Transition Metal Organometallics in Catalysis and Biology
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Lecture – 53
Olefin Polymerization (Part 14)

Welcome to this course on transition metal organometallics and catalysis and biology, we have been discussing about olefin polymerization in the last few lectures and in this regard, we have been particularly, looking at the catalyst development that happened during the course of evolution of olefin polymerization particularly, for polyethylene and polypropylene polymerization.

And we have noted that this olefin polymerization started with a Ziegler Natta discovery of heterogeneous $TiCl_4$, diethyl aluminium chloride being able to polymerize ethylene at ambient conditions, room temperature and one bar pressure producing high density polyethylene and subsequent neither Ziegler Natta catalyst also could polymerize propylene to give isotactic polypropylene which is a sticky regular propylene with all the methyl group pointing in the same direction of the backbone.

And then we have focused on evolution of the catalyst as a course of evolution of the field as well and what we had observed that the focus shifted from heterogeneous catalysis to homogeneous catalysis, the reason being though heterogeneous catalysis was extremely good in terms of exhibiting very high activity for the polymer but a one major drawback to the heterogeneous catalysis for olefin polymerization was the fact that these are multi-site catalysis.

As a result, very broad distribution of the molecular weights of the polymer were obtained and consequently, the polymers were not really well behaved or the property wise, there was a need to make more narrow or distribution polymer for polyethylene as well as for poly propylene and as the need, they required the shift then, the research focus then shifted from multi-site catalyst to single site catalyst.

And that is why the homogeneous catalyst is came in picture now, the metallocene complexes of titanium and zirconium did a great job in terms of finding a homogenous solution to poly ethylene polymerization in a multi single site catalysis manner and as a result, with the advent of MeO as well as boron acetate, tri phenyl boron reagents what we saw was the evolution of metallocene type catalyst for which are homogeneous in nature.

And they are also single site catalyst for producing polyethylene as well as polypropylene in high activity, so this is what we had been discussing about and for poly propylene, the following 3 catalysts that we had spoken in the previous lecture is worth mentioning as they give propylene of different structures.

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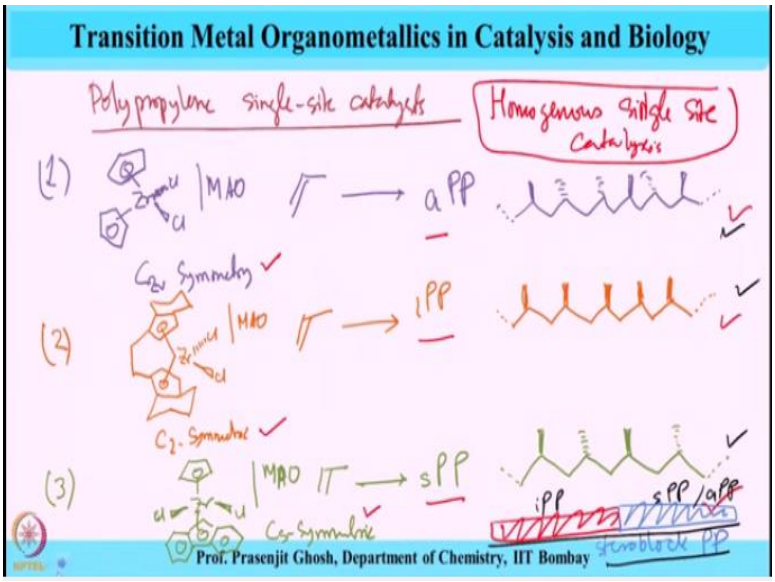

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For example, the first to note was these zirconium with MAO could give, this is of C2v symmetry gave propylene to atactic polypropylene; atactic means that the methyl groups are randomly oriented, something like that. Then, the next one that we had spoken about is these bridge sensor compound, this with MAO, this is C2 symmetric that propylene to isotactic polypropylene which is stereo regular.

And then, we had also looked into these famous zirconium catalyst; zirconium catalyst with MAO that gave propylene to syndiotactic propylene, I will draw this one properly and what is that meant was; so, alternating methyl group and so, this is a very interesting observation and that can give through insight into the type of polypropylene that could be obtained by changing the symmetry from going from C2v and this one the last one is Cs symmetry, this one is Cs symmetric.

So, one can see that on changing the symmetry from C2v, one gets atactic from C2 symmetric, one gets isotactic and from C2Cs symmetric one gets syndiotactic polymers, so now this is a finest example of how designing of catalysts can lead to polymer of very high activity with very extremely narrow or distribution range and extremely a good properties that one sort of wants to have in the polymer.

And this has all been achieved using homogeneous single site catalyst; catalysis, so this is the strength of organometallic chemistry at particularly, the homogeneous catalysis in being able to produce so many different types of polypropylene polymers by on the basis of symmetry catalyst structure and so forth. So, based on these we are going to now focus on another extremely a nice example by a professor Waymouth in 1995 by which he could make stereo block polymers.

And this is a beautiful elucidation of rationalisation, chemical modification and its resultant output in terms of the polymer that one could produce. Now, stereo block polypropylene means that this is 2O polymer segments of polypropylene, one may be this, the other; in cartoon I am giving of another colour, so this is a stereo block polypropylene and the idea is that these 2 are sort of a combination of either of the 3.

So, it can be; one block can be let us say isotactic, other can be syndiotactic or it can be atactic, so a combination of 2 different chains of any of this type, that would allow formation of stereo block of polypropylene, a very nice example of this as given by Professor Waymouth in 1995.

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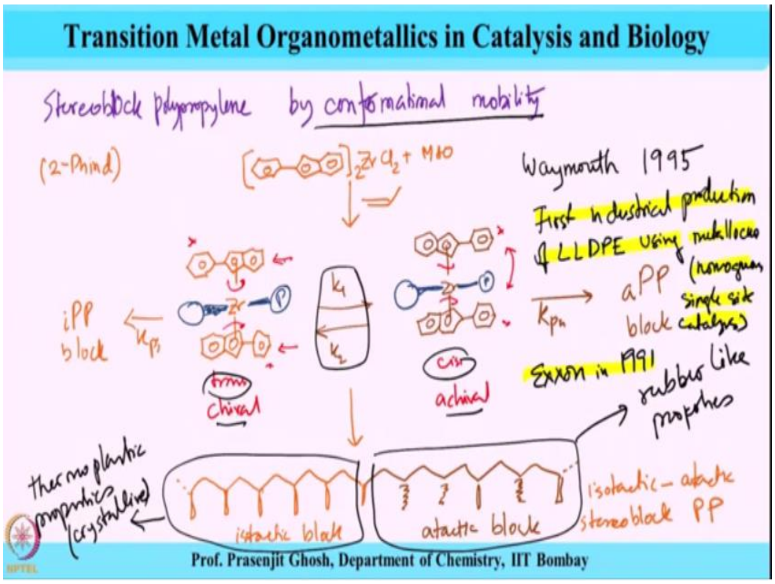
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Stereo block polypropylene by mobility and this was the fine demonstration of polymerization was carried out using these catalysts and this is illustrated by the equation, this ligand is called 2 phenyl indane or 2Phind, this ligand complex of zirconium MAO, actually resulted in 2 types of complex, zirconium of this in which these 2 phenyl moiety are in trans conformation and it would have the these would react with propylene would give one side the polymer chain.

And other side a vacant site and there can be 2 possible confirmations present of this which can be in mutual equilibrium and the other confirmation would be this, so what is literally happened is that there is a conformational rotation that happens between these 2 ligands along the zirconium axis such that these 2 phenyl rings can be trans as well as these 2 phenyl ring can be in the cis, this position, as it shown over here.

And the corresponding the polymer chain would be as here this being the vacant site now, these 2 change is dependent on temperature k1 and k2 now, what is important over here is to note that when one goes from cis to trans, the symmetry of the complex changes to the extent that this one remains C2 symmetric chiral and this one becomes achiral and since there is no anca bridging ligand between the 2 zarconia's in ligands, so this free rotation is very much possible going to 2 conformation in which when it is cis, it is a chiral.

When it is trans, it is chiral and as a result, when the polymerization occurs in this conformation, then atactic polypropylene is obtained, so atactic block of polypropylene is obtained and when the conformation polymerization occurs in this conformation Kpi, then isotactic polypropylene block is obtained and as a result, the overall polymer which comes out of these is something like that.

And then the other block, so this is atactic block and this one over here is isotactic block, so what is important over here is that stereo block polymer containing isotactic, atactic block polypropylene can be obtained and now, this is very interesting because point to note over here is that the conformational mobility that may exist between 2 forms; the transform and the cis form that is taken that has been exploited or taken advantage of to produce polypropylene having 2 blocks one is isotactic and the other is atactic.

And that is done in a controlled fashion, so by raising or changing the temperature concentration, one can control this equilibrium, the rate of exchange between the cis and the trans and then can control the length of the stereo block as per will and also one should take note of the fact that only one of the conformation is chiral which is giving this isotactic block and the other is achiral which is giving this atactic block.

So, this seminal, beautiful elegant example that take advantage of this conformational mobility was reported by professor Waymouth in 1995 which took advantage of this conformational mobility for producing a stereo block polypropylene and these 2 blocks, these 2 isomers are of comparable in energy, so they could be varied by changing the temperature, pressure and the R groups.

And property wise, this isotactic portion of the block; isotactic portion responsible for or more responsible for thermoplastic properties which is more crystalline whereas, atactic portion of the block is more rubber like properties and this, so this is sort of the power of homogeneous single site catalysis being able to produce polymers of 2 different tacticity in the same polymer chain.

And this was sort of recognized by the first fact that the first industrial production of LLDPE using metallocene single site homogeneous catalysis was reported by Exxon in 1991, so first industrial production of LLDPE linear low-density using metallocene homogeneous single site catalysis reported by Exxon in 1991. So, you know this is a significant discovery in the sense that we are; one is more familiar with heterogeneous catalysis being used for industrial scale application.

But here, catalyst is based on homogeneous catalyst which is not often the case in most of the situations was even built by Exxon for producing LLDPE, so this is tremendous success for homogeneous catalysis. There are further modification for example, Elf Atochem in 1999 used metallocene catalyst and caught on to heterogeneous process so, in a heterogeneous surface bed for producing this polymerizing olefin.

And this is the case, where homogeneous catalyst has been heterogeneous for the industrial scale production. So, with this we come to an end of today's discussion where we have looked into a nice example by Bob Waymouth that showed how conformational mobility by a suitable choice of ligand could be exploited for producing stereo block isomers on the same poly propylene backbone chain one of it; by varying the temperature, concentration, pressure one could modulate the chain length such that 2 studio blocks of different tacticity can be obtained in the same polymer chain.

And this takes advantage of this phenomenon of conformation changes from cis to trans that occurred in the catalyst in which one gives a chiral environment, the other becomes achiral resulting in isotactic and atactic stereo block polymer and this isotactic stereo block polymer is more crystalline and this is a thermoplastic properties to the polymer whereas, atactic is more rubber like.

So, 2 different opposing properties present in the same polymer and this is a beautiful elucidation of the chemistry that takes advantage of conformational mobility. So, with this I come to the conclusion of today's talk, we are going to look at more on this catalyst development aspect that we are looking in Ziegler Natta catalyst in (()) (18:25) polymerization starting from the Ziegler Natta catalyst’s, when we meet next, till then good bye and thank you.