand the different aspects of various techniques.

For example, whether the technique is relative or absolute, relative in the sense that the reported molecular weight values are in relative to some other known values or it is an absolute value. For relative measurement, we require a calibration curve form polymer molecules polymer chains with known molecular weight, but for absolute technique, we do not require any calibration curve form known molecular weights.

You also need to know that what are the type or types of molecular weight data the technique can provide, whether any additional data it can provide and what are the limitation which includes range of molecular weight of polymers which can be determined by that particular technique and what are the special cares should be taken to accurately measure the molecular weight.

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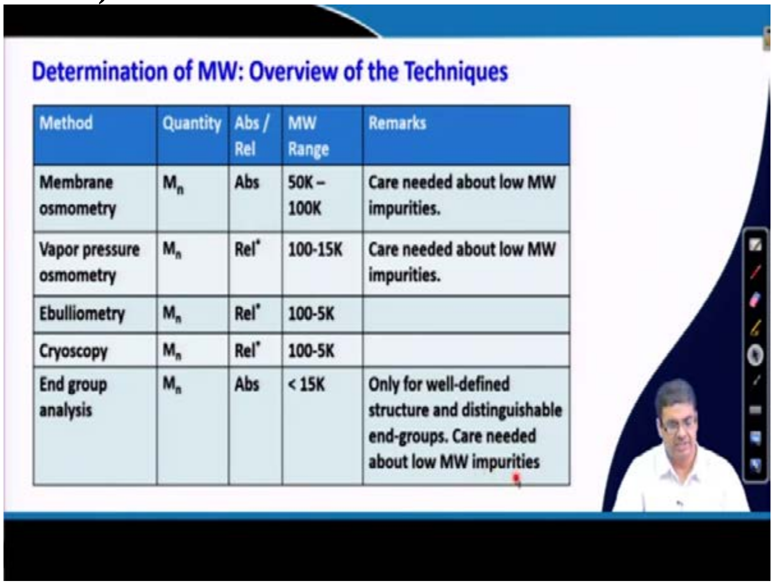

Determination of MW: Overview of the Techniques

Method	Quantity	Abs / Rel	MW Range	Remarks
Membrane osmometry	M_n	Abs	50K – 100K	Care needed about low MW impurities.
Vapor pressure osmometry	M_n	Rel*	100-15K	Care needed about low MW impurities.
Ebulliometry	M_n	Rel*	100-5K	
Cryoscopy	M_n	Rel*	100-5K	
End group analysis	M_n	Abs	< 15K	Only for well-defined structure and distinguishable end-groups. Care needed about low MW impurities

So, I will give you the overview of the various techniques. These first four techniques are based on measuring the colligative properties of polymer solution, which depends on the number of solute molecules in this case polymer molecules in solution. So, these techniques give number average molecular weight. Membrane osmometry is an absolute technique, whereas, the other three are relative techniques. Now, this * means that, although in principle it should be able to provide absolute value without any calibration curve, but, in reality, when we want to measure, we require parameters which need to be optimized or calibrated using known molecular weight. That is why these are relative techniques. And the molecular weight range for which these techniques are applicable are given in the table. In all these techniques, we need to be very careful about the low molecule impurities, because as I described, these are colligative properties and the property of this nature depends on the number of solute molecules. Hence, if there are low molecular weight impurities, which will effectively, increase the number of solute molecules in solution to much larger extent and there will be large error in these techniques.

End group analysis is done using some chemical techniques. And this also gives number average molecular weight, and this is the absolute measurement technique for polymers with low molecular weight especially if for MW the value is less than 15,000. The restriction is that we need to have techniques, which can quantify the end groups very effectively. So, to apply this technique of molecular weight determination, we need to have polymers will distinct end groups, which can be quantified by any chemical methods, and of course, care need to be taken about low molecular impurities.

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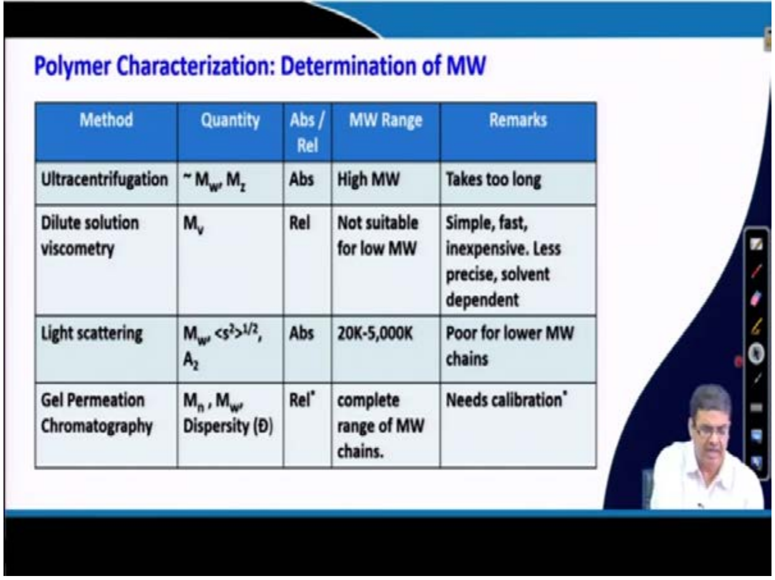

Polymer Characterization: Determination of MW

Method	Quantity	Abs / Rel	MW Range	Remarks
Ultracentrifugation	~ M_w, M_z	Abs	High MW	Takes too long
Dilute solution viscometry	M_v	Rel	Not suitable for low MW	Simple, fast, inexpensive. Less precise, solvent dependent
Light scattering	M_w, $\langle s^2 \rangle^{1/2}$, A_2	Abs	20K-5,000K	Poor for lower MW chains
Gel Permeation Chromatography	M_n , M_w, Dispersity (Đ)	Rel*	complete range of MW chains.	Needs calibration*

Similarly, ultra centrifugation technique is used to measure weight average molecular weight and Z average molecular weight is an absolute technique and is only applicable for high molecular weight polymers; the disadvantage is that it takes too long time. Dilute solution viscometer is very easy technique and it gives as, we discussed in few minutes back, viscosity average molecular weight. It is a relative technique, which is not very suitable for low molecular weight polymers. The advantage is that it is simple, fast, inexpensive technique, but disadvantage is that it is less precise and solve dependent. Light scattering techniques can be used to measure the weight average molecular weight, radius of gyration and polymer solvent interaction parameter from which we can also get the value of χ parameter. This is absolute technique and this is applicable to medium to higher range of molecular weight; disadvantage is that it does not give good accuracy for lower molecular weight polymers.

One of the best techniques for polymer molecular weight determination is gel permeation chromatography or GPC; it gives number average molecular weight, weight average molecular weight and also, the entire distribution of molecular weights, which indirectly gives the dispersity. Gel permeation chromatography technique can be either relative or absolute depending upon how we use. In most instances, in most laboratories, GPC techniques are used as relative technique; molecular weight measurements are done using a calibration graph, which is generated from known molecular weight of polymers. It is applicable for complete range of molecular weight of polymers and disadvantage is while we use this as a relative technique, we need calibration for which we need lot of polymer standards, which are narrow dispersed polymer molecules with known molecular weight.

We can also use GPC as absolute technique, for that, we need this very expensive and sophisticated instrumentation. Now, for this course, I will only discuss about the techniques, which are of practical utility as of now. Nowadays, although these techniques are all available, but generally we do not use some of these techniques for measuring polymer molecular weight.

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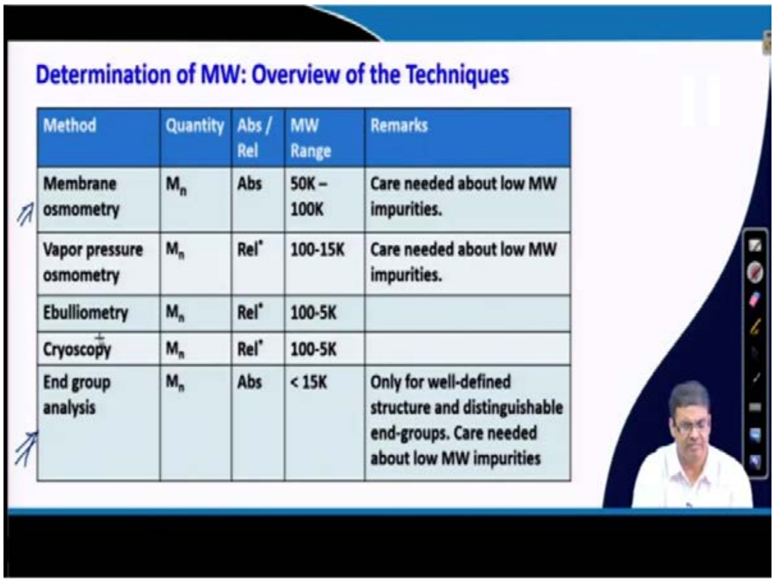

Determination of MW: Overview of the Techniques

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Ebulliometry	M_n	Rel*	100-5K	
Cryoscopy	M_n	Rel*	100-5K	
End group analysis	M_n	Abs	< 15K	Only for well-defined structure and distinguishable end-groups. Care needed about low MW impurities

Nowadays one of the techniques, which is used very frequently, is end group analysis, so, I will discuss end group analysis. As a representation from these four colligative property based techniques, I will briefly discuss the Membrane Osmometry; but these four techniques are not used very frequently nowadays, as representative, I discussed this membrane osmometry. Dilute solution viscometry is very easy technique and can be used commonly in lab for a crude way of measuring molecular work or quick way of measuring molecular weight which may not require very accurate results, so this is used nowadays for quick measurements of approximate molecular weight. So, I will discuss, dilute solution viscometry. I will also discuss light scattering and Gel permeation chromatography. I will stop now from next lecture onwards, I will discuss these five techniques, which I marked now for determining polymer molecular weight.