Principles of Polymer Synthesis
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Lecture - 02
Molecular Weight Determination of Polymers

Welcome back to this course on Principles of Polymer Synthesis. In the first class we have talked about how the polymer science evolved from knowing nothing about polymer structures yet synthesizing polymers, yet exploiting the properties in the early 18th and in the early 19th and late 19th century and even the early 20th century. To knowing precisely what the structures are to be able to put precisely the monomer units the way you want and to be able to evolve the properties the way you want with relationship to the structure of the materials.

Now, in this class I am going to talk about Molecular Weight Determination of Polymers, this is the topic of this class. So, I am not going to start with molecular weight of polymers per say I am going to start with as promised towards the end of the last class the classification of polymers by different ways.

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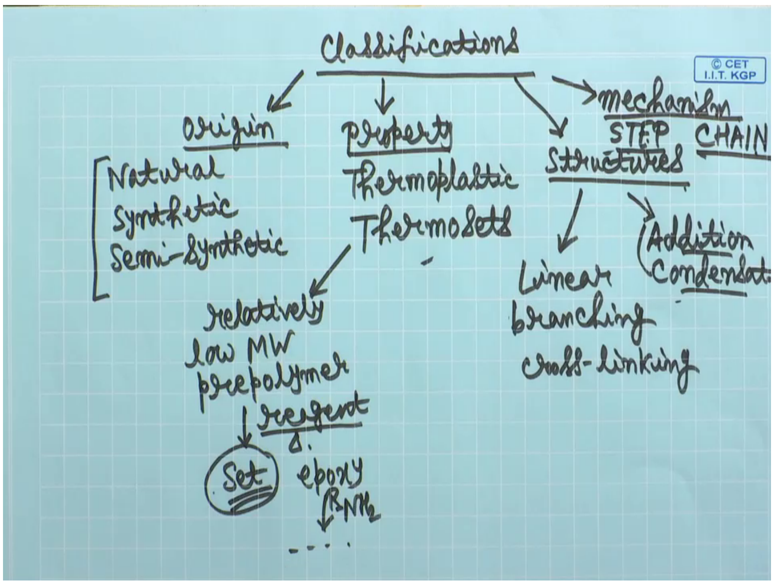

So, let me begin with that so how you can classify different polymers of course, this is different from whatever we talked about when we told commodity polymers, speciality polymers, or when we talked about engineering polymers those are different kinds of classifications. Now you can classify polymers on the basis of their origin this is something we already discussed in the previous class. So, we can have natural polymers say for example, polysaccharides example could be you know starch could be cellulose, we could have natural rubbers or completely synthetic polymers say for example, Bakelite a condensation product of phenol and formaldehyde or we can have semi synthetic polymers. Take for example, a cellulose nitrate about which we discussed a lot in the previous class and we also talked about you know the celluloid films that are actually made of a combination of cellulose nitrate and camphor camphor plasticizers the material. So, those things we discussed before.

So, on the basis of origin we could have this kind of classification natural synthetic semi synthetic. Also on the basis of property we can have polymers which are say thermoplastic. So, these are materials when you heat they become mouldable and when you cool they becomes more rigid. So, an example could be you know polyethylene terephthalate; we will talk about that in details when we talk about synthetic processes or we could have thermo sets.

So, typically these are materials with low polymer low molecular weight materials and these materials I mean the starting point is low molecular weight materials. So, it is you know relatively low molecular weight what you can tell as pre polymer and then this material you treat with some reagent maybe you heat the material also, you heat it and then it becomes set into a particular structure. So, basically this reagent helps it to cross link.

So, when you have a cross linked 3 dimensional 3 dimensional extensive cross linking between different polymer chain. So, it gets set into this particular structure. So, that is called thermo set, an example could be the reaction of epoxy with amine and then you have materials where you have cross links so those are thermo set materials. And you can also classify on the basis of structures it could be linear polymer or you can have some branching of the polymer or you could have cross linking also.

Now, on the basis of structure there could be another way to classify this, some say this is also on the basis of mechanism, but typically I can tell that this is on the basis of structure see you can have addition polymers, addition polymerization or you could have condensation polymerization and finally on the basis of mechanism. So, addition condensation and on the basis of mechanism you can have step growth polymerization or you can have chain growth polymerization. Now we are going to talk about these things later on in detail mostly we will talk about this step growth and chain growth polymerization and some of them can be actually dubbed as addition or condensation and this kind of classification of step growth and chain growth is better than addition and condensation this kind of classification here. And we will explain that a little later.

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Alright, so before going into further details of this when we as promised in the starting topic start discussing about the molecular weight. I would like to talk a little bit more about addition, condensation, polymerization and the classification when we do (Refer Time: 07:02) your step growth and the other one chain growth polymerization. And then we will come to slowly the other aspects. Say this this kind of classification on the basis of structure addition polymerization and condensation polymerization this was actually introduced by Carothers somewhere around 1929.

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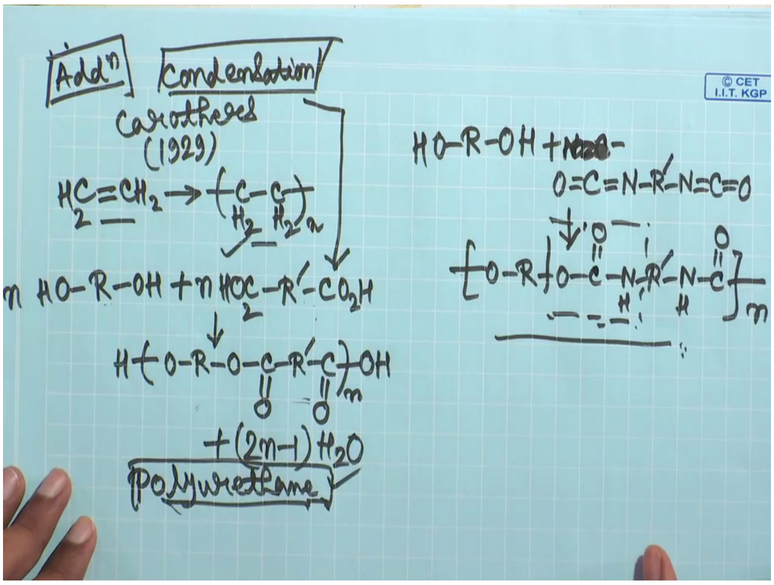

So, addition polymerization basically it means that whatever monomers you have whatever monomers you have all the monomers get incorporated into the polymer. So, basically the monomeric structure will be the same as the repeat unit structure, say you take an example you take ethylene and you polymerise. So, this is the monomer and then in the polymer you have C H 2 C H 2 whole in. So, the repeat unit has not lost any of the atoms from the starting monomer. So, this is your addition polymer.

Condensation polymer basically it is a condensation reaction. So, if you react a diol say you have a diol and you are reacting with a Diacid you know alcohol and acid react to form asters. So, if you do this reaction so by functional monomers if you are doing this reaction. So, basically you have this kind of polymer that is produced. So, what happens is that in this particular reaction you see this repeat unit this repeat unit does not have certain atoms that were present in the starting monomers.

So, you have a condensation reaction. So, the repeat unit is slightly different in structure then you are starting monomers basically here a small molecule is liberated 2 n minus one molecules of water. So, that way the condensation polymers are polymers where small molecules are liberated in that particular reaction. Now a problem with this kind of classification is that this cannot account for all the kinds of polymers, say if you are looking for polymers which are of the class polyurethane.

So, polyurethane actually I am going to talk about that here so Polyurethanes. So, you are reacting say an alcohol diol with the diisocyanate. So, then what happens is that so you in this particular reaction, you basically have this kind of urethane linkage that is produced and you see that no small molecule is actually eliminated. So, what we call this particular reaction is this a condensation reaction or an addition reaction. So, typical which term suggests that this is this reaction is slightly different at least if you talk about the mechanism then your polyurethane formation reaction.

So, this is not a complete way of describing the polymerizations in that case as far as the classification goes so. In fact, there is another way to describe this kind of polymerizations that is on the basis of Mechanism, which was suggested by flori on the basis of mechanism.

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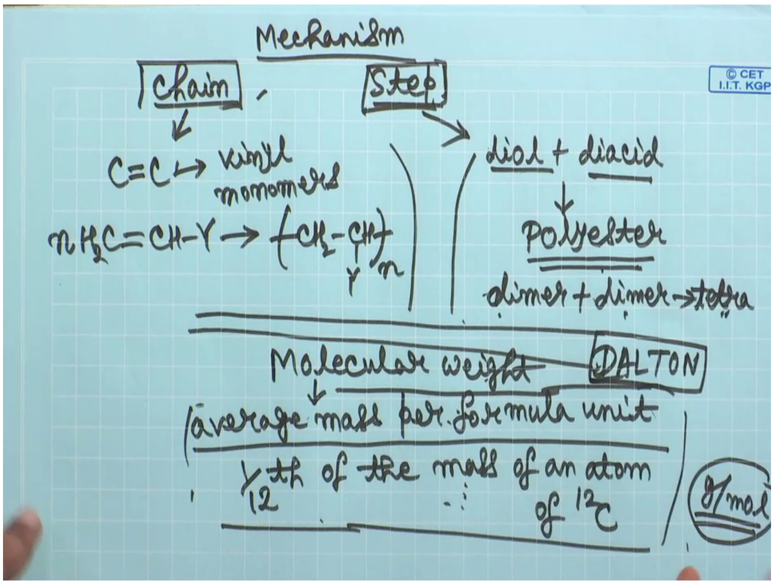

So, it is either chain growth polymerization or step growth polymerization. So, basically if you are looking at chain growth polymerizations, typically you have this kind of C double bond C units in the monomer, which is a vinyl based on vinyl monomers. Now these vinyl monomers when you polymerize, these vinyl polymers when you polymerize they will create these kind of product I mean very similar to I mean if you have ethylene you have this polymer. So, this is chain polymerization.

So, what happens is that you have an initiator that initiates the polymerization process and then what happens is that the successive addition of monomer units in a chain reaction occurs and then this particular process is called chain polymerization. The other process is step polymerization, the other mechanism mechanistic way of describing the different kinds of polymers. One is chain polymerization, one is step polymerization now step polymerization is basically most of the condensation polymers are also step polymers. So, as I told you if you are reacting a diol and you are reacting with diacid this diol.

So, basically you have a polyester the structure of which I have drawn previously. Now this is called step polymerization, because you know the polymerization occurs in steps say you create a dimer diol and diacid react and create a dimer and that dimer can react say with another dimer and it can create a tetramer or dimer can react with tetra tetramer or dimer could react with trimmer.

So, all these species of different what you say as molecular weights are present during the reaction, which is quite different from your chain growth polymerization. So, with this kind of classification then the polyurethanes they becomes step growth polymerization and not chain growth polymerization, the reason I talked about this is because next several classes we are going to spend talking about first the mechanistic aspects of step growth polymerization, the dealing with the kinetics of this polymerizations for example. And then we will also talk about chain growth polymerizations. And afterwards we will try to apply these principles in the synthesis of different industrial polymers, but now is the time to talk about the main topic that I am going to deal with. In the next few classes, the reason I discussed some of these things at the earliest is because these directly concern with many discussions that we will have later on ok.

So, we are going to talk about molecular weight you know you have done a reaction suppose you want to create a polymer you want to create a polymer. Now several of the monomer units have come together to create this polymer the polymer that you have got how do you characterise these polymer. One of the main things that you do is you try to find out the molecular weight of this polymer and there are different ways to determine the molecular weight and also I will tell you that the molecular weight is basically an average molecular weight very unlike the you know whatever small molecules that we deal with it is very different, small molecule synthesis and polymer synthesis they are very different.

So, Firstly, then we will start with what is molecular weight; the molecular weight by it is very definition it is basically like this average mass per formula unit divided by 1 12th of the mass of an atom of 12 C. So, that way molecular weight does not have a unit like gram per mole, you basically tell that as molecular mass has this unit, but still it is quite prevalent that people will use gram per mole for molecular weight and I do not see any problem in that because basically that does not change the signs that we discuss, but it is important to keep in mind that molecular weight that way we use something call DALTON. So, there is a mass on the up and there is a mass of the on the denominator so numerator by denominator.

So, basically the unit of the mass gets cancelled. So, gram per mole is the molecular mass, but molecular weight also we use this unit gram per mole or you can use dalton also although this is not correct that way, but we use this is quite prevalent.

Now, one thing that you should keep in mind is the following as I was telling unlike preparation of small molecules when you are creating a polymer chain say hundreds of monomer units are coming together through covalent linkage. It is almost impossible to create a polymer molecular which has a fixed molecular weight in a way. So, several chains you are creating by the synthesis, by the polymerization, all these chains will have a slightly different molecular weight, because of the inherent statistical process that is there in the preparation of polymers. Which will mean suppose you have 100 number of units in a polymer chain, another polymer chain can have different number of units maybe 100 and 10 maybe 100 and 5 or maybe 98. So, like this.

So, when you are creating a polymer you have a distribution of molecular weights in all this polymer chains. So, it is important to recognise that when we talk about molecular weight of a polymer we basically talk about an average molecular weight of the polymer and there are techniques through which you can determine this average molecular weight, we will come to that and we will discuss only specific techniques not all the techniques some of the important techniques we will discuss.

Now, certain things you should keep in mind that what are we dealing with we are dealing with this property.

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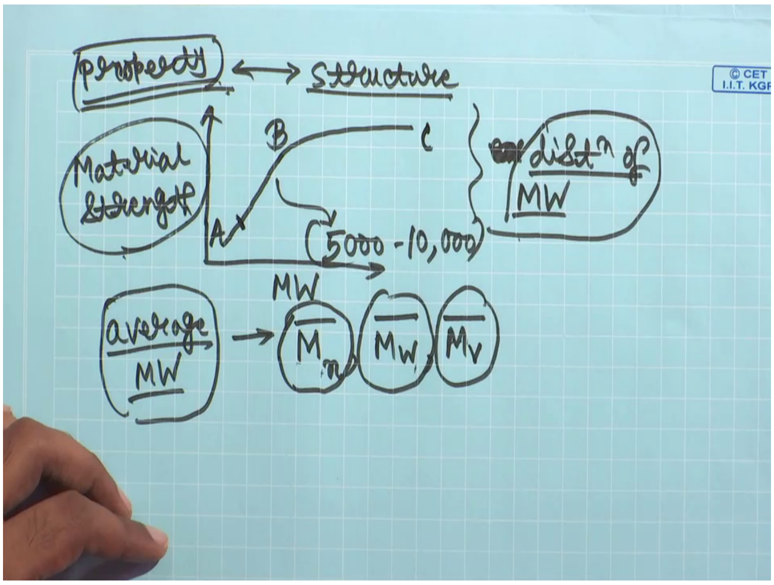

What we are interested in is to create the property that we want in the polymer and what is it is relationship with structure. Now different properties of the polymer they will vary in different ways, with the molecular weight say one of the properties that are very important that I want to talk about here say material strength verses say molecular weight. It will be something like this say point A, point B, point C.

So, if your polymer is of very low molecular weight then you do not have this kind of materials strength. So, somewhere here if you have molecular weight your material strength is not good enough for any kind of industrial application. So, you need at least a certain molecular weight. So, that the properties they have started to evolve and this is typically again this are approximate say between 5,000 to 10,000 so at least you need this kind of molecular weight in order to get certain properties that become relevant for applications and after that they may become slowly saturated so on and so forth.

So, from this discussion also then it is important to understand, that ultimately what we want is that we want an we want a distribution we want to know, what is the distribution of molecular weight in the polymer sample that we have prepared. Now we will come to that after first let us talk about this thing average molecular weight. So, when say average molecular weight there are different kinds of averages that we deal with. One of them is number average molecular weight, which we can designate as M n bar this is number average molecular weight and then we can have what you call as weight average molecular weight, we can have viscosity average molecular weight, these are some of the main molecular weight averages.

Now, if you are using if you are actually trying to find out say M n or M w or M v you are basically using different kinds of experiments in order to determine these different molecular weights. So, let us say we before we come to the different experimental parts let us try to have an expression of these means what are the expressions of these different averages.

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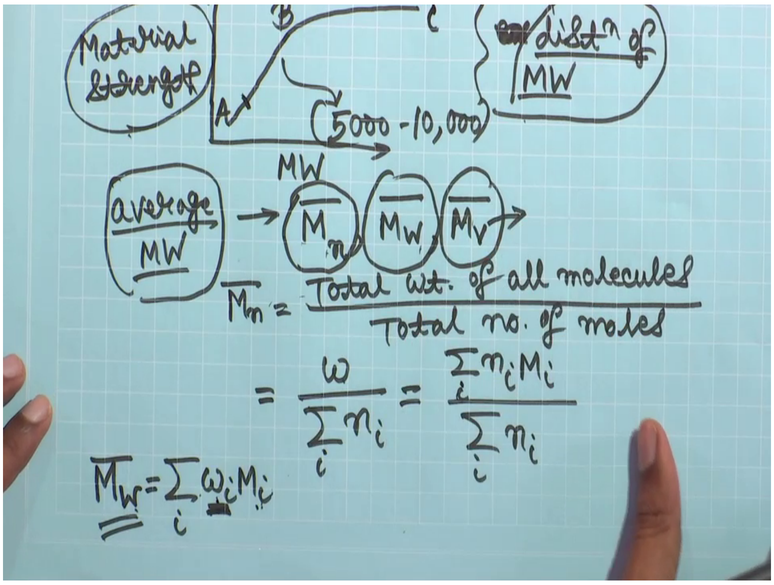

Say when you talk about M n number average molecular weight it is basically total weight of all the molecules in the sample all the molecules, in the samples divided by total number of moles total number of moles. So, which is nothing, but w which is total weight divided by say total number of moles. So, all different kinds of molecules different kinds means not by the structure means they are all the polymer molecules, but they have different molecular weights, because you know there will be species of different molecular weights and you are taking the average of these molecular weights and you are determining M n see in this case.

So, let me write down the expression and then I will explain. So, this is sum over n i M i divided by sum over n i. So, this means you are summing over all i's. So, maybe you may have n i moles of molecules which have molecular mass M one you have n 2 moles of molecules molecular mass M 2 like that. So, you are summing up.

So, suppose you have 10 kinds of molecules of molecular weight M 1 M 2 M 3 up to M 10 and the corresponding number of moles are n 1 n 2 n 3 up to n 10, then this is a summation the total weight is basically number of moles into molecular mass and then you sum it up and divided by total number of moles. Now this is the expression of M n, if you are trying to have an expression of M W weight average molecular weight.

So, if you are looking at M W then what is the expression of M W it is W i M i. Now do not confuse this W i with this W i this is the weight fraction of molecules having molecular mass. So, weight fraction. So, if you have 10 kinds of molecules. So, weight fraction of molecules. So, if you have 10 kinds of molecules. So, the weight fraction of molecules W 1 which have the molecular weight M one weight fraction of molecules W 2 which have the molecular weight M 2 so on and so forth. So, if you add them up together then you basically have your molecular weight which is the weight average molecular weight. Viscosity average molecular it will come after afterwards. So, let me give you an example of this suppose you have a suppose you have a polystyrene sample.

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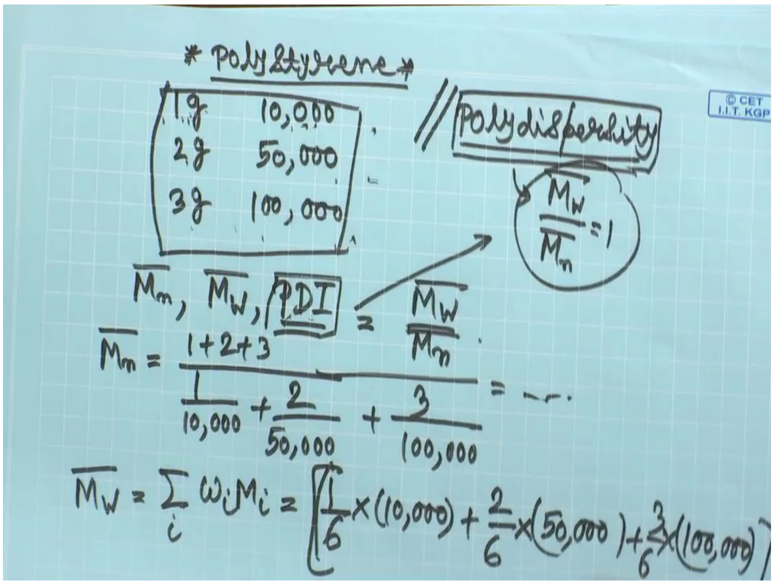

I am just trying to work out a problem here. So, suppose you have a polystyrene sample and this polystyrene sample is composed of this, say 1 gram of polystyrene which has molecular weight of 10,000, 2 grams of polystyrene which has molecular weight of 50, 000, 3 grams of polystyrene which has molecular weight of 100,000.

Now, these are not exact molecular weights of course, there is something called polydispersity. So, which means if the polydispersity index which is defined by M W by M n, if this is the if this is higher than one the more the value the more is the dispersity; that means, the more is the distribution of the molecular weight among different polymer chains. If this ratio is one that would mean all polymer chains have actually the same length. So, this in practice is never 1, but this can be close to one by different controlled processes you can actually create polymers which are close to 1.

So, still you are actually talking about average, but the molecular weight is very narrow down the dispersion the distribution of molecular weight. So, there you can tell they are Fairley mono disperse samples so polystyrene sample. So, you have 3 Fairley mono disperse samples of 1 gram of 10,000 2 grams of 50,000 molecular weight and 3 grams of 100,000 molecular and they are mix it up.

So, then the question is in this particular sample with all this 3 together what is the value of M n that is number average molecular weight what is the value of M W whatever is the molecular weight and what is the value of PDI, that is Polydispersity index we will talk about it little bit later, now I am going to give you the formula this is the formula M W by M n is the formula now M n M W.

So, in order to determine this value of M n so it is total weight divided by total number of moles. So, total weight is 1 plus, 2 plus, 3 divided by total number of moles. So, this is one divided by 10,000 so 1 gram. So, number of moles is this plus 2 grams by 50, 000, plus 3 grams divided by 100,000. So, this value I have not actually calculated you can calculate actually. So, this is the value of M n that you will get.

So, what is the value of M W, I am trying to work out this this problem in order to give you an understanding about the formula that I have drawn and try to understand what is the significance of that formula in terms of the problems here. So, M W is a sum over all the weight fractions corresponding multiplied by M I, which is the molecular weight. So, the weight fraction so total weight is 6 grams. So, weight fraction of the first sample is one divided by 6 that multiplied by the molecular weight 10000. So, like this you add all of them up 2 by 6 into 50, 000 plus 3 by 6 into 100,000 and then you get the value of M W and the polydispersity index is basically equal to M W, by M n that you can work out.

So, I have given you the expressions of number average molecular weight; average molecular weight and worked out a problem for you which gives you an understanding of how the things, basically work; and if you have this kind of problems how do you solve some of these things.

So, what now is the time to conclude this particular class? So, before conclusion I am trying to give you a (Refer Time: 28:12) of what is going to come in the next class; in the next class I will actually talk about.

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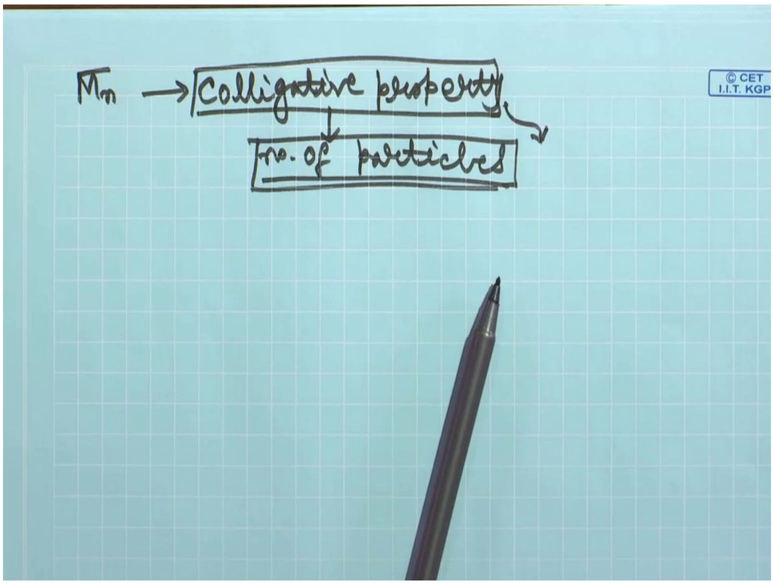

How we can determine M n this number average molecular weight and there you will see that we basically rely on colligative properties colligative properties of the polymer solution. Now these colligative properties they actually depend on the number of particles of the solute present in the solution. And so, these kind of experiments that you do they are biased towards the low weight fraction part of the sample, because your sample as I told you can have say a say 90 percent of polymer molecules, which have very high weight or maybe 10 weight percent raise best of that may be of low weight.

So, basically some of the experiments that we do colligative properties are one of them we can talk about M W also, some of the different experiments that we do for the molecular weight determination, some of them are biased towards low molecular weight fractions of the polymer sample and some of them are biased towards high molecular weight fractions of the polymer sample. And you will see as you can understand from what I have told already colligative properties that depend on the number of particles. So, they basically are biased towards the low molecular weight fractions.

So, we will conclude here and we will start with the different experimental techniques to determine the number average molecular weight in the next class.

Thank you.