Transition Metal Organometallics in Catalysis and Biology
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Lecture – 54
Olefin Polymerization (Part 15)

Welcome to this course on transition metal organometallics in catalysis and biology, we have been discussing about olefin polymerization and in particular, we have covered ethylene polymerization and propylene polymerization in the last few lectures. With regard to both of these ethylene polymerization as well as propylene polymerization, we have come a long way, let me just briefly summarize as to what has been discussed so far.

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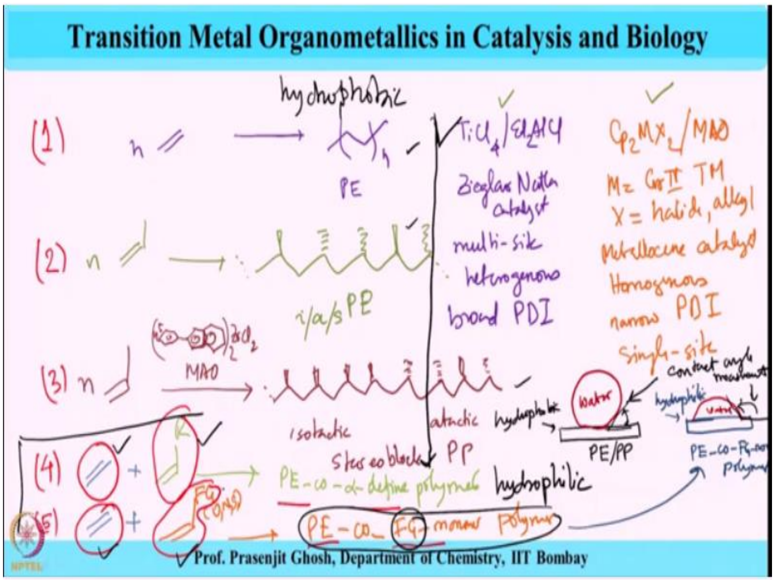

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And that where we proceed from here and what we have seen is for with respect to ethylene, we have made polyethylene of various types and for this, there have been 2 types of catalysts mainly, this is the famous Ziegler Natta catalyst whereas and these are mainly a multi-site homogeneous catalyst sorry, heterogeneous catalyst; catalyst and we have also seen metallocene catalyst.

And they are of the formula, MAO, there of the formula M equals group 4 transition metal as well as X can be halide, alkyl and so on and so forth and these are called metallocene catalysts and they are homogeneous in nature and they provide narrow PDI polymer whereas, the heterogeneous provide broad PDI polymer and these are single site catalyst, so these and the system evolved from one to other.

So, these are the 2 catalysts; 2 types of catalysts, one can is heterogeneous, homogeneous, Ziegler Natta, metallocene, broad PDI, narrow PDI, high activity, low activity, so these are the 2 types of the catalyst trajectory that we have discussed. Now, using these 2 catalysts we had done elaborate study on polyethylene polymerization using this, we have also looked at these are poly propylene, it can be isotactic, atactic or syndiotactic depending on the distribution.

And we had seen how the catalyst evolved for both of these types of catalysis and each of these, both the Ziegler Natta type as well as the metallocene types were equally capable of carrying out this kind of polythene polymerization in a very nice way and broad way. We had also discussed another interesting example which is the catalyst is a metallocene catalyst (()) (06:04), so we had also seen this phenyl, indanyl zirconium dichloride with MAO that giving atactic, isotactic stereo blocks, isotactic, stereo block polymer polypropylene.

So, what we saw a nice application of various types of polymer being produced on demand and at will using some variation of these 2 type of catalysts, one is heterogeneous and homogeneous where one can produce not only polyethylene of various grades, not only similarly, polypropylene of various grades, one can also have a stereo block polymer of different tacticity attached from the same polymer chain using these catalysis.

So, this is a nice, fine demonstration of the scope and capability of organometallic chemistry that can be put in use, so fantastic demonstration that champions, the field of organometallic chemistry for utility in achieving very different difficult or challenging reactions. So, today having covered all of these today, we are going to take a look at 2 more types of polymerization particularly, the ones that I am talk about so, we have talked about 2 types of polymerization process 1, 2, 3.

The 4th one that we would talk about is polymerization between olefin and alpha olefin resulting in poly ethylene co alpha olefin polymer, so these is a polymer that is obtained from copolymerization of 2 different monomers, this is one, another one and the polymer would have now 2 fragments; one is the polyethylene fragment as well as the poly olefin fragments and the 5th one that we would talk about is copolymerization of olefin with functional monomers.

So, in that case again, one can have ethylene plus another poly olefin with functional group; functional group means oxygen, nitrogen, sulphur, hetero atom containing functional more groups beings polyethylene, copolymer, functional group polymer, so here to there are 2 monomers; one is this functional group bearing olefin, co polymerizing giving poly olefin and monomer inserted functional group polymer.

So, the emphasis then became important for developing such types of polymer now, one reason for such development is that the surface properties becomes different, one when one goes for copolymerization for example, for the 5th process, since the functional group is present, so the co polymer backbone would have a functional group and functional groups are usually a polar in nature, so that will render hydrophilicity to the polymer.

So, any polymer with hydrophilic application for those purpose, this functionalization, copolymerization with olefins and alpha olefins bearing functional groups are important because all of these polymers as one says, they are all hydrophobic in nature whereas, if one can make a polymer with surface functionalized functional group, then those polymers would instead be hydrophilic in nature.

So, these are the reasons where which led to the need for being able to copolymerise olefins with alpha olefins as well as ethylene with a monomer bearing functional group, just to illustrate my point about the hydrophilicity for example, all of these this, all of these from here all the way up to here, they are hydrophobic whereas, the this last one will be hydrophilic.

Because of the presence of the functional group on the polymer backbone, so to illustrate my point let me just explain this with this cartoon, so if one makes a film with poly olefin PE or PP versus one makes a another film with copolymerised PE, copolymerized FG, a monomer so with a film at this polymer, this surface is hydrophilic whereas, for polyethylene surface is hydrophobic.

And if one puts a drop of water molecule on top of it so, the water molecule this being a hydro will have a concave surface because it will not wait the polymer surface whereas, for this kind of poly olefin with functional group, if one puts of water on it so, it will be hydrophilic and it will have a shape like this. So, in this case the water will wet the surface that means, it will spread over a larger area of the poly olefin comonomer surface.

Whereas, water will be limited because these being hydrophobic, the water will just have a minimum surface contact with this polyethylene or polypropylene surface and one can do lot of experiments to demonstrate the wetness of the surface and one is called contact angle measurement, where they measure this angle between the water surface and the polymer which is called the contact angle.

That will give some indication as to how wet this surface or to what extent the functional monomer has been incorporated in the catalyst. So, now this this provides the basic platform based on which for the development of these 2 polymerizations; one is olefin with alpha olefin and olefin with alpha loop in olefin bearing functional monomers, where to be done.

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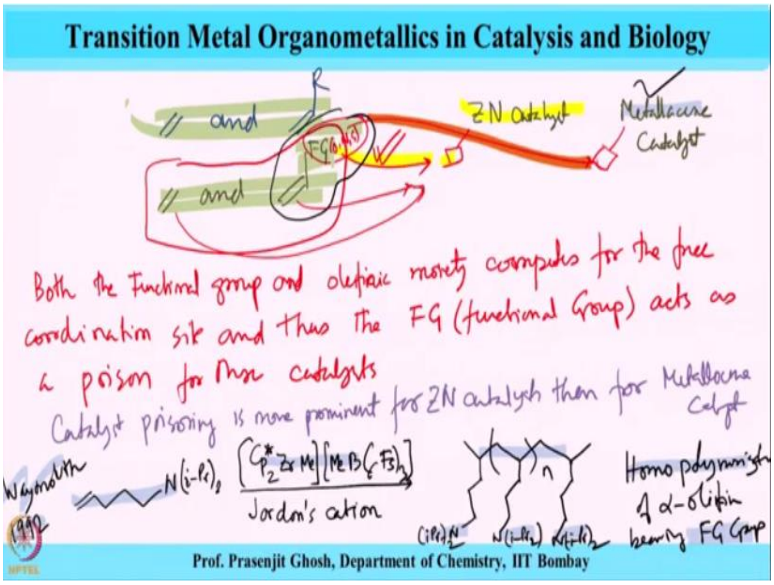

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Both the Functional group and olefinic moiety competes for the free coordination site and thus the FG (functional Group) acts as a poison for these catalysts

Catalyst poisoning is more prominent for ZN catalysts than for Metallocene Catalyst

Homo polymerisation of α-olefin bearing FG Group

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Now, when one talks about this polymerizing olefin and olefin with alpha olefins are one talks about polymerizing olefin and olefin with functional monomers which as a functional group using the catalyst which is a Ziegler Natta catalysts or metallocene catalyst, then the challenges which one faces are different for example, if one were to consider this case of; for example, if one were to consider this case of polymerizing, copolymerizing olefin with a functional group, then the problem which one faces is that this functional group bearing oxygen, nitrogen, sulphur atoms they compete in binding to the vacant site of this catalyst.

Each of these catalysts would have vacant site may be depicted by this metallocene also which have a vacant site, so they compete the functional group, competes with binding to this vacant site as well as of the olefin and the olefin of the functional group and it so happens that this functional group binding to the Lewis acidic metal centre, this outweighs the binding of the olefin to the vacant site.

So, these binds over here and as a result, the functional group poisons the catalyst as a result, the functional group poisons the catalyst, both the functional group and olefin moiety is compete for the free coordination site and thus the functional group acts as poison for these catalysts. So, what happens is this functional group binds more strongly to this Lewis acidic site over here as well as over here.

And it poisons the metallocene catalyst and does not allow the polymerization, so that is a nascent challenge for this type of copolymerization processes and what it turns out that these poisoning of the catalyst; catalyst poisoning by this functional group is more prominent for Ziegler Natta catalyst, then for metallocene catalyst. Catalyst poisoning is more prominent for Ziegler Natta catalyst, then for metallocene catalyst.

So, this is an interesting observation that in both the cases, in this case as well as in this case as well, this poisoning do happen but the poisoning of Ziegler Natta catalyst is more acute and more prominent and wins over and taking advantage of this process, Waymouth in 1992 reported at the following polymerization, where one could produce, one could do a polymerization of alpha olefins and a bearing functional monomer.

So, what Waymouth did taking advantage of this process, Waymouth did homo polymerization of just this functional group using metallocene catalyst, so the Waymouth chemistry using Cp star to zirconium methyl boron C6 F5 whole 3 and this is called Jordan’s cation, Waymouth polymerized this heteroatom bearing amino functionalized alpha olefin.

So, this was a great discovery a belt on which people went back and started working on the copolymerization even though, this is a homo polymerization of alpha olefin bearing functional group, this was a big discovery by itself because now, what Waymouth; this was reported by Waymouth in 1992, what Waymouth demonstrated is that these metallocene catalyst can homo polymerize alpha olefins.

And the functional group did not poison the metallocene catalyst; this metallocene catalyst and was able to give the homo polymer; homo polymer bearing functional group, so this was a very important and interesting discovery which sort of led way to the parent problem and the parent problem was of being able to go polymerize first ethylene with alpha olefins and then ethylene with alpha olefins bearing functional group.

So, this copolymerization was further developed on the backbone of Waymouth’s results which could polymerize alpha olefins bearing functional group. Sp, with this we come to the end of today's lecture and what we have demonstrated is the fine feet of organometallic chemistry and how the organometallic chemistry, organometallic catalyst triumph forward the requirement for producing different types of polyethylene polymer.

And we had seen that how this catalyst evolved on going from polymerizing ethylene or propylene by themselves which are called homo polymerization and then providing several grades of the homo polymerized products and then finally, how the need for developing copolymer with more polar surfaces and poly olefin backbone was developed and addressing that the challenges which remained was these functional groups were actually poisoning and the catalyst.

But one observation was made that the extent of poisoning was more significant for Ziegler Natta catalyst heterogenous than for metallocene catalyst and taking advantage of this knowledge, what Waymouth’s first date is paved the way for developing this further with copolymerization and what Waymouth showed was taking a metallocene catalyst, he could successfully homo polymerize alpha olefins bearing amine functional group all that in modest yield.

So, with this I come to the conclusion of today's lecture, we are going to be talking more about this homo polymerization and copolymerization with olefins and alpha olefins and olefins and alpha olefins bearing functional group, how this really took off and how more improved catalysts were developed for the copolymerization process, all of these interesting stuff when we meet next, until then goodbye and thank you.