Polymer Reaction Engineering
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Lecture - 07
Molecular Weight and It's Distribution

Welcome to the molecular weight and its distribution under the head of polymer reaction engineering. In the previous lecture, we started about the things related to the molecular weight and we discussed about the importance of a molecular weight as per this particular slide that all molecular weight plays a very vital role in deciding the mechanical and chemical thermal properties of the polymer.

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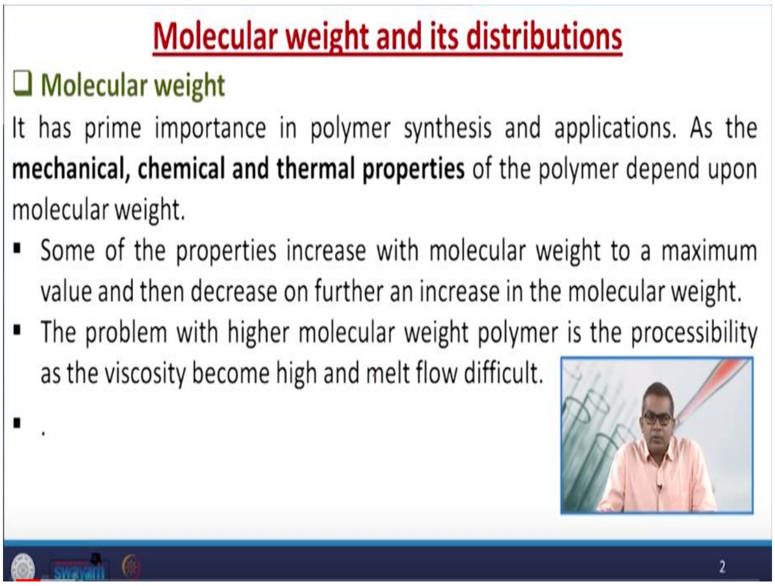

And moreover, its change or this molecular weight also affects the processability of the polymeric system. So, we go ahead with this particular molecular weight approach in this particular segment. And we discuss about the various kind of molecular weight, how it distributed among the different type of system, we will discuss in the due course of time.

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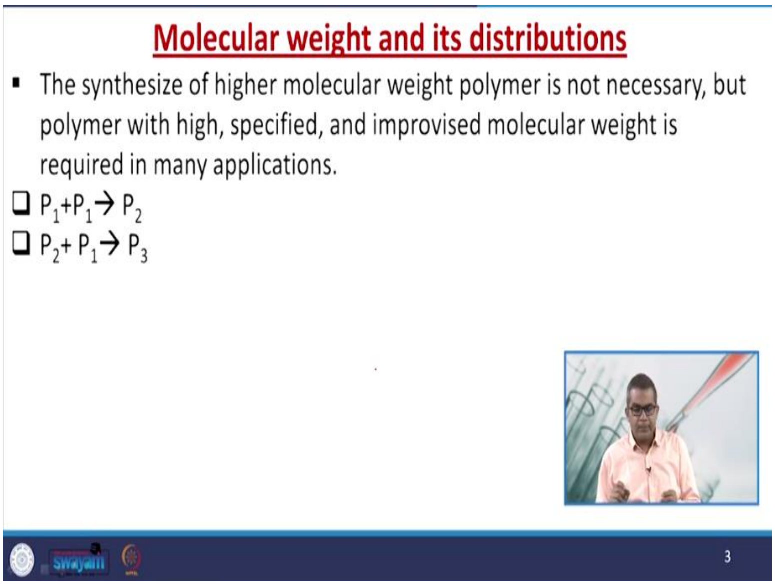

Now, the synthesize or synthesis of higher molecular weight polymer is always not necessary. But polymers with high specified and improvised molecular weight is required for the many application. Now, why I am saying the polymers they do not possess any kind of fixed molecular weight. The reason is that let us go to the this particular whiteboard and we will see that lets this P_1 represents the monomer.

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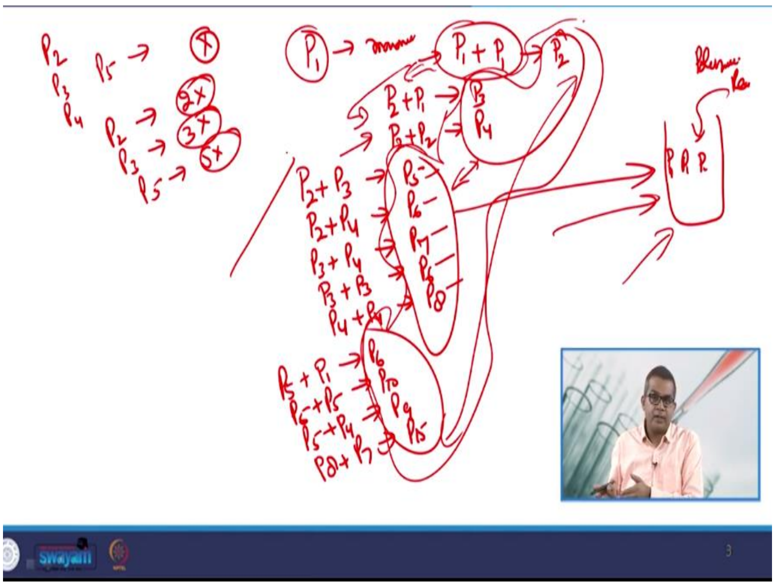

So, when we start the polymeric system or polymerization process, so, this is one repeating unit. Now, this P_1 at the start at the outset, it may get combined with this P_1 to give you P_2. Now, this is my reactor polymerization reactor. Now, here now, if you see that initially the P_1, P_1, P_1, etc., they were present but when the reaction was started or the polymerization process initiated.

In that case, there may be this formation of P_2 that means 2 repeating units are combined. Now, at the carry on this particular polymerization little further then the reaction mass may have P_2 may get combined with P_1 to give you P_3. Similarly, P_2 may have an option to combined with P_2 to give you P_4. And obviously, this option is always there. Now, you see that in the reaction mass you are having P_2, P_3, P_4 apart from P_1.

Now, if you proceed further see the complexity of this particular system. If you proceed further, then P_2 may get combined with P_3 to give you P_5. Similarly, P_2 may combine with P_4 which is earlier developed P_6. Similarly, P_3 may have a chance to combine with P_4 to give you P_7. Similarly, the P_3 may have a chance to combine on its own gave you P_6.

Similarly, P_4 may have an option to combine on its own. So, give you P_8. Now, if you see this profiling apart from this, these products available in the reaction mass, there are additional polymeric chains having 5 repeating units, having 6 repeating units, having 7 repeating units and another one is the having the 8 repeating units. So, as a whole if we talk about after some time, then this polymer system may have this type of a polymeric chains.

Now, if you proceed further, then you see that the complexity may be like this P_5 may combine to give you P_6. Similarly, P_5 may combine with P_5 to give you P_{10}. P_5 may have an option to combine with P_4 to give you P_9. Similarly, P_8 may have an option to combine with P_7 to give you P_{15}. So, by this way, the chains of the polymer may have an ability to enhance themselves with respect to the different type of monomeric units or repeating units.

Now, if you see, just after say Stage 3 or 4, now you see that how much different polymer chains are available in the reaction mass. Now see every chain like whether it is P_2, P_3, P_4, P_5, etc., it represents the different number of monomeric unit. Now, let us have an example of suppose one monomer unit is having the molecular mass of x. So, P_2 will have the molecular mass of 2x, P_3 will have the molecular mass of 3x, P_5 may have the molecular mass of 5x and so on.

So, this is the molecular weight. Now, at the outset, there are 2 options, either you truncate the polymerization reaction at the desired level of viscosity as the desired level of the function or you keep on polymerizing different segments for the longer period of time. So, if you keep on setting this particular polymerization process for a longer application, then there may be a chance that higher molecular weight chain may get processed.

In that case, the molecular mass of that particular polymer would be on the higher side, it may create the problem of processability as I discussed in the previous slide. Now, in that case, you are compelled to truncate or this particular polymerization process or terminate that particular polymerization process at some juncture.

So, when you truncate this particular polymerization process, there may be a chance that your polymer mass may consist of a different chain with the different chain lengths, maybe P_2 maybe P_3, P_4, P_5, P_6, P_7 up to P_n and so on. So, in that case, you may not have an opportunity to analyze that how many numbers of chains are there, how many repeating units are there, etc.

And that is why there is a usually a range of molecular weight for every kind of a polymeric system. And this may be from say 10 to 10 lakhs etcetera. So, it all depends on that how much the physical and chemical property you require in this particular polymerization process. So, it is a very crucial thing. And that is why if you recall that I discussed that initially, the polymeric systems they are having the 3 different steps, initiation, propagation and termination.

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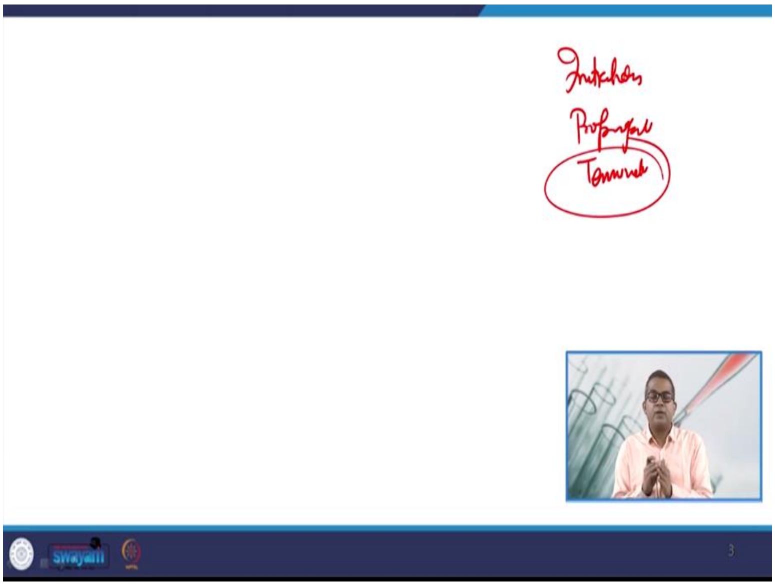

Now, initiation as I told you in previously, this this is your initiation step. Now, subsequent processes when you started this initiation process, the subsequent processes are termed as propagation. Now, when you achieve the desired property based on your requirement with respect to the thermal, chemical, mechanical or the processability aspect or viscosity aspect then you try to truncate.

You can you cannot carry out this particular polymerization process for infinite period because I told you that it may create a bulky mass. So, in that case, you prefer the termination. So, at the outset, when there is a termination process in that case, you need to calculate the molecular weight because, one time we are saying that molecular weight plays a very vital role for the deciding the properties.

So, the determination of this molecular weight is extremely important to carry out the further processing of any kind of polymeric system. So, based on this particular approach, there are different type of molecular weight things are given. And they discuss about the different type of distribution pattern for the molecular weight. I told you that from P if at any point of time, your molecular mass may consist of P_1 to say P_n.

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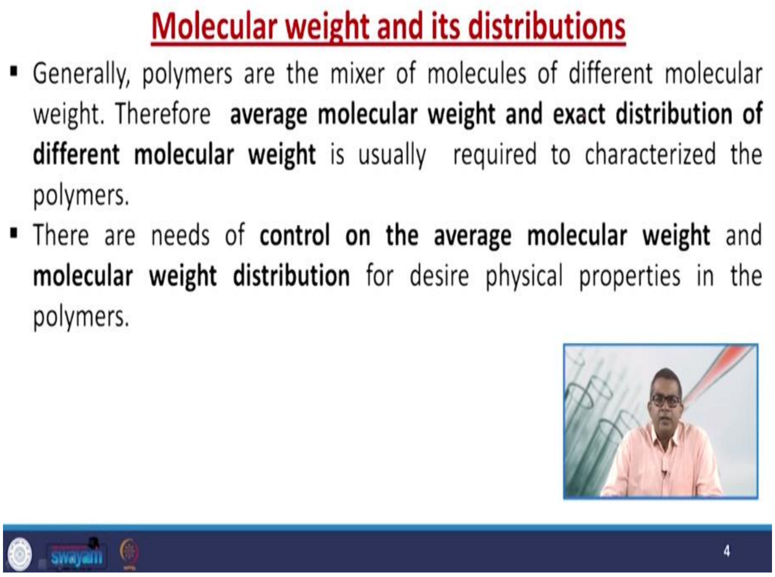

So, that is why there is a distribution pattern for these molecular weights. So, based on this particular nothing, we already discussed that polymers, usually they are a mixture of molecules of a different molecular weight, just because attributed to the different polymeric chains having the different number of monomers.

So, therefore, the average molecular weight and exact distribution of a different molecular weight is usually required to characterize the polymer rather than the specific molecular weight of those polymers. So, there are need as I discussed, there is a need to control on the average molecular weight because of the processability because of the thermal, chemical and mechanical properties.

So, that is why we are always looking for the proper molecular weight distribution to carry out the desired physical properties in those polymers. So, usually this concept of average molecular weight is biased towards the larger and smaller sized molecules. So, various methods are used to determine the average molecular weight of polymers, sometimes colligative properties, sometimes light scattering things, sometimes the viscosity measurements etc.

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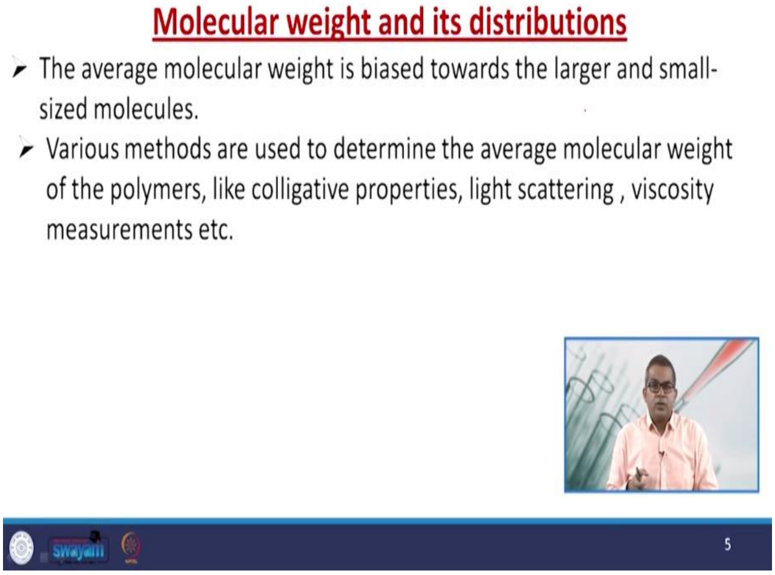

So, based on your requirement, you may choose the different protocols for calculating the molecular weight distribution. But before we discuss this, the protocol for the determination of these molecular weight. Let us have that how we can classify these molecular weight distributions. So, there are different methods or different protocols are available for this molecular weight distribution.

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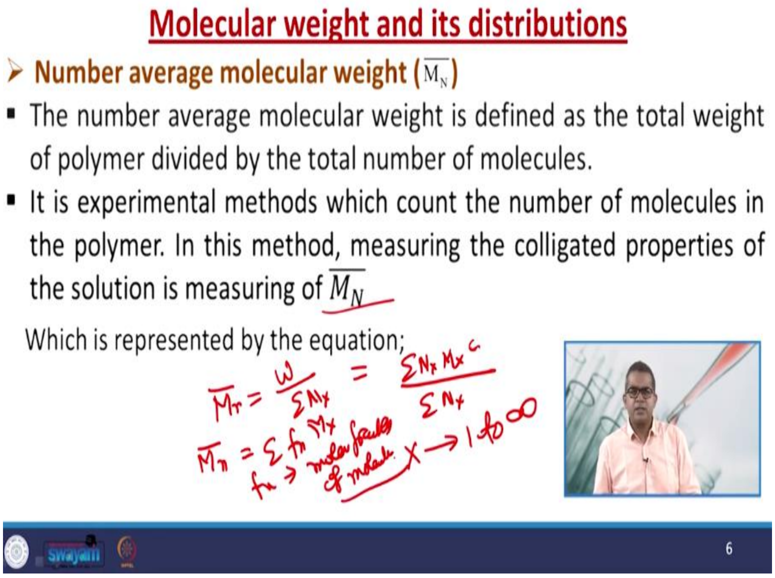

1 is that number average molecular weight. Now, that number average molecular weight is usually defined as the total weight of polymer divided by the total number of molecules. Now, it is usually the experimental method, which usually count the number of molecules in the polymer. So, in this method, the measurement of the colligative properties of the solution is measuring by M_N.

Now, this particular approach is represented by this particular equation. Now, before we go into the detail of this number average molecular weight, let us give you a typical plot of mechanical strength versus molecular weight distribution. There is a useful plot because, by this particular plot, you will be able to learn more and more specifically about the importance of this molecular weight distribution.

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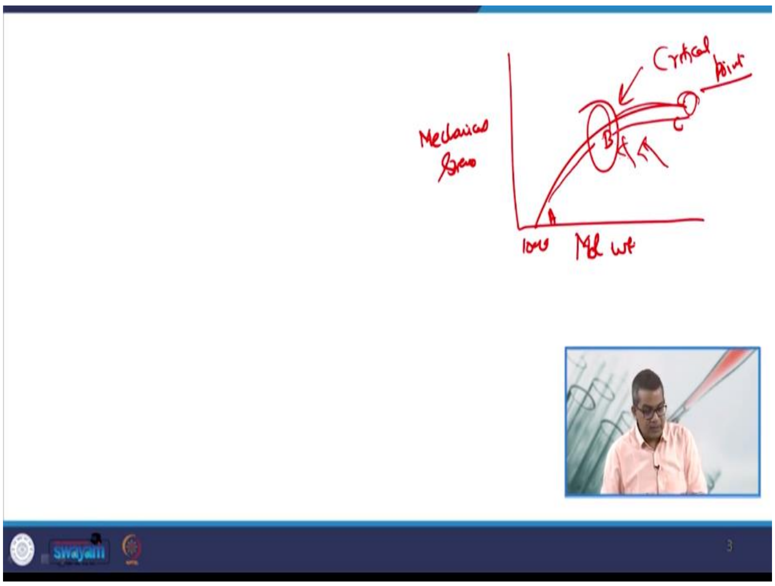

So, let us say that this is the molecular weight and here this is the mechanical strength. Now, here this plot is having 2, 3 different sub segments. Now, A is the minimum molecular weight of polymer. This may be say 1000 etc. Above A, usually the strength increases rapidly up to the point B. After this point, the this increases a bit slowly and reach to the limiting value of C.

Now, this shows the critical point correspond to the minimum molecular weight of a polymer to exhibit the sufficient strength. Now, this particular concept is important. Because there are certain limitations and these limitations you cannot carry out as I told you cannot carry out the experimentation or polymerization process for a longer time. Because of the efficiency of a process you require the optimum strength optimum property versus desired molecular weight.

So, the critical point approach is extremely important in this case. No doubt, you may have a higher molecular weight and sometimes a slight enhancement in the mechanical strength. But, if you carry on up to from point B to point C, certain quantum of energy economics, these **(()) (14:10)** may get involved in this process. So, sometimes you may not get the feasibility to carry out this particular process from B to C.

So, that is why the important point to carry out to analyze is the critical point. Now, this critical point is always useful while deciding the feasibility of any kind of a polymerization process. Now, go back to the number average molecular weight. Now, we discussed this particular approach in this particular slide where we are discussing about the number average molecular weight.

$$\overline{M_n} = \frac{W}{\sum N_x} = \frac{\sum N_x M_x}{\sum N_x}$$

$$\overline{M_n} = \sum f_x M_x$$

f_x →molar fraction of molecules

Where x→1 to ∞

Now, here this the equation where or sometimes it is referred as now that here N_x is the number of moles whose weight is usually the M_X. This is the summation over the overall different size of a polymer molecules from say x to extends from 1 to infinity. So, in other words, if we carry out this particular approach with respect to the mole fraction, it is represented as bar Mn where this is the mole fraction of molecules.

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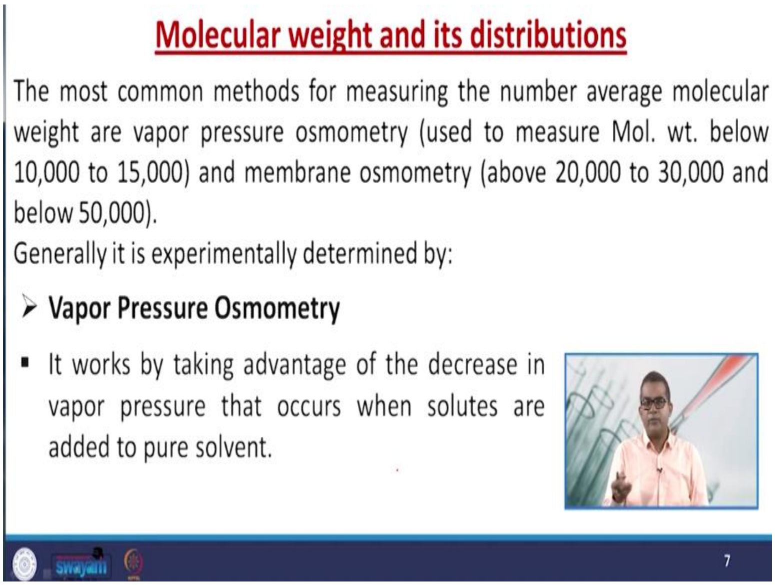
Equation Mn



So, this type of approach is again important. Now, the most common method for measuring the number average molecular weight are the vapor pressure osmometry. Usually measures the molecular weight below 10,000 to 15,000. And another approach is the membrane osmometry for above say to 20,000 to 30,000 and some below 50,000. So, generally, it is determined with the help of experimental tools.

And let us have a brief look about these vapor pressure osmometry and a membrane osmometry. Vapor pressure osmometry, it works by taking advantage of the decrease in vapor pressure that occurs when solute are added to your solvent. It is a very common phenomena of a chemistry.

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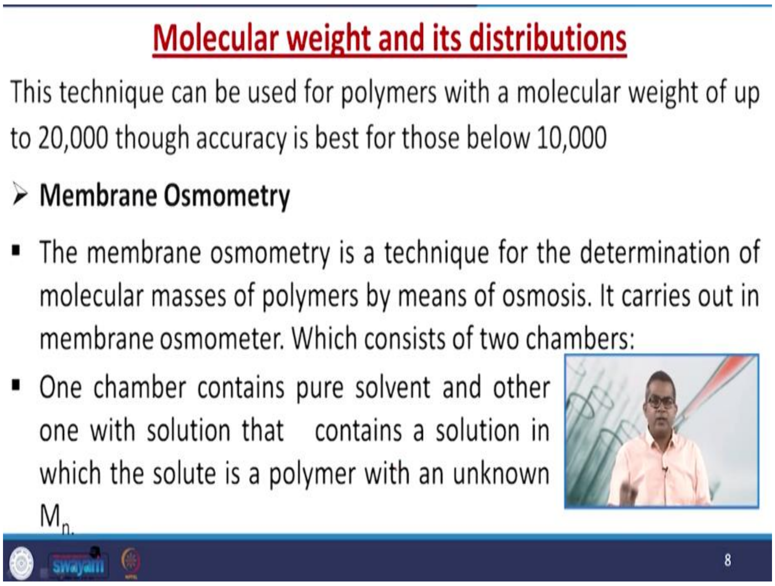

Now, this technique is used for the polymer with the molecular weight they may have up to 20,000. Though accuracy is best below as I told you in the previous slide that below 10,000. The next approach for determination of this is the membrane osmometry. Now, this membrane osmometry is a technique for the determination of molecular masses of polymer by means of osmosis membrane osmosis.

It carries out in a membrane osmometer. Usually, this membrane osmometer consists of 2 chamber, one chamber contains the pure solvent and other one is solution. And there is a barrier in between is that is attributed to the semi permeable membrane. Now, this the solution container contains a solution in which the solute is polymer with an unknown number average molecular weight.

Now, sometimes you may need to form the solution with the different type of a solvent like sometimes hexane, sometimes of a different hydrocarbon solvent being used for that different type of a dilution to carry out this membrane osmometric process. Now, by measurement of osmotic pressure across the semi permeable membrane, this gives the information about this number average molecular weight.

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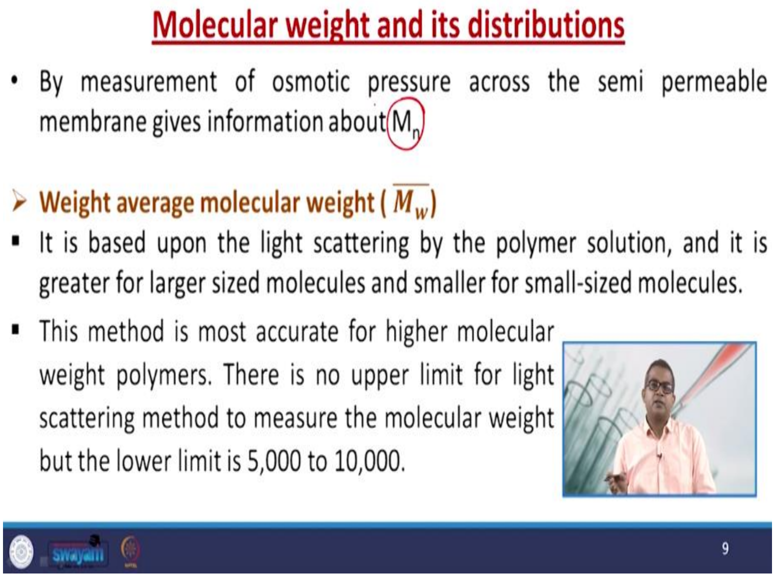

Now, another segment of determination of molecular weight distribution that is called the weight average molecular weight is a very common practice for the determination of or representing the molecular weight distribution. Now, it is usually based on the light scattering by the polymer solution and it is a greater for large sized molecule and is smaller for small sized molecule.

So, this method is usually accurate for higher molecular weight polymers. Usually, we do not prefer to have any upper limit of light scattering method to measure the molecular weight but for lower limit it is 5000 to 10,000. Now, this weight average molecular weight referred as bar Mw. This can be described as the product of weight fraction fx of the molecule whose weight is Mx.

$$\overline{M_w} = \sum f_x \, M_x$$

f_x → weight fraction of molecules whose weight is Mx

$$\overline{M_w} = \frac{\sum C_x M}{\sum C_x} = \frac{\sum C_x M_x}{C} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

C_x →weight concentration of M_x molecule

C → total weight concentration of all polymer molecules

$$C_x = N_x M_x$$

$$C = \sum C_x = \sum N_x M_x$$

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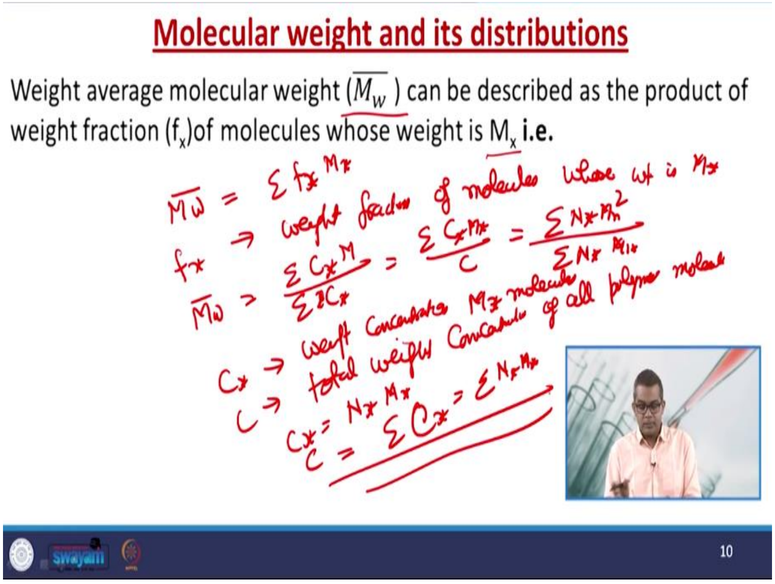

Now, the mathematically it is represented as now, this f_x is the weight fraction of molecules whose weight is M_x or this bar M_w is concentration. This C is the concentration of x component. And this is summation $N_xM_n^2$ upon summation N_xM_x. Now here the C_x is the weight concentration of M_x molecule. C is the total weight concentration of all polymer molecules.

Now, C_x can see that is equal to N_x, M_x and C is. So, this is the mathematical representation of weight average molecular weight how we can represent this weight molecule is respect to the polymeric system. And other the third approach is referred to as the viscosity average molecular weight.

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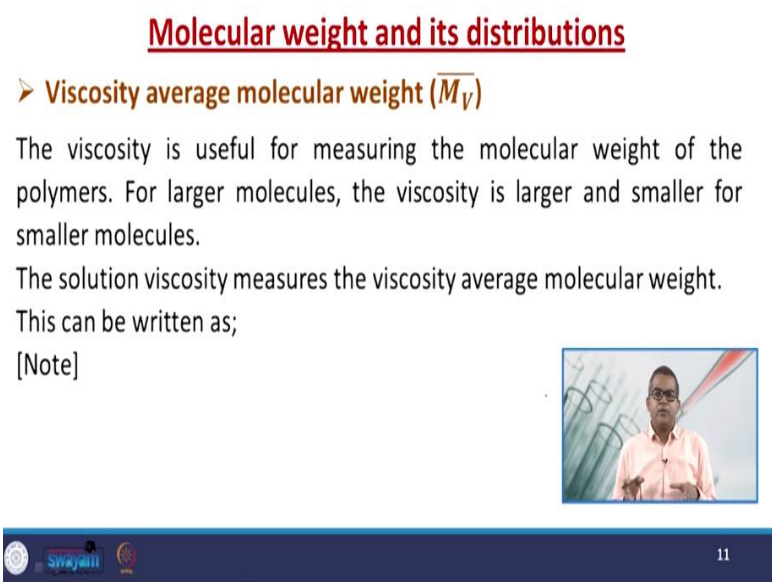

Now, as we know in the previous slide we discussed that viscosity plays a very vital role and if you carry on the polymerization process, sometimes viscosity may increase up to such a level that you cannot process that particular polymer. So, viscosity is a very useful thing for the measuring the molecular weight of polymer. So, for larger molecule viscosity is usually large and for a smaller molecule usually it is bit small.

Now, this solution viscosity usually measures the viscosity average molecular weight. Now, this solution average viscosity average molecular weight mathematically it can be represented as bar M_V. This is the rate of x component M_X. N_XM_X upon 1/a. Here a is constant. Now, viscosity and weight average molecular weights are equal when a is equal to 1.

$$\overline{M_v} = [W_x M_x]^{1/a} = \left[\frac{\sum N_x M_x^{a+1}}{\sum N_x M_x}\right]^{1/a}$$

a →Constant

a=1 then viscosity and weight average molecular weight are equal

$\overline{M_v} < \overline{M_w}$ if $0.5<a<0.9$

It is usually 20% of $\overline{M_w}$

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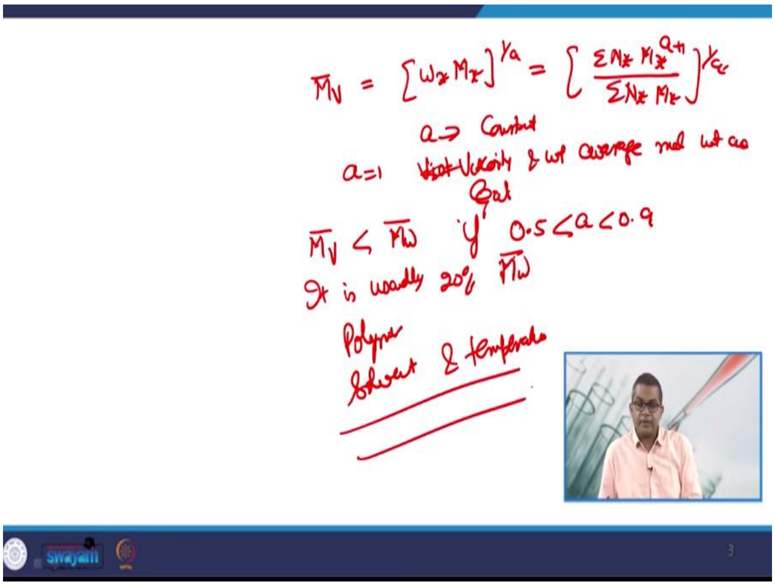

So, viscosity and weight average molecular weight are equal. Now, sometimes we may encounter this type of a scenario where viscosity average molecular weight is less than the weight average molecular weight. So, this scenario happens when a is in between 0.5 to 0.9. Now, it is usually 20% of weight average molecular weight and it varied with the polymer solvent and temperature.

So, you can say that the different controlling parameter for this viscosity average molecular weight is the polymer solvent and temperature. So, these are the governing factor for this viscosity average molecular weight. Now, another important part of this particular concept is the polydispersity index.

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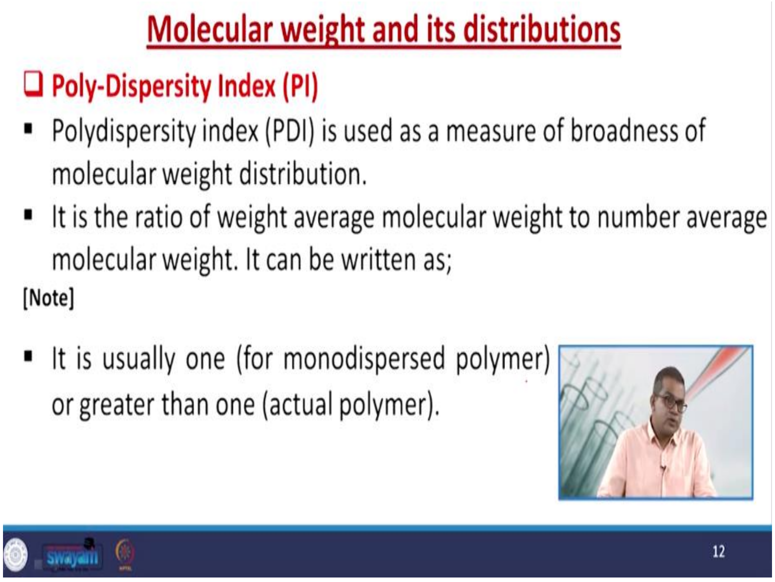

Now, this polydispersity index it offers a very vital role when we discuss about the polymerization process and the distribution of molecular weight etcetera. So, this is used as a measure of broadness of a molecular weight distribution, how large or how enhanced this one. Usually, it is the ratio of weight average molecular weight to the number average molecular weight.

$$Polydispersity\ Index = \frac{\overline{M_w}}{\overline{M_n}}$$

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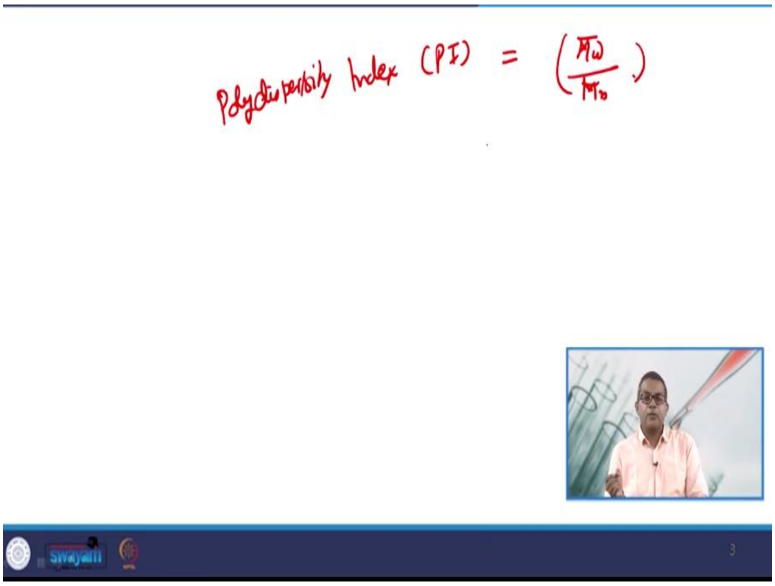

Now, it can be written as polydispersity index, PI. This is now this ratio depend upon the breadth of the distribution curve. Now, sometimes this particular curve plays a very vital role we will discuss this particular curve later on. Now, this is usually 1 for mono dispersed polymer or greater than 1 for actual polymer. So, it depends on the class of polymer which are being questioned.

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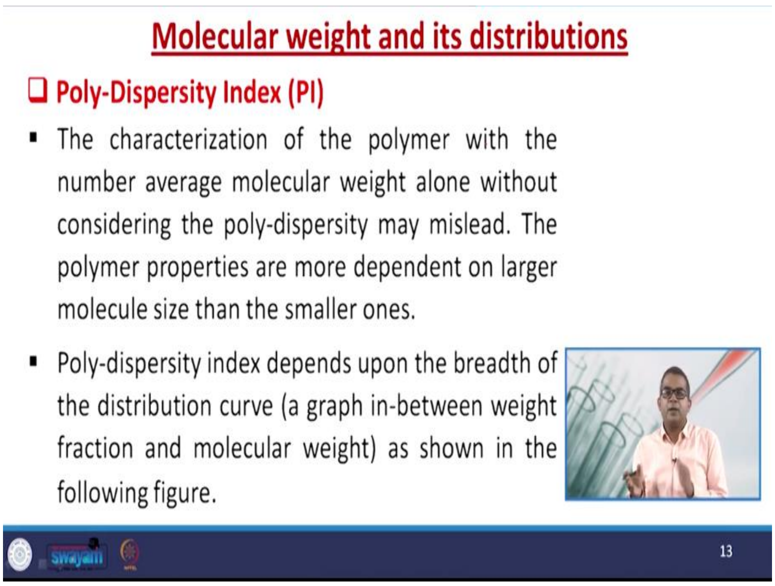

Now, the characterization of the polymer with the number average molecular weight alone without considering the polydispersity index may sometimes give you a misleading information. The polymer properties they are more dependent on a larger molecular size than the smaller one. Because then they are switches towards the monomer side. So, polydispersity index depends on the breadth of the distribution curve graph in between the weight fraction and the molecular weight.

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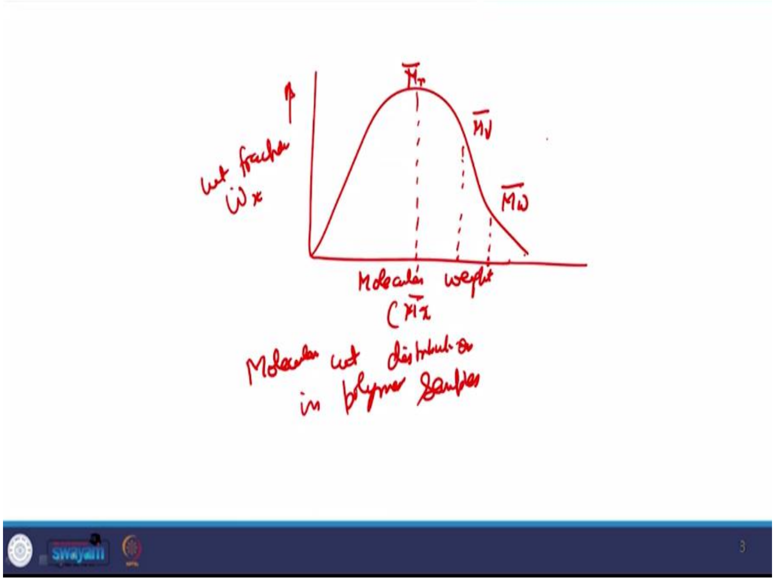

Now, we can have a look about this particular graph, which we are describing here. Now, here this is the molecular weight and this is the weight fraction. Now, here this is the number average and this is the viscosity average and this one is the weight average. So, this is the molecular weight distribution in polymer samples.

Now, this particular graph is important in this context that sometimes, because of the complexity of the nature you may require all 3 type of molecular weight distribution pattern. So, for this particular plot or this particular curve is extremely important to have an analysis. Because sometimes you may require to have a vetting of a data during the polymerization process and this particular approach is extremely useful to carry out this analysis.

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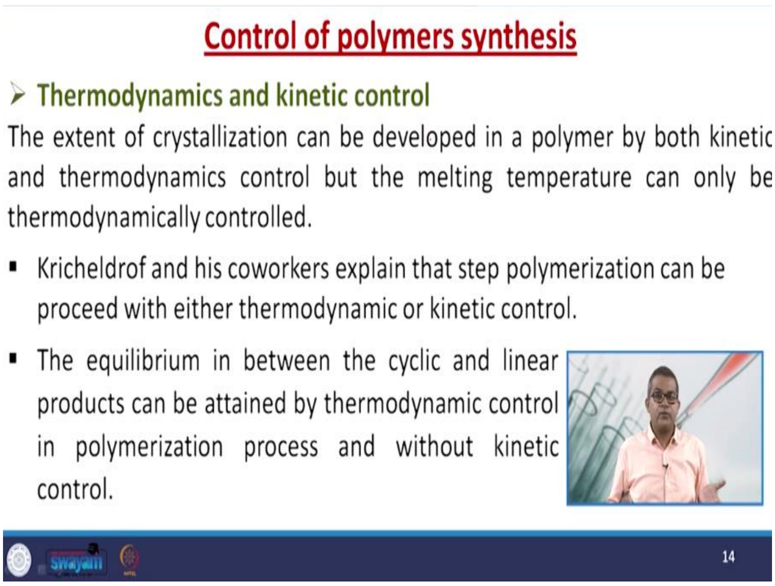

Now, when we discussed about this particular approach related to the molecular weight distribution, and I told you about the importance of this particular molecular weight concept approach and how sensitive this particular approach is. That is why we discussed the different type of molecular weight distribution pattern like number average, weight average and viscosity average.

So, you can sensitize the thing that based on the polymerization process, based on the desired property of the polymers, based on the processability aspect, the molecular weight distribution plays a very vital role. Because sometimes you may have a bulky chains then you may face a problem of processability, you may require certain other things sometimes the molecular mass becomes so thick that it may not be possible to remove that particular molecular polymeric mass from the reactor.

So, that is why the molecular weight distribution is extremely important. Now, how to carry out this molecular weight distribution effectively, and how to control this molecular weight distribution, we will discuss this particular thing in the control of control methodologies of polymer synthesis in the next lecture.

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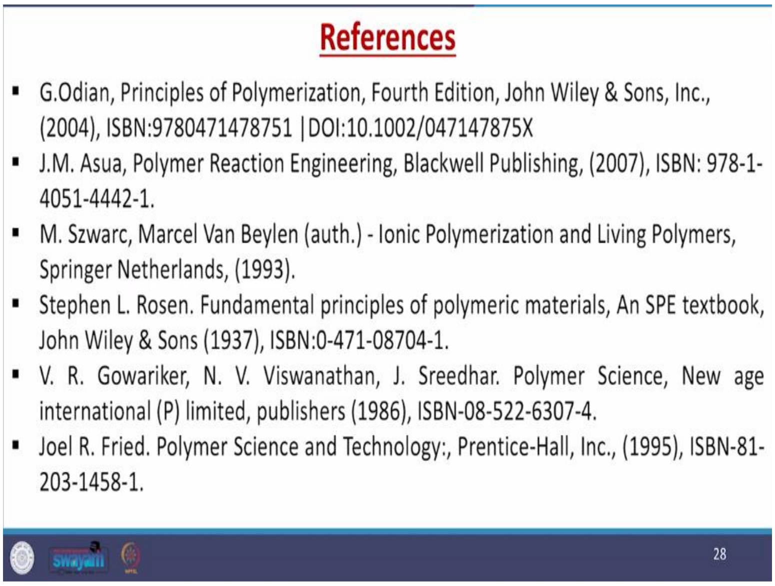

So, in this particular lecture, we have discussed about the molecular weight distribution, we have discussed about the efficacy of this molecular weight distribution to the polymeric system. We analyzed that how we can determine this molecular weight may be number average, may be weight average, may be viscosity average mathematically.

Because there are several experimental tools available as on date through which you can determine these molecular weights. And in the last slide, we discussed that sometimes you may require all 3 molecular weight distribution for in particular polymeric system for to carry out the feasibility of that particular polymerization process. So, we have gained the knowledge about these molecular weight distributions in this particular lecture.

In next slide, because, we have discussed about the efficacy of this molecular weight distribution, we will discuss that how we can control these molecular weight distribution pattern, how we can control the polymeric synthesis. So, we will discuss this particular approach in the next lecture, thank you very much.