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

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Lecture 6

Common Polymerization Protocol and Mechanism (Contd.)

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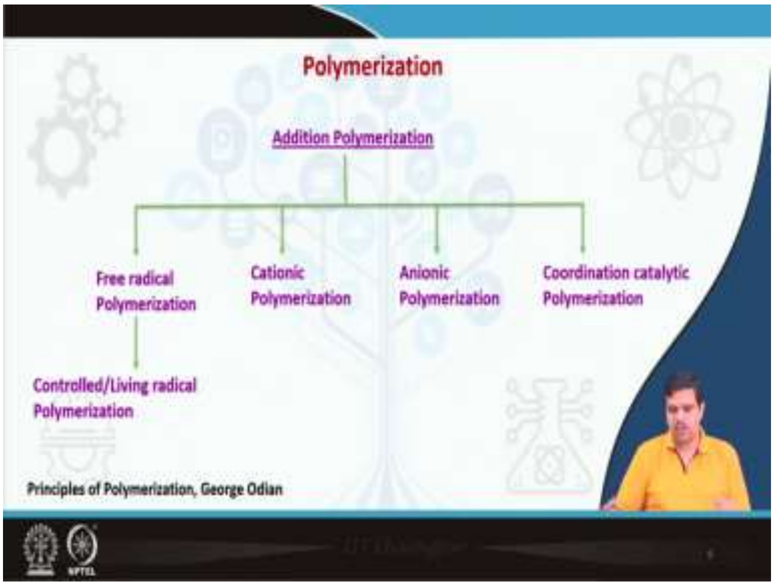
Lecture 06: Common polymerization protocol and mechanism.....Continued



Polymerization

Addition Polymerization

Free radical Polymerization

Cationic Polymerization

Anionic Polymerization

Coordination catalytic Polymerization

Controlled/Living radical Polymerization

Principles of Polymerization, George Odian

So, far we have discussed the Step Growth Polymerization, the uniqueness of the step growth polymerization, the basic criteria condition and the mechanism you will see that a versatile polymers can be synthesised in a different method.

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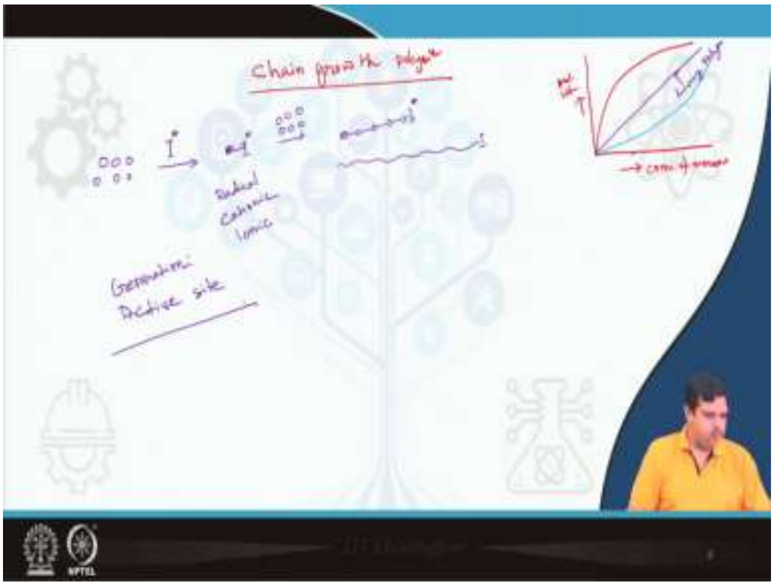

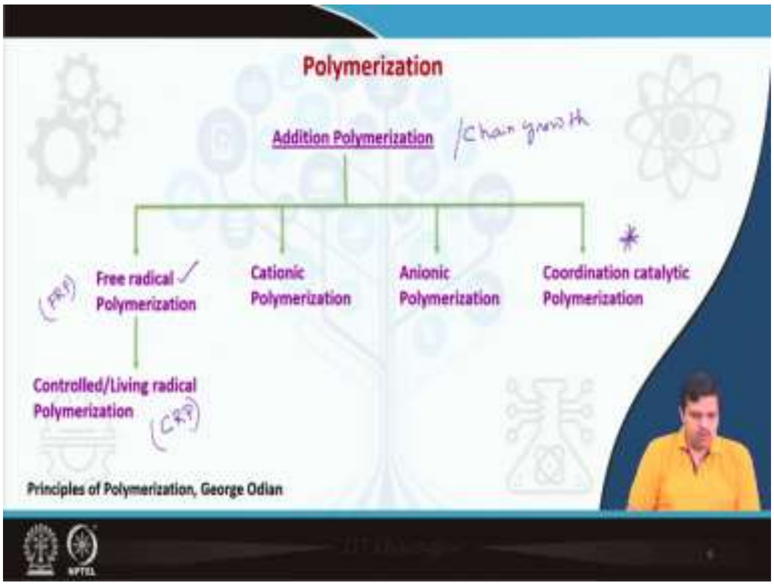

Polymerization

Addition Polymerization /Chain growth

- Free radical Polymerization ✓ (FRP)
  - Controlled/Living radical Polymerization (CRP)
- Cationic Polymerization
- Anionic Polymerization
- Coordination catalytic Polymerization *

Principles of Polymerization, George Odian

So, before that I just want to highlight that chain growth polymerization and then I will come to the different chain growth polymerization. So, here as you see from the step growth polymerization, now, it is very clear that in the if you plot this is the molecular weight of the polymer and this is the conversion of monomers. So, if you are, if my rate is chain growth polymerization, you will get like this one that graph I am not doing any scale it just to qualitative.

But this is good enough to understand and this one is like this one. So, later so, here you will see that the blue one is the step growth polymerization and the red one is the chain growth polymerization where, the reactive species exist and these are very highly reactive, it immediately reacts with monomers and after reactive in the monomer it and again react with another monomer and the reactive species basically at the end of the oligomer.

So, the reaction is very rapid and at the particular time of the polymerization at a specific time you will see that molecular weight of the you are getting a quite high molecular weight of the polymer, although as I told that both have advantages disadvantage, the main disadvantage of the step growth and chain growth polymerization is that you cannot really control the polymerization.

So, you if you have a specific length or I if I need a specific architecture or you need a specific PDI of the polymer, it is very difficult to handle with these kinds of polymerization. So, in the ideal condition, I will prefer to have polymerization where the molecular weight is linearly dependent on the conversion of the monomer that means, I if I feed a particular mole of the polymer, of the monomer I should be able to know that what how much molecular weight polymer I am getting.

So, this is called the living polymerization, living or control polymerizations where you will get the well defined polymer. So, eventually this we will discuss later how we can make the chain growth polymerization to living polymers, essentially the living polymerizations or either would be chain growth or step growth, but the polymerizations will be here the leaving control to get the oil defined polymer with a specific PDI or controlling the structure of the polymer backbone.

So, let us understand what are the chain growth polymerization. So, here you will see that as I told that if you have a monomer here there a lot of monomer. And I, if I make this monomer needs not to be highly reactive, but I have to make it reactive by doing by reacting with some initiator in most of the cases it is a radical, or maybe other cationic, anionic.

So, these have to make a reactive site like reactive species this may be radical this may be cationic this may be ionic what it may be metal catalysed but I have to make a highly reactive species and then what it will do it will react with monomer available and then this one you will get see so, this one like that like that. So, this will not stop to oligomer, monomer, dimer, trimer and hexamer it will actually grow in a like that.

So, you will get the high molecular weight polymer by this chain growth polymerization So, as I told that initiation propagation and the termination is quite visible in this kind of polymerization where in a particular time let us say the like this this time here you will get the chain you will get the high molecular weight polymers along with some monomer left, but the step growth the scenario was different.

So, the main point I am telling that there has to be active site. And this active site you have to generate by different ways. That we will discuss in the following classes and very brief way, because before going to the coordination catalytic polymerization, that metal catalytic polymerization, we should understand the other protocols otherwise we cannot really make a difference or make we cannot understand the concept of the polymerization. So, here the addition polymerization is a basically in some book you will see that this is the added chain growth polymerization.

So, this is actually similar concept twice. So, you will see that there are several chain growth or addition growth polymerization are possible like free radical polymerization we sometimes call the FRP cationic polymerization we call CP and anionic polymerization called AP. Then coordination catalyst polymerization that is basically our aim in this course, and free radical polymerization are recently developed to the control radical polymerization on some we call CRP controlled radical polymerization. So, that I will try to give a very brief overview of the different addition polymerization.

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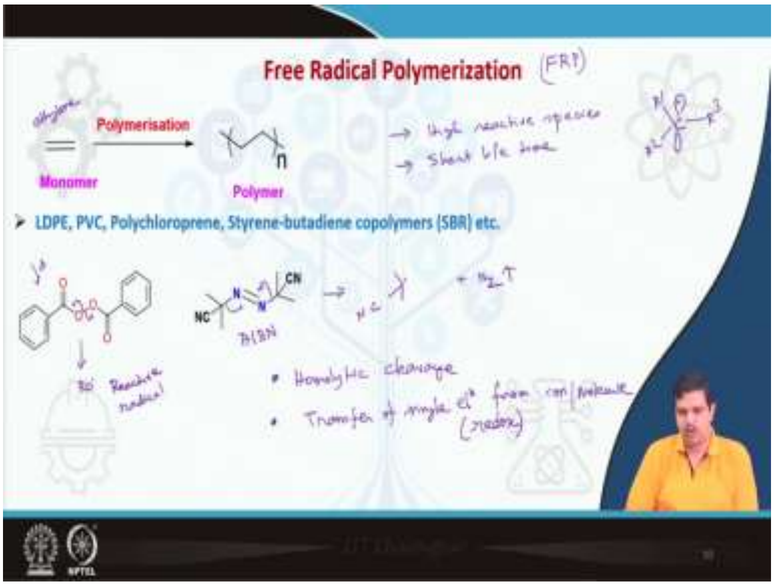

Free Radical Polymerization (FRP)

- LDPE, PVC, Polychloroprene, Styrene-butadiene copolymers (SBR) etc.

So, in as I told you that in the polymer, chain growth polymerization that one like see like this is my ethylene monomer and you know it is you can polymerize by the free radical polymerization that we called the FRP. So, here we routinely use some initiator as example like this is your benzo peroxide. So, what happens if you if we give some heat this undergoes the homolytic fission so, homolytic cleavage and you will get the like that, so, you will get the highly reactive. So, this is basically the reactive species. So, here you this is here, this is the reactive radical here. So, as I told that this in the free radical polymerization, a highly reactive species, you have to make it highly the reactive species, radical species obviously, we just short life time in carbon based radicals.

So, this is the scenario where the radicals the free, the unpaired electron, the free radical is housed in one of the P orbitals. So, this one the free radicals now reacts with monomer and this is also another initiator we routinely use that is called AIBN. So, this is you know that this is the azo, this is a azo type of initiator, so, you see that the what is the driving force it is very easily we can make the corresponding radical. So, what happens here you like that and you make this one and nitrogen comes out dinitrogen So, these are the driving force. So, these the radicals we routinely we use for initiate the polymerization in the free radical polymerization.

So, I will just give some examples of the free radical polymerization and I will try to give the basic properties or the unique criteria for these kinds of polymerization. So, let us so, now, it is clear that what kind of what prerequisite, so, prerequisite is that I have to make, I have to initiate the monomer by a reactive radicals. So, radicals can be formed easily by the homolytic cleavage like here in this case, so, two ways we can do that is the homolytic here all these two examples are basically through by the homolytic cleavage and other one we can do the transfer of single electron from iron or molecule from iron or molecules. So, this one is called the electron single electron transfer.

So, two ways homolytic cleavage or electron transport eventually this one is basically redox reaction. So, if suppose one species will giving the electron to make the radical cationic and anionic so, that also possible so, these are the two ways we can make or we can generate the reactive species fine.

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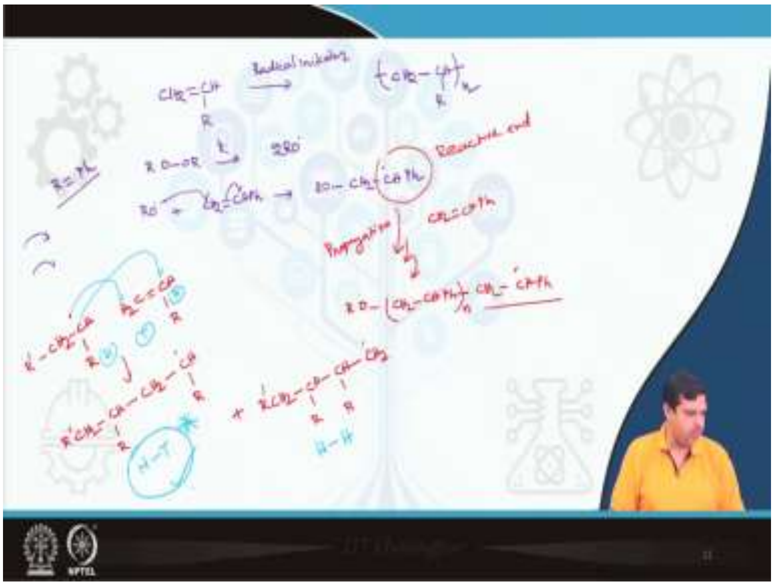

So, let us give take some examples like this kind of monomer, we can do the radical polymerization if you use the radical initiator, you can make the polymers, now I will just show one examples, where R is equal to let us say phenyl where it is. So, these polymers will be polystyrene. So, and the monomer will be styrene, then we will understand the what are the mechanism of what are the steps involved and what is the advantage or disadvantage. So, what happens so, you first is the initiation, generation of the initiator. So, I am just writing in a simple way. So like a peroxide type of initiator. So, this is the initiator.

So, you will get that this radical now, you this one we will, I am sure if you have taken any polymerization course you have studied this, I just try to just trying to refresh your knowledge on this polymerization so that it will be easier at later stage. So, here now what you are getting so, this is basically the reacting with the monomer and you will get the this. So, you have see that this attack on this attack here and then so you have to this is a radical attack. So, you have to careful we, this is the convention is like that if there is anion then we do like this one I am sure you know this one. So, it is a present basically single electron attack. So, then you will see that it first we attack here because they just regularly favoured here phenyl group is there.

So, attack at the less sterically position and then it undergoes further then it undergoes this rearrangement and why because this is more stable because this is a conjugated with the phenyl group there. So, now you will see that this is my reactive end so, there this is my reactive end. So, now as it is reactive end so, this is now will react to it another monomer and similarly it will react with sequential, sequentially with other monomers and eventually you will get the like this and still you will see that this is my monomer this is my the polymers with still active end. So, here you will now this is the active end. So, this is the propagation step, this is the initiation step.

Now, this one can undergo the termination or can also possible the chain transfer I will show very briefly, but here you have there we have to consider the other one on important point like for when this kind of radical species when react with the monomer raised to CHR, I am putting here this one. So, there is two possibilities one this can react here or these can react here.

So, that two possibilities, I will show you how to be the difference in structure. So, this is my R and this is, first time writing the two possibilities and then you, I will explain what is the difference, fine. Now, you will see that now, you will see formation of this one, how it is happening, this is happening by reacting with this one. So, if we consider this is head and this is tail side.

So, this is basically head to tail attack. Now another possibilities, if we consider this is head so that means this is head in this monomer so and other possibilities that this can attack with this one and eventually you will get this product so this is the product with head to head up, but as I told because this is less sterically favoured, so head to tail is the most favoured way of the attack. So, in the radical in this kind of scenario you will get mostly head to tail attack.

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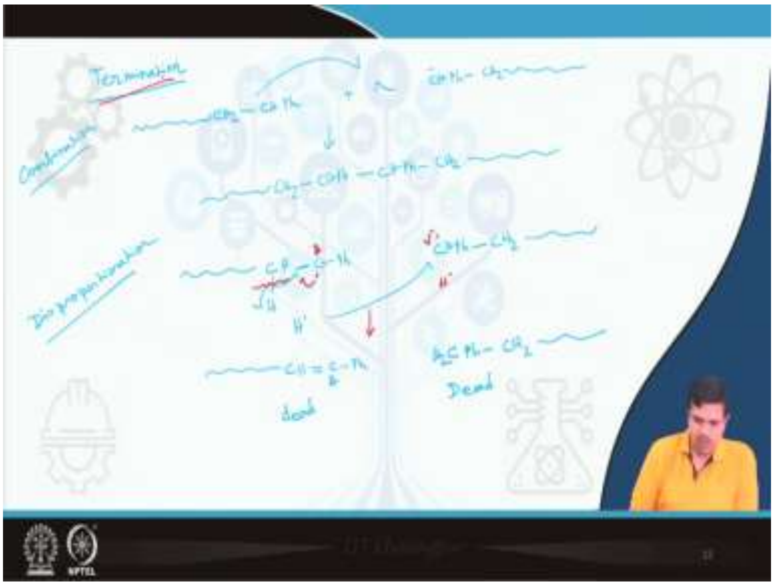

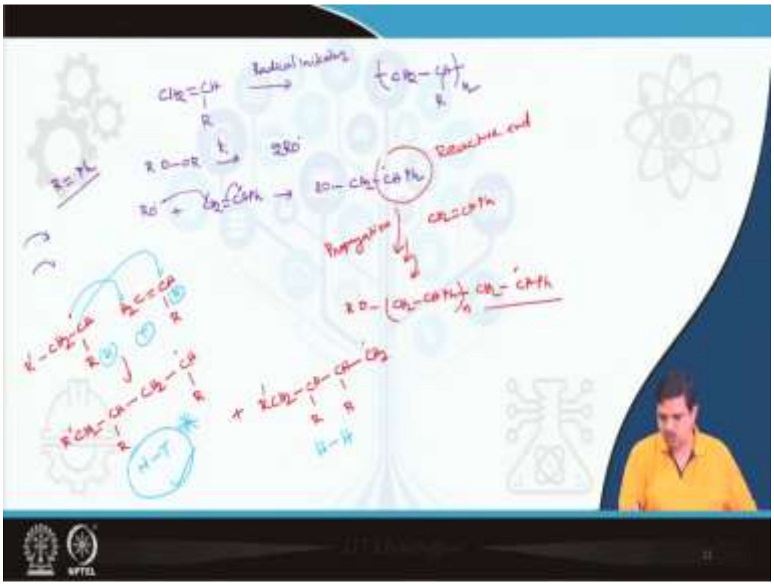

Now, in very quickly I will show tell you the termination so, here you will see that I am not writing the whole polymers, I am just writing already the active end of the polystyrene. So, here you see CH, Ph if you recall the last slide, so, this is the CH2 CH Ph. Now, this is the radical, so, this is a very active so, we can imagine that there is another, because there are a lot of these kind of active species the polymers with active end are there. So, this one then like this one, so, this one now can react and eventually what you will get, you will get so, basically you are getting this is one termination, so, coupling of the two radical and you will be getting a polymer with just double molecule weight.

So, that is the one way of combinations. So, this is just a combination or coupling of the two radicals and the other one is possible is the disproportionation. How it is possible very interesting. So, again I am writing the only active end and they are like this one. Now, what I will be doing here I am just doing this so that it is easy to understand. So, I am writing this way. So, this is Ph. Now, this is my radical here this H is homolytic cleavage and this H. And now this you are getting H dot here and this H dot is basically coupled with this radical, this is active end and there is a formation of the double bond. So, you are getting here the double vinyl function the polymer with the double bond end.

So, here you are getting the double bond here and here it is H is there and in this case, you are ended with so, both are dead polymers. So, this is also dead polymer this is also dead polymers. So, I am just repeating again because there was not clarity in the drawing. So, in this disproportionation reactions you will see there is, this is the radical. So, what happens, this H there is a homolytic cleavage here, this is the homolytic cleavage of the CH1. And this one, this radical, this free electron reacts with the free electron available after the homolytic cleavage of the CH1 so, H dot is free now, this H dot reacts with this end, and forms the dead polymer end and here You are getting the polymer all the dead polymer, but with the one alkene bond. So, this way that terminations are possible and also there is another possibility of the chain transfer.

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That is again I am writing with another end with the reactive end and suppose if there is any species which can react with this active end this X-A maybe monomer this X may be solvent or any other impurities or reagents. So, what may happen this can give the reactions like CH2 Then CH, Ph and this X and this A dot now, this is called the chain transfer here the this is also another possibility in the free radical polymerization these are one of the disadvantage. So, here you see this is my dead polymer, but this one is reactive.

So, this then again can initiate or you can tell reinitiate the polymerization. So, you will get then in a quite broad molecule distribution in the polymerization. So, this is the summary. So, this free radical collaborations is very well known and widely used in the polymer synthesis. But problem is that you cannot really have a good control over on the polymerization polymer architecture and the molecular weight.

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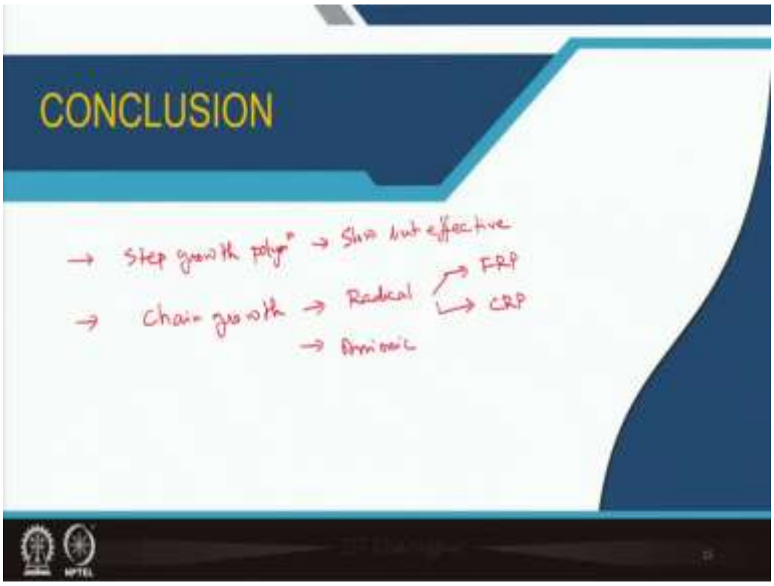

CONCLUSION

→ Step growth poly^n → Slow but effective

→ Chain growth → Radical → FRP
→ CRP

→ Anionic

So, in the conclusion that the step growth polymerization, you will see step growth polymerization. The, it is a quite slow process. And it is very, it is a quite slow process but effective to make the polymers very well developed well-studied and very useful polymers like nylon, other fibril type of polymers, PET, and many, many of them now chain growth polymerizations. There are several possibilities are there. One is the radical polymerizations, that may be free radical, FRP, they are maybe the controlled that we will discuss in the next class, there maybe the anionic polymerization.

That also we will discuss in the next class, but as its summary, what I want to tell that in the chain growth polymerization, you will see we can make the high molecular weight polymers by the chain growth polymerization protocol where the different initiatives are involved for the reaction the polymerization rate is quite high and you can make it a very useful method for a versatile to get the versatile polymers.

So, in the next class, we will discuss about the control radical polymerization where you have you the all the disadvantage associated with the with the free radical polymerization where the control the main disadvantage of the making the polymerization of the free radical polymerization is the not having the controls that will be solved per shell and then we will discuss the anodic polymerization to make you see that more living in nature so, that the controlling and to get the well-defined polymers will be quite useful according to our willness, according to other properties we are aiming for, and obviously the application aiming for. So, thank you very much and let us meet in the next class again.