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

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Lecture 19

Coordination Polymerization of Olefin and Stereoregularity

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

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Lecture 19: Coordination polymerization of olefin and stereoregularity

Welcome learners to the course Metallocene and Metal-carbene based Compounds for Advanced Polyolefin Catalysts. So far, we have discussed the reactivities and the unique properties of bent metallocene catalysts, which are, which will be our main focus to study in this course. Today, we will discuss about the coordination polymerization by different metal catalysts and how the stereoregularity is maintained or governed by the catalyst system in alpha olefin polymerization. And we will try to find out that what is the origin of this stereoregularity. How does it happen? How does stereo centre a specific stereo centre is created.

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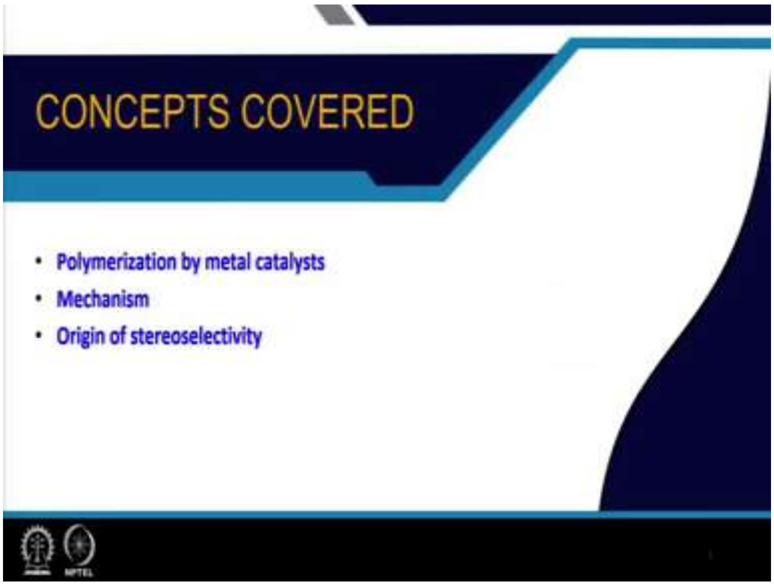

CONCEPTS COVERED

- Polymerization by metal catalysts
- Mechanism
- Origin of stereoselectivity

So, the concept will be covered in this lecture is a polymerization by metal catalysts. And specifically, we will try to understand the mechanism and which steps or which basic properties are responsible for the stereoselectivity.

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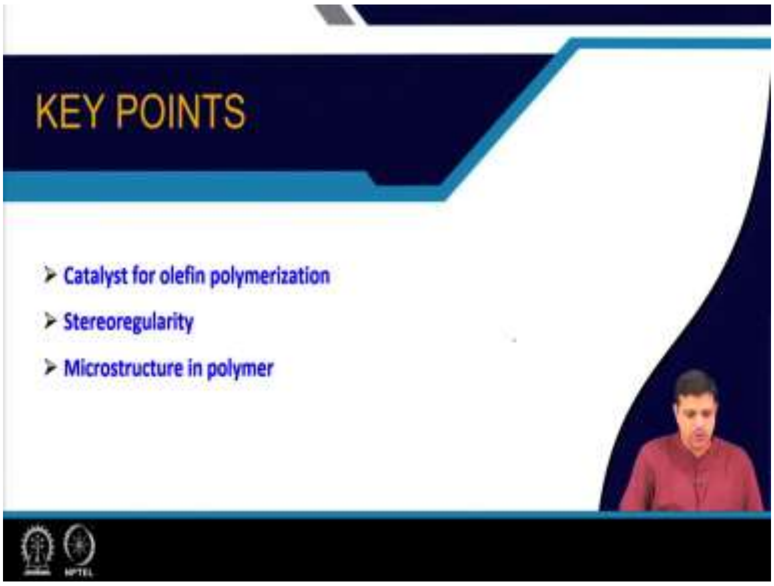

KEY POINTS

- Catalyst for olefin polymerization
- Stereoregularity
- Microstructure in polymer

So, the key points, we will learn here, the stereoregularity, microstructure in polymer, if you recall in our previous classes, we discussed and very briefly that what is the stereoregularity and how the microstructure is created or depends on the polymerization mechanism. So, that we will try to understand here and we will try to see that how the different catalysts not only the different catalysts, the catalysts of following the different condition can govern the stereoregularity in olefin polymerization, let us see.

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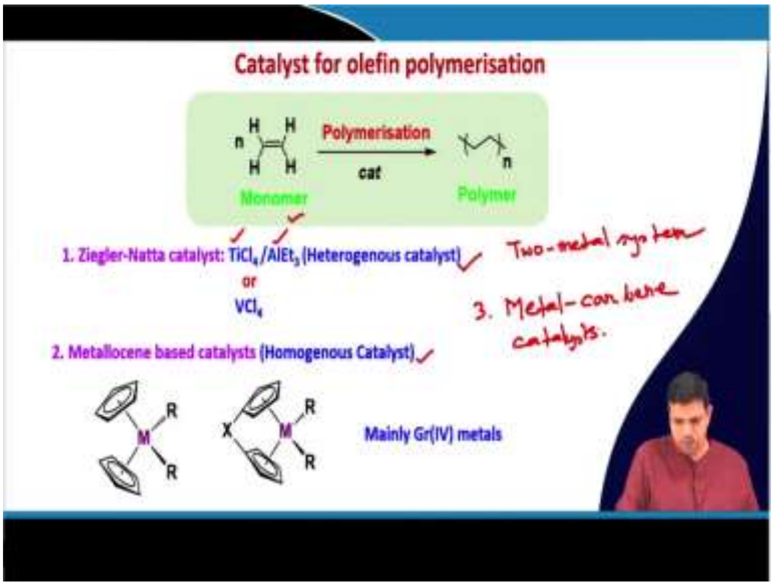

Catalyst for olefin polymerisation

1. Ziegler-Natta catalyst: $TiCl_4/AlEt_3$ (Heterogenous catalyst) ✓
or
VCl_4

Two-metal system

3. Metal-carbene catalysts.

2. Metallocene based catalysts (Homogenous Catalyst) ✓

Mainly Gr(IV) metals

So, you know that this is the polymerisation, we will are interested here that is the alkene. And this one is the polymer and this polymer can be synthesized following different polymerization protocol as example, radical polymerization, free radical polymerization, controlled radical polymerization, anionic polymerizations and also by the coordination polymerization where you will be using a organometallic or transition metal complexes for as catalysts. So, this is one of the very well-known polymerization catalyst is the Ziegler-Natta catalyst that is the heterogeneous catalyst and metals we will be using titanium or vanadium and also here we have to use a co catalyst. So, here the two metal system.

So, two-metal system. One you see the titanium and also you need a aluminium catalyst and the aluminium trialkyl aluminium is called the co catalyst both are required. And another very famous category of the catalyst is the metallocene based catalysts, which we will be discussing shortly after getting the information and understanding this basic feature of the Ziegler-Natta catalyst.

Of course, the third category is the metal-carbene catalyst. So, we will discuss step by step that how these catalysts are become so popular in industrial polymer synthesis and what is the beauty and what is the structural feature and the reactivities are associated with this kind of catalyst system. So, we will try to understand in on the basis of this mechanism reactivity and the cons, using the concept of the organometallic chemistry.

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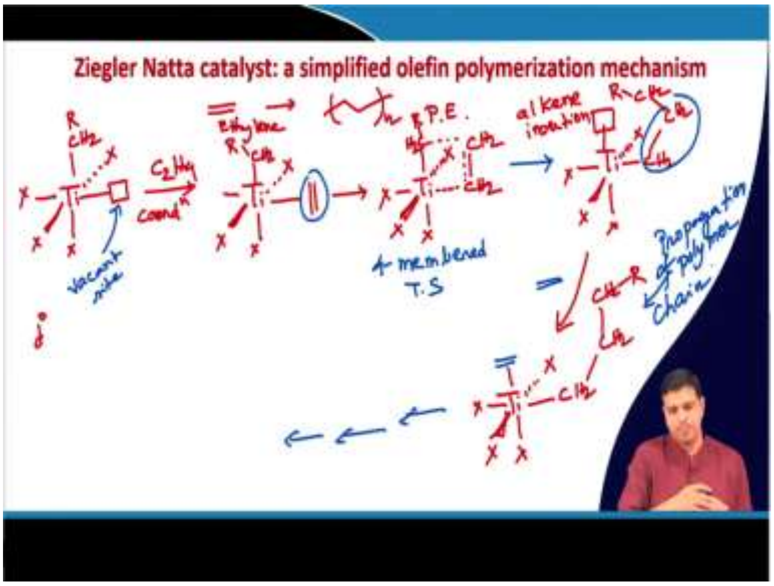
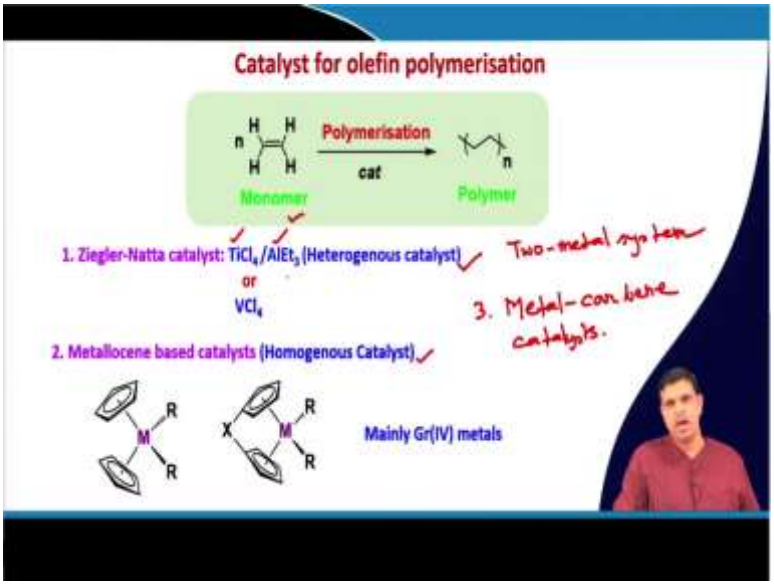


Ziegler Natta catalyst: a simplified olefin polymerization mechanism



Catalyst for olefin polymerisation

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Two-metal system

2. Metallocene based catalysts (Homogenous Catalyst)

3. Metal-carbene catalysts.

Mainly Gr(IV) metals

So, as I told first let us understand try to understand the Ziegler-Natta catalyst which is one of the popular catalyst used in polymer synthesis. So, you know that Ziegler-Natta catalyst is as I told the system is TiCl4 titanium chloride and the alkyl aluminium co catalyst and a simplified mechanism you all probably will be ever but I will just try to recall that what are the key steps of the Ziegler-Natta polymerization.

So, what we are going to do we are trying to do these polymerizations, so, this is ethylene and this is polyethylene. And let us try to understand what are the basic steps we will the bond forming and bond breaking process then we will try to understand how these catalyst systems are governing the stereoselectivity. So, now we will try to understand only the steps, we will not discuss the stereoselectivity factors.

So, you can do like this one, so here is any alkyl group, and this side is actually chloride group so, I am not writing I am just writing x. And this is actually the vacant site we will discuss in the following slides, how this vacant site is created? Why it is needed? And what is the specific position or site of the vacant sites and how important it is for the stereoregularity.

So, as it is a vacant site here and you know that this system is the d0 system. We discussed in the last classes, so, it can act as so empty orbitals, no lone pair. So, not there is no electron in an nonbonding molecule orbital. So, it can act as a acceptor pi acceptor. So, if we put the ethylene here the C2H4 then what will happen, So, ethylene will coordinate like this. So, this is basically you see the coordination of ethylene.

Now, second step is a forming a transition state. So forming a transition state here the four-member transition state, like that. So, this is there here x that is the Ti chloride maybe chloride maybe bromide. So, here what is happening here, there is a formation of a four membered transition state. So now do not consider the stereoselectivity we will discuss later. You try to understand now the what is the bond breaking and bond forming process.

And next step is the migration reactions and how does it happen you see the titanium and so, here is as usual these are the halides and what will happen here you will see that CH2, CH2. So, there is a migration reactions. So, it is basically the alkyne migration alkene insertion reaction and what happened here you are getting the vacant site.

So, this one is the alkene insertion reactions now, again you see there is a vacant site here and again this one so, I have now this was is the halide, this is the halide and you have a CH2, CH2, CH2, R and you have now the vacant site here. So, try to understand what is done here. So, here you will see that this (())(11:46) has been inserted here and this one you see that there is a vacant site here so, it can coordinate another alkene and it form the again the alkene complex here and that is the way it will propagate n number of times and the propagation is you see that is the propagation of polymer chain.

So, here important step the alkene coordination forming a transition state four-member transition state and then the insertion reactions. We will discuss the migration steps in the next few slides you will try to understand that how the stereoregularity is maintained depending on the catalyst system.

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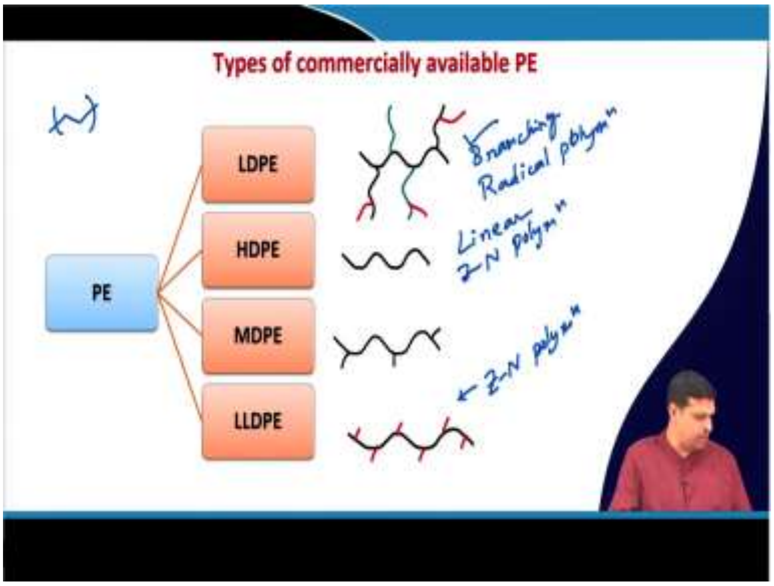

Types of commercially available PE

PE

LDPE

HDPE

MDPE

LLDPE

So, now we know all from our previous discussion that although the same composition that is the polyethylene. The polyethylene depending upon the polymerization protocol, a different type of microstructures are possible as example, like here you will see that this is the low density polyethylene where you will see there are a lot of branching and for the low density polyethylene, we generally prefer the polymerization protocol that is the free radical polymerization, free radical polymerization.

Now for high density polyethylene you will see there is no branching it is linear, we generally follow the Ziegler-Natta polymerization and for LLDPE, you will see that there is a strategic branching has been employed, controlled branching not like the LDPE. So, here also we follow the Ziegler-Natta polymerization and that is the reason we discussed in the previous classes, why these are important it has different properties and as properties govern the applications. So, for different applications, we need the different polyethylene with different architecture. And that is why it is very important to understand that what polymerization protocol will follow depending upon your targeted applications of the polymer of the same composition.

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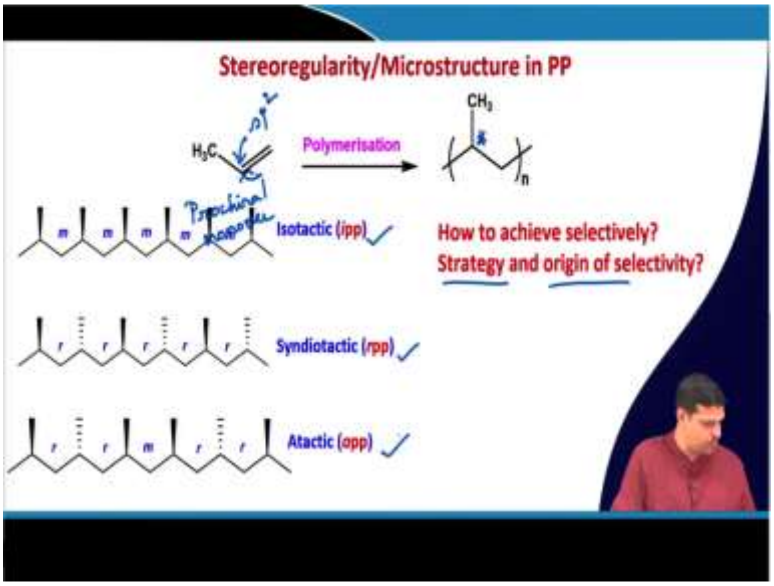

Stereoregularity/Microstructure in PP

How to achieve selectively?

Strategy and origin of selectivity?

The more interesting features where you will have a monomer like this one, as all you know probably this is a prochiral monomer because you need you know this is sp2. So, if you now add one more atom or substituent here at this position it will become sp3 and that center will be stereocentre, tetrahedral sp3 centre with different substituents so, it will be chiral.

So, like here you will see this should be a chiral centre and you will get the stereo selectivity or polymer in polymerization, which also it is very interesting because depending on the stereo select, stereoregularity in the polymer, your properties are changed in very much we have discussed the crystallinity, solubility, hardness, softness. So, how to do the strategic, develop the strategic pathway to make the polymer as particular stereoselective.

Or how to make the polymer atactic depending on your what you need and what is the origin of the selectivity and how we can do the selectively that is the most important and challenging and most interesting part, so, that we will discuss here. So, as I told that, depending on the stereoregularity, you may get isotactic polymer you may get syndiotactic polymer I you all discussed I am not going repeating again and these are the atactic polymers. So, you will see that now, how to control how to get only the isotactic or syndiotactic or with a higher percentage of the stereoregularity.

So, there is a possibility that the same catalyst they had might have a mixture and it is actually more common you will get like 80 percent isotacticity, 20 percent syndiotactic. So, how to get the more percentage of the stereoregularity that means, like say how to get 90 percent isotactic polymer. So, that we will discuss how it is possible in a organic metallic point of view and mechanism point of view.

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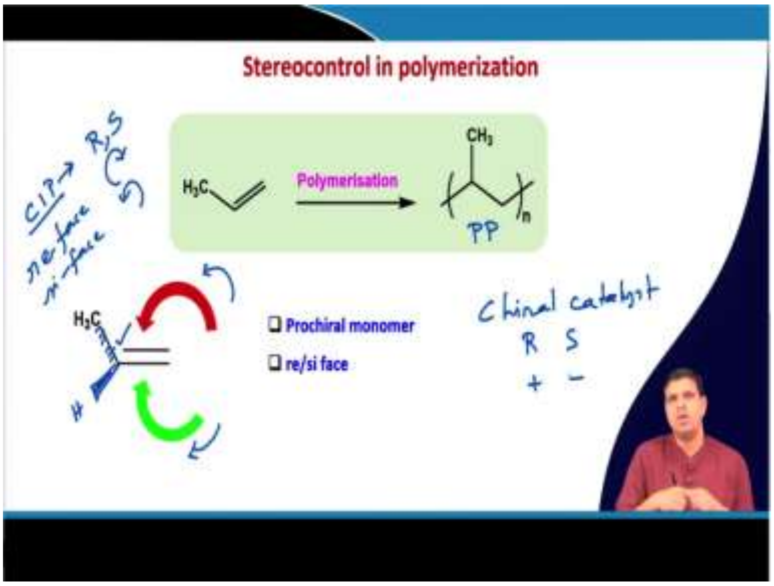

Stereocontrol in polymerization

☐ Prochiral monomer

☐ re/si face

So, let us try to understand, why how it is possible and what strategy we will follow. So, here you will see that this is the polymerization we are trying to this is called the polypropylene and this is the propylene monomer. And you see carefully here that this one has two face, so, if we like this one is H and this is like that, so, this is a planner molecules and this if the plane of the computer screen is the plane of the molecules and so, hydrogen is from my side and the methyle is to towards your side. So, the planner molecules now, if there is any catalyst or any other reagent each can approach two ways either from this one or from this one. So, depending on that approach, depending on the attack, it will give the two different isomers what is called stereo isomers or more precisely enantiomers.

I will give an example in the next slide, you will understand very common example. So, here one is called re face and one is called si face. So, if we all know that CIP protocol CIP rules that is the based upon the priority rules we assign the configuration R or S. So, if it is clockwise then we tell the re face so, that if it is clockwise and if it is si face, then it is if it is anti-clockwise, then it is si face. So, you have to same CIP protocols you have to apply here on this centre, and then you see that which one and you can assign.

So, now, whether you will how the depending on the attack, it will give a different enantio selectivity. So, let us see how it is possible I will give a very common example. Now, this is fine that now it is understandable that your let us say your catalyst here because we or your any reagent which will be reacting with this prochiral moiety it can attack from the lower this side or the upward side.

Now, if you see the or if you have encountered or carefully, have you seen that this is fine for the chiral catalyst the chiral catalyst if we use then that is with a specific R or S also called plus or minus. So, the chiral catalyst will have a specific site it is called the enantiomeric selectivity and it will give a particular stereoisomers whether depending about the enantio selectivity it will give the R or S now, many cases it is observed that although your catalyst is not chiral, but still we get the stereo selectivity stereocenter in the resultant product how it is possible.

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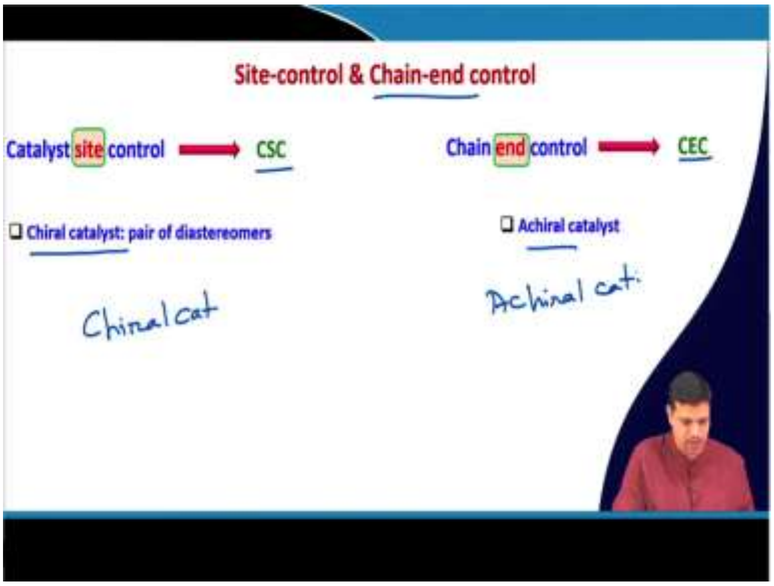

Site-control & Chain-end control

Catalyst site control → CSC

Chain end control → CEC

❑ Chiral catalyst: pair of diastereomers

Chiral cat

❑ Achiral catalyst

Achiral cat.

To understand this one, we have to clearly understand the concept of the site control and chain end control. So, what is site control and chain end control here you will see in the catalyst site control there will be chiral catalyst involved and this chiral catalyst basically induces the stereo selectivity of the substrate This is called the CSC that is the site control.

And for the Achiral catalysts many case examples are there for Achiral catalyst. Although catalyst is not chiral you will see there is a stereogenic centre is formed in my product and how it is done here it is created through chain end control what is called CEC. So, two mechanisms are operated, one is the catalyst side control that is for the chiral catalyst and one chain end control that is the Achiral catalyst. So now we will try to understand how this CSC and the CEC are operated in some of the well-developed reaction to understand more clearly. So let us see.

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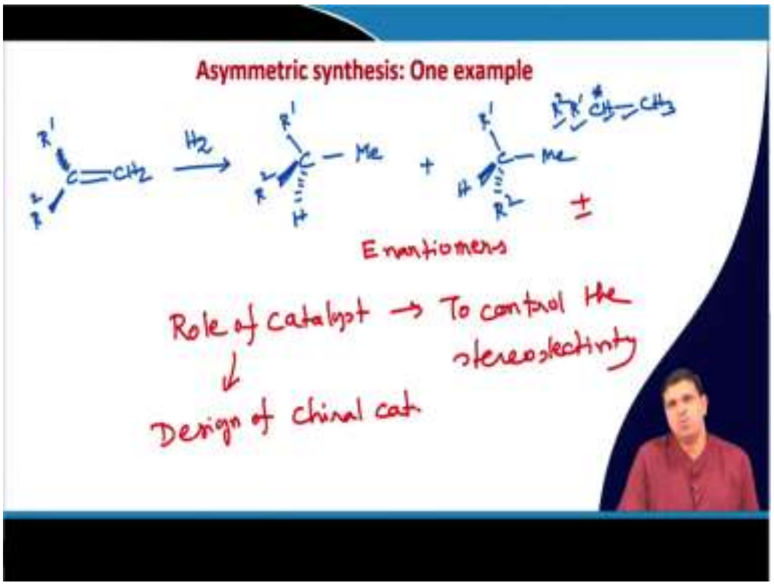

Asymmetric synthesis: One example

Enantiomers

Role of catalyst → To control the stereoselectivity

↓

Design of chiral cat.

So I will give one basic example. How the Asymmetric synthesis are operative? So, I will give one example of let us say, and here R1, and R let us say 2. So this is. Now what will happen if you do the hydrogenation I am not writing the condition. I am just doing addition of the H, H. So, I am doing the hydrogenation So, what are the possible the compound we know that it will form the R1, R2 H and CH3 so that would be the product.

But you see that this is the stereogenic centre because you have a one, two, three and four different substituents at that tetrahedral centre carbon centre. So, how does it possible you will see that here, so and this one and another one what are the possibilities another possibilities are R1, R2. So, here you will see that these two compounds. What are they what are the relation between these two these are enantiomers and you know that these enantiomers are the properties are exactly same for the enantiomers.

So, it is really difficult to isolate and purify both the enantiomers and most of the cases it remains as a racemic mixture if there is no stereo selectivity in the reaction. So, here is the role of the catalyst. So, we will try to understand the role of catalyst how to control the, to control the stereo selectivity and thus will try to understand the design of chiral catalyst how to make my catalyst which will act as this stereoselective catalyst to give one enantiomer on priority basis.

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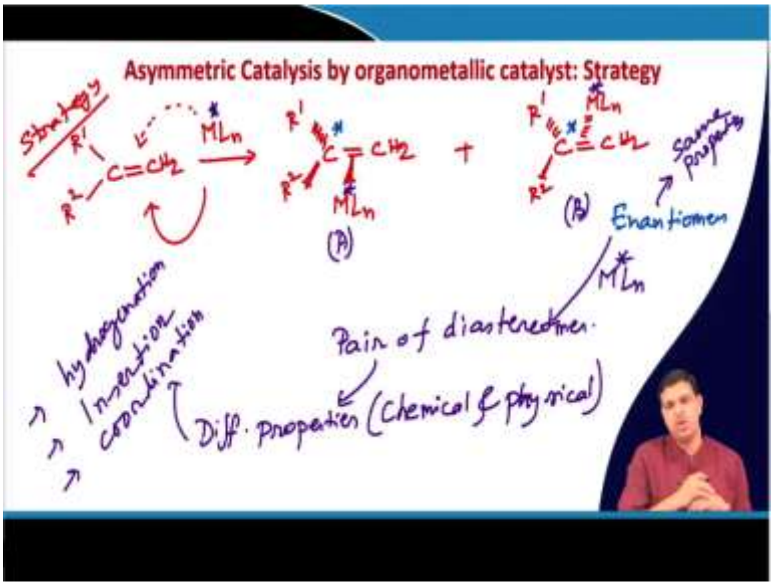
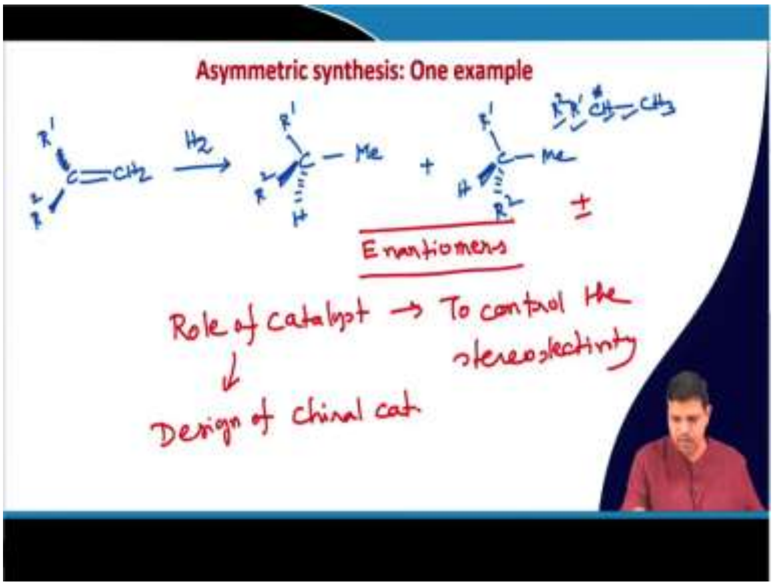

Asymmetric Catalysis by organometallic catalyst: Strategy

Strategy

Pair of diastereomer.

Diff. properties (Chemical & physical)


Asymmetric synthesis: One example

Enantiomers

Role of catalyst → To control the stereoselectivity

Design of chiral cat.

So, we will discuss with one strategy that how it can be done. So, in the last slide you will be saw that these are the enantiomers and the properties are exactly same. Now, how we can make different the properties chemical and the physical properties any idea? Yes, we have to make diastereomers How it is possible? So, let us take one example just we basically rather we will discuss the strategy.

So, now suppose I am now react, I am now reacting with one metal center MLn. This is I am trying to show in a very general way. So, we will discuss later with specific metals and ligands. So, what will happen now, this one can coordinate in it will be better to show like this one and here you will see that this will MLn. Now, another one as I told that this one is reacting from the downwards and another possibility this can react as upwards. So, what will happen then now.

So, what has happened in this case? In this case basically now, it has become the stereogenic centre and these are enantiomers, but now think how to make the diastereomers. If my this one is a chiral with the particular R or S. So, this will be chiral. Now what will happen now this enantiomer in presence after coordination with a chiral catalyst what will form, a pair of so, this is suppose A this is suppose B so it will form pair of diastereomers.

Now if it is pair of diastereomers then what will happen the in this case the same properties now here different properties chemical and physical. So, and that is why there is the different in the reaction step as example like in the last, in the last slide you will see hydrogenation either hydrogenation or in our case insertion and the coordination of the polymer. So, this is the strategic way for asymmetric catalysis where you can preferentially get one enantioselective one particular stereoisomer.

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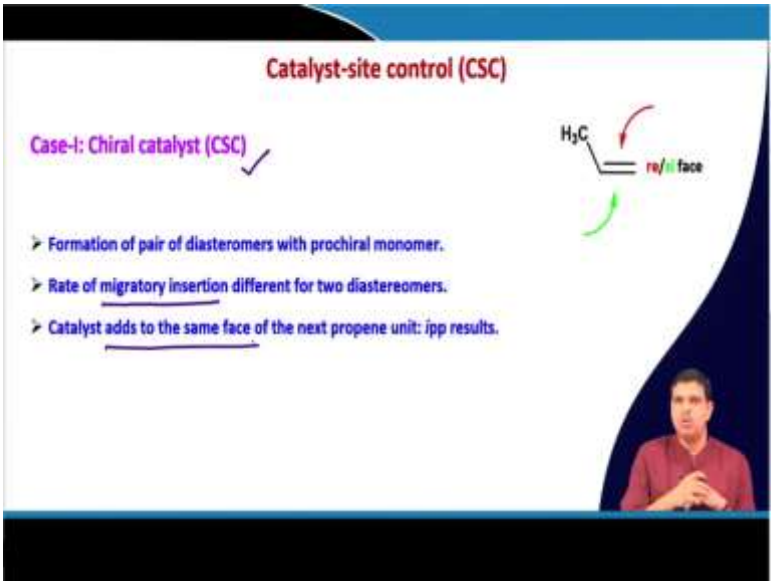
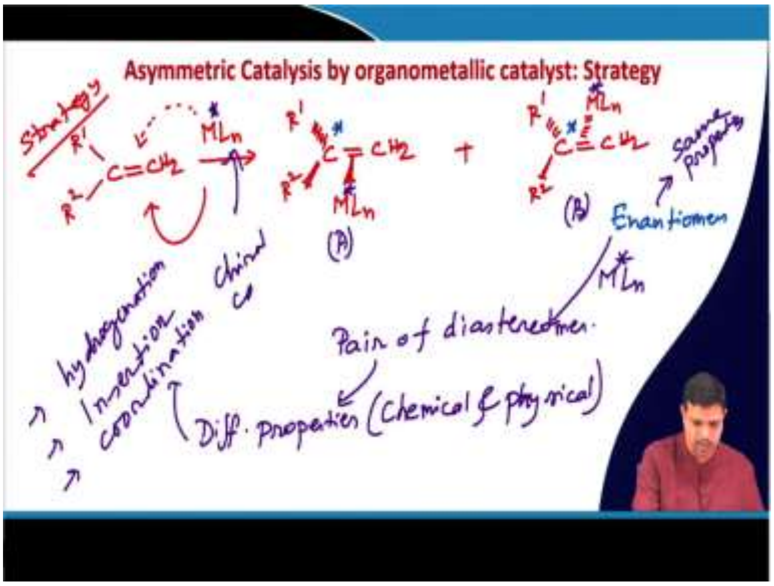


Catalyst-site control (CSC)

Case-I: Chiral catalyst (CSC) ✓

- Formation of pair of diasteromers with prochiral monomer.
- Rate of migratory insertion different for two diastereomers.
- Catalyst adds to the same face of the next propene unit: *ipp* results.



Asymmetric Catalysis by organometallic catalyst: Strategy

So, this one you will see this is called the catalyst site control where you are using a chiral catalyst. So, this one is the chiral catalyst here as you see here we are I am taking as a this is the chiral catalyst. So, in a summary the catalyst site control where you will be using a chiral catalyst. So, what is happening you are forming a pair of diastereomers with prochiral monomer here propylene and for particular this polymerization reactions what we are doing, we are basically making two different situation where the migratory insertion rate will be different and that is why you will get.

So, one diastereomers will have a higher rate of migration and one other one will have the lower rate of migration. So, that is why you will get will get a stereoselective polymer using the chiral catalyst. Because the catalyst adds to the same face of the next propene unit. And that is the way we will get the isotactic polypropylene.

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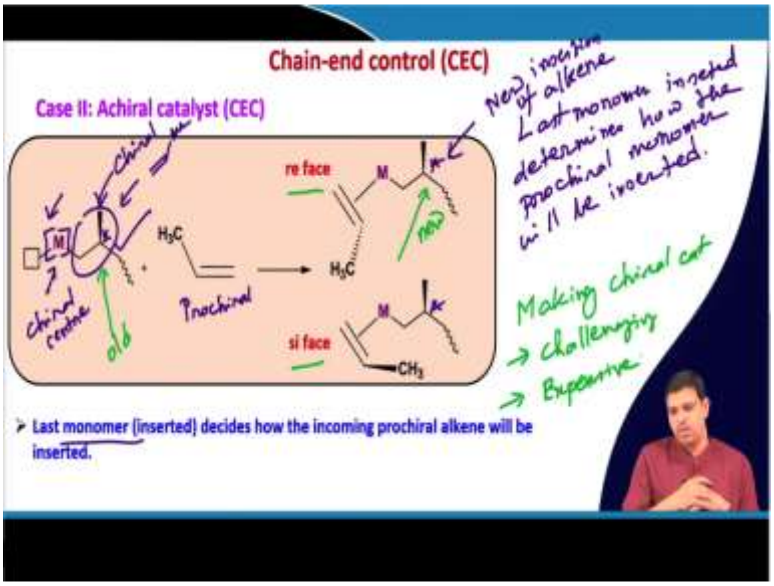

Chain-end control (CEC)

Case II: Achiral catalyst (CEC)

- Last monomer (inserted) decides how the incoming prochiral alkene will be inserted.

Now, in the other case, that is the chain end control where we will be not using chiral catalyst, but still will be getting the stereo selectivity how it is possible very interesting. So, here you will see that let us see this one this this is the metal centre and this catalyst is not chiral but still we will be getting the chiral catalyst chiral centre. So, how it is possible let us see, this is the prochiral and this is not the chiral centre.

Now, in this case, you will see that the last step of the monomer insertion last monomer will dictate the coordination of the next alkene and here you will see the last monomer inserted determines how the prochiral monomer will be inserted So, here you will see that this has been formed this centre has been formed by the alkene the propylene coordination, so, that is the last step and as it is a stereo centre this one, so, this one is the stereo centre.

So, this is not the chiral but this environment is the chiral environment. So, this chiral environment will basically dictates the specific site of the alkene coordination and that is the way the way it actually tunes or creates the stereo centre of the incoming monomer. So, here you will see that was the previous and here you will see that is formed after the new insertion of alkene. So, here this case, this case the stereo centre is formed from just last insertion of the alkene and this stereo centre again it is formed after the insertion of the new alkene. So, this is the old the last one and that is the new as this centre is the chiral.

So, the addition of the alkene is happening on the chiral environment and that is why the it is preferentially give either the re face attack or si face attack depending on the stereogenic environment and that is the way the prefers the particular stereoregularity in the polymer that is actually more interesting than the CSC and advantage is that you no need to make a chiral catalyst designing making a chiral catalyst is more challenging and also expensive because you have to make the chiral ligand for that and that chiral ligand making is expensive pathway.

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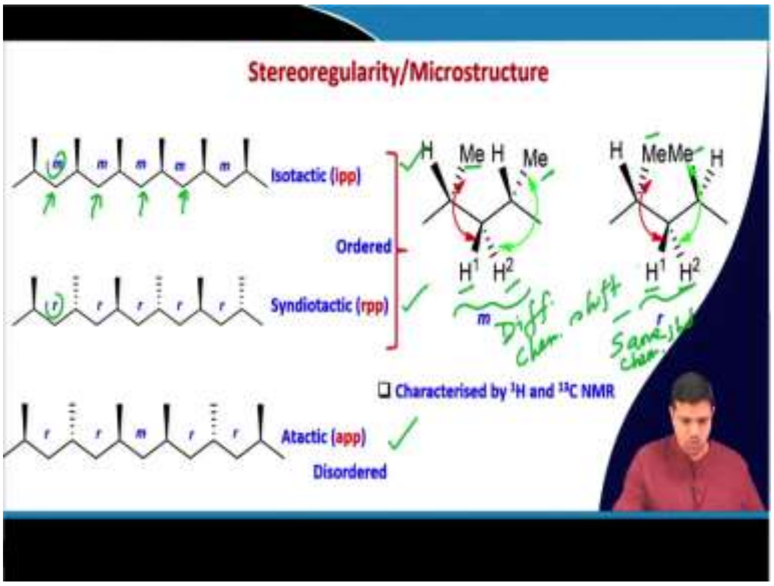

Stereoregularity/Microstructure

Isotactic (ipp)

Ordered

Syndiotactic (rpp)

☐ Characterised by ^1H and ^{13}C NMR

Atactic (app)

Disordered

So, we discussed in the last classes, but just want to recall that depending on the pathway, you can make isotactic, syndiotactic or atactic polypropylene and as you know that we can assign this CH2 as m meso r in this to using the two small words that is the m or the r and how it is how we can give the meso here you will see that in this case where this H2 and this methyl both are below and here this H and this methyl is one is above and one is below that means these two hydrogens will feel different chemical shift in the proton NMR and this case is this H2 and this methyl one is above and below and here H1 and methyl one above and below So, this will be the same chemical shift and here it will be different chemical shift. So, this one we discussed in the last class I will not go in depth now.

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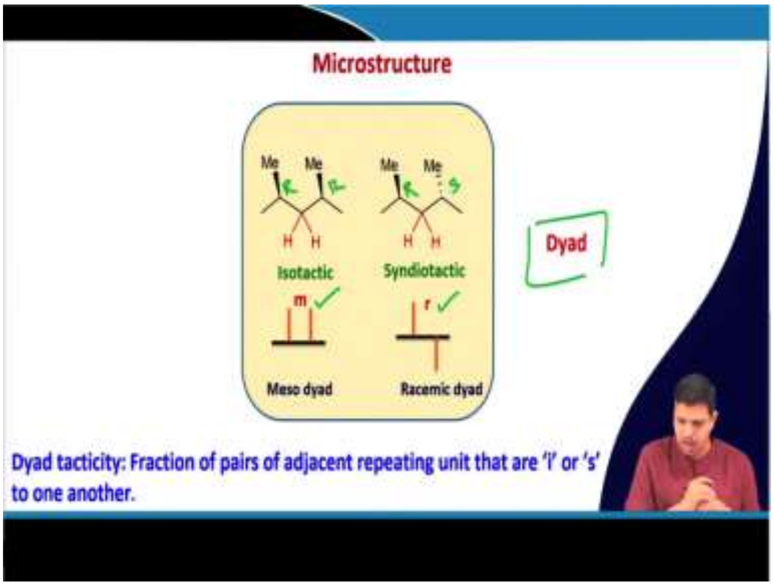
Microstructure

Dyad tacticity: Fraction of pairs of adjacent repeating unit that are 'i' or 's' to one another.

Now, and according to this convention, you can designate the Dyad where here you will see for this is for the meso this is we call m and this is the r where you will see this is if it is r and r then it is meso and if it is r and s this is the r. So, here the Dyad tacticity we put the name meso or the r so this is the meso dyad and this is racemic dyad. So we call i and this call also s the pair of dyad.

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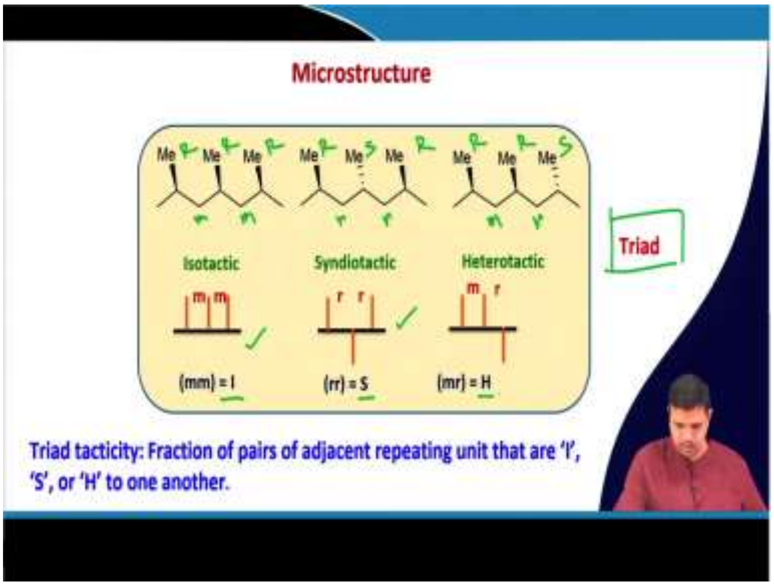
Microstructure

Triad tacticity: Fraction of pairs of adjacent repeating unit that are 'I', 'S', or 'H' to one another.

Similarly, you can make the triad. This is isotactic where both CH2 are m and m and this one is the syndiotactic where you have here r this is the r and this is the r that means here r r r here r s r, so this is the syndiotactic and this is the atactic r r s So, in this case what you are getting, you are getting m and you are getting here r like that. So, this is the triad. So, these are very useful for calculating how much trio regularity present in your polymer. So, this will be very important for our future discussion. So, this is called I, this is called S, this is a capital I, S, H isotactic syndiotactic or hetero atactic.

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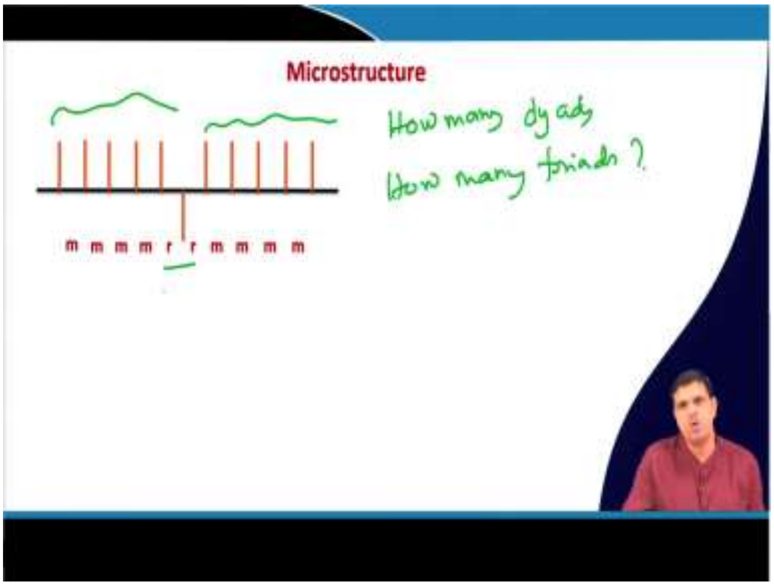

Microstructure

How many dyads

How many triads ?

So, in this way you can calculate also that how many dyads and traids are possible. So, here it is a how many dyads and how many triads we discussed in the previous classes. And you can see here this portion is the m and here again this portion is the m and this is the r and this knowledge is required because I told you that in many cases you will see there is a defect in the stereoregularity. So, that how much defect is there how much stereoregularity there this information is very much important to calculate the stereoregularity.

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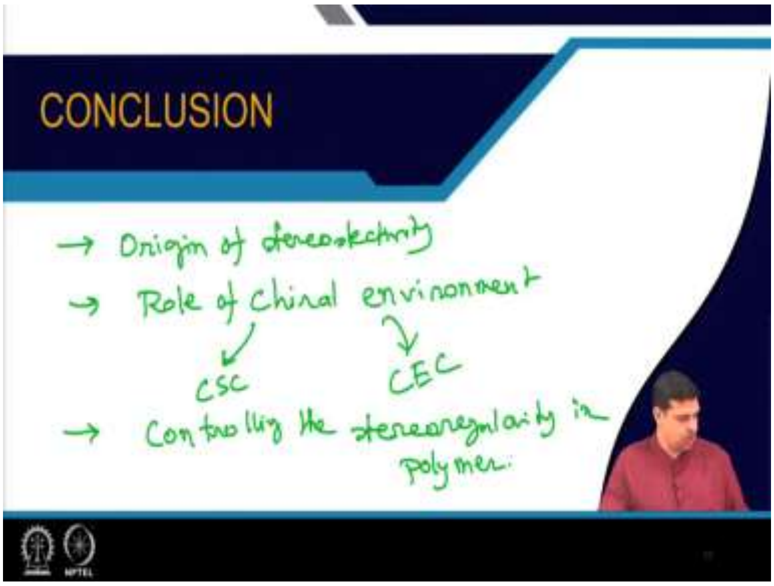

CONCLUSION

→ Origin of stereoselectivity

→ Role of chiral environment

CSC

CEC

→ Controlling the stereoregularity in polymer.

So, in conclusion, we have discussed the origin of stereoselectivity, role of chiral environment either catalyst site control or chain end control. So, this will eventually give why the controlling the stereoregularity in Polymer while you will be using prochiral monomer.

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- Organotransition metal chemistry from bonding to catalysis by John Hartwig, University science books, 2010 ✓
- Principle of polymerisation by George Odian, Jhon Wiley & sons, 4th edition, 2004 ✓
- Basic organometallic chemistry by Gupta and Elias, University Press. ✓
- Polyolefins: 50 years after Ziegler and Natta II by Walter Kaminsky, Springer, 2013 ✓

So, we have discussed this section of the lecture from these books you can read all are easily available. So, thank you and in the next class we will be discussing the Ziegler-Natta catalysts. Where you will see how stereoregularity is possible with this catalyst. So, we will see you again in the next class. Thank you very much.