Polymers: Concepts, Properties, Uses and Sustainability
Prof. Abhijit P. Deshpande
Department of Chemical Engineering
Indian Institute of Technology-Madras

Lecture - 05
Molecular Weight and Distribution

Hello and welcome to this lecture on molecular weight. In this lecture, we will look at molecular weight and its distribution. This is the first week of our course on polymers. And we are mainly trying to answer these questions, what are polymers and what are their unique features. And this is a course, in which we are looking at different aspects from concepts to properties to applications and sustainability.

This particular lecture focuses on estimation, quantification and therefore properties.

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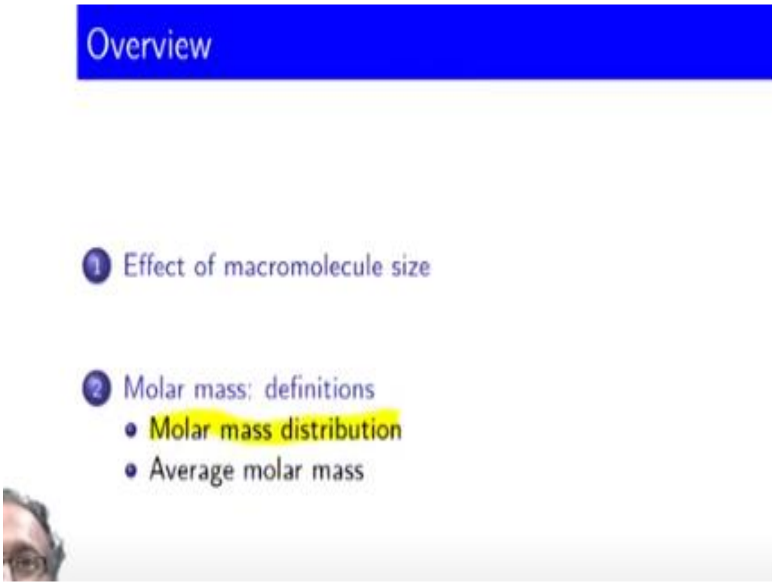

And we will do this by first just briefly reviewing what is the effect of molar mass or molecular weight. And then we will look at how do we define a distribution and therefore, both distribution and an average is defined.

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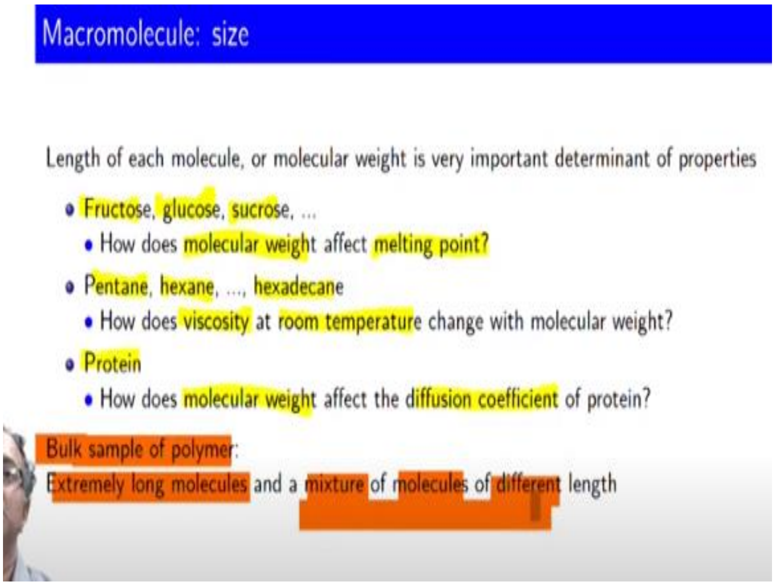

What is the influence of size of a molecule on properties? We can think of this problem by looking at some other sets of molecules also. So for example, if you look at sugar molecules, so if you look at fructose, glucose, sucrose, you can look up molecular weights of each of these and size of each of these. Now the question that you can ask is, how does molecular weight of these different compounds affect the melting point?

Do you have a guess? For example, if you change the molecular weight, will the melting temperature increase or decrease? I think most of you probably will say that molecular weight if it is higher, the melting temperature will also be higher. We will require more thermal energy to make the molecule mobile.

So clearly we understand that molecular size has a very important role in terms of determining the properties of a material. Let us look at other class of materials. In this case, these are alkanes; pentane, hexane, hexadecane. What happens to viscosity of these liquids at let's say 25 degree Celsius when we look at it as a function of molecular weight? Again, do you think the viscosity will be influenced?

In which way will be influenced? You can just go look up viscosities of these kind of compounds and see whether it meets your expectation in terms of viscosity being higher if molecular weight is higher. An important example is related to biological world, proteins. Proteins need to reach select places within cells. And therefore, they have to diffuse. Now some proteins are small, some proteins are large.

The question that we can ask is how does molecular weight affect diffusion coefficient of a protein? Diffusion coefficient is a property which determines how much protein can move. So flux of a protein will be diffusion coefficient times the concentration gradient. So therefore, diffusion coefficient is an important determinant of how fast or slow a protein is diffusing by quantification using flux.

So the question in all of these cases are what happens when we change the molecular size, what happens to properties? And just to remind ourselves that a bulk sample of polymer will have extremely long molecules and generally it will be a mixture of molecules of different length. This is not so always in case in natural world.

Just to remind ourselves protein for example, if it is a specific protein of a specific species, it has a fixed molecular weight as opposed to a distribution of molecular weight. But we also have biopolymers like starch. Depending on the species, depending on which part of the body for a tree let us say or another, in case of human, let us say collagen tissue, which is made using collagen as a material.

So molecular weight and many other properties of macromolecule may vary depending on the location and the specific role that the biomacromolecule is able to play. So generally, in this lecture, we will focus on those sets of polymers, where there is a distribution of molecular weight and synthetic polymers by definition belong to this class where bulk sample of polymer will always have a mixture of molecules of different length.

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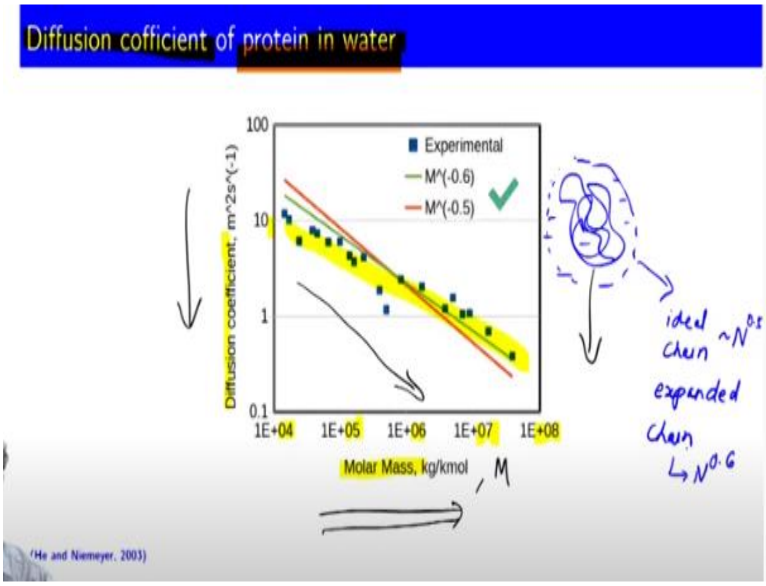

Just looking at data again to highlight this point of how size influences the diffusion coefficient. What we are looking at here is diffusion coefficient, as I explained, which determines basically the flux or the amount of protein that can diffuse in water. And this is experimental data, which are all these blue data points where the diffusion coefficient is plotted as a function of the size, molar mass or the length of the macromolecule.

You can notice that its orders of magnitude different. So protein can have molecular weight which is 10,000 to molecular weight, which is 10^7 and even higher. So that is the range of molecular weights that is possible in macromolecules. And so it is quantification is very important. Now what is very nice and beautiful with this experimental data is that you have a very nice trend.

The larger the protein molecule, the lower is the diffusivity. So there is an overall decreasing trend, as you increase the molecular weight, the diffusion coefficient comes down. And again, from the point of view of conceptually just making sense of this, as the size is increasing, the bulkiness of the protein macromolecule will also increase. And therefore, its diffusion coefficient decreases.

So qualitatively of course, we can immediately reconcile to this information that it makes sense. Now what is very nice about polymer science is that we can explain this quantitatively. And in this lecture, we are not going to look at this aspect, but just to help you see this when you we will look at this in a future lecture is look at the two lines that are drawn in this figure.

One line is related to $M^{-0.5}$. And other underline is related to $M^{-0.6}$. M is the molar mass. So we know that diffusion coefficient varies with molar mass. These two lines, the red and the green signify how much quantitatively does diffusion coefficient vary as a function of molar mass. It is negative power because it is decreasing.

One is 0.5 and one is 0.6. And you can see that 0.6 is closer to the experimental data. But of course there are there is a minor difference, but these two come from quite simplistic theories of how a polymer conformation and the size of the polymer is in a solution. We are looking at protein in water. And therefore, what we are looking at is some protein molecule which is surrounded by water.

And what is the diffusion coefficient of this particular protein? How does it move? And so we can think of the protein molecule as being encompassed in some sort of a size, spherical or cylindrical depending on the shape of the protein molecule, we can think of it as a spherical or cylindrical object. And then, we need to say how this sphere or cylinder is diffusing in water medium?

And so we will see later on this shape of this sphere or the size of this sphere is closely linked to the molecular weight based on theories of either ideal chain or expanded chain. So ideal chain says that the radius of this sphere is proportional to $N^{0.5}$, where N is the degree of polymerization or how many repeating units are there on the polymer. And for expanded chain, it is $N^{0.6}$.

Degree of polymerization capital N is directly related to molar mass M through the number of repeating units. So you can see that, how theories can be used to quantitatively explain the behavior which is observed. So molecular size is very important in terms of defining the properties of a macromolecular system. Let us look at this molar size in more detail.

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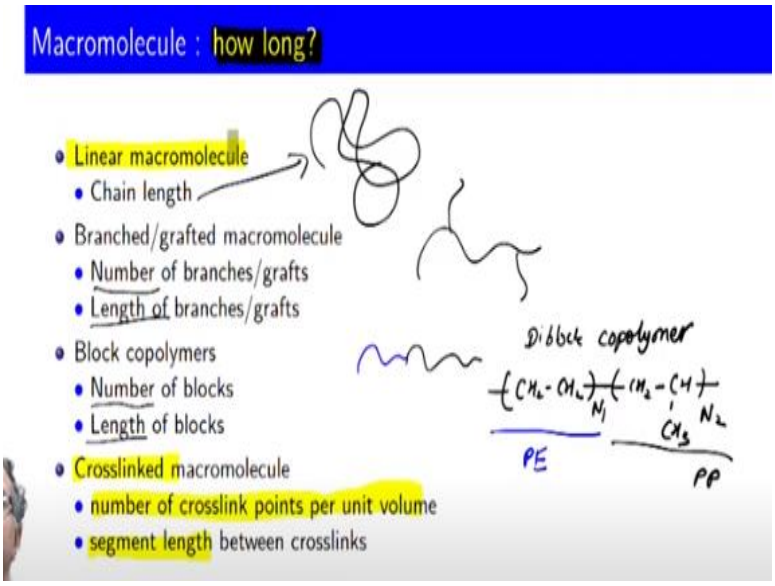

So how long is a macromolecule? Now if it is just a linear macromolecule, then we just need to look at its chain length. But if it is a branched molecule, then we need to look at the number of branches and also length of each branch. So in terms of size of a macromolecule, we need to specify different things depending on what is the molecular architecture of that particular macromolecule.

If you have a block copolymer, in which case, we will have a block of one type of monomer, attached to another type of monomer. And what I have drawn here is an example of a diblock copolymer. So in this case, we need to specify the number of blocks as well as the length of the blocks. And whether it is triblock or diblock will give us the number of the blocks.

Whether it is, and the length of each of these is specified. So for example, if I make a block copolymer of polyethylene and polypropylene, then I would write it like this, where I will say that CH_2-CH_2 a block is combined with CH_2CH_3, which is propylene. And so N_1 and N_2 are lengths of blocks. And in this case there are two blocks. There is a polyethylene block and then there is a polypropylene block.

So we have a PP and PE. And you can look this up. This is EPR. It is a very important application for again elastomeric applications. If we have a cross linking system then we need to know what is the number of cross links per unit volume or alternately we also need to know the segment length between cross linking points. So in each case, the question how long will be answered by quantifying different sets of things.

So lot of discussion now that I am going to introduce in the next few slides is related to mainly linear macromolecules. And, but same concepts are applicable to all the other molecular architecture also except that instead of talking of one particular macromolecule, we talk of length of branch, length of cross-link and so on.

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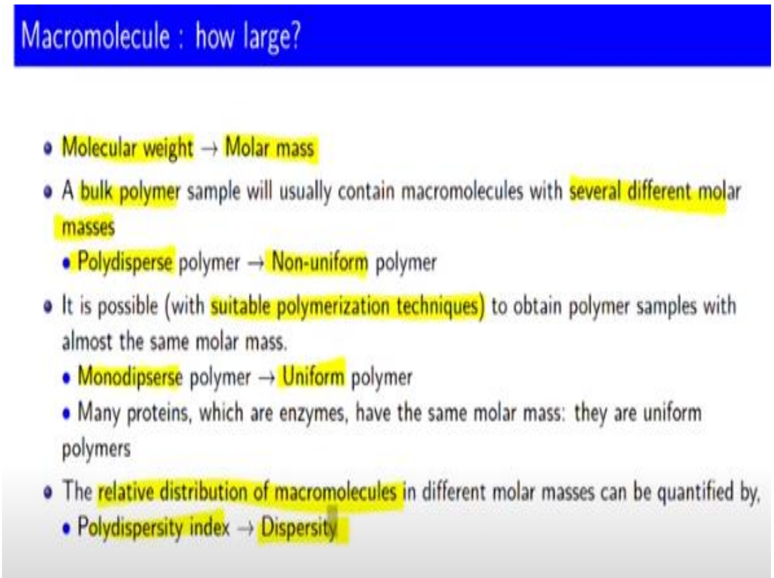

So let us start looking at quantitatively about how long can the macromolecules be. We have already stated that molecular weight is important for polymers because they are extremely large molecules, macromolecules. And we have also stated that in a bulk sample, there may be each macromolecule with a different molecular weight. Just to begin with some terminology, molecular weight and molar mass.

Scientifically speaking, molar mass is the term which is used. But in common parlance as well as in practical usage, molecular weight is used. So in this course also we will try to use both these terms, so that we are aware of the scientific usage as well as common parlance usage. So bulk polymer will contain macromolecules with several different molar masses.

And therefore, this polymer is called a polydisperse polymer or also scientifically non-uniform polymer. Immediately you can see that, since there is a non-uniform polymer there is a uniform polymer and uniform polymer traditionally is called monodisperse polymer. So therefore, mono disperse polymer, can you think of a monodisperse polymer? In fact, protein is a very good example of monodisperse polymer.

The reason in our biological world, proteins do very specific tasks. And all their properties are dependent on the specific structure that they have, which is dependent on molecular weight or molar mass. So the biological polymerization machinery is such that, we get precisely the same protein with exactly the same molecular weight. By the way, this is not always the case in the biological world.

For example, polysaccharides are not exactly the same molecular weight. There is a molar mass distribution in case of polysaccharides. So if we have suitable polymerization techniques, we can obtain a monodisperse or uniform polymer. When we say it is a uniform polymer, we take a bulk sample of it, each and every macromolecule in that sample will have exactly the same molar mass.

And the relative distribution of macromolecules in a bulk sample is measured using polydispersity index and scientifically which is called dispersity. So in the next few minutes of this lecture, we will try to define these terms precisely.

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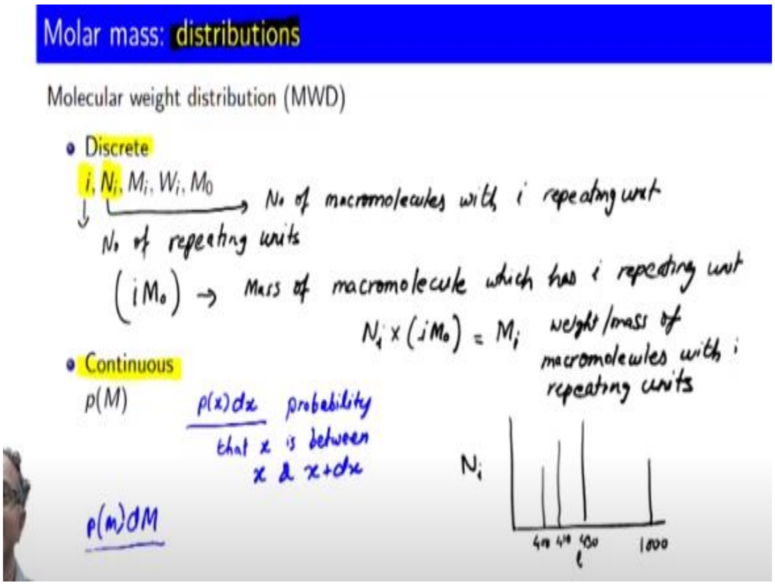

So let us first look at what do we mean by a molar mass distribution. And there are two ways to describe it. Discrete, in which case we have number of macromolecules given that we can count these macromolecules. Then we can talk in terms of number and number of macromolecules of each and every repeating unit. Then in that case, we call it discrete. Continuous implies that they all the infinite sets of molar masses are present in the sample.

Why is continuous required because in reality, a macromolecule will have let us say 10 repeating units or 50 repeating units, 10,000 repeating units. So it is a discrete number. When we say continuous, it implies that all numbers, real numbers are possible. So discrete molar mass distribution is what we will see in reality, and when we measure also we will get discrete molar mass distribution.

But from a theoretical point of view, it is quite useful to talk about continuous distributions, because we can then use lot of mathematical equations and mathematical equalities and principles to try to derive some important results which are useful in terms of understanding macromolecules. So we will start with discrete in this course and focus mostly on the discrete.

So most important variables are as follows; `i' is the number of repeating units. So in a macromolecular sample, some macromolecules may have 400, some others may have 405 and so on. So this is depicted by i. And then if we take a bulk macromolecular sample and I say what is the number of macromolecules which have 405 units? So that is called N_i. So therefore, N_i is the number of macromolecules with i repeating units.

So in fact the distribution is completely specified if I can specify i and N_i. Because then I know in the bulk sample how many number of macromolecules have how many repeating units. And,

$i*M_0$ is nothing but the mass of molecules which have i repeating unit. Because M_0, so this is molar mass of macromolecule which has i repeating units. So can you guess what is M_0?

Sure enough, all of you would have recognized that M_0 is the molar mass of repeating unit. Therefore, i times M_0 is the macromolecule which contains i units. So now using this information, we can construct the distribution and more importantly estimate averages also. So if I ask the question what is the mass of macromolecules in a bulk sample, which have i repeating units?

So what you have to do in this case is take all the macromolecules which have i repeating units and find their mass. So since N_i is the number of molecules, which have i repeating units, and then each of them weighs, $i*M_0$ this is the weight of macromolecule which contains i repeating unit. So that is why M_i is the weight or mass of macromolecules with i repeating units.

So therefore, now we can continue and define what are the averages based on such a distribution? We can also plot this distribution by saying, what is the number of repeating units for many of the macromolecules and then what are the numbers corresponding with it. And so if we quantify this, we can then have the complete distribution of the molar mass in the sample.

So for example, this distribution may look something like this, that at some i equal to let us say 400, some numbers are there, then 410 some other numbers are there and 430 some other numbers are there, and 1000 repeating units also some molecules are there. So this way is a distribution of the molar masses. How about continuous distribution? I am sure all of you are familiar with probability and distribution.

And you would have seen that a probability density function P(x) is usually denoted like this and P(x)dx is the probability that x is between x and x + dx. So therefore P(x) is a probability density and P(x) describes the distribution of a random variable x. So describing molar masses, we similarly now have a macromolecular sample in which there are all kinds of macromolecules with all kinds of molar masses M.

So therefore, P(M)dM has same meaning as P(x) dx that you are familiar with. So can you write in words, what does P(M)dM would imply?

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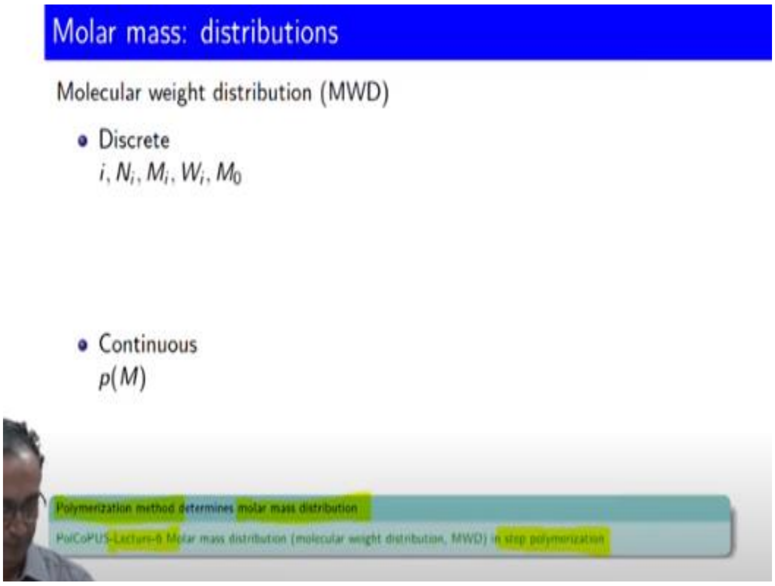

So let us continue and look at the distribution of molar masses on a discrete basis and define averages. It is very important to note here that polymerization method will determine what is the molar mass distribution. We will see an example of this in upcoming lecture, where we will see, how in a step growth polymerization the molar mass distribution varies.

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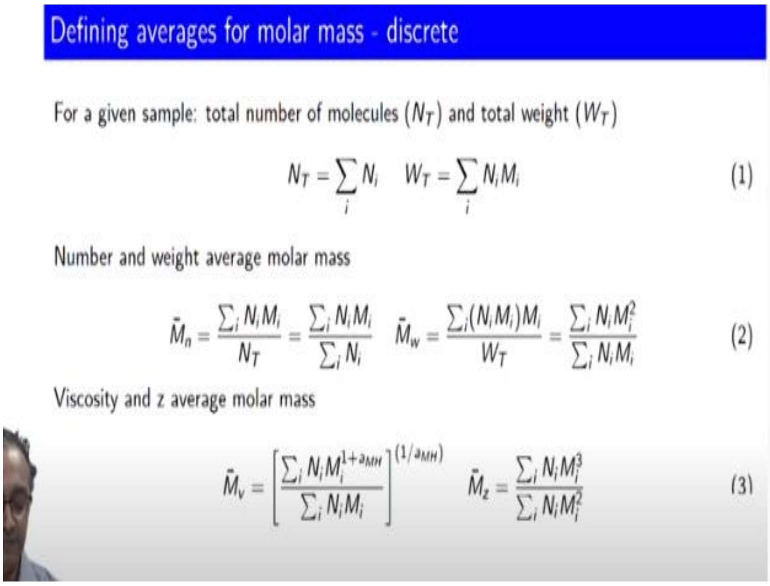

So let us start defining the average and this can be done by using the quantities that we had defined earlier.

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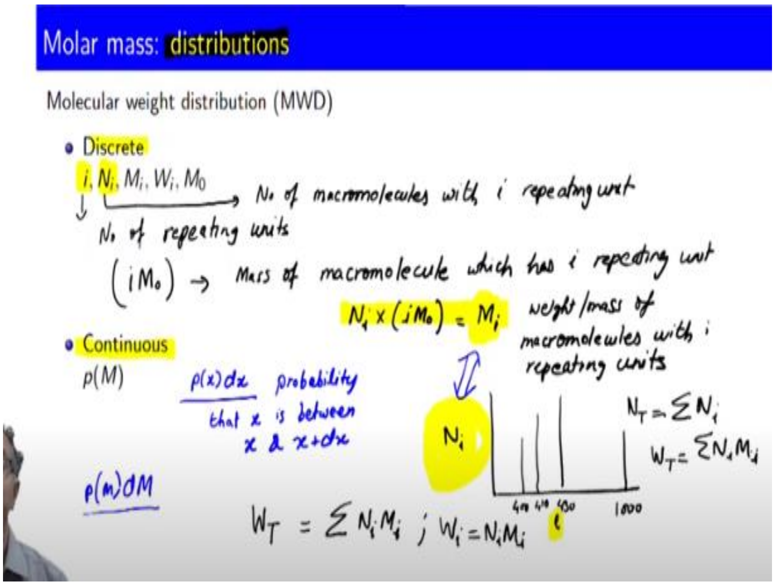

So we had said that we have N_i as the number of macromolecules which contain repeating units i. And then we had also defined the mass of macromolecules which contain the i repeating units. So if I have to sum all the mass which is there in this macromolecular bulk sample. So if we want to calculate the averages, we will need to calculate the mass in a bulk sample.

And we can do that by counting the number of macromolecules with i repeating units and if I know the mass, so using these two numbers, then we can find out what is the overall mass. So for example, if we think of what does this sum tell us? So N_i is the number of macromolecules which have i repeating units. M_i is the mass of such macromolecules.

So N_iM_i tells us the mass of all the macromolecules which contain i units. And if I sum this overall then I will get the overall mass of the sample. And mass of macromolecules which contain i repeating unit is just N_i*M_i. So this is one clear ratio, right? W_i/W_T tells me the ratio of the weight of macromolecules, which contain i repeating unit to the total weight.

So we will see that averages can be constructed by looking at many of these sums and dividing by a particular quantity. So the first thing we can do is we can calculate it based on numbers. So in this case what will happen is the numerator will be the overall mass of macromolecules divided by the total number. So in this case we are focusing on the number of macromolecules and therefore, the denominator is number.

So in that case, the possibility of denominators that we have is:

Total number (N_T) = ΣN_i and

Total weight (W_T)= $\Sigma N_i M_i$

And so these are two most common ways of defining average molar mass.

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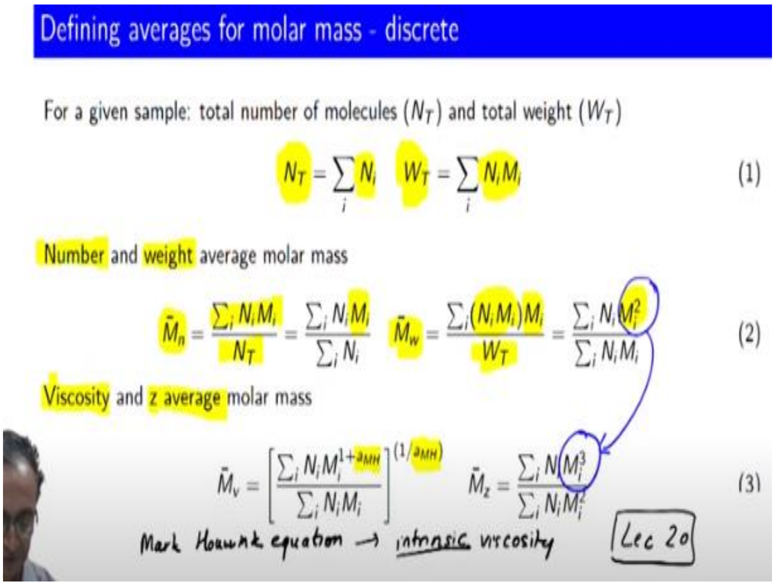

So let us look at the expressions. So N_T is the total number of macromolecules present in the sample because we just sum over all the macromolecules with i repeating units. Similarly, W_T is the total weight of the polymer and that is $\Sigma N_i M_i$. So now we can define a number average molar mass, which is the overall mass or weight of the macromolecules divided by the total number.

$$M_n = \frac{\Sigma N_i M_i}{N_T}$$

And then we can define a weight average molar mass where we are saying of what is the mass of macromolecules with i repeating units and the weighting factor is the molar mass of the same number of repeating units.

$$M_w = \frac{\Sigma (N_i M_i) M_i}{W_T} = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

And if you notice the difference between the two, we have M_i^1 in the first definition while we have here M_i^2 in the second case.

Now if you remember statistics in which you would have learnt many of the quantities which are defined, whenever we have a variable which takes several different possibilities, we can define the series and it is measured using variables such as mean, standard deviation, mean square and so on. Can you think which of this relates to the quantities that I mentioned just now?

What is mean square and what is mean? I am sure you can immediately spot that number average molecular weight or number average molar mass is the mean, because it is just ΣM_i. While M_i^2 is mean square. So therefore, standard deviation is related to weight average molar mass. Mean is related to number average molar mass. We also have other definitions of molar masses.

These are based on the measurement technique as well as from the application point of view. Given that macromolecules have this distribution of molar masses, it is very challenging to figure out which part of, which fraction of molar mass will play a crucial role in which application. What I mean is if we are looking at a mechanical property, which fraction of macromolecules is going to play a major role?

So therefore, distribution is important and quantification of distribution in terms of single number in terms of average may not always work. So therefore, we define different types of molar mass which are average quantities, and then we try to correlate an engineering property with such average molar masses.

So that is why we have number average molar mass, weight average molar mass, viscosity average molar mass and the z average molar mass. The viscosity average molar mass is based on viscosity measurement. And if you look at z average, you can clearly see that as opposed to mean square, now you have a higher moment.

So if many of you are not familiar with some of these, you have to go and read in terms of distribution, random variables, and series of random variables and measures associated with such random variables. So in the equation for viscosity average molar mass given as,

$$M_v = \left[\frac{\Sigma N_i M_i^{1+a_{MH}}}{\Sigma N_i M_i}\right]^{(1/a_{MH})}$$

we have this parameter a_{MH}. This is a very important parameter from the point of view of a solution behavior of a polymer solvent system.

And it gives very good indication of polymer solvent interactions also. In this case H and M stand for Houwink and Mark. And in general we will learn more about this later on, where historically this was called Mark-Houwink relation for viscosity. We will define this. There is a specific term called intrinsic viscosity. Why intrinsic? We will learn about this in the 20th lecture.

So lecture number 20, we will learn about this Mark Houwink equation. In fact, it is also called Kuhn-Mark-Houwink-Sakurada equation to acknowledge various scientists who have contributed. You can see that if a_{MH} is 1, it reduces to something else, which is on the same slide. So just think about it. Let us go continue further.

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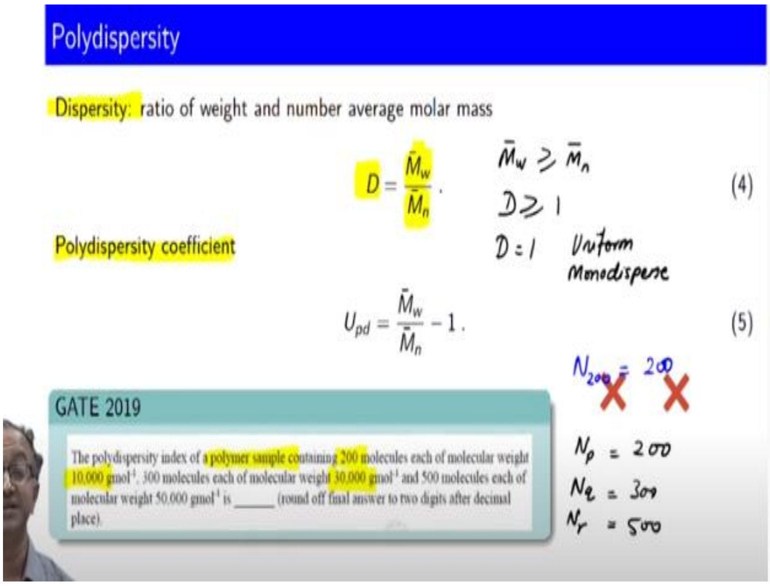

So based on what I said in terms of molar mass distribution being important, and several different fractions of molar masses might contribute differently to a property. For example, when it is considered flowability, moulding capability of a polymer, the low molar mass fraction is sometimes important, because it makes the flow to be easier.

From a mechanical property point of view, such as strength, high molar mass may be important. So in general, not only do we need to know average molar mass, but we need to know the distribution also. And taking the distribution in terms of having all the details is sometimes very cumbersome. So therefore, we define these averages and we define some other variables which are based on these averages.

And one of the most important variable which is used quite commonly is called polydispersity index in general usage or dispersity in scientific usage. We define dispersity as the ratio of the weight average molar mass to number average molar mass. And you can see that weight average molar mass is going to be always greater than or equal to number average molar mass. Think about it, why is this statement possible?

You can also think in terms of what is the relationship between root mean square and mean. Why is it that root mean square will always be greater than mean of a random set of numbers. If you think about that, you will get answer to this also. So therefore, D generally will be 1 or greater value. And whenever D is 1, we have a uniform polymer or monodisperse polymer.

So that is why D is a very good measure of quantifying the distribution. We can also define a number which is called polydispersity coefficient, which is just based on dispersity itself. Just to think in terms of how we get these numbers, you can look at this question here, where the polydispersity index of a polymer sample is being asked in this exam question.

And what is being given is the number of macromolecules and instead of giving you the number of repeating units, directly what is being given is the mass of each and every molecule. So just think about it in the notation of our lecture, which of these quantities how are how are they related? So for example, can you just go back to the slide where we defined the variables and then come back and tell yourself what is 200?

What is 500? And what is 300? So just to start you on this, for example, N_{200} is 200. Is that correct? No, think about it carefully. 200 is the number of molecules. We do not even know the repeating units in this case. So therefore, all we know right now in this case is some repeating units are there, but the number of those molecules we know. So therefore, N_{i1} is 200.

Instead of calling it N_{i1}, let us just call it N. We will just use some indexes. So let us use N_1, N_2 and N_3. This is where some of the notation can become tricky. N_1 in our definition implies number of molecules with 1 repeating unit. So again, this is not correct. So let us just use N_p, N_q and N_r; also, we do not know p, q, r. But we know that number of macromolecules with p repeating unit is 200.

And then 300 molecules of some other repeating unit are there and then 500. So you can continue and then find out for example what is 10,000, 30,000 and 50,000. And therefore, you can calculate in the end what is D based on whatever we have covered.

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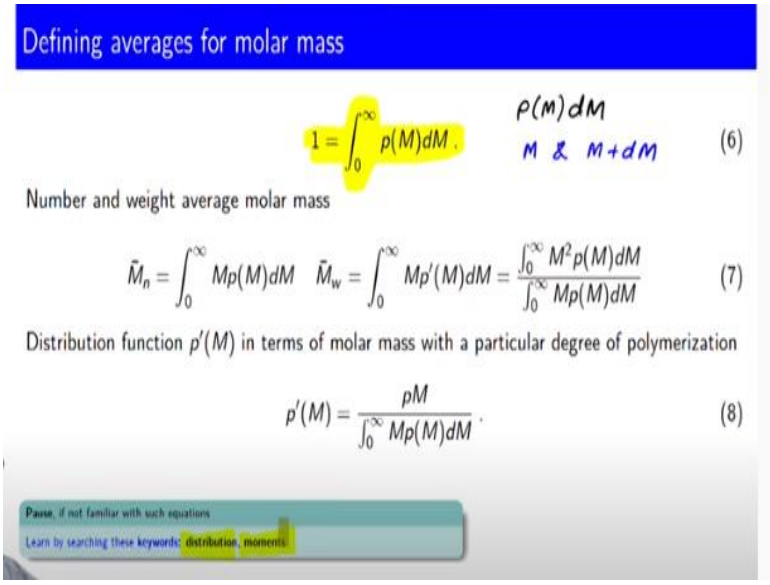

So I leave you to **do** finish this calculation. As I mentioned earlier, the continuous distribution is very useful theoretically. And again, this is something which should be familiar to you. If you answered my question related to what is the meaning of p(M)dM, you should be able to justify immediately that y is an integral of p(M)dM for all the values of molar masses is equal to 1.

So just to recap, p(M)dM is the probability of finding a macromolecule with molar mass between M and M+dM. So if I sum all these probabilities from 0, which means smallest macromolecule to infinity, which means the largest macromolecule, then the probability has to be 1. And so therefore this is what is called the normalization of a probability density function.

And so p(M) is a normalized probability density. So in case you are not familiar with, you can do some search related to these terms and pick up some of the theoretical concepts related to these continuous distribution. For our course purposes, it suffices to learn about discrete molar mass distribution and then some of the average quantities which are based on this.

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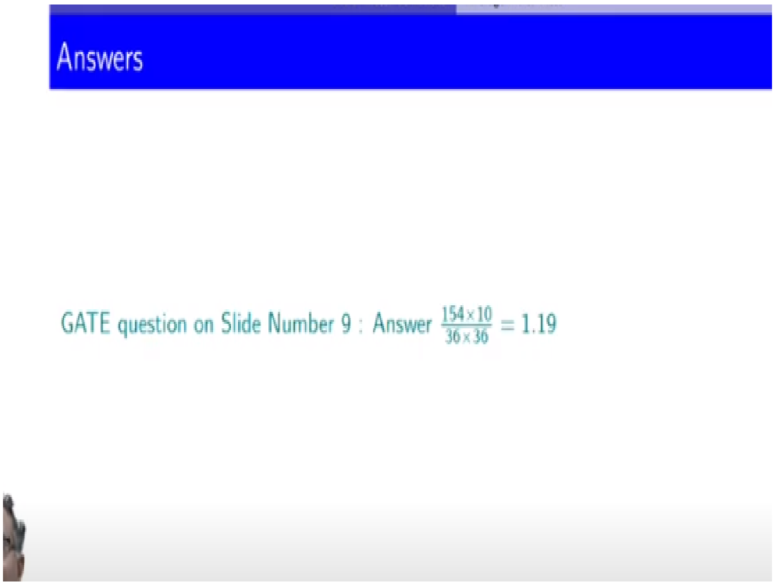

Leave you with the answer on the question. So if you have done all your algebra correctly, you should be able to get the correct answer. Thank you.