Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts
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Lecture 02
A Brief Introduction to Polymers (Contd.)

Welcome to second lecture my students. So, the title of this course as you know the Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts. In the first class, I gave a very brief interaction about the polymers and you realize that how important and the field of polymerase and how the exciting development happened in the field of the polymers.

In this class, which is basically the continuation of the first class is we will discuss about the basic properties of the polymers and how different it is from the monomeric or the small molecules, so let us try to understand.

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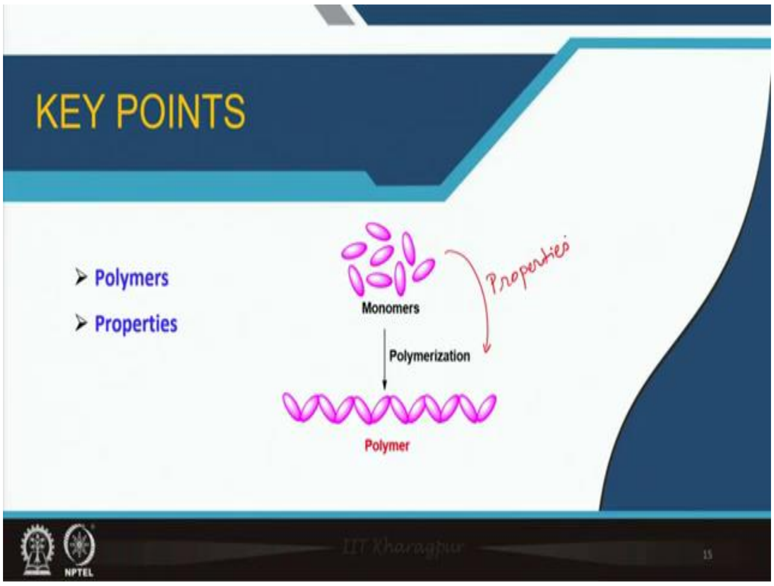

So, what we will do? we will, the concepts we will cover the polymer, the unique properties of the polymers as I already told, and we will try to understand that how different it is from the monomers as you see that these are, you can assume this is a monomer that is a small molecules and these are the polymer that is a big macro molecules, and the properties we will try to understand how different can be. So, let us see how, what are the basic difference in properties.

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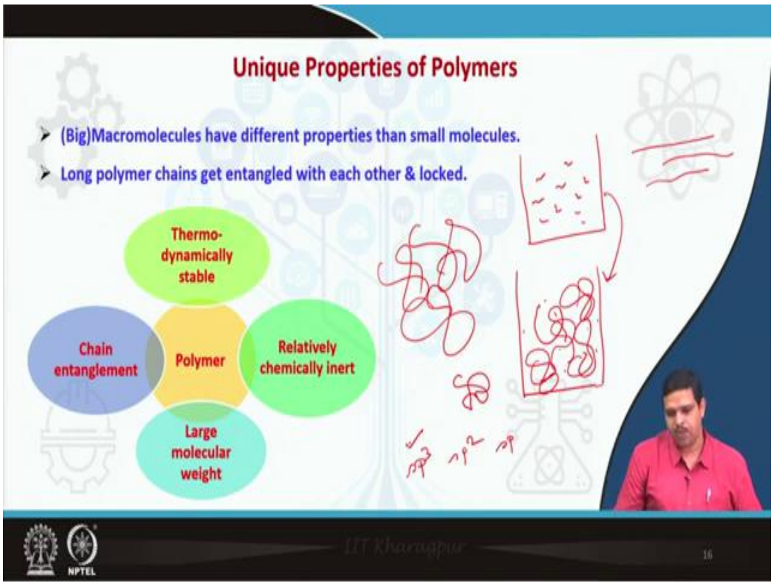

So, this is a large view of the unique properties of the polymers, so you will see, this is very obvious that what can be the difference in the basic properties because as you see from the application perspective, like if you look around your classroom, you will see that the tables, chairs, the foams are just made of polymers. Your pen made of polymers, your toothbrush the first material or item we use in the morning is the toothbrush made of polymers.

So, obviously, very obvious as that these are very stable that is why you are using for the daily life and household applications, so these are should be kinetically stable, chemically stable, thermally stable, thermodynamically stable, and obviously this depending on the applications, the properties whether it is hard, whether it is flexible, whether it is soft, is that is very obvious.

If we use like a rubbery material, you will see these are soft, if you think is a household materials like chairs, tables are hard, so what, how we engineer the polymers and what are the basic, what is the relation between the application and the properties of the polymer, that we will try to understand.

So, you see that the small molecules, you see these are kind of a free, you can tell like these are like a small molecules, if you keep in a beaker, let us say in a this is a in a beaker, and this in a solvent let us say, so this is a small molecules it remains like this one. Now, same thing if you do, like in this is in your any, the beaker and your polymer, let us say is your this is your polymer and this polymer will remain like this one, so this is like that, and there will be solvent if it is soluble.

Now, you see that the polymers is actually remains as a coil like or the best composition will be like a snake, the snake how does it stay, it just stay like that one, like that. So, similarly, the polymer stays in solution like this one, so in the entangled, this is the basic properties, this is the basic phenomena in the polymer in solution and that actually one of the reason how the solution behaviour is different from the small molecule to polymer. So, that we will try to understand how different it is. So, most of the polymers remains as a coil like polymers like this one.

Some of the polymers which are rigid polymers as example, like polyacetylene type of metal of polyline those actually remains as a kind of a rod like polymers, like that one, but that is not very common, so most of the polymers remain as a coil like polymers where you have a SP 3 hybridized, if you are, if you have, if you just refresh your memory that SP 3, SP 2, SP hybridized carbon or nitrogen centers, SP 3 if you have a carbon that is more flexible as example like polyethylene, but if you take the polyacetylene where in the polymer you have a double bond, so that means that carbon center is SP 2, that means more rigid in nature.

So, if you have a acetylene that will be more rigid in nature, so then that polymer cannot, polymer chain cannot fold, so you, that polymer will remain as a coil. So, that is the basic difference in nature of the small molecule for to the big molecules, macro molecules or polymers.

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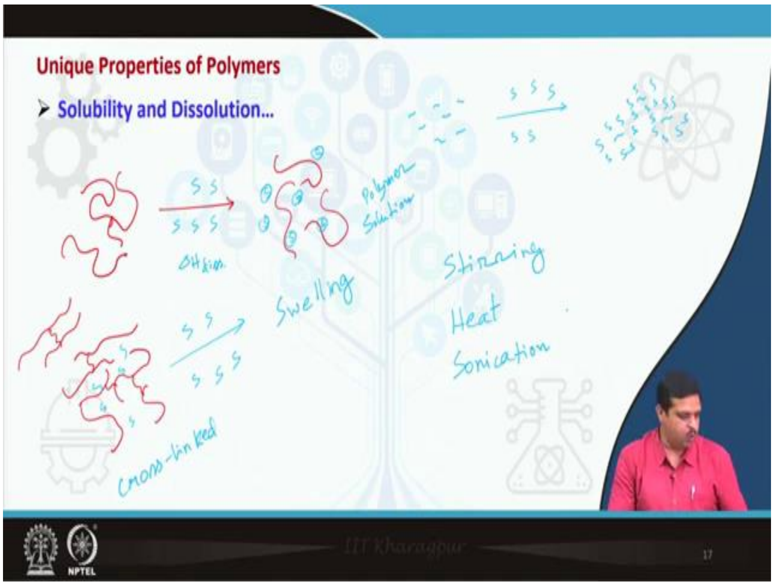

So, let us see how we get the different observation when we try to make the solution of the polymers. As I told, that polymer is remains as like this one, like that one, so this is a separate polymer chain. Now, if you try to solubilize it, let us say I am adding some solvent, let us say I am adding some solvent, so this is my, the blue one is the solvent molecules I am just writing SSS, so now what will happen these solvent molecules will penetrate in the environment of the entangle entangles polymers.

So, what will happen if the penetration is good enough, then solvent molecules will be here like that and this process that is the you can say delta h solution is much higher than the small molecules. That means you need to have a extra effort to solubilize the polymeric materials compared to the small molecules materials.

Because you see from here if you have a small molecules as example like, you will see that this is your small molecules like that and you have a solvent, then you will see that is there is no problem in solver is in solubilizing or the solvation what we will tell like the small molecule, so it is very easy to make, to make it soluble. But in polymer, the scenario was very different due to the entanglement of the polymeric chain.

And this is more difficult when the polymer has like a cross linking materials, you will see that cross-linking means that each of the polymer again is threaded with covalently by another reagent or another backbone. So, if you see this is the pure polymer chain and if you thread it by chemically by covalent bond that then it is cross linked polymer.

So, this is again, it is more difficult to solubilize, because if you put solvent now, then, now if you put your solvent molecules, let us say THF or dichloromethane, tetrahydoviron, dichromethane chloroform, then what will happen you see that this will be more difficult to enter in the polymer vicinity, because it is very tightly packed due to the cross linking.

And that is why, you will see when there is a free chain then it is the, you can make the polymer solution. But in the case of the cross link polymers you really cannot make the solution, it only undergoes the swelling, Anyway, but this has its own advantage and disadvantage as example like cross linked polymeric materials give the gels very easily, so it has a its own applications. This I just want to emphasize the basic properties of the polymeric materials.

So, just take-home message is that making solution of a polymer, sometimes you have to have some extra effort, it is not like the small molecules. So, as you see why this from, this easy pictorial diagram it is, I am sure it is now very obvious to you why it is difficult to make the polymeric solution. So, sometimes also you need to do have a starting, sometimes you need to warm it or heat it little bit, sometimes you have to do sonication because that solvent molecule needs to penetrate in the entanglement environment of the polymer. However, this kind of problem is not there for the small molecules.

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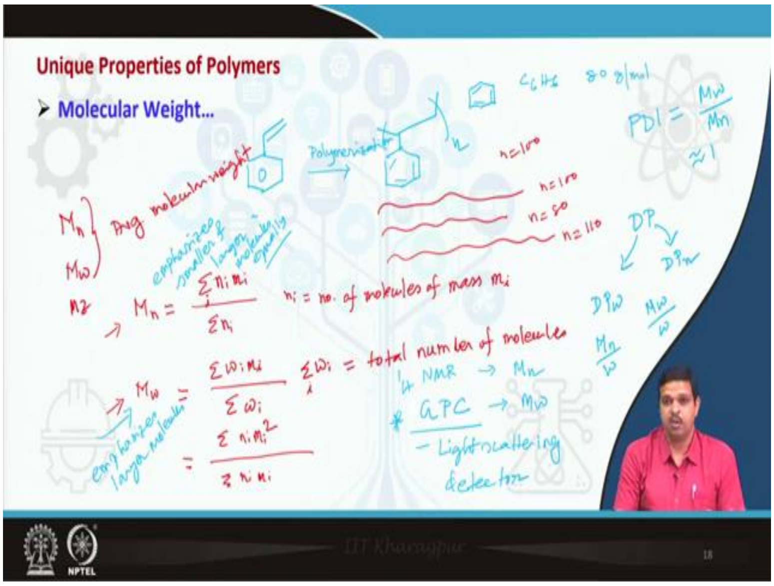

So, not only the solubility, you will see that molecular weight, there is a very interesting in the molecular rate of the polymers, you just take a Benzene molecule, the small molecules just like a Benzene, I know I am sure all of you know that what is the Benzene, so this is the Benzene, this is C6 H6.

So, now you see that not considering the isotopic distribution, the what is the molecular rate or molar mass of the Benzene, it is basically 80 gram per mole. So, what about the way you prepare the Benzene, you will guess that always the molar mass of the Benzene is 80 gram per mole, so that is the unique like a constant. But the polymer, chemistry is different. Suppose, you are making the polystyrene, I will discuss later, the polymeration protocol, just let us think that assume that I am making the polymer by like this by radical polymeration or anionic polymeration, no need to worry about the what polymeration I am considering.

So, this is my styrene, polystyrene polymer. So, you will see that when I am making the polymer like a small molecules, now I am making a macromolecules like this part. Now, there is no zero T that all the polymer chain will be the same length, it entirely depends on the mechanism on the polymerization protocol what we are using and also depend on the condition even though you are following a very well defined polymeration protocol, it also depends to hand to hand, depends on the reaction condition, depend temperature many on many aspects.

So, suppose I am targeting the n, let us say is like a n 100, but when you do the polymer, polymerations, in the polymer you may get some polymer chain with n 100, some will get n

80, you may get some n 110 like that. That means I am telling that you will get a distribution of the chain length.

Now, if you see the distribution of the chain length then you will not have a defined molar mass or molecular weight as you see for the small molecules. So, that is the another difference, and due to this difference there is the polymeric, the properties of the polymers of the same skeleton also differs. So, that is why the new convention in the polymer molecular weight have been defined and you will see the multiple molecular rates are described to define the molecular rate of the polymer.

I am sure some of you have taken the basic polymer codes and you have understood, here I am just trying to keep the feeling about the different molecular weight of the polymers, particularly for the students who have not taken in the polymer course. So, here you will see generally the three kinds of molecular rate in the polymers are quite popular to define the polymeric chain length, one is the Mn, one is the Mw and one is the Mz, and among these, the two are very popular. So, for our future discussion, if you have an idea about the Mn and Mw, that will be good enough.

So, here all these molecular weight Mn Mw and Mz is actually the average molecular weight. This average molecular weight concept is not required for the small molecules, because as I told is a very specific the molecular weight for the small molecules. So, what is the Mn? Mn is basically the, this is, so Mi here, so summation ni mi by summation ni. So, what is the a ni, ni is the number of molecules number of molecules or number of the polymer chain links of mass mi, so that is the mn, that is called number average molecular weight, the number here n denotes the number, average molecular weight.

And, what is the Mw? Mw is the wi and wi summation mi summation, so you can just convert it to the ni mi, so this is my ni mi and this is my ni mi square. So, what is the wi? is the total number of molecules. So, you see that there is two molecular weight, generally, we use for polymer to define the polymer chain length one is the Mn and one is the Mw and this Mn and Mw, this actually emphasizes smaller and larger molecules equally and Mw is actually, emphasizes larger molecules.

So, generally Mn and Mw, the Mn molecular weight is actually emphasizes the smaller and larger molecules equally, but the Mw emphasizes, the larger molecules only. So, this, many properties can be explained accurately by considering the Mw or Mn. So, now how we will know that what is the Mw and what is the Mn or the molecular weight. So, routinely we use the GPC, as you know I will not discuss much about the GPC because this is not the basic polymer course, this we know that GPC that is the gel permission chromatography or size exclusion chromatography, from this techniques this we routinely use in our laboratory and also in our industry to get the Mw.

And we also use the, and you will get the more accurate molecule rate if your GPC is equipped with Tetra, light scattering detector, so this is the most modern technology of the GPC, that is the light scattering detector, equipped with light scattering data you will get the absolute molecular weight of the polymer. And we also use routinely like NMR, proton NMR which actually give your Mn, that is the number average molecular weight and also other techniques we use these are the routinely used and out of these, this is the mostly used technique to understand the Mw and Mn.

Some other terms in the polymer, I am sure you know that is the PDI. So, PDI is nothing but Mw by Mn. So, if your polymeration is well defined that means the number of polymer chain links are same for a particular molecular weight, then you will get the PDI of almost 1. So, that means what I am telling, suppose you are targeting n 100, and if you get your polymer chain length where n is equal to 100 or near by 100 like 95 or 105, then you will get the PDI is much more closer to 1, less than 1 is not possible it is the best PDI may be 1.01, 1.04, sometimes 1.22, so this is the called poly dispersity index.

But do not be confused with the PDI value, this PDI, it does not mean that that PDI, the polymer with PDI of one is always good it depends on the practical utility. Sometimes, we make the PDI purposefully 2, which the properties I need to like make it flexible, like for your polyethylene. If I use, let us say for packaging materials, soft materials, I will use the flexible material that means the PDI will be much more 1.

If the PDI is nearby 1, then the polyethylene will be more rigid due to the high crystallinity, more brittle. So, it depends on the applications what kind of polymer we need, but yes if PDI is close to 1 that means your polymeration method is more well defined, more control, fine. And also, another term you are familiar that is the degree of polymeration, that is basically this n, how you can, so again this DP may be two types, one is the DPw, weight average degree of polymeration, and this is the number average degree of polymeration.

And, how we will calculate is Mn by w, Mn is the number average molecule to the polymer and the denominator is w, that is the molecular weight of the repeating unit. And for DPw, what you will calculate the Mw by w, that is the weight average molecular weight by the molecular weight of the repeating unit. So, we can calculate, you can get the idea of the degree of polymeration, that is the n value once you have the molecular rate, two types of molecular weight of the polymers, fine. So, I am sure you have now a good idea about the molecular rate of the polymers which are little different than the number average, and then the small molecules.

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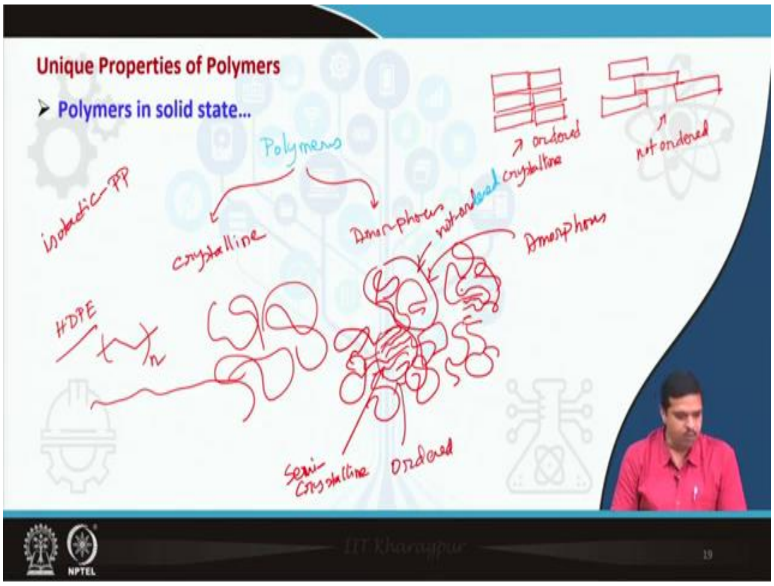

So, this, so far, we have understood that how the polymers behave in a solution, the solubility and also we have understood that how different the molecular weight of the polymers compared to the small molecules. Now, we try to understand that how, what is the difference and what is the special behavior of the polymers in the solid state. So, let us try to understand.

In polymers, the materials, these polymers may be as I already mentioned that small molecules we know the concept of the crystallization. We tell routinely, if you make in your laboratory, you suppose synthesize the small molecules organic or organometallic and inorganic, we tell that we have purified by registration. I am sure you have done it in your project or laboratory, you have recrystallized your product and to get the more pure product.

Obviously, there are other methods of purification like chromatography, distillation, sublimations, that is but recrystallization also another method. So, this is very hard so to believe that the polymer also may be crystalline. So, we will discuss how this crystallinity is possible in the polymer, some of the polymer.

Why I am discussing this because this will be very important to understand the nature of the polyolefin and how this polyolefin synthesis I can protocol, polymeration protocol ions I will select depending on the properties and depending on the application. Suppose, if I need crystalline polyethylene, what method I will choose? and what characterization techniques I will confirm? I choose to confirm that, yes, this is crystalline polymer.

So, that is a that is why a good knowledge is required to understand the polymer behaviour and the strategy of the polymers, let us try to see. As I told that polymer may be amorphous which is very common, and as I told in some polymers, in special cases that may be crystalline. So, all we know that what is the crystalline materials? crystalline materials comes from the orderness of the molecules or atoms or species, whatever.

So, like I am sure you have studied in your courses about the crystallinity and the origin of the crystallinity. I will give a very famous and very well-known pictorial diagram. So, let us assume like that this is your, a molecules, so if your is crystalline, then how does it undergoes the arrangement in the solid state? like that, so it is like a ordered structure. I am sure you have seen how the wall is constructed, so it is putting one brick to another brick in a well ordered manner.

Similarly, this in the crystalline state, the molecules are ordered like this one. If these molecules are not ordered, then how will be the scenario? it will be like this one, that means this is not ordered and this is ordered, so this is crystalline and this is amorphous. So, this is a very qualitative pictorial presentation to understand the ordered and not ordered structure.

So, similarly in polymer, some of the polymers this is also possible if the polymer undergoes the order arrangement, then it can exhibit the crystallinity. As an example, if you see the polyethylene, so polyethylene the structure is this one. As I told that suppose this is my high density polyethylene, the HDP, that means there is no branching, completely linear, no branching, that means I like this one.

Now, I told that polymer chain does not stay like a straight or free, it gives, it remains as a entanglement like that in the solution, and also obviously in the solid state. Now, what happens some of the polymers, one example is the high density polyethylene, in some domains this kind of scenario may exist, why? what kind of things? I will just show you, like this one.

Now, see very carefully, this now, this very, see very carefully, suppose this is my polyethylene chain as remain in the solid state. You see this portion and you see here this portion, this one is ordered and this one is not ordered structure, so that means this one is crystalline domains, the crystalline, and this one is amorphous. So, you see that if the in a particular condition the polyethylene may exist in crystalline domain or amorphous domain and this crystallinity originates from the orderness of the polymer chain.

So, here you will see, although that it is crystalline, but this crystallinity will be much less than the small molecule, because this kind of domains will be very less and compared to the amorphous region. So, it is better to use the term semi crystalline materials, and this domain is called crystallites, that is a small portion of the crystalline phase, that is called crystallites. So, due to this scenario some of the polymers may be crystalline in nature, and one of the example is the HDP, and later I will give the example isotactic polypropylene.

I am sure you have heard that isotactic polypropylene is crystalline polymer, so we will discuss in more depth when I will discuss about the polypropylene. So, here you will see, I am sure it is now well understood that how the polymers may be crystalline, and this basically originates from the orderness in the polymer chain which comes from the ordered domain in the…

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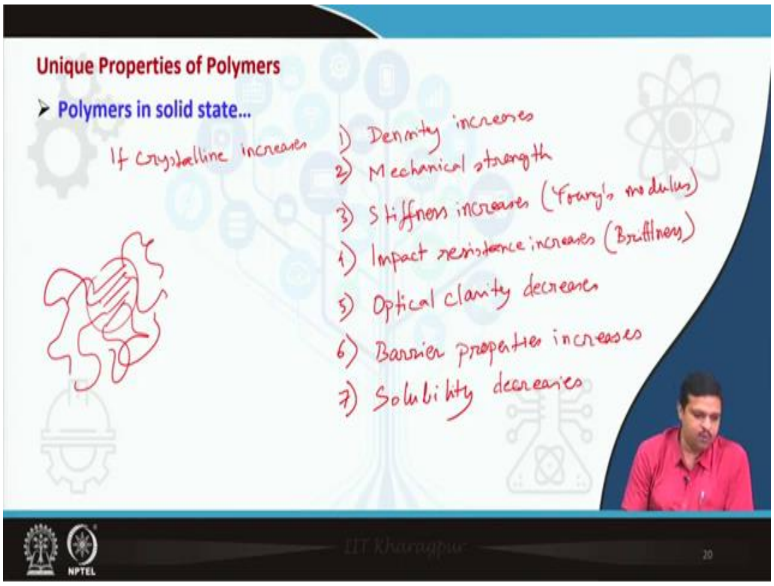

Due to this crystalline, some interesting properties evolved in the polymer. As example, if the polymer circular crystalline, if crystalline increases what happens then? so what is the output if the crystallinity increases for some particular polymers? density increases and very obvious why density increase because it is more tightly packed. Then mechanical strength increases, why I am discussing this? because suppose if I need to induce more mechanical strength of the polymer, I will try to induce the crystallinity and that the way I will design my Polymer and that the way I will select my polymerization protocol and consequently, I will select my the catalyst or the initiator.

Stiffness increases that is the Young's modulus, impact resistance increases that means brittleness increases. So, if it is crystalline, the metal is more brittle in nature, optical clarity decreases, why? Because if the crystalline materials, so suppose like this one, then what happens due to this crystalline? the solubility decreases and there may be chance of light scattering, so that is why optical clarity decreases.

Then barrier property increases, that means diffusion is difficult, so permeability is difficult, and definitely solubility decreases. So, you see that how the crystalline governs the properties of the polymers and these are in, these are I am not telling this advantage or disadvantage. So, according to the properties or application you are trying to make the polymer you have to select the pollination protocol and the mono model, so that I want to give the message.

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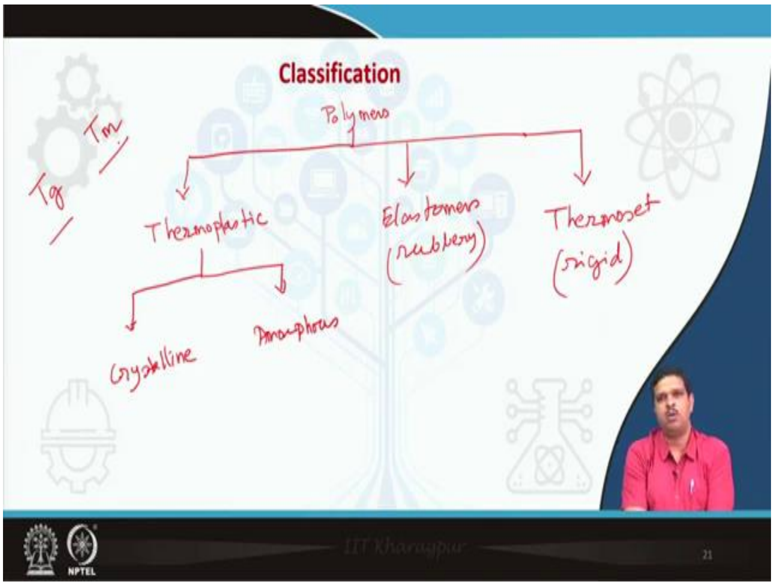

So, you will see depending on the physical properties of the polymers, you can actually classify the polymers into some broad category categories. So, I just very briefly I will tell you the classification, this is the thermoplastic, like normal plastic we actually thermoplastic polyethylene, polypropylene, this thermoplastic can be divided into two categories that is the crystalline, like polyethylene is on a crystalline thermoplastic and amorphous, thermoplastic materials the polymers actually become soft, all liquid on Heating.

Then this is the elastomers, elastomer polymers are actually rubbery materials that means soft at room temperature, you can stretch it, so it is basically rubbery materials. And the third category is the thermoset polymer, that is the rigid one, very rigid, very hard polymeric materials. And these are basically the, depends on the polymer leak all the properties come from the, how the polymer is the chemical structure of the polymer, what functional group is there? what is the nature of the polymer? how much crystallinity is there? How, what is the TG of the polymer?

So, you should have a good concept about the TG and TM, that is the glass transition temperature and that is the melting point of the polymer. So, this TG and TM again, depends on the polymeric structure, the chemical structure and TM depends on the crystallinity of the polymer.

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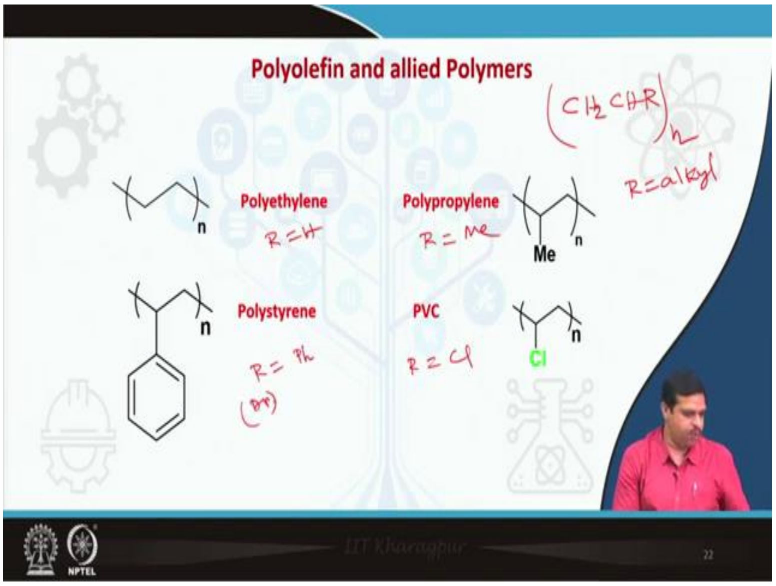

So, these are the common polyolefin and allied polyolefin polymers. So, you know the general formula of the polyolefin is this one, CHR, this is, so if you see if you if we categorize strictly as a polyolefin, R should be alkyne group. So, if R is alkyne, then it is actually strictly polyolefin, so that is why you call the allied polymers. So, if you follow this convention, then polystyrene should not fall in the polyolefin or you can tell the polyolefin allied polymers. So, all these you see what R is equal to here is for polyethylene, R is equal to hydrogen, here polypropylene is methyl, PVC is chloride, and here actually R is equal to PH is actually aryl group.

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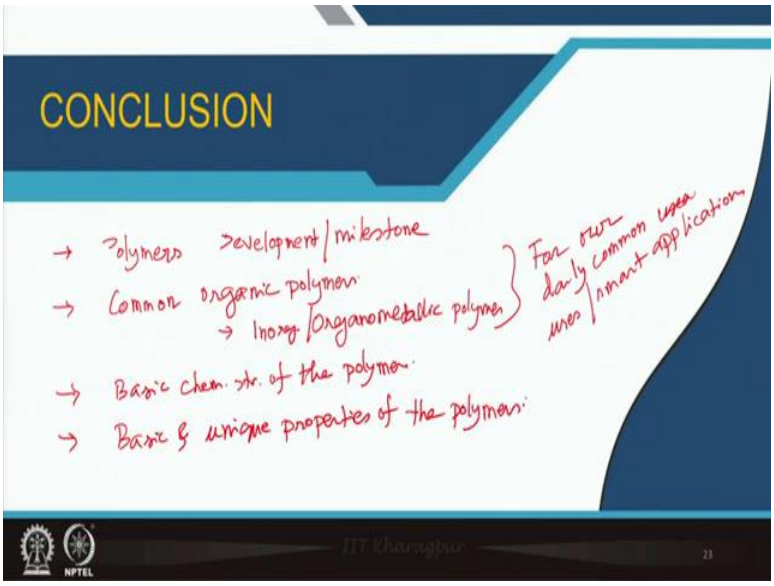

So, in conclusion, so far what we have discussed, we have discussed the in the lecture 1 and 2, we discuss the about the polymers, the development and milestone, common organic polymers, and also very briefly we have discussed common inorganic organometallic polymers for daily common uses and the smart applications. Then, the basic chemical structure of the polymers, how does it look likes? Then you have to discuss the basic and unique properties of the polymers.

I just want to mention that I have only covered the unique properties of the polymers which will be required for our future discussion. So, there are lot of properties of the polymer for the, if you consider the aspect of the physics or chemistry of the polymers, but I have only in the last class, two classes, I have only discussed the very basic properties of polymers in a very easy way, so that in the next classes will be more easy to understand.

So, thank you very much, in the next classes we will discuss the polymeration protocol, and then we will enter to the polyolefin chemistry. But before that, I just touch very quickly about the stereochemistry and structure, chemical structure of the polypropylene, which will be used in the later part when you will come to the Metallocene Catalyst, and how the Metallocene Catalyst governs the stereochemistry of some of the polymers where it is applicable. So, thank you very much, we will see in the next class again.