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

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Lecture 23

Symmetry of metallocene and Stereoregularity in polyolefin

Welcome to our class. So, in the last class if you remember we have discussed the role of catalyst that is the metallocene based catalyst that is the main catalyst and also role as co-catalyst that is the MAO or the Boron based catalyst which is also called as a Lewis acid based co-catalyst. So, we have discussed in depth what is the individual role of the catalyst and main catalyst and the co-catalyst and we discuss the mechanism in detail.

And we understood that how the metallocene compounds act as a polymerization of cat, as a polymerization catalyst for olefin compounds as example like ethylene, polyisopine and others similarly. We also discussed that what is the origin of the demand of the metallocene based catalyst, what was the disadvantage of the very famous catalyst for Nobel winning, Nobel winning, Nobel prize winning catalyst that is the Ziegler Natta catalyst. So, we discussed very detailed.

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Lecture 23: Symmetry of metallocene and Stereoregularity in polyolefin

Today we will discuss one more very unique feature of the metallocene based catalyst which make this category famous and that is the stereo selectivity. As you remember for theZiegler Natta catalyst, the stereo selectivity, the origin of the stereo selectivity was to understand the mechanism was really very difficult and also to tune the stereo selectivity it is very difficult as you saw that the titanium TI cl3 that is the active species of the polymerization catalyst that is really very difficult to understand because the stereo selectivity depends on the crystal in phases.

And you see that beta Ti cl3 that is the brown phase that is the performance of that beta Ti cl3 is poor than the Alpha, Gamma and Delta. But the most advantageous and the unique properties of the metallocene based catalyst is that you can regulate the stereo selectivity by changing the structure and the symmetry and how it is that we will discuss.

So, today we will discuss about the symmetry of metallocene and stereoregularity. So, you see these two points, the two words, one is the symmetry and one is the stereoregularity. So, what is the correlation between this, how we can tune the stereoregularity by changing the catalyst symmetry and the catalyst design that will discuss in the following classes.

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CONCEPTS COVERED

- Catalyst design ✓
- Symmetry of *ansa*-metallocene ✓
- Origin of stereoselectivity in polyolefin ✓
- Mechanism

So the concept cover will cover the catalyst design that is very important because according to your, our need we will design our catalyst choosing the right the ligands, the right the (())(3:37) units and obviously the metal center and the more specifically, the changing the substance on the CP or the fused CP ring that we discussed.

So, we will see that how the selectivity is correlated, can be correlated with the symmetry of the catalyst molecule and obviously, we will try to understand that which, in which mechanism it the polymerization propagates.

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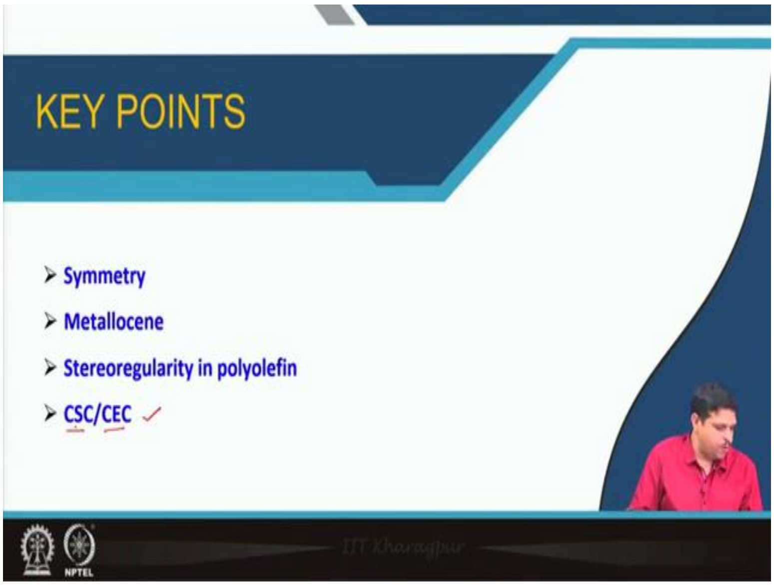

KEY POINTS

- Symmetry
- Metallocene
- Stereoregularity in polyolefin
- CSC/CEC ✓

If you remember that we discussed in the previous classes about the CSC that is the catalyst site control and CEC that is the chain end control, so this that how these two mechanism can be operated depending on the symmetry of the catalyst and my the resultant polymers which actually you are targeting for.

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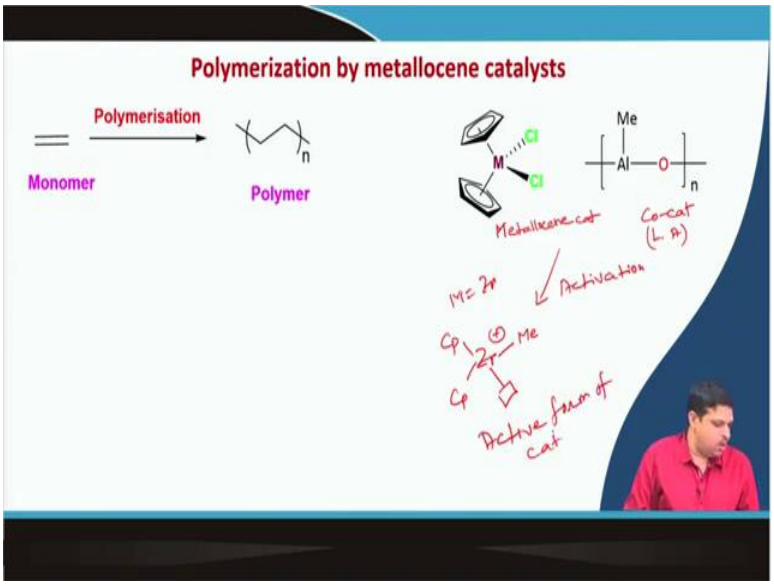

Polymerization by metallocene catalysts

So, now we are very clear that this kind of polymerization can be done by this catalytic system that is the metallocene that is the most simple metallocene based catalyst and this is the co-catalyst, that is the Lewis acid and in the last classes we learned that this co-catalyst is very much important to activate the main catalyst.

So, after activation what you will get, you will if metal is zirconium, then you will get this one, so I am writing just as a CP and here so we learned in the last class that MAO has a dual role; one first roll is the activation, first roll is the methylation and the second rule is the abstraction of the methyl to make the catalytic center is positive and as well as coordinatively unsaturated. So, this is my vacant site so this is the active form of catalyst.

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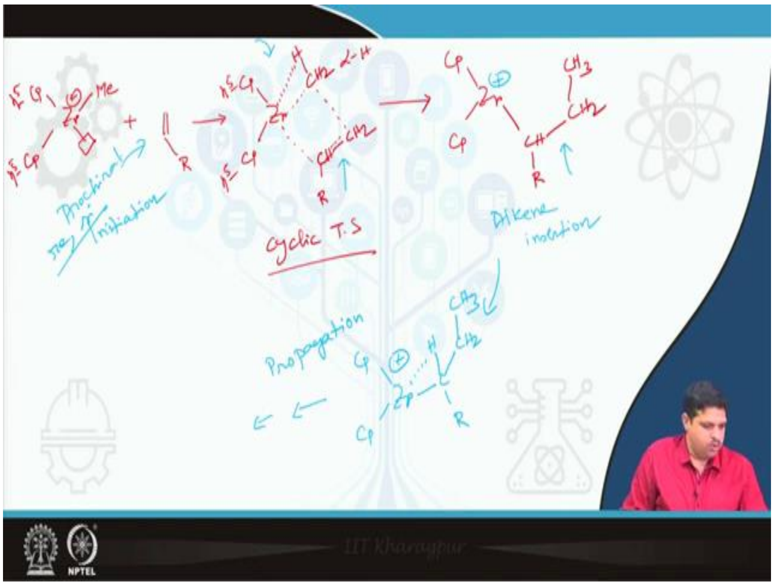

Now how the polymerization happens I just try to refresh your memory. So, if you have now this the active catalyst, so as I told that this is actually the eta phi and this is the and this is the positive charge and you have a vacant site here so if now if I let us say do the polymerization of any (())(6:28) molecule as example like propylene, if R is equal to methyl, then what will happen?

So, it will the undergo through a cyclic transition state like this one, so and you have a CH2, so I am writing as this one. Now this CH2 this is the alpha hydrogen, this alpha hydrogen can undergo a agostic interaction that is very unique with zirconium methylation bent methylation complex that it can undergo the alpha hydrogen agostic interaction, we have seen that the beta H agostic interaction is very much common.

Then it actually undergoes through a, the reaction through a four member transition state and this one like that and then so this is my the cyclic transition state and then this will be as is well the CP. And now this one will be CH R and CH2, CH2 and this will be the CH R CH2 and this will be actually CH3, because that carbon is, now that hydrogen is now here so this will be now CH3.

Now, what you saw here if you notice carefully so what happened? So, this has been this alkene has been inserted here, so this is the alkene insertion, fine. Now, so this is the positive charge as usual and then similarly what happened? So, you have a CH2, now CH3, now you have the R here and this hydrogen can again undergo the agostic interaction like here and this is the way it will undergo the polymerization reaction, so it will be. So, this is the basically the initiation step and after this would be propagation step.

Now, remember here so this will if it is pro chiral, so we discussed in depth in the last classes that it can undergo the reaction by attack by reface or psi phase and if the catalyst is the chiral then it will favour a specific attack either on re phase or psi phase and that is the origin of the stereoregular polymerization following the catalyst site control and if the catalyst if it is (())(10:46) control then the chiral environment after inserting to the, of the last pro chiral monomer will dictate the attack of the second monomer and that is the chain end control that we have discussed in the last classes.

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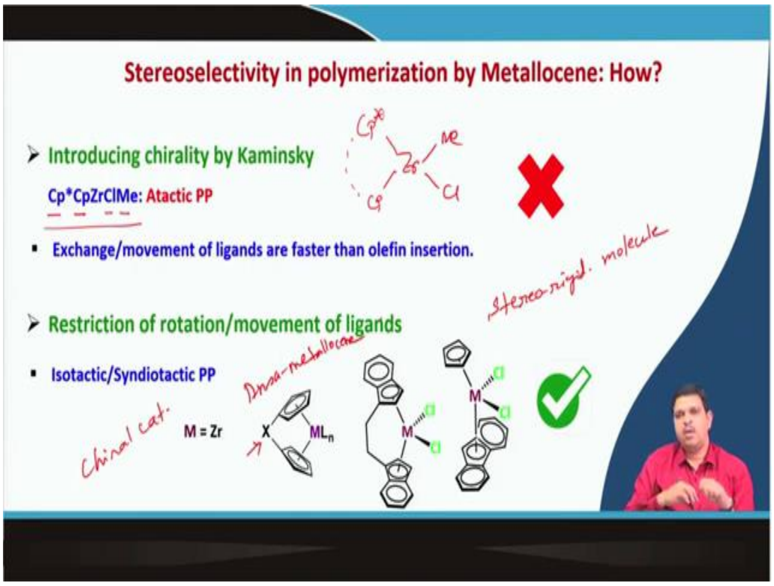


Stereoselectivity in polymerization by Metallocene: How?

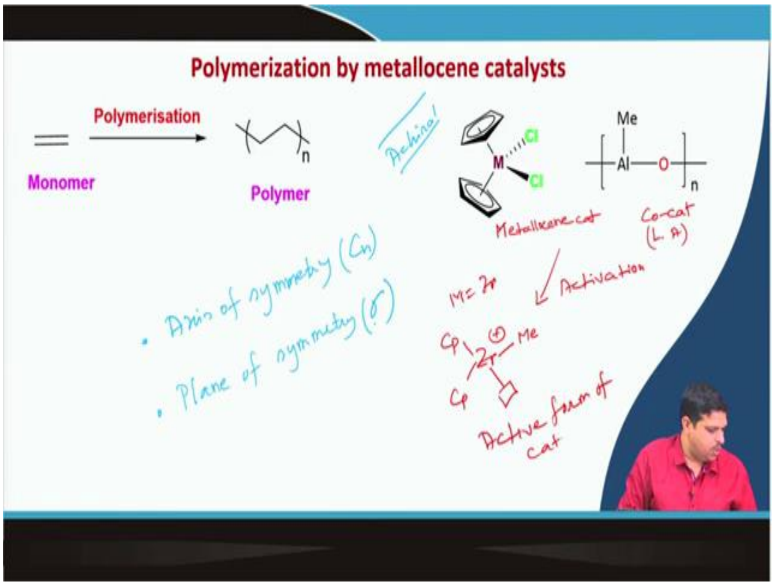
- Introducing chirality by Kaminsky

  Cp*CpZrClMe: Atactic PP

  - Exchange/movement of ligands are faster than olefin insertion.

- Restriction of rotation/movement of ligands

  - Isotactic/Syndiotactic PP



Polymerization by metallocene catalysts

- Axis of symmetry (Cn)
- Plane of symmetry (σ)

Now, the most unique and beauty is that how we can make it the stereo regular polymers, how, what I have to do on the metallocene because you see that this metallocene the simple, this metallocene this one, this is achiral so there is no way that you can get the stereoregular polymer, this is obvious, very obvious region you have a plane of symmetry and here you have to have a knowledge about the axis of symmetry in the following classes, plane of symmetry.

And I am sure that you know that axis of symmetry designate as Cn and plane of symmetry with designate as sigma, sigma can be Sigma H, Sigma V that is horizontal, vertical all those things. Now, how we can make it the chiral catalyst or induce the chirality in the catalyst so that we can get the stereoregular polymerization. So, there was a attempt to make the chiral polymer.

So, here the first one Kaminsky tried that we discussed that you put two different CP molecules and two different the substance of the zirconation, but very surprising that atactic polymer was formed not, so in the molecule it looks like that there is no plane of symmetry but what happens that due to the very rapid exchange and rotation of the these two CP rings, it is that the exchange is so fast that it is faster than the alkyl insertion and that is the reason that there is no stereoregularity observed in this kind of structure.

So, we have to do some strategy that how we can make this polymer as a stereo, how we can make this catalyst stereo-rigid catalyst so that we can get a permanent chiral environment. How we can do it? Very simple, we have to bind these two CP rings so just like a thread, thread it two CP rings so that there is no rotation or exchange. So, we are basically restricting its first rotation and first exchange.

So, you see that just simple restricting by the by putting the bridging unit just threading the two CP rings and then what will happen you will make the stereo-rigid molecule, molecule means here this here it is the metallocene molecules, so by bridging the two CP rings it is the easiest strategy, however, we can also make the non bridged CP metallocene compounds with the more strategic, strategistic design.

So, here you see that we can make the chiral catalyst however, in the last classes also we told that to make the stereoregularity, the absolute chiral molecule is not necessary, it can also undergo the stereoregularity, stereoregular polymerization by following the chain end control that will discuss later. So, as you know these are all falls in the category of Ansa metallocene that is means the two CP rings are threaded by a bridging units.

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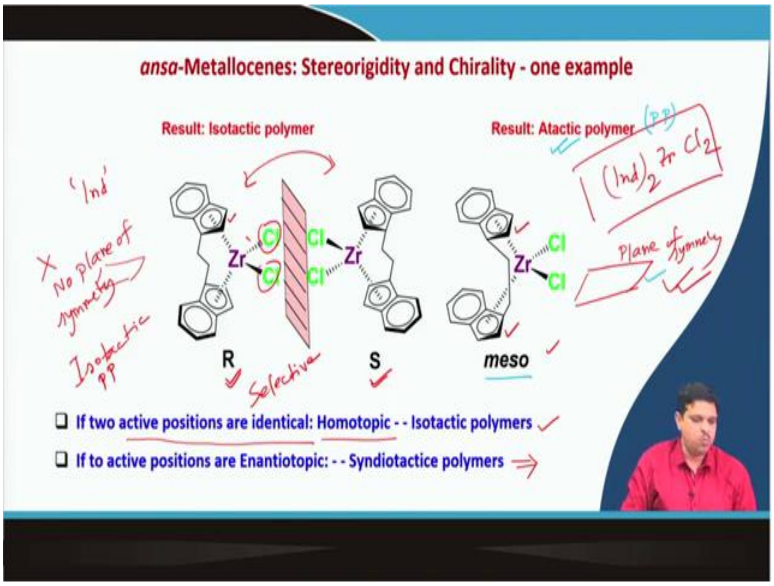

ansa-Metallocenes: Stereorigidity and Chirality - one example

Result: Isotactic polymer

Result: Atactic polymer

- ☐ If two active positions are identical: Homotopic - - Isotactic polymers
- ☐ If to active positions are Enantiotopic: - - Syndiotactice polymers

So, to understand in more depth let us take a case study where you see that these two CP rings are basically the indenial CP rings and here you see that we see very carefully that this one and this one is actually the chiral, because there is no plane of symmetry because you see this CP and this one the this benzene, this CP falls on the benzene ring, it does not fall on the CP ring.

That means here in this plane if you see this is no plane of symmetry, no plane of symmetry. So, it actually exists as R S form and you can get a, if you put a mirror so these two are actually, these two are actually the enantiomers, R and S; so super impossible mirror image. Now, if you see this one so this is like ind 2 Zr Cl 2 this is the composition of this catalyst.

Now, if you see this structure so this is actually see these CP rings are, this CP rings has basically just fall on above each other. So, that means there is a plane of symmetry exist, so this is there is a plane of symmetry exist here, but here no plane of symmetry. So, that means this is selective catalyst, catalyst and with this one we will get the iso tactic polymer we will discuss later how we will get it, I am just now trying to give a flavour that same composition, same ligands but how we can get a different conformer of the catalyst.

And what will be the difference in symmetry, so from, if you use this catalyst, you will get a isotactic polypropylene no matter whether you use the pure R or pure S or resmic mixture because in the resmic mixture, both R and S will do the polymerization individually. So, you will get in both the cases like individual R or individual S or resmic mixture of R S catalyst you will get the isotactic polymer.

Why, what is the reason? Because in this case two active positions are identical and that is why what you will get these are the homotopic, this two active position means I am telling this one and this one, these are the active positions because the your monomer actually in one side it coordinates and then it undergo the insertion to the other side, this side let us say. So, that we discussed in the last classes. So, you will get the isotactic polymers.

If you specially design you can also get the, you can make the two active position enantiotopic and in that case you will get the syndiotactive polymers that you need to design or induce the special symmetry on the metal region that will discuss in the next slide. Now, you come to the third one. So, third one is obviously you see that here there is a plane of symmetry so this is basically the meso isomer of this in denial zirconium CL2 metal machine and this one you will get the atactic polymer because this is not a chiral catalyst, this is the acrylic catalyst.

So, in here you this polymerization will undergo through catalytic site control mechanism and you will get the atactic polymer if you, if your monomer is let us say propylene, pro chiral monomer, so you will get the atactic PP. So, this, with this example you will see that if you design your catalyst you can get a different type of the tacticity in the, on the same polymers. So, this is a one example, we will discuss in a very strategic way how we can induce the chirality and if you, if I give one catalyst how we will know that what polymer we will get or if you had target for a one particular tacticity what catalyst you will design or what catalyst you will select for your polymerization, fine.

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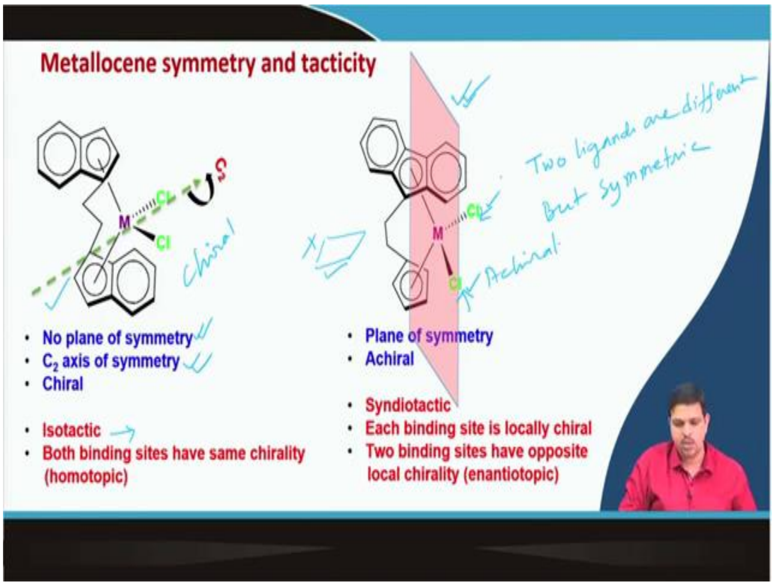


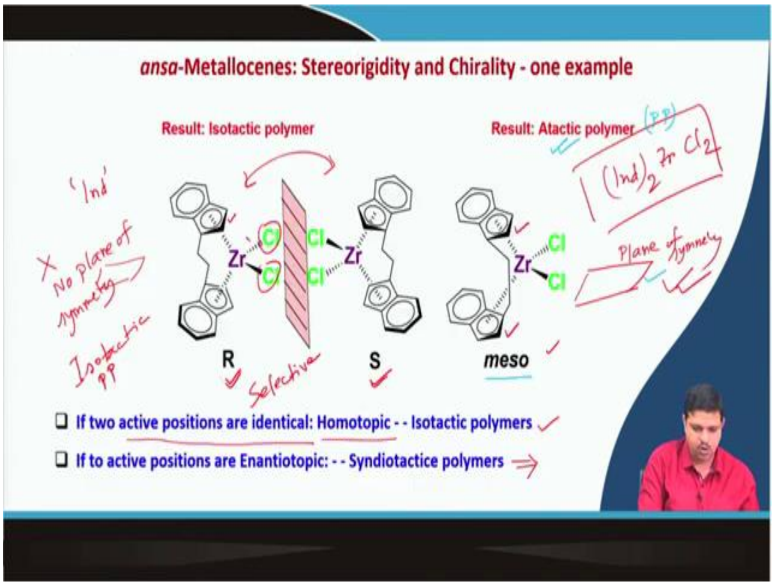
Metallocene symmetry and tacticity

- No plane of symmetry
- C_2 axis of symmetry
- Chiral

- Isotactic
- Both binding sites have same chirality (homotopic)

- Plane of symmetry
- Achiral

- Syndiotactic
- Each binding site is locally chiral
- Two binding sites have opposite local chirality (enantiotopic)



ansa-Metallocenes: Stereorigidity and Chirality - one example

Result: Isotactic polymer

Result: Atactic polymer

- ☐ If two active positions are identical: Homotopic - - Isotactic polymers
- ☐ If to active positions are Enantiotopic: - - Syndiotactice polymers

So, this one as I here, you saw here there are no plane of symmetry here, no plane of symmetry there is the same molecule actually I draw it here and it has a C 2 axis of symmetry that will discuss in the following classes, so that you will get the isotactic polymers because both binding sides have the same chirality and those are homotopic. Now, as I told that if you have, if you design in a very strategic judiciously, then you can also get the syndiotactic polymers and what you have to do let us see in this catalyst.

So, this catalyst you will see here, here the two CP rings are different but symmetric, the two ligands, two ligands are different but symmetric individually. So, you will have a, you do not have a plane of this plane of symmetry you do not have, this one, but you have this plane of symmetry, so this is actually achiral because you have a plane of symmetry. In this case, no plane of symmetry, so this is actually the chiral, this is the chiral molecule and this is the achiral molecule.

Now, each binding site is locally chiral here and two binding sites have opposite local chirality and this that is why this site and this site has a two opposite local chirality and that is why you will get the syndiotactic polymers, it in, it is you will not get atactic polymer because here the two sites because these you do not have this plane of symmetry but you have this plane of symmetry and the two binding sites this one and this one is actually is have a local chirality and have the opposite local chirality and that is why you will get the syndiotactic.

That is if one methyl is oriented R and another methyl in the polypropylene, it will be the neighboring methyl will be oriented as S opposite direction so R S, R S like that. So, if you design your catalyst, you can get the syndiotactic, you can get the atactic and you can get the isotactic polymer. That is the most beauty in this metallocene based kind of polymers.

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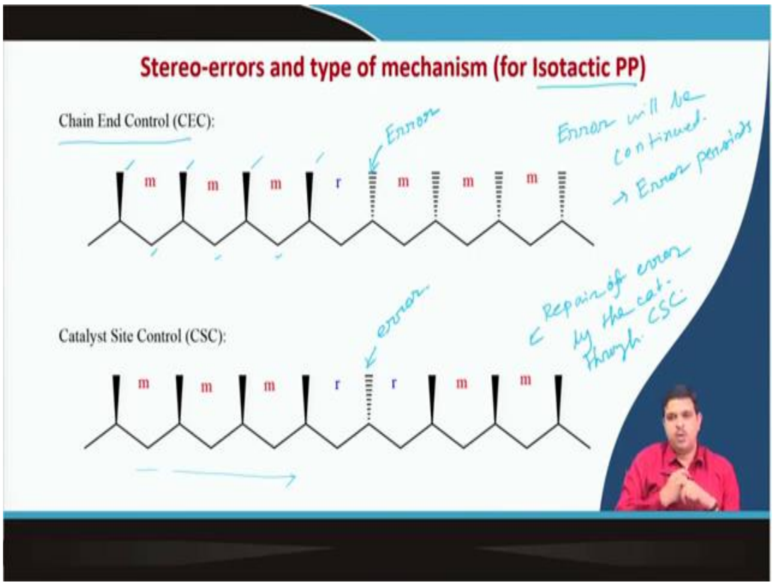

Stereo-errors and type of mechanism (for Isotactic PP)

Chain End Control (CEC):

Catalyst Site Control (CSC):

And you can use as a toolbox that whatever you need you select your catalyst and you do the polymerization, you will get your target polymers. Now, in many cases what happens this tacticity also depends on the temperature, and also the solvent and also sometimes depends due to various reason there you may observe some error. So, we are like for isotastic polypropylene, all the methyl should be on the same orientation that means you, we should get all like a r r r r like that in according to the CIP priority rules.

But many time what happens there is a errorness, that errorness is due to the various reason. Now, this is also very important because this is also helpful to understand that whether this polymer chain is undergoing through CSC mechanism or chain end control mechanism, whether catalyst site control or chain end control. So, this error is also advantageous sometimes, let us try to understand what is this error and what is the relation between the type of mechanism, that is the CSC or CSC.

So, let us first consider the isotactic polypropylene. Now, if it is going through a chain end control let us say, so I am first targeting chain end control. So, let us say for isotactic polypropylene what will, what is the ideal scenario that all the methyl will be on the same direction. That means this CH2 will be m m m m. Now, suppose there is a error, so this is my error, so error means you see that this one will now in a different orientation.

So, as it is a chain end control, that means, the last inserted monomer will dictate the insertion of the next monomer. So, what will happen this will after this insertion this methyl will be on the same orientation as the methyl which was inserted as error. So, this error will be preserved. So, in this case you will see the error will be continued or persist.

But in the site chain that is the catalyst site chain control, what you will see that if you for if you targeting for isotastic polymerization now it is going on fine no problem. Now this is the error. Now, if you consider the catalyst site control if you remember that the propagation for the stereoregular polymerization is induced by the chirality of the catalyst, so it does not matter how the last monomer was inserted.

So, this will actually now repair its error but this one is error persists. So, you see that for catalyst site control if you are targeting for isotactic polymerization if there is a error, then that error will be repaired by the catalyst, repair of error by the catalyst through CSC is interesting now, yes, very interesting.

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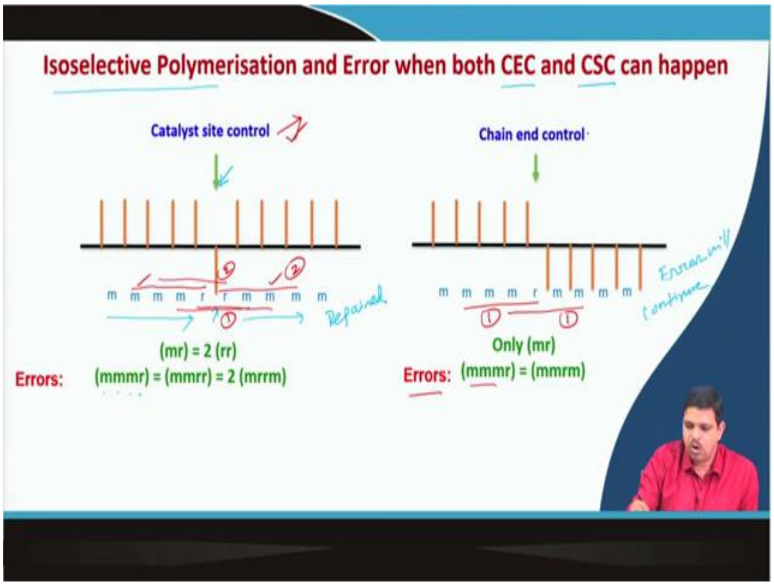


Isoselective Polymerisation and Error when both CEC and CSC can happen

Catalyst site control

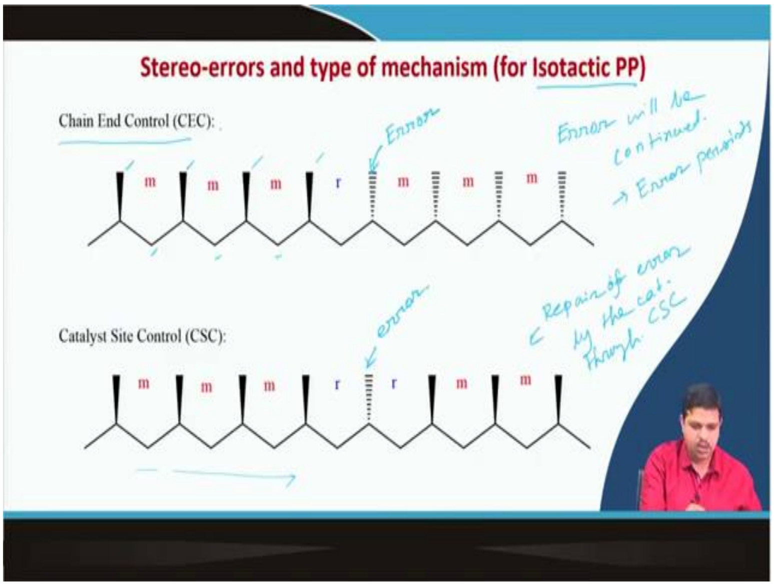
Chain end control

(mr) = 2 (rr)

Errors: (mmmr) = (mmrr) = 2 (mrrm)

Only (mr)

Errors: (mmmr) = (mmrm)



Stereo-errors and type of mechanism (for Isotactic PP)

Chain End Control (CEC):

Catalyst Site Control (CSC):

Now, shown here in a very simplified way that is the call line drawing we have learned in the last classes. So, this is the isoselective polymerization when both CEC and CSC that is the site chain and end control are operating, as I showed in the last, in the last slide you see that this if you consider this is the chain end control so here you will see this is my error, so all will be first m m m, that is no problem going, fine. Now this is my error and then what happened as it is a catalyst site control so it is repaired again, so it is now repaired.

And this is the chain end control so it is not repaired the error will continue, error will continue. Now, this one how you will identify, this can identify by proton and 13C spectra. Now, you will see here is a very simple calculation or observation so here you will see the error m you see that so we learn in the last classes diad, triad and now here you will see here the m m m r, m m m r, so this is, I will change the link then it will be more easily understandable.

So, here you will see triple m this one, m m r r this one, now m r r, m r r m, so you see m r r m is one unit, this is one unit. Now, triple m r, so this triple m r, this triple m r so that means two unit and m m r r, m m r r if you go from this site one and if you goes this site then all these also tune it.

So, by looking at very carefully the proton and C13 spectra you will get the, you will get to know that whether it is the polymerization undergoes through catalyst site control or chain end control. And in this case if you see the what will be the error, you will see that m m r here triple m r and here m m r this 1, so this is basically same number, so this one, so you will get this one 1 and this one you will 1 so by looking at the intensity of the corresponding CH2 protons you will able to know that whether it is following the catalyst site control or chain end control.

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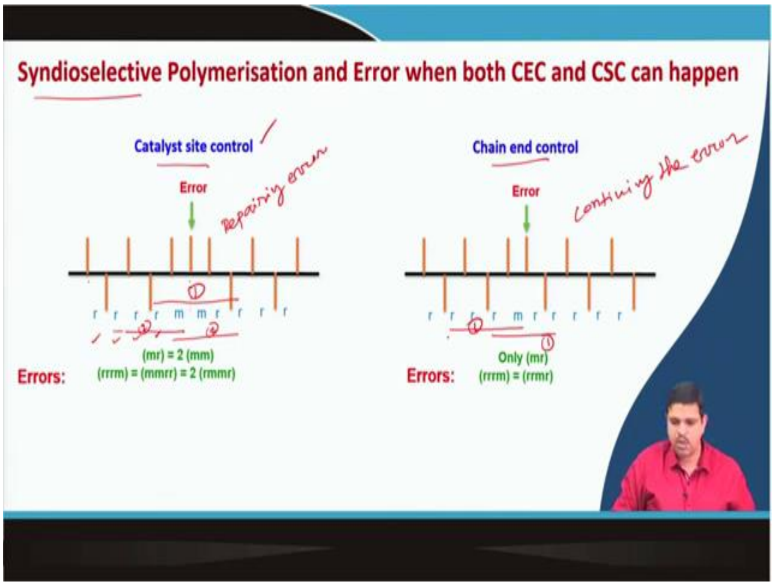

Syndioselective Polymerisation and Error when both CEC and CSC can happen

Errors: (mr) = 2 (mm)
(rrrm) = (mmrr) = 2 (rmmr)

Errors: Only (mr)
(rrrm) = (rrmr)

Similarly, for if you, for syndioselective polymerization if there is any error, then for catalyst type control you will see that for syndioselective so this is my r so in a alternate orientation of the methyl groups, so r r r r, now this is my error see this is my error. So, this one supposed to be here but it is not there, so as it is a catalyst site control it will repair so here again you will see after this one it is the repairing error.

And opposite scenery happens for chain end control, here there is no repairing that will be continuing, continuing the error. And due to this one what you will get, you will see that r r r m that is this one that is the m m r r, m m r r this one you will get the two units, this is also two units if you come from this site and this one r m m r that one you will get 1 unit so by looking at the intensity of this CH2 protons or that CH2 carbon you will be able to know that whether it is undergoing through catalyst site control or not.

And in this case, you will see the triple r m this one and r r m m r that is the this one if the number of this kind of quadrates will be same, so this is also 1, this is also 1. So, this is one of the way by proton and C13 spectra although you need a high resolution spectra at least 400 or 500 megahertz NMR spectroscopy you will be able to know whether what mechanism it is undergoing, fine.

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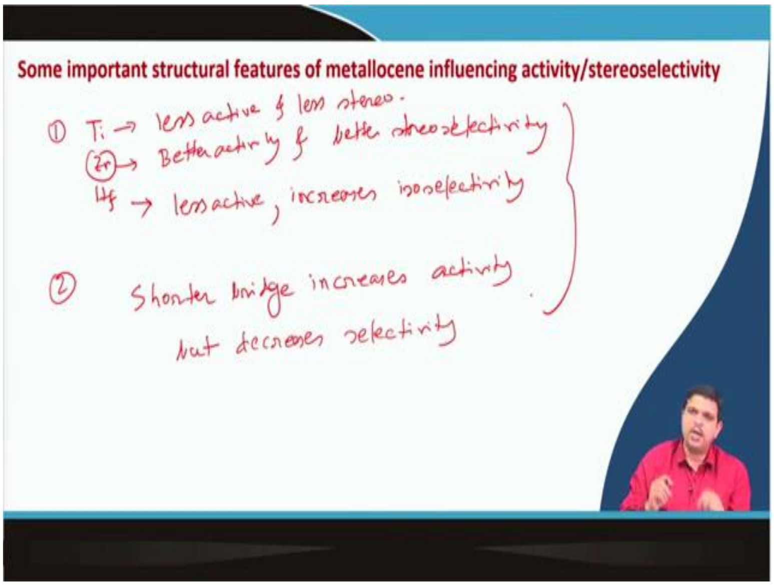

Some important structural features of metallocene influencing activity/stereoselectivity

① Ti → less active & less stereo.
Ⓩr → Better activity & bette stereoselectivity
Hf → less active, increases isoselectivity

② Shorter bridge increases activity
but decreases selectivity

So, you some of the important points you have to consider for this kind of catalyst, one is that I just very briefly I will mention that if we have titanium, zirconium or hafnium of the same group and if you consider the same ligands, so always the zirconium actually shows the better activity and better stereoselectivity, always. Titanium has less active and also less stereoselectivity. And hafnium also less active but increases iso selectivity. And another important point that shorter bridge increases the activity but decreases selectivity.

Why? Because if bridge is shorter then your openingness on the active sites will be more, so then there will be preferential attack of the whether the re or psi phase that will be the less selective and due to that one your, the bridging should be in a critical length it should not be very short and also it should not be really big long. So, you have to have proper design of the catalyst. So, these two points are also important for designing your effective catalyst which will give the better activity and also the better selectivity.

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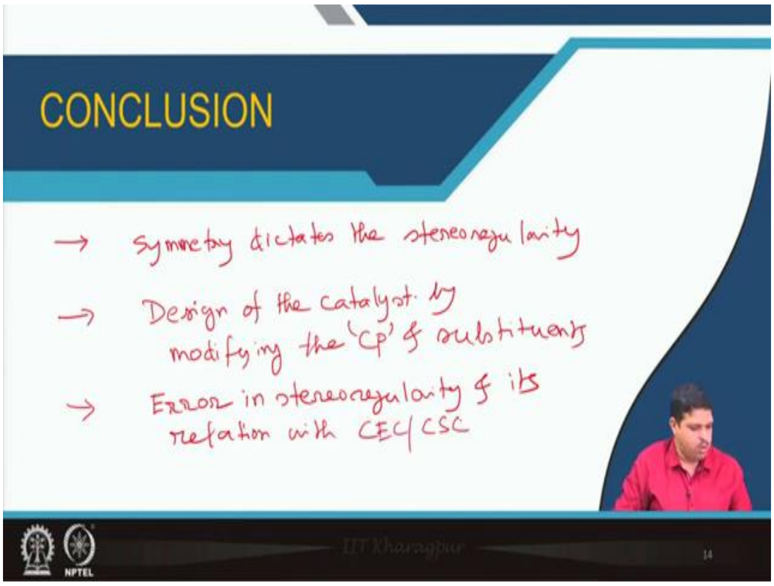

CONCLUSION

→ Symmetry dictates the stereoregularity

→ Design of the catalyst by modifying the 'Cp' & substituents

→ Error in stereoregularity & its relation with CEC/CSC

So, in today's class we, what we have learned? We have learned the how the symmetry dictates the stereoregularity and is basically we learned the design of the catalyst by modifying the CP and substituents. And we also discussed that the error in stereoregularity and its relation with chain end control and catalyst site control mechanism.

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So, in the next class we will continue the symmetry the correlation between the metallocene symmetry and the stereoregularity, we will discuss by case to case with a specific category of the metallocene molecules and then we will see what symmetry are there and what symmetries are responsible for getting the isotactic or syndiotactic or atactic polymers. So, see you in the next class which will be very exciting and important. Thank you.