Metallocene and Metal-Carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

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Lecture 5

Common Polymerization Protocol and Mechanism

Hello learner, welcome to the course, Metallocene and Metal-Carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts. So, in the last class we have discussed about the microstructure and tacticity of the polyolefin polymers, where it is possible like polypropylene, we have seen also different types of variation in chemical structure that is due to the position of the double band and the radio isomer which is possible in like polyisoprene or polybutadiene polymers. The most interestingly we found that where you have you are using the prochiral monomers; you will have a different stereo regularity in the polymer backbone.

So, as we discussed that these controlling of the micro structures and the difference in the chemical structure in the backbone can be varied by following different polymerization protocol. So, before going to the Metallocene and other organometallic based polyolefin synthesis, we should know about the existing and very well developed mechanism and synthesis protocols so, that we understand the basic concept of the polymerization. So, in this class, I will go in a very brief I will not have the opportunity to discuss the kinetics, I hope that you have if you have taken the basic polymerization course, that will be helpful if you have not taken that also no problem I will try to discuss in a very simple language, so, that you can understand the basic concept of the polymerization, so, let us start.

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So, as I told that, today's class will be the common polymerization protocol and mechanism. So, here you will see that what will be the concepts I will cover, I will cover the polymerization protocols. The two polymerization protocols are exist, you probably are familiar with that one if you have taken polymerization course that is the step growth and chain growth those the main common polymerization protocol. And then we will discuss the different mechanism or synthetic protocols addition, free radical, controlled radical, anionic and obviously the metal catalyzed, that is our, the main focus of this course.

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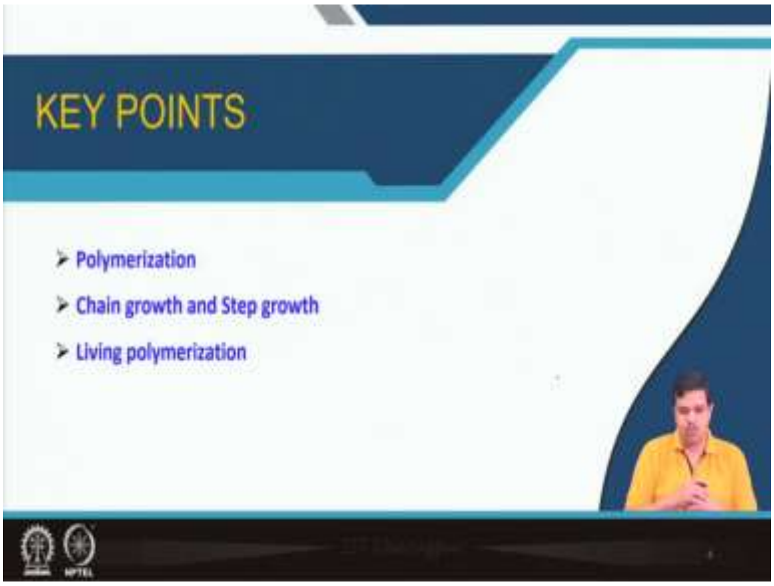

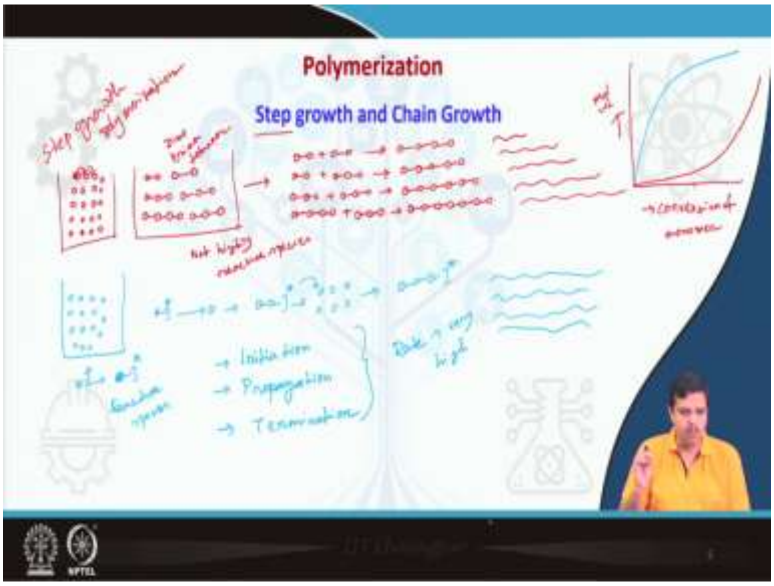

The key points will cover the polymerization and chain growth and step growth. And we will understand that how controlled it is. And then we will try to understand the different control polymerization protocol including the living polymerization where we can actually tune and control the architectures of the polymers. So, let us start the two very well-known polymerization mechanism operated during the polymerization. So, you know, that I will try to discuss in such a fashion show that you can understand the basic difference of the step growth and chain growth. Let us try to do, let us try to understand or to understand the basic concept of this two this mechanism, two type of mechanism one is step growth, one is chain growth, as the name suggests the step growth.

So, what is that, so, the polymerization will be like a as a step. So, suppose I have monomer in the polymerization, if I have monomer in the polymerization reactor, let us say these are the small rounds are polymers. This small rounds are the monomer sorry, so, this is my polymerization reactor. While you are doing the polymerization, now, the polymerization may happen in two ways. This is the one and the other one is, is one let us say here, here also monomers are there like that. Now, first I try to explain very qualitative way what is the step growth polymerization. So, let us so, these monomers obviously has to be active.

So, there should be functional group or we have to make it active. So, that we will discuss in the later part. So, now if it is active let us say this is reactive monomer so, it will react with the other monomers or other monomer So, let us say there will be formation of the dimer. Now, there will be formation of dimer there may be a lot of dimers and this one also they may and then this reactivity can also react with other monomer so, it will be then also trimer formation so, like that similarly, they are maybe tetramer formation like that. So, in a similarly, so, there you will see that there are possibilities of dimer, tetramer, trimer like that here so, here you see that all are equally reactive.

So, not, I come to the chain growth polymerization where you have a very reactive centres or this may be propagating site or monomers or activated the monomer but in this case in a step growth polymerization all are equally reactive there is no way highly reactive species, but all are equally reactive. So, they are all are not highly reactive species exist here. And here you will see the distribution of dimer, trimer tetramer are there. Now, the next step you can think what will happen. So, this dimer can react with another dimer and you will get basically a tetramer now this dimer it can react with another trimer and then you will get basically pentamer.

Now, this trimer can react with another trimer and you will get hexamer like that, then again so, tetramer can react with trimer and you will get the heptamer like that. So, what is happening here you are at any time you will be getting a different length of polymer like that polymer chain. So, it is like that. So, that is why so, this process is quite slow as I told that there is no really highly reactive species out there. And at any time, you will get a quite broad distribution of the molecule weight and as the process is slow, you will if you plot like this one that this is my, the molecule weight of the polymer and this is the conversion of monomer means how much percent is of the monomers the moles are converted to the polymer. So, what how, what kind of what, what kind of trend you will get, you will basically get a trend like this one.

So, that means, that you will see here it is quite slow process and you will get at the particular time let us at this time, you will get quite low molecular weight polymer where also you will see the conversion of the monomer is quite slow. So, this is it called step growth polymerization. However we, you I will give some example, here you will see the step growth polymerization is very useful and routinely used for some of the common polymers I will show you on the next slide some example you will see that there are many polymers which are used in daily life are synthesised by the step growth polymerization protocol, just to understand and to get the concept of the difference between step growth and chain growth polymerization.

I will also discuss and a very qualitative way as I told I not go in detail on the kinetics that here very unlike to the state growth polymerization, the chain growth polymerization what happens these monomers first has to be, has to be react with some initiator where is the active species formed. So, this one actually this one first react with some initiator let us say I dot and forms a actives species which is basically very reactive species. Now, this one with the active species these can react with one monomer and then it form the like that, then this one will have a lots of monomers. So, this one then again react with this one and then you will get like this one.

So, what will happen you will see that if there is no termination or no other side reactions, you will see that these polymerization is very rapid and because it involves the very highly reactive species and eventually what you will get you will get the long molecular weight polymers with relatively narrow molecular distribution relatively I am telling not unlike the step growth polymerization. So, now, if you plot like this one the if this is for the step growth polymerization and for chain growth polymerization what will the scenario you will get basically like that means, at a particular time you will see the conversion of even at the low conversion of the monomer that means.

Let us say the premature polymerization condition, you will get a quite high molecular weight polymer because this polymerization rate is very high and in this case, you will get the initiation, propagation and termination that we all know that these are the although other steps are possible. That is like chain transfer and DTC. These are the main steps in the polymerization that the initiation propagation and termination what the steps are clearly visible in case of the chain growth polymerization. So, you will see that in chain growth polymerization, the polymerization is quite rapid, sometimes very uncontrolled, but this also kind of these polymerization also very, very highly used in some of the polymers as example, like polyolefin.

So, it is widely used process for the polyolefin type of polymerizations. In even in industry, but it has its own advantage and disadvantage that we will discuss and that was that is why the new catalyst like Metallocene or Ziegler Natta catalysts, or other Metal-Carbene based catalysts developed to exclude the disadvantage. Fine. So, I, students, I hope I have given some favour to understand that what is the state growth and chain growth collaborations very qualitatively, although I am not going in depth in kinetics now, what, I will give is some more depth on the step growth polymerization with some examples and the possibilities.

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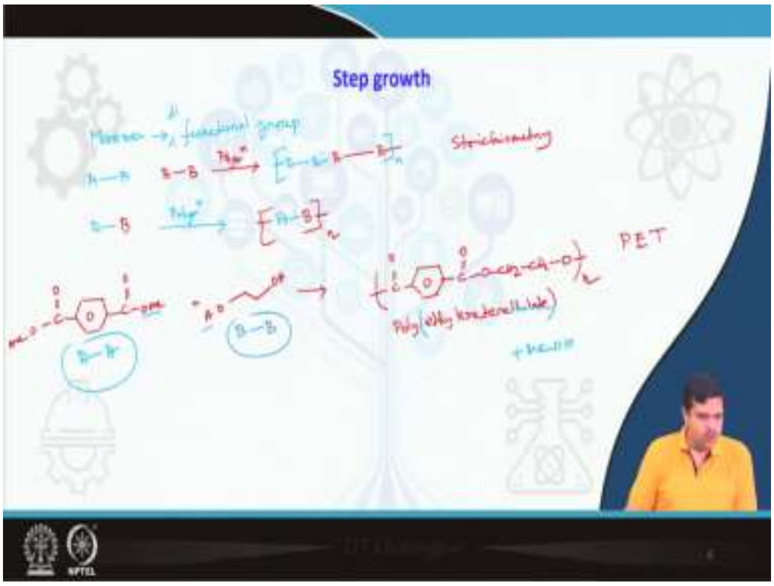

Let us understand, so, as I told that in a step growth polymerization one monomer you will react with another monomer and so, there should be some functional groups. Although it is not very highly reactive but it should react with another monomer then form dimer then trimer then dimer plus dimer, dimer plus trimer like that. So, two types of possibilities may be there as example the monomer first let us say monomer should exist functional group which can react that to another functional group this functional group and this functional group should maybe same type like this is one monomer let us see and another monomer is let us see the like that.

So, here you see that the monomer should be difunctional, so difunctional and monomers to two monomers maybe they are one is the AA one is the BB that means one monomer exist same type of functional groups, but difunctional and another monomer should make these two functional groups at the end, but the same functional groups. And another possibility is maybe there is like this one were like that. Now, it is obvious that if you do the polymerization, obviously, here it is step growth polymerization. So, you will get like so, A will react with B functional group and you will get like this kind of polymerization.

So, A-A B-B, so, this is possible, where you have bifunctional, but with different monomers, now, single monomer but with two different functional groups at the two end, so, in this case, what kind of how what kind of polymer you will get, if you do the polymerization step growth polymerization. So, you will get like and so, this one. So, obviously, from here you will see that polymerization depends on the stoichiometry. So, you have to follow the stoichiometry very carefully, like here, you have to get the 50, 50 percent like that and the stoichiometry will highly depend on the, molecular weight will highly depend on the stoichiometric here you have to maintain the stoichiometry and also there should not be any side reaction between A functional group and B functional group.

So, these two things you have to be keep in mind. And as I told you that none of the functional groups should be highly reactive, so, no reactive intermediates exist in this step growth polymerization. So, as a I now I will give some examples here you will understand that what kind of monomers we can give the step growth polymerization with the some examples in for in real life as example, we all know the PET polymers. The terethalate, polyethylene terethalate polymers, so, you all know, can you tell me the one use of the PET polymer, it is everywhere. The water bottles, everywhere. So do you know the chemical structure of that PET? Can you guess what kind of so polyethylene terethalate, so terethalate that moiety, so let us see, here that PET is synthesized by the step growth polymerization, what are the monomers?

So obviously, the ester group and the diol so polyethylene terethalate it is this polyethylene is coming from here thalate is coming from here now if you do the step growth polymerization you will get the polymers like this one and you will CH2, CH2. So, this is there will be this O will there. So, this is my PET. So, this is commonly known as PET that is the polyethylene terethalate, can you Poly ethylene terethalate. So, this is the polymer widely used and why and in synthesised following the step growth polymerization of these two monomers.

So, obviously you see this is I can regard as this is the B-B monomer B-B type monomer like this one and this is the A-A type monomer like that one fine and most of the cases you will see in the in this kind of polymers a very common reagent if a common product is also eliminated most of the cases is water some cases methanol like here you will see that methanol is coming out methanol is coming, methyl this methyl and this OH this OME and this OH in many cases water is coming out. So, it is like a condensation polymerization.

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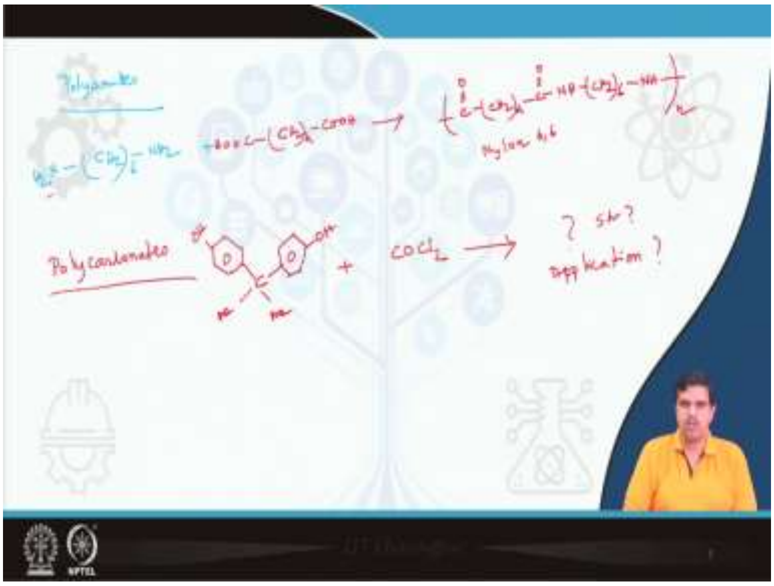

So, you will see there are a lot of examples for the step growth polymerization leading to the very common polymers which we use actually in daily life, one of the other polymers category the polyamides, when I call the polyamides the first thing comes in mind is the nylon 66 it is highly used in textile industry and other domain of applications.

So, do you know the chemical structure of the polyamide nylon polymer nylon 66, what are the monomers let us try to understand what are the monomers. So, simple amine with diamine, so, here see CH2 6, so 6 CH 2 and here NH2 here NH2. So, this is a diamine again A-A type monomer and the other one it is basically the diacid dicarboxylic acid and here CH2 4 and COH carboxylic acid dicarboxylic acid, then it is what polymer you will get, you will get the CO CH2 4 then CO other end and NH, CH2 6 and then the other end that this end NH and you will get these polymers. So, this is we called nylon, 66 polymers it is highly used in textile industries. And in fibre and cloth applications.

So, this you can easily synthesise this one, even in a just without in much precaution you can make it this polymers in your laboratory. Similarly, the polycarbonates also you can make it by very easily by step growth polymerization and here the monomers you know that. So, this is and the other monomer is the. So, this is you know the phosgene gas the COCL2 the phosgene and this is a biphenyl, and you will get this polymer, let us this is you can do it when after the class what are the polymer structure, the structure and the application if you know this is fine if you do not know, this when we treated as a assignment. So, it is now quite clear to understand that it is step growth polymerization you will have the polymerization is quite slow you can you have to have the monomer with bifunctional groups here at a particular time in the polymerization.

There is exist of the monomer the different type of polymer chain length oligomeric or tetramer hexamer like that and the polymerization is quite late and the conversion of the monomer is quite slow. So, this is the general criteria general properties of this kind of step growth polymerization. So, reaction is quite slow. It is sometimes you have to do the polymerization in few hours, few days like that, fine, but this is very easy, that is the probably the main advantage this is very easy, you can make it your own you can do in your lab, so, no problem at all.

So, now we have some kind of basic concept about the step growth polymerization. So, in the next class, we will discuss about the chain growth polymerizations. What are the mechanism what are the protocols? So, far, we have discussed the step growth polymerizations or the disadvantage, the main criteria and main the polymerization conditions. Thank you.