Molecular Arrangements and States of Polymers

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Lecture - 16
Structure of Biopolymers

Welcome to the course on polymers. In this course, we are looking at the concepts related to polymers, their properties, their uses, and also focus on the sustainability aspects. After having looked at initial definitions and factors which are involved in polymeric systems, what are the advantages and disadvantages of polymeric systems, what are some of the different applications of polymeric systems. We have also looked at a single macromolecule and how conformations in a single macromolecule is very useful in terms of describing many of its properties for a melt or rubber like system wherever there is segmental motion possible. Now, in this week what we will do is start looking at some of the properties in the solid state. So, because of the macromolecular flexibility in the solution or the melt, the solid state that we get is also influenced by the conformations. So, therefore, what we have learnt in conformation is again useful while describing the solid state of these polymeric systems. However, once the solid state is reached, the structure gets frozen. And we will see that it can be a glassy amorphous system, it can be crystalline system and in polymers quite often it’s combination of the two.

So, in this week, we will look at what are the possible concepts associated with structure and the confirmations of systems polymeric systems in the solid state. And so, let’s begin by just doing a survey of the structures in biopolymers. As we have been saying in this course, that sustainability requires for us to take inspiration from many of the biopolymers, which are already present. So, let’s look at what are the structures.

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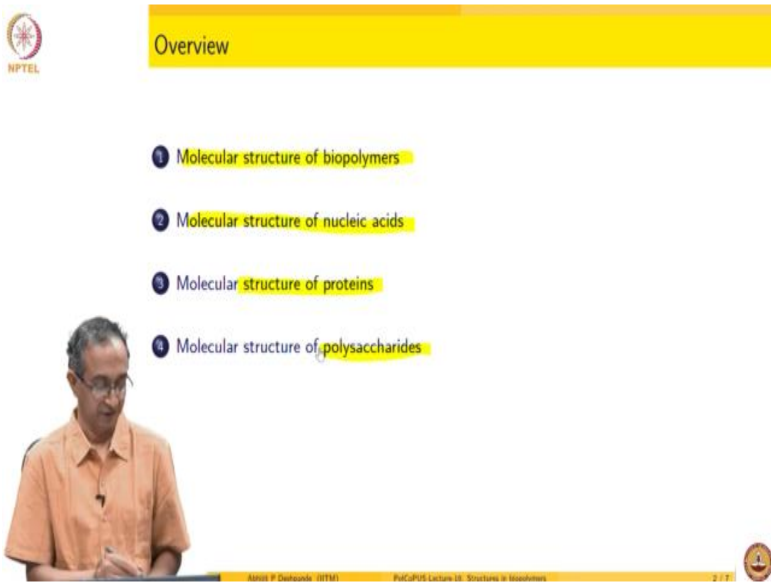

So we will do this by looking at quickly the molecular structure, which we have already talked about, so I will quickly review it and then we will look at some of the aspects of DNA as a molecule, which can be used for engineering and summarize, what do we mean when we say structure of proteins. And we will look at in a little more detail an example of polysaccharide which is pectin and how complicated structure at the macromolecular level is very useful for its function.

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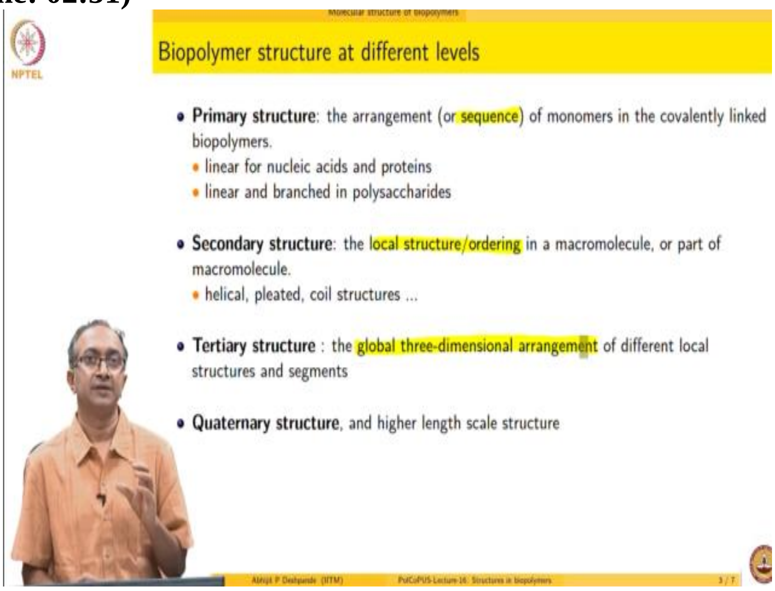

So, biopolymer structure can be looked at different levels and this is something which you may be familiar with from your earlier courses on biology and physical chemistry. So, we can have the primary, secondary and tertiary structure and this just depends on the sequence of how the monomers are attached to each other. Or what is the local structure and ordering? And of course, what is the global three dimensional arrangement? So, I suggest that you read about these structures related to proteins, which are described in great detail.

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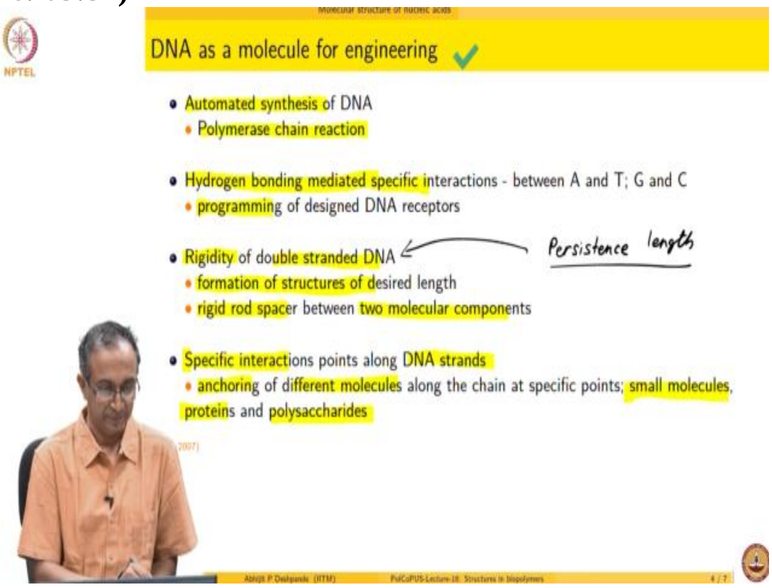

And we will move on to look at just some aspects of DNA, the nucleic poly nucleic acid as a molecule for engineering. So, of course, this is something which all of us are familiar with, I am recording these lectures in the midst of a COVID pandemic and PCR is the term which is quite often used and so, this is nothing but automated synthesis. So, DNA is a molecule can be used for automation and engineering. Some of the terms which we are quite commonly used in manufacturing and fabrication and so on. And all of this is possible because of these hydrogen mediated very specific interactions which are present in the DNA. So, therefore, you can actually do program in terms of which part of DNA molecule will interact with what kind of species? And the other important aspect is related to the flexibility of the macromolecular system. In this case, we know that DNA exists as a double stranded species and its rigidity or lack of molecular flexibility is very high and therefore, we can actually form structures of control length. And more importantly, this rigidity can be controlled depending on whether we go from single stranded to double stranded or if we change the ionic environment. And we could also place this rigid component as a spacer as something separating different molecular entities, so, again like an engineering at the molecular scale. Just to remind you, we have discussed this earlier, we have defined something called persistence length. And I would urge you to go and look at what is the persistence length of a DNA molecule? And compare it with persistence length of polyethylene. And then you will be able to see why polyethylene is called a flexible molecule and double stranded DNA is a rigid molecule. And so, what is crucial in DNA as a molecule for engineering is the fact that we have very specific interactions along these DNA strands and so we can in fact anchor different molecules and these molecules can be small molecules, proteins or polysaccharides and in fact, this is the basis of life, that all these interactions can be done in a very controlled manner using DNA.

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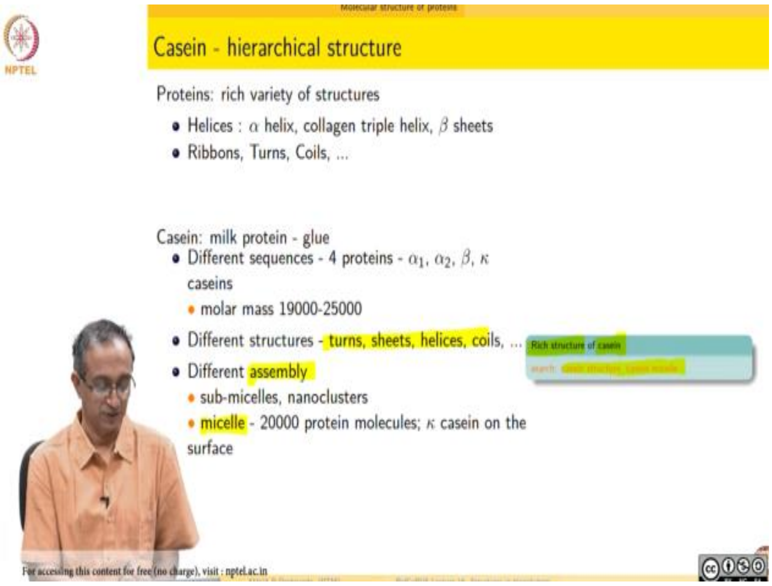

Now, let us look at proteins and here we will look at examples of casein. And of course, from your earlier knowledge of proteins, you know that they exist in alpha helix, and beta sheets and they can exist in all these different form. Again, the best way to learn about this is just do a search on these and look at the images. There are fascinating rich variety of images, which can immediately make you understand what is meant by each of these structures. And all of these structures get formed specifically because of interactions along the macromolecular chain. And these interactions could be hydrophobic, could be ionic, could be hydrogen bonding, and so on. And we will learn about some of these interactions in the 19th lecture where we will summarize some of these interactions which are possible. So let’s, in this lecture focus on casein, and casein is a protein and, of course, it is part of milk. And so it is known for thousands of years. And in fact, it’s used also and one of the common examples in addition to the food cheese making, or variety of applications related to food, it’s very commonly used as glue.

And in fact, one of the applications where it is used as glue is in transformers, in insulation boards. Can you think of reasons why would casein as a substance, as a glue be used in transformers as an insulation? And what is an insulation medium? So, generally insulation is wooden or cellulosic material. And if we need a required thickness then you may like plywood we make, we actually put several layers of cellulosic material together to make a solid rigid substance and that's what is insulation, paper based insulation and in between different layer casein is used. And important aspect of providing insulation is also oil in transformers. You must have heard of transformer oil and therefore, this paper based insulation needs to interact very well with oil. And so, casein clearly has sufficient hydrophobic groups so that it can interact with oil. So, just to highlight again hydrophobicity is required and interaction with oil is required. Now, why then casein alone? We can use many other hydrophobic substances, which can be used in as a glue. The key here is bonding with cellulose. And once bonding with cellulose is involved, we need hydrophobic and hydrophilic groups also, because cellulose as we have seen contains carbohydrate, it's a basically polysaccharide and so, therefore, we need hydrophilic groups also. So, casein has just the right amount of hydrophobic hydrophilic combination, which can serve as adhesive between cellulosic materials and as an insulating material with oil, very fascinating.

And the issue with casein is also it's a complex structure. In fact, it can have different sequences, so there are different types of caseins. So, different sequences of amino acids are used and in biology and therefore, whether it's cow or goat or any other mammal which is producing milk, there are different varieties of caseins which are produced and the molar masses are also different depending on the origin of the casein. And then so, this is the sequence level the primary structure itself is a combination of several things, then they combine to variety of secondary structures. So, we can have sheets, turns, coils, whatever we have discussed earlier are all present here and then these molecules macromolecules and these secondary structures combine to give an assembled clusters. By cluster we mean combination of several molecules, and so, we some of these turns and sheets and casein macromolecules get together to form a smaller entities called sub micelles or nanocluster and these combine where 20,000 protein molecules are involved in one micelle and in fact in milk, because casein is largely a hydrophobic substance, it forms these micelles and then it can be dispersed in a aqueous medium which is what milk is.

And generally the Kappa casein which we have seen is on the surface of such micelles. So, if you look at this casein extremely rich structure, there is sequence difference, there are secondary structures which are different and then finally assembled into a complex micellar structure. And again if you just do search on casein micelle or casein structure, you will see how rich variety of structures which are present in casein. So, in addition to being used as glue, casein can also be used in a variety of biomedical applications given that it has this, combinations of hydrophobic and hydrophilic interactions and it has presence of a micellar behavior and more importantly this micellar behavior can be manipulated by changing pH or ionic environment. And so, when we change pH or ionic environment we manipulate the hydrophilic and ionic interactions and therefore, we can arrive at different sorts of assemblies. So, you can see that a bio macromolecule like casein gives us such a wide ranging capability of manipulation and can such things be also achieved in a synthetic polymer can also synthetic polymers give us wide ranging response where the right combination hydrophobic and hydrophilic interactions are present. So that's a challenge for us to look at.

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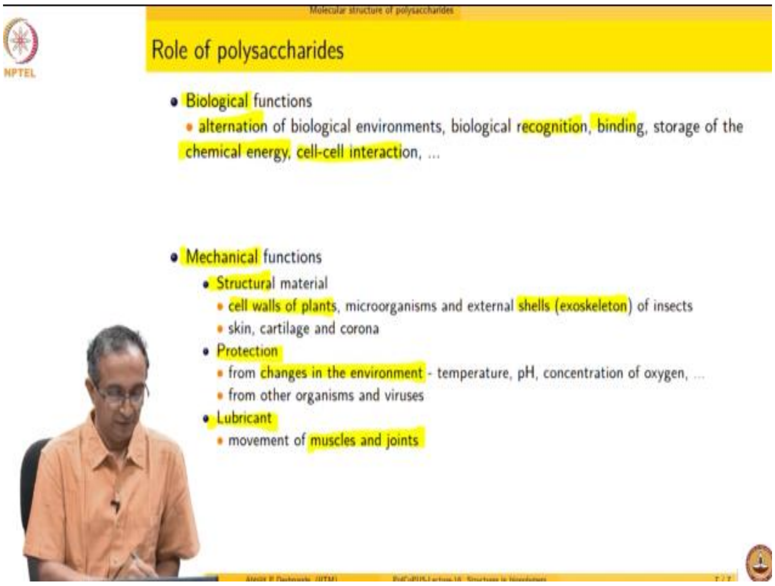

So, let's finish this lecture by looking at the role of polysaccharides and one example of a polysaccharide. So polysaccharide plays several roles in biological systems, whether it's plants or animals. Biological roles are things like recognition, alteration of biological environment, binding, storage of energy, and also mediating interactions between cells. So, they play a very important biological function, but quite often they also play a role of mechanical function. So in our joints, for example, the synovial fluid is actually a polysaccharide based system. So movements of muscle and joint lubricants are used very mechanical function. We also have cell walls of plants, the cell walls are rigid compared to the cell contents itself and it gives us the shells. So therefore, many protection based systems, which serve a mechanical role also are made up of these macromolecules, which are basically polymers of sugars.

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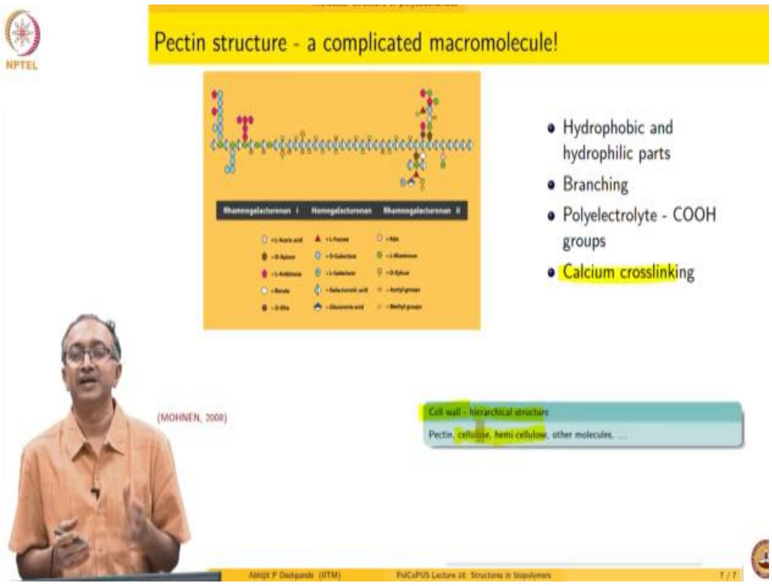

And let's look at one specific example called pectin. Pectin is there in several fruits and vegetables. The commercial pectin which is available is quite often made from either orange or apple. In case of, for example, many parts of India we eat leaf vegetable, which in different languages in it's called gongura, it's called ambadi. So you can go and look up this leaf and this plant also produces pectin. So pectin is a very fascinating polysaccharide and here I am showing you the sequence that is involved in pectin. And what you can see is, it's a rich building block using several components, it has been assembled together, where we have hydrophobic and hydrophilic parts, we have branching, we have poly electrolyte, because there are carboxylic acid groups and there is possibility of calcium cross linking using these carboxylic groups.

So, you can see that there are galactose groups, there is galacturonic acid, there are methyl or acetyl groups which are more hydrophobic and lot of combinations of several things using which this pectin molecule has been assembled. And you might wonder, why is such complex arrangement needed? And again the answer is in terms of function. In fact, the ripening of the fruit we know for example, that the skin will go from a very hard skin to a soft skin. And in fact, pectin plays a very important role in such softening. The way the pectin backbone and the branches are arranged, and how whether it's the carboxylic acid groups or methylated or acetylated groups, this distribution pretty much determines whether pectin will give you a soft gel like behavior or rigid film like behavior. And so, when we go from hard skin to a soft skin actually the enzymes in the fruits are playing a role of changing its side groups from carboxylic acid to methylated side group, and that changes the interaction. We go from a hydrophilic interaction between different carboxylic acid group to hydrophobic interaction, and that therefore changes just the structure of a pectin system. So therefore, pectin is a very important component of the cell wall. And what's interesting is, it has a hierarchical structure, there is macromolecular level information in terms of sequence, in terms of branching, in terms of different groups being present, and how they assemble with this calcium cross linking and more importantly, how they combine with hemi-cellulose and cellulose. And later on in this course, we will have a chance of looking at composites as a material and composites that we used from aerospace to sporting goods, just looking at cell wall as a natural engineered composite material, which has possibility of manipulating its own properties, depending on the requirement. It's an excellent example to take inspiration from.

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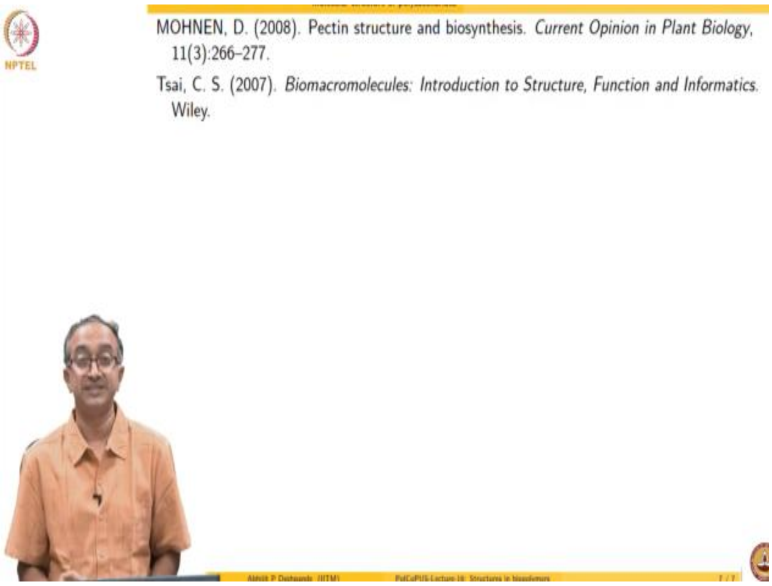

So with this, we will close this lecture and we will continue our look at structure **of** macromolecular systems in the next few set of lectures.

Thank you.