Simple Concepts Related to Single Macromolecules
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology - Madras

Lecture - 10
States of Interest

Welcome again, we continue our journey to understand the concepts related to polymers. In this case, we are in the week 2, where we will be focusing on single macromolecules. And in this lecture which is related to concepts, let us just focus on what are the states of interest in which single macro molecular behavior will be important and what is the nature of that single macro molecule behavior that we need to keep in mind.

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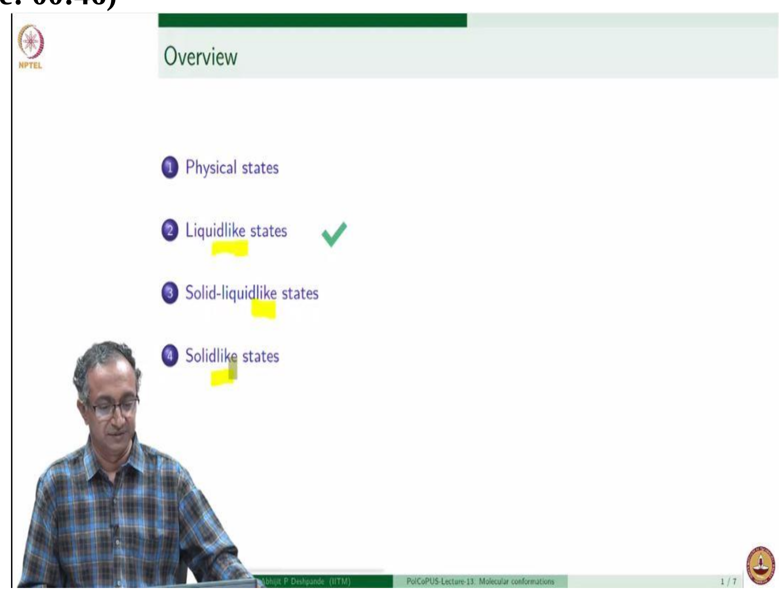

And we will do this by just quickly listing what are the physical states of interest, when we think of polymeric system. And, then we will look at liquid like states and this is an important distinction which cannot be overemphasized in the context of polymers. We can have liquid states, but which will have certain characteristics of solid materials. And these characteristics are in terms of several features, there could be micro-structural features or behavioral features.

So, for example, order - molecular order, whenever we say that we think of solid like crystalline materials, so, therefore, that is a micro-structural aspect. Sometimes we think in terms of property like elasticity, so, that is a behavioral feature. So, we could have solid like feature in a liquid like material. And that is why in all of these, we will use this phrase "like" to remind ourselves that nothing is 100% one way or the other. And, this is challenge associated with understanding of polymers.

And so, the polymeric materials which are made up of single covalent bond to begin with, with segments, branches and macromolecules and to the bulk have multiplicity of timescales and then scales of response. And, due to this both liquid like and solid like mechanisms are always present in case of polymers. So, therefore, we will look at these 3 broad class of examples of material system and try to see where is single macro molecular behavior important and relevant.

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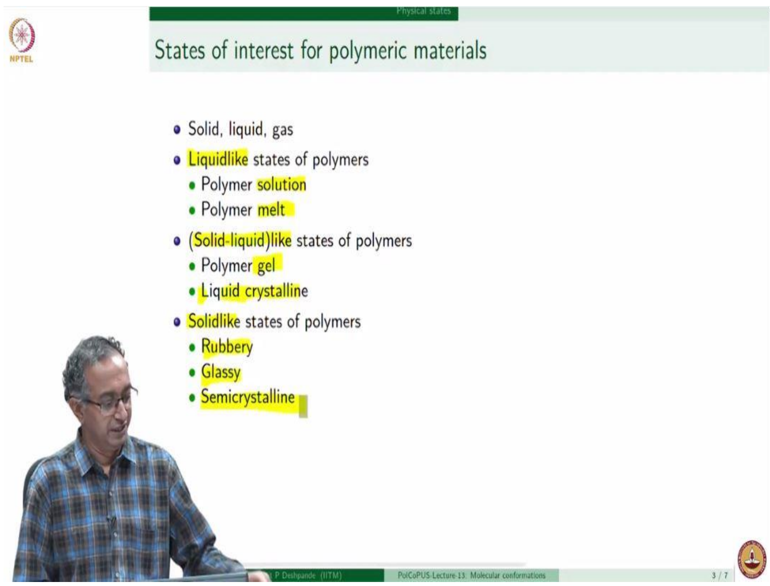

So, generally when we think in terms of states of interest, since middle school or maybe even earlier we have been taught to think in terms of solid, liquid, gas. And in when we look at polymers, the states of interest that we will focus on in this course, will be a few states which are liquidlike and those are solutions and melts of polymers. And remember that some of these may be related to fabrication and processing of polymeric materials, but some of them could be related to direct application.

Can you think of direct application in which case a polymer solution is used? Polymer melt - I am sure you can see that, you know, it is only related to fabrication and processing. Is polymer solution also only related to processing? Think about it because in one of the earlier lecture, we have already talked about polymer solution as an application. So, just think and carefully try to answer that question. Now, the solid, liquid like states of polymers will be gel or liquid crystalline so there is liquid, but there is crystalline order.

And then, of course, solid like states of polymers. When we think of plastics and rubbers, this is the case, which is most important. And we think generally in terms of their application as solid materials. So we can have a rubbery, glassy or semi-crystalline states. So let us look at some of the examples of this and what are the key features that might be of interest to us when we think of a single macro molecular behavior.

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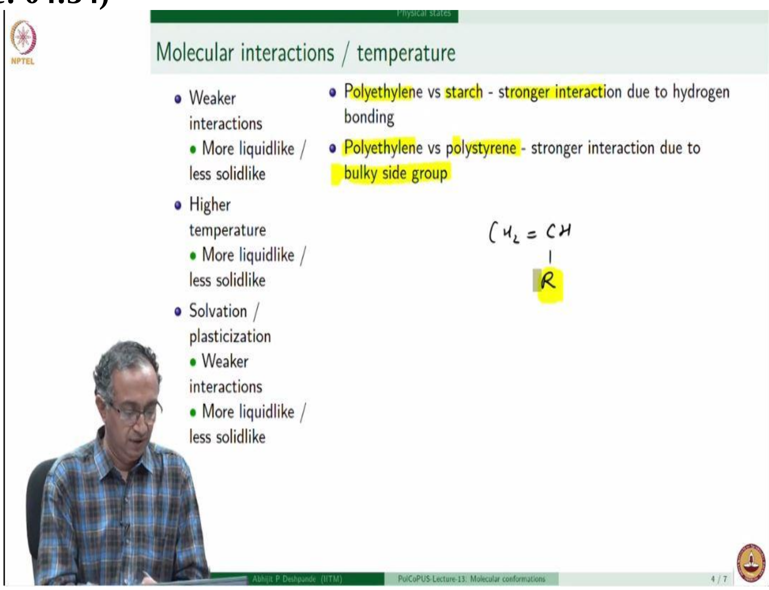

So, when we think in terms of why these states are behaving the way they are, one important thing is to remember what is the underlying mechanism and underlying set of interactions which are present which lead to a more liquid like or a more solid like response? So in this slide, I am trying to give you 3 possibilities. So, we could have interactions which are different. And if we have stronger interactions, then we have more solid like. Or, the way it is mentioned on the slide, If we have weaker interactions, then we have more liquid like response.

So, when we go from a liquid to solid, this is what happens in a liquid state the interactions are weaker molecules can randomly go about. In solid, the molecules interact with each other more strongly and they are frozen in a single position, which is of minimum energy configuration. So therefore, liquid to solid is again a transition which can be thought of as a transition in terms of interactions. Of course, the interactions are always related to what is the thermal energy present for molecules to change their states.

And in case of solid, the molecule becomes frozen in its position but thermal energy still sufficiently available for doing just vibration. While, in the liquid state, the molecules can just go around. Thermal energy is sufficient. So, by changing temperature again we can go from one or the other state. And the ability of other molecules to influence the interaction is also there. So, a solvent if it is present or a plasticizer molecule, which is very important in case of polymer applications, if these are present, then what they do is they reduce the interactions.

And therefore, they will lead to more liquid like and solid like response. So, therefore, whether we have more liquid like or more solid like response depends on these conditions. And just to give you example, we can see how each of these influences. So, let us look at interactions. So, if you look at polyethylene and starch what is the difference between these 2 in terms of interactions, and this we have already alluded to when I when we talked about polyethylene and natural fiber like jute fiber, We already talked about how these 2 are different.

So same thing here also, that in case of starch, there is stronger interaction, and therefore, starch has a far more solid character. In fact, that is the challenge of getting starch films in place of a polyethylene grocery bag, because starch film will be very brittle due to these strong interactions. And so it is much more solid like response while for a grocery bag we need a flexible, little more liquid like response. Polyethylene versus polystyrene, again, both of these are examples of vinyl polymers. This is the monomer. R can be different for propylene, styrene, PVC.

So many of these are examples of these family of polymers. So why is it one of them is more solidlike than the other? So, polystyrene is a solid like material and we will see that it is remains in glassy state at room temperature. In fact its glass transition temperature is around 75-80 degrees Celsius. On the other hand, polyethylene is negative 80 degrees Celsius. So, why is that the case why is polyethylene at room temperature more liquid like compared to polystyrene and the answer lies again, stronger interaction due to in this case, bulky side group.

So, if this R is of different size, then interactions will be different the way macromolecule single macromolecules can change conformation the way it interacts with other macromolecules will be very different. And so, single macromolecular behavior will influence the overall properties of the material on a bulk scale.

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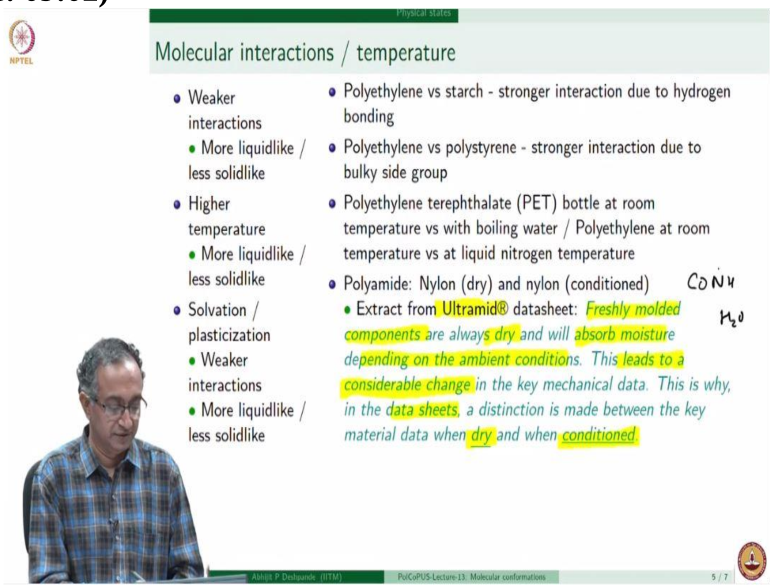

Let us continue and look at temperature. So, PET bottle which is used for soft drinks at room temperature versus if we add something which is boiling very hot - sambar or very hot dall is added, we know that the PET bottle will deform and it will no longer be able to retain the shape that it has. And that is associated again with the solidlike response at room temperature but at 90 degrees Celsius it becomes more liquidlike and it starts deforming very easily.

And in fact, if you search on net, you will see a lot of examples of subjecting some materials which are flexible to liquid nitrogen condition and they shattering. So, giving more solid like brittle response as opposed to flexible response so, leaves petals, polyethylene many of these you will see there will be videos where you dip it in liquid nitrogen and throw it and it will shatter like glass. And so that is again where thermal energy is being manipulated to lead to more solidlike response. At liquid nitrogen temperatures the thermal energy available is much less for bond rotation or any of the conformational changes that make macromolecules flexible.

And plasticization example is very important for nylon, because nylon has polyamide and polyamide has this -CONH as part of the repeating unit and this can interact strongly with water.

And so, nylon can absorb significant amount of solvent which in this case, which is water and the presence of water can influence nylon properties a lot. And just to highlight how practical this is, I have taken this statement from a commercially available polymer.

So, you could in fact, go and dig further and look at what does a commercial nylon literature look like. So, for example, the the datasheet highlights that freshly molded components are always dry and once processed, and of course, they are shipped and used, they eventually will absorb moisture and more importantly, the amount of moisture will depend on what is the weather condition.

So, in a very dry weather like in Rajasthan, the amount of moisture which is absorbed will be very different compared to a very humid weather, let us say in Cochin. So, therefore, you you will have the same nylon part will have different amount of moisture in the 2 cases. You can see this is a challenge in terms of designing a performance of a product. So, the different amount of water will lead to considerable change in the mechanical data. And so, range of mechanical properties are possible.

So data sheets will always give you properties which are under dry condition, just to give you an idea that what happens when all the moisture is removed to some conditioning. Because, it is difficult to give you data for all different types of weathers, what companies will do is they will say that look, we are conditioned it at 25 degrees Celsius in 65% relative humidity and so you know, what is the amount of water present. And based on that, then you can try getting your design process through.

So, one of the key things that you think at this point is why is water playing such an important role in terms of determining mechanical properties? Because it is the macromolecule with its large length which is responsible. Then what is water doing? And water as you know, will interact through hydrogen bonding with the -CONH. So what makes water change the behavior of a single macromolecule? So why does a single macromolecule become flexible, and why can it change its conformation more easily when water is present?

So you can see that while describing the bulk behavior of polymeric materials, we are taking recourse to phenomena which are happening at a single macromolecular level. And so that is why in this lecture I am trying to highlight how the behavior of a single macromolecule in different states is very important in terms of describing the bulk behavior.

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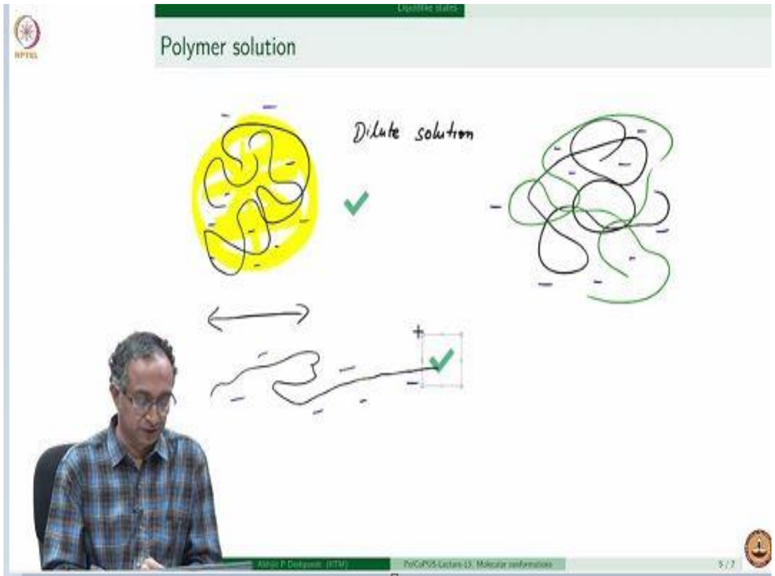

And so let us look at some of the examples of these states by quickly going through and getting a picture of what a single macromolecule may look like in many of these cases. So when we think of a polymer solution, we have basically a macromolecule and which is surrounded by solvent. And so, this is a picture of a dilute solution, because I have not drawn any other polymer. If we have concentrated solution, then we will have macromolecule and I hope all of you are now familiar with this drawing of polymers where I have not drawing any group, but just depicting the macromolecule using just a set of curves.

So, in this case, when we have concentrated polymer again we will have polymers interacting with each other as well as solvent and polymer interacting with each other. So, in this case, what you can see is, here for example, there is a rough size approximate size of this polymer. And, this size is determined based on what kind of conformational changes a single macromolecule can take.

Just look up polyether ether ketone, and see how along the backbone there are bulky groups. And so, such polymers then cannot exist in such a coil like states, but what will happen is they will in general occupy more extended states or rod like states. So, depending on the macromolecular details, a single macromolecule can change its conformation as in case of a coil or it may be a little more in terms of extended state and therefore less changes in terms of conformation.

And so, you can see that single macromolecular conformations will be very important in terms of determining the overall shape of the molecule and how much its size. And therefore, this is important in describing polymer solution response.

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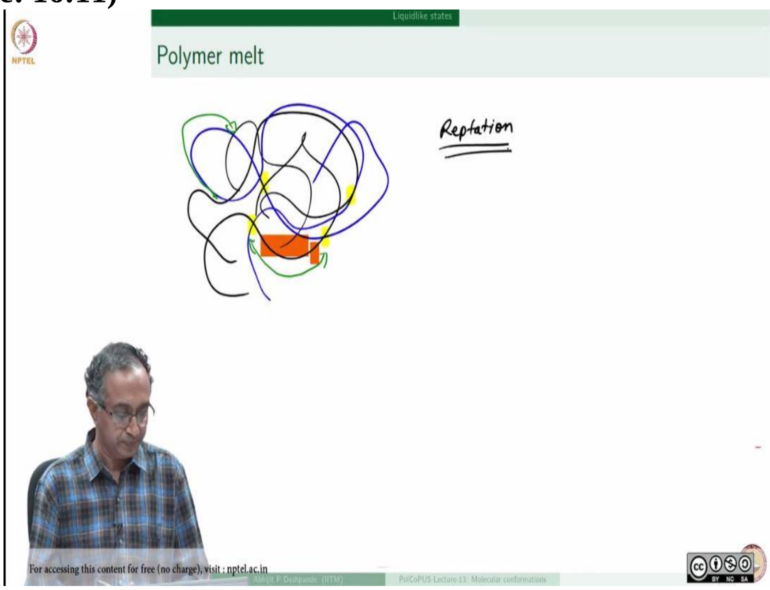

So, let us look at another liquid like state, which is polymer melt, in which case we have macromolecules which are entangled with each other. And in this case, there is no solvent. And what we can see in this case is a macromolecule which, since the entanglements are present everywhere, the physical interactions between polymers lead to these entanglements and so what will be crucial is, so, this is the segment, let me just draw it and show it more clearly.

So, this is the length of segment. We can also see another segment here, where this is one entanglement point, this is another entanglement point and these are segments again. So, in the molten state macromolecules are entangled with each other, and they may have limited way of moving. And that is why we have a model called reptation, which describes how a macromolecule moves in an entangled polymer melt system.

But the segments between the 2 entanglement points can change conformations. So, again, a single macromolecular behavior at the level of segments can determine a lot of behavior of the polymer melt.

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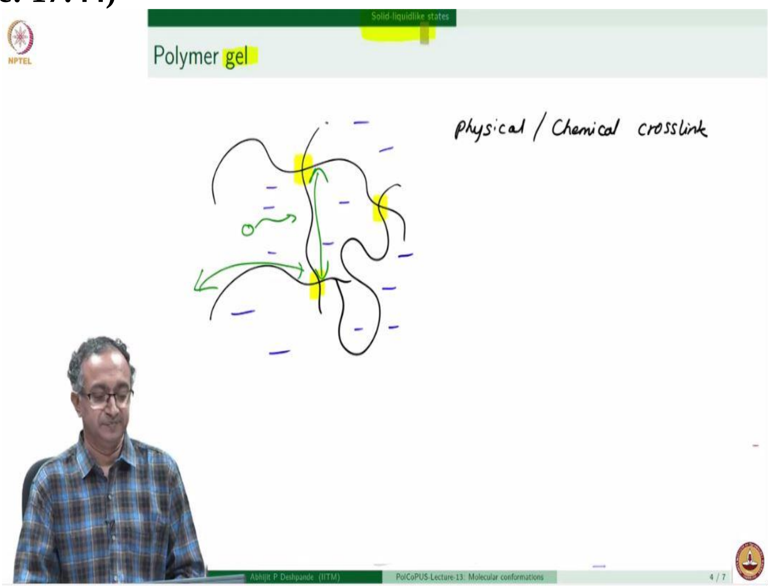

Let us move on to solid-liquid like systems. Here, we are highlighting them as solid-liquid like because there seems to be behavior which is describing both these properties. So if you look at the gel as a material, generally it is a solid like system. So when we take a jam or jelly in to eat on a slice of bread, it sits like a solid. We can cut it, we can scoop it all using a spoon, but once we start spreading it, it also is a fairly soft solid. It spreads like a liquid almost. And if you look at the molecular level picture, again there are several liquid like features.

So, polymer gel generally is a set of polymers, which are cross linked together through physical or chemical cross links. So, there are what are called physical or chemical cross links. We have already seen sulfur vulcanization is an example of chemical cross link. So, physical cross link also possible through various intermolecular interactions. And this you will say is very similar to a polymer solution.

So, what is the difference between a polymer solution and a polymer gel? It is the strength of interaction at these points, if strength is higher than we get a gel like response, because then this becomes like a cross link. While in case of polymer solution, which is concentrated, there will only be some amount of entanglement and the strength of the interaction will not be so high for us to call it a cross link. Of course, what makes it a soft material is the presence of large amount of solvent in the cross link network.

Again, a feature which looks very much like a polymer solution, but because of the cross links, there is ability of materials to give solid like response. So, here now, the behavior of a segment again between crosslink point is what is important and due to this, the features at molecular scale are very liquid like. The coils, the segments can change the information very much like liquid, the solvent can move around pretty much like liquid. If I have sugar or salt, small molecules which are added they can also diffuse around very easily.

So, if I add some small molecule it can diffuse through this network. So lot of lot of liquid like features. But if you look at because of the crosslinks, here, the crosslinks lead to give it a solid. So therefore, this is an example of a solid-liquid like state.

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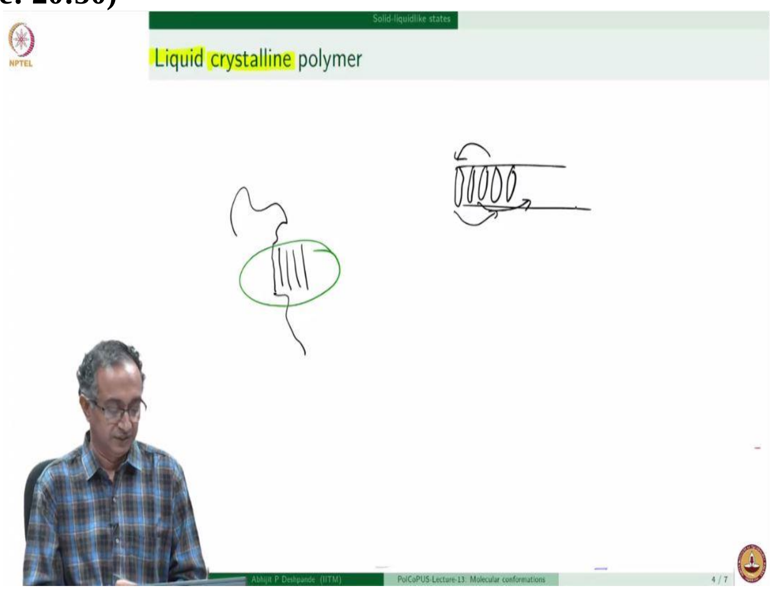

Another example of a solid liquid like state is liquid crystalline polymer. So it is liquid or molten state but at the same time there is a crystalline order. And you can think of what kind of polymers will lead to liquid crystalline behavior. Because I have already talked about in 2 lectures that there is something associated with polymer backbone and the groups which are on it. If there is just C-C bond, then bond rotation is possible and it is a flexible chain, but if I have bulky groups like benzyl groups, then we have a rigid rod like chain.

So, can you think of what will be a macro molecule which will give us liquid - which means flexibility, crystalline - which means order? So, both of these in a single macro molecule is it achievable? So, I want you to think about this. In this case, you can see that if I am drawing macromolecule there may be flexibility and then there may be rigidity how is this possible? So, we will see that if you have flexible and rigid segments in a polymer you can achieve liquid crystalline order.

Where some parts of the chain can come together in order 1 key difference between a solid crystalline state and liquid crystalline state is the fact that the region which I have drawn with crystalline order there is some amount of diffusion of molecules. This is easier to explain using small liquid crystal. So, for example, if we have some rod like molecules and they align with each other to form this order, when I say there is diffusion possible these can exchange places. And so, there is diffusion possible.

But if you look at the overall plate in which all these are ordered that ordering and orientation all remains crystalline. So, therefore, liquid crystalline is a mixture of movement of molecules like in the liquid state, but an order which is a solid state feature.

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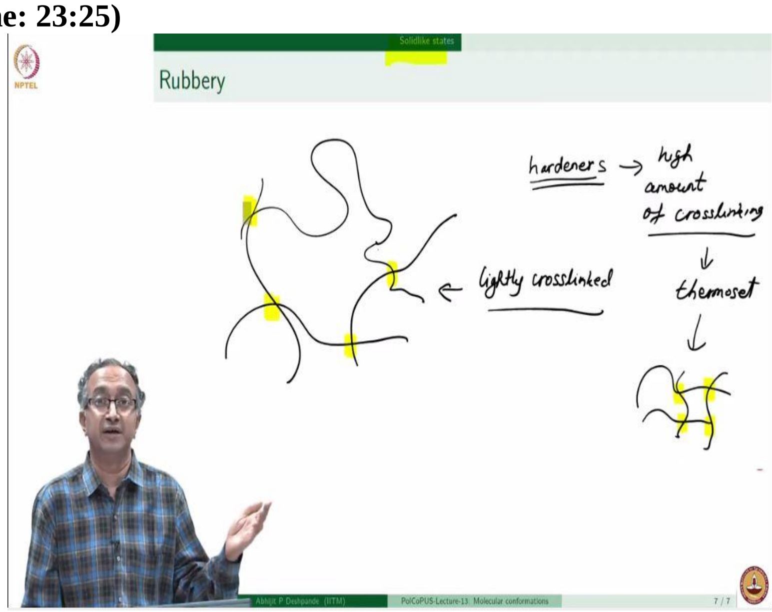

Now, let us look at from the performance point of view the important states which are solid like states. And the first solid like state example, we will look at is rubber. And when I draw rubber, which I have drawn several times, we again have basically a set of segments which are cross linked. And cross link point in case of natural rubber we saw sulfur. So, in case of epoxy or polyester we will have multifunctional what are called hardeners so, which are used as cross linking agent.

So, you can go and search for in the context of epoxy which is a very important adhesive which is used and what is a hardener. So, hardener is the one which will provide these cross links and therefore, it will make the material solid. The difference between epoxy and hardener and rubber is the fact that rubber is lightly crosslinked material. While hardener will lead to a very high amount of crosslinking. And therefore, these materials we call them thermoset.

So, when I draw thermoset and crosslink polymer some of the feature may look similar. So, in case of a thermoset if I draw the crosslink density will be very high. So, the segment length between cross link point will be very short, very small segments. And therefore, its behavior is much more solidlike compared to rubber like. In case of rubbery materials, the conformation between these crosslink points can be changed.

So, a segment is free to move and therefore, the rubber like materials or flexible rubber band, or they can be used as vibration mounts as we saw an example related to polyisoprene where segments moving can allow dissipation of energy. And again, it is a behavior of a single macro molecular segment, which is useful in terms of describing the bulk response.

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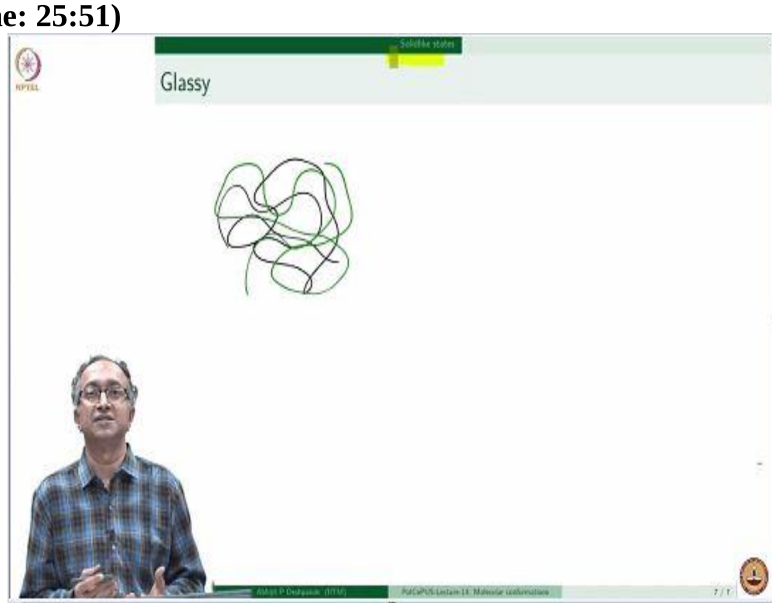

When we think of a glassy state, here we have again the same coil like states of macromolecule which are frozen and there is no macromolecular segmental flexibility. So between rubber and glass, in terms of ordering and in terms of macromolecular shapes, it looks pretty much coil like and random. But in terms of ability of a C-C bond to rotate or any other macromolecular confirmation to change in glassy state, it is not possible. In rubbery state, it is possible and therefore, glassy state is where solid like response will be more dominant.

However, this is again to highlight the fact that it is only solid like given the random arrangements and given that we will see glassy state being a non equilibrium state where some amount of moleculer rearrangement will happen over time. And therefore, some of the features in the glassy state will also have liquid like response. So, liquid like response, which generally implies energy dissipation is also possible in case of glassy polymers.

So, that is why when we talk in terms of these liquid and solid like features, we will talk in terms of molecular arrangements, which is like whether ordering is there, whether it is random whether it is coiled, like whether it is changing conformations. So, that is at the structural feature, we talk in terms of behavior, whether it is can withstand stresses, whether it is appearing to be rigid, whether it is allowing a small molecule to diffuse through, so this is related to behavioral pattern. And also we can describe the overall phenomena using energy arguments. That is energy being stored or energy being dissipated. And in case of a glassy state energy can be stored because macromolecules can move apart from each other and store energy. So, therefore, elasticity is also possible. But at the same time viscous behavior is also possible because given some amount of time some of these macromolecules will start rearranging themselves and dissipate energy.

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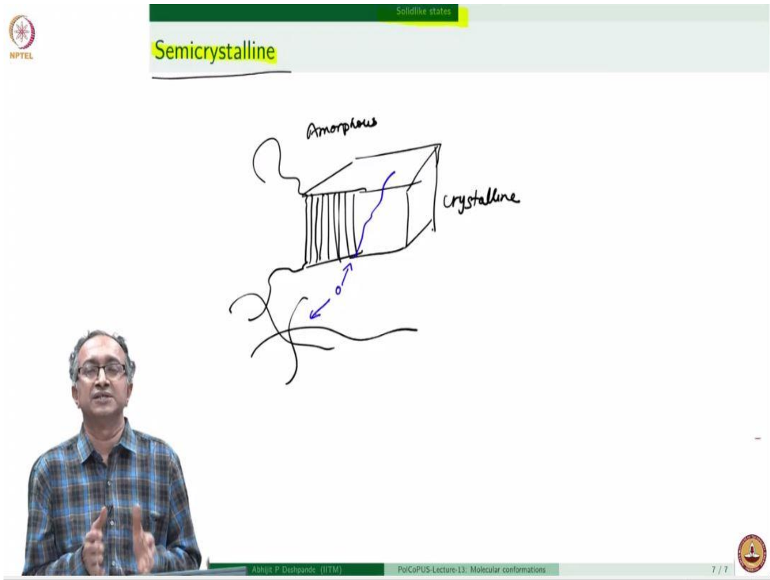

On the other hand a crystalline segment, dissipation modes are not present, because a crystalline material will have very definite order and in this definite order all the segments are perfectly aligned with each other. So, the so that we can think of a unit cell and the same unit cell repeating everywhere and these are frozen. So, only vibration of molecules around mean positions is possible, while the amorphous state can have again more flexibility in terms of some molecular rearrangement.

Polymers are challenging because they are always semi-crystalline, in the sense that amorphous part will always exist together with the crystalline part. And so, this is an example where polypropylene and PET and so many polymers are examples of important semicrystalline materials, which are very important class of solid like states from engineering materials point of view.

And if you think in terms of behavior here if a small molecule is diffusing and you can see a small molecule diffusing depending on the interaction that the small molecule has and the size it has, it may find very difficult to diffuse through this crystalline domain. But on the other hand, the amorphous domain it may find easy to diffuse. So, the solvent resistance or barrier properties may change a lot depending on whether a crystalline order is there or amorphous state is there.

So, again how a single macromolecule is organized and how single macromolecule can change its conformation determines the bulk behavior of the materials. So, with this we have given a broad overview of why single macromolecule behavior is important in terms of considering physics of polymeric systems as well as the response of polymeric systems. So, in the next few lectures, we will focus on the single macromolecular behavior. Thank you.