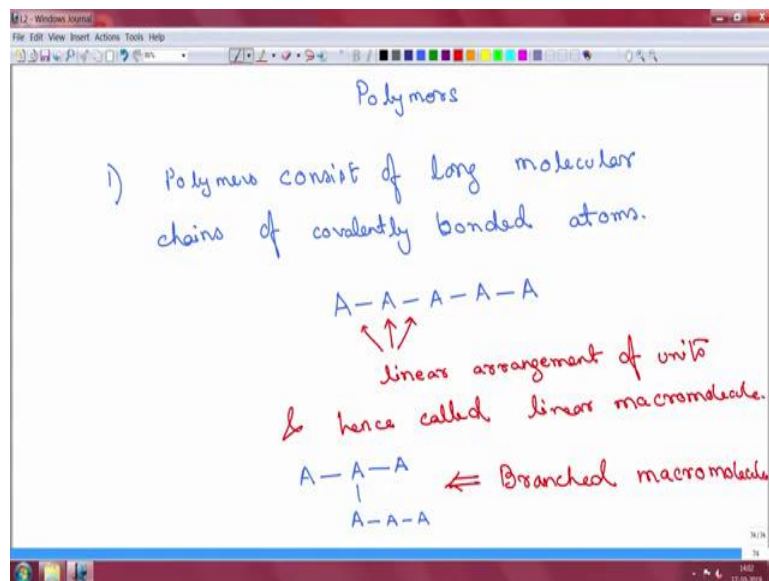


Introduction to Soft Matter
Professor Dr. Alope Kumar
Department of Mechanical Engineering
Indian Institute of Science, Bengaluru
Lecture No 14
Polymers Cont

So, welcome back to one more lecture on Introduction to Soft Matter. And today what we are going to see. So, last class, we were discussing polymers. So, we will just quickly review a couple of important points that we were discussing.

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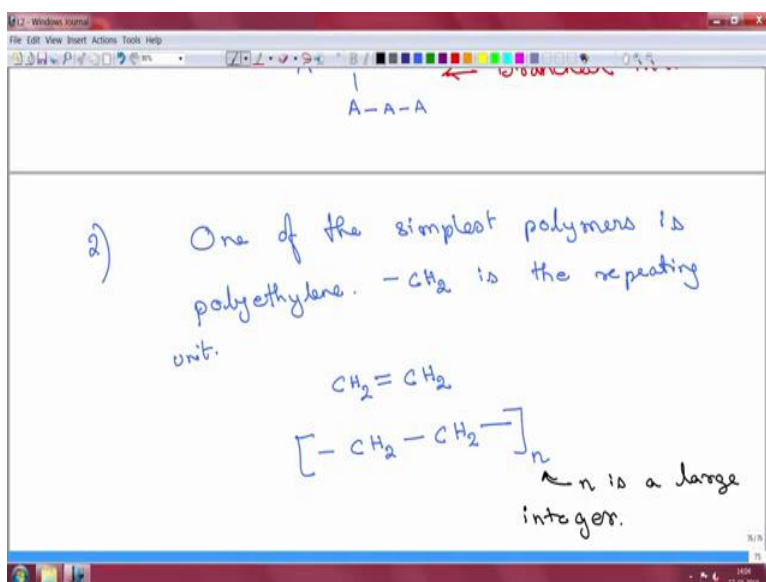
And so, we are looking at polymers. And some of the important points, the issues that we discussed is that polymers basically consist of, polymers consist of long molecular chains of covalently bonded atoms. And essentially the idea is that there is some structural unit or this a unit of a polymer, let us just call it A for the time being and this A is going to covalently bond with another A and it is going to keep on going on and this becomes a polymer.

Now, in a situation like this, where A structural unit. So, this is a Structural unit it is bonded to two other only two other structural units and that is repeated again and again this is known as a linear polymer whereas, so this is linear arrangement, okay of units and hence called linear macromolecule or linear Polymer. Now, the linear word does not mean that the chain is, in reality that is how the polymer really looks like a straight line. That is what not, it does not mean that.

But of course, when we say linear that means that some other form is probably also possible. That is why we have to give a special name to this and that is true because you can have what

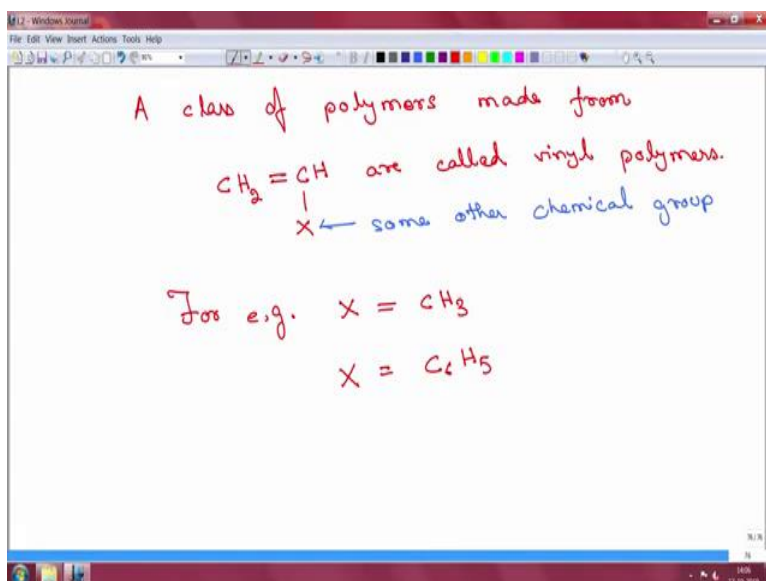
is called is a Branched arrangement where you have an A and then you can have another sequence of here I am running out of space, so I am just going to, so this is a Branched arrangement. Okay. So, this is a Branched macromolecules.

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Another important point that we discussed last time, was that one of the simplest polymers is Polyethylene and here your CH_2 is the monomer, is the monomer is the repeating unit and it is basically made using ethylene and through the polymerization of ethylene and this polymerizes and this becomes a repeating chain that just continues for some n where this n is a very large number, large integer and this is how the polyethylene molecule is formed.



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This also brings us to another class of polymers made from this molecule where I have taken 1 H out and instead I am going to replace with an X, where this X is some other group, is some other chemical group. So, a class of polymers made from this is known as Vinyl compounds or so or Vinyl polymers are called Vinyl polymers.

So, what can X be for, so for example, your ex can be different groups? It can be for example as CH₃ group, it can even be part of a benzene ring with one hydrogen removed. So, you can have these different Vinyl groups possible. So, maybe we should look at some examples of common polymers. Okay.

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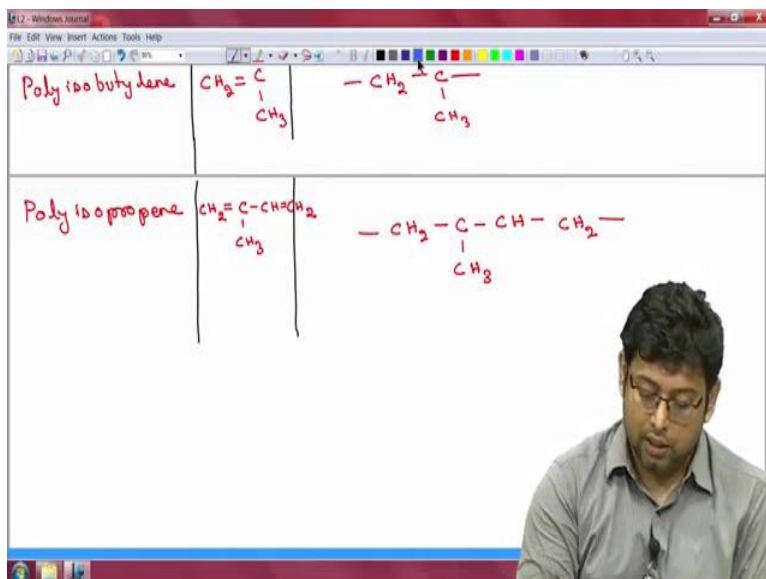
Polymer	Monomer	Structure
Polyethylene	$\text{CH}_2=\text{CH}_2$	$-\text{CH}_2-\text{CH}_2-$
Polystyrene	$\text{CH}_2=\text{CH}$ 	$-\text{CH}_2-\text{CH}-$ 
Polyacrylamide	$\text{CH}_2=\text{CH}$ CONH_2	$-\text{CH}_2-\text{CH}-$ CONH_2
Polyvinyl chloride	$\text{CH}_2=\text{CH}$ Cl	$-\text{CH}_2-\text{CH}-$ Cl
Polyisobutylene	$\text{CH}_2=\text{C}$ CH_3	$-\text{CH}_2-\text{C}-$ CH_3

So, what I will do is I will create a section. Okay, so for a name of the polymer and here we will put the monomer and this is what the structural or the structure of the polymer looks like. So, let us say, so we obviously started with Polyethylene, so let us just populate it with that. Polyethylene monomer was CH₂ CH₂ and here you have. So, how about, so another one is called Polystyrene, one of the famous polymer in this case your X takes on becomes a benzene ring.

So, instead of 1 H we have now a benzene ring. So, when this polymerizes you have, so, I am just missing a 2 here. Another one is called Polyacrylamide and here your X takes on the value CONH₂, this is your NH₂ and you have a structured looks like following. Another example is Polyvinyl chloride where we take the X as chlorine atom. So, this is called polyvinyl chloride and in this case, X is a chlorine atom. So, this is obviously it is just going to be this one.

Then you have Polyisobutylene where both the hydrogen atoms are taken out in this case and are replaced by CH₃. So, obviously, you know how to draw the structural unit for this we will now have a CH₃, two CH₃ units.

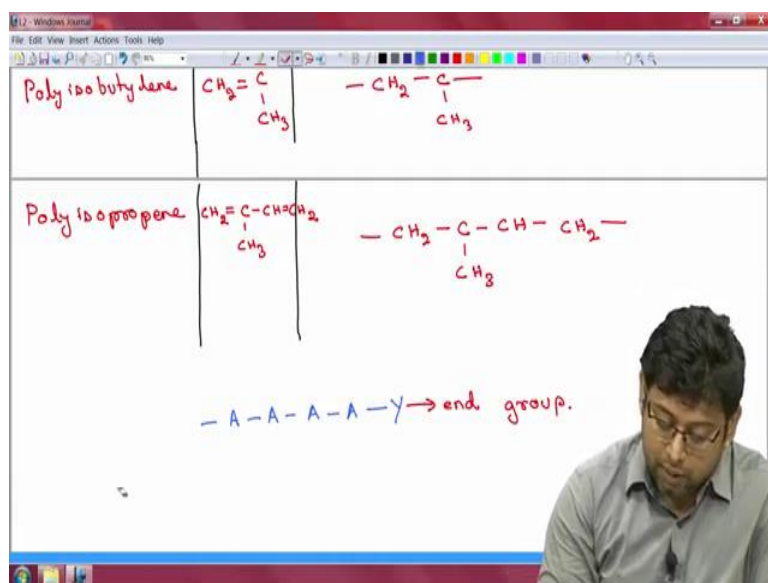
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And here and this is Polyisopropene and here, your chain slightly more complicated. So, you have a CH₂, then you have a CH, you have a CH₃ here, but this carbon is now attached to CH CH₂. So, if you had to polymerize this then you will take this particular bond here the two double bonds and use that to cause polymerization. So, your polymerization should look like CH₃. These are some of the examples, the common examples of very, of the polymers.

So, if you are working with a polymer in the lab, it is good, just good to know what is the chemical formula for this. And that will help you in many, evaluating many of the important properties.

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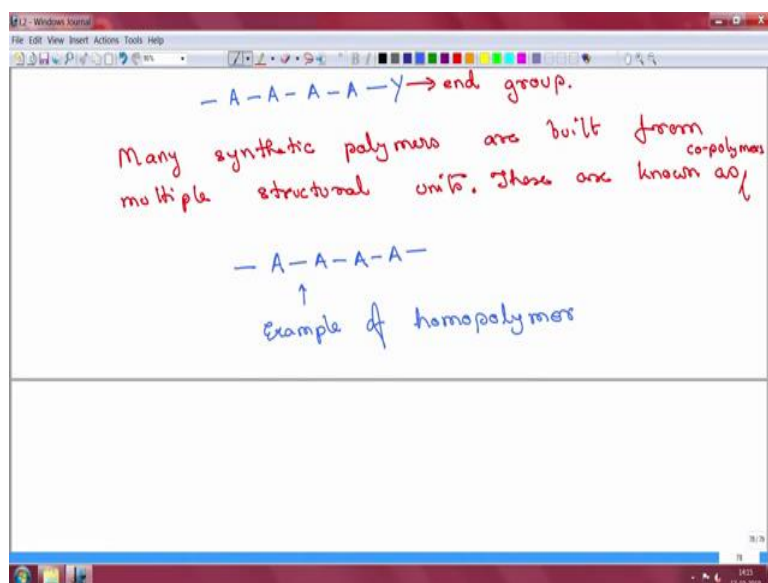
Now, just quickly going back to that point that a polymer is basically made up of structural units. So, let us just say that there are these structural units A, which are repeating again and again. So, at some point, this chain has to end. And when the chain ends, then you, it might not always end in the same structural unit. So, here you might have, so I have already used X for something else, so maybe I will use the symbol y.

So, it ends in y, which is a special unit and this is also called the end group, okay. So, these end groups are usually different than the repeating unit. So, this is a end group. So, polymers, where chains terminate special groups can be found and these end groups can be very, very important in also determining, let us say the overall charge and other properties of the polymer molecule.

So, we can already see that there is quite a bit of complication. So, you have the polymer molecule, the macro molecule, but it is not just sufficient to know which monomer it is, because the monomer is obviously going to be there, but how is the monomer causing the (poly) or participating in the polymerization that is important. So, you have to know the formula, but at the same time, you also have to understand how, whether it is a linear molecule or is it branched, and then whether what any group does it have.



So, till now but this example is basically relating to a polymer which is just made up of one structural unit, which is repeating again and again. But then there are many polymers which are not composed of just one structural unit. It can be composed of many different structural units which can also go on repeating.

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So, many synthetic polymers are built from multiple structural groups, structural units. These are known as co-polymers, co-polymers. So, in contrast a polymer like this, which is made up of only one structural unit. This is known as a Homopolymer Okay. So, this is an example of Homopolymer.

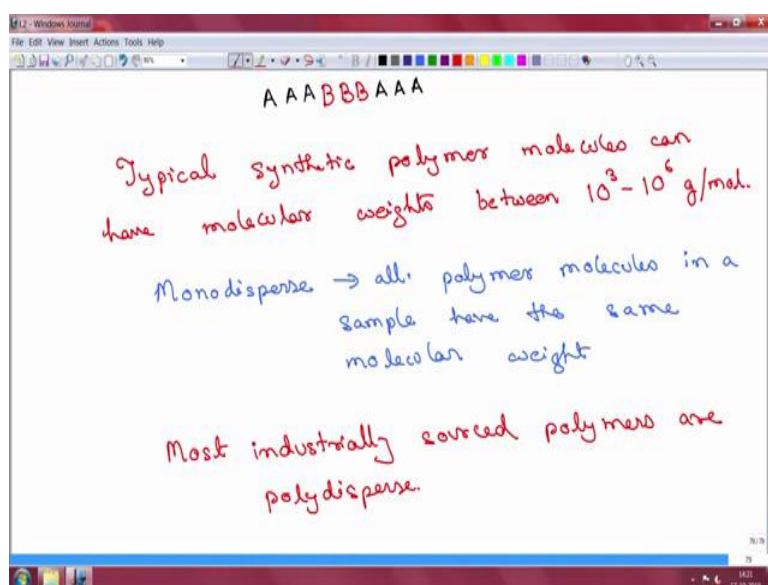
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Polymer	Monomer	Structure
Polyethylene	$CH_2=CH_2$	$-CH_2-CH_2-$
Polystyrene	$CH_2=CH$ 	$-CH_2-CH-$ 
Polyacrylamide	$CH_2=CH$ $ $ $CONH_2$	$-CH_2-CH-$ $ $ $CONH_2$
Polyvinyl chloride	$CH_2=CH$ $ $ Cl	$-CH_2-CH-$ $ $ Cl

\leftarrow Homo polymers

So, all the examples that we just did. These are all homopolymers, okay? So, maybe we will just make a note. So, these are Homopolymers.

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In a copolymer, you can have a situation where you have, for example, two structural units, maybe let us just call them A and B. So, if you have that you can have a situation where you have A, A, A repeating and then you have another and then after some time again. So, copolymers can also be of different types random co-polymer, etc. grafted co-polymers, we are not going to discuss too much about that, that also takes us into the chemistry of how we should be making these polymers that is outside of the scope of this particular course, but it is useful to know that these exist and you might need them and if you need them, then you have to look into the specifics of how they are made.

Now, the typical synthetic polymer, okay. So, the typical synthetic polymer, a polymer which is made through an industrial process can have many different molecules or structural units together. So, typical synthetic polymer molecules can have molecular weights between let us say 10,000 to easily a million, or even more, at times, grams per mole this is just an example value. And a tobacco mosaic virus, for example, is of the order of 10 to the power 7 grams per mole.

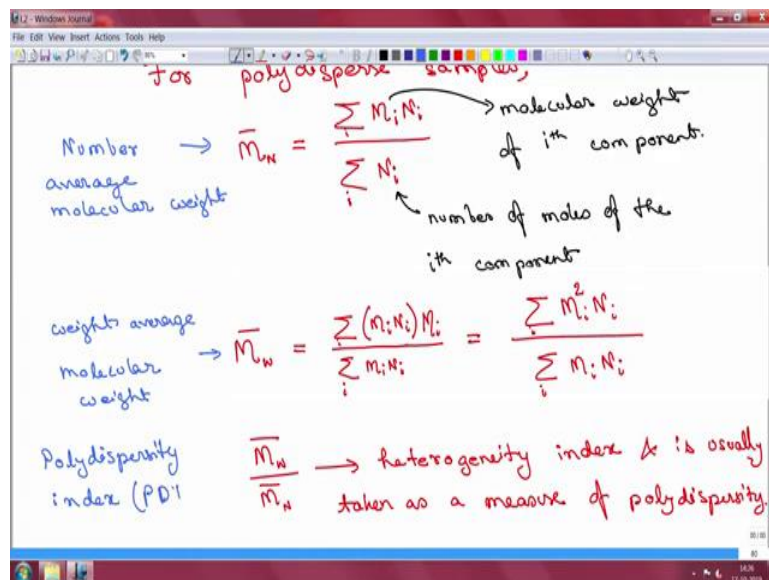
So, these large molecules can have a lot of very high molecular weight, just contrast it to the simple molecule, let us say oxygen, let oxygens, molecular weight is about 32 approximately 32 grams per mole is what it weights. But for a polymer it can be 10,000, or even 1 million. So, that gives you a contrast as to how big the polymer molecules are in contrast to some of those simple molecules.

Now, when you are making these polymers in an industrial process, there is no reason or it depends on how the polymer is going to be manufactured, that you might end up with a polymer, a set of polymers, which are not the same molecular weight. You can also have a molecular, a process of fabrication in which perhaps, all the polymers are going to have the same number of repeating units. And in that case, you would call it a monodisperse polymer because all the polymer molecules has the same n in that sense.

So, the number of times of the mer is (rep), is repeated. But usually you not get that, okay, so in any tradition, in any manufacturing process, you are not likely to get a set of molecules which have the same molecular weight. So, we quickly discuss these two terms. So, monodisperse is another important term, monodisperse is when all polymers molecules, all polymer molecules in a sample have the same molecular weight.

So, obviously, the contrasting word would be polydisperse, but most industrially sourced polymers, sourced polymers are polydisperse. So, the moment you have a dispersion then you must have some way of calculating an average molecular weight because now you have a whole set of molecular weights that is there in solution.

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For polydisperse samples,

Number average molecular weight $\rightarrow \bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$

where M_i is molecular weight of i^{th} component and N_i is number of moles of the i^{th} component.

Weight average molecular weight $\rightarrow \bar{M}_w = \frac{\sum (N_i M_i) M_i}{\sum N_i M_i} = \frac{\sum M_i^2 N_i}{\sum N_i M_i}$

Polydispersity index (PDI) $\frac{\bar{M}_w}{\bar{M}_n} \rightarrow$ heterogeneity index & is usually taken as a measure of polydispersity.

So, for polydisperse, so, for polydisperse samples, so for Polydisperse samples, we can define a number average molecular weight. So, let us say we divide, define this quantity mN which is an average quantity and that is given as a summation of I am going to divide this that is why it is going to become average N_i , okay. N_i is the number of moles of the i^{th} component.

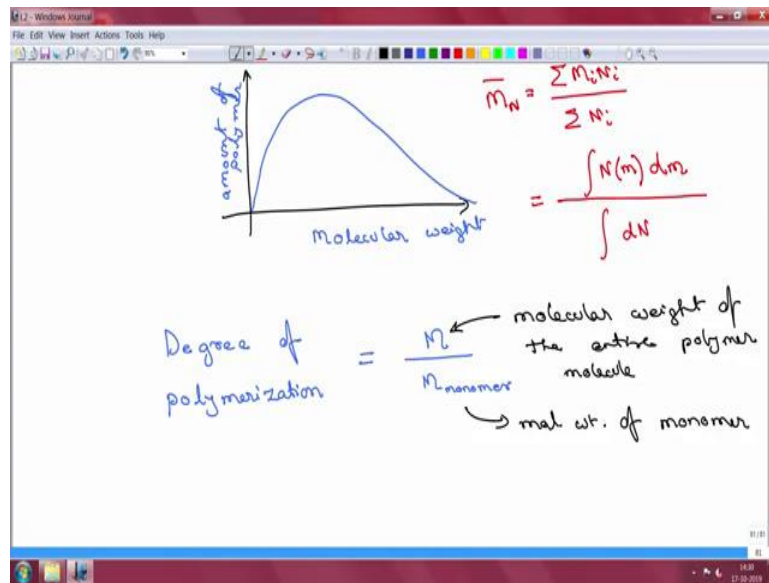
On the top you can probably guess that you would have an M_i , which is stand for in this case both of them are being the summations are being done over i and this m is the molecular weight of i th component. So, some people argue that this is not always a very good measure, because it biases the sample, if the sample has molecular weights or samples or components which have very low molecular weight versus and all very high molecular weight. So, then this m average can vary a lot.

So, then the other suggested average is what is called as a weight average molecular weight in which case we define this as and weight is a slightly misleading term it is suppose should be mass, okay so if you want to understand it in terms of that, so, let us say you have $M_i N_i$ and $M_i N_i$ as the same as we discussed before, this is summation sign. On, on the top you have, again $M_i N_i$, which is, in some measure of mass of the i th component, and that is multiplied again by the number of moles of that number average molecular weight.

And the other one is usually called the weight average. And this ratio of the two averages is usually taken as a very another, its becomes an another important number. So, this ratio mW by mN average this is, it represents certain heterogeneity in the sample. It is a heterogeneity index and is usually taken as a measure, taken as a measure of Polydispersity.

So, obviously, if you had a sample where there is only one molecule present with one molecular weight then your, this ratio would just be one right and the more it deviates from one it means that the sample has more and more molecules have different molecular weights. So, this is sometimes also called the polydispersity index or PDI. So, so also called Pollydispersity index or PDI okay.

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So, in a normal situation you may have a very large distribution. So, sometimes when we source these polymers from an industrial location or an industrial source, what we end up getting is not a set of molecular distributions, but entire curve of molecular distributions. So, let us say this axis is molecular weight and on this you have the amount of Polymer. So, then this average quantity that you had just discussed, which was initially we were writing it as a summation.

So, in this case, the summation is obviously not going to work. So, instead, we are going to replace this N with a dN and then you have to put the limits for that and then it is a summation of Nm . Another quantity that people often encounter is called the Degree of polymerization. So, how do you calculate the degree of the polymer, polymerization for a given polymer?

You take the molecular weight of the entire polymer okay. So, this is m of the polymer and you divide it by the molecular weight of the monomer. So, this is molecular weight of the entire molecule and this is molecular weight of monomer. So, as a degree of polymerization changes, then your property should change.

So, coming back to the degree of polymerization. So, let us take polyethylene, okay. Polyethylene or ethylene, the monomer itself at normal room temperature is a gas and then as you keep on polymerizing it the polymer would become liquid at normal room temperature and pressure. And if you keep on doing it if you increase the degree of (())(27:50) to even higher numbers, then at some point, this natural state, when we say natural state means that

state of the material at room temperature and pressure will become that have a solid body right.

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The slide shows a handwritten formula for the Degree of Polymerization (DP) and a table with three columns: DP, M_n , and Character.

Formula:
$$\text{Degree of polymerization (DP)} = \frac{M_n}{M_{\text{monomer}}}$$

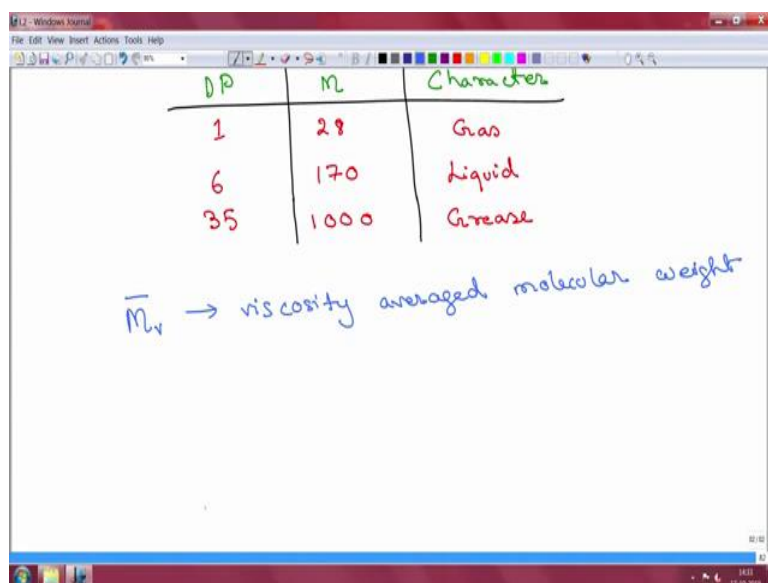
Annotations: M_n is labeled "molecular weight of the entire polymer molecule" and M_{monomer} is labeled "mol wt. of monomer".

DP	M_n	Character
1	28	Gas
6	170	Liquid
35	1000	Grease

So, maybe, so, from literature, we know that. So, let us just call this DP degree of polymerization. So, I will just quickly draw. So, this is, let us say degree of polymerization DP. Here is your molecular weight, and then this is character. Now, from literature and this is some data that I have taken from the book of Brinson and Brinson. So, first of course, if you have a DP of 1, then you are dealing with polyethylene itself, the molecular weight is 28 and here you have a Gas.

If you have molecular weight of 6, then you will end up with 170 and in this case it becomes a liquid. See, it is not a simple multiple of 28 by the way, because you have the end of the molecule to take care of. So, and if you have 35, then your molecular weight again it depends on the particular system that you are dealing with, you will end up with Grease. So, that is why this polymerization is very important and how, how much is the molecular weight these numbers are very, very important when you are working with any of these polymeric, any of these components.

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A screenshot of a software window titled 'Paint' showing a handwritten table. The table has three columns: 'DP', 'M', and 'Character'. The rows are as follows:

DP	M	Character
1	28	Gas
6	170	Liquid
35	1000	Grease

Below the table, the text $\bar{M}_v \rightarrow$ viscosity averaged molecular weight is written in blue ink.

Now, there is also one more molecular weight, which is viscosity average molecular weight, so, I will just mention it here. So, this is called viscosity So, sometimes you will find that manufacturers will report the polydispersity index, whenever they report an average molecular weight you must ask yourself or you must ask the manufacturer which particular average value are they reporting is it the number average? Or is it the weight average? Or is the viscosity average?

More often than not it is weight average but in some cases they can also report viscosity average. The viscosity, the equation relevant to this I will discuss at a slightly later stage because I have to introduce a few other things with that in that case. What we saw today is we take a quick review of that, we looked at some common polymers, polyethylene, polystyrene, we discussed what the structures look like.

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Typical synthetic polymer molecules can have molecular weights between $10^3 - 10^6$ g/mol.

Monodisperse \rightarrow all polymer molecules in a sample have the same molecular weight

Most industrially sourced polymers are polydisperse.

Then, we discussed some of the terms that you encounter again and again in polymer literature and copolymer, homopolymers, monodispersity, polydispersity.

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Number average molecular weight $\rightarrow \bar{M}_n = \frac{\sum M_i N_i}{\sum N_i}$

M_i molecular weight of i^{th} component.
 N_i number of moles of the i^{th} component

Weight average molecular weight $\rightarrow \bar{M}_w = \frac{\sum (M_i N_i) N_i}{\sum M_i N_i} = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$

Polydispersity index (PDI) $\frac{\bar{M}_w}{\bar{M}_n} \rightarrow$ heterogeneity index & is usually taken as a measure of polydispersity.

And then we looked at a couple of important quantifiers, which are the number average molecular weight and the weight average molecular weight and the polydispersity index.

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DP	M	Character
1	29	Gas
6	170	Liquid
35	1000	Grease

$\bar{M}_v \rightarrow$ viscosity averaged molecular weight

And also the degree of polymerization. So, next class will, will have a little bit more discussion on polymers. We will keep this going. Okay, we will stop here today.