Transition Metal Organometallics in Catalysis and Biology
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Lecture – 51
Olefin Polymerization (Part 12)

Welcome to this course on transition metal organometallics in catalysis and biology, we have been talking about olefin polymerization in particularly, polyethylene and polypropylene polymerization and we have been looking at it from the perspective of catalyst development for this polymerization process as a course of time.

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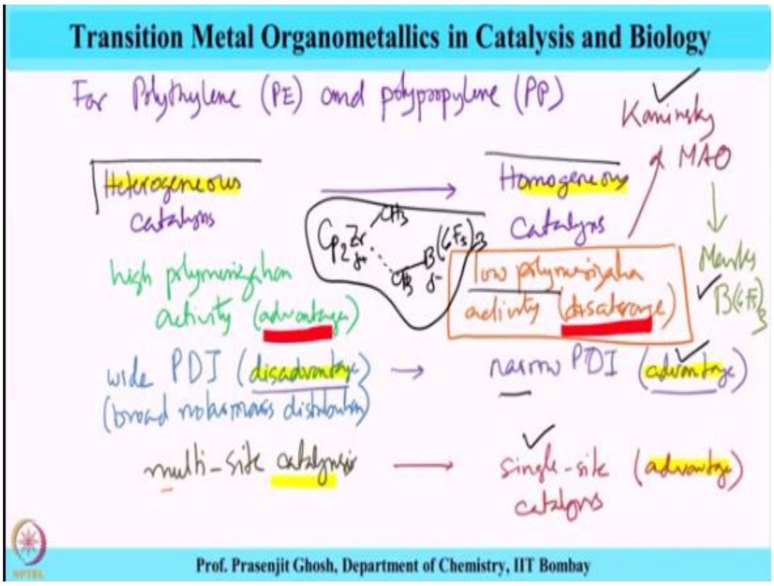

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For Polyethylene (PE) and polypropylene (PP)

Heterogeneous catalysis → Homogeneous catalysis

high polymerization activity (advantage) — low polymerization activity (disadvantage)

wide PDI (disadvantage) (broad molar mass distribution) → narrow PDI (advantage)

multi-site catalysis → single-site catalysis (advantage)

Kaminsky MAO

Marks $B(C_6F_5)_3$

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In this context, we have observed that for both for polyethylene and polypropylene for this, how the polymerization process moved from heterogeneous catalysis to homogeneous catalysis and each has its own advantages and the in the course of the struggle, what we had observed that heterogeneous catalysis though exhibited very high activity that is to its advantage.

But on the same time exhibited broad molar mass distribution, wide polydispersity index or broad distribution, so these is seen as a disadvantage and hence because of this the efforts were on to move on to homogeneous catalysis and in the also, this broad poly molar mass distribution has been attributed to the presence of multi-site catalysis and hence the effort were on to move on to the homogeneous catalysis system.

And which meant that the exactly, opposite attributes were wanted for example, narrow PDI, so this turns out to be advantage so, this is how this disadvantage can be converted to advantage narrow PDI. Similarly, the thing which this offered is single site catalysis and this is also considered to be advantage whereas, what in the earlier days; what homogeneous catalysis struggled with was low polymerization activity.

And this is supposed to be disadvantage, so we saw how on moving from; one moving from homogeneous to heterogeneous, how these disadvantages like single site, multi-site catalysis could be converted to the respective advantages and this advantage which was of the high performance becoming disadvantage, in case of the homogeneous catalysis. Now, in our study we had also seen that this disadvantage was finally overcome.

Overcome by the work of Kaminsky, who brought about the advent of methyl alumina oxane, MAO and then subsequent improvisation by Marks using a boron C6 F5 whole 3 reagent, this disadvantage of low activity was finally overcome to get homogeneous catalyst with extremely high activity. So, we had seen the beauty about organometallic chemistry as to how the things evolved from something heterogeneous to homogeneous where it had its advantages in terms of narrow PDI, single site catalysis.

But its own disadvantage was low activity and which was also finally, overcome by the advent of MAO by Kaminsky followed by using boron tri penta floro phenyl methyl boron by Marks which sort of gave a highly active single site catalyst of the structure something like CP2 zirconium methyl CH3 BC6 F5 whole 3, so this is a del positive, a del negative, so this is the catalyst which sort of became the final evolved structure through all of these processes.

And we had discussed this in great detail in our previous class, in this context also what is important is the fact that this answer be bleached, tetra hydro indane zirconium catalyst which could give atactic polymer.

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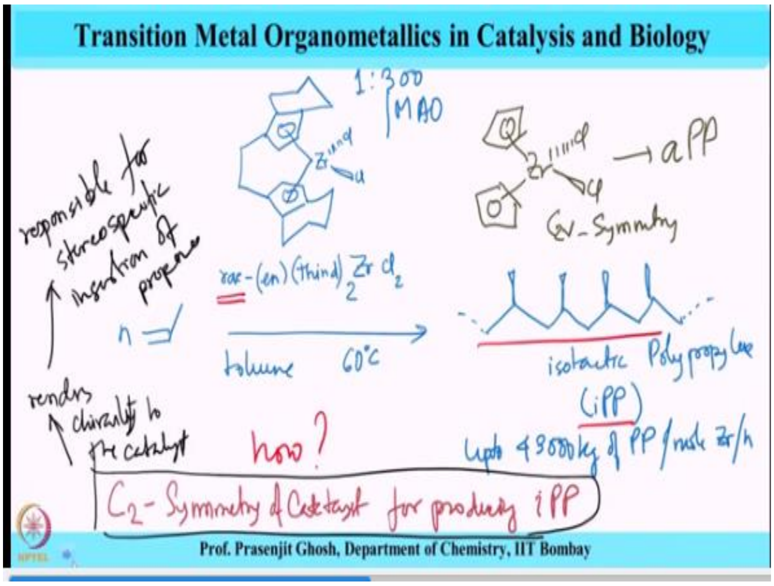

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So, this the catalyst which is drawn over here, these (()) (09:27) are catalysts, this is called racemic en for ethylene breached, this ligand is Thind, tetra hydro indane whole twice zirconium dichloride, this with MAO in 1 is to 300 ratio could give polymerized propylene at fairly low temperature of 60 degree centigrade in toluene to give atactic polypropylene, isotactic poly propylene or iPP.

And now, what is important over here is this, the question of; and this is extremely high active catalyst up to 4th to 3,000 kilogram of polypropylene produced per mole of zirconium per hour. So, this extremely high active; highly active catalyst which was producing iso propyl; isotactic polypropylene and the question is how; the question with regard to this is how, how is it possible that when we take a racemic catalyst that one gets isotactic polypropylene?

So, that is the main intriguing feature about it and the answer to that is guided by the C2 symmetry, the answer is provided by the C2 symmetry nature of the catalyst; C2 symmetry of catalyst that produced this isotactic for producing isotactic polypropylene. In this thing, it is to be noted that if that is the rational, then it is to be noted that a catalyst which is BCP zirconium, similar catalyst produced, we can may gave atactic polypropylene.

So, this has C2v symmetry now, this is best explained by the presence of C2 symmetry in the catalyst which renders chirality to the complex, this C2 symmetry renders the catalyst and these catalyst which is responsible for the stereospecific insertion of propane and this is best explained in the diagram shown in the next page.

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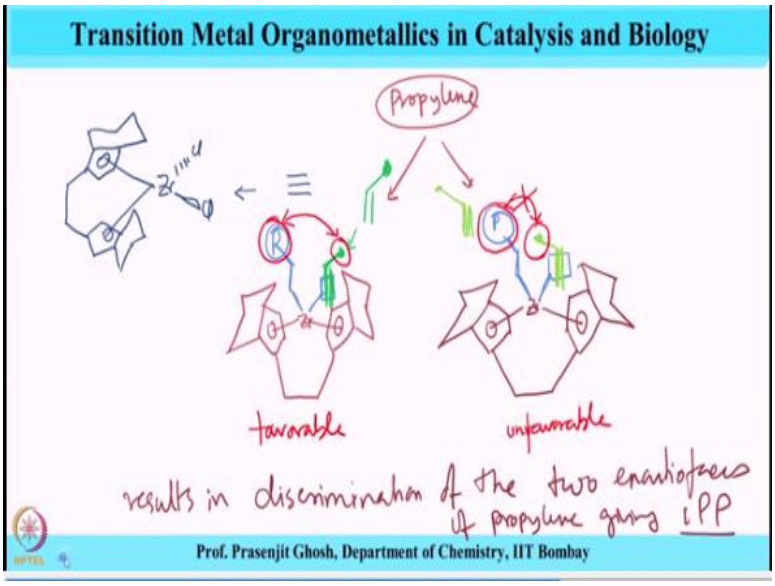

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results in discrimination of the two enantiofaces of propylene giving iPP

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This catalyst as is given below, the catalyst; this zirconium chloride can have when viewed from this side can sort of the represented by the following 2 diagram as is shown below and so this is bound to zirconium and it can have 2 sites, maybe I will draw with a different ink, it can have 2 sites, one something like this and the other site is a vacant site where the olefin can come and bind.

And I draw the same structure over here as is drawn over here, this again will have polymer as is shown over here and a weak inside now, the question is that polypropylene, when it approaches these catalysts, how would it occupy or bind at this site? So, possibility is there are 2 possibilities; one possibility is when a propylene comes, it will approach in this fashion and would sit in the vacant site in the fashion shown, as opposed to it can also approach in this fashion and occupy the vacant site and in a fashion like this.

Now, a careful look could quickly reveal that this orientation is less favourable because of steric repulsion between the methyl group and the polymer chain rendering this approach to be unfavourable whereas, compared to relative to this approach where the methyl groups are further apart, this becomes the favourable orientation of approach in terms of the energy.

And hence, these results in discrimination of the 2 faces; enantio faces of propylene giving isotactic polypropylene, so this is how these racemic catalyst with C2 symmetry steers the approach of propylene to give isotactic polypropylene.

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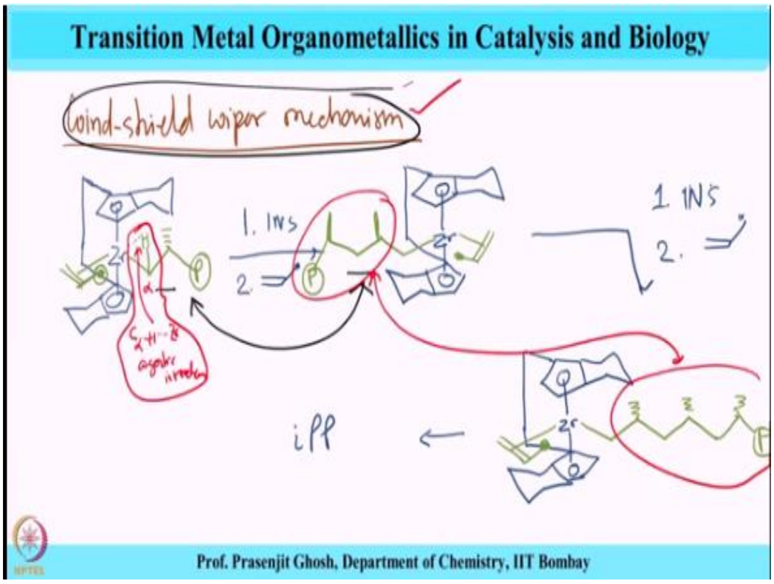

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Now, this is based summarized by a mechanism which is popularly called as a windshield wiper mechanism, which is popularly called as windshield wiper mechanism and is illustrated below, this is the catalyst bound to zirconium and this is how the 2 ligands are connected. Now, on one side I will use a different colour is bound to zirconium with the methyl moiety pointed in this direction.

And other side it is bound to a polymer chain, which exhibit C alpha H agostic interaction, so there is a special interaction over here which is called, this interaction is called C alpha H zirconium agostic interaction. Now, when this catalyst when olefin is bound in this fashion, the first, the migratory insertion of propylene occurs and the whole chain shift to the other side and a molecule of propylene then binds on the opposite side to what is shown over here.

This is best illustrated by the diagram shown over here, zirconium as is shown and then again, we will illustrate now, the polymer chain has shifted to the other side and the insertion has happened as it shown over here and in this side, second propylene is bound. So, what one sort of notices over here that as the insertion and binding of propylene happens, the polymer moves from one side to other and this is what is called the windshield wiper mechanism?

And subsequently, again the another insertion happens with the propylene being bound and the catalyst as it is shown here with zirconium and the ethylene, again comes to this site and in this site, the polymer chain grows and this is how the insertion or the reaction prepares to give iso polypropylene. So, this windshield wiper mechanism is very much evident by the fact that the stereochemistry of the polymer chain goes from one side of the catalyst to the other.

And the configuration sort of remains the same as it flips over, so this is this windshield wiper mechanism and this is stabilized or this is propagated by the presence of this zirconium alpha CH, agostic introduction which helps it propagate to give isotactic polymer; so polypropylene. So, with this we have seen how the single site catalyst is improved homogeneous to give polypropylene of higher stereo specificity.

And how symmetry plays a great role in distinguishing between the face; enantio face of the propylene that alpha olefin that approaches and results in highly regular; stereo regular structure producing poly propylene in high stereo specificity. So, with this we have also seen the role of answer; ligand which has a bridging ligand how it helps in opening up the cyclopentadienyl ring say, for better approach of the polymer chain and the catalysis.

So, more of this and this is a very nice demonstration of good thinking in chemistry, how it can lead to catalyst improvement, so more of this catalyst development on the polymerization mechanism of a polypropylene as we take this topic in bit more detail when we meet in the next class. I once again thank you for being with me in this class while we discussed the various stereo specific addition of propylene to give polypropylene.

And how there has been improvement in the catalyst structure as one went about correcting things in terms of polymer requirement and demand and the properties and more of these discovery on polypropylene would continue as we take this topic up in bit more detail when we meet in the next class, till then goodbye and thank you.