Transition Metal Organometallics in Catalysis and Biology

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Lecture – 56

Homo and Co Polymerization; Functionalized olefins, Cycloolefins and Diolefins

Welcome to this course on transition metal organometallics in catalysis and biology we have been talking about olefin polymerization and in this context we have covered a lot of grounds particularly with respect to homo polymerization we started off with ethylene homo polymerization with using Ziegler Natta system has also moved on to propylene homo polymerization with the Ziegler Natta system then to metallocene system then we had seen advent of MAO and boron based gradients metallocene catalysts which were extremely active for ethylene as well as propylene homo polymerization.

We had also observed how the stereospecificity of the poly propylene polymerization could be controlled using a variety of metals in catalyst and then subsequently in the last few lectures we have moved into a co polymerization reactions of these olefins. And to this extent we have looked into copolymerization of two different kind of olefins for example diolefins one can be ethylene other can be alpha olefin as well as now we have also looked into copolymerization of cyclic olefins which are which could also be used.

So in this context we have spoken about one type of cyclic olefins which were obtained in the previous class which was obtained using 2 reactions one is Diels-alder reaction followed by co polymerization of the cyclic olefins. So let me just focus on what we had finished in our previous class and then we will to move into moving to the other routes of making this kind of cyclic a polyolefin polymers.

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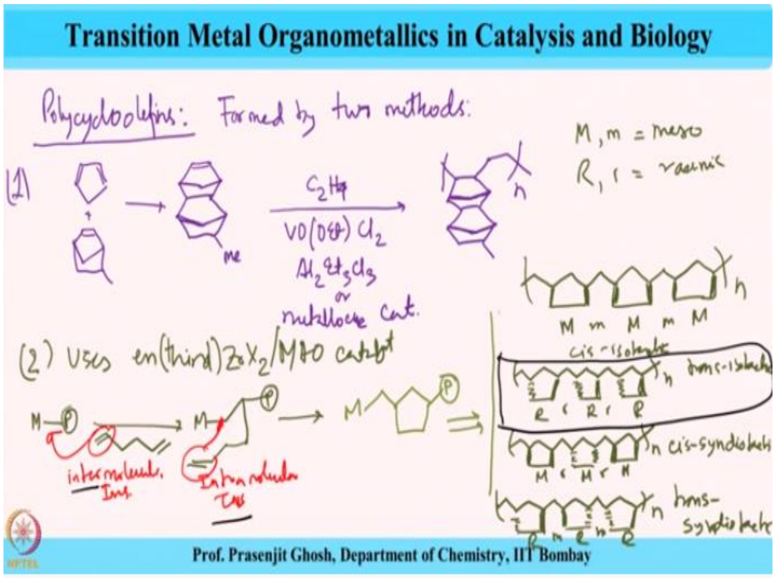

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They can be a formed by 2 ways by 2 methods and these are really a very interesting method. The one we had discussed in the last class involves 2 reactions this is method 1 or metallocene catalyst and that could give this polymer of this type. So we have seen how these polymers are important for magnetic applications and we are going to now take a look at the other pathway using zirconium catalysts. The second pathway uses in the zirconium x2 MAO catalyst and the reaction is shown over here.

So it already has a polymer chain building on it and then this olefin comes the first is the insertion of this olefin on the metal polymer chain length and then that gives this inserted product. Now then what happens is the first this is called intermolecular insertion and now intramolecular insertion would happen. Now this will now insert in this bond to give this product and subsequently this insertion would follow through.

So there are 2 types of insertions and that would give rise to various kinds of products possible products which are shown here it can be this where the stereochemistry can be a meso within the ring M,m capital M or small m for meso are and smaller for racemic like this. So this is a cis isotactic the other possibility can be like this where it can be hard. So this is trans isotactic similarly it can be MrMrM this is cis syndiotactic and the last can be and this can be RmRmR and this is called trans syndiotactic.

So the these insertion can happen in 4 ways as its shown over here and these are 2 types of insertion as has been mentioned in this so one is in in intramolecular the other is intermolecular and these gives optically active polycyclic olefins and the best one which is produced by this method exclusively is trans isotactic. So this is the one which is exclusively produced this is the trans isotactic.

So this is an interesting result we have seen that there are 2 ways in which polycyclic olefins one can be through copolymerization by Diels-alder and then using the VO vanadium catalyst the other can be using a non-conjugated dying and doing intramolecular and intermolecular catalyst with chiral answer bleached zirconium zirconocene catalyst. So that exclusively it gave the trans isotactic products.

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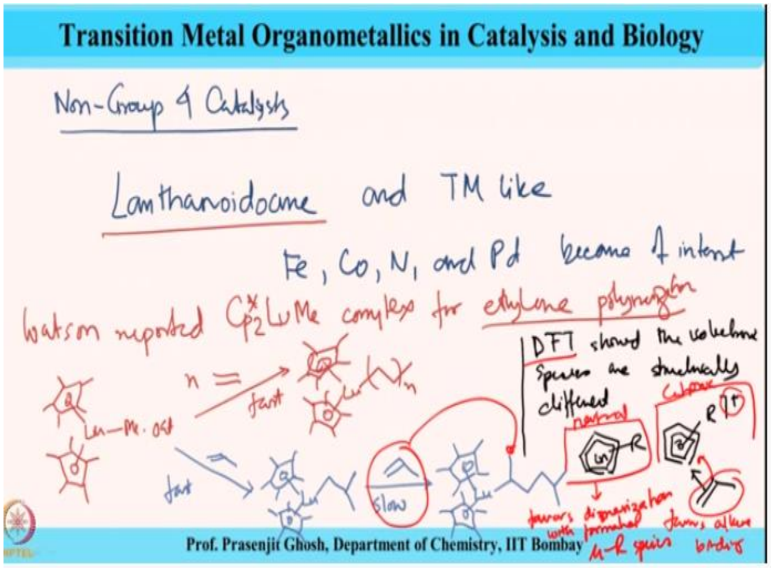

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Non-Group 4 Catalysts

Lanthanoidocene and TM like

Fe, Co, Ni, and Pd became of interest

Watson reported Cp^*_2LuMe complex for ethylene polymerization

DFT showed the cationic species are structurally different

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So apart from this there are several efforts were made in trying to diversify the metal learning this regard. The emphasis were developed on generating non-group 4 catalyst and in these regards the several metals were looked into but what emerged out are this lanthanum DCN lanthanum derivatives are called lanthanoidocene and other metals are the transition metals like iron, cobalt, nickel and palladium became of interest.

Now so when the quest for other types of metallocene’s were developed then this lanthanum based the catalyst as well as other transition metals like iron, cobalt, nickel became of interest.

So developing so we are going to focus right now on the first part which is this lanthanum based metallocene catalyst and the question was though there was a nice work by Watson who sort of the developed Watson reported Cp star 2 Lu methyl complex for ethylene polymerization.

So but this is a interesting complex there is the Cp star complex the complex could take ethylene and like you know polymerize it fast polymerization to give Cp star. So it could successfully polymerize ethylene very fast, but the interesting thing is that it could only do one insertion single insertion with propylene. So with propylene it could first give these alkenes complex and then the second ethylene of insertion was surprisingly very slow to give a slow complex of this type.

So and beyond this it did not proceed and then this is a very unusual behavior in terms of the earlier observation that only 1 ethylene insertion and could take place and the reaction did not proceed. So the and then the thing which was contrasting is that corresponding metallocene complexes for zirconium could allow several insertion of propylene to give the product and this was finally explained by Ziegler using DFT calculations which should have said that coordination in the neutral alkene zirconium cationic zirconium complex is more favorable for further reaction than in the neutral lanthanum species.

So this is explained by Ziegler by DFT calculations and DFT showed the isoelectronic species are structurally different. That is for lanthanum its a neutral compound whereas for zirconium there is a approach of olefin that could abide for zirconium because of this cationic nature. There is a free side where it could bind favors alkene binding and these for the lanthanum series because it is the isoelectric is neutral in nature.

So they are less favorable to olefin binding and favors dimerization with formation of mu R species. So there is a fundamental difference between the lanthanum complex as well as there is zirconium catalyst which could polymerize olefin and the reason was finally answered by DFT which sort of showed that this is a neutral complex. This is neutral and this is cationic and being cationic it favors olefin binding.

Whereas this neutral these does not favor olefin burning to great extent on the other hand there is a decomposition of the catalyst through formation of R alkyl bridges is observed in cases of lanthanum. So these was a great difference between the lanthanoidocene chemistry as well as the transition metals zirconium chemistry. In case of lanthanoidocene alkyl compound sigma bond metathesis is also observed.

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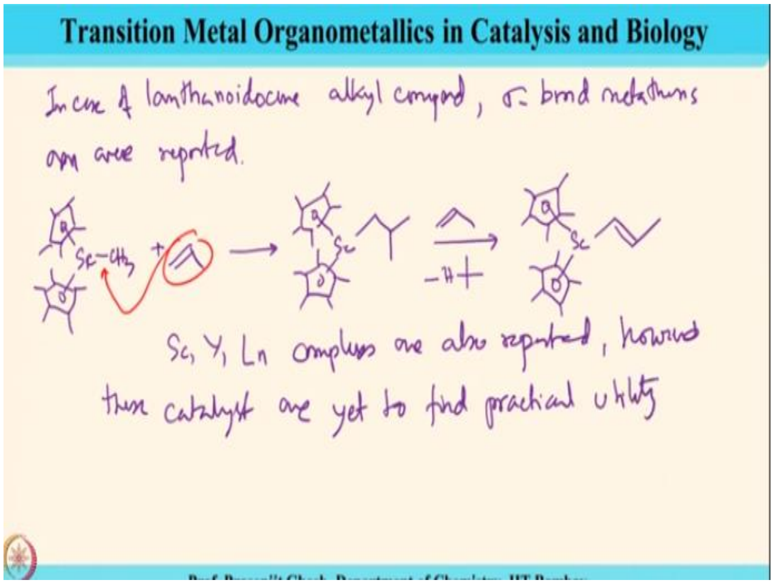

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In case of lanthanoidocene alkyl compound, σ- bond metathesis are also reported.

Sc, Y, Ln complexes are also reported, however these catalyst are yet to find practical utility

Another interestingly activity of lanthanoidocene catalyst is in case of lanthanoidocene alkyl compound instead of polymerization sigma bond metathesis reactions were reported and how this and of the first in this is the insertion into the alkyl bond as is shown to give the corresponding species that in presence of another propylene gave this sigma bond metathesis reaction to give the compound which is this and for yttrium plays a role and then several metals of this type.

For example scandium, yttrium, lanthanum complexes also reported to exhibit this polymerization activity. However these catalysts are yet to find practical utility I would this complexes that yet to find practical utility. Now these are startlingly different in terms of behavior with respect to the early transition result zirconium organism catalyst and the main thing what we had seen that though they may be able to polymerize ethylene.

These cannot undergo subsequent propylene insertion and, in some cases, only one insertion of propylene could be obtained and in other cases even that is not observed just after first insertion the second insertion does not happen and just sigma bond metathesis reaction takes place. So with this we come to the end of lanthanum chemistry for designing polypropylene catalyst as a part of these non-group 4 transition metals non-group 4 metals for polymerization purpose.

And now we move on to the effort that describes other non-group 4 metallocene catalyst and they involve other transition metals for example iron, nickel, cobalt, palladium so on and so forth. Now the story a sort of first focuses on iron by a catalyst given by Gibson Brooker and Gibson they are fantastic catalysts and then the focus a sort of from lanthanum shifts to.

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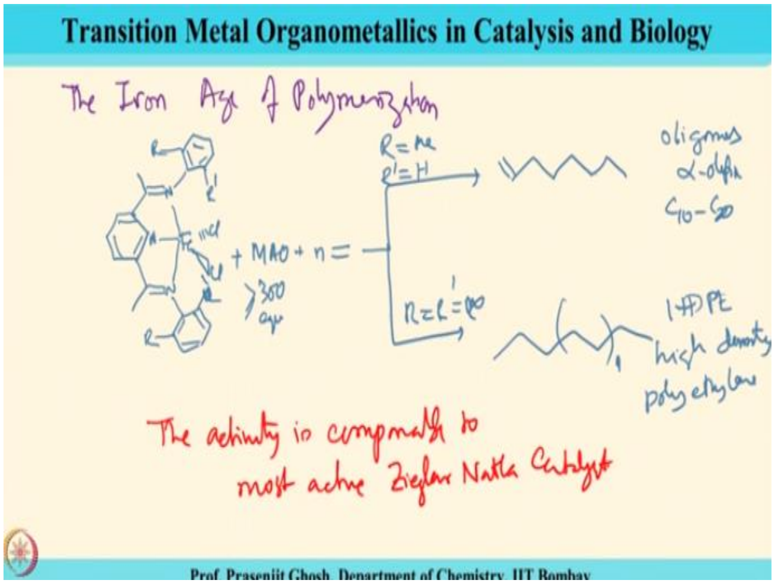

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The Iron Age of Polymerization

The activity is comparable to most active Ziegler Natta Catalyst

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Iron Age of polymerization and these are our two like a very important catalyst is given by where R is a bulky group is equal to isopropyl or bulky group. This with MAO and MAO greater than 300 equivalents and n ethylene when R=methyl this is R and R dash 2 different substituent this R= methyl and R dash = hydrogen it could give oligomers alpha olefins c10 to c20 and when R = R dash = methyl then it could give H high-density HDPL high density polyethylene.

And this is activities the important thing is the activity of is very similar to the activity is comparable to most active Ziegler Natta catalyst. So this is a important discovery in the sense that the iron right now can be used to produce oligomers as well as ethylene a high density polyethylene of extremely high activity. So with this we come to the end of todays discussion where we have looked into development of non-group 4 metal based catalyst for olefin polymerization and how we have seen that how landscape changed on going from lanthanum to iron.

So more of these non-group 4 transition metal catalysts as we take up the discussion in the next class in which we will move beyond iron and see other metals like nickel, cobalt so on and so forth being present for these developing polyolefin polymers. So with this I can thank you for being with me in this class and I look forward to being with you in the next class where we take up this non-group 4 transition metals in more details thank you.