Introduction to Soft Matter
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Lecture No 15
Polymers Cont

So, welcome back, we were discussing about polymers, we will keep this discussion going on today. And we will discuss some of the other important terms and issues that you would encounter with polymers when you deal with them.

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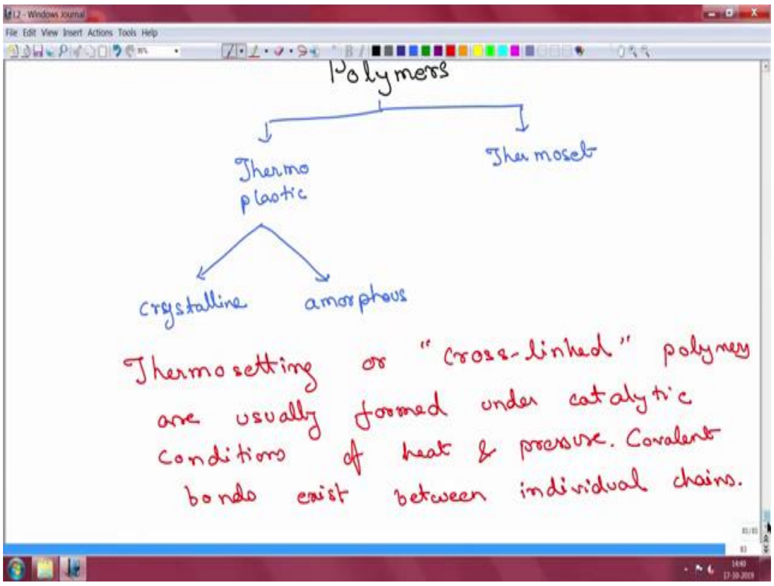

Thermosetting or "cross-linked" polymers are usually formed under catalytic conditions of heat & pressure. Covalent bonds exist between individual chains.

So, most of these polymers, so polymers can be classified. So, we discussed this homo polymer and the copolymers and others, but we and we also discussed that you have these different forms the straight, the linear macromolecule and the branched macromolecule but overall these polymers can be classified into two general broad under broad engineering names and one is called a thermoplastic.

And another is called a thermoset, in the, under the thermoplastics you can also have crystalline and amorphous polymers, amorphous. So, what gives rise to these different forms? Now, when I say amorphous is an indication that when you let us take a polymer and you cool it down, then what is the state of the cooled solid body that you are getting or the condensed form.

In an amorphous form, you would have a lot of disorder within the molecules whereas, a crystalline name usually refers to some kind of structure that is there amongst the molecules. So, but under thermoset I did not draw any of this, so, why is that? So, thermosetting and there is a reason for that and the reason is that the thermosetting or which is also called the cross-linked polymers, polymers are usually formed under catalytic conditions of heat and pressure.

And the reason we are mentioning this formation is because what this formation does is that during the polymerization process, it causes a formation of covalent bonds between individual chains okay. So, covalent bonds exist between individual chains.

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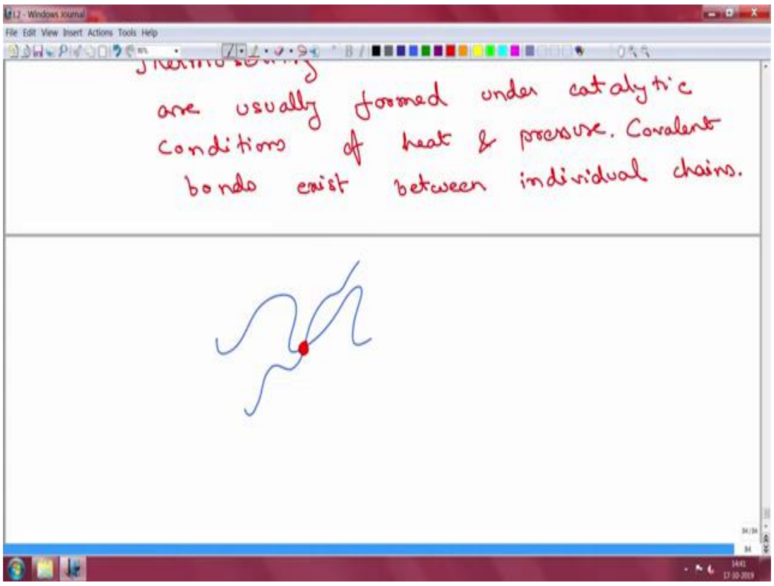

are usually formed under catalytic conditions of heat & pressure. Covalent bonds exist between individual chains.

So, if you were to look, if you were to take us go down to the atomic scale, what you would find is let us say you have a Polymer this is a chain. And let us say this is another chain. Now, at some point, they have come into close contact with each other. It is right here in the thermoset Polymery or cross-linked polymer at this location, you have another covalent bond between this chain and other chain, okay.

And that what that does is basically now what you are looking at is a large molecule, an even larger macromolecule than the original polymer itself, because the polymers have now been cross linked with each other. So, they are covalently bonded. So, breaking the bonds is going to take a lot of energy. And in contrast to the covalent bond, covalently bonded cross-linked polymers exists a different class.

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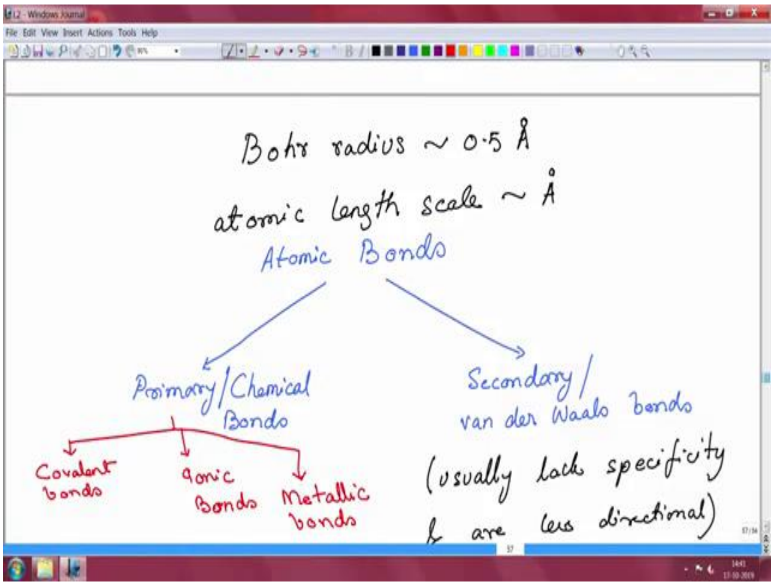

Bohr radius ~ 0.5 Å

atomic length scale ~ Å

Atomic Bonds

Primary/Chemical Bonds

Covalent bonds

Ionic Bonds

Metallic bonds

Secondary/ van der Waals bonds

(usually lack specificity & are less directional)

I remember when we were discussing bonds we are discussing, there are two types of bonds. So, we will just quickly go back to that right. So, we had said that there are, in atomic bonds, there are two types of bonds the primary and the secondary type of bonds.

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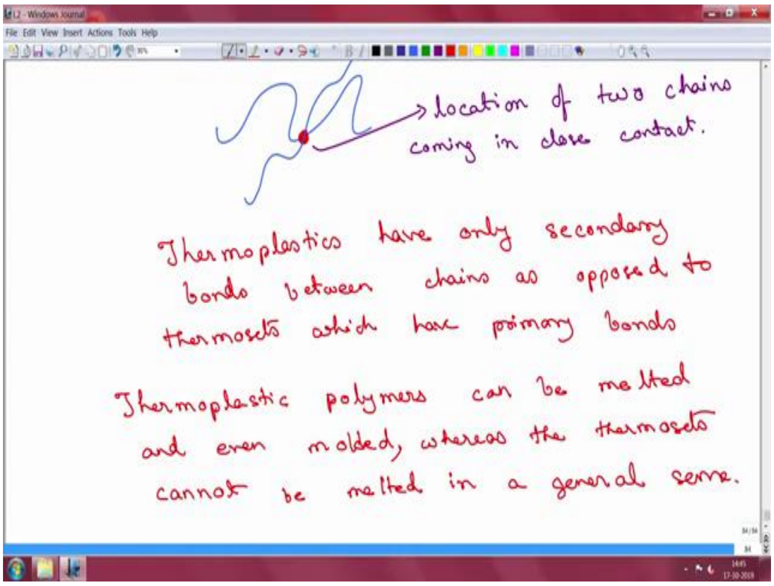

location of two chains coming in close contact.

Thermoplastics have only secondary bonds between chains as opposed to thermosets which have primary bonds

Thermoplastic polymers can be melted and even molded, whereas the thermosets cannot be melted in a general sense.

So, when we come back to our system like this, you can have at this location, you can either have a primary bond or a secondary bond, okay. And that gives rise to the difference between the two polymers. If you have a secondary bond, you end up with a thermoplastic because in that case, the bonds weaker bonds and those bonds can be broken with less energy. Whereas for a thermoplastic case, a thermal, sorry thermoset case there exists covalent bonds between the different polymer chains.

How many cross-links you have not said that, so, that itself can vary, but, the moment you have covalent bonds you end up with it requires you a lot, it requires a lot of energy input to break these bonds. So, most of the thermosetting polymers exist as solid bodies at normal room temperature and pressure example will be bakelite, rubber. Whereas, for the, for the other case the poly, the actually, maybe I should define it right now. So, the other case is the thermoplastics.

So, thermoplastics, thermoplastic have only secondary bonds between chains as opposed to thermosets which have primary bonds. So, this location of overlap, location of two chains coming in close contact. So, at this location you can have either a primary bond or a secondary bond and that makes the difference between the two.

So, thermoplastics the slide, the chains can also slide past each other and that is why these plastics are the thermoplastics can be melted and even molded. So, thermoplastic polymers, thermoplastic polymers can be melted and even molded whereas the thermosets cannot be melted in a general sense. Okay.

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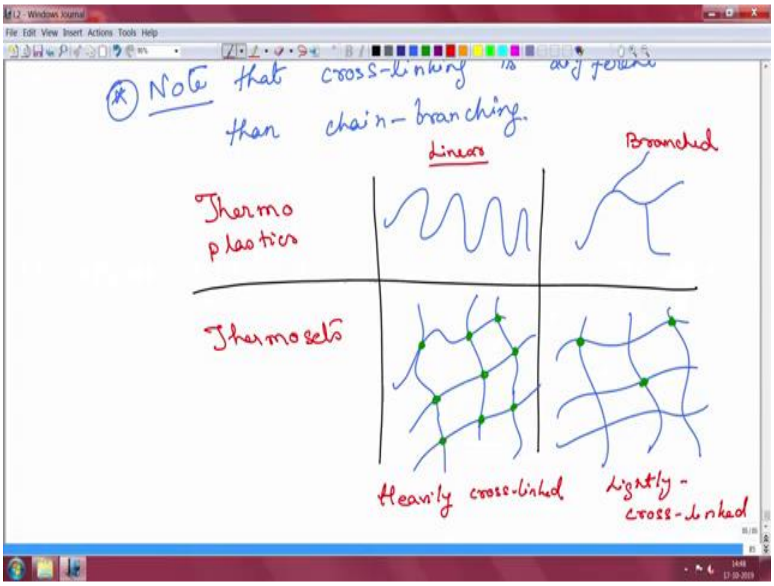

(*) Note that cross-linking is different than chain-branching.

And you want to note that so, note that cross linking is different than chain branching because in a chain branching situation, the branches are supposed to be small with respect to each other. So, let us contrast one more time these two. So, you have thermoplastics, the thermosets and within the thermoplastics you can have a linear chain. This is linear or you can have a branch system. This is your branch.

But in this case, in this case of the thermosets, the moment you have these polymer molecules you can have these are, this, these are all locations of covalent bonding and the number of covalent bonds can be high or low and that depends upon how you have manufactured them. So, you can have another case where very similar situation let us say and here the number of covalent bonds are lower. So, this will be called a heavily cross-linked thermoset and this is a lightly crosslink.

So, we can see that the very fact that your molecule is becoming large is leading to so many issues and so many other configurations that are possible. So, all these complications simply arise because now your molecule is large. So, the variation that can be there in the molecular structure is also becoming large. And we have not even talked about isomerization.

So, you can have molecules that exists in different isomeric forms and that would also lead to a whole different set of confirmations that are possible. So, we are not, isomorphism is also an issue, but we are not going to discuss that here. So, let us, since we are trying just trying to familiarize ourselves with the polymer literature, we are going through all the different terms that are important to in this particular area. And let us just go ahead and familiarize ourselves with a couple of more.

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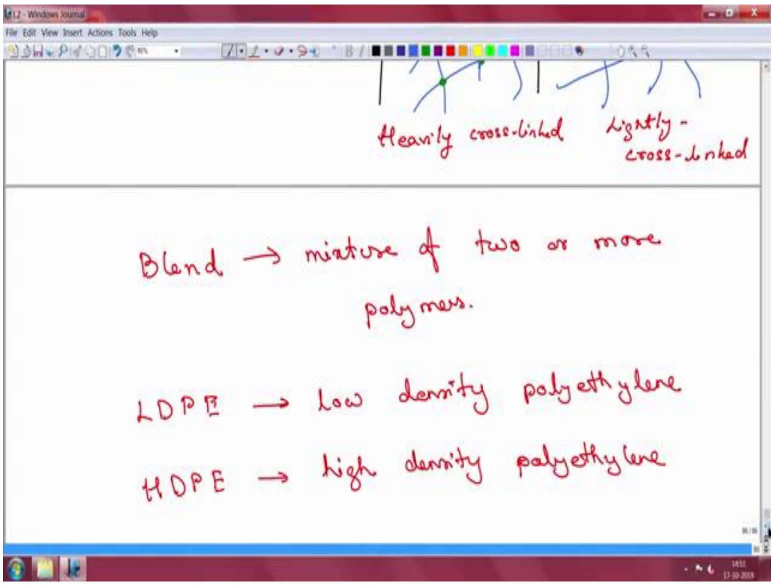

Heavily cross-linked

Lightly - cross-linked

Blend → mixture of two or more polymers.

LDPE → low density polyethylene

HDPE → high density polyethylene

So, for example, in an industrial setting, you would call you have something called a blend, okay. And a blend is a mixture of two or more polymers, obviously, different polymers. Then you have terms like LDPE which is used for low density in this case it is low density polyethylene.

You have HDPE, and the reason we are going through all this, these sundry facts is because just to give you an idea that the moment you have these large molecules, how many different complications are possible and that can lead to all these different issues that you have to take care of so, high density.

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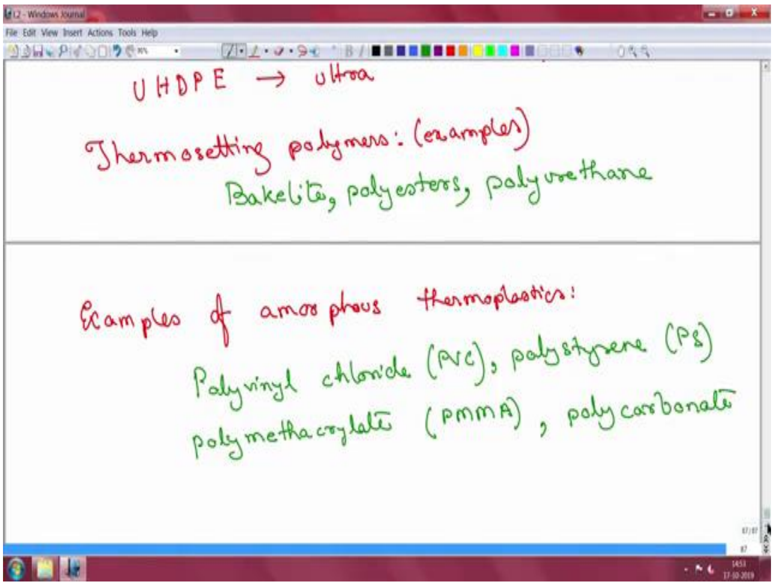

UHDPE → ultra

Thermosetting polymers: (examples)
Bakelite, polyesters, polyurethane

Examples of amorphous thermoplastics:
Polyvinyl chloride (PVC), polystyrene (PS)
polymethacrylate (PMMA), polycarbonate

And if you place a U here then it becomes ultra-high density. So, there is something called UHDPE so say changing the structure is going to lead to all these so I am not going to copy this just say ultra-high density polyethylene. Thermosetting polymers, some examples perhaps. So, thermosetting polymers examples of the common examples for this are bakelight, polyesters I am sure you have heard of the term polyester?

Goes into making of clothes, sometimes polyurethane, examples of amorphous thermoplastics are polyvinyl chloride part of the vinyl chloride, vinyl polymers, the polyvinyl chloride PVC, polystyrene PS, so polystyrene something you might have encountered quite a bit, polymethacrylate PMMA, and polycarbonate.

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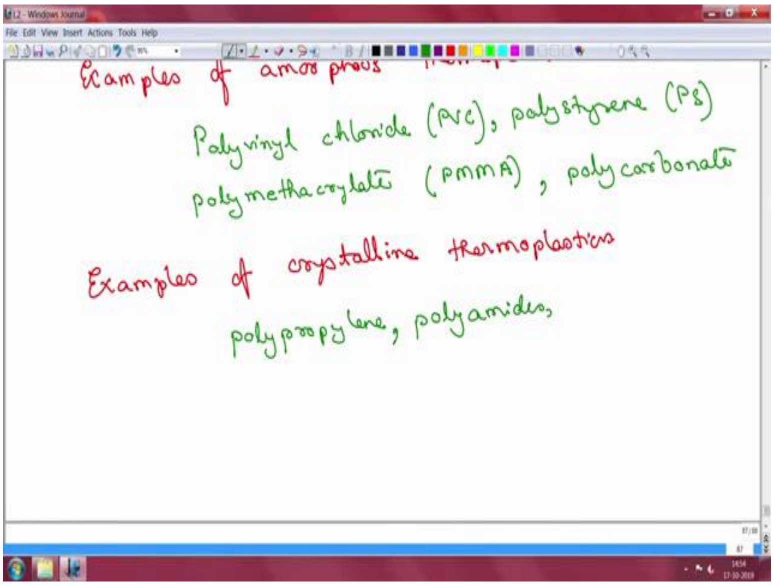

Examples of amorphous

Polyvinyl chloride (PVC), polystyrene (PS)
polymethacrylate (PMMA), polycarbonate

Examples of crystalline thermoplastics

polypropylene, polyamides,

And examples of crystalline thermoplastics would be polypropylene, polyamides, etc. So, what we have done is we have encountered a lot of different terminologies with respect to polymers, specifically some of the engineering related terminology, thermoplastics, thermoset and so, we have seen that this cross-linking or not, other not, the presence of the secondary or primary bond can be an important classifier here. But what about the individual chain itself okay. So, we have not discussed isomorphism so much, but the individual chain can exist in a number of different forms.

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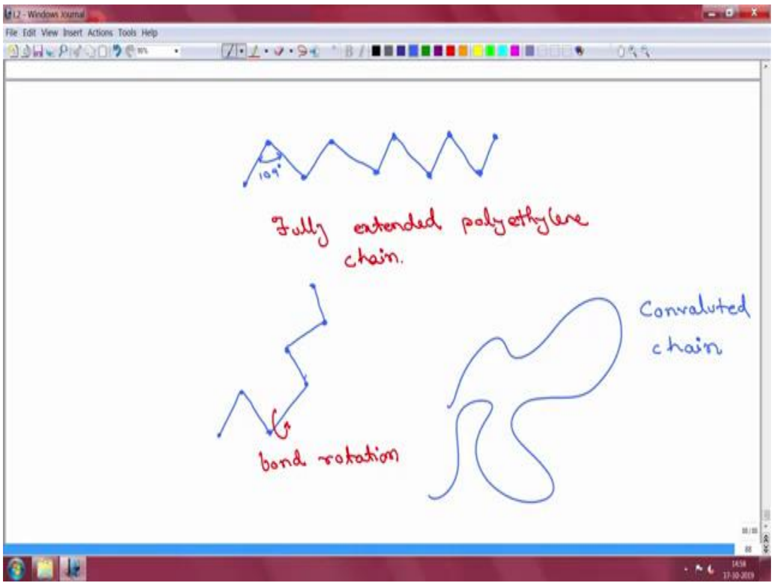

So, the individual polymer chain, if you so, the carbon so, I am just drawing the carbon carbon (back) backbone okay, so this is the carbon carbon backbone. You might recall that this angle has to be 109 degrees approximately. So, a linear or fully extended chain would have a backbone like this. So, this is your linear, sorry, is a linear molecule, sorry fully extended polyethylene chain but you do not expect atoms. So, this is a crude diagram because the angles are always supposed to be 109 degrees.

Now, atoms are always moving, they are never stationary. So, at any finite temperature they cannot remain stationary. So, there is always a tendency to move and we know that the single carbon carbon bond allows for rotation. So, once it allows for rotation, you can actually have rotations of this that are possible. So, for example, in a due to this thermal motion of the atoms itself, maybe I will just draw it a little bit down due to the thermal motion of the atoms this I have to draw like that.

But the second one I can draw in this fashion. So, this, this bond has undergone rotation. This is and if all the other bonds are also undergoing rotation, you can end up with a chain like this, so this keeps on going. So, your final chain, which is going to consist of a very very large number of bonds can look like this convoluted chain and this is what usually if you take a polymer molecule and when it is in solution or when it is in a even in solid phase, this chain molecule will be in some convoluted form is specifically then numbers of a degree of polymerization is very, very high.

So, it is not, never going to be this extended molecule. So, let us say your degree of polymerization is 10,000. So, the carbon carbon bond we know is about Angstrom, so that is 10 to the power minus 10. So, if you have a degree of polymerization of 10,000 10 to the power 4 then if the chain were to be fully elongated, it would be of a length of 10 to the power minus 10 into 10 to the power 4, which is 10 to the power minus 6. So, that is almost 1, that is 1 micron.

1 micron, at what stage can you start seeing with your eye? About 100 microns is something that is in a human eyes resolution and 10 to, 10,000, we just discusses a small number for polymerization. So, if you have a polymer chain whose degree of polymerization is now let us say take a million, 10 to the power 6 that would be 100 (mole) 100 microns.

So, if you have a polymer chain, and its degree of polymerization is 1 million then if you were able to stretch it out, you would actually be able to see it with your naked eye. So, 1 molecule you will be able to, single molecule will be something that would be within the grasp of your human eyes resolution. And obviously, a million is small. So, you have chains which have a billion up to a degree of polymerization, then if you stretch that out, then that could be 10 to the power 3 microns, this almost this millimeter. So, you can actually see it on a small scale.

So, but a polymer is never going to be that big, because there is no force you need something to stretch it out. For that, polymers are always coiled up. A human DNA is a polymer with a very large degree of polymerization. So, if all of them had to be of that if they were stretched out, then humans, average human cell would have to be much bigger than a micron. Or sorry, a millimeter. So, we know that that does not happen.

So, in reality in the natural state, the polymer molecule never exists as an extended chain, but rather as a crumpled up ball. And the important question is then that what is the size of this ball? So, that is something that we will see in the next class. So, we will end today’s class here. And in the next class, we will just try to see discuss a little bit more on polymers and some of the other classes of stock materials. Okay, so we will stop here today.