Introduction to Materials Science and Engineering
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Lecture – 42
Crystallinity in Polymers

Polymers are can be either amorphous or crystalline.

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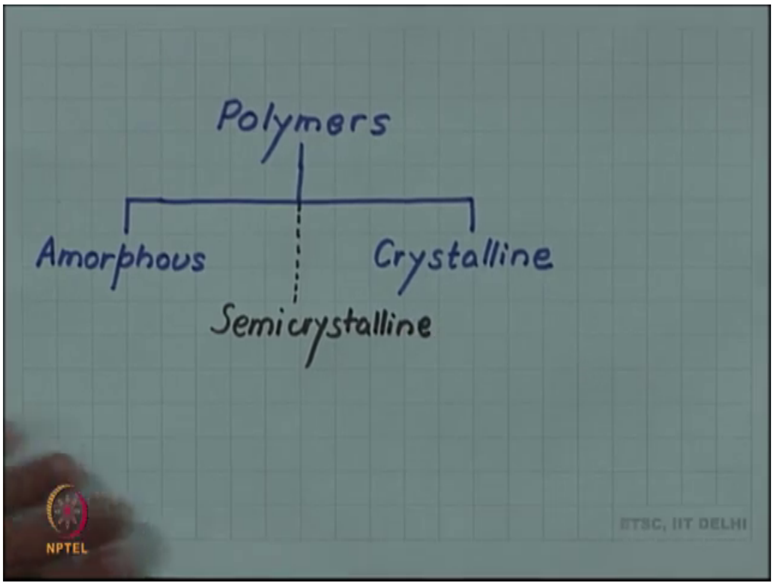

In fact, a given polymer is never fully amorphous or fully crystalline, a given sample of polymer may have regions of amorphous field and regions of crystalline phase, such a state is called semi crystalline semi crystalline.

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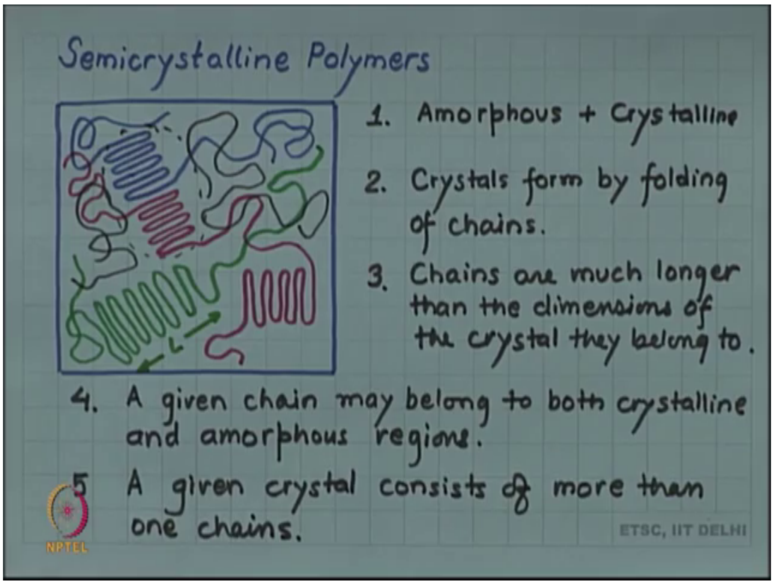

So, here we schematically a 2-dimensional schematic of a semi crystalline polymer is shown, what you should know here is that the crystals form by folding of the chain, you can see this blue chain or the red chain are folding. So, the first point is that there are both amorphous region, you can see the amorphous plus crystalline region.

So, where we have I am showing this parallel chains, I am trying to represent crystalline region and where I have shown these randomly wiggling chains that is the amorphous region, in the same polymer sample. Then the crystalline region the crystals form by chain folding, by folding of chains, which really means and it is a very, very important point, that length of a given chain it is much, much longer than length of the crystal.

So, for example, the green chain if you see, is much, much longer than the length of the green crystal which is much smaller. So, the chains are much longer than the dimensions of the crystal, they belong to this is a very, very important point, historically as well because this was a big issue when Schrodinger and proposed the macromolecule or long chains as basic structure of polymers, because when crystal structure was determined using x ray diffraction the unit cell size and the crystal size, was found to be much smaller than the chain size.

This led to the confusion that how come in a in a small unit cell or in a small crystal long chains can fit. So, then this folding mechanism was thought of, and gave an explanation for long chains fitting into smaller unit cells or smaller crystals. So, chains are much longer than crystals they belong to, and a given chain if you see for example, the green chain is part of both crystalline and amorphous region. So, a given chain may belong to both crystalline and amorphous regions, and at the same time, if you look at a given crystal. So, for example, this crystal look at this crystal, this is a single crystal, but then part of it is coming from the blue chain, and the part of it is coming from the red chain.

So, a given crystal can be formed from more than one chain. So, a given crystal consists of more than one chains. So, these are basic aspects of a semi crystalline polymer.

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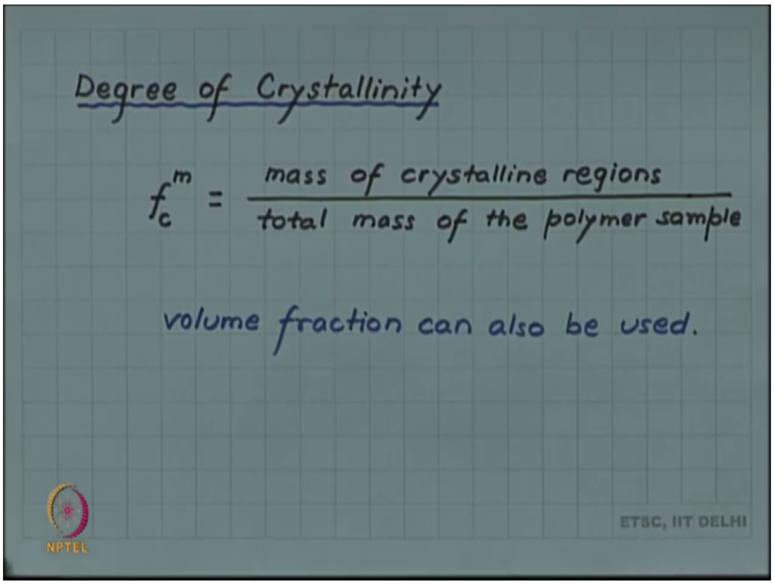

A factor called degree of crystallinity is defined, which is simply mass of crystalline region by total mass of the polymer sample, this tells us that in a semi crystalline polymer what fraction is crystalline and what fraction is amorphous, instead of mass fraction one can use volume fraction as well.

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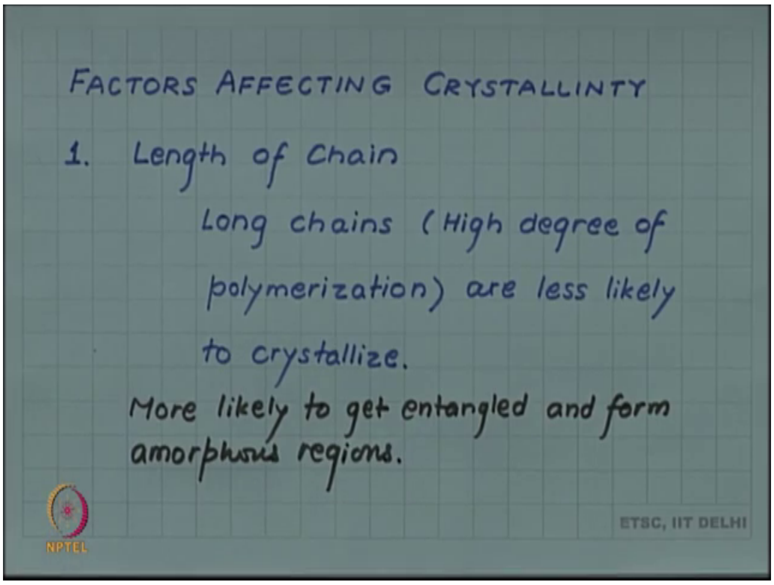

Now, what are the factors there are certain aspects of polymer certain aspects of crystallization of polymers, which depend upon the structure of polymer, a structural aspects of polymer. So, these factors are now listed. So, one of the factors is length of the chain, if you have long chain that is if you have high degree of polymerization then these chains are less likely to crystallize, this is simply be called long chains are more likely to get entangled, and form amorphous regions.

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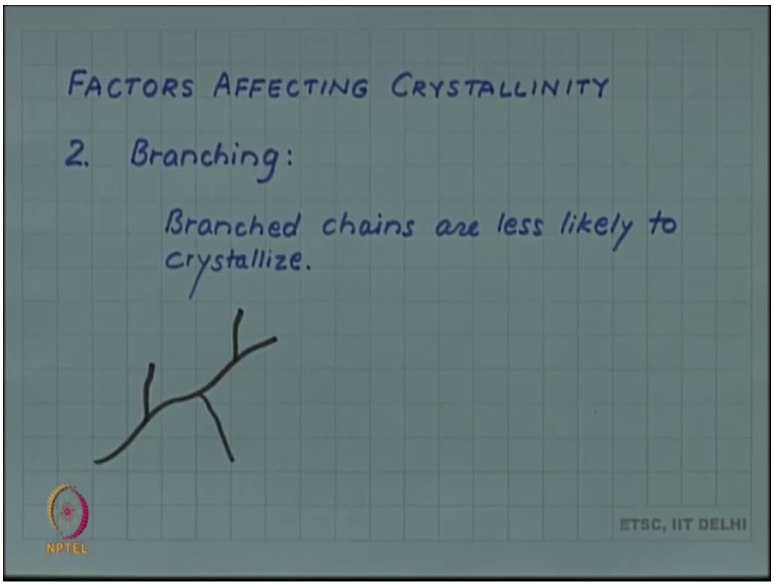

So, longer chains are less likely to crystallize. Another factor which affects is branching if you recall there is a polymer backbone, and on that backbone sometimes you can have side branches we have discussed this. So, if you have now branched chains like this, it will be more difficult to fold them and pack them periodically. So, these branches will come in the way of packing crystalline packing of the polymer chains. So, branched chains are less likely to crystallize.

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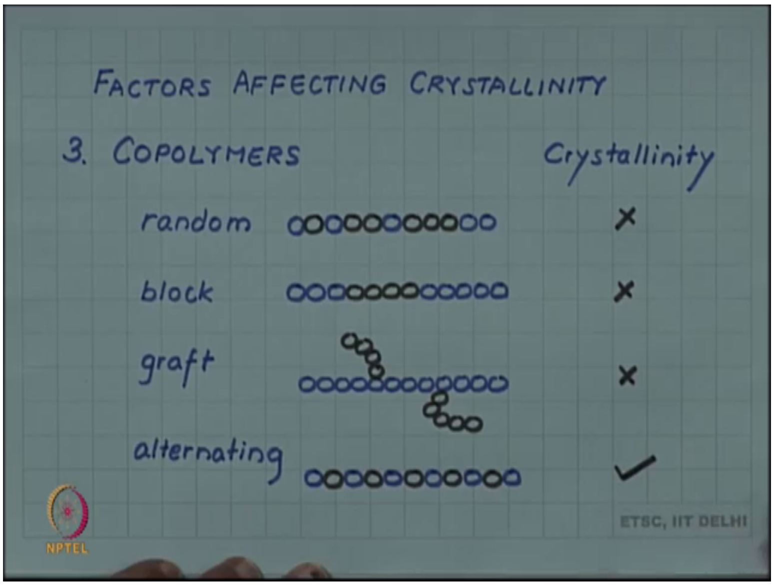

Now, if you have copolymers then we discussed variety of copolymers random block graph, and alternating you can see that in random copolymer the monomers the black and the blue circles are now representing monomers. So, the monomers come in some sort of random sequence. So, a given chain itself has a random arrangement of monomers. So, crystallinity is much less likely. So, it will not be forming a crystalline structure, the block copolymers also has monomer blocks of monomers coming in a random sequence.

So, this is also unlikely to form crystalline polymer graft polymer is like a branched polymer you can see and these branches will come, in the way of packing like the crystalline structure. So, the only alternating copolymer in which the monomers are alternating has an inherent periodicity within the chain itself, and then one can think of folding and periodically arranging them. So, this may crystallize.

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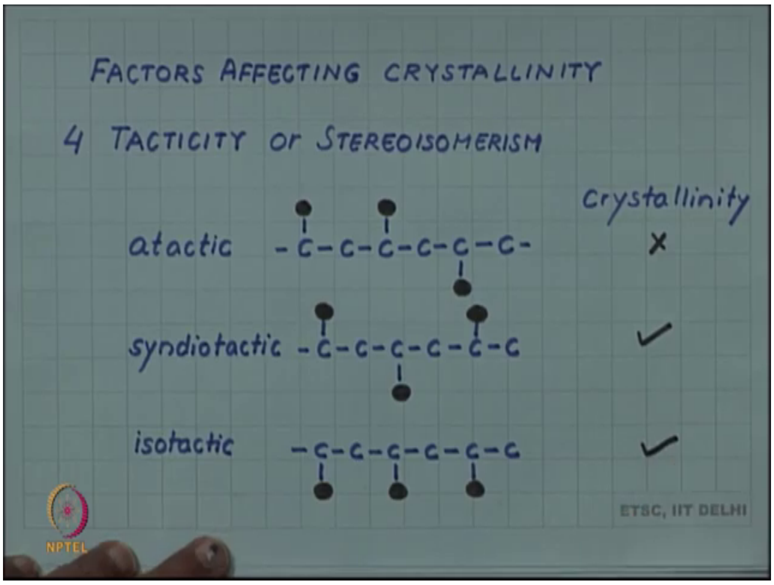

We have discussed tacticity or stereoisomerism, and if there is a special fide group those specified group can come on either side of the main backbone, if they are coming randomly on either side then you have a tactic, if they are coming alternately on each side you have syndiotactic and if they are coming all on the same side it is isotactic.

You can see that if in a tactic chain or an a tactic polymer since because of the randomness of the side group, the main backbone or the main chain itself is random and will not be possible to arrange them in a crystalline form. So, a tactic and will not be crystallizing, where a syndiotactic because it is coming alternately. So, has an inherent periodicity within the chain, and one can think of packing them in a crystalline way and same is true for the isotactic.

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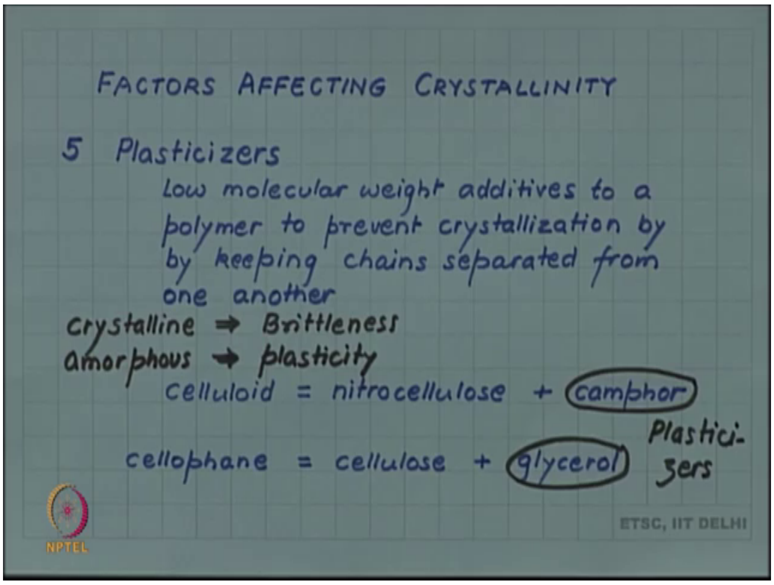

The final factor which affects crystallization of polymers is plasticizers, sometimes low molecular weight additives are added to polymers to prevent crystallization, crystalline regions the crystalline polymers are usefully brittle, crystalline implies brittleness, where as amorphous leads to lends plasticity to the polymer plasticity. So, they can be deformed easily. So, these low molecular weight additives are called plasticizers because they prevent the chains, they come in between the chains and prevent them from coming together.

So, that therefore, a crystalline periodic packing of these chains are not possible, and by promoting amorphousness they make the plastic or make the polymer more plastic. So, that is why they are called plasticizers. So, some well-known Bayer plasticizers and polymers made out of those plasticizers are celluloid, which has nitrocellulose as it is polymer, but camphor is added as plasticizer. Another polymer cellophane has cellulose as it is main chain, but glycerol is added as plasticizers. So, both camphor and glycerol these are plasticizers in these polymers, and they promote amorphous structure