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

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Lecture 24

Symmetry of Metallocene and Stereoregularity in polyolefin (Contd.)

Welcome once again. So, in the last class we started to understand the correlation between the symmetry of the metallocene and the stereoregularity in polyolefin. And this is very important, this knowledge because you see, that if we, if I take a pro chiral monomer, then how we will control its stereoregularity and whether we can control by taking a particular catalyst or the condition.

So, we understood from the last class that if you, that little variation in the metallocene based molecules, you can change the tacticity which is the most beautiful and the unique properties of this metallocene based catalyst. And here actually, the metallocene catalyst wins over the Ziegler Natta catalyst. So, today we will continue and try to understand in a more depth and by taking a specific example in a very strategic way, one by one.

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Lecture 24: Symmetry of metallocene and Stereoregularity in polyolefin
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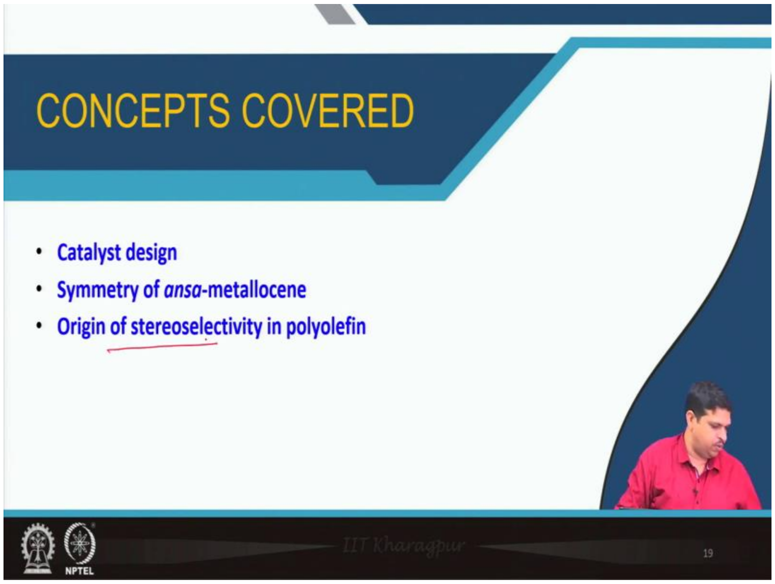
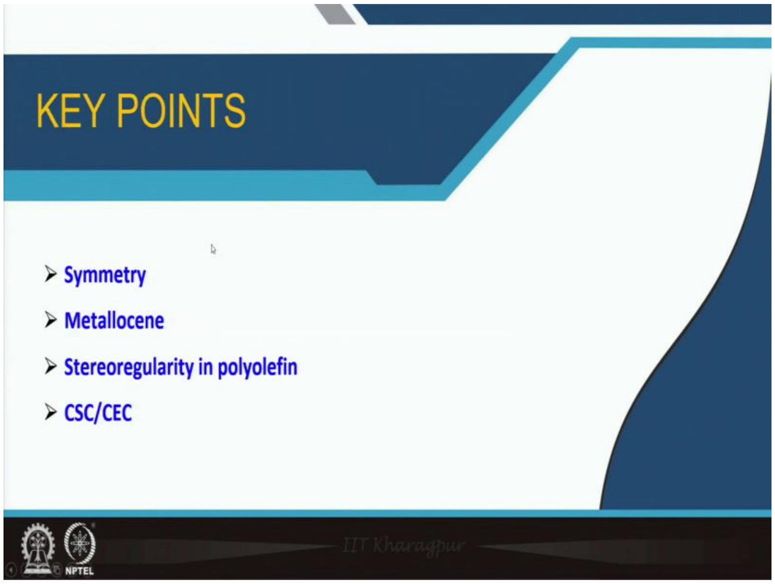


CONCEPTS COVERED

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



KEY POINTS

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

So, today we will try to understand in more detail about the catalyst design and the symmetry of the metallocene. And obviously, to understand the origin of the stereoselectivity. So, in the last class obviously we have, we now know that what kind of what is the basic structure of the metallocene, what are the variation of the ligands, what is the need of threading these two ligands by a bridging or special, that is to make the ansa metallocene based catalyst, and we also learned that how is the basic polymerization steps, the mechanism.

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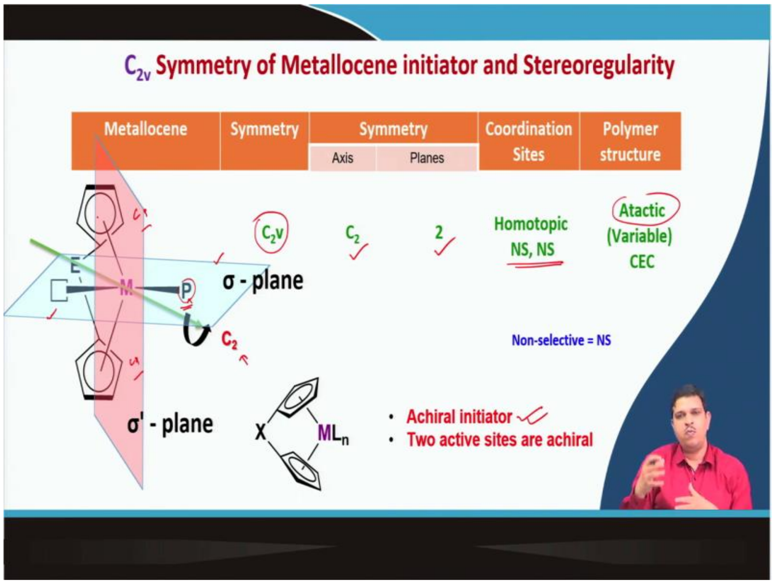

C_{2v} Symmetry of Metallocene initiator and Stereoregularity

Metallocene	Symmetry	Symmetry		Coordination Sites	Polymer structure
		Axis	Planes		
	C_2v	C_2	2	Homotopic NS, NS	Atactic (Variable) CEC

Non-selective = NS

- Achiral initiator
- Two active sites are achiral

So, let us start one by one. So, I am sure that you have a basic knowledge about the symmetry, very common symmetry elements like axis of symmetry, the plane of symmetry, like Cn or the sigma, they are different type of plane of symmetry are there. The inversion, center of inversion, I. So, that you have, I am sure that you have came across through physical or organic courses or stereochemistry courses. So, I will not go in depth to explain what are the symmetry operators, but this knowledge will be very, very useful to understand for today's class.

So, now, you, let us understand this basic structure. So, here this two Cp rings, this is one Cp ring, and this is one Cp ring. And here, actually I have shown, this p means the polymerization N, where it is a kind of intermediate species during the polymerization. And this is the vacant species. So, you can consider, it is like a two sides, there is no substituent, just imagine that only this Cp ring you have, Cp ring you have, and these two sides are vacant. Just imagine like that. And then you try to understand what are the symmetry.

So, so again I am telling that this P is not phosphorous or something, it is like, I am designating it as a polymer chain where the polymer propagation is there. And this one is the active side for the olefin coordination. Now, this one, if I show, this one has a C2 axis if you rotate through this axis, you will get the same conformer of this structure. So, you will basically, you will get a indistinguishable structure, if you rotate through this axis. This is C2, means 180 degree, through this axis.

Not only that, you have the one sigma plane here and also another sigma plane here. So, this blue sigma plane is basically the cutting to equal halves, identical halves, and also, if we consider the pink plane, it is also cutting this molecule into two equal halves. So, you have two sigma. One is sigma H, that is, and one is the sigma V. And that is why the symmetry of this molecule is basically C2 V. So, what axis you have, the symmetry elements? You have C2 and you have two planes.

As you have the two planes, that means this is a achiral molecule. So, initiator will achiral. So, you do not consider this one here. You just consider that two sides, let us say like two chlorides are there. Then you try to think that what is the symmetry. So, this is the achiral molecules or achiral metallocene initiator. So, two active sites are obviously the achiral and as the these are achiral So, you will get the non-selective propagation. That means you will get the atactic polymers if you start the polymerization with the propylene.

So, if symmetry, so where your both ligands are same, whether it is a bridged or unbridged, then if you have a symmetry like C2 and the two planes, then you would have a C2 V symmetry. And C2 V symmetry metallocene will give the atactic polymer. So, you no need to suppose you are trying to exp, develop the catalyst, metallocene based catalyst and you are targeting for atactic polymers, you should not do any trial an error. You have to understand logical way that what will be my symmetry and basic structure of my metallocene. Accordingly, you, either you select or you design your catalyst and go for the synthesis and the next step.

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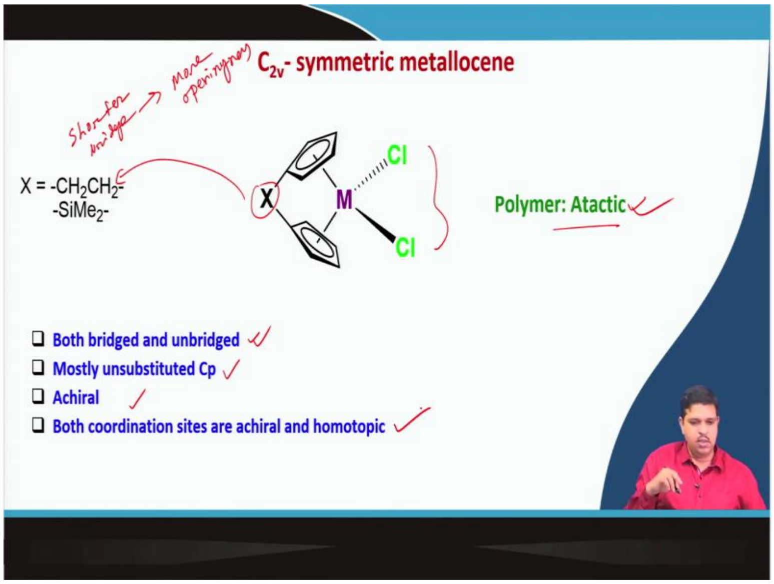

C_{2v}- symmetric metallocene

Shorter bridge → more openingness

$X = -CH_2CH_2-$
$-SiMe_2-$

Polymer: Atactic ✓

- ☐ Both bridged and unbridged ✓
- ☐ Mostly unsubstituted Cp ✓
- ☐ Achiral ✓
- ☐ Both coordination sites are achiral and homotopic ✓

So, in more detail here you will see that this, as I told that this is the C2 V, and why it is C2 V, I explained here that what are the symmetry elements are here, and you will see that this may be bridged or non-bridged. And for bridged like this X is the either the CH2CH2 ethane or the SiMe2, this kind of. One thing in the last class I told, that the selectivity also depends on the number of atoms in the bridging units because you see that if there is a shorter bridge, then means more openingness this side, more openingness.

That means there will be no, much stereoselectivity. Although this is achiral polymer. So, here there is no question of the stereoselectivity, but this is the good information, important information. So, the bridging unit also plays a role to induce or to tune the stereoregularity.

However, in this case, there is no question of the stereoregularity or you will get the atactic polymer, whether both bridged or unbridged, but mostly unsubstituted and symmetric Cp, molecule is achiral and why it atactic? Because both coordination sites are a chiral and homotopic. And that is the reason this C2 V symmetric metallocene initiators only will always give the atactic polymers.

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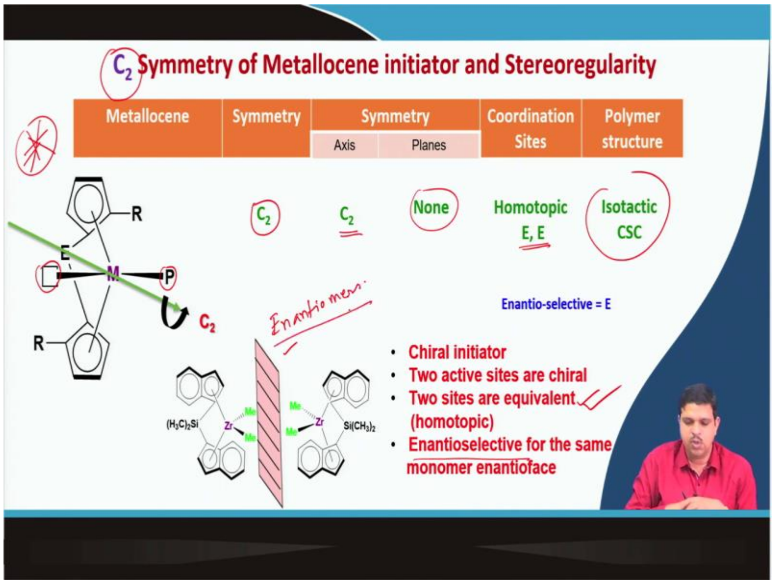

C_2 Symmetry of Metallocene initiator and Stereoregularity

Metallocene	Symmetry	Symmetry		Coordination Sites	Polymer structure
		Axis	Planes		
	C_2	C_2	None	Homotopic E, E	Isotactic CSC

Enantio-selective = E

- Chiral initiator
- Two active sites are chiral
- Two sites are equivalent (homotopic)
- Enantioselective for the same monomer enantioface

Now this one is very important, this category, this is the C2, the earlier case is the C2 V. This C2 is actually the very popular and most successful catalyst, the category of the metallocenes which will give you a isotactic polymer. It is very limited. Only two symmetry, one is the C2 and one the C1 will give the isotactic polymers. And C2 is the most famous and most successful metallocene chemistry, which gives the almost 100 percent isotacticity in the polypropylene.

So, what will it look like? What will be the ligands and how will the structure look like? So, it is like this one. So, what symmetry should be here, you have to have C2, and there is no plane of symmetry. That means the molecule is chiral molecules. And the, and here you will see that two active sites are chiral, means these two active, side this one and this one, two active sites are chiral because there is no plane of symmetry, and two active sites are equivalent, that means homotopic.

And ensure, and these two active sites which are equivalent and homotopic, these are actually enantioselective, that is for the same monomer enantio phase. And that is the reason that you will get the isotactic polymer for the C2 symmetry metallocene initiator. So, E means enantioselective. That means the, it is for the chiral molecules. We will get the isotactic polymers. So, this as I told, this is the most important category of the metallocene compounds where to get the isotactic polymers.

So, as I told, these are very limited, only the C2 symmetry is the most successful and partially is the C1, and why it is partially, I will discuss at the last, for the C1 category of the metallocene. So, as it is chiral because you will see it can exist into two enantiomers as you know, enantiomers, non-superimposable mirror image relation.

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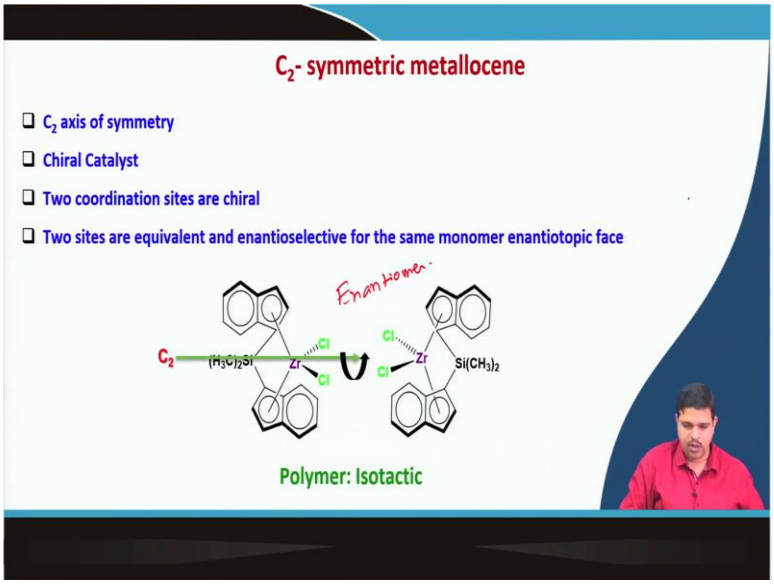

C_2- symmetric metallocene

- ☐ C_2 axis of symmetry
- ☐ Chiral Catalyst
- ☐ Two coordination sites are chiral
- ☐ Two sites are equivalent and enantioselective for the same monomer enantiotopic face

Polymer: Isotactic

So, so I will just give one example here in more detail. So, this is you, saw that two, one axis and there is no planes. So, there you will see that this is the enantiomers, and why the enantiomers you will see that because it is a relation of the plane of, if you, these are non-superimposable mirror image, and you will see that if you rotate like this one through the C2 axis, you will get the same indistinguishable structure. And this is the chiral catalyst. And that is why you will get the isotactic polypropylene.

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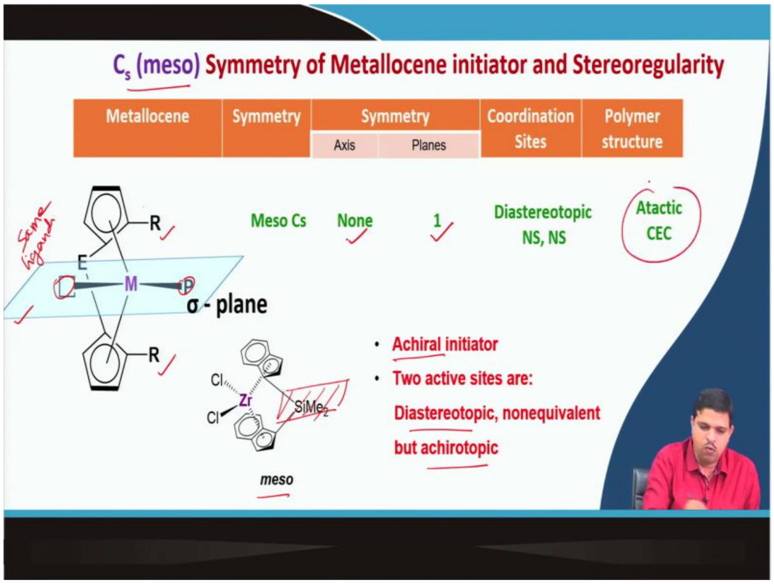

C_s (meso) Symmetry of Metallocene initiator and Stereoregularity

Metallocene	Symmetry	Symmetry		Coordination Sites	Polymer structure
		Axis	Planes		
	Meso Cs	None	1	Diastereotopic NS, NS	Atactic CEC

- Achiral initiator
- Two active sites are:

  Diastereotopic, nonequivalent

  but achirotopic

So, next the category is the Cs. Cs, two types, one is the meso and one is the Cs. I will, next slide I will tell you what is the Cs. Now let us try to understand what is the meso Cs. So, so far what we have learned, we have learned C2 V, we have learned C2, now is a Cs category of the metallocene, and more specifically this is Cs meso. So, what are the criteria here? So, here you will see that you have the symmetrical ligand shape. So, is a symmetrical, same ligand, sorry, not symmetrical, the same ligands. On, here also same ligand, same ligands.

Now, here you will see that how it is meso, because you will see there is a sigma plane, this one, the blue one, and that actually makes the molecule achiral. So, this is the achiral because it has a plane of symmetry. So, no C2 axis here, but there is a one plane and that is why it is achiral molecule. One real example you will see, this one, the meso because it has the plane of symmetry here. So, this is the meso.

And two active sides, that is this one, and this one, the two active sites are diastereotopic and nonequivalent, but achirotopic. So, these two active sides are diastereotopic but achirotopic. And as it has a plane of symmetry, you will get the atactic polymer for the Cs meso.

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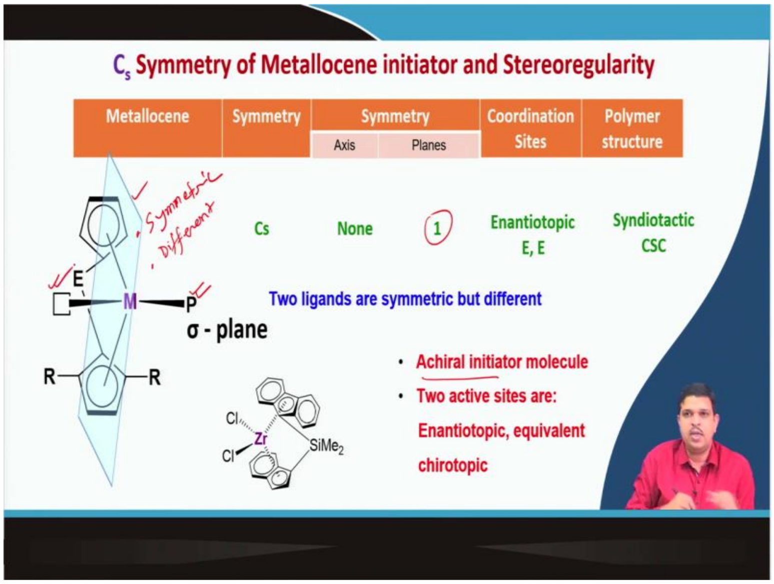


C_s Symmetry of Metallocene initiator and Stereoregularity

Metallocene	Symmetry	Symmetry		Coordination Sites	Polymer structure
		Axis	Planes		
	Cs	None	1	Enantiotopic E, E	Syndiotactic CSC

· Symmetric

· Different

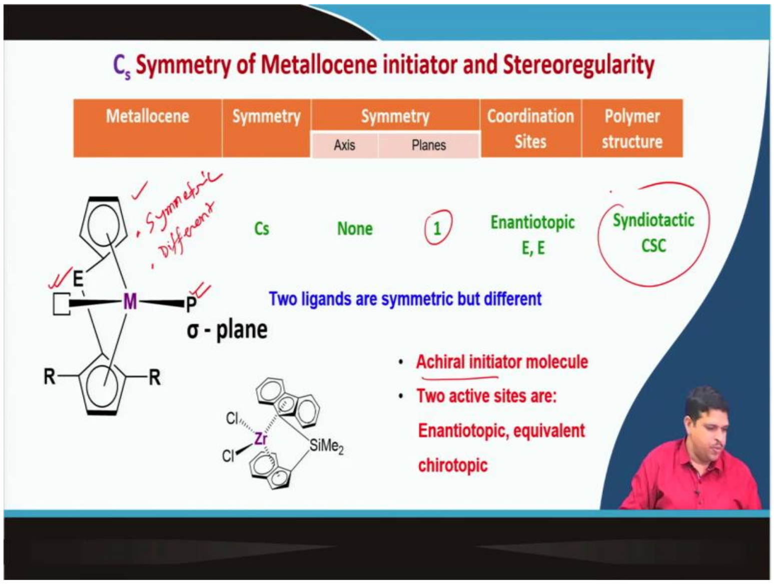
Two ligands are symmetric but different

σ - plane

- Achiral initiator molecule
- Two active sites are:

  Enantiotopic, equivalent

  chirotopic



C_s Symmetry of Metallocene initiator and Stereoregularity

Metallocene	Symmetry	Symmetry		Coordination Sites	Polymer structure
		Axis	Planes		
	Cs	None	1	Enantiotopic E, E	Syndiotactic CSC

· Symmetric

· Different

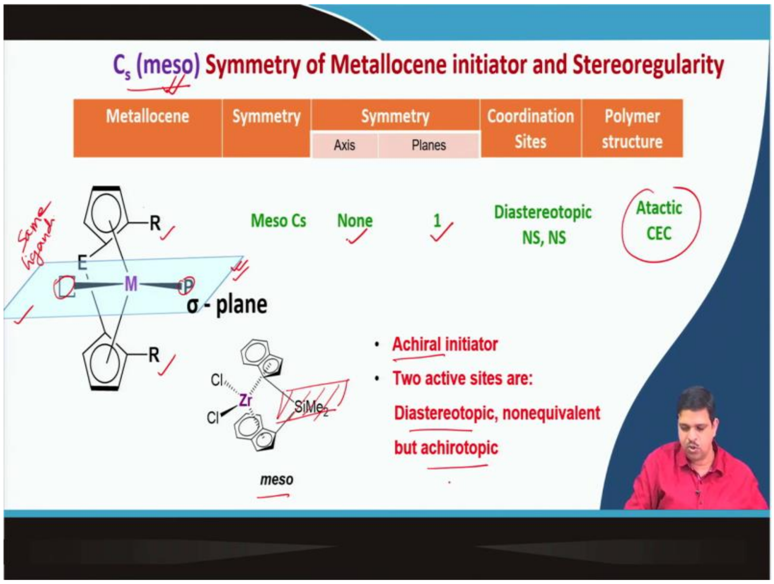
Two ligands are symmetric but different

σ - plane

- Achiral initiator molecule
- Two active sites are:

  Enantiotopic, equivalent

  chirotopic



C_s (meso) Symmetry of Metallocene initiator and Stereoregularity

Metallocene	Symmetry	Symmetry		Coordination Sites	Polymer structure
		Axis	Planes		
	Meso Cs	None	1	Diastereotopic NS, NS	Atactic CEC

- Achiral initiator
- Two active sites are:
  Diastereotopic, nonequivalent
  but achirotopic

One, and the as I told, the Cs, two category one is Cs and one is Cs meso. So, this one is the Cs meso. So, how you can, what is the difference in structure, you see that the two ligands are symmetric individually, individually symmetric, but different. So, here, you will see that you have the plane but the plane, the earlier one in the meso, the plane is this one, that is the, your, through your, the plane is through your metal and two active sites. But in this case, the plane is different.

Here, basically the, through the metal center, cutting the two active sites. So, this is the blue one. So, this and how you can impose the shape symmetry, you have to take the ligands, symmetric ligands individually, but the two different ligands you can, if you can take, you will get the Cs symmetry. So, this is again, as you have a plane of symmetry, so this is achiral molecules, but two active sites are enantiotopic, equivalent and chirotopic.

And due to this one, as plane of, plane of the symmetries here, so this is basically the enantio, this one and this one is the enantiotopic. In the last case, that is the Cs meso this plane is here. So, this, that is why this is diastereotopic and non-equivalent. But here, it is equivalent. And that is why it is give the syndiotactic polymer. So, here you will see the Cs meso will give the atactic polymer, but Cs symmetry metallocene will give the syndiotactic polymers. This is very important.

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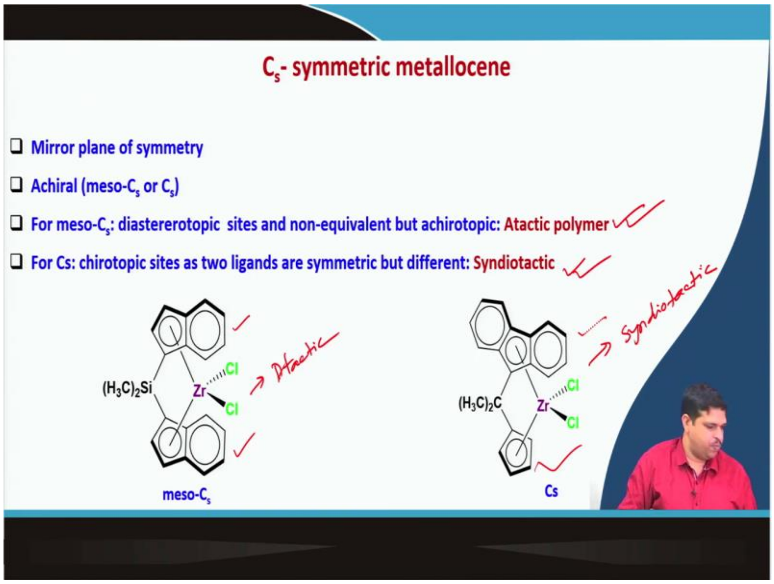

C_s- symmetric metallocene

☐ Mirror plane of symmetry

☐ Achiral (meso-C_s or C_s)

☐ For meso-C_s: diastererotopic sites and non-equivalent but achirotopic: Atactic polymer

☐ For Cs: chirotopic sites as two ligands are symmetric but different: Syndiotactic

So, here one example of the Cs symmetric metallocene. So, this one as we saw. So, this is two Cp links, two ligands are same. So, that is why it is a meso and this one is the CH here, two ligands are same but individually symmetric. So, that is the Cs. Both are achiral, because there is a mirror, plane of symmetry at there. But for meso Cs, the two active sites are diastereotopic nonequivalent, and that is why you are get the atactic polymer.

But for Cs, the two active sites are chirotopic and equivalent, and enantiotopic, and that is why you will get the syndiotactic polymers. So, in this case, the meso, you will get the atactic polymer, and this one, you will get the syndiotactic polymers. So, this is really very interesting. You will see how, you can see here that how these different symmetry actually dictates the stereoregularity of the polymers.

This is the most unique and beauty in the, and the most advantageous properties of the metallocene based catalyst. So, you can basically use as a tool box for, to access the different tacticity in the polymers.

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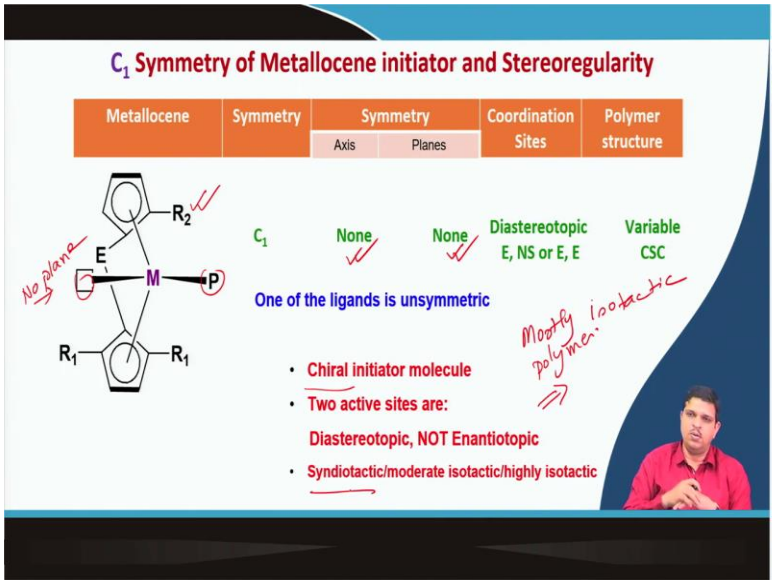

C_1 Symmetry of Metallocene initiator and Stereoregularity

Metallocene	Symmetry	Symmetry		Coordination Sites	Polymer structure
		Axis	Planes		
	C_1	None	None	Diastereotopic E, NS or E, E	Variable CSC

One of the ligands is unsymmetric

- Chiral initiator molecule
- Two active sites are:
  Diastereotopic, NOT Enantiotopic
- Syndiotactic/moderate isotactic/highly isotactic

Mostly isotactic polymer.

So, this is the last category that is the C1 symmetry of metallocene. And here C1 means as you know that there is no symmetry here. So, you will see there is no axis, and there is no plane. That means there is no plane, plane of symmetry, that means it is a chiral. So, this is a chiral molecule. So, you see that very limited, one is the C2 and one is the C1.

So, here you will see that how you will, so in this case you see one of the ligands is unsymmetric here. So, here you see that difference here, that in the Cs symmetry here you will see that both the ligands are symmetric, but different. And in this case, here, what we have done that this one again is a, make, made as unsymmetrical. Two ligands are different, but also the one ligand is unsymmetrical. Other one is symmetrical. Then you can make the C1.

So, C1 again, these two active sides are the diastereotopic but non-enantiotopic because you do not have the plane here, no plane. So, in this case, you we generally get the isotactic polymers but it is sometimes also variable, it also depends on different condition like temperature and others. So, mostly we will get here the isotactic polymers but also we can get the syndiotactic polymers to some extent. So, as I told that C2 and C1, these two categories of the metallocene can only give the isotactic polypropylene.

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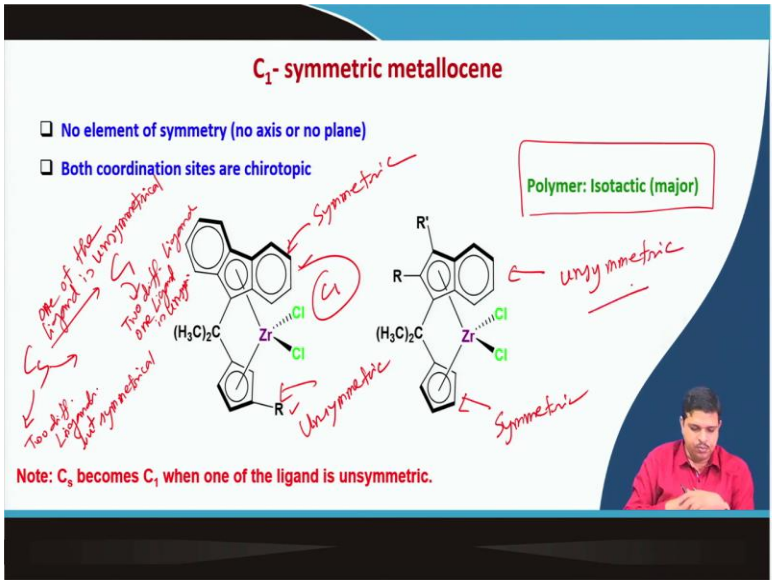

C_1- symmetric metallocene

- ☐ No element of symmetry (no axis or no plane)
- ☐ Both coordination sites are chirotopic

Polymer: Isotactic (major)

Note: C_s becomes C_1 when one of the ligand is unsymmetric.

So, here again just to discuss in more depth, about the C1. So, here what you, what we have seen here, if you have a Cs or metallocene, how we are convert to the C1, is basically when one of the ligand is unsymmetrical. So, in Cs case, what we have done here in Cs case, that here, in the Cs case, two different ligands, but symmetrical. And in this case, two different ligands, but one ligand is unsymmetrical.

So, if you see carefully here, that this one and this one, this is symmetric, and but this one is unsymmetric. And that is why this is, falls in the C1 symmetric metallocene. So, no element of symmetry, no axis or no plane, and both coordination sites are chirotopic as we discussed here. And this is a diastereotopic, the active sites are the diastereotopic. And due to this one, the polymer will get the isotacticity in meso but also, we get sometimes syndiotactic polymers also. So, here also you see that this is the symmetric and this is unsymmetric.

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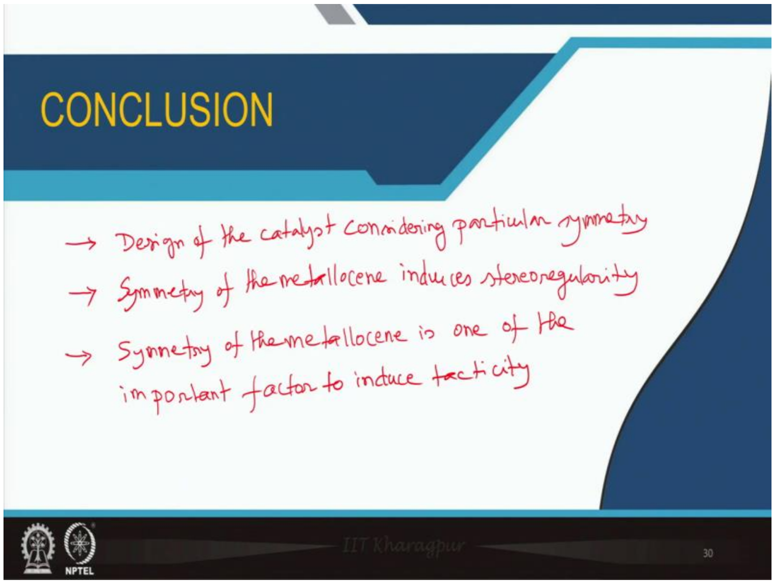

CONCLUSION

→ Design of the catalyst considering particular symmetry

→ Symmetry of the metallocene induces stereoregularity

→ Symmetry of the metallocene is one of the important factor to induce tacticity

So, you will see here that how we can design the catalyst by inducing a particular symmetry. So, from the class, this class what we have learned? We have learned that the design of the catalyst considering particular symmetry, and the symmetry of the metallocene induces the stereoregularity.

And the symmetry of the metallocene is one of the important factors to induce tacticity because as I told that if, suppose I want to, I am targeting for a particular kind of polymer as say like a isotactic polymers. So, I have to design my catalyst in such a way that this, I have a, first thing, that I have to have this two digit criteria of the metallocene and the metallocene should have C2 or C1. The most preferred is the C2 for isotactic polymers.

And suppose if I want to make a atactic, so you have to take a C2 V or Cs meso. So, this, these are important factors in catalyst design. So, before doing the polymerization and considering the target, what we are looking for, you have to select your catalyst. So, you can use this catalyst as a toolbox. So, you should say, you have a set of the different libraries of the catalyst and according to your need, you have to take the catalyst.

So, these are very, very important factors and you have to keep in your mind when you are doing the polymerizations, especially I am conveying this message to the industry personals who are involved in polymer industry that before doing the polymerizations, you have to select your catalysts properly so that you can fulfill your, the product whether what you are getting, whether isotactic, tactic or syndiotactic.

And also, you have to keep in your mind that suppose I am, sometimes I need to have a mixture of a blend of isotactic, isotacticity or syndiotacticity. So, you can also use a mixed catalyst at a particular time. So, that also you have to kind of a judge that yes how much I, tacticity I am looking for it. And accordingly, I have to charge my catalyst in the polymerization reactor.

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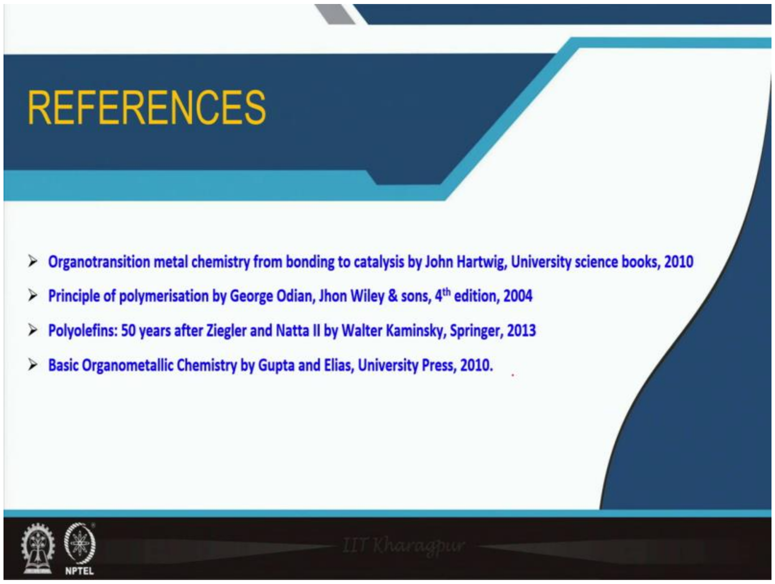

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So, I very much confident that you have learned that how you can design your catalyst and how you can select your catalyst for a particular set of polymers where you are looking for a particular tacticity. So, these are the books you can read for, to understand in more depth, for the last, what we discussed in today, this class, at the last class.

And in the next class we will discuss the, further, the metallocene, but there will be no two Cp rings, there will be half metallocene catalysts. This is called constant geometric catalyst. And also, we will discuss the non-metallocene based catalyst which are actually the recent trend in the catalyst development of the polyolefin.

So, why is the non-metallocene, because one of the, there are lot of advantage, or advantageous properties of the metallocene catalyst but one disadvantage is the cost of the catalysts. So, to replace the metallocene catalysts, one of the suitable and most cost effective is the non-metallocene where we will not be using expensive ligands or expensive metal centers. So, that also now in a kind of very active area of research, developing the non-metallocene based catalyst for the polyolefin catalyst. So, that we will discuss in the next class. So, thank you, and see you in the next class. Bye.