Transition Metal Organometallics in Catalysis and Biology
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Lecture – 52
Olefin Polymerization (Part 13)

Welcome to this course on transition metal organometallics in catalysis and biology, we have been talking about olefin polymerization particularly, in the context of polyethylene and polypropylene polymerization and from the perspective of the catalyst development that we have been talking about in the last few lectures and in that regard, we have been talking about this zirconium catalyst C2 symmetric zirconium catalysts which could give iso tactic polypropylene.

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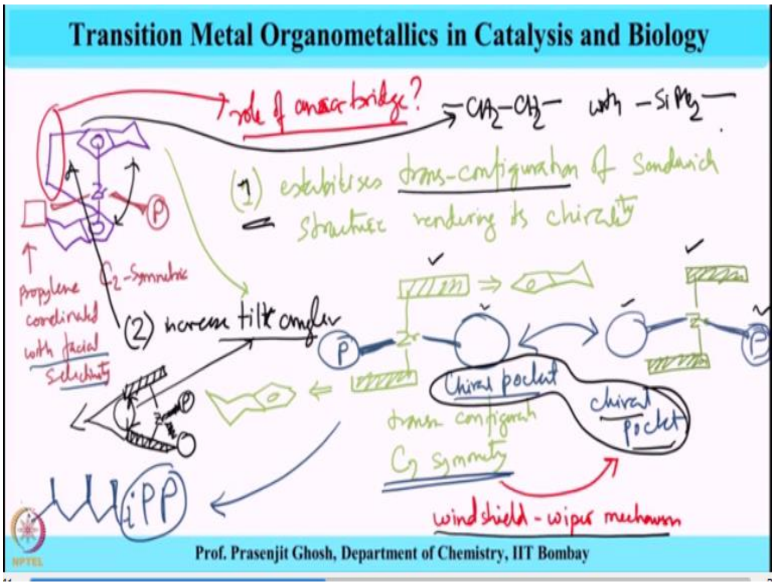

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And the catalyst that we have been discussing is this zirconium ethylene bridge complex as is shown over here, the catalyst that we have been discussing is this zirconium anca complex as is shown over here and this has these anca bridge which was playing an important role. Now, the way if this catalyst is progressed, is this the function of this anca bridge which had two armed binding sites.

The one that contained the polymer site and the other that contained the vacant site where the propylene coordinated with facial selectivity, so and this is C2 symmetric catalyst, now what is important over here is this the role of this anca bridge or the bridging ring clone. What is important is the role of an anca bridge, so what is its role? Now, the way it works is this, the first this anca bridge establishes trans configuration; configuration of sandwich structure rendering its chirality.

And what is that supposed to mean is; if we look at the catalyst and if we depict that the taller upper CP ligand as this, then zirconium and so, this is the top CP ligand and this is the bottom CP ligand which right now is in trans configuration imparting C2 symmetry with one side occupied by a polymer chain and the other side with a chiral pocket which can carry out facial selectivity of propylene.

Now, what we had discussed which is an important point that as a part of insertion via windshield; windshield wiper mechanism, what we had seen that when the insertion happens, then the polymer moves on to the other side; polymer moves on to the other side with this side having the chiral pocket. What is interesting to note is that for C2 symmetric catalyst, the chirality of these 2 pockets are same as a result, they are of same chirality?

Because of the C2 symmetric nature of this catalyst as a result, the propylene which is obtained is isotactic something all the methyl groups reside in the same side, isotactic polypropylene because the origin is that the chirality is the same, so this is an important role of played by this anca ligand, this is number 1 role which we have discussed that it keeps the ligand in the trans configuration as is shown over here.

And because of windshield wiper mechanism as the polymer chain goes from one side to another and the pocket moves from another to another however, the chirality of the pocket remains unchanged, the chirality of the pocket remains unchanged resulting in similar kind of insertion. Now, the second function is to increase the tilt angle, the second function of this anca ligand to increase tilt angle. So, what is tilt angle?

Tilt angle is the angle between 2 CP rings for example, if this is the top CP ring, this is the bottom CP ring, they are joined by ligand, so that and this is where the metal is bound to one site polymer chain, other site vacant site, so this angle is called the tilt angle. So, this bridge opens up the angle between the metal centre or make it the larger tilt angle which helps in polymerization.

For example, replacement; for example, replacing over in this catalyst, replacing CH2 CH2 linker as is shown with dimethyl Si Me2 increases the tilt angle further and result in isotactic polymer.

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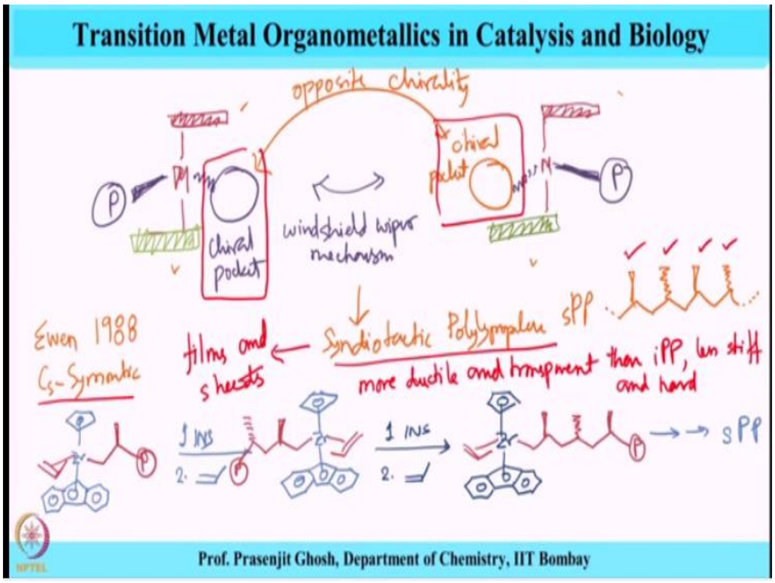

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Now, when one goes back to the drawing board and one can conjecture that if this is the configuration of the top metallocene ligand bound to a metal and if there is another metallocene ligand over here and in one side is up, in one side is a polymer chain and other side is a chiral pocket. So, if through windshield wiper mechanism, if one builds the polymer such that the top ligand remains the same metal.

And the bottom ligand, remains the same however, now the polymer has changed sides and moved on to the other side and the chiral pocket too has moved side and has moved to the other side but the symmetry of the ligand system is such that these 2 pockets are of opposite chirality, then the facial binding of the propane would be through different phases at each of this pocket.

And that should give the product as syndiotactic polypropylene or sPP which means, the methyl groups would be alternatingly incorporated, so this is a very nice conceptual extension where the principle which is said is that this ligand is chosen as such with the different symmetry that the chiral pockets are of opposite chirality resulting in the binding of propylene through different phases.

And as a result, alternating incorporation of the methyl group; one top, other bottom again, top bottom would occur result in syndiotactic polypropylene using this configuration. Indeed the nice demonstration of this syndiotactic polypropylene was given by Ewen in 1988, where Cs symmetry catalyst, this catalyst was used for producing syndiotactic polypropylene and this is best illustrated below.

For example, for these complex CP zirconium, this with 2 arms for example, polypropylene is another case and this being bound to zirconium which would undergo one insertion and second propylene binding that would give catalyst as is shown here. So, now the polymer arm has moved on to the other side with 2 methyl alternatingly, occupying the position and then subsequently, another insertion with propylene would occur.

And that would give the catalyst as shown over here with the polymer chain, again moving to the other side as is shown here and the olefin insertion happening and this perpetually propagating to give syndiotactic polypropylene. So, what is important over here is that the symmetry; the Cs symmetry; a defect of Cs symmetry results in 2 different kind of chiral pocket of different chirality, opposite chirality.

As a result, the polypropylene produced has the signature of alternating methyl group placed around each other and that arises because selective differentiation of the 2 faces of the polypropylene being produced resulting in syndiotactic polypropylene, the syndiotactic polypropylene is very useful because they are more ductile materials and transparent. Then, isotactic polyethylene, they are less stiffen; less stiff and hard.

And these are more suitable for applications a films and sheets and these are more suitable for applications of films and sheets, so this was a nice demonstration where one could control the microstructure of this polymer insertion using symmetry. So, what we saw is that C2 symmetric catalysts produced isotactic polypropylene whereas, Cs symmetric catalyst produced syndiotactic polypropylene.

And then, the catalyst development moves on to another level whereby the as per using different strategies, one could prepare polymers of use and Waymouth in this context, Waymouth had shown that conformational flexibility could give rise to formation of stereo block polypropylene.

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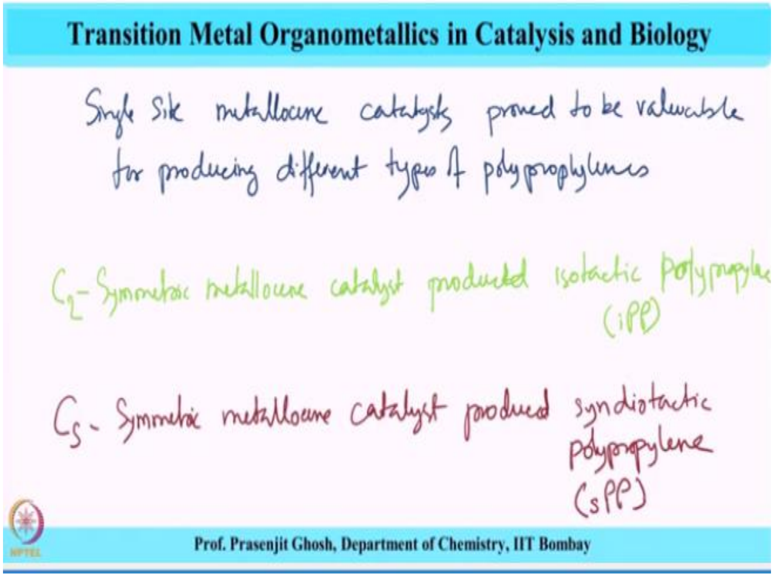

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Single Site metallocene catalysts proved to be valuable for producing different types of polypropylenes

C_2- Symmetric metallocene catalyst produced isotactic Polypropyle
(iPP)

C_s- Symmetric metallocene catalyst produced syndiotactic polypropylene (sPP)

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So, single-site catalyst, metallocene catalyst proved to be valuable for producing different types of poly propylenes for example, C2; for example C2 symmetric metallocene catalysts produced isotactic polypropylene or iPP and Cs symmetric metallocene catalysts produced syndiotactic propylene or sPP. So, with these, this was a nice demonstration of the scope of symmetry; modulation of symmetry resulting in incorporation of polymer in a stereo regular fashion.

The top one showed incorporation of polymer through one particular phase of the propane whereas, the bottom one showed incorporation of propylene through simultaneously, alternating between 2 different phases of the propane, so with this we come to an end of today's lecture where we had seen the effect of C2 symmetry in producing isotactic polymer as well as, see a nice work by Ewens which showed the effect of Cs symmetry producing alternating syndiotactic polymers.

Syndiotactic polymers are more soft, more ductile and transparent than isotactic polymers and has relevant application in for films and sheets and these are made by metallocene based homogeneous catalysis bearing Cs symmetry. So, with this I come to the end of today's lecture, we are going to be looking at the effect of catalyst design on the polymer properties in bit more detail, the catalyst evolution of metallocene single site metallocene based catalyst starting from Ziegler Natta heterogeneous catalyst for propylene polymerization.

The story continues and we are going to be looking at these catalysts development in bit more detail when we take up this discussion again in the next class, so till then thank you and good bye.