Introduction to Soft Matter
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Lecture No 13
Polymers

So, welcome back everybody. So, in the last class, we were looking at a crystalline structure and we were asking ourselves that if we look at a crystalline structure in a very simple, as a simple lattice that is held, being held together by spring forces, then what is the relationship between the modulus and spring constant and if we represent, if you know the pair potential, then can we relate these two?

And what we found out eventually was that the modulus can be thought of as energy density where your numerator has a potential energy and the denominator has a volumetric type of term. Now, why is, why is this important? It is important because this tells us about the overall idea of a crystalline material. The crystalline material is something where energy can be input and it can be held inside the volume of this material for some time.

This idea of looking at a structure in a crystalline, in this particular in the viewing the modulus as an energy density is very helpful if you specially want to understand how is it that materials which flow over a long time have finite modulus at any given point. Because if eventually everything is flowing. If we go back to that old analogy of Deborah that even the mountains are going to flow over time, then what is the point of having a modulus?

If everything is flowing, so, you should just be done with one viscosity term or one something that describes the dissipation forces and that should be it. But, what happens is that the moment you put energy into a system the energy is going to get locked in and depending on obviously, what kind of material it is, if your material has a behavior that overall even though, even if over a long period of time it starts flowing, the instantaneous energy can be or the energy put in can be, can be stored inside the, the volume of the material for an instant of time and it can be stored there.

It can decay over a much longer period, but it can be stored for some time. And that, because of that reason, you can assign a kind of modulus or an instantaneous modulus, which is related to this storage of energy at a given instant of time. So, in a perfectly crystalline solid by the way, there is no mechanism by which the stress can ever relax.

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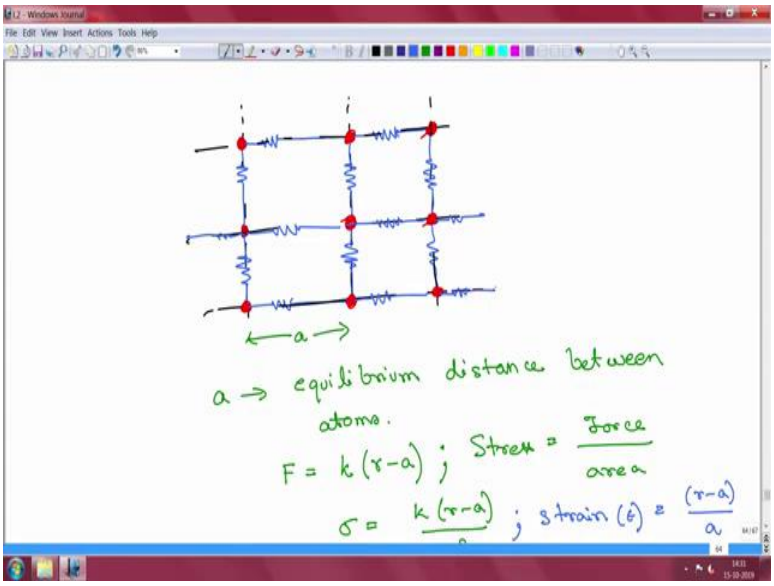

So, if you go back to this, go back to our simple idea of a crystalline solid, we are holding all of these atoms together with the springs. Now, the springs have no mechanism by which they can relax.

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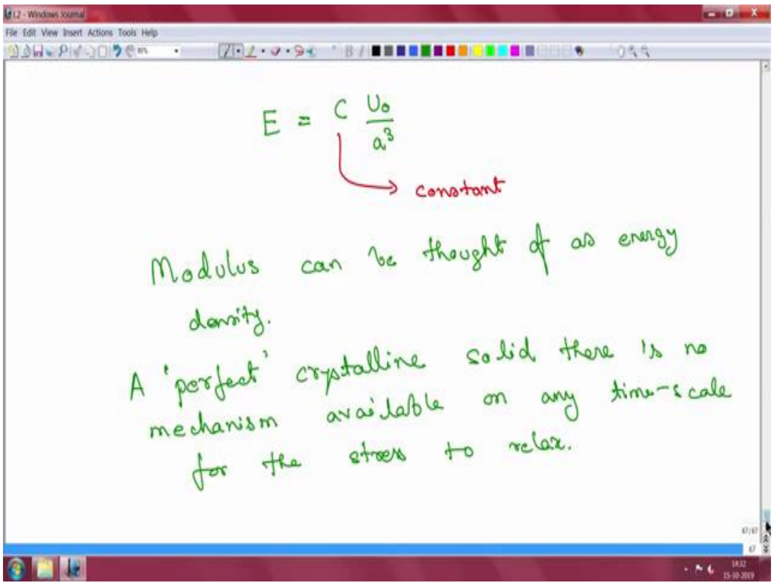

So, the idea of a perfectly crystalline material is a, is an ideal situation and in this ideal situation so perfectly or a perfect just a second I am going to rewrite this. So, a perfect crystalline and perfect I am just going to put here in quotes because what we mean is a very idealized condition. So, in a perfect crystalline solid there is no mechanism available on anytime scale for the stress to relax.

So, for solid bodies if you have a solid which is, which has inherent relaxation time of the order of years. If you are doing an experiment in the lab, the timescale is not very important, you are just looking at the energy you put in and how much energy is getting stored. So, assigning young's modulus or a modulus for such materials, makes perfect sense. But even for other cases where you can see something in your experiential timescale, if a material is moving, even then you can assign a modulus for these based on this idea of energy density.

But let us quickly contrast it. So, the idea of the crystalline solid is to be contrasted with that of a viscous liquid. So, in a viscous liquid, this stress, whatever stress you put in, is going to relax and is going to relax quickly. So, they do not have any mechanism by which they can store energy and that is the contrast between that.

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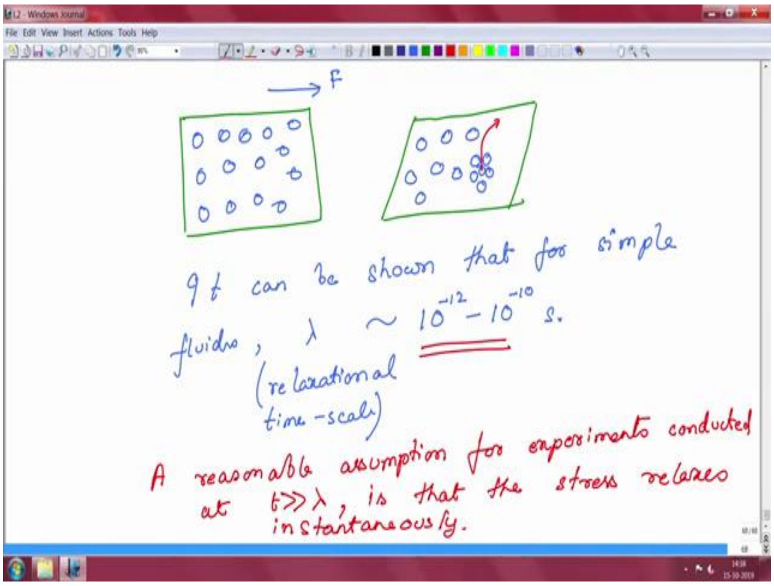

So, let us say you have a fluid. So, this is let us say a control volume and or an imaginary box which are and these are these different fluid particles, which are distributed some random fashion and you are applying some kind of a force on them then what happens? So, here what happens is, in a simple fluid, let us say water, this volume will distort and your molecules or atoms will move to slightly new places where they will be displaced.

And it can so happen that in the disordered form, there was some intramolecular distance between the different atoms, but here what you can have is, you can have a suddenly a cage type it can form where an atom get trapped in a very close packed structure, but this atom does not like it. So, it is going to jump back to some other available location and it is going to move and the moment it is able to move this, this is the place where your stress has built up and the stress is going to relax.

So, this timescale and we can show that I am not going to go into details of the calculation, so it can be shown. It can be shown that for simple fluids and simple fluids, the example will be water, for simple fluids this lambda which is the relaxation timescale. So, relaxation timescale is of the order of 10 to the power minus 12 minus 10 seconds okay. So, basically what is this lambda?

The lambda is basically the time where these molecules are going to readjust and going to distribute them again in such a way that they appear very similar to the way they were distributed before the application of the force itself okay. So, that is the time lambda is basically the time for molecular rearrangement in this particular case. So, now, you can see this time scale is actually really small. For experiments done in the lab, these time scales are way too small.

And you can assume, in many cases in an idealized cells that for simple fluids, the stress relaxes instantaneously, okay. So, reasonable, a reasonable assumption for experiments conducted at, at t much, much greater than lambda. So, let us say you are doing an experiment where your measurements or your data is being sampled at seconds or maybe minutes or hours, in that case 10 to the power minus 12 is way too small.

So, if you are doing an experience such way, in such a way that the data sampling rate is so much slower than lambda, then we can assume reasonable assumption for experience conducted at sorry, okay let me just be consistent is that the stress relaxes instantaneously, okay.

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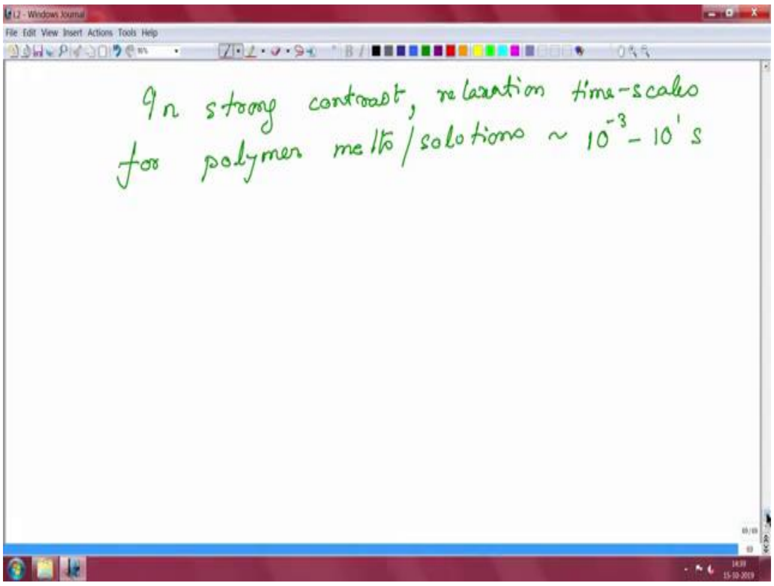

But this behavior is going to stand in contrast to the soft materials that we are going to see. And in fact, in, in strong contrast time scales of relaxation, time scales for polymer melts or polymeric solutions. We are later on going to do some experiments in the lab with polymeric solutions. We are going to see how they behave. So, in strong contrast relaxation timescales for polymeric melt solutions can be often of the order of the milliseconds to seconds, okay.

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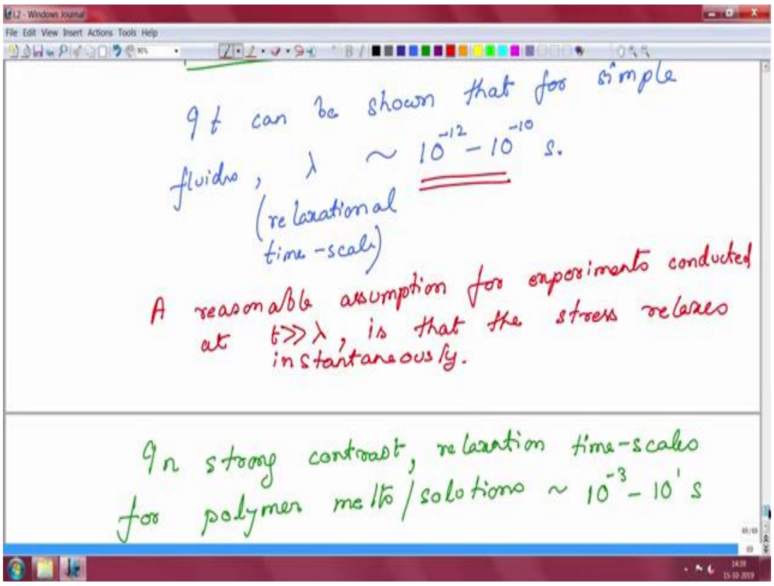

So, you can see how different these values are, 10 to the minus 12 versus this. Now, these are again, actual in an actual experiment, these values have to be measured, and they can even be lay, lie outside of this range. I am just giving an approximate range for many of the common polymerics melts and solutions that people encounter.

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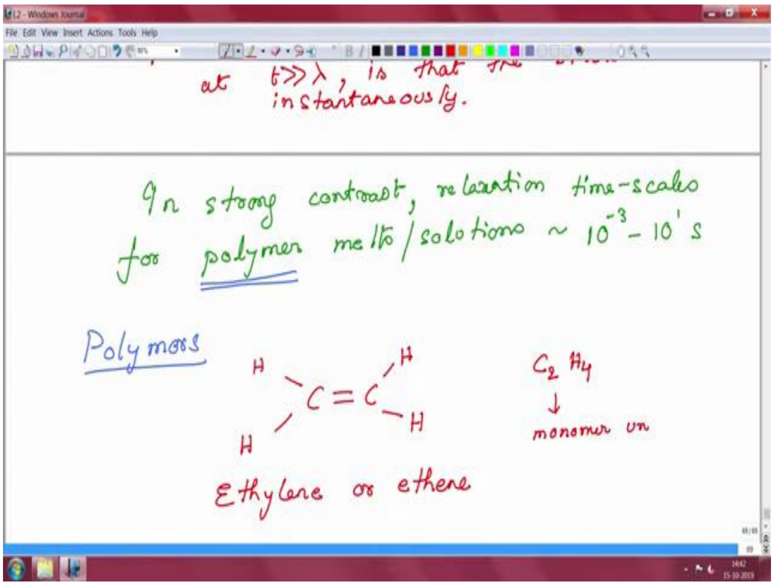

So, this is a very nice segue for us to segue into a topic called polymers. So, we see that polymers is, polymers are some materials, which are now going to display soft material type characteristics, but what are polymers? So, let us take a look at polymers in general and this is a very good, the polymers are very good example materials for understanding soft materials and viscoelastic behavior because they have been very well studied.

And more importantly, they have produced at a very, very large scale industrially. So, because their industrial usage and you might have heard of all the now the problems with polythene. And how it is becoming a huge problem for our environment and the reason it is becoming a problem for the environment is because of the scale of use and the scale of industrial production is massive.

So, these polymers are materials which have been produced or we have understood how to make them very well, we are, we have understood how to control the properties of these materials to very very fine degree, we have come up with many different manufacturing techniques for them and as a result of which they have been very widely studied and very widely categorized.

So, there are very interesting class of materials to begin with to understand some of these soft materials. So, to understand polymers we will take a very simple molecule, okay. And the simple molecule is this one, C2H4, so this is one of the simplest of the alkynes and this is also called Ethylene or ethene. And this C2H4. And we will see what this is, this is, for us this will be for the monomor. I will just write this right now and I will explain why I am writing this.

So, this is a very widely used material and its produced on a very large scale industrially and it is used to make a polymer which looks so, once you so, if you take the polythene, poly, sorry, the Ethylene molecule and polymerize it and you probably already know what polymerization means, then you have to take these monomor molecules and keep on adding them together till the actual molecule becomes very very large.

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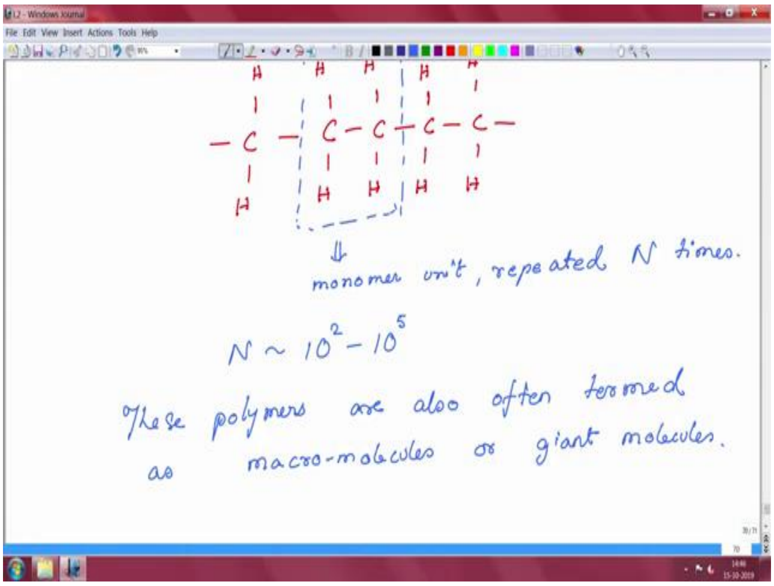

So, in this particular case, you would create such kind of a large molecule by bringing together all the different different carbon bonds, carbon atoms and this can just go, keep on going, okay. So, you can recognize this is your monomor unit right here, which is now going to be repeated we will say N times in the polymerization process and this N usually can be very, very large. Okay.

So, you are going to polymerize it and your N often can be easily of the order of 10 to the power 2 to 10 to the power 5 even higher sometimes. So, you end up producing very, very large molecules to do this process. Such large molecules are different than our simple molecules that we are accustomed to. Simple molecules are oxygen O2, very simple structure you have two atoms nitrogen N2, again having two atoms, water H2O having three atoms, those are also important components.

So, there is, exists a class of materials, where the actual molecular structure is very simple, simple in a relative term. Obviously, this, there is still research going on into structures of water etc. But for the perspective of the molecular structure and the unit of the material, its rather simple, but here this monomer unit keeps on repeating, the monomer unit actually keeps on is being repeated for a large amount of, by a large number.

So, end of the day what you will end up with is a molecule that is very very long, that is composed of a backbone of carbon carbon, in this particular case carbon carbon chain and that chain would have a huge number of carbon molecules. So, compared to your simple molecules, these molecules are extremely large, they are much larger and therefore, an appropriate name for these class of materials is also macromolecules okay.

So, these polymers are also often termed as macromolecules. And some researchers have even called them giant molecules. There is actually a very nice book called giant molecules by two Russian authors Alexander Grosberg and Alexei Khoklov if I pronounce it correctly, it is a very nice book for leisure reading of these materials.

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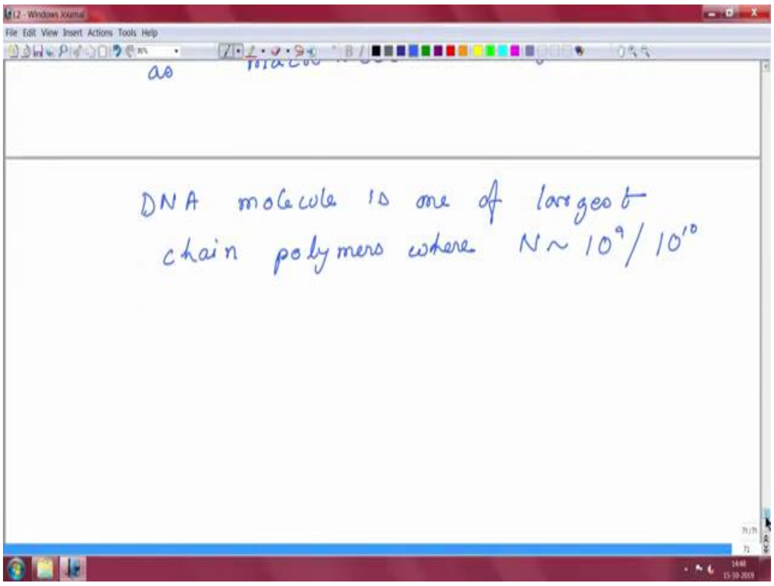

Now, another example of such polymers is DNA for example, DNA is also, DNA is one of the, DNA molecule is one of the largest chain polymers where this N can be of the order of 10 to the power 9 or 10 to the power 10, okay.

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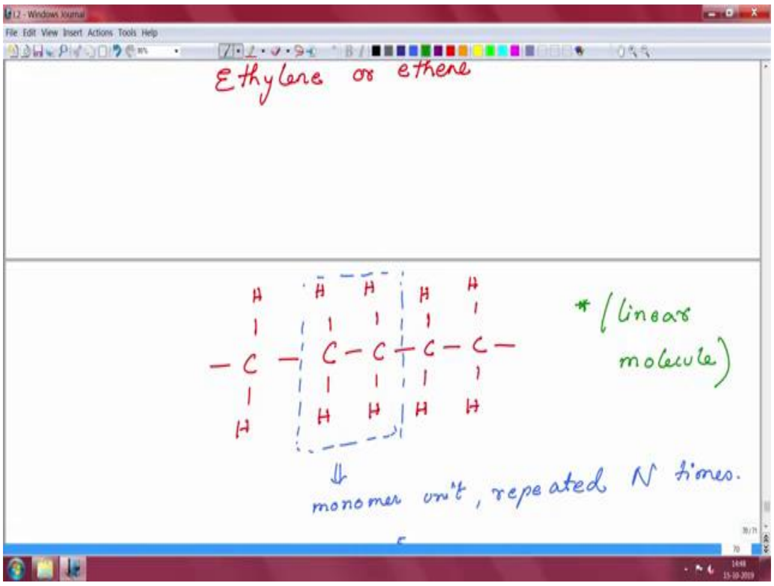

So, this is how our long polymer chain is going to form, this is, this kind of an arrangement is also called a linear arrangement. So, all the carbon carbon bonds are laid out next to each other so, this is a linear molecule. So, we have drawn and this is a linear chain, okay.

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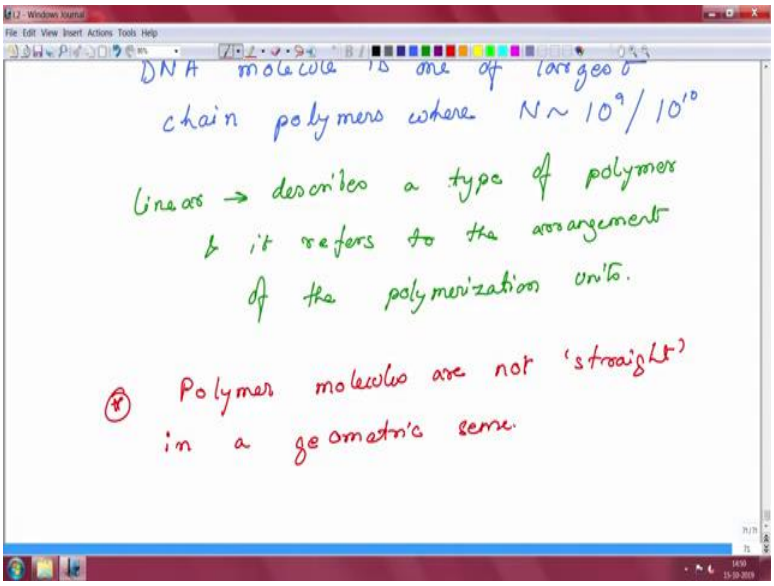

So, I will just make a quick note of this that linear here, linear does not mean that the molecule itself is like a straight line. Linear here describes a type of polymer, a polymeric, polymer or polymer material and a disk and it refers to the arrangement of the polymerization units.

The reason we are specifying this is because other types of structures are also obviously possible. So, we will later on contrast them with the linear models. And just to make a note is Polymer molecules are not straight in a geometric sense, which means that if you take some polymer if you put it in Water.

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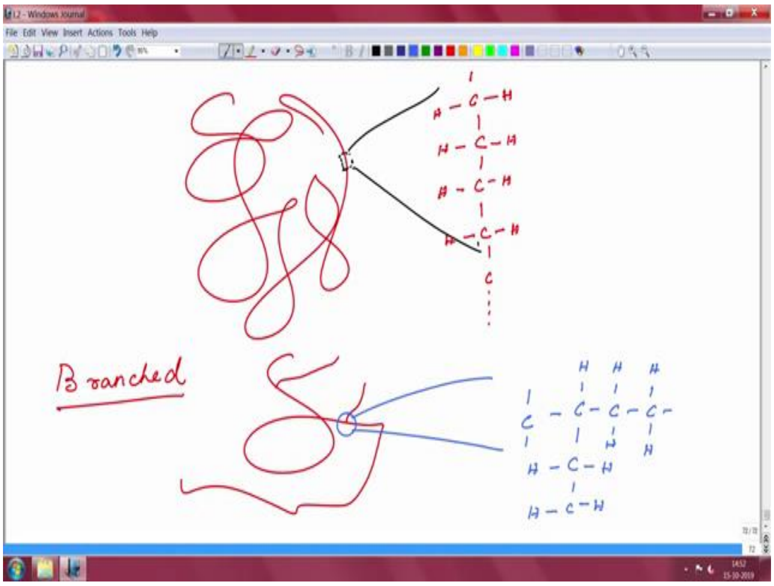

This polymer chain itself might look something like this. Okay. And this is a long and cold Polymer. But if you look at some small portion of this, and if you zoom in here you will just find these are again, the carbon carbon bonds are all arranged in some linear fashion. This is once again polyethylene. And obviously, this keeps, keeps on going. So, this is important from that perspective for us to understand the structure. Later on we will be referring to these.

So, you can also have, so in contrast to the linear molecules, you can also have a branched So, this is, so you can have a branched polymer molecule and a branch polymer molecule example, you can also have, so, you have these branches at different locations. So, if you zoom in into this small bit, what you will see is that you have the carbon carbon bonds obviously.

And then suddenly at some location there will be another branch of carbon which will be going off and forming a short chain so, this is a branch structure in contrast to the linear arrangement. So, in branched polymers, there are many different varieties that are possible and some of these are named just because of the manner in which the polymer molecules themselves are look in a schematic diagram.

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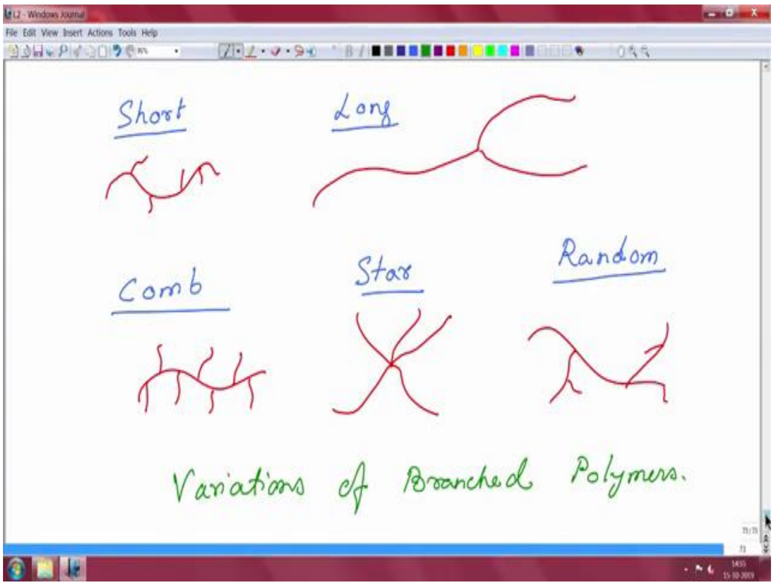

So, for example, short branched, so in a short branched, you will have maybe a chain and then you will have these short branches going off this is one morphology and you can also have what is called as a long chain. And in this case, you can have a branch, sorry a backbone and then it branches off but the other branches are also very, very long. So, that is one kind of morphology.

Another morphology which some people have called a comb morphology is, you have a backbone structure. But then you have different branches going off as if it appears like a comb. Then you can also have what is called as a star structure where different branches coming off from a very small location. So, this, it looks like a star obviously, that is why it is being called a star.

And then finally you have random distribution here well as the name suggests there is no (perf), there is no real structure that you can assign on morphology that it appears like. The branches occur at random at various locations or the main. So, these are all by the way, these are variations of branched polymers.

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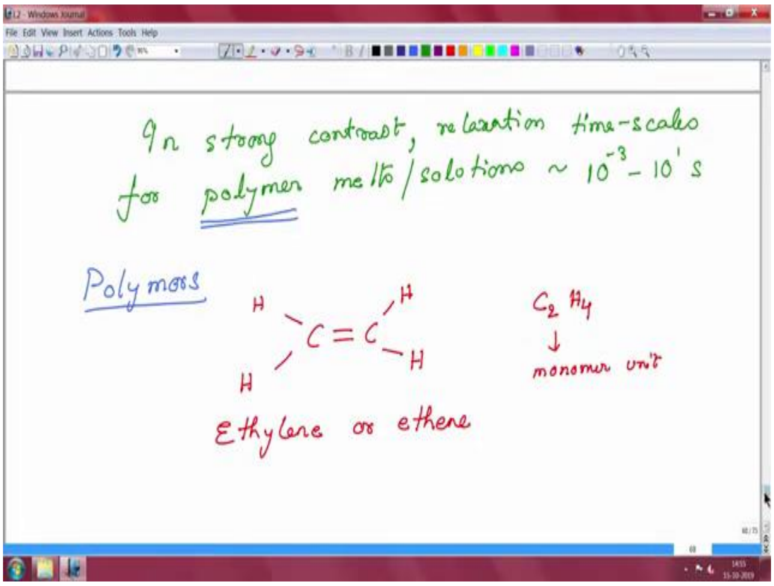

So, what we are trying to discuss here basically finally, was that we have these polymer molecules and these polymer molecules, we took an example of Ethylene.

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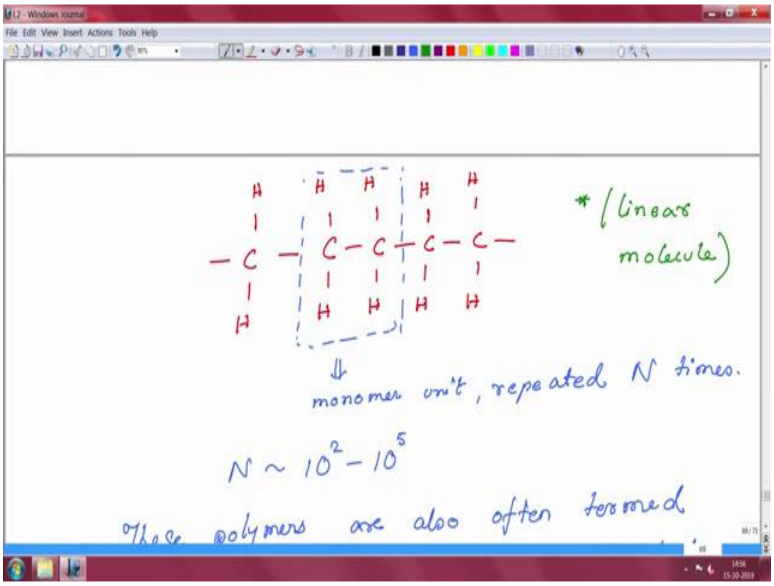

And we showed that this is one particular arrangement of the polymer molecules will be this linear combination.

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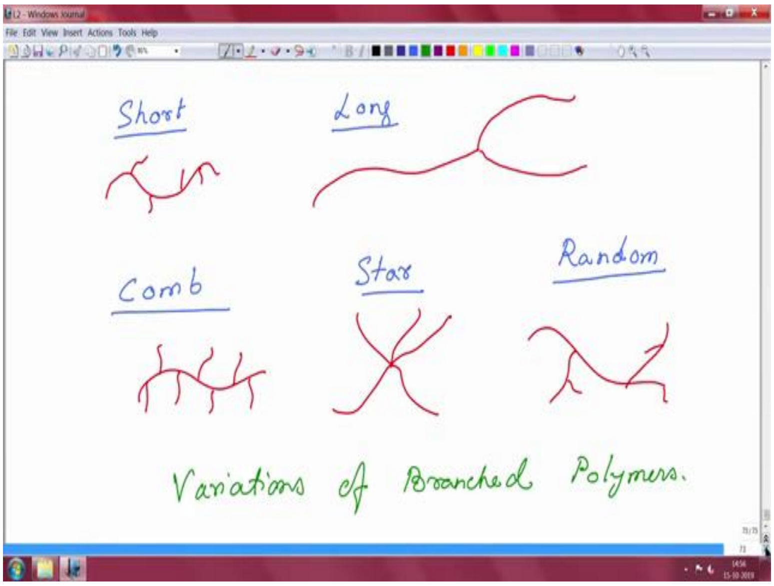

And there are other ones obviously, that are possible and we discussed some of the different morphologies of the branched polymers and they can have these different forms. The reason we are discussing this is because different manufacturing techniques or different polymerization techniques will lead to different kinds of overall or final structure of the polymer itself.

And the final or the structure of the polymer chain also influences very strongly its physical properties. So, it will affect its density, its affect its soft material behavior as well. So, it is very important to know, in a given situation, if you are doing an experiment with say, polyethylene oxide and you are making solutions of polyethylene oxide, it is very important that for a set of experiments, the material be made in or manufactured in the same way.

So, that whatever its structure, whatever is a branch structure or a linear structure be the same throughout the different experiments. Right. So, if you are a person who is conducting experiments, you have to make sure that you have to source it from the same vendor perhaps at times to maintain the, the similarity between the different experiments or else even if you source the same polymer with the same degree of polymerization, it is possible to get different structures, we should have very different properties.

And then if you have a mixture of these, which were originally manufactured in different ways, okay, so the N could be the same for, So you have, let us say you have gone into the lab and there are three bottles in the lab, and all of them have an N of the 10 to the power 4 but all of them have come from different manufacturing sources and you do not know how they were manufactured.

You cannot take those three different polymers and say oh because the N are similar I will do the experiments between them and they should come out to be the same, they will not most likely they probably differ from each other because the final atomic structure the molecular structure changes, then the physical behavior will also change. So, we will stop here today Okay, thank you.